

Alkaline Earth- and Rare Earth-Transition Metal Complexes

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The work described in this Thesis was carried out in the Chemistry Research Laboratory, University of Oxford from October 2009 to February 2013 under the supervision of Professor Philip Mountford. All work is my own unless stated to the contrary, and has not previously been submitted for any degree at this or any other university.

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Abstract

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This Thesis describes the synthesis and characterisation of new alkaline earth- and rare earth-transition metal complexes. Experimental and computational studies were performed to investigate the structure and bonding in these complexes. Their reactivity was also studied.

Chapter 1 introduces metal-metal bonded complexes and current alkaline earth- and rare earth-transition metal bonded complexes.

Chapter 2 describes experimental and computational studies of new alkaline earth- and lanthanide-Fe complexes possessing the $[\text{CpFe}(\text{CO})_2]^-$ anion.

Chapter 3 presents experimental studies of the reduction of $\text{Fe}_3(\text{CO})_{12}$ with Ca.

Chapter 4 describes experimental and computational studies of new alkaline earth- and lanthanide-Co complexes containing the $[\text{Co}(\text{CO})_3(\text{PR}_3)]^-$ anion.

Chapter 5 presents full experimental procedures and characterising data for the new complexes reported.

Appendix describes the attempted synthesis of $[\text{Ca}\{\text{CpRu}(\text{CO})_2\}_2(\text{THF})_x]_y$ and study by DFT of $[\text{CaR}_2(\text{THF})_3]_2$

CD Appendix contains .cif files for all new crystallographically characterised complexes described.

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Abbreviations

General

Å	Ångstrom
atm	atmosphere(s)
avg.	average
<i>ca.</i>	<i>circa</i> , about
calcd.	calculated
<i>cf.</i>	<i>confer</i> , compared to
Cp _{cent}	computed cyclopentadienyl ring carbon centroid
CSD	Cambridge Structural Database
°	degrees
°C	degrees Celsius
d	day(s)
e.s.d	estimated standard deviation
g	gram(s)
h	hour(s)
K	Kelvin
mbar	millibar(s)
min	minute(s)
mL	millilitre(s)
mmol	millimole(s)
RT	room temperature
s	second(s)
<i>vs.</i>	versus

Chemical

Ae	alkaline earth metal
An	actinide
Ar	aryl group
bian	bis[(2,6-diisopropylphenyl)imino]acenaphthene
Bu	<i>n</i> -butyl
COD	cyclooctadiene
COT	cyclooctatetraene
Cp	C ₅ H ₅

Cp'	C ₅ H ₄ Me
Cp*	C ₅ Me ₅
cy	cyclohexyl
DABCO	1,4-diazobicyclooctane
dipp	2,6-diisopropylphenyl
DME	1,2-dimethoxyethane
dppe	Ph ₂ PCH ₂ CH ₂ PPh ₂
en	ethylenediamine
Et	ethyl
fc	1,1-ferrocenyl
Fp ⁻	[CpFe(CO) ₂] ⁻
HMPA	P(O)(NMe ₂) ₃
ⁱ Pr	<i>iso</i> -propyl
IPr	C{N(dipp)CH} ₂
L	a supporting ligand (set)
Ln	lanthanide
M	metal
Me	methyl
Mes	2,4,6-C ₆ H ₂ Me ₃
NacNac	[{(Ar)NC(Me)} ₂ CH] ⁻
OTf	CF ₃ SO ₃ ⁻
P	generic phosphine ligand
Ph	phenyl
PMDTA	pentamethylethylenetriamine
PPN	[Ph ₃ PNPPh ₃] ⁺
Pr	<i>n</i> -propyl
priso	[(Ar)NC(NR ₂)N(Ar)] ⁻
py	pyridine
pz	pyrazolyl
R	generic aryl or alkyl
Rp ⁻	[CpRu(CO) ₂] ⁻
TBDMS	SiMe ₂ ^t Bu
^t Bu	<i>tert</i> -butyl
^t Bu _{py}	4- ^t Bu(C ₅ H ₄ N)
THF	tetrahydrofuran

TM	transition metal
TMEDA	tetramethylethylenediamine
Tol	4-C ₆ H ₄ Me
Tp	tris(pyrazolyl)hydroborate
tren	N(CH ₂ CH ₂ NSiMe ₃) ₃
Ts ^{Xy}	HC {SiMe ₂ N(3,5-Me ₂ C ₆ H ₃)} ₃
X	Generic halide
Xy	3,5-C ₆ H ₃ Me ₂
Xyl	2,6-C ₆ H ₃ Me ₂

Calculations

AIM	atoms-in-molecules
BCP	bond critical point
DFT	density functional theory
<i>H</i>	energy density
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
MO	molecular orbital
MP2	Moller-Plesset perturbation theory (second order)
ρ	electron density
$\nabla^2\rho$	Laplacian of the electron density

Mass Spectrometry

EI	electron impact
<i>m/z</i>	mass to charge ratio
MS	mass spectrometry

Nuclear Magnetic Resonance Spectroscopy

¹³ C{ ¹ H}	proton-decoupled ¹³ C
app.	apparent
br	broad
COSY	correlation spectroscopy
d	doublet
DOSY	diffusion ordered spectroscopy
HMBC	heteronuclear multiple bond correlation

HMQC	heteronuclear single quantum correlation
Hz	Hertz
<i>i</i>	<i>ipso</i>
<i>J</i>	coupling constant
<i>m</i>	<i>meta</i>
m	multiplet
MHz	Megahertz
NMR	nuclear magnetic resonance
<i>o</i>	<i>ortho</i>
<i>p</i>	<i>para</i>
ppm	parts per million
q	quartet
s	singlet
sept	septet
t	triplet
VT	variable temperature
δ	chemical shift in ppm

Infrared Spectroscopy

br	broad
FT-IR	fourier transform infrared red
IR	infrared
cm^{-1}	wavenumber
m	medium
s	strong
w	weak
ν	frequency
$\nu(\text{CO})$	carbonyl absorption band

Notes

Literature compounds described in this Thesis are numbered **1.x**, **2.x**, **3.x**, **4.x** according to the Chapter in which they first occur. The new compounds described in this Thesis are numbered **1 – xx**. Model systems used in calculations are denoted by **#Q**.

X-ray crystallography data was collected, solved and refined by the author with help and guidance from Prof. Philip Mountford. Data for compound **3** was collected by Dr Andrew Schwarz. Molecular drawings were produced by Prof. Philip Mountford.

Diffusion (DOSY) NMR spectroscopy was performed in collaboration with Dr Timothy Claridge of the University of Oxford's NMR service.

DFT calculations were performed in collaboration with Prof. Nikolas Kaltsoyannis at University College London.

Chapter One

Introduction

1.1 General Introduction

The study of metal-metal bonding has played a pivotal role in the advancement of chemistry for decades,¹⁻⁴ furthering our understanding of structure and bonding, catalysis and bioinorganic processes. Whilst structurally authenticated transition metal-transition metal interactions are numerous, relatively few metal-metal bonds involving the alkaline earth or rare earth elements are known.⁵⁻⁷ Owing to their potential to give similar structures and reactivities to some of the divalent rare earths, the heavy alkaline earths are being pursued as a more economical and sustainable alternative to the former.⁸⁻¹⁸ The application of metal-metal interactions involving the alkaline earth elements for chemical transformations is in its infancy.¹⁹⁻²³

This thesis describes the synthesis of heterobimetallic alkaline earth- and rare earth-transition metal complexes. Use of single crystal X-ray diffraction has enabled the structural authentication of these complexes and subsequent support for or against the presence of direct interactions between these metal centres to be elucidated based on their structures. IR spectra for these complexes in solution and the solid state have been recorded to enable, along with NMR spectroscopic data, the composition of the bulk material and the difference between its solution and solid state form to be investigated. Reactions with small molecules and DFT calculations have been carried out for selected complexes. Some of this work has been published.²⁴

This Chapter introduces landmark complexes with transition metal-transition metal bonding, followed by complexes with alkaline earth-alkaline earth bonding. Complexes with alkaline earth-main group metal interactions are compared to their rare earth counterparts. Rare earth-transition metal complexes are also introduced.

1.2 Criteria

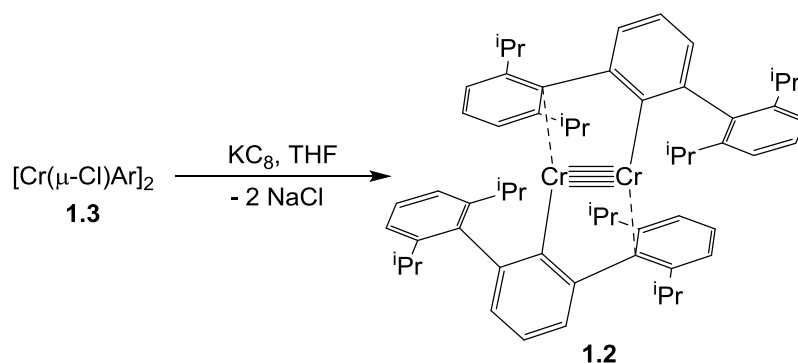
Whilst some substances that have not been structurally authenticated will be discussed, this study places much importance on structural characterisation by single crystal X-ray diffraction. This is particularly important in distinguishing between metal-metal interactions and bridging interactions between the metal centres. In some cases, even with a molecular structure this may remain ambiguous.²⁵⁻²⁸ To ensure consistency throughout one set of empirically determined values will be used for each of the covalent radii and ionic radii.^{29, 30} Covalent radii are sourced from a report by Alvarez *et al.* in 2008 where values have been compiled based on distances between

given elements and the reference elements C, N or O for structures deposited in the Cambridge Structural Database (CSD). Note that no single element forms a significant enough number of bonds to all of the elements to be used as a reference throughout. Thorough criteria were followed and the methodology is detailed in depth in the publication. The ionic radii are sourced from a report by Shannon in 1976 and were determined from crystallographic data for halides and chalcogenides, utilising plots of radii *vs.* volume, radii *vs.* coordination number and radii *vs.* oxidation state to take into account the influence of factors such as coordination number and valence. Again, details of the thorough criteria used to compile these data are detailed in the publication.

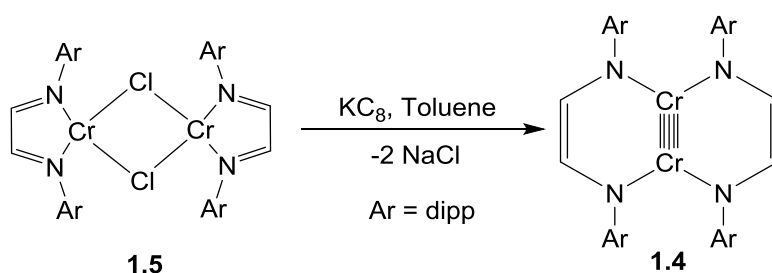
The e.s.d. (estimated standard deviation) of the difference of two values having e.s.d.s x and y is given by $\sqrt{(x^2+y^2)}$. The e.s.d of the difference of two averaged values having e.s.d.s x and y is given by $\sqrt{\{(x^2+y^2)/n^2\}}$ where n is the number of values, in this case two.³¹

1.3 Transition metal-transition metal complexes

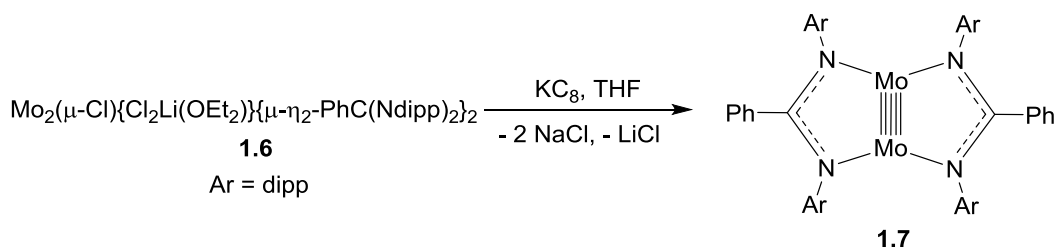
The report of $\text{K}_2[\text{Re}_2\text{Cl}_8]\cdot 2\text{H}_2\text{O}$ (**1.1**) in 1965 by Cotton *et al.* represents the first structurally authenticated complex containing a metal-metal quadruple bond.³²⁻³⁵ Whilst a number of other quadruply bonded transition metal species have been reported since, it was not until 2005 that the first structurally authenticated example of a quintuple bond, between the two Cr centres in $[\text{CrAr}_2]_2$ (**1.2**, Equation 1.1, Ar = C_6H_3 -2,6-bis(dipp) and dipp = 2,6-diisopropylphenyl), was reported by Power *et al.*³⁶ This unsupported Cr-Cr quintuple bond (1.8351(1) Å) was synthesised by the reduction of $[\text{Cr}(\mu\text{-Cl})\text{Ar}]_2$ (**1.3**) with KC_8 and represents a landmark in metal-metal bonding chemistry. The molecular structure determined by single crystal X-ray diffraction coupled with DFT analysis and temperature-independent paramagnetism support the existence of five filled molecular orbitals between the two Cr $3d^5$ centres. Whilst there may be some interaction between the Cr centres and the neighbouring terphenyl groups, indicated with a dashed line in Equation 1.1, this is unlikely to be responsible for the short distance between the metal centres, as evidenced by the considerably greater distances accommodated by the same supporting ligands for the Co and Fe analogues.

Equation 1.1³⁶

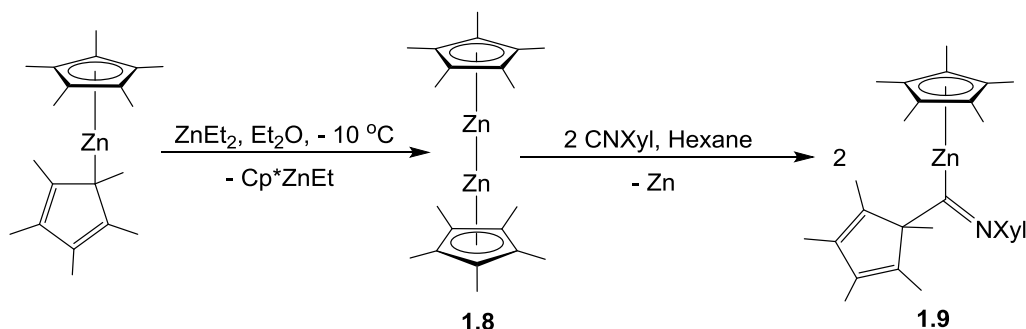
Following **1.2**, the structure of $[\text{Cr}(\mu\text{-}\eta^2\text{-L})]_2$ (**1.4**, Equation 1.2, $\text{L} = \text{N,N}'\text{-bis-(dipp)-1,4-diazadiene}$) was reported,³⁷ containing a Cr-Cr interaction (1.8028(9) Å) with some degree of quintuple bonding, where analysis by DFT gives a bond order of 4.28. Complexity in assigning this results from delocalisation of electron density within the structure. At present this represents one of the shortest molecular inter-metal distances known, resulting from a combination of direct metal-metal interactions and ligand enforced geometric constraints. As with **1.2** this was synthesised *via* KC_8 reduction of a metal chloride precursor, $[\text{Cr}(\text{L})(\mu\text{-Cl})]_2$ (**1.5**).

Equation 1.2³⁷

Complexes with Mo-Mo quintuple bonds have also been reported.³⁸ For example, reduction of quadruply bonded $\text{Mo}_2(\mu\text{-Cl})\{\text{Cl}_2\text{Li}(\text{OEt}_2)\}\{\mu\text{-}\eta^2\text{-PhC}(\text{Ndipp})_2\}_2$ (**1.6**, Equation 1.3) with KC_8 afforded $[\text{Mo}\{\mu\text{-}\eta^2\text{-PhC}(\text{Ndipp})_2\}]_2$ (**1.7**). This results in a decrease in the Mo-Mo distance from 2.0756(8) Å (**1.6**) to 2.0157(4) Å (**1.7**), one of the shortest inter-transition metal distances known beyond the first row.⁵

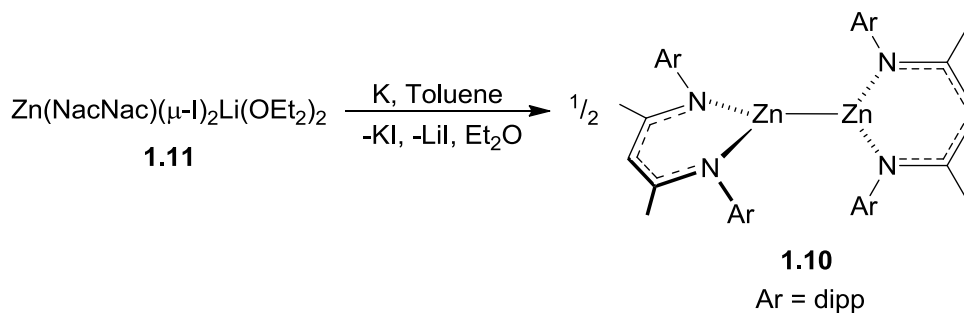
Equation 1.3³⁸

Recent efforts in inorganic chemistry have not only sought to increase the bond order in bimetallic species, but to achieve unprecedented oxidation states. Carmona *et al.* reported the first Zn(I) complex $[\text{Cp}^*\text{Zn}]_2$ (**1.8**, Scheme 1.1),³⁹ with a Zn-Zn distance of 2.305(3) Å, isolated in 45% yield from the reaction of ZnCp^*_2 with ZnEt_2 . This material was found to be susceptible to decomposition in solution and the solid state at temperatures above 0 °C, although storage under argon or vacuum was reported to permit stability at RT. Compound **1.8** was shown to react with CNXyl (2,6-dimethylphenyl isocyanide) to afford the half-sandwich complex iminoacyl species **1.9** as the only product.



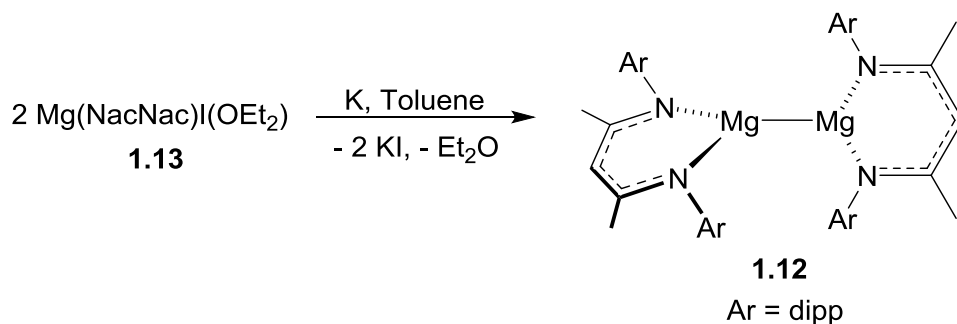
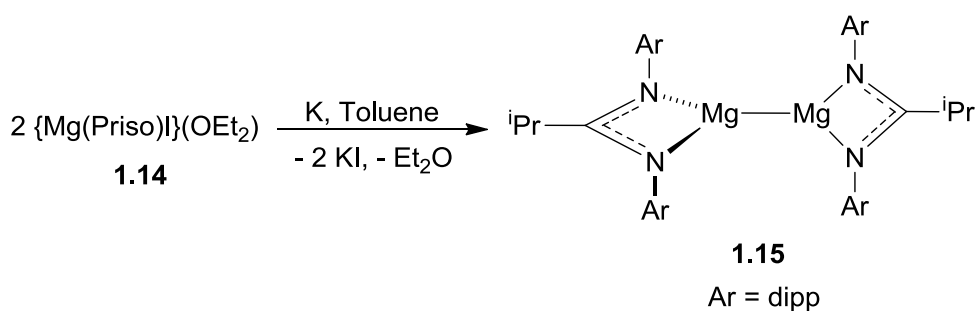
Scheme 1.1. Formation of Zn-Zn bonded **1.8** and its reaction with CNXyl to afford **1.9**.³⁹

The preparation of other Zn-Zn bonded complexes has since been reported.⁴⁰⁻⁴⁶ One example, $[\text{Zn}(\text{NacNac})]_2$ (**1.10**),⁴⁷ with a Zn-Zn distance of 2.3586(7) Å (Equation 1.4), utilises the sterically encumbering NacNac supporting ligand. The NacNac ligand has the formula $[\{(\text{Ar})\text{NC}(\text{Me})\}_2\text{CH}]^-$ (for **1.10** and all other complexes Ar = dipp unless stated otherwise). Whilst still extremely air- and moisture-sensitive, **1.10** is more thermally stable than **1.8**. As with **1.2**, **1.4** and **1.7**, **1.10** was synthesised by reduction of a metal-halogen precursor ($[\text{Zn}(\text{NacNac})(\mu\text{-I})_2\text{Li}(\text{OEt}_2)_2]$, **1.11**), albeit using K/Hg rather than KC_8 .

Equation 1.4⁴⁷

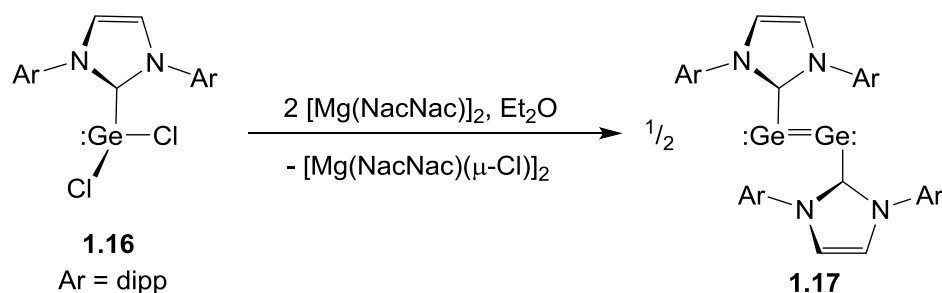
1.4 Alkaline earth-alkaline earth complexes

The NacNac ligand was also employed by Jones *et al.* in 2007 in the synthesis of $[\text{Mg(NacNac)}]_2$ (**1.12**) by reduction of two equivalents of Mg(NacNac)I(OEt) (**1.13**, Equation 1.5) with excess K metal.²³ By analogy, reduction of $\{\text{Mg(Priso)I}\}_2(\text{OEt}_2)$ (**1.14**) gave $[\text{Mg(Priso)}]_2$ (**1.15**, Equation 1.6). Priso = $[(\text{Ar})\text{NC}(\text{NR}_2)\text{N}(\text{Ar})]^-$ where Ar = dipp and R = isopropyl. Compounds **1.12** and **1.15** represent the first examples of molecular Mg-Mg bonded complexes, with distances of 2.8457(8) and 2.8508(12) Å, respectively. These represent not only the first Mg(I) complexes but Ae(I) complexes also, a major milestone in Ae chemistry (Ae = alkaline earth metal).

Equation 1.5²³Equation 1.6²³

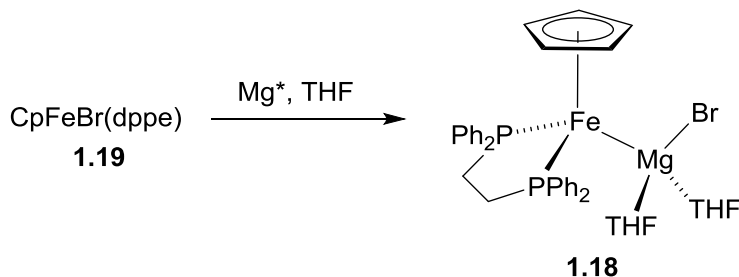
The reactivity of these Mg(I)-Mg(I) complexes with organic substrates and use as

reducing agents has also been demonstrated.^{20-23, 48} For example,⁴⁹ the reduction of $\text{GeCl}_2(\text{IPr})$ (**1.16**) using elemental Na or KC_8 gave reduction to elemental germanium with formation of free IPr, where $\text{IPr} = \text{C}\{\text{N}(\text{dipp})\text{CH}\}_2$. However, reduction with **1.12**, a soluble and milder reducing agent, afforded $[\text{Ge}(\text{IPr})]_2$ (**1.17**, Equation 1.7), albeit in low yields. Complex **1.17** possesses tentatively assigned doubly bonded $\text{Ge}(0)$ centres based on computational calculations and structural features including the near orthogonal coordination of the IPr ligands to the Ge_2 fragment ($\text{C-Ge-Ge} = 89.87(8)^\circ$). Other Ae(I) complexes are yet to be reported.⁵

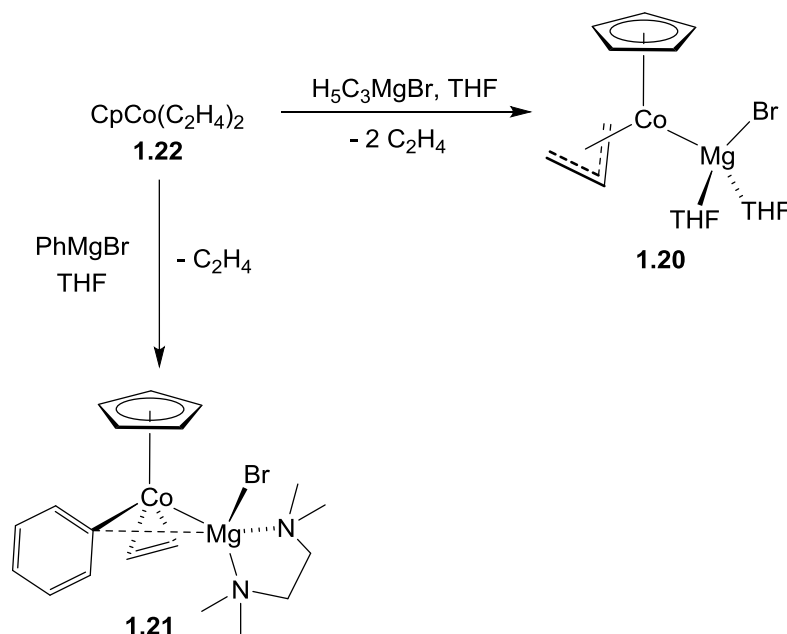
Equation 1.7⁴⁹

1.5 Alkaline earth-transition metal complexes

Despite the expanse of transition metal-transition metal and main group-transition metal bonds known,⁵ little attention has been paid to the area of alkaline earth-transition metal bonding. The first complex bearing a direct Ae-TM bond, $\text{CpFeMgBr}(\text{dppe})(\text{THF})_2$ (**1.18**, Equation 1.8) was reported by Felkin *et al.* in 1974,⁵⁰ synthesised by the reaction of $\text{CpFeBr}(\text{dppe})$ (**1.19**) with an excess of Mg, activated with $\text{BrCH}_2\text{CH}_2\text{Br}$, in THF. The insertion of Mg into the Fe-Br bond is akin to the insertion of Mg into a C-Br bond in the synthesis of organic Grignard reagents.⁵¹ Compound **1.18** contains a four-coordinate Mg centre with a distorted tetrahedral geometry with bonds to two THF ligands, Br and Fe. The Mg-Fe distance of 2.593(7) Å is shorter than the sum of the respective covalent radii (2.73(4) Å).²⁹

Equation 1.8⁵⁰

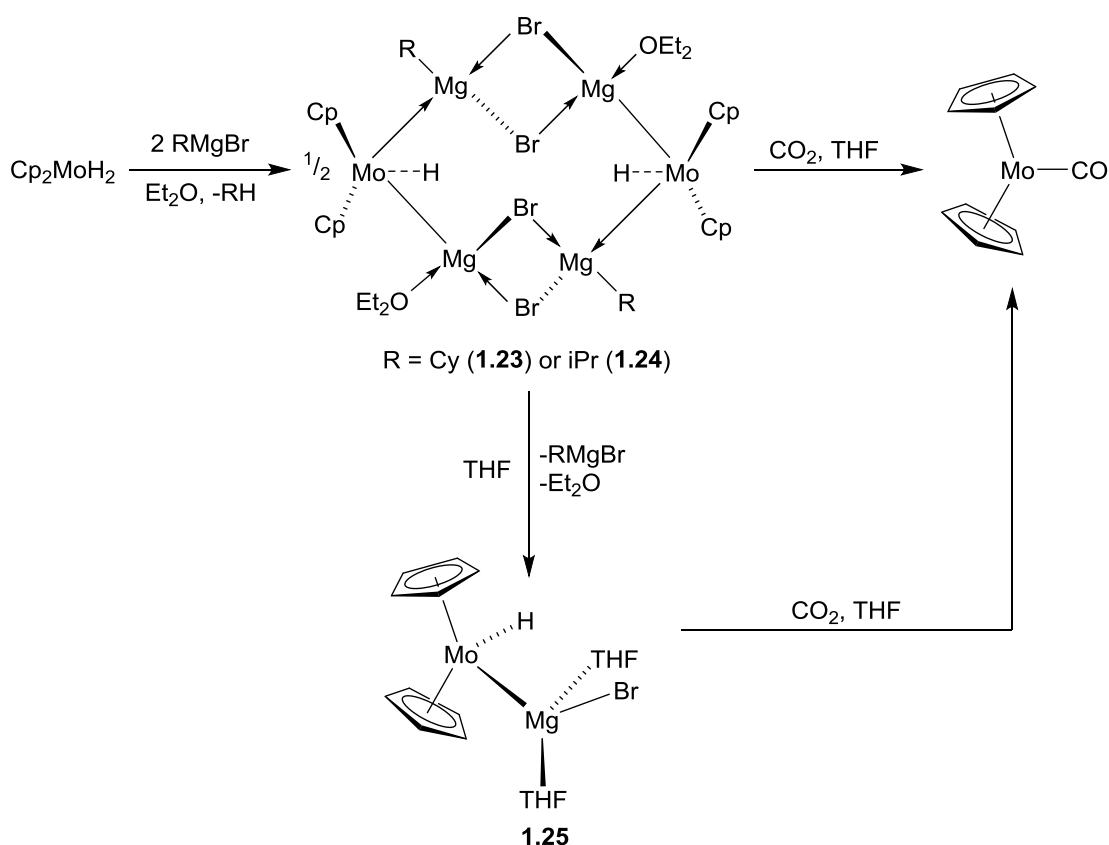
In 1986, Jonas *et al.* reported two structurally authenticated Mg-TM complexes, $\text{CpCo}(\eta\text{-C}_3\text{H}_5)\text{MgBr}(\text{THF})_2$ (**1.20**) and $\text{CpCo}(\text{C}_2\text{H}_4)(\text{Ph})\text{MgBr}(\text{TMEDA})$ (**1.21**) with Mg-Co distances of 2.480(4) and 2.565(3) Å, respectively.⁵² They were synthesised by the reaction of $\text{CpCo}(\text{C}_2\text{H}_4)_2$ (**1.22**) with the corresponding Grignard reagent RMgBr , where $\text{R} = \text{C}_3\text{H}_5$ or Ph , resulting in transfer of the R group to Mg and concomitant Mg-Co bond formation, eliminating ethene in the process (Scheme 1.2). Both of these Mg-Co distances are shorter than that for **1.18** (2.593(7) Å), consistent with the decrease in TM covalent radius, and that predicted for the sum of the respective covalent radii (2.67(8) Å).⁴⁵ Comparing **1.20** and **1.21**, the Mg-Co distance is substantially longer for **1.21**, a consequence of the Mg-Ph interaction, whilst the analogous interaction involving the allyl group in **1.20** is absent. Jonas described the Co-Mg bond in **1.21** as the result of a Lewis acid-base pairing between the electrophilic $[(\text{TMEDA})\text{BrMg}]^+$ cation and $[\text{Cp}(\text{C}_2\text{H}_4)(\text{Ph})\text{Co}]^-$ anion.



Scheme 1.2. Synthesis of $\text{CpCo}(\eta\text{-C}_3\text{H}_5)\text{MgBr}(\text{THF})_2$ (**1.20**) and $\text{CpCo}(\text{C}_2\text{H}_4)(\text{Ph})\text{MgBr}(\text{TMEDA})$ (**1.21**) from $\text{CpCo}(\text{C}_2\text{H}_4)_2$ (**1.22**).⁵²

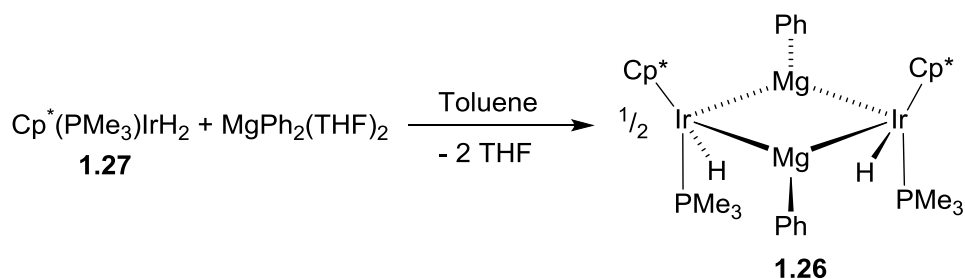
Green *et al.* synthesised the cyclohexyl and isopropyl derivatives of $[\text{Cp}_2\text{Mo}(\text{H})\{\text{Mg}(\text{R})\text{Br}(\text{OEt})_2\}_2]_2$ (Scheme 1.3),⁵³⁻⁵⁵ where $\text{R} = \text{Cy}$ (**1.23**) or $i\text{Pr}$ (**1.24**), *via* the reaction of Cp_2MoH_2 with the corresponding Grignard reagent in Et_2O . Despite complications with the quality of the data, citing problems with disorder and space group determination, the connectivity of the solid state structures are unambiguous. The Mg-Mo distances of 2.853(7) and 2.737(6), and 2.76(3) and

2.81(3) Å for **1.23** and **1.24** are consistent with a direct interaction based on the sum of the covalent radii (2.95(9) Å).²⁹ The difference between the Mg-Mo distances within **1.23** and **1.24** reflect the different substituent effects of the alkyl and the Et₂O groups. The hydrides were not located in the difference map and were thought to lie in the Mg-Mo-Mg plane within the ring. These hydrides have been included in Scheme 1.3 and have been positioned in accordance with the original report. Similar complexes to **1.23** and **1.24** were synthesised using an analogous route with variation of the Grignard reagent (RMgX, where R = ⁿBu, Me or Ph). The reactivity of these complexes with small molecules was investigated. For example, reaction with CO₂ afforded Cp₂Mo(CO), consistent with reactivity for alkali metal-TM bonded complexes.⁵⁶ Dissolving **1.23** or **1.24** in THF followed by recrystallisation afforded monomeric Cp₂Mo(H){MgBr(THF)₂} (**1.25**) with an approximately tetrahedral four-coordinate Mg centre with a direct Mg-Mo bond (2.732 Å).^{57, 58} The Mg-Mo distances in **1.23**, **1.24** and **1.25** are longer than the Mg-TM distances in **1.18**, **1.20** and **1.21**, consistent with the larger covalent radius of Mo compared to Fe or Co.²⁹ The reaction of **1.23** or **1.24** with CO₂ was also shown to afford Cp₂Mo(CO). Reactions between Cp₂WH₂ and Grignard reagents (R = Me, ⁱPr, Ph) were also performed and the resulting products reacted with small molecules, these complexes were not structurally authenticated.



Scheme 1.3. Synthesis of $[\text{Cp}_2\text{Mo(H)}\{\text{Mg(R)Br(OEt)}_2\}_2]_2$ (R = Cy (**1.23**) or iPr (**1.24**)) and $\text{Cp}_2\text{Mo(H)}\{\text{MgBr(THF)}_2\}$ (**1.25**) and their reaction with CO_2 to afford $\text{Cp}_2\text{Mo(CO)}$.^{53, 55, 58}

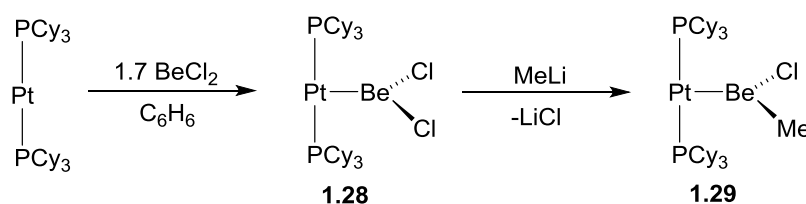
A more recent report of $[\text{Cp}^*\text{Ir(PMe}_3\text{)}(\text{H})\text{MgPh}]_2$ (**1.26**, Equation 1.9) by Bergman *et al.* contains the first example of structurally authenticated Mg-Ir interactions,⁵⁹ with distances of 2.660(2) and 2.750(2) Å, consistent with the sum of the respective covalent radii (2.82(9) Å).²⁹ This is the first and only example of a structurally authenticated direct interaction between Mg and a 3rd row TM.⁵



Equation 1.9⁵⁹

In 2009 Braunschweig *et al.* published the first structurally authenticated example of a

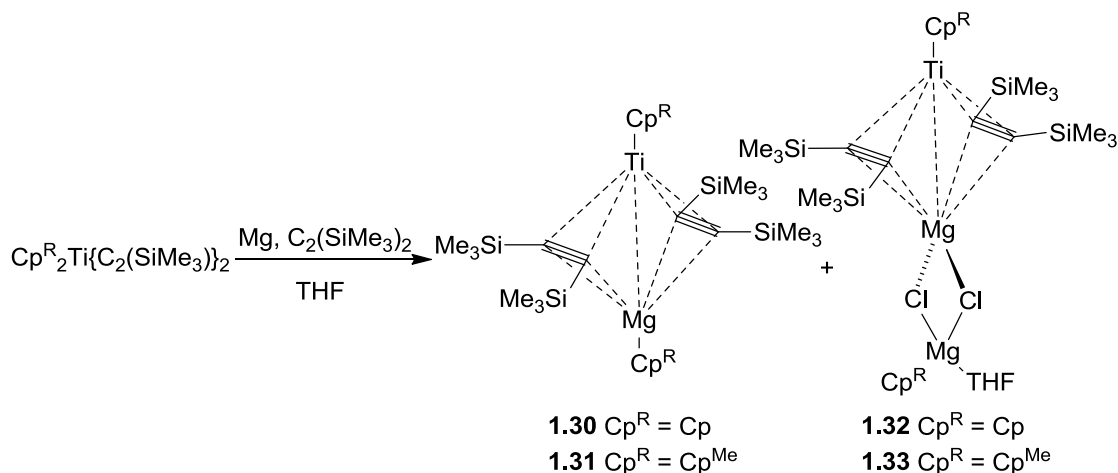
Be-TM bonded complex, $\text{Pt}(\text{PCy}_3)_2\text{BeCl}_2$ (**1.28**, Scheme 1.4), synthesised by the reaction of $\text{Pt}(\text{PCy}_3)_2$ with an excess of BeCl_2 , with a Be-Pt bond distance of 2.168(4) Å.⁶⁰ Complex **1.28** was shown to react with MeLi to form $\text{Pt}(\text{PCy}_3)_2\text{BeMe}(\text{Cl})$ (**1.29**), maintaining a Be-Pt bond (2.195(3) Å). Both of these Be-Pt distances are consistent with that expected based on the sum of the respective covalent radii (2.32(6) Å) and represent the shortest Ae-TM interactions known to date.²⁹ The Be-Pt distance for **1.29** is longer than that for **1.28** and the Cl-Be-C angle (123.70(17) °) for **1.29** is wider than the Cl-Be-Cl angle (118.61(18) °) for **1.28**. DFT calculations involving hypothetical models with smaller phosphine ligands gave shorter Be-Pt interactions and wider Cl-Be-X angles. The calculated bond dissociation energies for **1.28** and **1.29** of 77.6 and 47.8 kJ mol⁻¹ are consistent with the shorter interaction for **1.28**, consistent with its greater Lewis acidity. Unlike the aforementioned work of Felkin and Jonas,^{50, 52} the synthesis of **1.28** and **1.29** do not represent redox processes. Indeed, the Lewis acid-base pairing has been demonstrated for other direct Pt(0)-main group metal interactions using the $\text{Pt}(\text{PCy}_3)_2$ moiety.⁶¹⁻⁶⁵



Scheme 1.4. Reaction of $\text{Pt}(\text{PCy}_3)_2$ with BeCl_2 to afford $\text{Pt}(\text{PCy}_3)_2\text{BeCl}_2$ (**1.28**) and its reaction with MeLi to give $\text{Pt}(\text{PCy}_3)_2\text{BeMeCl}$ (**1.29**).⁶⁰

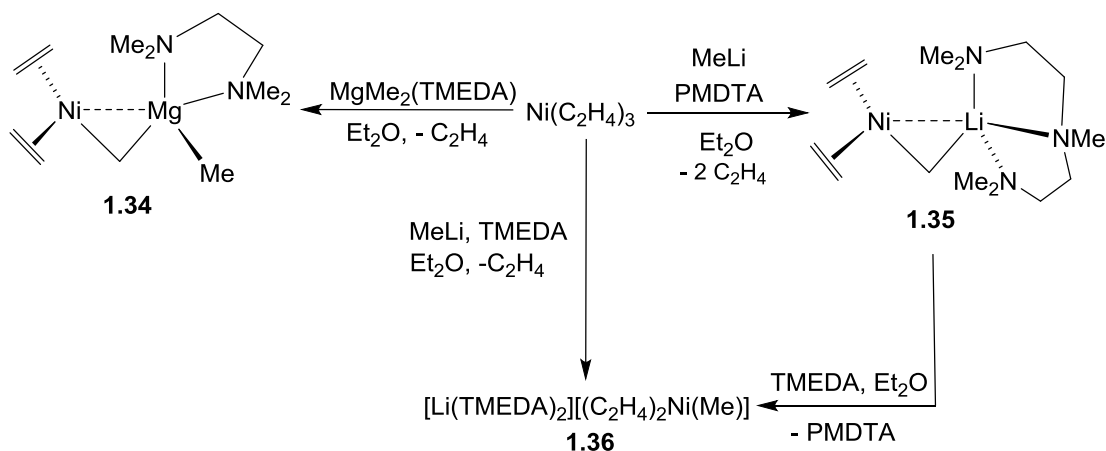
Other structurally authenticated complexes have been reported with potential Ae-TM interactions albeit significantly supported through other interactions such as bridging groups between the metal centres despite having a separation otherwise consistent with a direct interaction. For example, the binuclear complexes $\text{Cp}^{\text{R}}\text{Ti}\{\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_2(\text{SiMe}_3)_2\}_2\text{Cp}^{\text{R}}\text{Mg}$ where Cp^{R} is $\eta^5\text{-C}_5\text{H}_5$ (**1.30**) or $\eta^5\text{-C}_5\text{H}_4\text{Me}$ (**1.31**) and trinuclear complexes $\text{Cp}^{\text{R}}\text{Ti}\{\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_2(\text{SiMe}_3)_2\}_2\{\text{Mg}(\mu\text{-Cl})_2\}\text{Cp}^{\text{R}}\text{Mg}(\text{THF})$, where Cp^{R} is $\eta^5\text{-C}_5\text{H}_4\text{Me}$ (**1.32**) or $\eta^5\text{-C}_5\text{H}_3\text{Me}_2$ (**1.33**), show a range of $\text{Mg}\cdots\text{Ti}$ distances (2.755(4)-2.768(2) Å).²⁵ These values are relatively constant across the range of structures, where a bonding interaction is proposed to exist between the Mg(II) and Ti(II) centres with the Ti d² electrons delocalized in low energy π^* -orbitals. However, the C-C-Si angles (137.4(5)-139.9(16) °) are indicative of significant sp² hybridisation at the acetylenic carbons atoms, consistent with these ligands pulling the metal centres

closer together. Compounds **1.30-1.33** were obtained from the reaction depicted in Equation 1.10.



Equation 1.10²⁵

Reaction of $\text{Ni}(\text{C}_2\text{H}_4)_3$ with $\text{MgMe}_2(\text{TMEDA})$ afforded $\text{Mg}(\text{Me})_2\text{Ni}(\text{C}_2\text{H}_4)_2(\text{TMEDA})$ (**1.34**, Scheme 1.5) with a $\text{Mg}\cdots\text{Ni}$ distance of 2.615(1) Å,^{66, 67} consistent with the sum of the respective covalent radii (2.65(8) Å),²⁹ albeit with a bridging methyl group between these metal centres. This motif is similar to that observed in $\text{Li}(\text{Me})\text{Ni}(\text{C}_2\text{H}_4)(\text{PMDTA})$ (**1.35**, PMDTA = pentamethyldiethylenetriamine) with $\text{Li}\cdots\text{Ni}$ distances of 2.689(7) and 2.722(8) Å (two independent molecules in the asymmetric unit),²⁶ consistent with the sum of the respective covalent radii (2.52(8) Å).²⁹ Addition of TMEDA to **1.35** led to the displacement of PMDTA and formation of the separated ion pair $[\text{Li}(\text{TMEDA})_2][\text{Ni}(\text{C}_2\text{H}_4)_2\text{Me}]$ (**1.36**).

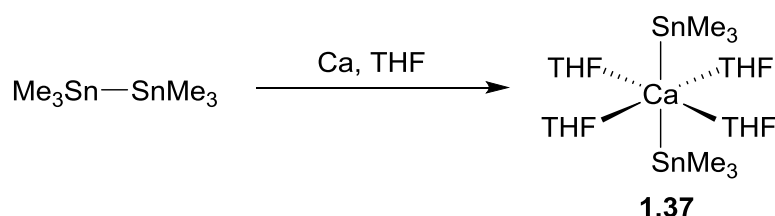


Scheme 1.5. Synthesis of $\text{Ni}(\text{C}_2\text{H}_4)_2\text{MgMe}_2(\text{TMEDA})$ (**1.34**), $\text{Li}(\text{Me})\text{Ni}(\text{C}_2\text{H}_4)(\text{PMDTA})$ (**1.35**) and $[\text{Li}(\text{TMEDA})_2][\text{Ni}(\text{C}_2\text{H}_4)_2\text{Me}]$ (**1.36**).²⁶

1.6 Alkaline earth-main group metal complexes

Including those complexes with partial direct Ae-TM interactions, it is evident that there are relatively few reports of these interactions in the literature, where those involving Ca, Sr and Ba are absent. However, structurally authenticated examples are known with direct interactions between Ae and main group metals.

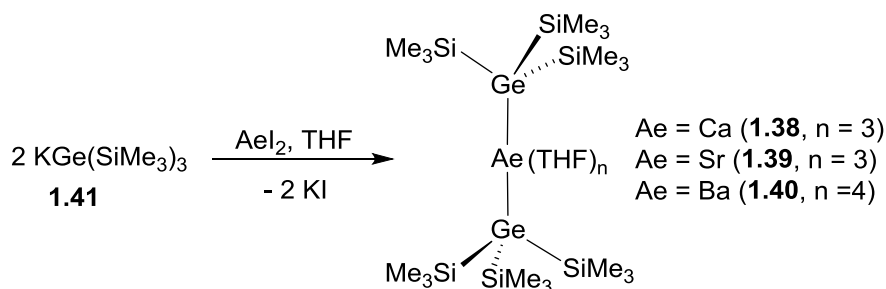
$\text{Ca}(\text{SnMe}_3)_2(\text{THF})_4$ (**1.37**, Equation 1.11) reported by Westerhausen *et al.* in 1994 contains the first structurally authenticated example of an Ae-main group metal bond.⁶⁸ This was synthesised by the insertion of elemental (distilled) Ca into the Sn-Sn bond of $[\text{SnMe}_3]_2$ to afford **1.37**, with approximately octahedral geometry at the Ca centre with *trans*-axial Ca-Sn (3.2721(3) Å) interactions and four equatorial THF ligands. The Ca-Sn distances are consistent with the sum of the respective covalent radii (3.15(11) Å).²⁹



Equation 1.11⁶⁸

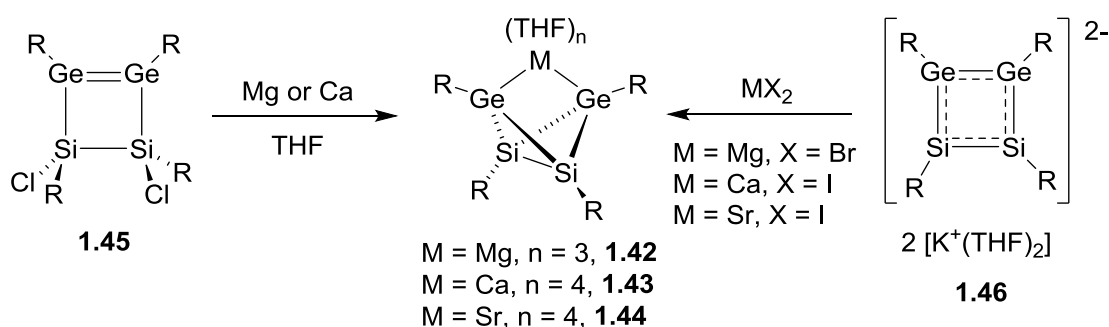
In 2004 Teng and Ruhlandt-Senge reported the series of complexes $\text{Ae}\{\text{Ge}(\text{SiMe}_3)_3\}_2(\text{THF})_n$, where Ae = Ca (**1.38**, $n = 3$), Sr (**1.39**, $n = 3$) or Ba (**1.40**, $n = 4$).⁶⁹ These were synthesised by the salt-metathesis reaction of two equivalents of $\text{KGe}(\text{SiMe}_3)_3$ (**1.41**) with the corresponding AeI_2 (Equation 1.12). Compounds **1.38**-**1.40** feature two Ae-Ge bonds with average distances of 3.022(2), 3.147(5) and 3.398(9) Å, respectively. These are consistent with that expected based on the sums of the covalent radii (2.96(11), 3.15(11) and 3.35(12) Å).²⁹ The structures of five-coordinate **1.38** and **1.39** are approximately trigonal bipyramidal and that of six-coordinate **1.40** is approximately octahedral. Comparing the O-Ae-O angles for the *trans*-axial THF ligands in approximately trigonal bipyramidal **1.38** and **1.39** with the Ga-Ba-Ga angle in approximately octahedral **1.40**, the extent of *trans*-angle compression, i.e. the deviation from the ideal 180°, increases on descending Group 2 (155.1(2), 150.13(10) and 140.52(2)°), consistent with increasing bond lengths that permit greater flexibility with reduced repulsion between the bulky groups in addition to increased ionic character that results in weaker Ae-Ge interactions. These contrast

with Westerhausen's **1.37**, with a Sn-Ca-Sn angle of 180°.



Equation 1.12⁶⁹

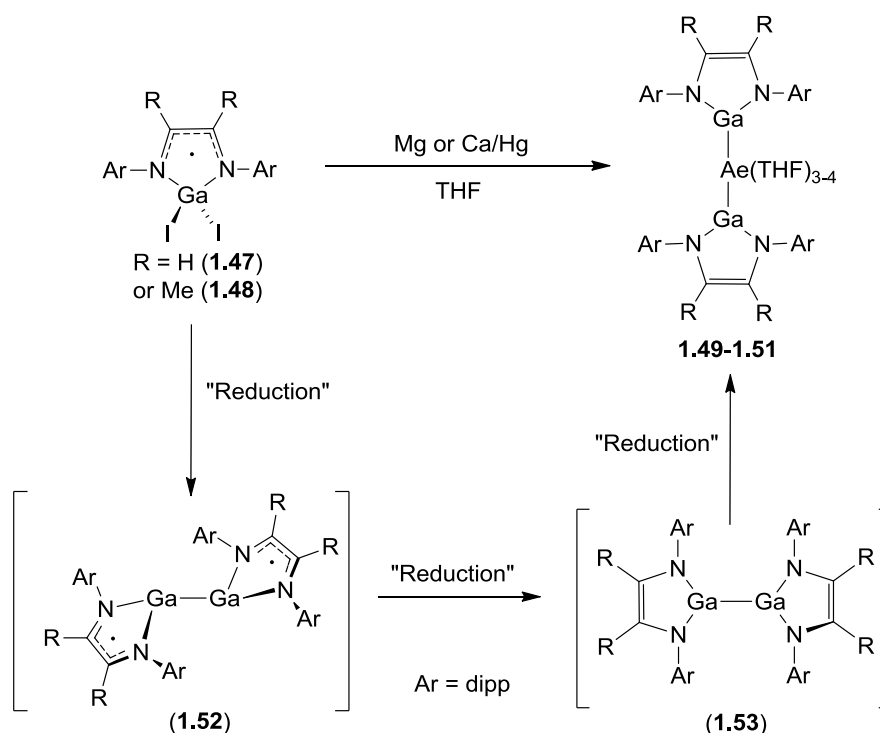
Also in 2004, Sekiguchi *et al.* reported the series of complexes $\text{Ae}\{(\text{GeR})(\text{SiR})\}_2(\text{THF})_n$, where $\text{Ae} = \text{Mg}$ (**1.42**, $n = 3$), Ca (**1.43**, $n = 4$) or Sr (**1.44**, $n = 4$) and $\text{R} = \text{SiMe}^t\text{Bu}_2$.⁷⁰ These were synthesised by the routes illustrated in Scheme 1.5, where reduction of $[\text{Ge}(\text{R})\text{Si}(\text{R})(\text{Cl})]_2$ (**1.45**) with elemental Mg or Ca gave **1.42** or **1.43**, respectively. Compounds **1.42** and **1.43** could also be synthesised by the salt metathesis reaction of $[\text{K}(\text{THF})_2]_2[\text{Ge}(\text{R})\text{Si}(\text{R})]_2$ (**1.46**) with the corresponding AeI_2 , also providing a synthetic route to **1.44**. For **1.42**–**1.44** the Ae occupies the bridgehead position to give two Ae-Ge bonds with five- (**1.42**) and six-coordinate (**1.43** and **1.44**) Ae centres. The average Mg-Ge (2.696(2) Å), Ca-Ge (3.038 Å) and Sr-Ge (3.128 Å) distances are consistent with that expected based on the sums of the respective covalent radii (2.61(8), 2.96(11) and 3.15(11) Å).²⁹ The acute interplanar Ge-Si-Si-Ge (φ) angles, **1.42** (98.90 °), **1.43** (102.30°) and **1.44** (104.90 °) are consistent with the increasing size of the Ae metal.



Scheme 1.5. Synthesis of $\text{Ae}\{(\text{GeR})(\text{SiR})\}_2(\text{THF})_n$, where $\text{R} = \text{SiMe}^t\text{Bu}_2$ and $\text{Ae} = \text{Mg}$ (**1.42**, $n = 3$), Ca (**1.43**, $n = 4$) or Sr (**1.44**, $n = 4$).⁷⁰

Jones *et al.* have synthesised complexes containing Ae-Ga bonds through use of Ga heterocycles.⁷¹ Reactions of $\text{GaI}_2(\text{ArNCR})_2$ ($\text{R} = \text{H}$ (**1.47**) or Me (**1.48**)) with an

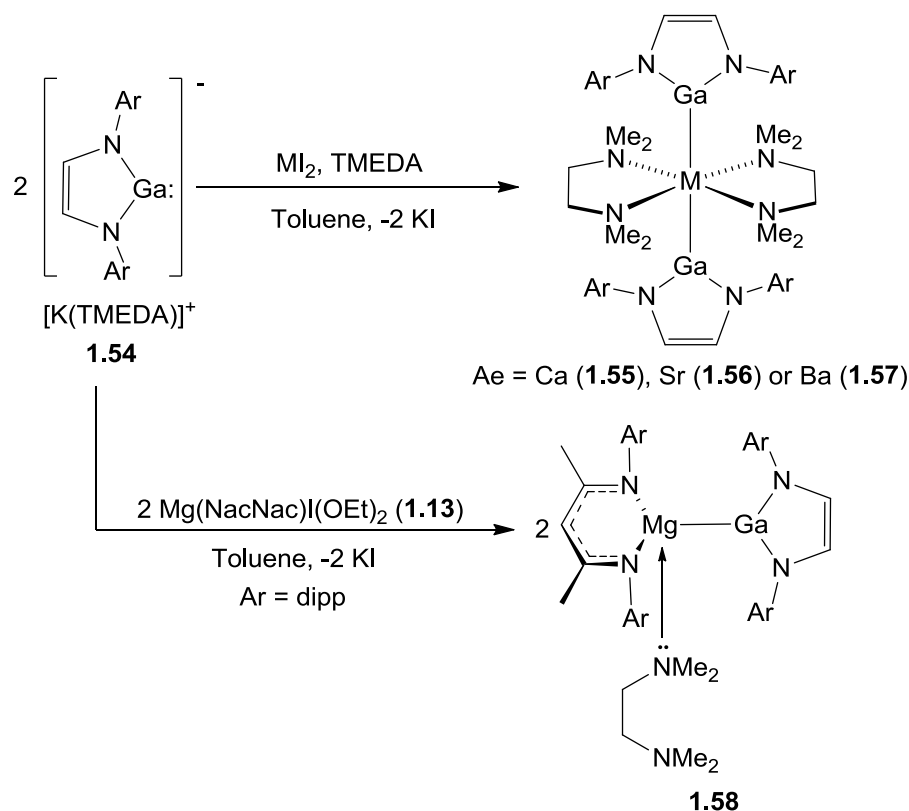
excess of Mg or Ca metal in the presence of Hg gave $\text{Ae}\{\text{Ga}(\text{ArNCR})_2\}_2(\text{THF})_n$ where Ar = dipp and Ae = Mg (**1.49**, R = H and n = 3) or Ae = Ca (n = 4) and R = H (**1.50**) or R = Me (**1.51**), as illustrated in Scheme 1.6. Compounds **1.49-1.51** represent the first structurally authenticated Mg- and Ca-Ga interactions. Investigations showed these to form *via* the intermediates **1.52** and **1.53** (for R = H or Me). Interestingly, attempts to form the Sr and Ba analogues of **1.50** and **1.51** were unsuccessful, forming **1.53** but failing to proceed beyond this even at higher temperatures, extended reactions times and using enhanced metal activation *via* sonication. As commented by Jones, given **1.53** was formed in these processes it cannot be a consequence of metal surface inactivity but a result of the differing reactivities of the elemental Ae. These observations are somewhat counterintuitive given the increased electropositivity of the heavier Ae metals. Compound **1.49** has a distorted trigonal bipyramidal geometry with the gallyl ligands in equatorial positions ($\text{Ga-Mg-Ga} = 127.32(6)^\circ$). Whereas **1.50** and **1.51** are very similar with octahedral geometries with *trans*-axial gallyl groups ($\text{Ga-Ca-Ga} = 180^\circ$). The Mg-Ga distances in **1.49** ($2.7174(15) \text{ \AA}$) are shorter than that for the Ca-Ga distances in **1.50** ($3.1587(6) \text{ \AA}$) and **1.51** ($3.1988(12) \text{ \AA}$), consistent with the increased covalent radius of the Ae metal centre. These distances are consistent with the sums of the respective covalent radii ($\text{Mg-Ga} = 2.63(8)$ and $\text{Ca-Ga} = 2.98(10) \text{ \AA}$).²⁹ The parameters associated with the gallyl fragments were found to be intermediate of those previously reported for the free and complexed heterocycle,⁷²⁻⁷⁸ consistent with significant ionic character in these Ae-Ga interactions. DFT calculations for model complexes were consistent this, where the ionic character increased from Mg to Sr.



Scheme 1.6. Reduction of GaI₂(ArNCR), where R = H (**1.47**) or Me (**1.48**) to Ae{Ga(ArNCR)₂}₂(THF)_n via intermediates **1.52** and **1.53**. For Ae = Mg, R = H (**1.49**) and n = 3. For Ae = Ca, R = H (**1.50**) or Me (**1.51**) and n = 4.⁷¹

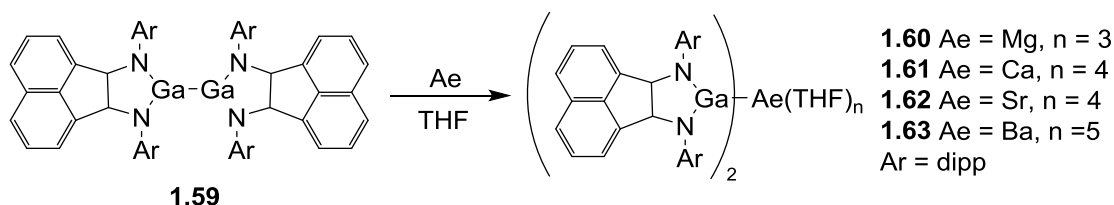
Jones *et al.* have extended their use of gallium heterocycles to increase the number of Ae-main group bonds known.⁷⁹ Reaction of *in situ* generated MI₂(TMEDA)_n, where M = Ca, Sr or Ba with two equivalents of [K(TMEDA)][Ga(ArNCH)₂] (**1.54**, Ar = dipp), afforded Ae{Ga(ArNCH)₂}₂(TMEDA)₂ for Ae = Ca (**1.55**), Sr (**1.56**) and Ba (**1.57**). The presence of TMEDA (tetramethylethylenediamine) in these reactions was found to be crucial to their success. Compounds **1.55-1.57** have isostructural octahedral geometries with two *trans*-axially bound gallyl groups and two equatorial bidentate TMEDA ligands. The average Ae-Ga distances show an increase Ca (3.228(1) Å) < Sr (3.324(1) Å) < Ba (3.464(8) Å), consistent with the increasing Ae covalent radii.²⁹ It is unsurprising that the Ca-Ga distances in **1.55** are greater than in **1.50** or **1.51**, given the greater steric bulk around the Ca centre in the former. The synthesis of the Mg analogue could not be achieved, unsurprising considering the sterically demanding nature of the gallyl and TMEDA ligands that would be required to occupy the Mg coordination sphere, smaller than that of its heavier congeners. However, reaction of **1.54** with Mg(NacNac)I(OEt₂) (**1.13**) afforded Mg(NacNac)(κ¹-TMEDA){Ga(ArNCH)₂} (**1.58**), bearing a direct Mg-Ga bond (2.7470(7) Å),

illustrated in Scheme 1.7.



Scheme 1.7. Synthesis of TMEDA stabilised Ga-Ae bonded species (**1.55-1.58**), where Ar = dipp.⁷⁹

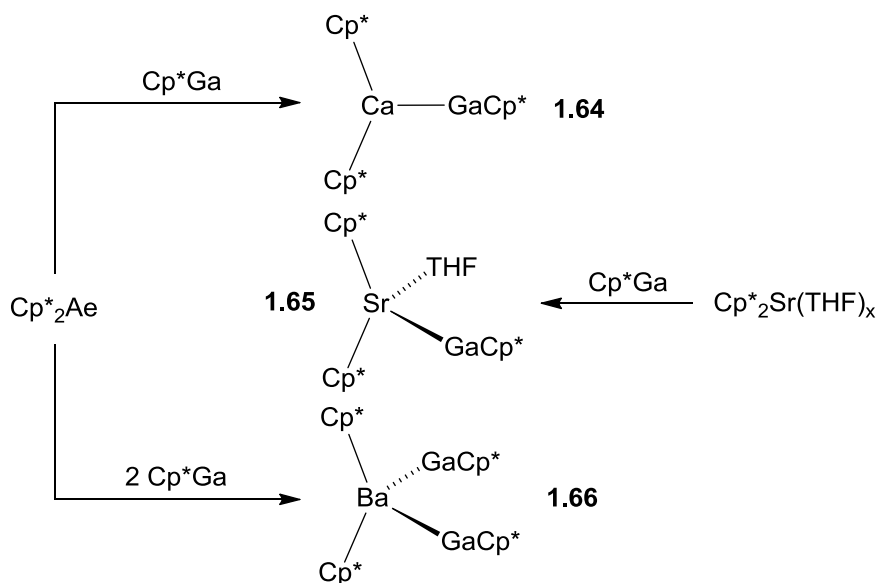
Fedushkin *et al.* have also utilised Ga heterocycles to afford complexes with Ae-Ga bonds.⁸⁰ Reaction of the digallane $[\text{Ga}(\text{dipp-bian})]_2$ (**1.59**), where dipp-bian is 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene, with elemental Ae in THF gave the complexes $\text{Ae}\{\text{Ga}(\text{dipp-bian})\}_2(\text{THF})_n$, where Ae = Mg (**1.60**, $n = 3$), Ca (**1.61**, $n = 4$), Sr (**1.62**, $n = 4$), Ba (**1.63**, $n = 5$) as illustrated in Equation 1.13. Of these, **1.63** was structurally authenticated and found to have an average Ba-Ga distance of 3.6199(9) Å.



Equation 1.13⁸⁰

Shortly after Jones' initial report of Ae-Ga bonding in 2006,⁷¹ Roesky presented a

different approach to achieving complexes with Ae-Ga bonds.⁸¹ Rather than using a heterocyclic Ga(III) moiety, Cp*Ga was reacted with the Cp*₂Ae(THF)_x (Ae = Ca, Sr or Ba) sandwich complexes to afford the corresponding Lewis adducts Cp*₂CaGaCp* (**1.64**), Cp*₂Sr(THF)GaCp* (**1.65**) and Cp*₂Ba(GaCp*)₂ (**1.66**), illustrated in Scheme 1.8. The increasing average Ae-Ga distances, where **1.64** (3.183(2) Å) < **1.65** (3.4348(7) Å) < **1.66** (3.5911(9) Å) and coordination numbers are consistent with the increasing Ae covalent radii, where that for Sr would appear to be intermediate of the requirement to afford a solvent free complex observed for **1.64** and coordination of additional Cp*Ga unit as for **1.66**. Attempted DFT calculations regarding the binding energy of **1.64** relative to Cp*Ga and Cp*₂Ca were unsuccessful, giving a linear structure for Cp*₂Ca and Ca-Ga distance 0.24 Å greater than that observed experimentally. This demonstrates the weak nature of this interaction composed of van der Waals dispersive forces. Alternative MP2 calculations reproduced the bent structure and a Ga-Ca distance 0.12 Å shorter than that observed experimentally.



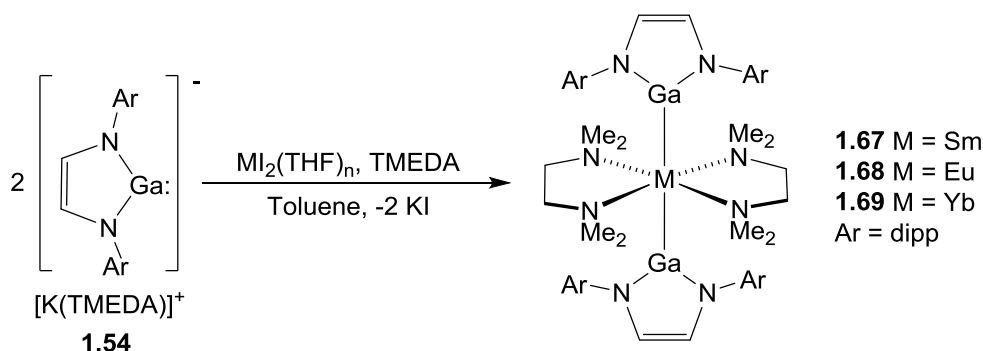
Scheme 1.8. Synthesis of the Ae-Ga Lewis adducts **1.64-1.66** by reaction of Cp*Ga with the corresponding Cp*₂Ae(THF)_x.⁸¹

1.7 Lanthanide-main group metal complexes

Pairings between certain divalent Ae and Ln (lanthanides) can be made based on similar covalent and ionic radii.^{29, 30} For example the covalent radii of Ca (1.76(10) Å) and Yb (1.87(8) Å) are similar, as are their effective ionic radii (Ca²⁺ = 1.00 and Yb²⁺ = 1.02 Å). For Sr the covalent radius (1.95(10) Å) is comparable to those for Sm

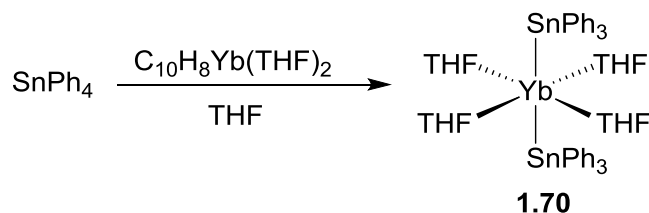
(1.98(8) Å) and Eu (1.98(6) Å). Also the effective ionic radius for Sr^{2+} (1.18 Å) is similar to those for Sm^{2+} (1.22 Å) and Eu^{2+} (1.17 Å). These observations have provided the impetus for studies investigating the structures and reactivities of complexes containing these comparable metals centres. The reader is directed to many excellent publications to this end.⁸⁻¹⁸

Comparable complexes containing Ae- or Ln-metal interactions have also been studied. The most pertinent examples are the $\text{Ln}\{\text{Ga}(\text{ArNCH})_2\}_2(\text{TMEDA})_2$ complexes published by Jones *et al.*,⁸² where Ar is dipp and Ln is Sm (**1.67**), Eu (**1.68**) or Yb (**1.69**) with Sm-, Eu- and (average) Yb-Ga distances of 3.3124(9), 3.3124(11) and 3.2262(10) Å, respectively. The distances for **1.67** and **1.68** are identical, consistent with the respective radii. These complexes are isostructural with their Ca (**1.55**) and Sr (**1.56**) analogues discussed in Section 1.6. The average Ca-Ga distance in **1.55** (3.228(1) Å) is identical within error to the average Yb-Ga distance in **1.69** (3.2262(10) Å). Based on the covalent radius of Yb (1.87(8) Å) *vs.* Ca (1.76(10) Å), one might have expected the Yb-Ga distance to be slightly greater than the Ca-Ga distance. The Sr-Ga distance of 3.324(1) Å in **1.56** is identical within error to the Sm- and Eu-Ga distances in **1.67** and **1.68**, respectively, consistent with the similar radii of Sr, Sm and Eu.



The molecular structure of $\text{Yb}(\text{SnPh}_3)_2(\text{THF})_4$ (**1.70**) published by Bocharov *et al.* in 1991 is comparable to Westerhausen's $\text{Ca}(\text{SnMe}_3)_2(\text{THF})_4$ (**1.37**).⁸³ Compound **1.70** possesses a six-coordinate Yb centre with a distorted octahedral geometry, with *trans*-axial SnPh_3 groups and four THF ligands in the equatorial plane. With the caveat that these structures bear different R-groups, one can compare the Ca-Ga (3.2731(3) Å) interaction in **1.37** with the Yb-Ga interaction (3.305(1) Å) in **1.70**. As expected, the Yb-Ga interaction is longer than the Ca-Ga interaction, consistent with the slightly

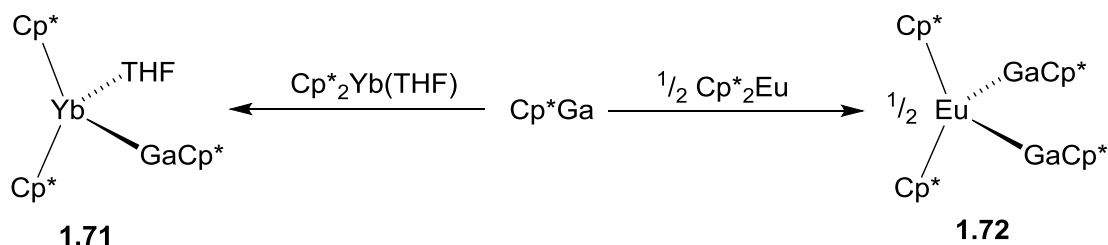
greater covalent and ionic radii for the latter. In contrast to the synthesis of **1.37**, **1.70** was synthesised by the reaction of naphthalene-ytterbium with SnPh_4 in THF, as illustrated in Equation 1.15.



Equation 1.15⁸³

Similarly, Roesky's $\text{Cp}^*_2\text{CaGaCp}^*$ (**1.64**) and $\text{Cp}^*_2\text{Yb}(\text{THF})\text{GaCp}^*$ (**1.71**) are comparable.⁸⁴ Unlike **1.64**, attempts to synthesise a solvent-free version of **1.71** were unsuccessful. Nevertheless, it is apparent that these metal-metal bonded species are structurally similar, where the bent ytterbocene interacts with the gallyl moiety in an analogous fashion to calcocene. The Yb-Ga distance (3.2872(4) Å) is longer than the Ca-Ga distance (3.183(2) Å) and consistent with the sum of the respective covalent radii (3.09(9) Å).²⁹

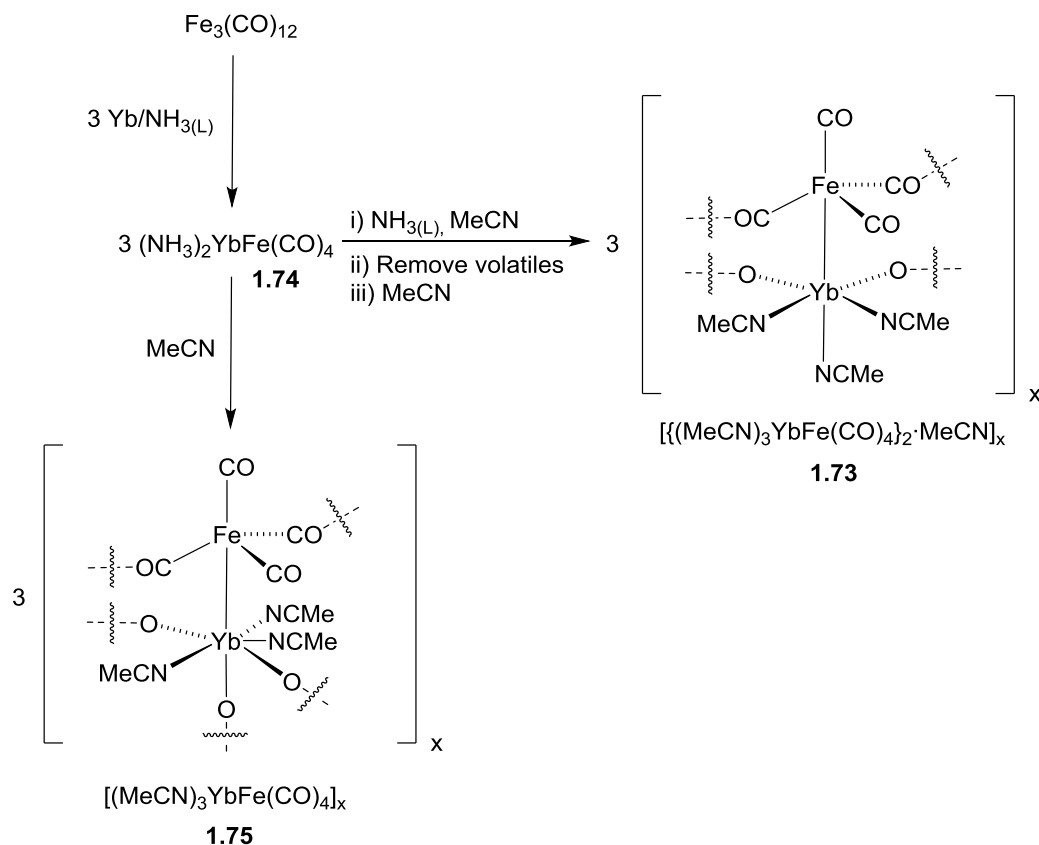
Unlike Jones' **1.56** and **1.68** ($\text{M}\{\text{Ga}(\text{ArNCH})_2\}_2(\text{TMEDA})$, M = Sr or Eu), the structures of $\text{Cp}^*_2\text{Sr}(\text{THF})\text{GaCp}^*$ (**1.65**) and $\text{Cp}^*_2\text{Eu}(\text{GaCp}^*)_2$ (**1.72**) show a distinct difference, where **1.72** coordinates an additional GaCp^* to afford a four-coordinate Eu centre, contrasting with **1.65** which is also four-coordinate but coordinates a THF ligand in place of a M-Ga interaction. Whilst the coordination spheres are different, it is interesting that the average Eu-Ga distance of 3.320(4) Å is shorter than the Sr-Ga distance of 3.4348(7) Å. Indeed, the structure of **1.72** is reminiscent of that for $\text{BaCp}^*_2(\text{GaCp}^*)_2$ (**1.66**).



Scheme 1.9. Synthesis of Lewis adducts $\text{Cp}^*_2\text{Yb}(\text{THF})\text{GaCp}^*$ (**1.71**) and $\text{Cp}^*_2\text{Eu}(\text{GaCp}^*)_2$ (**1.72**).⁸⁴

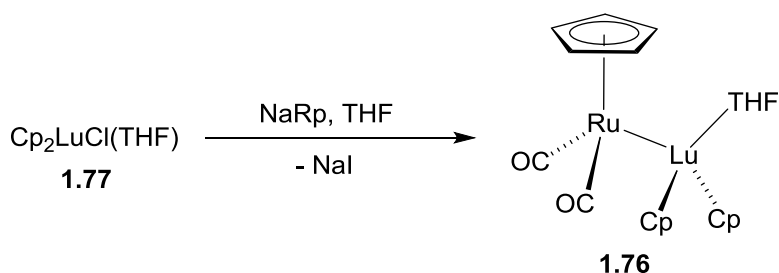
1.8 Lanthanide-transition metal complexes

The first example of a structurally authenticated Ln-TM interaction was reported by Shore *et al.* in 1991.⁸⁵ $[\{(\text{MeCN})_3\text{YbFe}(\text{CO})_4\}_2 \cdot \text{MeCN}]_x$ (**1.73**, Scheme 1.10) was synthesised by the reduction of $\text{Fe}_3(\text{CO})_{12}$ with $\text{Yb}/\text{NH}_3(\text{L})$ and subsequent treatment of the intermediate $(\text{NH}_3)_2\text{YbFe}(\text{CO})_4$, **1.74** with MeCN. Each Yb^{2+} is coordinated to two neighbouring $[\text{Fe}(\text{CO})_4]^{2-}$ units *via* isocarbonyl bridging and each $[\text{Fe}(\text{CO})_4]^{2-}$ to two neighbouring Yb^{2+} cations to give an isocarbonyl linked chain. Importantly, each Yb also has a direct interaction with an Fe centre on a neighbouring chain. The independent distances of 3.012(1) and 3.009(1) Å are shorter than the sum of the respective covalent radii (3.19(9) Å).²⁹ Three MeCN ligands are also coordinated to each Yb centre to give a distorted octahedral geometry. Overall this results in a solid state structure in the form of a polymeric ladder, where the Yb-Fe bonds form the rungs between the $\text{Yb}(\mu\text{-OC})\text{Fe}$ isocarbonyl linked chains. A later report of a slightly different treatment of **1.74** with MeCN, involving quenching of the reaction, afforded $[(\text{MeCN})_3\text{YbFe}(\text{CO})_4]_x$ (**1.75**).⁸⁶ This is similar to the solid state structure of **1.73** but isocarbonyl cross-linking occurs between the Fe and Yb centres on neighbouring polymeric chains to afford a sheet-like structure. Consequently, each Yb centre in **1.75** is seven-coordinate with distorted pentagonal bipyramidal geometry. For **1.75**, the Yb-Fe interactions are longer at 3.046(1) Å, consistent with the higher Yb coordination number for **1.75** compared to **1.73**.

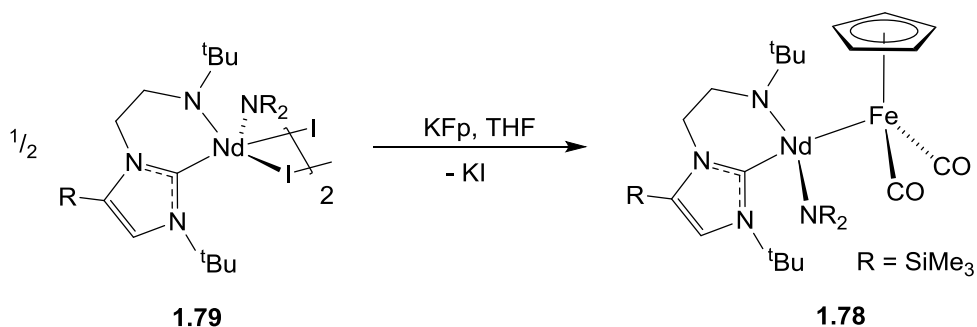


Scheme 1.10. Reduction of $\text{Fe}_3(\text{CO})_{12}$ with $\text{Yb}/\text{NH}_3(\text{L})$ to afford polymeric $[(\text{MeCN})_3\text{YbFe}(\text{CO})_4]_2 \cdot \text{MeCN}]_x$ (**1.73**) and $[(\text{MeCN})_3\text{YbFe}(\text{CO})_4]_x$ (**1.75**).^{85, 86}

In 1993, Beletskaya *et al.* reported the molecular structure of $\text{Cp}_2\text{LuRp}(\text{THF})$ (**1.76**, Equation 1.16), synthesised by the salt-metathesis reaction of $\text{Cp}_2\text{LuCl}(\text{THF})$ (**1.77**) with NaRp , where Rp^- is $[\text{CpRu}(\text{CO})_2]^-$.⁸⁷ Complex **1.76** contains a four-coordinate Lu(III) centre with approximately tetrahedral geometry with two Cp and one THF ligand, and a direct Lu-Ru interaction (2.955(2) Å) that is consistent with the sum of the respective covalent radii (3.38(11) Å).²⁹ This represents the first structurally authenticated example of an Ln-4d metal interaction and unsupported Ln-TM interaction.⁵ The analogous Lu-Fe complex was characterised in THF but a molecular structure was not obtained owing to decomposition within 1 h of preparation. IR spectroscopic analysis of this material in THF and showed two $\nu(\text{CO})$ bands at 1946 and 1859, compared to 2027 and 1965 cm^{-1} for **1.76**.

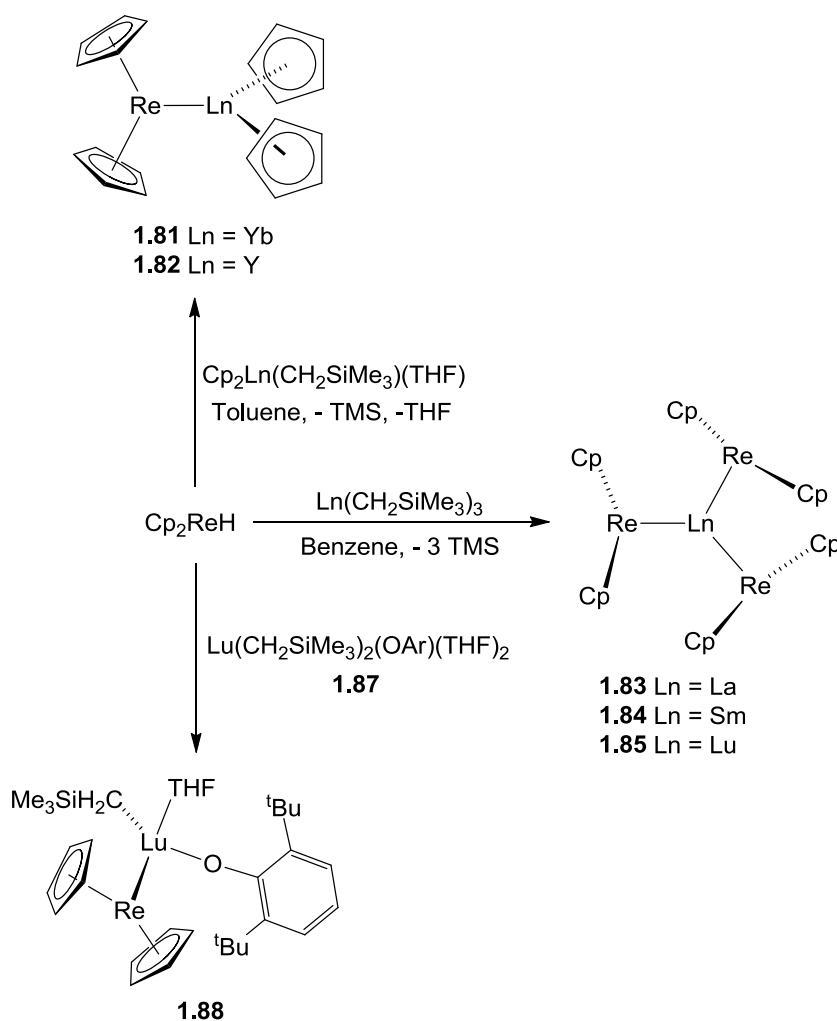
Equation 1.16⁸⁷

Similarly, Arnold *et al.* utilised the Fp^- anion to afford $\text{Nd(L)Fp}\{\text{N}(\text{SiMe}_3)_2\}$ (**1.78**, Equation 1.17), where L is $^t\text{BuNCH}_2\text{CH}_2\{\text{CNCSiMe}_3\text{CHN}^t\text{Bu}\}$, synthesised by the salt-metathesis reaction of $\text{Nd(L)I}\{\text{N}(\text{SiMe}_3)_2\}$ (**1.79**) with KFp .⁸⁸ **1.78** possesses a four-coordinate Nd centre with approximately tetrahedral geometry, coordinated to an amide, bidentate pendent functionalized carbene moiety and Fp^- anion. The latter interaction occurs *via* an Nd-Fe (2.994(1) Å) interaction, the first structurally authenticated example of an unsupported 4f-3d metal-metal bond, which is shorter than the sum of the respective covalent radii (3.33(7) Å).²⁹

Equation 1.17⁸⁸

Much has been contributed to the area of Ln-TM bonding by Kempe *et al.* Reaction of Cp_2ReH with $\text{Cp}_2\text{Yb}(\text{CH}_2\text{SiMe}_3)(\text{THF})$ (**1.80**) in toluene afforded $\text{Cp}_2\text{YbReCp}_2$ (**1.81**, Scheme 1.11),⁸⁹ with an unsupported Yb-Re bond. The Yb-Re distance (2.897(2) Å) is shorter than that for the Y analogue ($\text{Cp}_2\text{YReCp}_2$, **1.82**, 2.962(2) Å), and both are shorter than the sums of their respective covalent radii of (Yb-Re = 3.38(11) and Y-Re = 3.41(10) Å).²⁹ DFT analysis of **1.82** showed a Y-Re bonding basin with a population of 0.83 electrons. The contributions of electron density to this of 84% and 14% from the Re and Y atoms, respectively, are indicative of the strong polarity of this interaction. Analysis of the hypothetical $[\text{Cp}_2\text{Y}]^+$ and $[\text{Cp}_2\text{Re}]^-$ fragments shows the latter to be bent, affording a region of enhanced electron density in the region involved in Y-Re bonding. This contrasts with the linear geometry of the

relaxed $[\text{Cp}_2\text{Re}]^-$ anion, isoelectronic with ferrocene, therefore the bending is a consequence of the metal-metal interaction. Analysis of the $[\text{Cp}_2\text{Y}]^+$ fragment shows a minimum in the valence region that coincides with the direction of the Y-Re interaction. Therefore the Y-Re bond is classed as a donor-acceptor interaction. Given the similarity of **1.81** and **1.82**, it is appropriate to treat the calculations for **1.82** as an indication of the nature of the Yb-Re bond, that is, a polar donor-acceptor interaction. One notes that whilst Y is not a lanthanide, it is a rare earth metal and therefore shares similar properties as illustrated in this example.

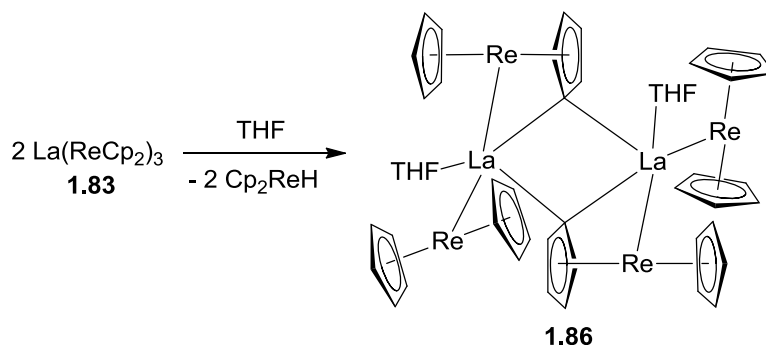


Scheme 1.11. Synthetic routes to Ln-Re bonded species **1.81-1.85** and **1.88**.⁸⁹⁻⁹¹

In a separate report, Kempe *et al.* reported the synthesis of $\text{Ln}(\text{Cp}_2\text{Re})_3$,⁹⁰ where Ln is La (**1.83**), Sm (**1.84**) or Lu (**1.85**), *via* reaction of the corresponding $\text{Ln}\{\text{CH}(\text{SiMe}_3)_2\}_3$ with three equivalents of Cp_2ReH (Scheme 1.11). Compounds **1.83-1.85** exhibit trigonal planar geometry, where Ln-Re distances decrease from **1.83** (3.0478(5) Å) to **1.84** (2.9734(6) Å) to **1.85** (2.8862(4) Å), consistent, albeit much

shorter, than the trend in the sums of the respective covalent radii (3.58(11), 3.49(11) and 3.38(11) Å).²⁹ The isolated yields of these materials were low (1-34%), attributed to their high reactivity, giving polymeric insoluble by-products (66-99%). Nevertheless their molecular structures clearly demonstrate the ability of the [Cp₂Re]⁻ anion to interact with the complete range of lanthanides in terms of size such that Ln-Re bonding is achieved. DFT analysis of **1.85** supported the existence of La-Re bonds, slightly more polar than those for **1.82**, comprising sizeable electrostatic and orbital terms.

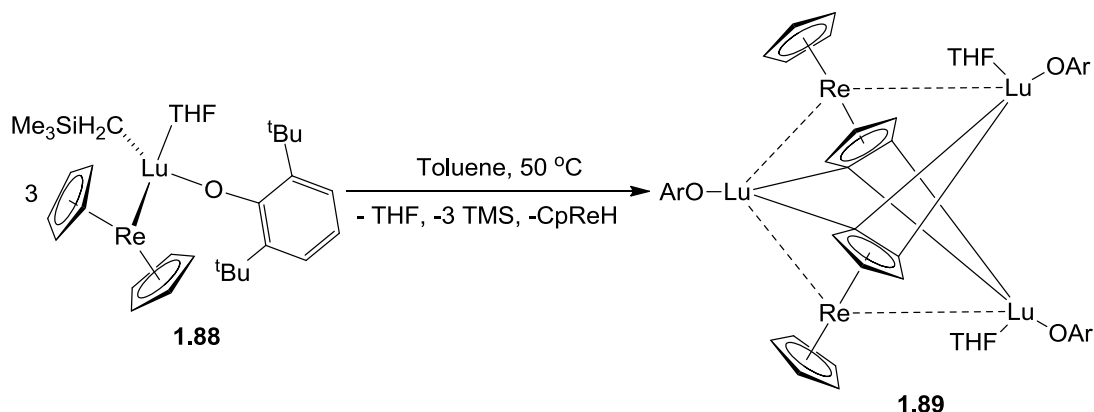
Reaction of **1.83** with THF afforded hexanuclear **1.86** (Equation 1.18) *via* decomposition of one of the metal-metal bonds per **1.83** and Cp₂ReH elimination. Compound **1.86** contains four La-Re interactions (3.0902(8), 3.1089(8), 3.0721(8) and 3.1017(9) Å) consistent with the sum of the respective covalent radii (3.58(11) Å).²⁹ In contrast **1.85** was found to be stable in THF, attributed to the smaller size of the low-coordinate Lu and better ligand shielding as a result. The reaction between **1.83** and Cp₂ReH in THF also afforded **1.86**, highlighting the importance of avoiding THF in these reactions. Compound **1.86** may give some indication of the insoluble polymeric products formed in the synthesis of **1.83-1.85**, albeit lacking THF.



Equation 1.18⁹⁰

The reaction of Lu(CH₂SiMe₃)₂(OAr)(THF)₂ (**1.82**), where ArOH is 2,6-di-tert-butylphenol, with one equivalent of Cp₂ReH afforded Lu(ReCp₂)(CH₂SiMe₃)(OAr)(THF) (**1.88**, Scheme 1.11), bearing a chiral four-coordinate Lu centre with tetrahedral geometry.⁹¹ VT-NMR studies confirmed the THF ligand to be labile at RT, enabling racemisation *via* a three coordinate intermediate. The Lu-Re distance of 2.8498(6) Å is significantly shorter than the average Lu-Re distance of 2.8862(4) Å in **1.85** and that of the sum of the covalent radii (3.38(11) Å).²⁹ The yield of this material (89%) is considerably greater than that

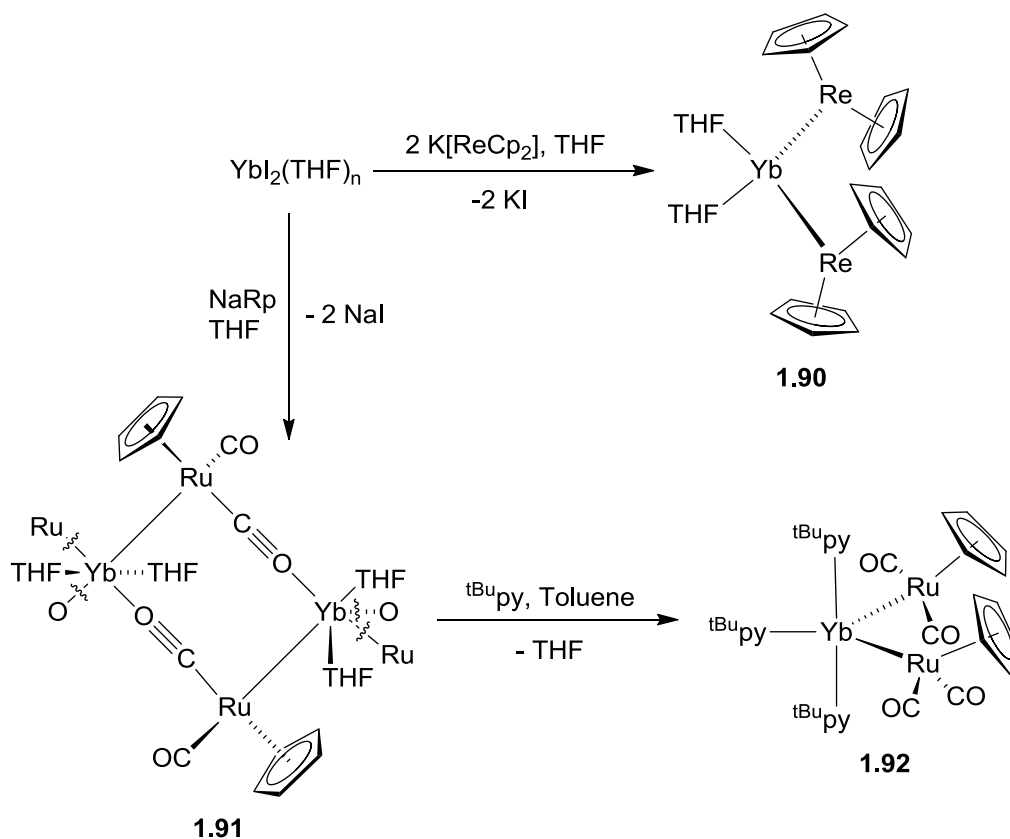
for the synthesis of **1.83-1.85**. However, heating a toluene solution of **1.88** to 50 °C resulted in the formation of the cluster compound (**1.89**) illustrated in Equation 1.19 *via* the elimination of TMS and Cp₂ReH. The Lu-Re distances (2.9981(4), 2.9842(4), 2.9120(4) and 2.9179(4) Å) are shorter than the sum of the respective covalent radii.²⁹ Note the unusual 1,2-bis-deprotonations of two of the Cp rings, rarely observed for a metallocene.⁹² DFT analysis was consistent with these bonds having a polar donor-acceptor character.



The reaction of two equivalents of K[Cp₂Re] with YbI₂(THF)_n gave Yb(ReCp₂)₂(THF)₂ (**1.90**, Scheme 1.12), demonstrating the ability of the Cp₂Re moiety to form bonds with Ln(II) as well as Ln(III) centres.⁹³ It also shows the ability to form these bonds using a salt-metathesis as well as alkane-elimination approach. Compound **1.90** bears a four-coordinate Yb centre with distorted tetrahedral geometry, with two direct Yb-Re interactions. The distances of 3.0366(7) and 3.0208(7) Å are consistent with the sum of the respective covalent radii (3.38(11) Å) and longer than those observed in **1.81** (2.897(2)), a result of the higher coordination number at the Yb(II) rather than Yb(III) centre, where the ionic radius of Yb²⁺ = 1.02 and Yb³⁺ = 0.868 Å.^{29, 30}

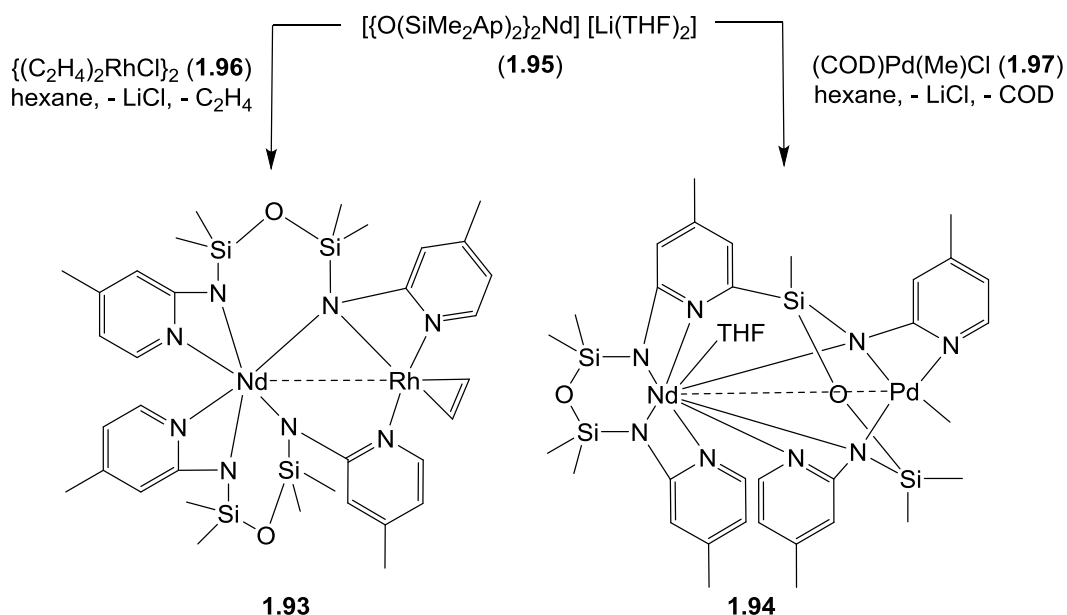
In the same report,⁹³ the reaction of two equivalents of NaRp(THF) with YbI₂(THF)_n to give [YbRp₂(THF)₂]_x (**1.91**, Scheme 1.12) was described. Compound **1.91** is polymeric in the solid state with each six-coordinate Yb having approximately octahedral geometry, coordinated to two THF ligands and four Rp⁻ anions. Two of these Ru···Yb interactions involve Yb(μ-OC)Ru isocarbonyl linkages and the other two comprise Yb-Ru bonds. These bond distances (3.1808(7) and 3.1391(8) Å) are consistent with the sum of the respective covalent radii (3.33(11) Å).²⁹ Addition of 4-

tert-butylpyridine ($t^{\text{Bu}}\text{py}$) to **1.91** broke up the polymeric structure to give $\text{YbRp}_2(t^{\text{Bu}}\text{py})_3$ (**1.92**), a monomer with direct Yb-Ru interactions only. The Yb-Ru distances of 3.1029(4) and 3.0626(4) Å are shorter than those in **1.91**, a result of the decrease from a six- to five-coordinate Yb centre. DFT analysis of both **1.91** and **1.92** are consistent with the Yb-Re and Yb-Ru bonds being classed as polar covalent.



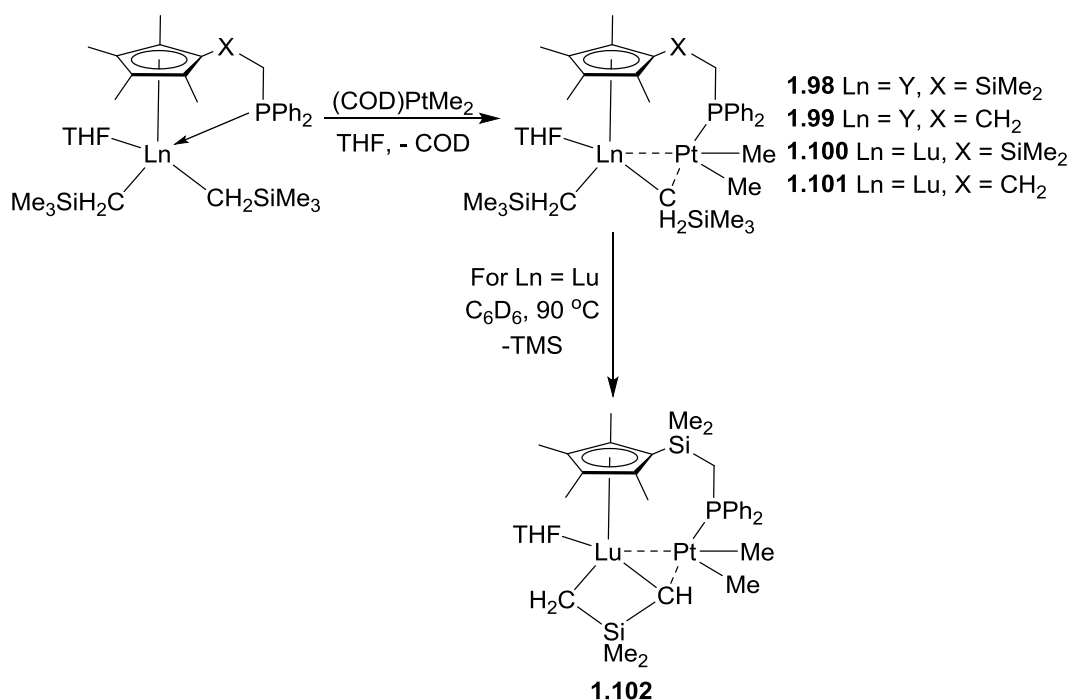
Scheme 1.12. Synthesis of Yb-Re ($\text{Yb}(\text{ReCp}_2)_2(\text{THF})_2$ (**1.90**)) and Yb-Ru ($[\text{YbRp}_2(\text{THF})_2]_x$ (**1.91**) and $\text{YbRp}_2(t^{\text{Bu}}\text{py})_3$ (**1.92**)) bonded complexes.⁹³

Kempe *et al.* have also synthesised $\{\text{O}(\text{SiMe}_2\text{N}-2-\text{C}_5\text{H}_3\text{N}-4-\text{Me})_2\}_2\text{NdRh}(\eta^2-\text{C}_2\text{H}_4)$ (**1.93**) and $\{\text{O}(\text{SiMe}_2\text{N}-2-\text{C}_5\text{H}_3\text{N}-4-\text{Me})_2\}_2\text{Nd}(\text{THF})\text{Pd}(\text{Me})$ (**1.94**),⁹⁴ by the reaction of $[\{\text{O}(\text{SiMe}_2)\text{Ap}_2\}_2\text{Nd}][\text{Li}(\text{THF})_2]$ (**1.95**) with $\text{Rh}(\text{C}_2\text{H}_4)(\text{Cl})$ (**1.96**) or $(\text{COD})\text{Pd}(\text{Me})(\text{Cl})$ (**1.97**), respectively, where $\text{O}(\text{SiMe}_2\text{ApH})_2$ is $\text{O}\{\text{Si}(\text{Me})\text{NH}(4-\text{CH}_3\text{C}_5\text{H}_3\text{N})\}_2$ and COD is 1,5-cyclooctadiene. Compounds **1.93** and **1.94** have close Nd $\cdots$ Rh and Nd $\cdots$ Pd separations of 2.974(2) and 3.035(2) Å, respectively, shorter than the sums of the respective covalent radii (Nd-Rh = 3.43(9) and Nd-Pt = 3.37(8) Å).²⁹



Scheme 1.13. Synthesis of $\{O(SiMe_2N-2-C_5H_3N-4-Me)_2\}_2NdRh(\eta^2-C_2H_4)$ (**1.93**) and $\{O(SiMe_2N-2-C_5H_3N-4-Me)_2\}_2Nd(THF)Pd(Me)$ (**1.94**) with short Nd...Rh and Nd...Pd distances, respectively.⁹⁴

Hou *et al.* reported the series of complexes $(C_5Me_4XCH_2PPh_2)Ln(CH_2SiMe_3)_2(THF)PtMe_2$,⁹⁵ where $Ln = Y$ and $X = SiMe_2$ (**1.98**) or CH_2 (**1.99**), or $Ln = Lu$ and $X = SiMe_2$ (**1.100**) or CH_2 (**1.101**). Of these, **1.98**, **1.99** and **1.100** were structurally authenticated and each contain a $Ln...Pt$ interaction with a distance of 2.8333(5), 2.8214 and 2.7870(11) Å, shorter than the sums of the respective covalent radii ($Y-Pt = 3.26(9)$ and $Lu-Pt = 3.23(9)$ Å). Compounds **1.98-1.101** were synthesised *via* the reaction of the corresponding $(C_5Me_4XCH_2PPh_2)Ln(CH_2SiMe_3)_2(THF)$ with $(COD)PtMe_2$. Heating **1.100** in C_6D_6 to 90 °C gave a thermal rearrangement with loss of $SiMe_4$ to afford $(C_5Me_4XCH_2PPh_2)Ln(CH_2SiMe_2CH)(THF)PtMe_2$ (**1.102**), with a shorter $Ln...Pt$ interaction (2.7668(5) Å) compared to that in **1.100**, a consequence of the stronger interaction of the $\mu-\eta^1:\eta^2-CH_2SiMe_2CH_2$ group with which Pt interacts.

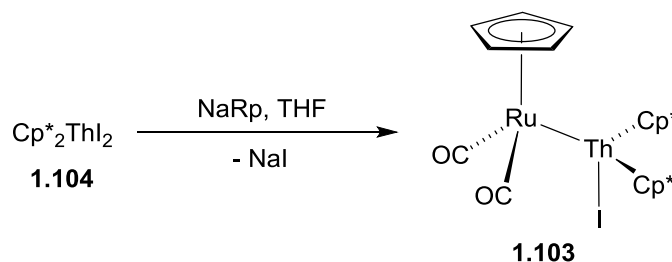


Scheme 1.14. Formation of $(\text{C}_5\text{Me}_4\text{XCH}_2\text{PPh}_2)\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})\text{PtMe}_2$ **1.98-1.101** and thermal rearrangement of $(\text{C}_5\text{Me}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})\text{PtMe}_2$ (**1.100**) to $(\text{C}_5\text{Me}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Lu}(\text{CH}_2\text{SiMe}_2\text{CH})(\text{THF})\text{PtMe}_2$ (**1.102**).⁹⁵

1.9 Actinide-transition metal complexes

The Actinide metals (An) cannot be paired with Ae metals owing to their lack of divalent states and differing covalent and ionic radii.^{29, 30} Nevertheless their ability to form hard Lewis acidic ions like the Ae and Ln,^{96, 97} and the relative paucity of structurally authenticated An-TM bonds warrants their introduction in this context.⁵

The report of $\text{Cp}^*_2\text{Th}(\text{I})\text{Rp}$ (**1.103**) by Marks *et al.* in 1985 represents the first structurally authenticated unsupported An-TM bond.⁹⁸ Complex **1.103** was synthesised by the salt-metathesis reaction of NaRp with $\text{Cp}^*_2\text{ThI}_2$ (**1.104**) and possesses a four-coordinate Th centre with a direct Th-Ru bond (3.0277(6) Å), shorter than the sum of the respective covalent radii (3.52(9) Å).²⁹ Independently performed theoretical calculations for the model complex $\text{Cp}_2\text{Th}(\text{I})\text{Rp}$ (**1.103Q**) were consistent with a dative donor-acceptor interaction between these metal centres. The IR spectra of the chloride analogue $\text{Cp}^*_2\text{Th}(\text{Cl})\text{Rp}$ (**1.105**) in heptane ($\nu(\text{CO}) = 2033$ and 1973 cm^{-1}) and THF ($\nu(\text{CO}) = 2023$ and 1959 cm^{-1}) were consistent with those for **1.103**, alas a molecular structure was not obtained.

Equation 1.20⁹⁸

In a later report,⁹⁹ Marks and Sternal reported a Th-Fe distance of 2.940(5) Å for Cp_3ThFp (**1.106**). However, further structural details were not provided. Analogous complexes using the Cp' ligand on Th and using the Rp^- anion were also synthesised but not structurally authenticated. As commented by Marks, the structurally authenticated complexes $\text{Cp}^*_2\text{Th}(\mu\text{-PPh}_2)_2\text{Ni}(\text{CO})_2$ (**1.107**) and $\text{Cp}^*_2\text{Th}(\mu\text{-PPh}_2)_2\text{Pt}(\text{PMe}_3)$ (**1.108**) were reported prior to **1.103** with short $\text{Th}\cdots\text{Ni}$ (3.206(2) Å)²⁷ and $\text{Th}\cdots\text{Pt}$ (2.984(1) Å)²⁸ distances. However, phosphido bridging between these metal centres resulted in some ambiguity regarding the extent of the metal-metal interaction in these complexes. In support of these interactions, the Th-P-Ni bond angles (75.8(1) and 75.8(1)°) in **1.107** and the analogous Th-P-Pt angles (69.1(1) and 67.8(2)°) in **1.108** are particularly acute, where these angles are much larger for non-metal-metal bonded complexes.^{100, 101} *Ab initio* calculations on model complexes further supported the presence of a Th-Ni interaction in **1.107**, consistent with a dative donor-acceptor interaction.

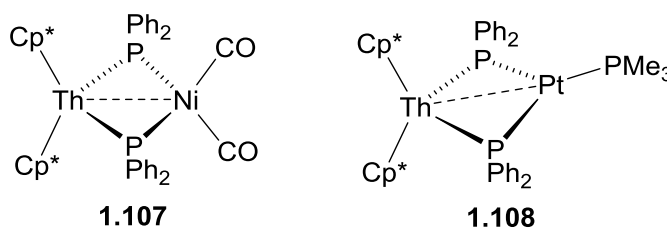
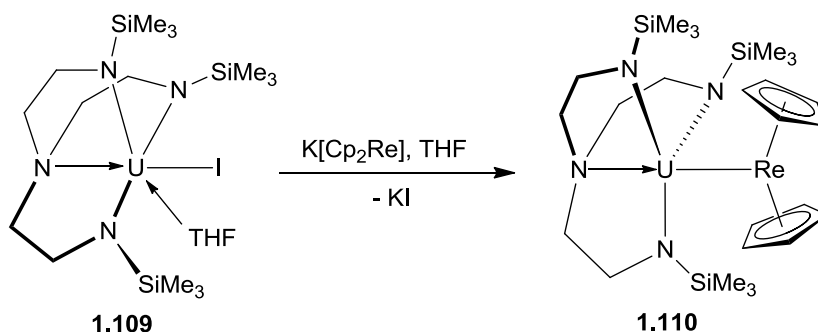


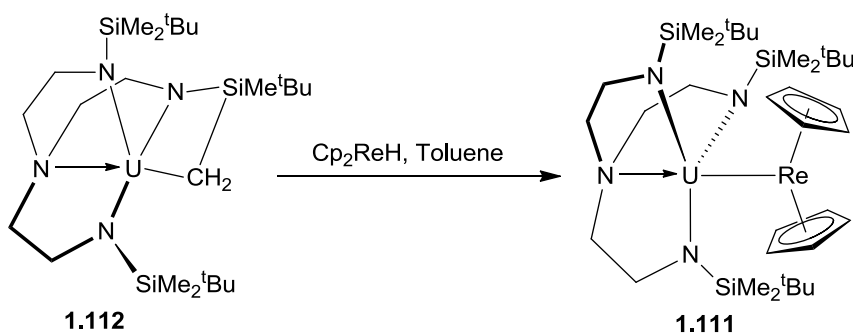
Figure 1.1. $\text{Cp}^*_2\text{Th}(\mu\text{-PPh}_2)_2\text{Ni}(\text{CO})_2$ (**1.107**) and (**1.108**) $\text{Cp}^*_2\text{Th}(\mu\text{-PPh}_2)_2\text{Pt}(\text{PMe}_3)$.^{27, 28}

The remaining An-TM bonds known are dominated by U-TM interactions. As with the contributions of Kempe *et al.* to Ln-TM bonding, Liddle *et al.* have set a precedent for complexes with An-TM bonding, namely U-TM bonding, utilising the Cp_2Re and Rp ligands for the TM component in these interactions. This chemistry has relied on the stabilising influence of multipodal, trianionic N-donor ligands on the U centre.

The first structurally authenticated U-TM bond was achieved by the salt-metathesis reaction of $(\text{Tren}^{\text{TMS}})\text{U}(\text{I})(\text{THF})$ (**1.109**) with $\text{K}[\text{Cp}_2\text{Re}]$, where Tren is $\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3$, to afford $(\text{Tren}^{\text{TMS}})\text{UReCp}_2$ (**1.110**, Equation 1.21) with a U-Re distance of $3.0475(4) \text{ \AA}$,¹⁰² consistent with the sum of the respective covalent radii ($3.47(10) \text{ \AA}$).²⁹ DFT analysis was consistent with U-Re bonding, with a calculated U-Re interaction energy of -561 kJ mol^{-1} and not insignificant orbital contributions (32%) with σ - and π -orbital interactions.

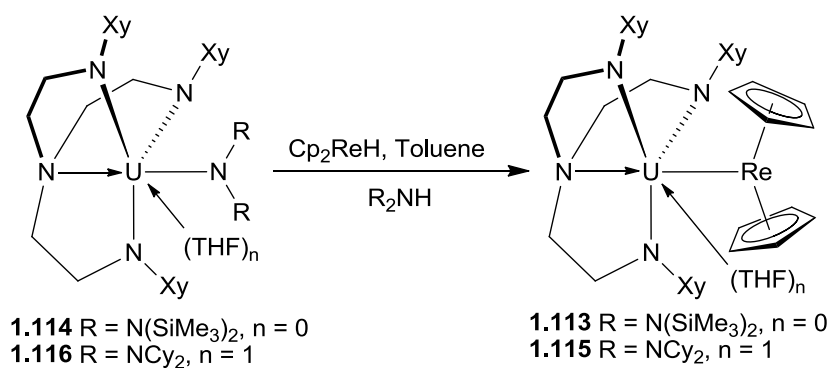
Equation 1.21¹⁰²

The bulkier analogue of **1.110**, $(\text{Tren}^{\text{TBDMS}})\text{UReCp}_2$ (**1.111**, Equation 1.22), has also been synthesised, where TBDMS is SiMe_2^tBu , bearing a U-Re bond with a distance of $3.0739(2) \text{ \AA}$.¹⁰³ Contrasting with the salt-metathesis reaction used to afford **1.110**, **1.111** was synthesised *via* alkane elimination in the reaction between Cp_2ReH and $\text{U}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2^t\text{Bu})_2(\text{CH}_2\text{CH}_2\text{NSiMe}^t\text{BuCH}_2)\}$ (**1.112**) in toluene. DFT analysis is consistent with a more ionic U-Re interaction in **1.111** compared to **1.110**.

Equation 1.22¹⁰³

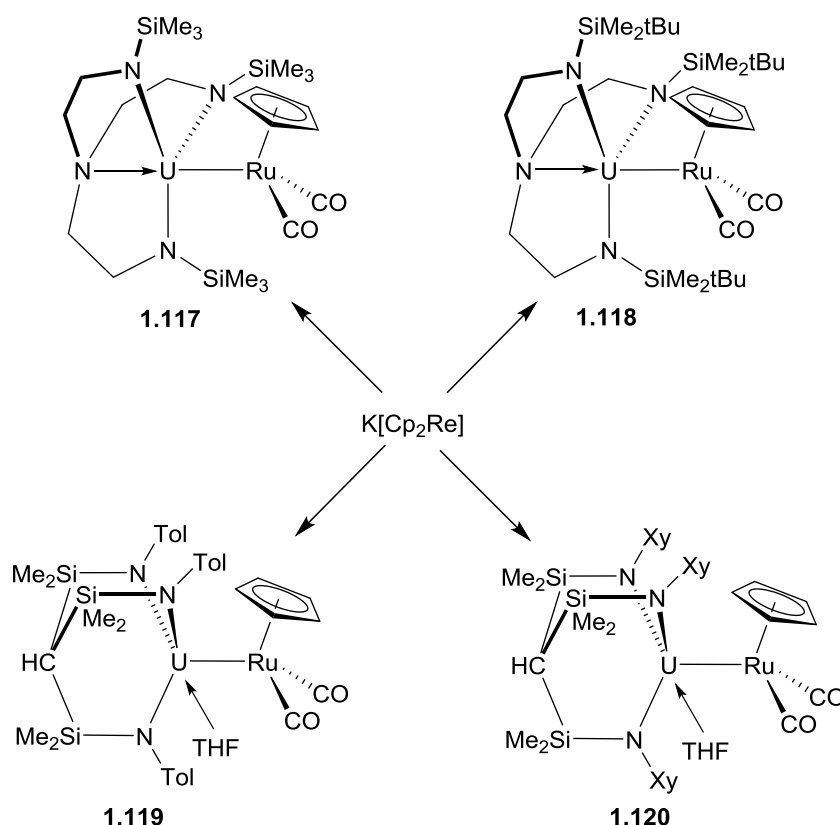
Amine elimination routes allowed the synthesis of $(\text{Ts}^{\text{Xy}})\text{UReCp}_2$ (**1.113**, Equation 1.23), where Ts^{Xy} is $\text{HC}\{\text{SiMe}_2\text{N}(3,5\text{-Me}_2\text{C}_6\text{H}_3)\}_3$, by the reaction of $(\text{Ts}^{\text{Xy}})\text{U}\{\text{N}(\text{SiMe}_3)_2\}$ (**1.114**) with Cp_2ReH .¹⁰⁴ The THF adduct (**1.115**) was also formed from the reaction of $(\text{Ts}^{\text{Xy}})\text{U}(\text{NCy}_2)(\text{THF})$ (**1.116**) with Cp_2ReH . The Re-U

distances for **1.113** (3.0021(8) and 2.9541(8) Å (two molecules in asymmetric unit)) and **1.115** (2.9307(8) Å) are shorter than the sum of the respective covalent radii (3.47(10) Å).²⁹ The greater distances for **1.115** are consistent with the higher coordination number at U compared to **1.113**. DFT analysis gave good agreement with the structures of **1.113** and **1.115**, consistent with bonding interactions between the U and Re metal centres.



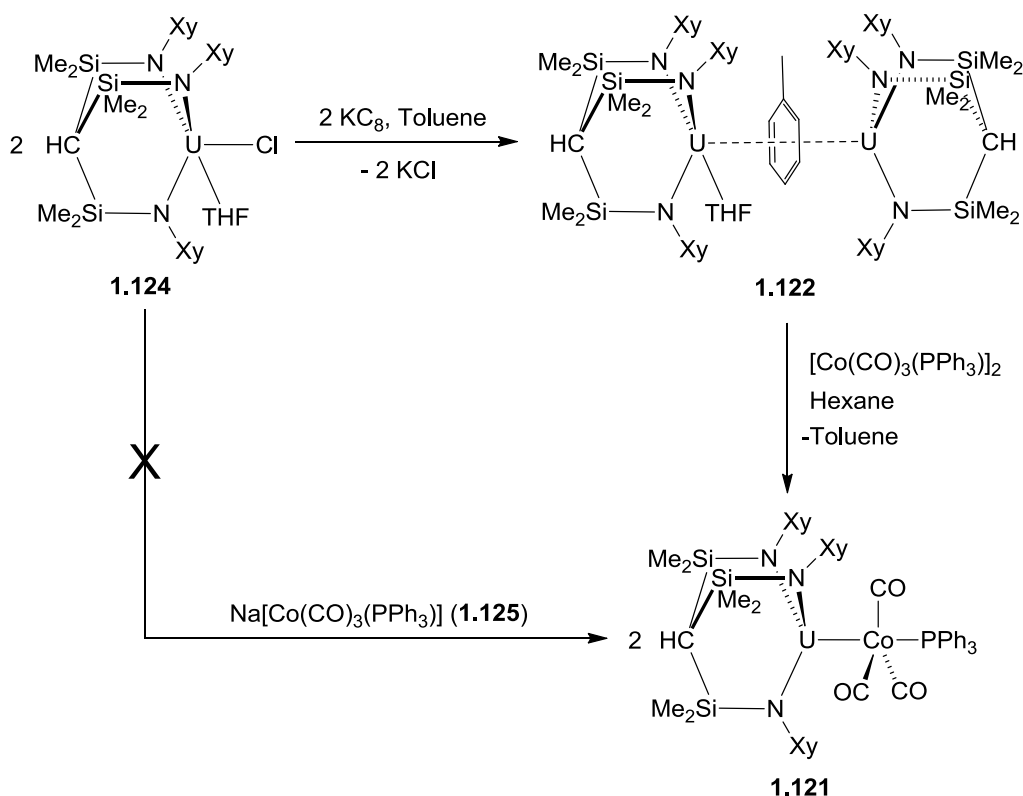
Equation 1.23¹⁰⁴

As mentioned, Liddle *et al.* have also reported structurally authenticated complexes with U-Ru bonds, through use of the Rp^- anion. Salt-metathesis reactions between KRp and the corresponding halide complexes afforded $(\text{Tren}^{\text{TMS}})\text{URp}$ (**1.117**), $(\text{Tren}^{\text{TBDMS}})\text{URp}$ (**1.118**), $\text{Ts}^{\text{Tol}}\text{URp}(\text{THF})$ (**1.119**) and $\text{Ts}^{\text{Xy}}\text{URp}(\text{THF})$ (**1.120**).¹⁰⁵ The U-Ru distances for **1.117** (3.0925(3) Å), **1.118** (3.0739(2) Å), **1.119** (2.9885(3) Å) and **1.120** (3.0062(5) Å) are shorter than the sum of the respective covalent radii (3.42(10) Å).²⁹ Attempts to form the U-Fe analogues *via* use of the Fp^- anion were unsuccessful, affording Fp_2 as the only identifiable decomposition product. It is thought that the valence orbitals of Fe may be too contracted to form a suitable bond with U, alternatively the Fp^- anion may act as a reducing agent.¹⁰⁶ DFT analysis of **1.117-1.120** was consistent with that observed experimentally, replicating the trend in U-Ru bond distances with orbital contributions of 25.6, 26.3, 25.9 and 26.2%, respectively, with charge transfer between the metal centres on bond formation. These bonds were classed as ionic with covalent character.



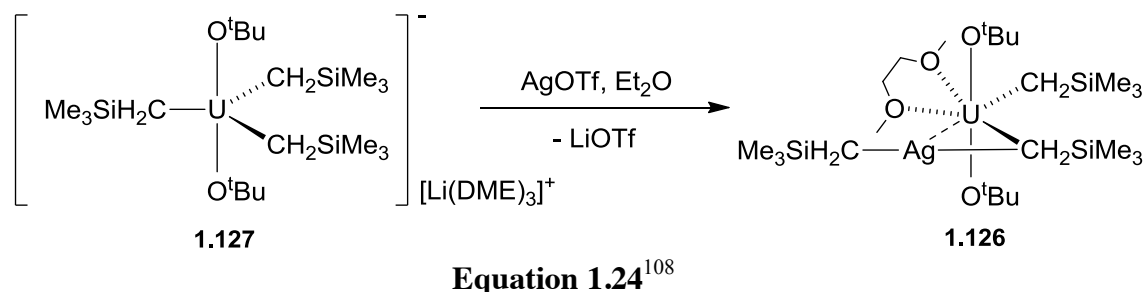
Scheme 1.15. Synthesis of **1.117-1.120** containing U-Re bonds *via* reaction of the corresponding halide precursor with KRp in THF.¹⁰⁵

Synthesis of $\text{U}(\text{Ts}^{\text{Xy}})\text{Co}(\text{CO})_3(\text{PPh}_3)$ (**1.121**, Scheme 1.16) was achieved by the reaction of the inverse-sandwich complex $[\{\text{U}(\text{Ts}^{\text{Xy}})\}_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_6\text{H}_5\text{Me})]$ (**1.122**) with $[\text{Co}(\text{CO})_3(\text{PPh}_3)]_2$ (**1.123**).¹⁰⁷ Complex **1.121** could not be formed directly by the salt-metathesis reaction of $\text{U}(\text{Ts}^{\text{Xy}})\text{Cl}$ (**1.124**) with $\text{Na}[\text{Co}(\text{CO})_3(\text{PPh}_3)]$ (**1.125**). The U-Co distance (2.9450(9) Å) is consistent with the sum of the respective covalent radii (3.22(8) Å).²⁹ DFT analysis was consistent with the experimental structure of **1.121**, with a total bond interaction energy of $-400.8 \text{ kJ mol}^{-1}$. This compares with an energy of ca. -600 kJ mol^{-1} for the other U-Re bonds analysed.¹⁰²⁻¹⁰⁴



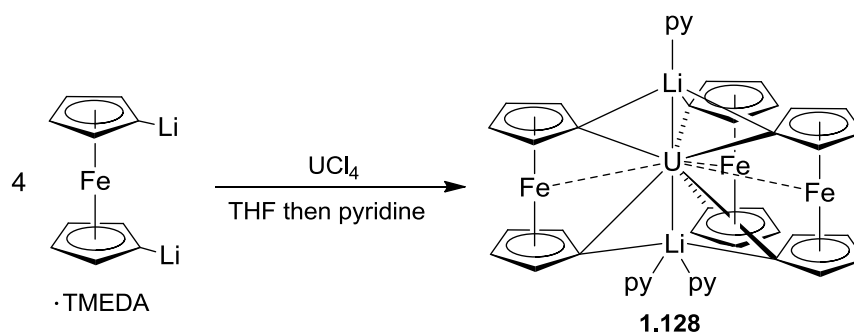
Scheme 1.16. Synthesis of the U-Co bonded $\text{U}(\text{Ts}^{\text{Xy}})\text{Co}(\text{CO})_3(\text{PPh}_3)$ (**1.121**) via $[\{\text{U}(\text{Ts}^{\text{Xy}})\}_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_6\text{H}_5\text{Me})]$ (**1.122**).¹⁰⁷

Hayton *et al.* have reported the structure of $(\text{Me}_3\text{SiCH}_2)\text{Ag}(\mu\text{-CH}_2\text{SiMe}_3)\text{U}(\text{CH}_2\text{SiMe}_3)(\text{O}^t\text{Bu})_2(\text{DME})$ (**1.126**, Equation 1.24), synthesised by the reaction of $[\text{Li}(\text{DME})_3][\text{U}(\text{CH}_2\text{SiMe}_3)_3(\text{O}^t\text{Bu})_2]$ (**1.127**) with a short U-Ag contact (3.1533(6) Å).¹⁰⁸ Whilst the interaction between U and Ag is supported by a CH_2SiMe_3 bridge, the acute $\text{U}(1)\text{-C}(1)\text{-Ag}(1)$ angle of $80.8(2)^\circ$ is consistent with an interaction between these metal centres.



Other structures are known that may possess some degree of Ln-TM interaction although in these cases it is ambiguous as to what extent the short distance between the metal centres may be a consequence of other interactions such as those of bridging ligands. The molecular structure of $\text{Li}_2(\text{py})_3\text{U}(\text{fc})_3$ (**1.128**), where fc is 1,1-

ferrocenylene, contains three U-Fe interactions with an average distance of 3.145(1) Å,¹⁰⁹ consistent with the sum of the respective covalent radii (3.28(8)).²⁹ Despite a lack of ring-strain there remains a significant amount of support between the Fe and U centres *via* the linked ferrocenophane units. Other structures have also been reported with short Fe-U distances with similar structural motifs.¹¹⁰



Equation 1.25¹⁰⁹

1.10 Summary and Objectives

This Chapter has presented literature examples of homobimetallic landmark transition metal-transition metal bonded complexes with high bond orders. Homometallic Mg(I)-Mg(I) complexes and selected examples of their application were introduced. The few structurally authenticated alkaline earth-transition metal bonded complexes that have been reported were also presented and alkaline earth-main group metal bonded complexes were compared with their rare earth-main group metal counterparts, demonstrating the potential for similar metal-metal bonded structures for those containing alkaline earth and certain divalent lanthanides. Complexes with rare earth-transition metal bonds were also discussed, as with the alkaline earth-transition metal bonds these are few in number and isostructural examples between these groups were unknown at the commencement of this research.

The work detailed in this thesis sets out to expand the number of structurally authenticated alkaline earth-transition metal bonded complexes. In addition, complexes with divalent lanthanides will also be investigated to enable comparison with their alkaline earth counterparts were applicable.

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Chapter Two

**Synthesis and study of Ae-Fe and Ln-Fe
complexes containing the $[\text{CpFe}(\text{CO})_2]^-$ anion**

2.1 Overview

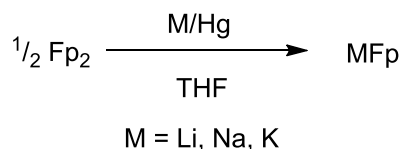
This Chapter describes the synthesis and investigation of new heterobimetallic complexes in pursuit of direct interactions between the alkaline earth and transition metals. Extensive use is made of the Fp^- anion generated by reduction of Fp_2 with alkaline earth metal amalgams or as KFp in salt-metathesis reactions. Analogous divalent Yb complexes are also studied, particularly with regard to structural similarities with their Ca counterparts. Use of the NacNac ligand to offer improvements in complex solubility and stability were explored. Simple reactivity studies were also undertaken to investigate the potential for insertions into and nucleophilic substitutions involving these metal-metal bonded species. Attempts to synthesise Ru analogues using the Rp^- anion were unsuccessful and are discussed in the appendix. Single crystal X-ray diffraction was employed to provide structural authentication of these complexes and aid in identifying interactions between the metal centres. In collaboration with Prof. Nikolas Kaltsoyannis of University College London, computational analysis was performed to further investigate the bonding in selected complexes. Comparable reports in the literature are also discussed.

2.2 Introduction

Literature examples of structurally authenticated complexes utilising the Fp^- anion are abundant. It is not the purpose of this introduction to provide an exhaustive list of these complexes given those of greatest relevance have been discussed in detail in Chapter One but to provide some background to use of the Fp^- anion in this role.

2.2.1 Group 1 metallates of the Fp^- and Rp^- anion.

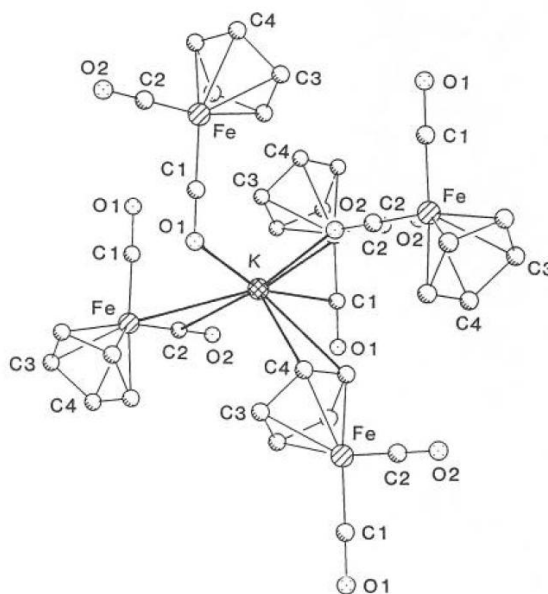
Fp_2 is commercially available at low cost providing a suitable starting point for the synthesis of the Fp^- anion, considered to be one of the most nucleophilic transition metal anions.¹ Numerous reactions of Fp_2 with activated Group 1 metals have been reported for this purpose. One established route, illustrated in Equation 2.1, uses a Group 1 metal amalgam to reduce Fp_2 in THF. This route is somewhat advantageous in allowing variation of the reducing metal (M) to afford MFp with an M^+ cation of choice.^{2,3} However, contamination with HgFp_2 has been reported.^{4,5}



Equation 2.1

Alternative routes include the reaction of Fp_2 in THF with KH ,⁶ $\text{NaK}_{2.8}$ alloy,⁷ K-benzophenone,⁸ KC_8 ,⁹ $\text{K}[\text{BR}_3\text{H}]$ ($\text{R} = \text{Et}$ or *sec*-butyl) and the elemental alkali metal as a dispersion in mineral oil or generated *in situ* using sonication.¹⁰⁻¹² Electrochemical reductions have also been reported.¹³

The solid state structure of KFp , synthesised by reaction of Fp_2 with KSi in DME, has been reported by Hey-Hawkins and von Schnering.¹⁴ This consists of infinite helical chains comprising K-O linkages. Van der Waals interactions between neighbouring chains give a three-dimensional network in which each K^+ cation is surrounded by five Fp^- anions as illustrated in Figure 2.1. The shortest $\text{K}\cdots\text{Fe}$ distances of 3.472(1) and 3.589(1) Å are longer than the sum of the respective covalent radii (3.35(12) Å).¹⁵



2.1. Ball and stick plot (arbitrary radius) of Fp^- anion interactions with one K^+ cation in KFp .¹⁴

Reduction of Fp_2 in THF with Na/Hg was reported to give $[\text{Na}\{\text{CpFe}(\text{CO})_2\}_2(\text{THF})_4]_x$ (**2.1**), with the solid state structure illustrated in Figure 2.2.¹⁶ As with that for KFp infinite chains are observed but with retention of the $\{\text{CpFe}(\text{CO})_2\}_2$ dimeric unit albeit in anionic form. These are linked *via* Na^+ cations that interact with μ_3 -bridging

carbonyl groups. Each Na is coordinated by four THF ligands and two independent $[\text{CpFe}(\text{CO})_2]^-$ anions to form the infinite chain. Interactions do not occur between these chains to give a network as observed for K₂Fp. The Na $\cdots$ Fe distances, for example Na(11) $\cdots$ Fe(1) (5.137 Å), are substantially greater than the sum of the respective covalent radii (2.98(9) Å).¹⁵

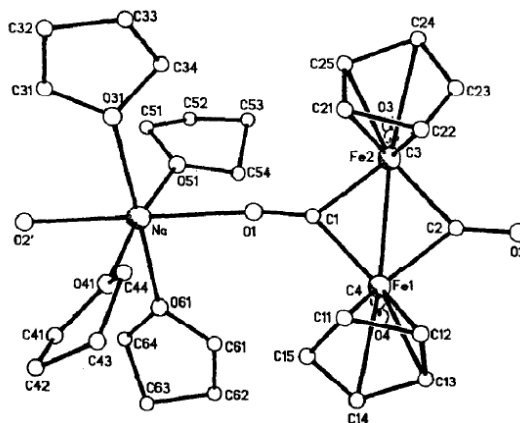


Figure 2.2. Section of the infinite chain of $[\text{Na}\{\text{CpFe}(\text{CO})_2\}_2(\text{THF})_4]_x$ (**2.1**).¹⁶

The molecular structure of $[\text{NaFp}(\text{TMEDA})]_x$ (**2.2**) (TMEDA = tetramethylethylenediamine) has also been reported,¹⁶ that is, the TMEDA adduct of NaFp, synthesised by addition of TMEDA to the THF solution that afforded **2.1**. Each Na^+ cation is coordinated to a bidentate TMEDA ligand and also interacts with two Fe centres indirectly *via* $\text{Na}(\mu\text{-OC})\text{Fe}$ isocarbonyl bridging. Similarly each Fe centre interacts indirectly with two Na^+ cations to form an infinite chain with $\{\text{NaFp}(\text{TMEDA})\}_2$ asymmetric units. The shortest Na $\cdots$ Fe distance (2.983 Å) occurs between Na and Fe" as depicted in Figure 2.3. This is consistent with a direct interaction based on the sum of the respective covalent radii (2.98(9) Å) which are absent in **2.1**.¹⁵

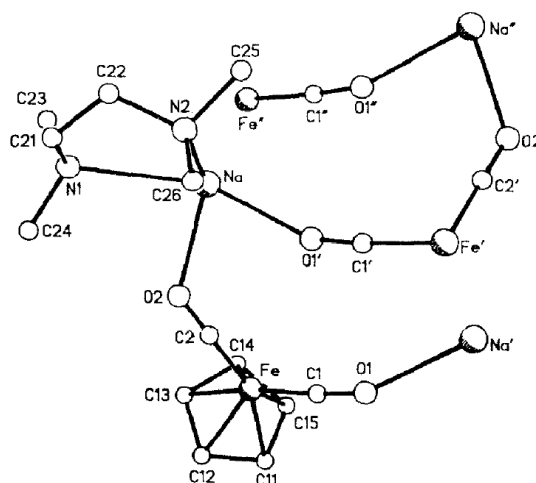


Figure 2.3. Portion of the infinite chain of $[\text{NaFp}(\text{TMEDA})]_x$ (**2.2**).¹⁶

Whilst considered to be less nucleophilic than the Fp^- anion,¹ structurally authenticated complexes have been reported that have a direct interaction between the Ru centre of the Rp^- anion and other metals.¹⁷ Despite their use in the synthesis of these complexes, the solid state structures of the Na^+ and K^+ metallates of the Rp^- anion are yet to be reported.

The THF solution behaviour of NaRp has been studied by IR spectroscopy and is consistent with a dynamic equilibrium between “tight”, “contact” and “solvent separated” (s.s) ion pairs (Figure 2.4).¹⁸ Note how these contrast with the solid state molecular structure of **2.1**. Increasing the number of equivalents of dibenzo-18-crown-6 in a THF solution of NaRp was observed to bring about an increase in the carbonyl stretching frequencies, consistent with a shift of this equilibrium towards that of the separated ion pair. Addition of DME to a THF solution of NaFp had a similar effect, consistent with a stronger interaction of DME with Na^+ over THF. Only two bands were observed for the carbonyl stretches of KFp in THF, consistent with this existing exclusively as the solvent separated ion pair.¹⁹

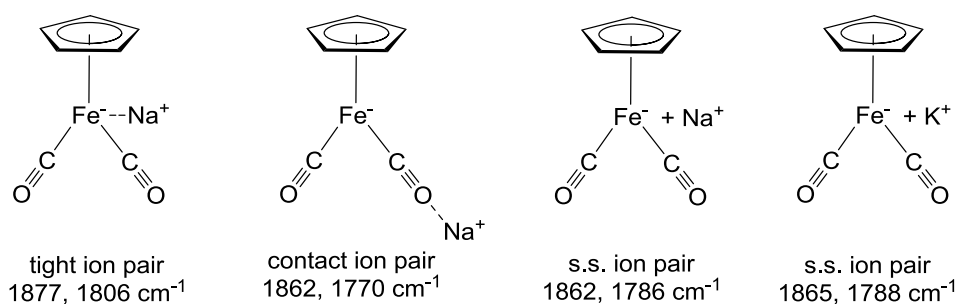


Figure 2.4. Tight, contact and solvent separated ion pairs of NaFp and KFp .^{18, 19}

2.2.2 Fp⁻ and Rp⁻ anions in metal-metal bonding.

Although discussed at length in Chapter One, the important role played by the Fp⁻ and Rp⁻ anions in landmark complexes with metal-metal bonding is worthy of reiteration at this point. Use of the Fp⁻ anion by Arnold *et al.* enabled the first structurally authenticated Nd-Fe bond (2.9942(7) Å), and as a result first unsupported 4f-3d bonded complex, to be achieved, namely Nd(L)Fp{N(SiMe₃)₂} (**1.78**, L = ^tBuNCH₂CH₂{CNCSiMe₃CHN^tBu}).²⁰ Marks *et al.* reported the first structurally authenticated unsupported An-TM bond in Cp*₂Th(I)Rp (**1.103**) (Th-Ru = 3.0277(6) Å).²¹ Kempe *et al.* reported the first example of a Yb-Ru bond (3.1808(7) and 3.1391(8) Å) and as such the first structurally authenticated 4f-4d bonded complex, namely [YbRp₂(THF)₂]_x (**1.91**).¹⁷

Use of the Fp⁻ anion has also enabled direct bonds between Fe and main group metals to be achieved. Examples include Al,²² Ga,^{23, 24} Ge,^{25, 26} In,²⁷ Sn,^{28, 29} Sb,³⁰ Bi,³¹ and Tl.³² Similarly, structurally authenticated examples of direct bonds between Ru and main group metals have been achieved using the Rp⁻ anion. Examples include In,³³ Sn,^{34, 35} Sb,³⁶ and Tl,³⁷ some of which are illustrated in Figure 2.5.

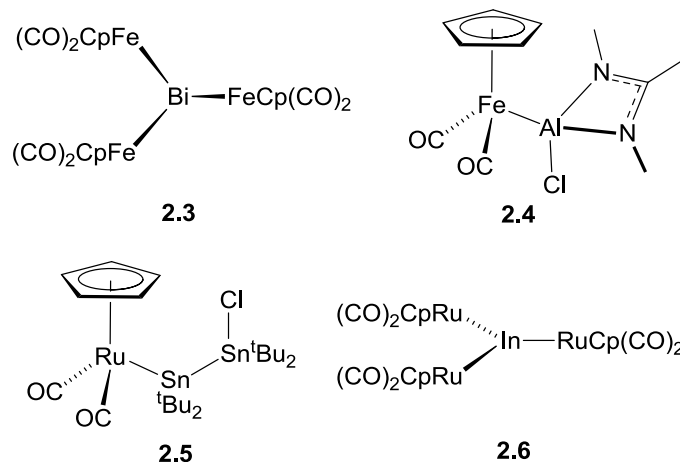


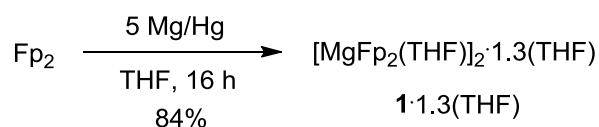
Figure 2.5. Selected examples of Fp⁻ and Rp⁻ complexes with Fe- and Ru-main group metal bonds.^{22, 31, 33, 35}

2.3 Reduction of Fp₂ with alkaline earth and Yb amalgams

As discussed in Section 2.2.1, reduction of Fp₂ in THF with activated alkali metals can afford metallates of the Fp⁻ anion. Use of amalgams enables the reducing metal to be easily varied. Whilst metallates such as Na and K are often used as precursors and reacted with metal halides to afford new interactions *via* salt-metathesis, it was

postulated that reduction of Fp_2 with an Ae or Ln amalgam could produce a metallate with direct Ae- or Ln-Fe interactions. Reassuringly, numerous examples of Ae and Ln amalgams had been reported prior to this investigation.³⁸⁻⁴¹ Whilst their reported use is very scarce for the reduction of Fp_2 , a report by McVicker in 1974 proposed the formation of $\text{MgFp}_2(\text{THF})_2$ (**2.7**) *via* reduction of Fp_2 with Mg/Hg to give a material with a direct Mg-Fe bond.⁴² Whilst this material was not structurally authenticated, elemental analysis, NMR and IR spectroscopy were performed to substantiate the claim.

Based on the report by McVicker, reduction of Fp_2 in THF with excess Mg/Hg afforded $[\text{MgFp}_2(\text{THF})]_2 \cdot 1.3(\text{THF})$ (**1**·1.3(THF)) in 84% isolated yield (Equation 2.2). This formula is consistent with elemental analysis of the bulk material.



Equation 2.2

Diffraction-quality crystals of **1** were grown from a concentrated benzene solution, in which **1** exhibited poor solubility, layered with pentane at RT. The molecular structure and selected distances and angles are shown in Figure 2.6 and Table 2.1.

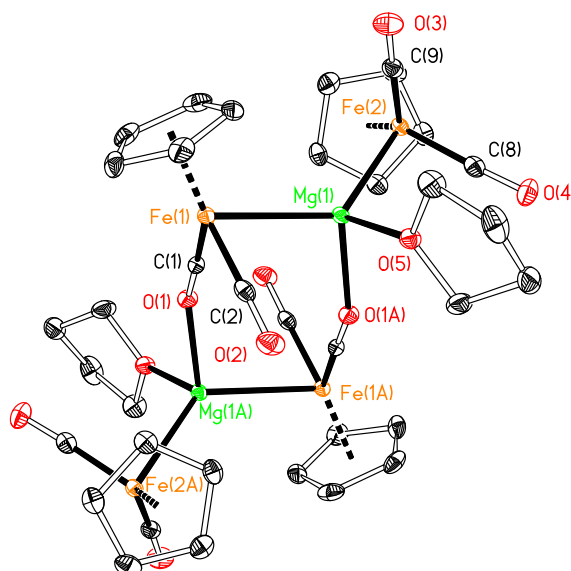


Figure 2.6. Displacement ellipsoid plot (35% probability) of $[\text{MgFp}_2(\text{THF})_3]_2$ (**1**). H atoms omitted for clarity. Atoms carrying the suffix “A” are related to their counterparts by the operator $2-x, 1-y, 1-z$.

Table 2.1. Selected distances (Å) and angles (°) for [MgFp₂(THF)]₂ (**1**).

Mg(1)-Fe(1)	2.6112(5)	Mg(1)-Fe(2)	2.5629(5)
Mg(1)-Fe(1A)	4.7879(5)	Mg(1)-O(1A)	2.1015(11)
Mg(1)-O(5)	2.0479(11)	Fe(1)-C(1)	1.7016(14)
Fe(1)-C(2)	1.7395(16)	Fe(1)-Cp _{cent} (1)	1.729
Fe(2)-C(8)	1.7359(16)	Fe(2)-C(9)	1.7279(15)
Fe(2)-Cp _{cent} (2)	1.718	C(1)-O(1)	1.1946(18)
C(2)-O(2)	1.164(2)	C(8)-O(4)	1.162(2)
C(9)-O(3)	1.1707(19)		
Fe(1)-Mg(1)-Fe(2)	128.70(2)	Fe(1)-Mg(1)-O(1A)	102.23(3)
Fe(2)-Mg(1)-O(1A)	108.76(4)	Fe(1)-Mg(1)-O(5)	107.34(4)
Fe(2)-Mg(1)-O(5)	109.01(4)	O(1A)-Mg(1)-O(5)	95.71(4)
Mg(1)-Fe(1)-C(1)	82.90(5)	Mg(1)-Fe(1)-C(2)	76.64(5)
Mg(1)-Fe(1)-Cp _{cent} (1)	116.58	Mg(1)-Fe(2)-C(8)	80.16(5)
Mg(1)-Fe(2)-C(9)	82.85(5)	Mg(1)-Fe(2)-Cp _{cent} (1)	116.33
C(1)-Fe(1)-C(2)	92.88(7)	C(1)-Fe(1)-Cp _{cent} (1)	135.29
C(2)-Fe(2)-Cp _{cent} (1)	129.47	C(8)-Fe(2)-C(9)	92.99(7)
C(8)-Fe(2)-Cp _{cent} (1)	138.02	C(9)-Fe(2)-Cp _{cent} (1)	133.01
^a Hinge angle	157		

^a Hinge angle = (Fe(1), C(1), O(1), Fe(1A), C(1A), O(1A))-(Fe(1), Mg(1), O(1A))

The molecular structure of **1** is dimeric in the solid state with two MgFp₂(THF) units connected by Mg(μ-OC)Fe isocarbonyl linkages and direct Mg-Fe interactions to form a centrosymmetric eight-membered ring. The geometry at each four-coordinate Mg centre is approximately tetrahedral, with bonds to two Fe atoms, a THF ligand and one μ-isocarbonyl group. The Mg–Fe bond distances of 2.6112(5) and 2.5629(5) Å are consistent with significant interactions, consistent with the sum of the respective covalent radii (2.73(8) Å).¹⁵ This represents only the second example of a structurally authenticated Mg-Fe direct interaction. The other being Felkin's Cp(dppe)FeMgBr(THF)₂ (**1.18**) with a Mg-Fe distance of 2.593(7) Å.⁴³ Other structurally authenticated reports of Mg-TM bonding include Jonas' Mg{CpCo(η³-C₃H₅)}(Br)(THF)₂ (**1.20**) and Mg{CpCo(η²-C₂H₄)(Ph)}(Br)(TMEDA) (**1.21**) with

Mg-Co distances of 2.480(4) and 2.565(3) Å, respectively.⁴⁴ The Mg(1)···Fe(1A) distance in **1** of 4.7879(5) Å is greater than the sum of the respective covalent radii (2.73 (8) Å).¹⁵ Although discussed in more detail in Section 2.3.1 it is important to highlight that the IR spectroscopic data for **1** and McVicker's **2.7** are consistent,⁴² strongly suggesting that these materials have identical molecular structures and importantly that **2.7** did contain direct Mg-Fe interactions.

For **1**, Mg(μ -O(1)C(1))Fe isocarbonyl interactions lead to a lengthening of the C(1)-O(1) distance (1.195(2) Å) relative to that for C(2)-O(2) (1.164(2) Å), a terminal carbonyl group. The Fe(1)-C(1) distance (1.7016(14) Å) is shorter than that for Fe(2)-C(2) (1.7359(16) Å). The C-O distances associated with C(8)O(4) (1.162(2)) and C(9)O(3) (1.171(2)) are identical within error to those for the terminal C(2)O(2). The Fe(2)-C(8) distance (1.7359(16)) is also identical within error to that for Fe(1)-C(2). The C(1)-Fe(1)-C(2) angle (92.88(7) °) is identical within error to that for C(8)-Fe(2)-C(9) (92.99(7) °).

This perturbation of C-O and Fe-C distances as a consequence of the Mg(μ -OC)Fe isocarbonyl interactions has been discussed for other M(μ -OC)TM isocarbonyl interactions in the literature.⁴⁵⁻⁵¹ In terms of **1**, donation of electron density from O(1) to Mg(1A) causes a decrease in the availability of electron density in bridging C(1)O(1). As a result the back donation of electron density from Fe(1) to C(1)O(1) is increased relative to that to terminal C(2)O(2). These synergic effects increase the electron density in the Fe(1)-C(1) bonding orbital and the C(1)-O(1) antibonding orbital, bringing about shortened and lengthened interactions, respectively. This is readily detected by IR spectroscopy and has been reported to cause a decrease in the carbonyl stretching wavenumber by around 100 cm⁻¹ for main group-transition metal complexes.⁴²

The Mg-O(THF) distance of 2.0479(11) is comparable with the average literature Mg-O(THF) distance of 2.08 (range: 1.96-2.29) Å.⁵² Compound **1** bears the first structurally authenticated Mg(μ -OC)Fe isocarbonyl interaction and is discussed with that for MgFp₂(THF)₄ (**2**).

The centrosymmetric eight-membered ring in **1** formed by isocarbonyl and direct interactions between the monomeric MgFp₂(THF) (**1'**) units has a chair-conformation where Fe(1), C(1), O(1), Fe(1A), C(1A) and O(1A) are coplanar. Mg(1) and Mg(1A)

can be considered as above and below this plane. The angle between these is referred to as the “hinge angle”, equal to 157° in **1**. This is indicated as angle “*a*” in Figure 2.7.

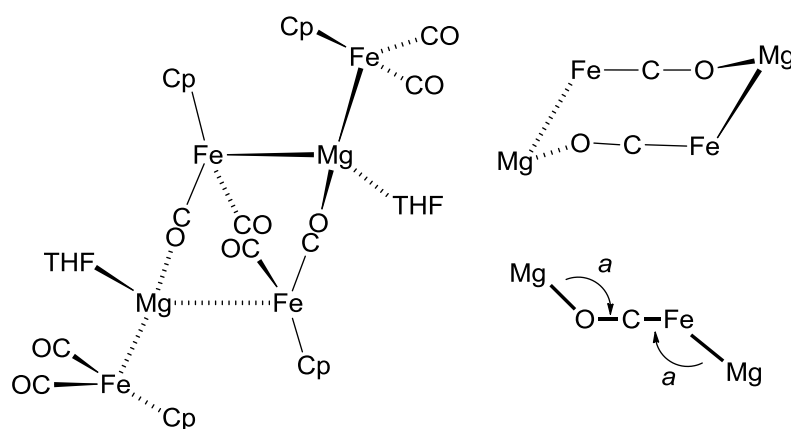


Figure 2.7. Molecular structure of $[\text{MgFp}_2(\text{THF})]_2$ (**1**) (left) and illustrations of the ring structure (right). Angle “*a*” denotes the hinge angle.

The eight-membered ring motif present in **1** is rare. Only one other structurally authenticated example exists with $\text{M}(\mu\text{-OC})\text{TM}$ μ_2 -isocarbonyl linkages where M is any metal and TM is any transition metal, namely $[\text{Pb}\{\text{Cp}^*\text{Mo}(\text{CO})_3\}_2]_2$ (**2.8**, Figure 2.8).⁵³ The dimeric molecular structure shares many structural similarities with that for **1** with two $\text{Pb}\{\text{Cp}^*\text{Mo}(\text{CO})_3\}$ units connected by two $\text{Pb}(\mu\text{-OC})\text{Mo}$ isocarbonyl linkages and two direct Pb-Mo interactions to form the eight-membered ring with a hinge angle of 151° . In addition, each Pb is bonded to a $\text{Cp}^*\text{Mn}(\text{CO})_3$ unit external to the ring.

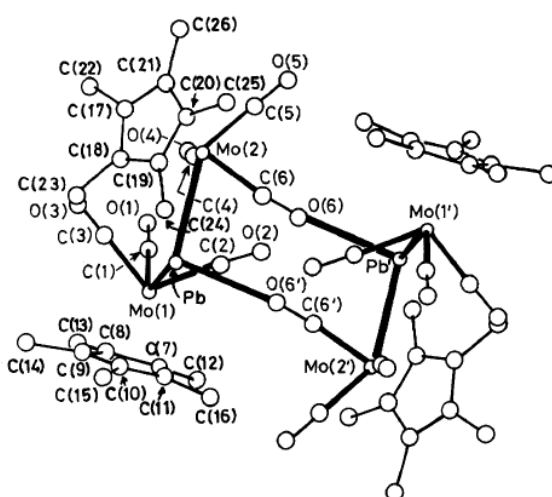


Figure 2.8. Ball and stick plot (arbitrary radius) of $[\text{Pb}\{\text{Cp}^*\text{Mo}(\text{CO})_3\}_2]_2$ (**2.8**).⁵³

Dissolving **1** in THF to give a concentrated solution enabled diffraction-quality crystals of $\text{MgFp}_2(\text{THF})_4$ (**2**) to be grown. The molecular structure and selected distances and angles are shown in Figure 2.8 and Table 2.2.

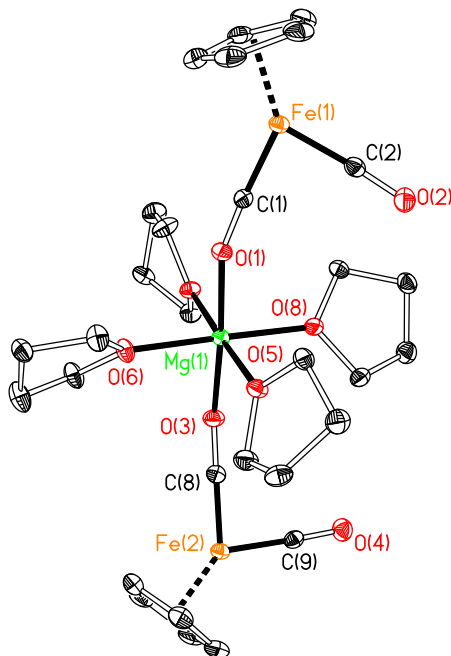
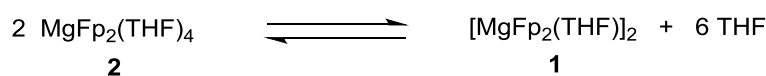


Figure 2.9. Displacement ellipsoid plot (20% probability) of $\text{MgFp}_2(\text{THF})_4$ (**2**). Minor disorder and H atoms omitted for clarity.

Table 2.2. Selected distances (Å) and angles (°) for MgFp₂(THF)₄ (**2**).

Mg(1)···Fe(1)	4.8033(14)	Mg(1)···Fe(2)	4.7796(13)
Mg-O(1)	2.029(3)	Mg(1)-O(3)	2.038(3)
Mg-O(5)	2.079(3)	Mg-O(6)	2.067(3)
Mg(1)-O(7)	2.081(3)	Mg(1)-O(8)	2.063(3)
Fe(1)-C(1)	1.684(4)	Fe(1)-C(2)	1.711(4)
Fe(1)-Cp _{cent} (1)	1.733	Fe(2)-C(8)	1.671(4)
Fe(2)-C(9)	1.725(4)	Fe(2)-Cp _{cent} (2)	1.729
C(1)-O(1)	1.199(5)	C(2)-O(2)	1.177(5)
C(8)-O(3)	1.207(4)	C(9)-O(4)	1.164(5)
O(1)-Mg(1)-O(3)	176.23(13)	O(1)-Mg(1)-O(5)	89.63(12)
O(5)-Mg(1)-O(6)	91.48(12)	O(5)-Mg(1)-O(8)	87.42(12)
O(6)-Mg(1)-O(7)	90.43(12)	O(7)-Mg(1)-O(8)	90.66(12)
C(1)-Fe(1)-C(2)	86.74(18)	C(1)-Fe(1)-Cp _{cent} (1)	137.91
C(2)-Fe(1)-Cp _{cent} (1)	135.34	C(8)-Fe(2)-C(9)	88.55(19)
C(8)-Fe(2)-Cp _{cent} (2)	136.67	C(9)-Fe(2)-Cp _{cent} (2)	134.72

The geometry at the six-coordinate Mg centre is octahedral, with *trans*-axial Mg(μ-OC)Fe isocarbonyl bridges to Fp⁻ anions and four coordinated THF ligands in the equatorial plane. The Mg(1)···Fe(1) and Mg(1)···Fe(2) distances of 4.8033(14) and 4.7796(13) Å, respectively, are significantly greater than the sum of the respective covalent radii (1.73(8) Å).¹⁵ Evidently additional coordination of THF results in a breakup of the dimeric structure (**1**) to give a monomeric structure (**2**). In the process, the Mg-Fe interactions are overcome to afford isocarbonyl interactions between the Mg and Fe centres only. The structure of **2** is likely to represent the form of **1** when in THF solution. Removal of THF results in dimerisation to reform **1** and direct Mg-Fe interactions (Equation 2.3). This is further discussed in Sections 2.3.1 and 2.3.4.

**Equation 2.3**

Analogous to **1**, the C(1)-O(1) (1.199(5) Å) distance is lengthened relative to C(2)-O(2) (1.177(5) Å) and Fe(1)-C(1) (1.684(4) Å) is shorted relative to Fe(1)-C(2) (1.711(4) Å). Compared to Mg(1)-O(1A) in **1**, the Mg(1)-O(1) (2.029(3) Å) and Mg(1)-O(3) (2.038(3) Å) distances in **2** are shorter. However, the average Mg-O(THF) distance in **2** (2.073(3) Å) is longer than that for Mg(1)-O(5) (2.048(1) Å). The C(1)-O(1) (1.199(5) Å) and C(8)-O(3) (1.207(4) Å) distances in **2** are identical within error to that for C(1)-O(1) (1.195(2) Å) in **1**. Whereas the Fe-C distances in **2** associated with C(1)O(1) (1.684(4) Å) and C(8)O(3) (1.671(4) Å) are shorter than the Fe(1)-C(1) distance (1.702(1) Å) in **1**.

The average Mg(1)-O(THF) distance of 2.073(2) in **2** is comparable with that for structurally authenticated literature complexes of 2.08(4) (range: 1.96-2.29) Å.⁵² Compounds **1** and **2** represent the first structurally authenticated examples of Mg(μ -OC)Fe isocarbonyl interactions. Only three examples are known that involve any TM; Burlitch's Mg{CpMo(CO)₃}₂(Py)₄ (**2.9**),⁵⁴ Theopold's Mg{Tp^{tBu,Me}Co(CO)}₂(THF)₄ (**2.10**)⁵⁵ and Braunschweig's recently reported Mg₂{Cym(BC₄Ph₄)₂}₂(THF)₅ (**2.11**) (Cym = Mn(CO)₃(η^5 -C₅H₃)),⁵⁶ illustrated in Figure 2.9. Of these, **2.9** exhibits close structural similarities with **2**, with a six-coordinate Mg centre with octahedral geometry possessing two *trans*-axial Mg(μ -OC)Mn interactions and four equatorial pyridine ligands. This was formed by reaction of Hg{CpMo(CO)₃}₂ with elemental Mg in THF to give an insoluble material that was recrystallised from boiling pyridine to afford **2.9**. The average Mg-O(isocarbonyl) distance of 2.047(2) Å is similar to that for **1** (2.034(2) Å) and is also similar to that for **2.10** (2.068(1) Å) but shorter than that for **2.11** (2.194(3) Å). However one must consider that **2.11** has a Mg(2)-O(3)-C(2) angle of 121.32(2) °, far from linear. For all of these complexes, an elongation of the Mg(μ -OC)TM C-O distances is observed relative to the respective terminal carbonyl groups.

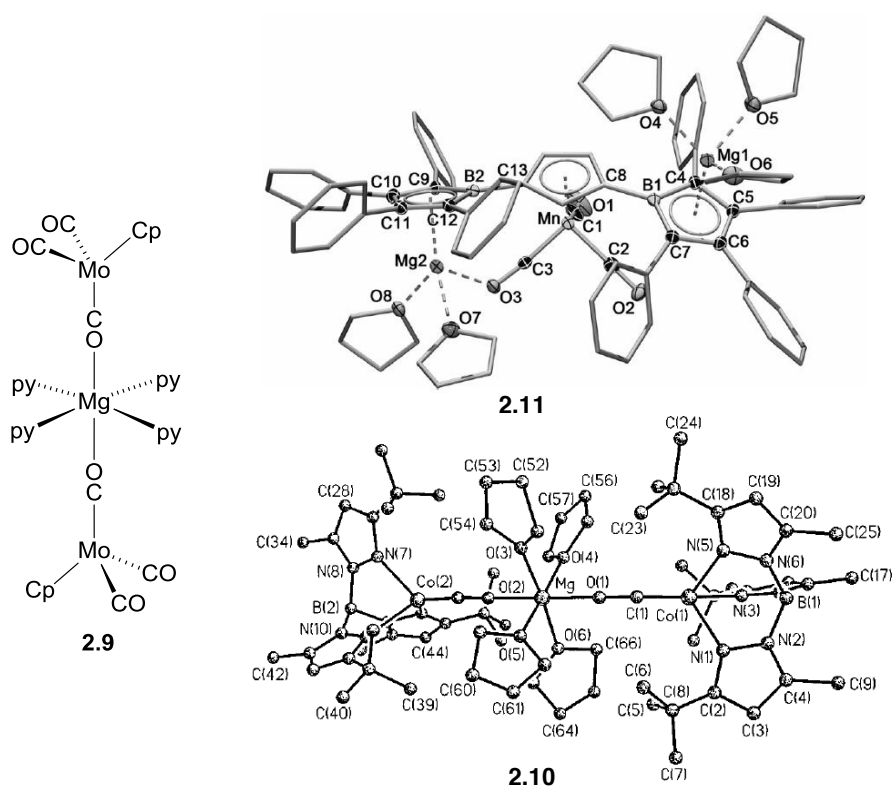


Figure 2.9. Molecular structure of $\text{Mg}\{\text{CpMo(CO)}_3\}(\text{Py})_4$ (**2.9**),⁵⁴ ball and stick plot (arbitrary radius) of $\text{Mg}\{\text{Tp}^{\text{tBu,Me}}\text{Co(CO)}_2\}_2(\text{THF})_4$ (**2.10**) and displacement ellipsoid plot (50% probability) of $\text{Mg}_2\{\text{Cym(BC}_4\text{Ph}_4)_2\}(\text{THF})_5$ (**2.11**).^{55, 56}

Reduction of Fp_2 in THF with excess Ca/Hg afforded $[\text{CaFp}_2(\text{THF})_3]_2$ (**3**) as a red solid in 65% isolated yield. Diffraction-quality crystals of **3** were grown from a concentrated THF solution at RT. The molecular structure and selected distances and angles are shown in Figure 2.10 and Table 2.3.

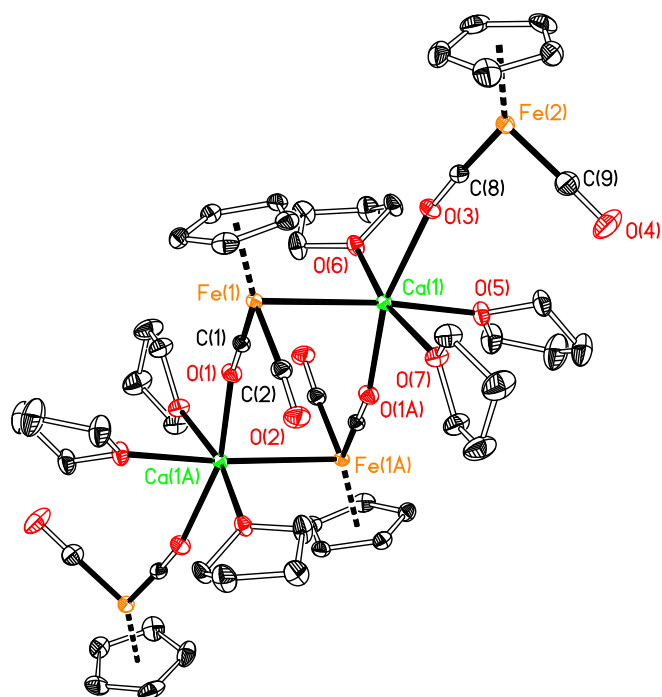


Figure 2.10. Displacement ellipsoid plot (25% probability) of $[\text{CaFp}_2(\text{THF})_3]_2$ (**3**). THF of crystallisation and H atoms omitted for clarity. Atoms carrying the suffix “A” are related to their counterparts by the operator $-x, 1-y, 1-z$.

Table 2.3. Selected distances (Å) and angles (°) for [CaFp₂(THF)₃]₂ (**3**).

Ca(1)-Fe(1)	3.0185(6)	Ca(1)···Fe(1A)	5.1260(6)
Ca(1)···Fe(2)	5.0634(6)	Ca(1)-O(1A)	2.3597(18)
Ca(1)-O(3)	2.3100(19)	Ca(1)-O(5)	2.3968(18)
Ca(1)-O(6)	2.3527(19)	Ca(1)-O(7)	2.3397(19)
Fe(1)-C(1)	1.705(2)	Fe(1)-C(2)	1.732(3)
Fe(1)-Cp _{cent(1)}	1.729	Fe(2)-C(8)	1.689(3)
Fe(2)-C(9)	1.724(3)	C(1)-O(1)	1.188(3)
C(2)-O(2)	1.159(4)	C(8)-O(3)	1.199(3)
C(9)-O(4)	1.163(4)		
Fe(1)-Ca(1)-O(1A)	96.30(5)	Fe(1)-Ca(1)-O(3)	102.62(6)
Fe(1)-Ca(1)-O(5)	174.92(6)	O(1A)-Ca(1)-O(3)	160.95(7)
O(1A)-Ca(1)-O(7)	92.50(7)	O(3)-Ca(1)-O(6)	85.19(8)
O(6)-Ca(1)-O(7)	168.00(7)	Ca(1)-Fe(1)-Cp _{cent(1)}	110.23
Ca(1)-Fe(1)-C(1)	79.43(8)	Ca(1)-Fe(1)-C(2)	84.19(9)
C(1)-Fe(1)-C(2)	92.07(13)	C(1)-Fe(1)-Cp _{cent(1)}	136.67
C(2)-Fe(1)-Cp _{cent(1)}	130.10	C(8)-Fe(2)-C(9)	88.43(13)
C(9)-Fe(2)-Cp _{cent(2)}	133.13	C(2)-Fe(1)-Cp _{cent(1)}	139.07
^a Hinge angle	146		

^a Hinge angle = (Fe(1), C(1), O(1), Fe(1A), C(1A), O(1A))-(Fe(1), Ca(1), O(1A))

The molecular structure is dimeric in the solid state with two CaFp₂(THF)₃ units connected by Ca(μ-OC)Fe isocarbonyl linkages. The geometry at each six-coordinate Ca centre is approximately octahedral with bonds to two μ-isocarbonyl groups, three THF ligands and one Fe centre. The Ca–Fe bond distance of 3.0185(6) Å is consistent with significant interactions, being shorter than the sum of the respective covalent radii (3.08(10) Å).¹⁵ This represents the first example of a structurally authenticated direct Ca-TM bond. The Ca(1)···Fe(1A) (5.1260(6) Å) and Ca(1)···Fe(2) (5.0634(6) Å) distances are considerably greater than the sum of the respective covalent radii. This structural motif is very similar to that for **1** with a centrosymmetric eight-membered central ring with two Ae-TM bonds and two Ae(μ-OC)Fe isocarbonyl linkages. Unlike **1**, **3** does not have direct Ae-Fe interactions external to the ring but a

Ca(1)(μ -OC)Fe(2) isocarbonyl interaction. As mentioned, **3** was formed *via* crystallisation from THF rather than a non-donor environment required to form the dimeric molecular structure of **1** with direct Mg-Fe interactions.

The Ca(μ -OC)Fe isocarbonyl interactions lead to a lengthening of Ca(1)-O(1) (2.3598(2) Å) relative to the terminal C(2)-O(2) (1.159(4) Å). Concomitantly the Fe(1)-C(1) distance (1.705(2) Å) is shortened relative to that for Fe(1)-C(2) (1.732(3) Å). A similar effect is observed with regard to the carbonyl groups bound to Fe(2). The Ca(1)-O(1A) distance is slightly longer than that for Ca(1)-O(3) (2.3100(19)). The C(1)-Fe(1)-C(2) angle (92.07(13) °) is slightly widened relative to C(8)-Fe(2)-C(9) (88.43(13) °). The THF ligand (O(5)) situated *trans* to the Ca(1)-Fe(1) bond has an increased Ca(1)-O(5) distance (Ca(1)-O(5) = 2.3968(18) Å) relative to those in the *cis* positions (Ca(1)-O(6) = 2.3527(19), Ca(1)-O(7) = 2.3397(19) Å). The average Ca-O(THF) distance of 2.3631(11) compares with the average literature value of 2.39(4) (range: 2.30-2.55) Å.⁵²

In addition to the first direct Ca-TM interaction, **3** also exhibits the first structurally authenticated example of a Ca(μ -OC)Fe terminal (μ_2 -) isocarbonyl interaction. Ca{Fe₂(CO)₇(PPh₂)₂}(THF)₄ (**2.16**) is the only reported structure bearing any Ca(μ -OC)Fe isocarbonyl interaction,⁵⁷ although this involves a μ_3 -carbonyl group bridging the Ca (κ_O) and two Fe (κ_C) centres, and is discussed in greater detail in Chapter Three. Nevertheless the Ca-O(isocarbonyl) distance of 2.298(4) is comparable with the average Ca-O(isocarbonyl) distance in **3** of 2.335(3) Å.

Dissolving [CaFp₂(THF)₃]₂ (**3**) in DME at 60 °C gave CaFp₂(DME)₃ (**4**) as a red solid in 88% isolated yield. Slow cooling of a concentrated DME solution to RT gave diffraction-quality crystals. The molecular structure and selected distances and angles are shown in Figure 2.11 and Table 2.4.

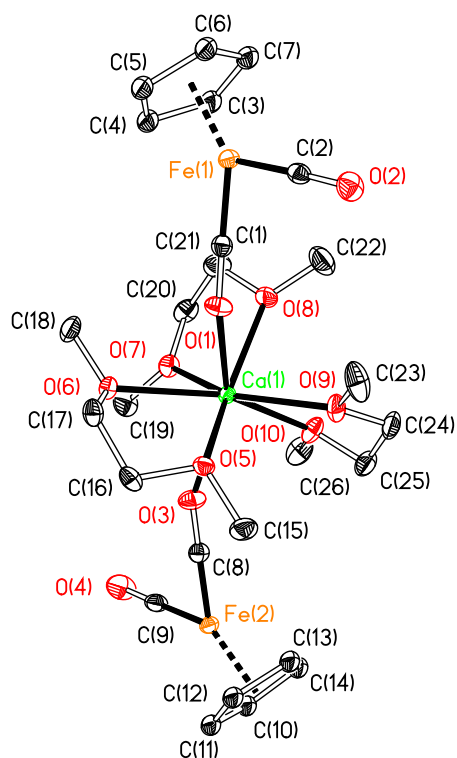


Figure 2.11. Displacement ellipsoid plot (25% probability) of $\text{CaFp}_2(\text{DME})_3$ (4). Second orientation of Cp rings and H atoms omitted for clarity.

Table 2.4. Selected distances (Å) and angles (°) for CaFp₂(DME)₃ (**4**).

Ca(1)···Fe(1)	5.0933(7)	Ca(1)···Fe(2)	5.1604(7)
Ca(1)-O(1)	2.409(2)	Ca(1)-O(3)	2.393(2)
Ca(1)-O(5)	2.514(2)	Ca(1)-O(6)	2.477(2)
Ca(1)-O(7)	2.450(2)	Ca(1)-O(8)	2.462(2)
Ca(1)-O(9)	2.430(2)	Ca(1)-O(10)	2.446(2)
Fe(1)-C(1)	1.685(3)	Fe(1)-C(2)	1.716(4)
Fe(1)-Cp _{cent(1)}	1.735	Fe(2)-C(8)	1.685(3)
Fe(2)-C(9)	1.711(4)	Fe(2)-Cp _{cent(2)}	1.738
C(1)-O(1)	1.198(4)	C(2)-O(2)	1.177(4)
C(8)-O(3)	1.202(4)	C(9)-O(4)	1.178(4)
O(1)-Ca(1)-O(3)	146.66(9)	O(1)-Ca(1)-O(5)	78.78(8)
O(5)-Ca(1)-O(6)	72.36(8)	O(5)-Ca(1)-O(10)	117.60(8)
O(6)-Ca(1)-O(7)	74.98(8)	O(7)-Ca(1)-O(8)	65.26(8)
O(8)-Ca(1)-O(9)	80.07(9)	O(9)-Ca(1)-O(10)	65.54(9)
C(1)-Fe(1)-C(2)	88.94(15)	C(1)-Fe(1)-Cp _{cent(1)}	136.24
C(2)-Fe(1)-Cp _{cent(1)}	134.64	C(8)-Fe(2)-C(9)	88.65(16)
C(8)-Fe(2)-Cp _{cent(2)}	136.56	C(9)-Fe(2)-Cp _{cent(2)}	134.79

Cp rings disordered over two sites, average values used for Fe(1)-Cp_{cent(1)}, Fe(2)-Cp_{cent(2)}, C(1)-Fe(1)-Cp_{cent(1)}, C(2)-Fe(1)-Cp_{cent(1)}, C(8)-Fe(2)-Cp_{cent(2)} and C(9)-Fe(2)-Cp_{cent(2)}.

Ca(1) is eight-coordinate with three DME ligands and two Ca(μ-OC)Fe interactions. The Ca(1)···Fe(1) (5.0933(7) Å) and Ca(1)···Fe(2) (5.1604(7) Å) distances are greater than the sum of the respective covalent radii. The bridging C(1)-O(1) distance (1.198(4) Å) is lengthened relative to that for C(2)-O(2) (1.177(4) Å). There is a concomitant decrease in the Fe(1)-C(1) distance (1.685(3) Å) compared to that for Fe(1)-C(2) (1.716(4) Å). A similar perturbation of the analogous distances occurs for Fe(2). The average Ca-O(DME) distance (2.463(1) Å) is longer than that for Ca(1)-O(1) (2.409(2) Å) or Ca(1)-O(3) (2.393(2) Å).

Evidently dissolving **3** in DME leads to a breakup of the dimeric structure with the loss of direct Ca-Fe interactions and displacement of THF for bidentate DME ligands.

The Ca-O(isocarbonyl) distances in **4** are longer than those for **3** where Ca(1)-O(1A) = 2.3597(18) and Ca(1)-O(3) = 2.3100(19) Å.

The molecular structure of **4** is reminiscent of that for **2**. As expected given the increase in covalent radii (Mg = 1.41(7), Ca = 1.76(10) Å) the Ca-O(isocarbonyl) distances are longer for **4** than **2**. However, the Fe-C and C-O distances associated with the Ae(μ -OC)Fe interactions are identical within error as are those associated with the terminal carbonyl groups.

The average Ca-O(DME) distance of 2.463(1) Å for **4** is comparable with the average literature value (2.45(5) (range: 2.36-2.60) Å)) for structurally authenticated complexes.⁵² The Ca(1)-O(1) (2.409(2) Å) and Ca(1)-O(3) (2.393(2) Å) Ca(μ -OC)Fe isocarbonyl bridging distances are also comparable with the only literature value (**2.16**) of 2.298(4) Å.⁵⁷

Reduction of Fp₂ in THF with excess Sr/Hg afforded [SrFp₂(THF)_x]_y (**5**) as an orange solid. Despite repeated attempts it was not possible to grow diffraction-quality crystals. Also a sample of **5** apparently reacted with the elemental analysis capsule, inhibiting these measurements. However, ¹H and ¹³C{¹H} NMR spectroscopic (THF-*d*₈) data were consistent with one species in solution. Due to these setbacks and the lack of solubility in solvents other than THF, it was not possible to determine the number of THFs “x” bound to Sr or the nature of the extended structure in the solid state. However, given the larger covalent radius of Sr (1.95(10) Å) compared to Ca (1.76(10) Å), it is likely to be dimeric (y = 2) or polymeric (y > 2) with x > 3.

As discussed in Chapter One, owing to their similar covalent (Ca = 1.76(10) and Yb = 1.87(8) Å),¹⁵ and six-coordinate divalent ionic radii (Ca = 1.00, Yb = 1.02 Å),⁵⁸ analogous Ca and Yb complexes have the potential to give molecular structures with very similar morphologies and bonding. To further investigate this phenomenon, Fp₂ in THF was reduced with an excess of Yb/Hg to afford [YbFp₂(THF)₃]₂ (**6**) as a brown solid in 85% isolated yield. Diffraction-quality crystals were grown from a concentrated THF solution at RT. The molecular structure and selected distances and angles are shown in Figure 2.12 and Table 2.5.

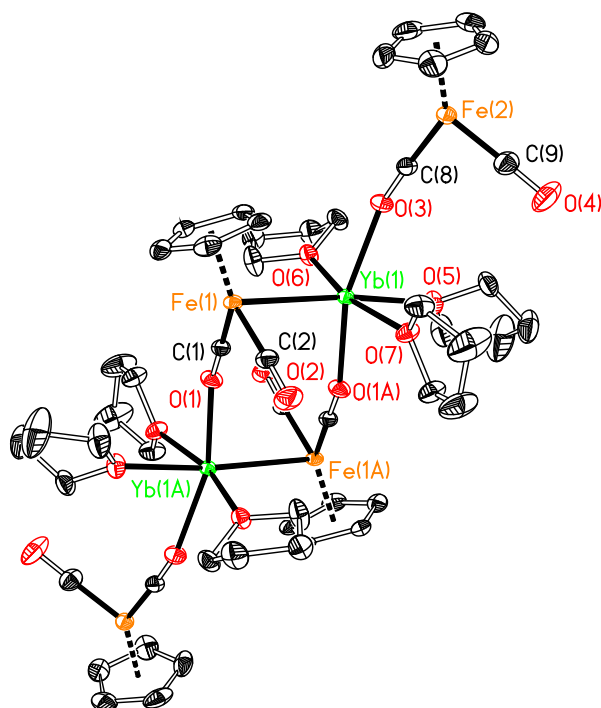


Figure 2.12. Displacement ellipsoid plot (35% probability) of $[\text{YbFp}_2(\text{THF})_3]_2$ (**6**). THF of crystallisation and H atoms omitted for clarity. Atoms carrying the suffix “A” are related to their counterparts by the operator $-x, 1-y, 1-z$.

Table 2.5. Selected distances (Å) and angles (°) for [YbFp₂(THF)₃]₂ (**6**).

Yb(1)-Fe(1)	2.9892(4)	Yb(1)···Fe(1A)	5.1605(4)
Yb(1)···Fe(2)	5.0867(4)	Yb(1)-O(1A)	2.4069(19)
Yb(1)-O(3)	2.356(2)	Yb(1)-O(5)	2.451(2)
Yb(1)-O(6)	2.408(2)	Yb(1)-O(7)	2.396(2)
Fe(1)-C(1)	1.699(3)	Fe(1)-C(2)	1.735(3)
Fe(1)-Cp _{cent} (1)	1.728	Fe(2)-C(8)	1.689(3)
Fe(2)-C(9)	1.718(4)	Fe(2)-Cp _{cent} (2)	1.724
C(1)-O(1)	1.195(3)	C(2)-O(2)	1.164(4)
C(8)-O(3)	1.201(4)	C(9)-O(4)	1.171(5)
Fe(1)-Yb(1)-O(1A)	96.99(5)	Fe(1)-Yb(1)-O(3)	103.89(6)
Fe(1)-Yb(1)-O(5)	174.26(6)	O(1A)-Yb(1)-O(3)	159.02(8)
O(1A)-Yb(1)-O(7)	92.24(7)	O(3)-Yb(1)-O(6)	84.30(8)
O(6)-Yb(1)-O(7)	166.13(7)	Ca(1)-Fe(1)-C(1)	79.15(9)
Ca(1)-Fe(1)-C(2)	84.20(10)	Ca(1)-Fe(1)-Cp _{cent} (1)	109.99
C(1)-Fe(1)-C(2)	91.66(14)	C(1)-Fe(1)-Cp _{cent} (1)	136.92
C(2)-Fe(1)-Cp _{cent} (1)	139.12	C(8)-Fe(2)-C(9)	88.07(15)
C(8)-Fe(2)-Cp _{cent} (2)	138.30	C(9)-Fe(2)-Cp _{cent} (2)	133.61
^a Hinge angle	144		

^a Hinge angle = (Fe(1), C(1), O(1), Fe(1A), C(1A), O(1A))-(Fe(1), Yb(1), O(1A))

The molecular structure of **6** is dimeric in the solid state with two YbFp₂(THF)₃ units connected by Yb(μ-OC)Fe isocarbonyl linkages. The geometry at each six-coordinate Yb centre is approximately octahedral with bonds to one Fe atom, two μ-isocarbonyl groups and three THF ligands. The Yb–Fe bond distance of 2.9892(4) Å is consistent with significant interactions, based on the sum of the respective covalent radii (3.19(9) Å).¹⁵ This represents only the third example of a structurally authenticated Yb–Fe bond. The other examples being Shore's polymeric [$\{(\text{MeCN})_3\text{YbFe}(\text{CO})_4\}_2 \cdot \text{MeCN}\}_x$ (**1.73**) and $[(\text{MeCN})_3\text{YbFe}(\text{CO})_4]_x$ (**1.75**) with Yb–Fe distances of 3.010(1) and 3.046(1) Å,⁵⁹ respectively. The Yb(1)···Fe(1A) (5.1605(4) Å) and Yb(1)···Fe(2) (5.0867(4) Å) distances in **6** are considerably greater than the sum of the respective covalent radii. It is highly apparent that the molecular

structure of **6** is very similar to that for **3** and shall be discussed in Section 2.3.3. The C(1)-O(1) distance (1.195(3) Å) in **6** is shortened relative to that for C(2)-O(2) (1.164(4) Å). As expected, the Fe(1)-C(1) distance (1.699(3) Å) is decreased relative to that for Fe(1)-C(2) (1.735(3) Å). A similar effect is observed with regard to the carbonyl groups bound to Fe(2). The Yb(1)-O(1A) distance (2.407(2) Å) is longer than that for Yb(1)-O(3) (2.356(2) Å). The distance of Yb(1)-O(5) (2.451(2) Å), *trans* to the Yb(1)-Fe(1) bond is lengthened relative to that for Yb(1)-O(6) (2.408(2) Å) and Yb(1)-O(7) (2.396(2) Å), both of which are *cis* to Yb(1)-Fe(1). The C(1)-Fe(1)-C(2) angle (91.66(14) °) is widened relative to that for C(8)-Fe(1)-C(9) (88.07(15) °).

The average Yb-O(THF) distance of 2.418(1) is comparable with the average literature value of 2.38(6) (range: 2.21-2.56) Å.⁵² The average Yb-O(isocarbonyl) distance of 2.389(1) Å is identical within error to that for Shore's **1.73** (2.374(7) Å) but shorter than that for **1.75** (2.481(4) Å).

Reduction of Fp₂ with Yb/NH₃(L) followed by extraction into THF was reported to afford YbFp₂(THF)₄ (**2.12**) with direct Yb-Fe interactions.⁶⁰ However this material was not structurally authenticated. The IR spectrum of **2.12** in THF showed two $\nu(\text{CO})$ bands at 1934 and 1860 cm⁻¹, different to that for **6** (1875 and 1711 cm⁻¹, Section 2.3.1). Given the proposed formula for **2.12**, one would expect a structure reminiscent of that for **2** with Yb(μ -OC)Fe isocarbonyl bridging only between the metal centres. As a result of the lack of structural authentication of **2.12**, further comparison cannot be performed.

2.3.1 Solid state and solution IR studies of [MFp₂(THF)_x]₂ complexes

The IR $\nu(\text{CO})$ bands recorded for [MgFp₂(THF)]₂ (**1**), [CaFp₂(THF)₃]₂ (**3**), [CaFp₂(DME)₃] (**4**), [SrFp₂(THF)_x]_y (**5**), [YbFp₂(THF)₃]₂ (**6**) and [Mg(HMPA)₄][Fp]₂ (**7**) in Nujol and THF are summarised in Table 2.6. The data for **7**, discussed in Section 2.5 and known to have separated ion pairs in both the solid state and THF solution, is also included.

Table 2.6. IR $\nu(\text{CO})$ (cm^{-1}) for $[\text{MgFp}_2(\text{THF})]_2$ (**1**), $[\text{CaFp}_2(\text{THF})_3]_2$ (**3**), $[\text{CaFp}_2(\text{DME})_3]$ (**4**), $[\text{SrFp}_2(\text{THF})_x]_y$ (**5**), $[\text{YbFp}_2(\text{THF})_3]_2$ (**6**) and $[\text{Mg}(\text{HMPA})_4][\text{Fp}]_2$ (**7**) in Nujol and THF.

Complex	$\nu(\text{CO})$ (cm^{-1}) in Nujol	$\nu(\text{CO})$ (cm^{-1}) in THF
1	1912 (s), 1855 (s), 1775 (m)	1875 (s, br), 1703 (s)
3	1899 (s), 1828 (s), 1744 (s)	1878 (s), 1703 (s)
4	1869 (s), 1733 (s)	1865 (s), 1703 (s, br)
5	1871 (s), 1808 (m), 1749 (m)	1878 (s), 1712 (s)
6	1897 (s), 1823 (s), 1744 (s)	1875 (s), 1711 (s)
7	1863 (s), 1789(s)	1865 (s), 1787 (s)

Figure 2.13 illustrates the molecular structures of **1** and **2**. These are postulated to be representative of the structure of **1** in the solid state and THF, respectively. Accompanying these diagrams are the DFT predicted $\nu(\text{CO})$ bands for these species. For **1** there are four predicted bands at 1926, 1909, 1864 and 1802 cm^{-1} . The band of lowest wavenumber at 1802 cm^{-1} corresponds to the bridging carbonyl groups and the former three values to the terminal carbonyl groups. Two $\nu(\text{CO})$ bands are predicted for **2** at 1881 and 1694 cm^{-1} , corresponding to the terminal and bridging carbonyl groups, respectively. The predicted decrease in stretching frequency as a consequence of coordination to the Mg centre is expected, consistent with the increase in $\text{M}(\mu\text{-OC})\text{Fe}$ C-O distances compared to those for the respective terminal carbonyl groups for the complexes synthesised in this Section. This effect was discussed in Section 2.3 for **1**.

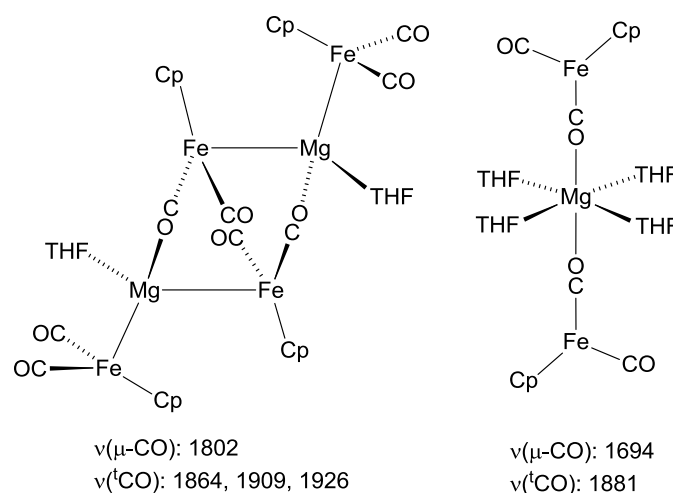


Figure 2.13. Molecular structures of $[\text{MgFp}_2(\text{THF})]_2$ (**1**) and $\text{MgFp}_2(\text{THF})_4$ (**2**) with DFT predicted absorption bands (cm^{-1}) for bridging ($\mu\text{-CO}$) and terminal (^tCO) carbonyls.

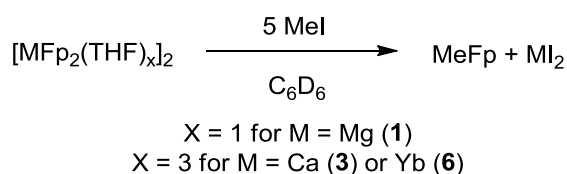
For **1**, the experimentally observed band at 1775 cm^{-1} is likely to correspond to the isocarbonyl bridged CO and the bands at 1912 and 1855 cm^{-1} to the terminal CO. Only two bands are observed in THF at 1875 and 1703 cm^{-1} for the terminal and isocarbonyl CO stretches, respectively. These bands are near-identical to those for McVicker's " $\text{MgFp}_2(\text{THF})_2$ " (**2.7**) commented on in Section 2.3 (1772 , 1854 , 1925 cm^{-1}).⁴² Therefore, it would appear that whilst the molecular formula proposed by McVicker is different, the material formed was in fact **1** and did contain a direct Mg-Fe interaction as proposed. Given **1** was isolated as a solvate i.e. $\mathbf{1} \cdot 1.3(\text{THF})$, the disparity between the McVicker's molecular formula and the actual molecular structure are understandable.

The three bands for **3** and **6** in Nujol are likely to correspond to the terminal CO, bridging CO external to the ring and bridging CO internal to the ring going from higher to lower wavenumbers. As with **2**, two bands are observed in THF. This is consistent with **3** and **6** switching from dimeric structures with direct metal-metal interactions to monomeric structures $\text{MFp}_2(\text{THF})_4$ ($\text{M} = \text{Ca}$ (**8**) or Yb (**9**)) with isocarbonyl bridging between the metal centres only. This is supported by the spectra for **4** in Nujol and THF which both exhibit two $\nu(\text{CO})$ bands, consistent with isocarbonyl bridging only as observed for the molecular structure (Figure 2.11). Compound **5** also follows the trend observed for **1**, **3** and **6** with three significant bands in Nujol and two in THF. Whilst this could suggest a similar form in the solid

state and THF to the analogous Ca and Yb complexes, this is not reliable evidence for or against the presence of direct metal-metal interactions in **5**. Reassuringly, none of the experimentally determined spectra match with that for **7** either in the solid state or solution, consistent with interactions between the Fe and Ae/Ln metal centres in all of these complexes, whether through isocarbonyl or direct metal-metal interactions. For some of these spectra, additional bands are observed that not might be expected based on the molecular structures and have not been reported in Table 2.6. These are often minor in comparison and may result from symmetry distortions from the idealised structures allowing more vibrational modes. All bands are reported for each of these complexes in Nujol in Chapter Five. This also applies to other new complexes discussed in this Thesis.

2.3.2 Reactivity of $[\text{MFp}_2(\text{THF})_x]_2$ complexes

NMR tube-scale reaction of **1** with MeI in C_6D_6 gave quantitative conversion to MeFp and MgI_2 . This was also successful for analogous reactions with **3** and **6** (Equation 2.4). For added confirmation, volatiles were removed from the product mixture for the reaction of **3** with MeI and redissolved in CDCl_3 . The ^1H NMR spectrum was consistent with literature values for MeFp synthesised from KFp,⁶¹ consistent with these complexes providing a source of the Fp^- anion.



Equation 2.4

2.3.3 Comparison of $[\text{MFp}_2(\text{THF})_x]_2$ complexes

It is highly apparent that **1**, **3** and **6** have very similar molecular structures and simple reactivity. All three possess a centrosymmetric eight-membered ring comprising two $\text{M}(\mu\text{-OC})\text{Fe}$ (M = Mg, Ca or Yb) isocarbonyl linkages and two M-Fe bonds. For **1**, two additional Mg-Fe bonds are observed per dimer, external to the ring whereas these Ae/Ln-Fe interactions manifest as isocarbonyl linkages for **3** and **6**. For **1** crystallisation from THF afforded **2**, monomeric with no direct Mg-Fe interactions. In contrast, **3** and **6** could be crystallised from THF to afford dimeric structures with direct metal-metal interactions. This allows the first experimental comparison of any alkaline earth-transition metal bond with that of a divalent rare earth analogue.

As summarised in Table 2.7, the parameters associated with the molecular structures of **3** and **6** are very similar to the point that these structures can be considered isostructural. Considering their unit cell parameters they are also isomorphous. This is expected given the similar covalent (Ca = 1.76(10) and Yb = 1.87(8) Å),¹⁵ and six-coordinate divalent ionic radii (Ca = 1.00, Yb = 1.02 Å),⁵⁸ are also similar. Despite these being slightly larger for Yb than Ca, the M-Fe bond distance is shorter in **6** (2.9892(4) Å) than **3** (3.0185(6) Å) whereas the M-O distances are longer as expected. For example the M(1)(μ-OC)Fe(1A) Ca-O distance is 2.3597(18) Å compared to an Yb-O distance of 2.4068(19) Å. This phenomenon was also observed for some of the isostructural divalent Ca- and Yb-main group metal bonded complexes introduced in Chapter One such as Jones' M{Ga(ArNCH)₂}₂(TMEDA)₂ (M = Ca (**1.55**) or Yb (**1.69**) and Ar = dipp), discussed in greater detail in Section 2.4.^{62, 63}

Table 2.7. Comparison of Selected distances (Å) and angles (°) for [MFp₂(THF)₃]₂ M = Ca (**3**) or Yb (**6**).

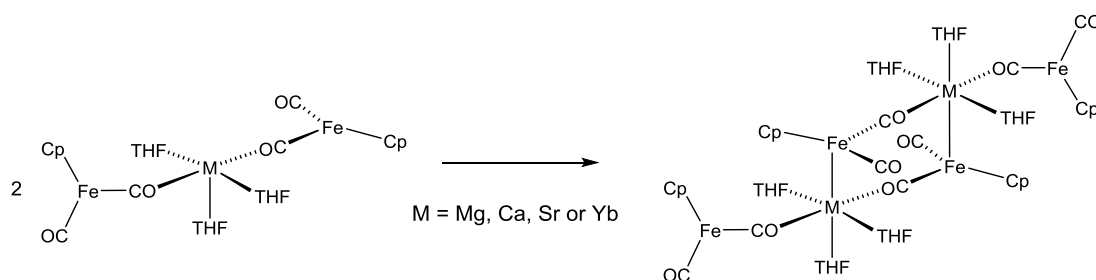
	3	6
M–Fe	3.0185(6)	2.9892(4)
M–O _{Fp} [Fe1(A)]	2.3597(18)	2.4069(19)
M–O _{Fp} [Fe(2)]	2.3100(19)	2.356(2)
M–O _{THF} [<i>trans</i> to M–Fe]	2.3968(18)	2.451(2)
M–O _{THF} [<i>cis</i> to M–Fe]	2.3527(19)	2.408(2)
	2.3397(19)	2.396(2)
Fe(1)–CO (bridging)	1.705(2)	1.699(3)
Fe(1)–CO (terminal)	1.732(3)	1.735(3)
Fe(2)–CO (bridging)	1.689(3)	1.689(3)
Fe(2)–CO (terminal)	1.724(3)	1.718(4)
OC–Fe(1)–CO	92.07(13)	91.66(14)
OC–Fe(2)–CO	88.43(13)	88.07(15)

2.3.4 DFT Computational Analysis of [MFp₂(THF)_x]₂ complexes

Gradient-corrected density functional theory (DFT) was employed to study **3** and **6** as full models, **3Q** and **6Q**, respectively, without symmetry constraints, the results of which are collected in Table 2.8. The agreement between the experimental and

computed structures is very good. In particular, the calculated Yb–Fe distances (2.965, 2.956 Å) are 0.021 Å shorter than those for Ca–Fe (2.984, 2.978 Å), consistent with the experimental structures (**3**: 3.019(1), **6**: 2.989(1) Å).

The Ziegler-Rauk energy decomposition scheme has been employed to probe the interaction between the two hypothetical [MFp₂(THF)₃] fragments at the converged geometries for M = Ca and Yb (Equation 2.5).^{64, 65} These data indicate a significant interaction energy between the two fragments (effectively a measure of the M-Fe interaction), which is 8.4 kJ mol⁻¹ larger per M-Fe bond in **6Q** than **3Q**, in agreement with the slightly shorter M-Fe distance in the former. Considering the relative contributions of the pre-relaxation electrostatic term and the post-relaxation orbital mixing term; it is unusual that the electrostatic term is the largest in the energy decomposition of interactions between neutral fragments. This suggests that the M-Fe bonds are predominantly ionic, and population analysis of the valence molecular orbitals supports this conclusion in finding no contributions from M larger than 1%. The difference in the Mulliken charges of the M and Fe(1) atoms in each [MFp₂(THF)₃] fragment is large, in keeping with the large electrostatic terms in the energy decomposition. The difference in the Mulliken charges of the M and Fe(1) atoms is large in each case, as expected for an ionic interaction, and also that the charges of M and Fe(1) are significantly different in [MFp₂(THF)₃]₂ than in the [MFp₂(THF)₃] fragments. This indicates that, on relaxation to self-consistency, there is a significant redistribution of charge within each fragment. This accounts for the favourable orbital mixing contributions to the M-Fe interaction energy, despite there being very little M character in the valence molecular orbitals. For **6Q** there is actually a decrease in the charge difference between the Yb and Fe centres in [YbFp₂(THF)₃]₂ compared to the [YbFp₂(THF)₃] fragments ($\Delta\Delta$ (charge M – charge Fe(1)) = -0.15). This contrasts with **3Q** where an increase in the charge difference is observed (0.06).

Equation 2.5^{64, 65}

Atoms-in-molecules (AIM) analysis supports the existence of Ca-Fe and Yb-Fe bonds in finding M-Fe bond paths.⁶⁶ Selected data at the M-Fe bond critical points (BCPs) are included in Table 2.8. The electron density ρ is slightly larger at the Yb-Fe BCP than the Ca-Fe BCP, in agreement with the shorter Yb-Fe bond and larger interaction energy. The small positive values of ρ and its Laplacian $\nabla^2\rho$ reinforce the molecular orbital and Ziegler-Rauk analyses in finding little covalency in the bonding. Following the approach of Vlasisavljevich *et al.*⁶⁷ and Bianchi *et al.*⁶⁸, the energy density H may be used to further classify the M-Fe interactions. Vlasisavljevich *et al.* used AIM to study a range of heterobimetallic Ln-M and An-M bonds, and found H values at the BCPs to be similar in magnitude to these results, but to be very slightly positive. H values close to zero indicate metallic bonding in the Bianchi approach. Hence the metal-metal interactions in **3** and **6** fit into this category, in agreement with the findings of Vlasisavljevich *et al.*

Table 2.8. Selected DFT computational results for [MFp₂(THF)₃]₂. M = Mg (**1aQ**), Ca (**3Q**) Sr (**5Q**) or Yb (**6Q**).

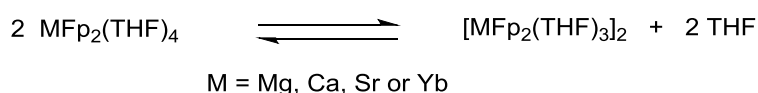
	1aQ	3Q	5Q	6Q
r(M–Fe) (Å)	2.815	2.984	3.197	2.965
	2.815	2.978	3.190	2.956
M–Fe interaction energy (per M Fe bond)	-150.5	-134.9	-116.1	-143.3
orbital mixing energy	-117.9	-91.1	-83.4	-107.4
electrostatic interaction energy	-207.6	-191.2	-185.2	-249.5
Pauli repulsion energy	175.0	147.4	147.4	213.5
charge M ([MFp ₂ (THF) ₃] fragment)	1.20	1.51	1.46	1.32
charge Fe(1) ([MFp ₂ (THF) ₃] fragment)	0.14	0.14	0.13	0.15
charge M	1.10	1.38	1.34	1.01
charge Fe(1)	-0.05	-0.05	-0.04	-0.01
Δ (charge M – charge Fe(1)) (fragment)	1.06	1.37	1.33	1.17
Δ (charge M – charge Fe(1)) (in complex)	1.15	1.43	1.38	1.02
ΔΔ (charge M – charge Fe(1))	+0.09	+0.06	+0.05	-0.15
ρ (electron density)	0.021	0.022	0.018	0.029
∇ ² ρ (electron density Laplacian)	0.039	0.041	0.038	0.040
H (energy density)	-0.003	-0.002	-0.0009	-0.006

All energies in kJ mol⁻¹. Orbital mixing (and hence total interaction) energies corrected for basis set superposition error (**1aQ** 9.1, **3Q** 7.2, **5Q** 8.7 and **6Q** 10.2). AIM data (atomic units) obtained at the bond critical point. Charges obtained from Mulliken analyses.

Also included in Table 2.8 are the values for hypothetical $[\text{MgFp}_2(\text{THF})_3]_2$ **1aQ** and $[\text{SrFp}_2(\text{THF})_3]_2$ **5Q** (Figure 2.14) based on the $[\text{MFp}_2(\text{THF})_3]_2$ structure observed for **3** and **6**. Structure **1aQ** is not observed experimentally, indeed $[\text{MgFp}_2(\text{THF})]_2$ (**1**) is observed when crystallisation is performed in a non-donor environment to afford a dimeric structure with only one THF per Mg rather than three as observed for Ca and Yb. Also two Mg-Fe bonds are present for each Mg in **1** but only one metal-metal bond exists to each Ca and Yb centre in **3** and **6**, respectively. However, the use of hypothetical **1aQ** allows the influence of altering the divalent metal within the same $[\text{MFp}_2(\text{THF})_3]_2$ framework to be investigated.

1aQ has shorter M-Fe interactions (2.815 Å) than that for **3Q** (2.984, 2.978 Å) or **6Q** (2.965, 2.956 Å). Indeed, the interaction energy per M-Fe interaction is greatest for **1aQ** (-150.5 kJ mol⁻¹). The electron density (0.021 au), its Laplacian (0.039 au) and the energy density (-0.003 au) at the Mg-Fe BCPs are consistent with there being little covalency in these interactions. Indeed, the values for these parameters are similar to those for **3Q**. The $\Delta\Delta$ (charge M – charge Fe(1)) for **1aQ** is also positive (0.09) like that for **3Q** (0.06) in contrast to that for **6Q** (-0.15).

Despite the stronger M-Fe interactions in **1aQ**, experimental findings show monomeric $\text{MgFp}_2(\text{THF})_4$ (**2**) is formed when **1** is crystallised from THF in contrast to the dimeric structures for **3** and **6**. To probe this further the transformations summarised in Equation 2.6 were assessed computationally for M = Mg, Ca, Sr and Yb. Since the (favourable) entropic contribution associated with the formation of the dimers in each case may be considered to be approximately constant, it is appropriate to consider only the enthalpy change rather than free energy change of the process. DFT finds that formation of **1aQ** from computed $\text{MgFp}_2(\text{THF})_4$ (**2Q**) is disfavoured by +48.9 kJ mol⁻¹. However, formation of **3Q** and **6Q** have favourable $\Delta_r H$ values of -11.9 and -33.5 kJ mol⁻¹, respectively, in agreement with experimental findings. The formation of **5Q**, discussed below, is favoured by -9.3 kJ mol⁻¹, similar to that for **3Q**.

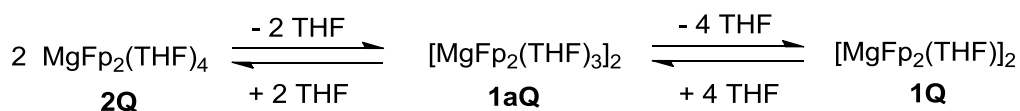


Equation 2.6

Equation 2.6 serves to illustrate the delicate balance between metal–solvent and metal–metal interactions in these predominantly ionic systems. The modest computed $\Delta_r H$ values for the conversion of **8Q** ($\text{CaFp}_2(\text{THF})_4$) or **9Q** ($\text{YbFp}_2(\text{THF})_4$) to **3Q** or

6Q, respectively, are consistent with the conclusion based on IR spectroscopy that **3** and **6** exist as monomeric THF adducts $\text{MFp}_2(\text{THF})_4$ ($\text{M} = \text{Ca}$ (**8**) or Yb (**9**) in solution.

As illustrated in Scheme 2.1, DFT finds that formation of **1Q** from **1aQ** is disfavoured by $\Delta_r H = +50.9 \text{ kJ mol}^{-1}$. However the entropy change associated with this is favourable, giving a free energy change of formation of $-152.9 \text{ kJ mol}^{-1}$, consistent with the formation of **1** in the absence of THF. The computed structure of $[\text{MgFp}_2(\text{THF})]_2$ **1Q** shows good agreement with that found experimentally (**1**). For example, the Mg-Fe distances in the eight-membered ring are similar (**1Q**: 2.633, **1**: 2.6112(5) Å) as are the external Mg-Fe distances ((**1Q**: 2.550, **1**: 2.5629(5) Å). However, the hinge angles are considerably different with the computed structure being closer to coplanarity (152°) than that determined experimentally (139°).



Scheme 2.1. Formation of **1Q** from **2Q** via hypothetical **1aQ**.

As discussed it was not possible to obtain diffraction-quality crystals of $[\text{SrFp}_2(\text{THF})_y]_x$ (**5**). To gain an insight into the possible Sr-Fe interactions in this material, the model structure $[\text{SrFp}_2(\text{THF})_3]_2$ (**5Q**) was analysed computationally (Figure 2.14).

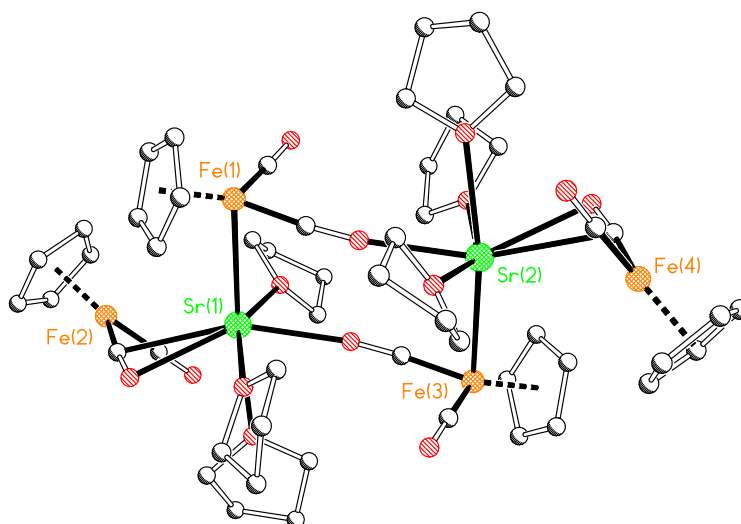


Figure 2.14. DFT calculated structure of $[\text{SrFp}_2(\text{THF})_3]_2$ (**5Q**).

The minimised structure of **5Q** contains an eight-membered ring in a chair conformation comprising two Sr-Fe direct interactions and two $\text{Sr}(\mu\text{-OC})\text{Fe}$

isocarbonyl interactions. The Sr-Fe distances of 3.197 and 3.190 Å are shorter than the sum of the respective covalent radii (3.27(10) Å) and the interaction energy per M-Fe bond of -116.1 kJ mol⁻¹ for M = Sr is the smallest of the calculated [MFp₂(THF)₃]₂ structures.¹⁵ For the monomeric fragment [MFp₂(THF)₃], the charge difference between the M and Fe centres of 1.33 for M = Sr is similar to that for M = Ca (1.37). This is also the case for the dimeric structure [MFp₂(THF)₃]₂ where the charge difference is 1.38 for M = Sr and 1.43 for M = Ca. Hence a slight increase (+0.05) in the charge difference occurs on bringing the monomeric fragments together. This is very similar to that observed for M = Ca (+0.06) and contrasts with that for **6Q** where a decrease occurs (-0.15). For M = Sr, the electron density (0.018 au) and its Laplacian (0.038 au) at the M-Fe BCPs are the smallest for the [MFp₂(THF)₃]₂ structures in Table 2.8. In addition, the small value for the energy density (-0.009 au) is consistent with an ionic Sr-Fe interaction with the lowest covalent contribution of these model systems.

Unlike the minimised structures for **1aQ**, **3Q** and **6Q** that for **5Q** (Figure 2.14) has side-on (η^2 -) carbonyl interactions between the Sr centres and Fp moieties external to the ring. Whilst this interaction is observed experimentally for [Sr{Co(CO)₃(PCy₃)₂}]_x (**35**, Chapter Four) it is possible that the experimental structure (**5**) has more than three THFs coordinated to each Sr centre. Alternatively or in addition, **5** may be polymeric in the solid state given the greater covalent radius of Sr (1.95(10) Å) compared to Ca (1.76(10) Å) or Yb (1.87(8) Å).

2.4 M{Ga(ArNCH)₂}₂(TMEDA)₂ Complexes

As discussed in Chapter One and illustrated once more in Figure 2.15, the gallyl complexes M{Ga(ArNCH)₂}₂(TMEDA)₂ (M = Ca (**1.55**) or Yb (**1.69**) and Ar = dipp) bear direct Ca-Ga (3.228(1) Å) and Yb-Ga (3.226(1) Å) interactions.^{62, 63} These distances are identical within error, consistent with the sum of the respective covalent radii,¹⁵ where Ca-Ga = 2.98(13) Å and Yb-Ga = 3.09(11) Å.

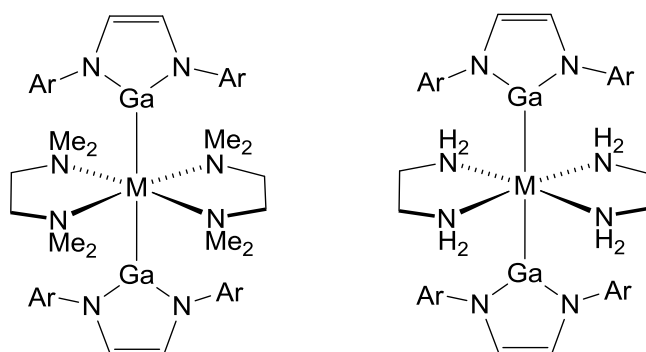


Figure 2.15. $M\{Ga(ArNCH)_2\}_2(TMEDA)_2$ (left, $M = Ca$ (**1.55**) or Yb (**1.69**)) and hypothetical $M\{Ga(ArNCH)_2\}_2(en)_2$ (right, $M = Ca$ (**1.55q**) or Yb (**1.69q**)), where $Ar = dippr$.^{62, 63}

Complexes **1.55** and **1.69** were modelled computationally as **1.55Q** and **1.69Q**, respectively. The data for these complexes and their less sterically encumbered analogues **1.55q** and **1.69q**, with ethylenediamine (en) rather than TMEDA ligands, are summarised in Table 2.9.

Table 2.9. DFT computed parameters for $M\{Ga(ArNCH)_2\}_2(TMEDA)_2$ ($M = Ca$ (**1.55Q**) and Yb (**1.69Q**)) and $M\{Ga(ArNCH)_2\}_2(en)_2$ ($M = Ca$ (**1.55q**) and Yb (**1.69q**)), where $Ar = dippr$.

	1.55Q	1.69Q	1.55q	1.69q
$r(M-Fe)$ (Å)	3.241	3.225	3.082	3.059
$M-N$ (Å)	2.614	2.641	2.550	2.564
charge M	1.32	1.18	1.33	0.99
charge $Ga(1)$	-0.16	-0.12	-0.04	0.02
Δ charge ($M-Ga$)	1.48	1.30	1.37	0.97
ρ (electron density)	0.018	0.023	0.022	0.028
$\nabla^2\rho$ (e.d. Laplacian)	0.027	0.025	0.036	0.031
H (energy density)	-0.0005	-0.003	-0.0008	-0.004

All energy densities in kJ mol^{-1} . AIM data (atomic units) obtained at the bond critical point. Charges obtained from Mulliken analyses.

Comparing **1.55Q** to **1.69Q**, the $M-Ga$ distance is shorter for $M = Yb$ (3.225 Å) than for $M = Ca$ (3.241 Å), despite the larger covalent radius for Yb and average $Yb-N$ (2.641 Å) distance relative to that for $M = Ca$ ($Ca-N = 2.614$ Å). AIM analysis gives

low values for the electron density, its Laplacian and the energy density at the BCPs in these structures, consistent with an ionic interaction between the metal centres. These parameters are smaller for $M = \text{Ca}$ than $M = \text{Yb}$. The charge difference between the metal centres is greater for $M = \text{Ca}$ (1.475) than $M = \text{Yb}$ (1.300), suggesting there is more covalent character associated with the Yb-Ga interactions compared to the Ca-Ga interactions. These observations are consistent with those for $[\text{CaFp}_2(\text{THF})_3]_2$ (**3Q**) and $[\text{YbFp}_2(\text{THF})_3]_2$ (**6Q**).

Substitution of the TMEDA methyl groups present in the full model structures **1.55Q** and **1.69Q** with H atoms gave **1.55q** and **1.69q**. As expected given the reduction in steric bulk, the average Ca-Ga (3.082 Å) and Yb-Ga (3.059 Å) distances are decreased, as are the average Ca-N (2.550 Å) and Yb-N (2.564 Å) distances relative to those in **1.55Q** and **1.69Q**. For **1.55q** and **1.69q**, the electron density, its Laplacian and the energy density at the BCPs is lower for $M = \text{Ca}$ than $M = \text{Yb}$, consistent with that observed for the full models **1.55Q** and **1.69Q**. As expected, for $M = \text{Ca}$ and $M = \text{Yb}$ these values are larger for **1.55q** and **1.69q** than **1.55Q** and **1.69Q**, respectively, although these interactions still have little covalency. The DFT calculated structures of $\text{Ca}\{\text{Ga}(\text{ArNCH})_2\}_2(\text{TMEDA})_2$ (**1.55Q**) and $\text{Ca}\{\text{Ga}(\text{ArNCH})_2\}_2(\text{en})_2$ (**1.55q**) are shown in Figure 2.16.

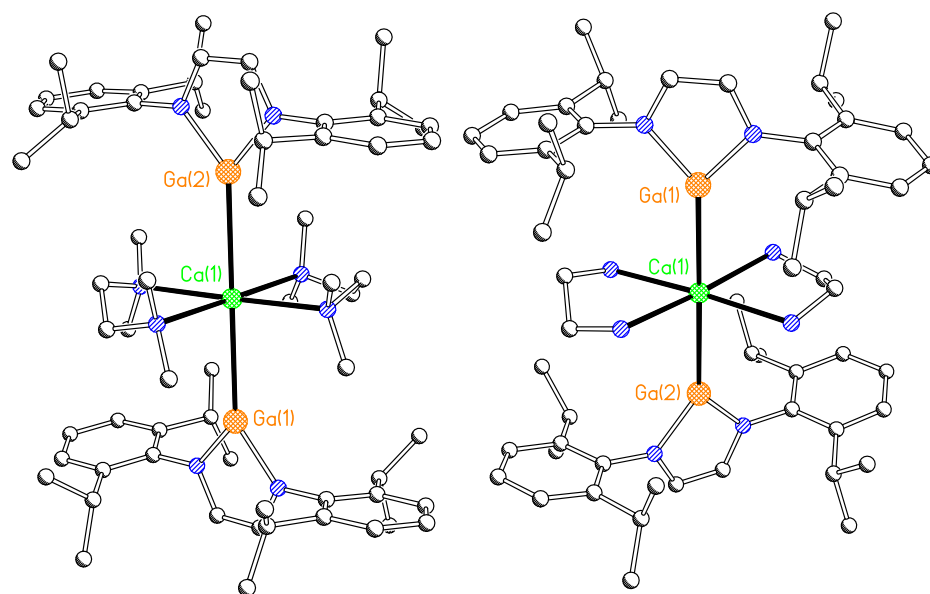


Figure 2.16. DFT calculated structures of $\text{Ca}\{\text{Ga}(\text{ArNCH})_2\}_2(\text{TMEDA})_2$ (**1.55Q**, left) and $\text{Ca}\{\text{Ga}(\text{ArNCH})_2\}_2(\text{en})_2$ (**1.55q**, right), where Ar = dipp. H atoms omitted for clarity.

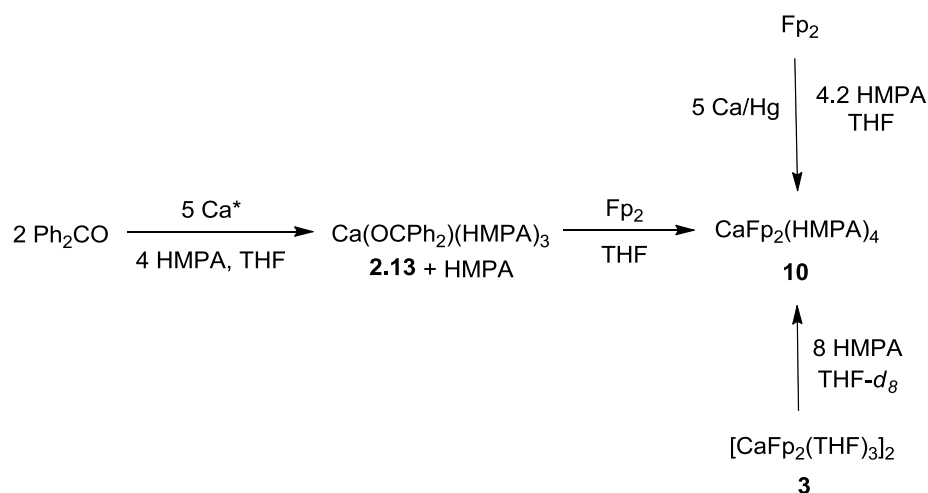
Calculations were also performed for **1.55q** and **1.69q** at their (otherwise) optimised geometries but with the M-Ga distances lengthened to the values for the full models **1.55Q** (3.241 Å) and **1.69Q** (3.225 Å). Compared to **1.55Q** and **1.69Q**, these modified structures **1.55aq** and **1.69aq** are destabilised by only 3.9 and 4.0 kJ mol⁻¹, respectively. Given the increase in these distances of 0.159 and 0.166 Å, this highlights the very soft character of these surfaces and the ease with which the distance of the interactions can vary.

Attempts to model **1.55Q** and **1.69Q** with the aryl ring *ortho*-ⁱPr groups substituted with H atoms were unsuccessful. The structures were unstable and did not maintain linearity along the M-Ga-M vector. This highlights the stability imparted by these groups together with the methyl groups on the TMEDA ligands and their likely influence on the bond lengths.

2.5 HMPA coordinated complexes

Whilst effective in activating the elemental alkaline earth metals (Mg, Ca, Sr) and Yb, an alternative to amalgamation was employed alongside the aforementioned reactions. Attempts to react KFp with CaI₂ were unsuccessful, apparently only returning unreacted KFp.

As mentioned in Section 2.2.1, KFp can be synthesised by the reaction of Fp₂ with K-benzophenone.⁸ The use of Ca-benzophenone has also been reported.^{69, 70} Given this, use Ca-benzophenone was investigated as alternative route to Ca/Hg reduction for the synthesis of Ca-Fp compounds. Unlike the formation of Na- or K-benzophenone, HMPA (P(O)(NMe₂)₃) is required in the presence of Ca-benzophenone to inhibit intramolecular coupling between the benzophenone ketyl radicals to give an undesired pinacol compound. Reaction between elemental Ca activated with CH₂I₂ and a THF solution of benzophenone and HMPA gave a deep blue solution containing Ca(OCPh₂)(HMPA)₃ (**2.13**). *In situ* reaction with Fp₂ in THF gave CaFp₂(HMPA)₄ (**10**) as a red solid in 41% isolated yield (Scheme 2.2).



Scheme 2.2. Synthetic routes to $\text{CaFp}_2\text{(HMPA)}_4$ (**10**).

Diffraction-quality crystals of **10** were grown from a concentrated THF solution at RT. The molecular structure is illustrated in Figure 2.17. Data of sufficient quality for a detailed structural analysis could not be obtained, although the connectivity within this structure is unambiguous. Elemental analysis and ^1H NMR spectroscopy of the bulk material were also consistent with **10** having this structure, the latter having one NMe_2 environment as a result of fast exchange of the HMPA ligands. The four HMPA ligands coordinated to $\text{Ca}(1)$ are sufficiently sterically demanding and Lewis basic such that only $\text{Ca}(\mu\text{-OC})\text{Fe}$ isocarbonyl interactions can take place between the metal centres.⁷¹⁻⁷⁵ This is unsurprising when one considers the $\text{Ca}(\mu\text{-OC})\text{Fe}$ isocarbonyl linkages observed in $\text{CaFp}_2\text{(DME)}_3$ (**4**).

It is not possible to carry out a comparison of the parameters associated with the molecular structure of **10** with structurally authenticated literature examples of Ca^{2+} dications ligated by HMPA. However, it remains to be said that they are known, including that of the intermediate $\text{Ca(OCPh}_2\text{)}_2\text{(HMPA)}_3$ (**2.13**).^{69, 76, 77}

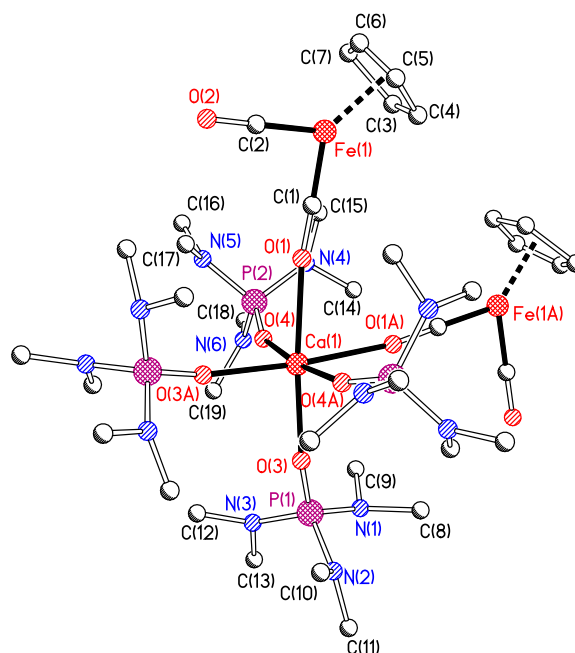


Figure 2.17. Ball and stick plot (arbitrary radius) of $\text{CaFp}_2(\text{HMPA})_4$ (**10**). H atoms omitted for clarity.

As illustrated in Scheme 2.2, it was also possible to synthesise **10** in 75% isolated yield using a Ca/Hg reduction of Fp_2 in the presence of HMPA. Alternatively, addition of HMPA to **3** gave quantitative conversion to **10** on the NMR tube-scale.

Reduction of Fp_2 in THF with excess Yb/Hg in the presence of excess HMPA gave $\text{YbFp}_2(\text{HMPA})_4$ (**11**) as an orange solid in 99% isolated yield. Diffraction-quality crystals were grown from a concentrated THF solution at RT. The molecular structure and selected distances and angles are shown in Figure 2.18 and Table 2.10.

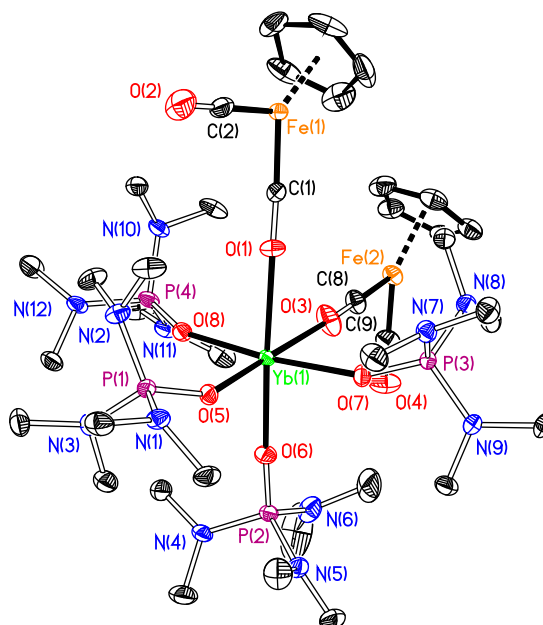


Figure 2.18. Displacement ellipsoid plot (25% probability) of $\text{YbFp}_2(\text{HMPA})_4$ (**11**). Other independent molecule and H atoms omitted for clarity.

Table 2.10. Selected distances (Å) and angles (°) for YbFp₂(HMPA)₄ (**11**).

Yb(1)···Fe(1)	5.2758(6)	Yb(1)···Fe(2)	5.3193(6)
Yb(1)-O(1)	2.449(3)	Yb(1)-O(3)	2.438(3)
Yb(1)-O(5)	2.323(3)	Yb(1)-O(6)	2.304(3)
Yb(1)-O(7)	2.328(3)	Yb(1)-O(8)	2.342(3)
Fe(1)-C(1)	1.699(5)	Fe(1)-C(2)	1.702(6)
Fe(1)-Cp _{cent} (1)	1.722	Fe(2)-C(8)	1.694(5)
Fe(2)-C(9)	1.728(6)	Fe(2)-Cp _{cent} (2)	1.726
C(1)-O(1)	1.190(6)	C(2)-O(2)	1.182(6)
C(8)-O(3)	1.189(6)	C(9)-O(4)	1.172(6)
P(1)-O(5)	1.488(3)	P(2)-O(6)	1.469(3)
P(3)-O(7)	1.477(3)	P(4)-O(8)	1.491(3)
O(1)-Yb(1)-O(3)	83.60(15)	O(1)-Yb(1)-O(6)	175.17(14)
O(3)-Yb(1)-O(5)	175.65(12)	O(3)-Yb(1)-O(8)	87.75(12)
O(5)-Yb(1)-O(7)	90.53(11)	O(7)-Yb(1)-O(8)	172.72(11)
C(1)-Fe(1)-C(2)	88.4(2)	C(1)-Fe(1)-Cp _{cent} (1)	136.70
C(2)-Fe(1)-Cp _{cent} (1)	134.94	C(8)-Fe(2)-C(9)	90.0(3)
C(8)-Fe(2)-Cp _{cent} (2)	136.64	C(9)-Fe(2)-Cp _{cent} (2)	133.36

The geometry at the six-coordinate Yb centre is approximately octahedral with four HMPA ligands and two Yb(μ-OC)Fe isocarbonyl interactions in a *cis*-arrangement. The Yb(1)···Fe(1) (5.2758(6) Å) and Yb(1)···Fe(2) (5.3193(6) Å) distances are longer than the sum of the respective covalent radii (3.19(9) Å).¹⁵ The C(1)-O(1) distance (1.190(6) Å), involved in isocarbonyl bridging, is lengthened relative to that for terminal C(2)-O(2) (1.182(6) Å). Concomitantly the Fe(1)-C(1) distance (1.699(5) Å) is shortened relative to that for Fe(1)-C(2) (1.702(6) Å). Similar observations occur for the carbonyl groups associated with Fe(2).

Whilst a quantitative comparison of the molecular structures of **10** and **11** cannot be carried out due to the poor quality of data associated with the former, it is apparent that they are isostructural. Both have a *cis*-arrangement of M(μ-OC)Fe isocarbonyl interactions accompanied by four HMPA ligands to give a complex with

approximately octahedral geometry. However, they are not isomorphous, having different unit cell parameters.

Structurally authenticated HMPA adducts of Yb have been reported in the literature,⁷⁸⁻⁸⁰ the most relevant example being that of $\text{Yb}\{\text{CpMo}(\text{CO})_3\}_2(\text{HMPA})_4$ (**2.14**).⁸¹ Analogous to the molecular structure of **11**, a *cis*-arrangement of $\text{Yb}(\mu\text{-OC})\text{Mo}$ isocarbonyl interactions is observed between the two $\text{CpMo}(\text{CO})_3$ anions and the cationic Yb^{2+} centre. Four HMPA ligands are also coordinated to Yb to give a distorted octahedral geometry. The *cis*-arrangement of anions in **2.14**, **10** and **11** is unusual. This is proposed to be a consequence of the sterically demanding HMPA ligands. Where a *trans*-arrangement of anions would position the four sterically demanding HMPA ligands closer together in the equatorial plane. Even as the *cis*-isomer, the anions are pushed towards each other by the HMPA ligands in these complexes as evidenced by the angle between the isocarbonyl groups in **11** ($\text{O}(1)\text{-Yb}(1)\text{-O}(3) = 83.6(2)^\circ$) and **2.14** ($\text{O}(5)\text{-Yb}(1)\text{-O}(6) = 81.7(6)^\circ$) being less than the average for that between the adjacent HMPA ligands of $92.02(5)$ and $90.6(5)^\circ$, respectively. The average $\text{Yb}(1)\text{-O}(\text{HMPA})$ distance of $2.324(2)$ in **11** is comparable with that for **2.14** of $2.33(1)$ Å. The $\text{Yb}(1)\text{-O}(1)$ ($2.449(3)$ Å) and $\text{Yb}(1)\text{-O}(3)$ ($2.438(3)$ Å) $\text{Yb}(\mu\text{-OC})\text{Fe}$ distances in **2.14** are longer than the average $\text{Yb}(1)\text{-O}(\text{isocarbonyl})$ distance in **6** ($2.418(1)$ Å) and Shore's $[(\text{MeCN})_3\text{YbFe}(\text{CO})_4]_2\cdot\text{MeCN}]_x$ (**1.73**, $2.374(7)$ Å) and $[(\text{MeCN})_3\text{YbFe}(\text{CO})_4]_x$ (**1.75**, $2.45(5)$ Å).

Reaction of HMPA with **1** in THF gave $[\text{Mg}(\text{HMPA})_4][\text{Fp}]_2$ (**7**) in 68% isolated yield. Diffraction-quality crystals were grown from a concentrated THF solution at RT. The molecular structure and selected distances and angles are shown in Figure 2.19 and Table 2.11.

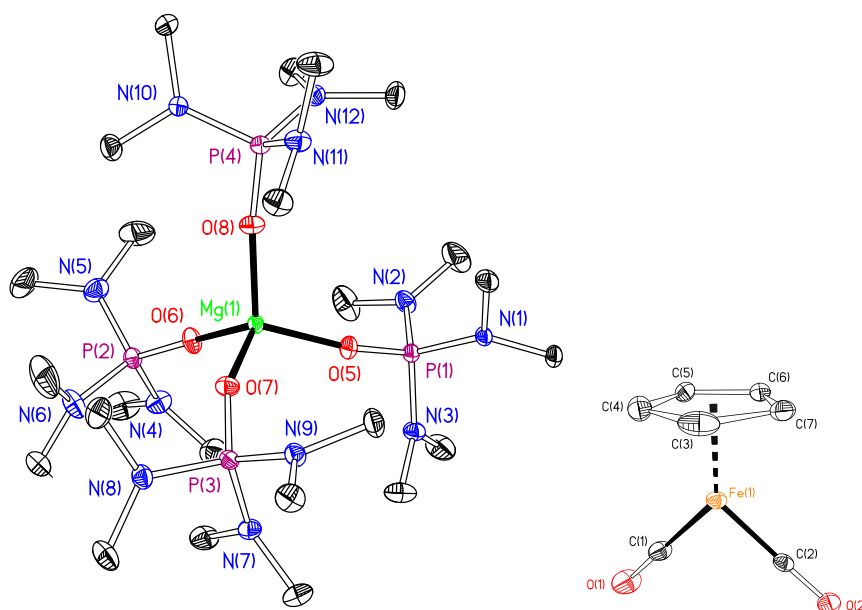


Figure 2.19. Displacement ellipsoid plots (35% probability) of $[\text{Mg}(\text{HMPA})_4]^{2+}$ (left) and one of the $[\text{Fp}]^-$ anions (right) of $[\text{Mg}(\text{HMPA})_4][\text{Fp}]_2$ (**7**). H atoms omitted for clarity.

Table 2.11. Selected distances (Å) and angles (°) for $[\text{Mg}(\text{HMPA})_4][\text{Fp}]_2$ (**7**).

Mg(1)-O(5)	1.887(2)	Mg(1)-O(6)	1.904(2)
Mg(1)-O(7)	1.908(2)	Mg(1)-O(8)	1.890(2)
Fe(1)-C(1)	1.711(3)	Fe(1)-C(2)	1.706(3)
Fe(1)-Cp _{cent} (1)	1.731	Fe(2)-C(8)	1.706(3)
Fe(2)-C(9)	1.707(3)	Fe(2)-Cp _{cent} (2)	1.730
C(1)-O(1)	1.178(4)	C(2)-O(2)	1.178(4)
C(8)-O(3)	1.176(4)	C(9)-O(4)	1.188(4)
P(1)-O(5)	1.495(2)	P(2)-O(6)	1.4744(19)
P(2)-O(7)	1.498(2)	P(2)-O(8)	1.495(2)
O(5)-Mg(1)-O(6)	107.75(10)	O(5)-Mg(1)-O(7)	110.95(10)
O(5)-Mg(1)-O(8)	110.49(10)	O(6)-Mg(1)-O(7)	108.89(10)
O(6)-Mg(1)-O(8)	111.31(10)	O(7)-Mg(1)-O(8)	107.46(9)
C(1)-Fe(1)-C(2)	91.25(16)	C(1)-Fe(1)-Cp _{cent} (1)	135.45
C(2)-Fe(1)-Cp _{cent} (1)	133.27	C(8)-Fe(2)-C(9)	89.24(15)
C(8)-Fe(2)-Cp _{cent} (2)	134.53	C(9)-Fe(2)-Cp _{cent} (2)	136.23

The geometry at the four-coordinate Mg centre is approximately tetrahedral with four HMPA ligands. The dication is flanked by two Fp^- anions which do not have any direct or $\text{Mg}(\mu\text{-OC})\text{Fe}$ isocarbonyl interactions with the Mg centres, and therefore **7** is a separated ion pair. Given the steric demands of the four HMPA ligands, it is unsurprising that isocarbonyl, let alone direct Mg-Fe interactions, are not observed. The switch from an isocarbonyl bridged monomeric complex (**10** and **11**) to separated ion pairs is a reflection of the change in covalent radius ($\text{Mg} < \text{Ca} < \text{Yb}$). As expected, the average Mg-O(HMPA) distance of 1.491(1) is considerably shorter than the average Yb-O(HMPA) distance of 2.324(2) Å for **11**. Consistent with the lack of interaction between the Fp^- anions and Mg^{2+} centre, the carbonyl C-O distances are identical within error as are the Fe-C distances.

Considering the abundance of structurally authenticated Fp containing complexes in the literature,⁵² it is somewhat surprising that the molecular structure of **7** represents the first example containing the non-coordinated Fp^- anion. As expected for the relaxed Fp^- anion, C(1), C(2) and the Cp centroid are coplanar (maximum deviation from plane = 0.02 Å (C(2))).

2.5.1 Solid state and solution IR studies of HMPA coordinated complexes

The IR $\nu(\text{CO})$ bands for $\text{CaFp}_2(\text{HMPA})_4$ (**10**), $\text{YbFp}_2(\text{HMPA})_4$ (**11**) and $[\text{Mg}(\text{HMPA})_4][\text{Fp}]_2$ (**7**) in Nujol and THF are given in Table 2.12. Reassuringly, the IR spectra for **7** in Nujol (1863 ($\nu_{\text{sym}}(\text{CO})$), 1789 ($\nu_{\text{anti}}(\text{CO})$) and THF (1865 ($\nu_{\text{sym}}(\text{CO})$), 1787 ($\nu_{\text{anti}}(\text{CO})$) exhibit near-identical $\nu(\text{CO})$ bands, consistent with a lack of interaction between the Fp^- anion in both THF solution and the solid state. These values are also consistent with those for KFp in THF (1865 and 1788 cm^{-1}) and NaFp in THF in the presence of crown ether (1862 and 1786 cm^{-1}), proposed to afford solvent separated ion pairs under these conditions.^{18, 19}

The IR spectra of **10** (1864 and 1781 cm^{-1}) and **11** (1863 and 1749 cm^{-1}) in Nujol also exhibit two $\nu(\text{CO})$ bands. The band at higher wavenumber can be attributed to terminal and that at lower wavenumber to $\text{M}(\mu\text{-OC})\text{Fe}$ $\nu(\text{CO})$ bands rather than $\nu_{\text{sym}}(\text{CO})$ and $\nu_{\text{anti}}(\text{CO})$ as assigned to those for **7**. Whilst they are similar to those for **7** in Nujol, the differences in THF are more distinct, for example **10** exhibits bands at 1787 and 1742, compared to 1865 and 1787 cm^{-1} for **7**. This is consistent with an interaction being maintained between the dicationic metal centres for **10** and **11** in

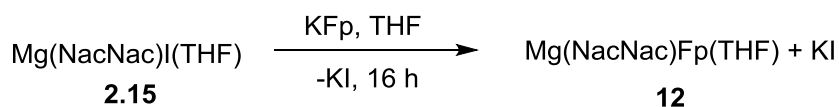
THF unlike for **7**. As expected, the bands for **7**, **10** and **11** in THF are different from their corresponding $[\text{MFp}_2(\text{THF})_x]_y$ complexes, **1**, **3** and **6**.

Table 2.12. IR $\nu(\text{CO})$, cm^{-1} for $[\text{Mg}(\text{HMPA})_4][\text{Fp}]_2$ (**7**), $\text{CaFp}_2(\text{HMPA})_4$ (**10**) and $\text{YbFp}_2(\text{HMPA})_4$ (**11**) in Nujol and THF.

Complex	$\nu(\text{CO})$ (cm^{-1}) in Nujol	$\nu(\text{CO})$ (cm^{-1}) in THF
7	1863 (s), 1789 (s)	1865 (m), 1787 (m)
10	1864 (s), 1781 (s)	1787 (s, br), 1742 (s)
11	1863 (s), 1749 (s)	1790 (m), 1746 (m)

2.6 NacNac supported M-Fp complexes

Reaction of KFp and $\text{Mg}(\text{NacNac})\text{I}(\text{THF})$ (**2.15**), synthesised following reported procedures,^{8, 82} in THF afforded $\text{Mg}(\text{NacNac})\text{Fp}(\text{THF})$ (**12**) as a yellow solid in 78% isolated yield (Equation 2.7).



Equation 2.7

Diffraction-quality crystals of **12** were grown from a concentrated benzene solution at RT. The molecular structure and selected distances and angles are shown in Figure 2.20 and Table 2.13.

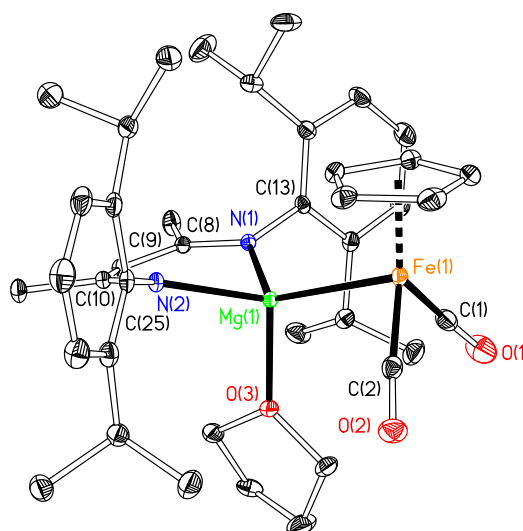


Figure 2.20. Displacement ellipsoid plot (20% probability) of Mg(NacNac)Fp(THF) (**12**). H atoms omitted for clarity.

Table 2.13. Selected distances (Å) and angles (°) for Mg(NacNac)Fp(THF) (**12**).

Mg(1)-Fe(1)	2.6326(4)	Mg(1)-N(1)	2.1024(11)
Mg(1)-N(2)	2.0971(11)	Mg(1)-O(3)	2.0706(10)
Fe(1)-C(1)	1.7224(17)	Fe(1)-C(2)	1.7233(16)
Fe(1)-Cp _{cent(1)}	1.709	C(1)-O(1)	1.170(2)
C(2)-O(2)	1.1665(19)		
Fe(1)-Mg(1)-N(1)	122.23(3)	Fe(1)-Mg(1)-N(2)	125.85(3)
Fe(1)-Mg(1)-O(3)	108.64(3)	N(1)-Mg(1)-N(2)	90.97(4)
N(1)-Mg(1)-O(3)	102.03(4)	N(2)-Mg(1)-O(3)	103.43(4)
Mg(1)-Fe(1)-C(1)	88.63(6)	Mg(1)-Fe(1)-C(2)	91.90(5)
Mg(1)-Fe(1)-Cp _{cent(1)}	107.36	C(1)-Fe(1)-C(2)	90.47(7)
C(1)-Fe(1)-Cp _{cent(1)}	133.22	C(2)-Fe(1)-Cp _{cent(1)}	131.05

The geometry at the four-coordinate Mg centre is approximately tetrahedral, with coordinated NacNac, THF and Fp ligands. Importantly, the Fp⁻ anion is coordinated directly to Mg *via* its Fe centre, rather than isocarbonyl linkage, to give a Mg-Fe bond of length 2.6326(4) Å, shorter than the sum of the respective covalent radii (1.73(8) Å).¹⁵ This is comparable with the Mg-Fe bond distances of 2.6112(5) and 2.5629(5) Å in **1** and represents only the third structurally authenticated Mg-Fe direct interaction

following those in **1** and Felkin's $\text{Cp(dppe)FeMgBr(THF)}_2$ (**1.18**) with a Mg-Fe distance of 2.593(7) Å.⁴³

The N(1)-Mg(1)-N(2) angle of 90.97(4) ° is comparable with other Mg(NacNac) complexes in the literature, for example Jones' $[\text{Mg(NacNac)H}]_2$ (**2.16**, 93.14(9) °) and $[\text{Mg(NacNac)}]_2$ (**1.12**, 91.78(5), 91.80(5) °),^{83, 84} Gibson's $\text{Mg(NacNac)N(SiMe}_3)_2$ (**2.17**, 95.11(6) °)⁸⁵ and Mountford's $\text{Mg(NacNac)(BH}_4\text{)(THF)}$ (**2.18**, 94.68(8) °).⁸⁶ As is evidenced by these complexes, the NacNac ligand has the ability to vary its N-Mg-N angle to accommodate different coordination numbers and interactions at the Mg centre whilst continuing to provide stability. In **12** the Mg centre sits out of the plane of the NacNac backbone by 0.764 Å, as has been observed and commented on for literature examples such as **2.18** (0.57 Å).⁸⁶ Other M(NacNac)Fp complexes with direct M-Fp interactions have been reported. For example, Al(NacNac)FpCl (**2.19**),⁸⁷ Ge(NacNac)Fp (**2.20**)⁸⁸ and In(NacNac)FpI (**2.21**)²⁷ with M-Fe distances of 2.480(1), 2.4961(17) and 2.5118(7) Å, respectively.

The Mg-O(THF) distance in **12** (2.0706(10) Å) is consistent with the average distance of 2.08 (range: 1.96-2.29) Å for structurally authenticated complexes.⁵² The carbonyl C-O distances are identical within error as are the Fe-C distances, consistent with a lack of $\text{Mg}(\mu\text{-OC})\text{Fe}$ isocarbonyl interaction.

2.6.1 DFT Computational analysis of Mg(NacNac)Fp(THF) (**12**)

DFT calculations on the crystallographically characterised **12** gave the full model structure **12Q**. The geometry and bonding parameters for this are in generally good agreement with those determined experimentally. For example, the Mg-Fe distance (2.581 Å) is only 0.05 Å shorter than that measured for **12** (2.6326(4) Å), and the N-Mg-N angle (92.4 °) is very similar to that for **12** (90.97(4) °). The Mg atom lies 0.72 Å out of the plane of the NacNac backbone, again consistent with that observed for **12** (0.76 Å). As with the calculations for **1Q** (Table 2.8, Section 2.3.4) the low values at the Mg-Fe BCP for the electron density (0.03 au), its Laplacian (0.062 au) and the energy density (-0.005 au) are consistent with a predominantly ionic Mg-Fe interaction.

Selected molecular orbitals (MOs) for **12Q** are shown in Figure 2.21 together with their associated energies. By way of comparison, the electronic structure for FpH was

also computed and selected MOs and energies are given in Figure 2.22. These are comparable to those computed previously.⁸⁹ The HOMO, HOMO-1 and HOMO-2 of FpH are predominantly metal-based, as expected for the formal Fe(+2), d^6 electronic description. MO-5 (-7.59 eV) corresponds to the Fe–H σ -bond. The LUMO of FpH (-1.99 eV) is Fe-ligand antibonding (HOMO-4 and HOMO-3, not illustrated, are Fe-Cp bonding MOs).

The electronic structure of **12Q** with respect to the Fe centre is related to that of FpH but with some important differences. The LUMO of **12Q** resembles that of FpH but lies at higher energy (-1.66 eV vs. -1.99 eV in FpH). The MOs corresponding to the d^6 electronic set of FpH (HOMO, HOMO-1, HOMO-2) find their counterparts as HOMO, HOMO-3 and HOMO-5 of **12Q**. However, as for the LUMOs of the two systems, the average energy of these MOs for **12Q** (-4.72 eV) is less negative than for the corresponding MOs of FpH (av. -5.40 eV). The Mulliken atomic charge for Fe in **12Q** (-0.164) is also more negative than that for FpH (0.0). Finally, whereas the Fe–H bonding MO of FpH (HOMO-5, -7.59 eV) is significantly stabilised relative to the three MOs housing the d^6 electrons, the corresponding MO (HOMO-1) of **12Q** is much less stable (-4.44 eV) and is predominantly Fe-based with effectively no contribution from Mg (in contrast to the HOMO-5 for FpH which features a significant 1s contribution). For comparison the electronic structure of the $[\text{Fp}]^-$ anion in the geometry found for FpH and **12Q** was also computed. As expected, the frontier MOs of $[\text{Fp}]^-$ feature four Fe-based MOs for the d^8 electron configuration (Figure 2.23). The HOMO of $[\text{Fp}]^-$ resembles the HOMO-1 of **12Q** and lies 1.06 eV *above* the HOMO-1. This in turn closely resembles the HOMO of **12Q**.

Whilst it is evident that coordination of the $[\text{Mg}(\text{NacNac})(\text{THF})]^+$ cation to the $[\text{Fp}]^-$ anion stabilises the HOMO of the latter by *ca.* 1.3 eV, the Fe–Mg interaction is nonetheless substantially ionic. Since the DFT results show that the orbital (HOMO-1) most responsible for any covalency lies within the manifold for the Fe-based electrons (HOMO, HOMO-3, HOMO-5), the electronic structure of Fe in **12Q** is best viewed as being between that of the Fe(0) centre in $[\text{Fp}]^-$ (d^8 configuration) and the formal Fe(+2) centre in FpH (d^6).

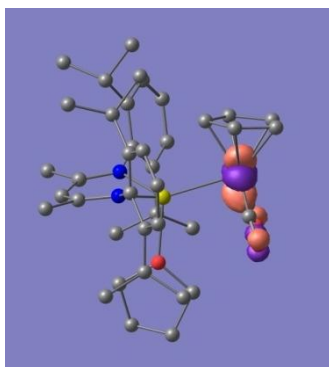
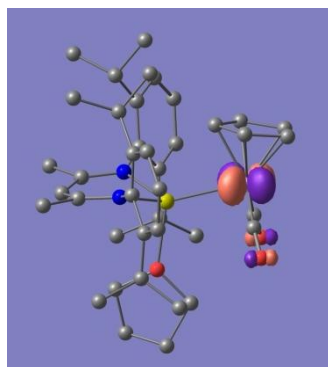
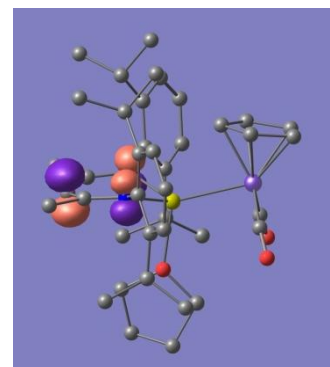
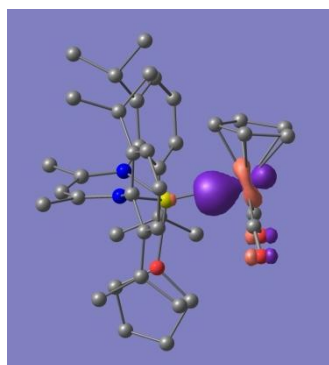
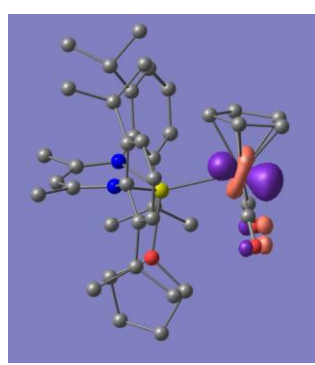
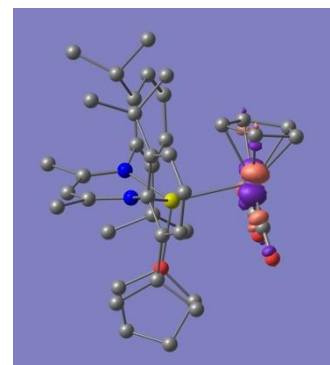
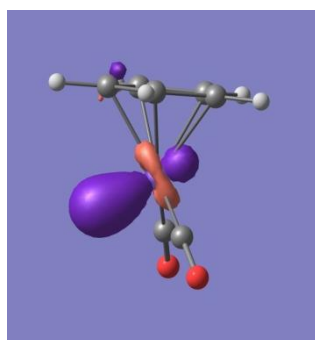
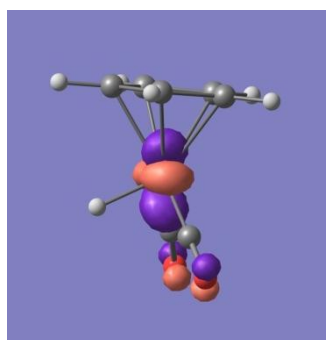
**HOMO-5: -5.36 eV****HOMO-3: -4.60 eV****HOMO-2: -4.57 eV****HOMO-1: -4.44 eV****HOMO: -4.20 eV****LUMO: -1.66 eV**

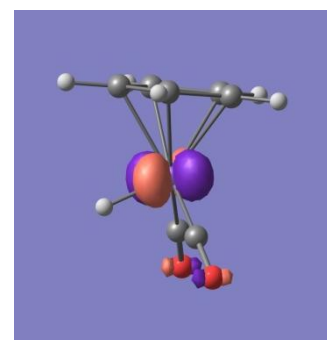
Figure 2.21. Isosurfaces and associated energies of selected molecular orbitals of Mg(NacNac)Fp(THF) (**12Q**). HOMO-2 and HOMO-4 (not shown) are ligand-based MOs associated with NacNac.



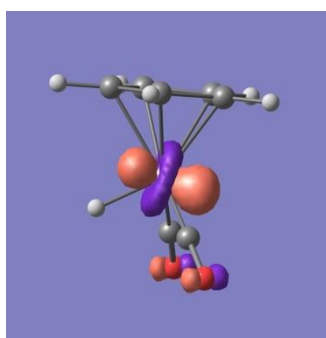
HOMO-5: -7.59 eV



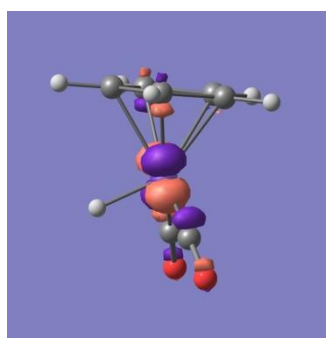
HOMO-2: -6.15 eV



HOMO-1: -5.52 eV

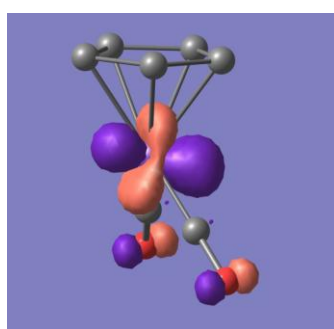


HOMO: -4.54 eV

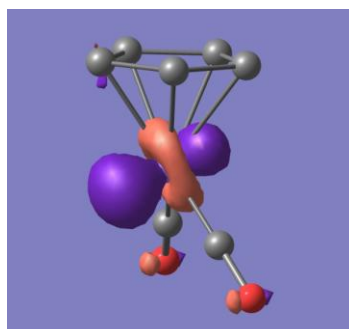


LUMO: -1.99 eV

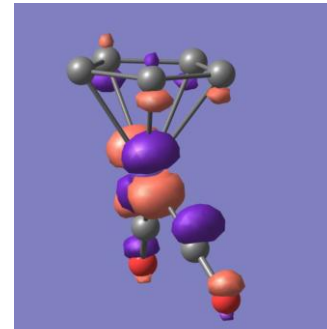
Figure 2.22. Isosurfaces and associated energies of selected molecular orbitals of FpH.



HOMO-1: 0.51 eV



HOMO: 1.57 eV



LUMO: 3.37 eV

Figure 2.23. Isosurfaces and associated energies of the LUMO, HOMO and HOMO-1 of $[Fp]^-$ in the geometry of the $CpFe(CO)_2$ moiety in **12Q** and FpH.

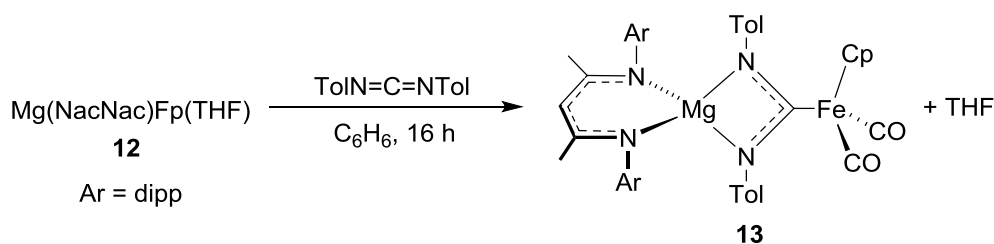
2.6.2 Reactivity of Mg(Nacnac)Fp(THF) (**12**)

Addition of excess of MeI to **12** on the NMR tube-scale gave immediate formation of Mg(Nacnac)I(THF) (**2.15**) and MeFp by ^1H NMR (Equation 2.8).⁹⁰ As with **1**, **3** and **6** this confirms **12** to act as source of the Fp⁻ anion.



Equation 2.8

Compound **12** was reacted with TolN=C=NTol (**2.22**, 1,3-di-p-tolylcarbodiimide) in benzene to afford Mg(Nacnac){(NTol)₂CFp} (**13**) as a yellow solid in 66% isolated yield (Equation 2.9). An NMR tube-scale reaction in C₆D₆ was consistent with quantitative conversion. The THF bound to Mg(1) is released in this reaction, consistent with the increase in steric bulk at the Mg centre. Despite repeated attempts it was not possible to obtain crystals of **13**. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (Figure 2.24) shows a singlet at 214.4 and 200.7 ppm assigned to the Fe-CN₂ and CO ligands, respectively.



Equation 2.9

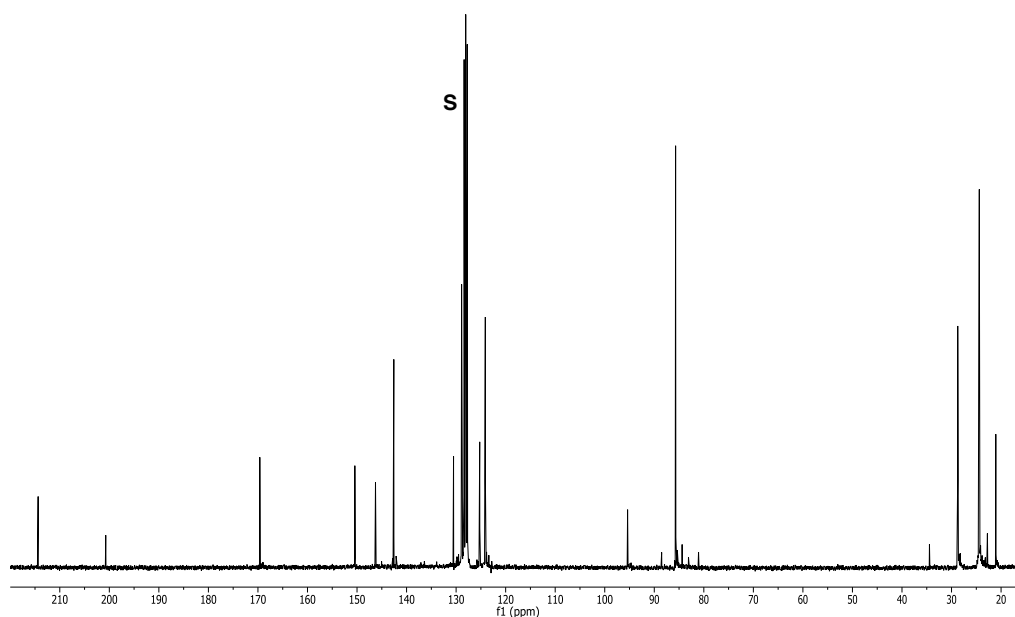
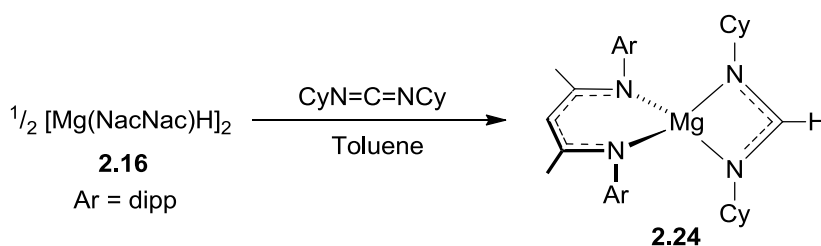
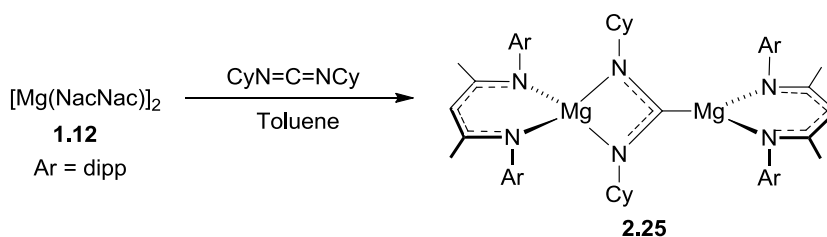


Figure 2.24. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75.5 MHz) for $\text{Mg}(\text{NacNac})\{(\text{NTol})_2\text{CFp}\}$ (**13**) in C_6D_6 (“S” denotes C_6D_6 ^{13}C resonances which overlap with certain tolyl resonances).

The reaction depicted in Equation 2.9 is comparable with the reaction of $[\text{Mg}(\text{NacNac})\text{H}]_2$ (**2.16**) with $\text{CyN}=\text{C}=\text{NCy}$ (**2.23**) to afford $(\text{NacNac})\text{Mg}\{(\text{NCy})_2\text{CH}\}$ (**2.24**) as illustrated in Equation 2.10).⁹¹ Similarly, reaction of $[\text{Mg}(\text{NacNac})]_2$ (**1.12**) with **2.23** gave $(\text{NacNac})\text{Mg}\{(\text{NCy})_2\text{Mg}(\text{NacNac})\}$ (**2.25**, Equation 2.11).⁸⁴

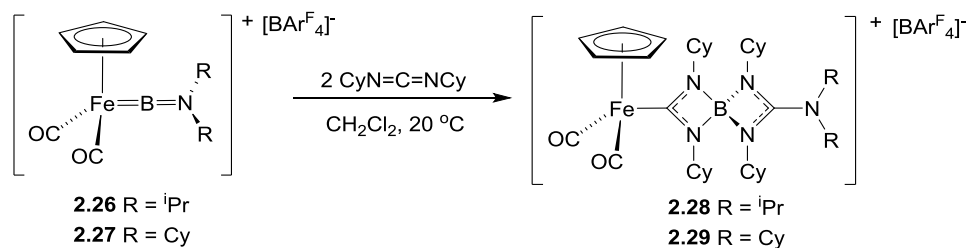


Equation 2.10⁹¹



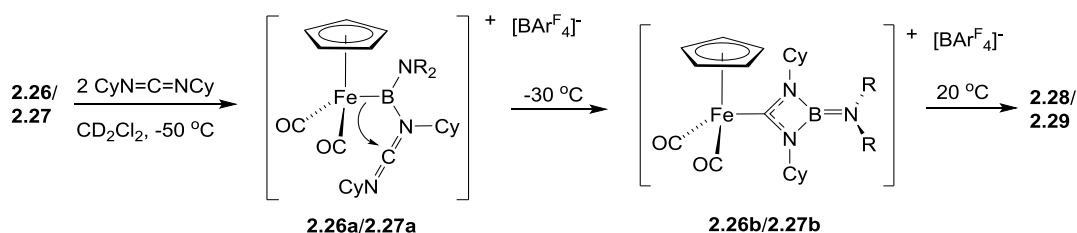
Equation 2.11⁸⁴

Aldridge *et al.* have reported the insertion of **2.23** into the Fp=B bond of the cationic terminal aminoborylene complexes $[\text{Fp}(\text{BNR})_2][\text{BAr}^{\text{F}}_4]$ where R = ⁱPr (**2.26**) or Cy (**2.27**) and $\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$ to afford $[\text{FpC}(\text{NCy})_2\text{B}(\text{NCy}_2)\text{CNR}][\text{BAr}^{\text{F}}_4]$ where R = ⁱPr (**2.28**) or Cy (**2.29**) (Equation 2.12).⁹²



Equation 2.12⁹²

Using VT-NMR, identification of the intermediates in the reactions depicted in Equation 2.12 was achieved and are illustrated in Scheme 2.3.⁹² The first intermediate (**2.26a/2.27a**) may be akin to that in the formation of **13** whereby carbodiimide N-coordination to the Mg centre results in adduct formation prior to insertion into the Mg-Fe bond.



Scheme 2.3. Intermediates (**2.26a/2.27a** and **2.26b/2.27b**) in the synthesis of $[\text{Fp}(\text{BNR})_2][\text{BAr}^{\text{F}}_4]$. R = ⁱPr (**2.28**) and Cy (**2.29**).⁹²

For **2.28** the $^{13}\text{C}\{^1\text{H}\}$ NMR exhibits singlets at 224.0 and 211.8 ppm corresponding to the Fe-CN₂ and CO ligands, respectively. For **2.29** these peaks are observed at 251.5 (NCN) and 209.6 (CO) ppm. Whilst the CO $^{13}\text{C}\{^1\text{H}\}$ resonance for **13** (214.4 ppm) is found at a similar position to those for **2.28** and **2.29**, the metalla-amidinate resonance is considerably further upfield (200.7 ppm), closer to that expected for quaternary amidinate or guanidinate ^{13}C resonances.⁹³⁻⁹⁵ For **2.28** and **2.29** this was ascribed to the partial carbenoid character of the Fe-C interaction, citing similar observations for the quaternary carbon in Gade's $\text{FpC}(\text{S})(\text{E})\text{ZrL}$ complexes where E = S or NPh and L = $\{(2\text{-FC}_6\text{H}_4)\text{NSiMe}_2\}_3\text{CH}$.⁹⁶

In contrast to that with TolN=C=NTol (**2.22**), **12** showed no reactivity with $^i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$ (**2.30**) on the NMR tube-scale. Heating at 50 °C gave a mixture of environments. Heating for a further 16 h did not give a satisfactory ^1H NMR spectrum. No reaction between **12** and H_2 was observed on the NMR tube-scale by ^1H NMR despite heating at 70 °C for 4 h. Consistent with this, **12** showed no reactivity on the NMR tube-scale with PhSiH_3 after heating at 70 °C for 16 h.

2.6.3 DFT Computational analysis of $\text{Mg}(\text{NacNac})\{(\text{NTol})_2\text{CFp}\}$ (**13**)

DFT analysis of the reaction shown in Equation 2.9 finds $\Delta G = -25.2 \text{ kJ mol}^{-1}$ with $\Delta H = -39.4 \text{ kJ mol}^{-1}$. The minimised structure (**13Q**) is shown in Figure 2.25. This possesses a four-coordinate Mg centre with approximately tetrahedral geometry, where the plane of the NacNac ligand is nearly orthogonal (86.3°) to the amidinate backbone. The Mg centre lies out of the plane of the NacNac ligand by $0.57 \text{ \AA}$, less than that observed for $\text{Mg}(\text{NacNac})\text{Fp}(\text{THF})$ experimentally (**12**, $0.76 \text{ \AA}$) or computationally (**12Q**, $0.72 \text{ \AA}$). The ArN-Mg-NAr angle of 94.4° in **13Q** is greater than that measured for **12Q** (92.4°) or **12** ($90.97(4)^\circ$), whilst the average Mg-NAr distance ($2.085 \text{ \AA}$) is shorter than that for **12Q** ($2.148 \text{ \AA}$) or **12** ($2.100(2) \text{ \AA}$). The Fe-C distance of 2.059 is considerably longer than the Fe-C distances of $1.948(2)$ and $1.938(3) \text{ \AA}$, in **2.28** or **2.29**, respectively. The calculated $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts for **13Q** for the CO (222.6 and 225.6 ppm) and Fe-CN $_2$ (207.7 ppm) ligands are similar to those recorded experimentally (214.4 and 200.7 ppm). The calculated IR $\nu(\text{CO})$ frequencies (1987 and 1949 cm^{-1}) are also consistent with those observed experimentally (2010 and 1956 cm^{-1}).

DFT calculations for **13Q** find an electronic structure consistent with a formal Fe(2+) centre and d^6 configuration. The Mulliken charge for Fe in **13Q** (-0.040) is significantly increased relative to that in **12Q** (-0.164) and is comparable to the value for FpH (0.0). The MO corresponding to the Fe-CN $_2$ σ -bonding interaction is found at -6.32 eV (*cf.* -7.59 eV for the Fe-H bond in FpH).

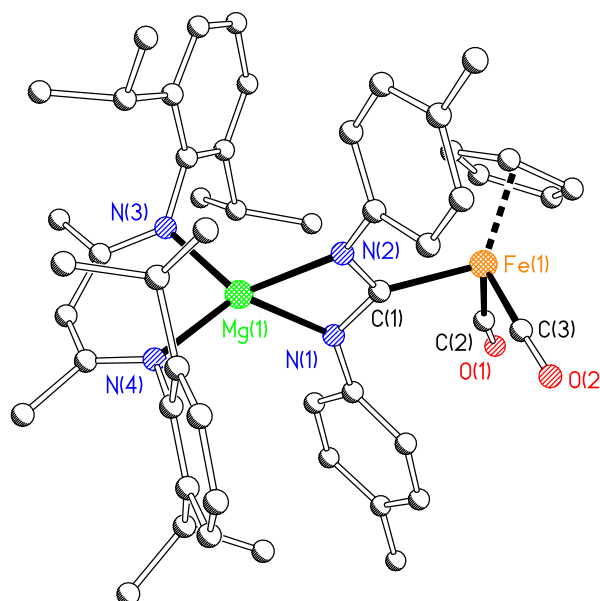
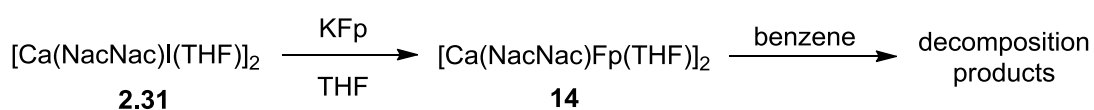


Figure 2.25. DFT Calculated molecular structure of $\text{Mg}(\text{NacNac})\{(\text{NTol})_2\text{CFp}\}$ (**13**). H atoms omitted for clarity.

2.6.4 NacNac supported Ca-Fp and Yb-Fp complexes

Reaction of KFp with $[\text{Ca}(\text{NacNac})\text{I}(\text{THF})]_2$ (**2.31**) in THF afforded $[\text{Ca}(\text{NacNac})\text{Fp}(\text{THF})]_2$ (**14**) as an orange solid in 68% isolated yield (Equation 2.13). The material was soluble in benzene such that NMR characterisation could be performed. However, the stability in benzene was not sufficient to allow the growth of crystals suitable for analysis by X-ray diffraction before decomposition, as evidenced by ^1H NMR analysis, contrasting with the stability of **12** under analogous conditions.



Equation 2.13

Complex **14** was dissolved in THF to give a concentrated solution which afforded diffraction-quality crystals of $[\text{Ca}(\text{NacNac})\text{Fp}(\text{THF})]_2$ (**15**). The molecular structure and selected distances and angles are shown in Figure 2.26 and Table 2.14.

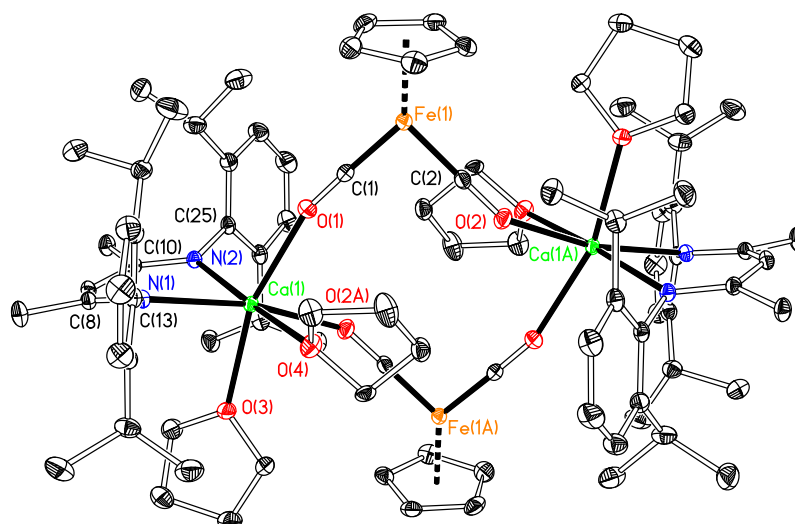


Figure 2.26. Displacement ellipsoid plot (20% probability) of $[\text{Ca}(\text{NacNac})\text{Fp}(\text{THF})_2]_2$ (**15**). H atoms omitted for clarity. Atoms carrying the suffix “A” are related to their counterparts by the operator $-x, 1-y, -z$.

Table 2.14. Selected distances (Å) and angles (°) for $[\text{Ca}(\text{NacNac})\text{Fp}(\text{THF})_2]_2$ (**15**).

Ca(1)···Fe(1)	5.2094(3)	Ca(1A)···(Fe1)	5.1012(3)
Ca(1)-O(1)	2.3915(12)	Ca(1)-O(2A)	2.3971(11)
Ca(1)-O(3)	2.4119(11)	Ca(1)-O(4)	2.4357(11)
Ca(1)-N(1)	2.4109(12)	Ca(1)-N(2)	2.4176(12)
Fe(1)-C(1)	1.7120(15)	Fe(1)-C(2) _{cent(1)}	1.7018(16)
Fe(1)-Cp _{cent(1)}	1.746	C(1)-O(1)	1.1869(19)
C(2)-O(2)	1.1914(19)	O(1)-Ca(1)-O(2A)	84.89(4)
O(1)-Ca(1)-O(3)	163.12(4)	O(2A)-Ca(1)-O(4)	83.48(4)
O(4)-Ca(1)-N(1)	98.11(4)	N(1)-Ca(1)-N(2)	79.92(4)
N(2)-Ca(1)-O(2A)	99.24(4)	C(1)-Fe(1)-C(2)	89.37(7)
C(1)-Fe(1)-Cp _{cent(1)}	136.60	C(2)-Fe(1)-Cp _{cent(1)}	134.03
^a Hinge angle	163		

^a Hinge = (Fe(1), C(1), O(1), Fe(1A), C(1A), O(1A))-O(1), Ca(1), O(2A), C(2A), Fe(1A)). Maximum deviation from plane = 0.343 Å (O(2A)).

Compound **15** is dimeric with two Fp[−] anions linking the six-coordinate Ca centres *via* Ca(μ-OC)Fe isocarbonyl bridging to give a centrosymmetric twelve-membered ring

in a chair-conformation. Each Ca centre has distorted octahedral geometry with a NacNac ligand and two THF ligands in addition to the $\text{Ca}(\mu\text{-OC})\text{Fe}$ groups. The $\text{Ca}(1)\cdots\text{Fe}(1)$ (5.2094(3) Å) and $\text{Ca}(1)\cdots\text{Fe}(1A)$ (5.1012(3) Å) distances are greater than the sum of the respective covalent radii. The $\text{N}(1)\text{-Ca}(1)\text{-N}(2)$ angle (79.92(4)°) is also smaller than the $\text{N}(1)\text{-Mg}(1)\text{-N}(2)$ angle (90.97(4)°) in **12**. The $\text{C}(1)\text{-Fe}(1)\text{-C}(2)$ angle (87.37(7)°) is smaller than that for **12** (90.47(7)°), a consequence of the doubly bridging nature of the Fp^- anion in the former. As anticipated, the carbonyl C-O distances are longer and the Fe-C distances are shorter in **15** than **12**. For example, for **15** $\text{C}(1)\text{-O}(1)$ = 1.187(2) and $\text{Fe}(1)\text{-C}(1)$ = 1.712(2) whereas for **12** $\text{C}(1)\text{-O}(1)$ = 1.170(2) and $\text{Fe}(1)\text{-C}(1)$ = 1.722(2) Å.

The structure of **15** can be compared with that for $[\text{CaFp}_2(\text{THF})_3]_2$ (**3**), where Fp^- anions link cationic Ca^{2+} centres in both of these dimeric structures but are singly isocarbonyl bridging in **3** and doubly bridging in **15** to give eight- and twelve-membered rings with and without direct Ca-Fe interactions, respectively. Evidently substitution of one of the Fp^- anions per Ca in **3** for NacNac is sufficient to disrupt the propensity to form Ca-Fe bonds. The average $\text{Ca}(\mu\text{-OC})\text{Fe}$ C-O distances in **15** (1.189(1) Å) and **3** (1.194(2) Å) are identical within error, as are the Fe-C distances of 1.707(1) and 1.694(2) Å, respectively.

Integration of the ^1H NMR (C_6D_6) spectrum and elemental analysis of **14** are consistent with one THF per Ca centre. In the absence of crystallographic data it is not possible to draw conclusions about the nature of the interaction of the Fp^- anion with the Ca centre.

The twelve-membered ring motif present in **15** with $\text{M}(\mu\text{-OC})\text{TM}$ μ_2 -isocarbonyl linkages is more common than the eight-membered ring observed in **1**, **3** and **6**, although examples involving the Fp^- anion are yet to be reported.⁵² As with the eight-membered rings, a hinge angle can be measured between the planar TM-C-O elements and the O-bound metals (M) at the vertices. For the centrosymmetric twelve-membered ring in a chair-conformation illustrated in Figure 2.27, the TM, C and O atoms along the *a*-edges are coplanar and therefore can be used to define a plane. Alternatively these atoms on the *b*-edges can be used to define another plane. For an ideal structure these should be identical but in practice this is often not the case. For the structures analysed in this study, the dominant angle, that is the one with the greatest deviation from 180°, will be used.

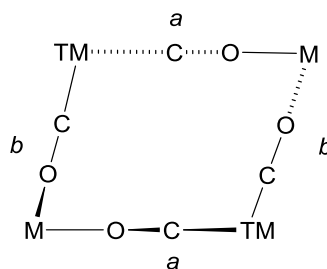
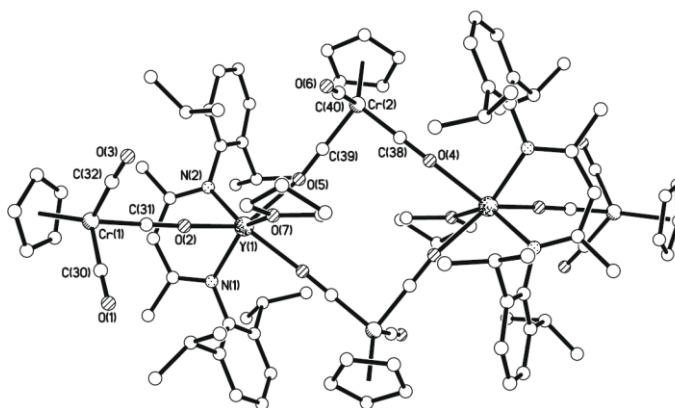


Figure 2.27. Representation of centrosymmetric twelve-membered ring motif in a chair-conformation.

There is one structurally authenticated literature example of a NacNac supported twelve-membered ring with the motif illustrated in Figure 2.26, namely Liddle's $[\text{Y}(\text{NacNac})\{\text{CpCr}(\text{CO})_3\}(\text{THF})]_2$ (**2.32**, Figure 2.28).⁹⁷ This was synthesised by the reaction of $\text{Na}[\text{CpCr}(\text{CO})_3]$ (**2.33**) with $\text{Y}(\text{NacNac})\text{I}(\text{THF})$ (**2.34**). The morphology of the molecular structure is similar to that for **15** with doubly isocarbonyl bridging $\text{CpCr}(\text{CO})_3$ units linking the NacNac ligated Y centres.



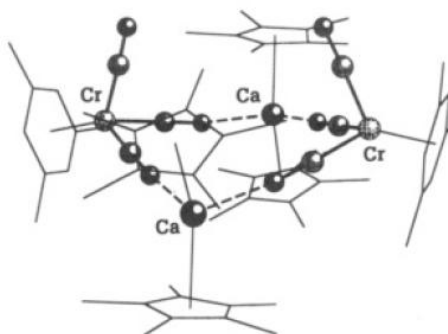


Figure 2.29. Molecular structure of $[\text{Cp}^*_2\text{CaCr}(\text{CO})_3(\text{Mes})]_2$ (**2.35**).⁹⁸

Literature reports containing $\text{Yb}(\mu\text{-OC})\text{TM}$ isocarbonyl bridges are also known. For example $[\text{Yb}(\text{Tp}^{\text{tBu,Me}})\{\text{Mo}(\text{Cp}')(\text{CO})_3\}(\text{THF})]_2$ (**2.36**), with a hinge angle of 147° .⁹⁹ $[\text{Cp}^*\text{Yb}\{\text{Mn}(\text{CO})_5\}]_2$ (**2.37**) also bears an isocarbonyl bridged twelve-membered ring.¹⁰⁰ However, unlike the aforementioned structures, a chair-conformation is not observed. Instead the ring is near-planar and actually exhibits a subtle boat conformation (172°), that is, both Yb centres are on the same face of the ring. Consequently sides *a-a* and *b-b* as depicted in Figure 2.27 are no longer coplanar. Interestingly this co-crystallises with $[\text{Cp}^*\text{Yb}\{\text{Mn}(\text{CO})_5\}]_x$ (**2.38**) where each Yb centre has three $\text{Yb}(\mu\text{-OC})\text{TM}$ isocarbonyl bridges, forming an infinite chain with planar twelve membered rings. Other literature reports of twelve-membered rings with $\text{M}(\mu\text{-OC})\text{TM}$ isocarbonyl linkages include $\text{Sm}\cdots\text{Fe}$,^{101, 102} $\text{Na}\cdots\text{Mn}$,¹⁰³ $\text{U}\cdots\text{Mn}$,¹⁰⁴ $\text{K}\cdots\text{Mn}$,¹⁰⁵ $\text{Ti}\cdots\text{Mo}$,¹⁰⁶ $\text{Zr}\cdots\text{Mo}$,¹⁰⁷ $\text{Al}\cdots\text{W}$,¹⁰⁸ and $\text{Ce}\cdots\text{W}$.¹⁰⁹

Whilst **14** is stable in THF, attempts to obtain crystals of the material or manipulate it in benzene gave a mixture of decomposition products as evidenced by ^1H NMR spectroscopy. To further investigate this, a concentrated benzene solution of **14** was allowed to stand for several days to afford black hexagonal crystals of $\{\text{Ca}(\text{NacNac})(\text{THF})\}_2\{\text{Cp}_4\text{Fe}_5(\text{CO})_8\}$ (**16**) amongst the precipitate. The molecular structure and selected distances and angles are shown in Figure 2.30 and Table 2.15.

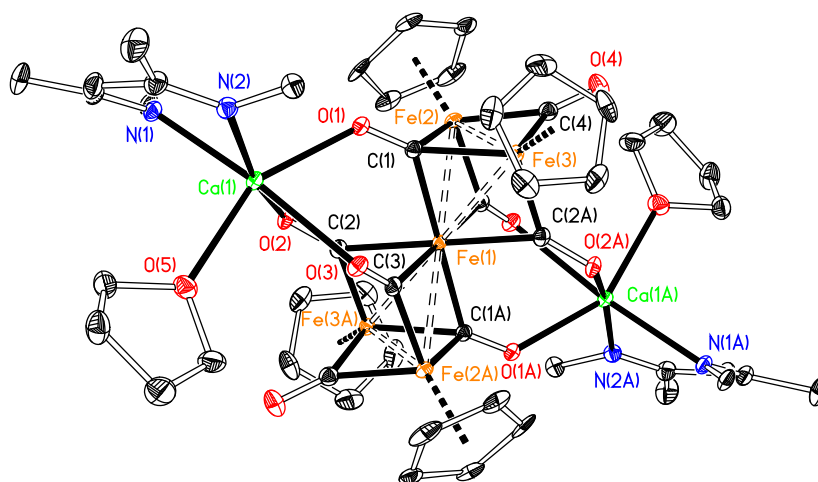


Figure 2.30. Displacement ellipsoid plot (20% probability) of $\{\text{Ca}(\text{NacNac})(\text{THF})\}_2\{\text{Cp}_4\text{Fe}_5(\text{CO})_8\}$ (**16**). Minor disorder, N-aryl groups and H atoms omitted for clarity. Atoms carrying the suffix “A” are related to their counterparts by the operator $1-x, 1-y, 1-z$.

Each six-coordinate Ca centre has distorted octahedral geometry with three isocarbonyl linkages (μ_3 -bridging carbonyl groups) to a $\text{Cp}_4\text{Fe}_5(\text{CO})_8$ core. In addition, each Ca centre is coordinated to a NacNac and THF ligand. The $\text{N}(1)\text{-Ca}(1)\text{-N}(1)$ angle ($79.79(4)^\circ$) is identical within error to that for **15** ($79.92(4)^\circ$). The $\text{Ca}(1)\text{-O}(\text{carbonyl})$ distances for **16** ($\text{Ca}(1)\text{-O}(1) = 2.2895(9)$, $\text{Ca}(1)\text{-O}(2) = 2.4384(9)$, $\text{Ca}(1)\text{-O}(3) = 2.4669(9)$ Å) span the range of distances covered by the $\text{Ca}(1)\text{-O}(\text{isocarbonyl})$ distances for **15** ($\text{Ca}(1)\text{-O}(1) = 2.3915(12)$, $\text{Ca}(1)\text{-O}(2\text{A}) = 2.3971(11)$ Å). The carbonyl groups interacting with $\text{Ca}(1)$ have Fe-C distances that are longer for **16** compared to those for **15** as expected given the μ_3 vs μ_2 -bridging modes, respectively, for example $\text{Fe}(1)\text{-C}(1) = 1.7120(15)$ in **15** and $2.0221(12)$ Å in **16**. The carbonyl C-O distances associated with the bridging carbonyl interactions to $\text{Ca}(1)$ in **16** exhibit a range of values ($\text{C}(1)\text{-O}(1) = 1.2295(16)$, $\text{C}(2)\text{-O}(2) = 1.1971(16)$, $\text{C}(3)\text{-O}(3) = 1.2032(16)$ Å).

The most distinct feature of **16** is the presence of interstitial $\text{Fe}(1)$ in the formally dianionic $\text{Cp}_4\text{Fe}_5(\text{CO})_8$ core supported by four side-on (η^2 -) carbonyl interactions. This highlights the extent to which **14** undergoes decomposition in benzene given the loss of Cp and both carbonyl groups that would have been bound as the Fp^- anion. Note that whilst the $\text{Ca}(1)\text{-Fe}$ distances are greater than the sum of the respective covalent radii ($3.08(10)$ Å),¹⁵ the $\text{Fe}(1)\text{-Fe}$ distances are shorter than the sum of the respective covalent radii ($2.64(4)$ Å), for example $\text{Ca}(1)\text{-Fe}(1) = 4.1872(3)$ and $\text{Fe}(1)\text{-Fe}(2) = 2.64(4)$ Å.

Fe(2) = 2.5524(2) Å. As such, direct interactivity may also take place between Fe(1) and its neighbouring Fe centres.

Table 2.15. Selected distances (Å) and angles (°) for {Ca(NacNac)(THF)}₂{Cp₄Fe₅(CO)₈} (**16**).

Ca(1)···Fe(1)	4.1872(3)	Ca(1)···Fe(2)	4.8967(3)
Ca(1)···Fe(3)	4.9247(3)	Ca(1)-O(1)	2.2895(9)
Ca(1)-O(2)	2.4384(9)	Ca(1)-O(3)	2.4669(9)
Ca(1)-O(5)	2.4148(10)	Ca(1)-N(1)	2.3911(11)
Ca(1)-N(2)	2.3855(11)	Fe(1)-C(1)	2.0221(12)
Fe(1)-C(2)	1.9875(12)	Fe(1)-C(3)	1.9976(12)
Fe(1)···Fe(2)	2.5524(2)	Fe(1)···Fe(3)	2.5412(2)
Fe(2)···Fe(3)	2.5307(3)	Fe(2)-Cp _{cent(1)}	1.744
Fe(2)-C(4)	1.9202(14)	Fe(2)-C(1)	1.9674(13)
Fe(2)-C(3A)	1.8591(13)	Fe(3)-Cp _{cent(2)}	1.745
Fe(3)-C(1)	1.9535(13)	Fe(3)-C(4)	1.9133(14)
Fe(3)-C(2A)	1.8724(13)	C(1)-O(1)	1.2295(16)
C(2)-O(2)	1.1971(16)	C(3)-O(3)	1.2032(16)
C(4)-O(4)	1.1794(17)	O(1)-Ca(1)-O(2)	71.49(3)
O(1)-Ca(1)-O(3)	72.14(3)	O(1)-Ca(1)-O(5)	151.50(4)
O(2)-Ca(1)-O(3)	80.30(3)	O(2)-Ca(1)-N(1)	93.44(4)
O(3)-Ca(1)-N(2)	107.33(4)	N(1)-Ca(1)-N(2)	79.79(4)
C(1)-Fe(1)-C(1A)	179.994	C(1)-Fe(1)-C(2)	84.21(5)
C(1)-Fe(2)-C(4)	97.42(5)	C(1)-Fe(2)-C(3A)	101.99(5)
C(1)-Fe(2)-Cp _{cent(1)}	120.89	C(1)-Fe(3)-C(2A)	102.05(5)
C(1)-Fe(3)-C(4)	98.12(5)	C(1)-Fe(3)-Cp _{cent(2)}	121.86
C(2)-Fe(1)-C(3)	73.47(5)	C(2)-Fe(1)-C(3A)	106.53(5)
C(2A)-Fe(3)-C(4)	83.49(5)	C(2A)-Fe(3)-Cp _{cent(2)}	121.95
C(3A)-Fe(2)-C(4)	84.73(6)	C(3A)-Fe(2)-Cp _{cent(1)}	123.39
C(4)-Fe(2)-Cp _{cent(1)}	120.47	C(4)-Fe(3)-Cp _{cent(2)}	121.07

For Cp_{cent(2)} average distances and angles are given to accommodate both orientations of the Cp rings.

Reaction of $[\text{Yb}(\text{NacNac})\text{I}(\text{THF})]_2$ (**2.39**) with KFp in THF afforded $[\text{Yb}(\text{NacNac})\text{Fp}(\text{THF})]_2$ (**17**) as a red solid in 88% isolated yield. As with **14**, stability in benzene was sufficient to allow NMR characterisation but not growth of crystals suitable for analysis by single crystal X-ray diffraction prior to decomposition. Therefore diffraction quality crystals of $[\text{Yb}(\text{NacNac})\text{Fp}(\text{THF})_2]_2$ (**18**) were grown from THF. The molecular structure and selected distances and angles are shown in Figure 2.31 and Table 2.16.

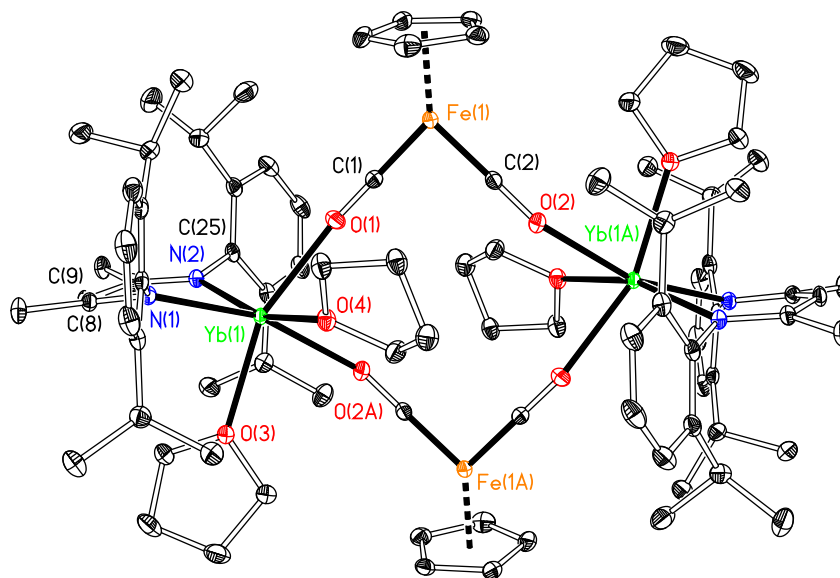


Figure 2.31. Displacement ellipsoid plot (20% probability) of $[\text{Yb}(\text{NacNac})\text{Fp}(\text{THF})_2]_2$ (**18**). H atoms omitted for clarity. Atoms carrying the suffix “A” are related to their counterparts by the operator $1-x, 2-y, 1-z$.

Table 2.16. Selected distances (Å) and angles (°) for [Yb(NacNac)Fp(THF)₂]₂ (**18**).

Yb(1)···Fe(1)	5.1718(5)	Yb(1A)···Fe(1)	5.2267(4)
Yb(1)-O(1)	2.437(2)	Yb(1)-O(2A)	2.4617(19)
Yb(1)-O(3)	2.469(2)	Yb(1)-O(4)	2.4671(19)
Yb(1)-N(1)	2.422(2)	Yb(1)-N(2)	2.434(2)
Fe(1)-C(1)	1.709(3)	Fe(1)-C(2)	1.707(3)
Fe(1)-Cp _{cent} (1)	1.742	C(1)-O(1)	1.191(3)
C(2)-O(2)	1.190(3)	O(1)-Yb(1)-O(2A)	80.58(7)
O(1)-Yb(1)-O(3)	157.21(7)	O(2A)-Yb(1)-O(4)	82.23(7)
O(4)-Yb(1)-N(1)	94.65(7)	N(1)-Yb(1)-N(2)	77.97(7)
N(2)-Yb(1)-O(2A)	109.56(7)	C(1)-Fe(1)-C(2)	90.31(13)
C(1)-Fe(1)-Cp _{cent} (1)	134.31	C(2)-Fe(1)-Cp _{cent} (1)	135.35
^a Hinge angle	158		

^a Hinge = (Fe(1), C(2), O(2), Fe(1A), C(2A), O(2A))-(O(2), Yb(1), O(1A), C(1A), Fe(1A)). Maximum deviation from plane = 0.394 Å (O(1A)).

Compound **18** is isostructural with the molecular structure for **15** with two Fp[−] anions linking the six-coordinate Yb centres via Yb(μ-OC)Fe isocarbonyl linkages to give a twelve-membered ring. Each Yb centre has distorted octahedral geometry with a NacNac ligand and two THF ligands in addition to the Ca(μ-OC)Fe groups. The Yb(1)···Fe(1) (5.1718(5)) and Yb(1)···Fe(1A) (5.2267(4)) distances are greater than the sum of the respective covalent radii. Compared to **15**, the distances around Yb(1) are longer than those around Ca(1), consistent with the increase in covalent radius. For example Yb(1)-O(1) = 2.437(2) whereas Ca(1)-O(1) = 2.3915(12) Å. The N(1)-Yb(1)-N(2) angle is slightly smaller at 77.97(7) compared to 79.92(4) ° in **15**. The C(1)-Fe(1)-C(2) angle of 89.37(7) ° is greater than that in **15** (87.37(7) °) but still slightly shorter than that for **12** (90.47(7) °). The carbonyl C-O and Fe-C distances in **18** are very similar to those in **15**. For example C(1)-O(1) = 1.191(3) and Fe(1)-C(1) = 1.709(3) for **18** and C(1)-O(1) = 1.1869(19) and Fe(1)-C(1) = 1.7120(15) Å for **15**.

Analogous to **14**, substitution of one of the Fp[−] anions per Yb in [YbFp₂(THF)₃]₂ (**6**) for NacNac is sufficient to disrupt the propensity to form Yb-Fe bonds. Consistent with the observations for the molecular structures of [CaFp₂(THF)₃]₂ (**3**) and **6**, and

$\text{CaFp}_2(\text{HMPA})_4$ (**10**) and $\text{YbFp}_2(\text{HMPA})_4$ (**11**), it is apparent that the structure for **18** is very similar to that for **15** further supporting the principle that analogous divalent Ca and Yb complexes have the potential to be isostructural.

Analogous to **15**, **18** has a dimeric structure with two THF ligands bound to each Yb, whilst ^1H NMR spectroscopy (C_6D_6) and elemental analysis of **17** are consistent with one THF per Yb. As with **14**, in the absence of crystallographic data it is not possible to draw conclusions about the interaction of the Fp^- anion with the Yb centre in the molecular structure of **15**, postulated to be dimeric.

Very surprisingly, cooling a dilute pentane solution of **17** to $-30\text{ }^\circ\text{C}$, afforded red crystals of $\{\text{Yb}(\text{NacNac})(\text{Fp})(\text{THF})\}_2(\mu\text{-YbFp}_2)$ (**19**) suitable for analysis by X-ray diffraction. The molecular structure and selected distances and angles are shown in Figure 2.32 and Table 2.17.

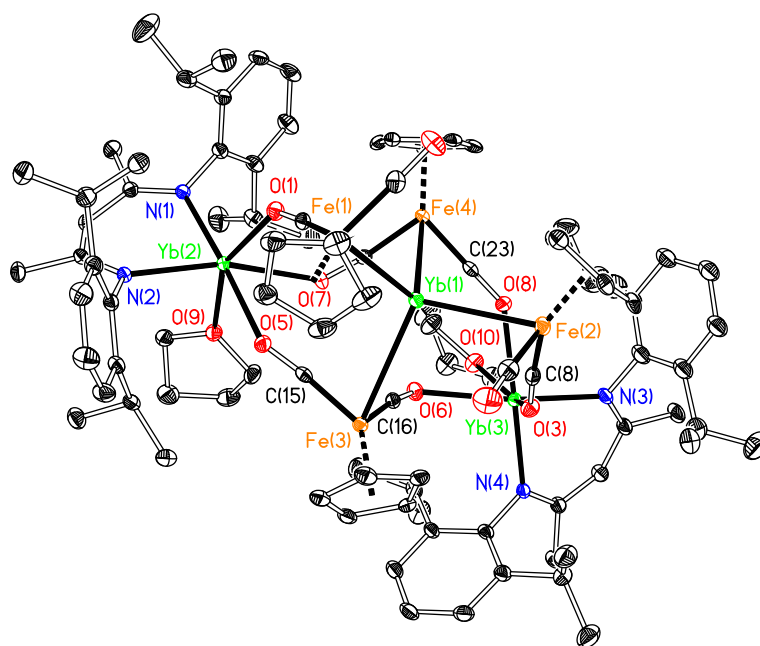


Figure 2.32. Displacement ellipsoid plot (20% probability) of $\{\text{Yb}(\text{NacNac})(\text{Fp})(\text{THF})\}_2(\mu\text{-YbFp}_2)$ (**19**). Pentane of crystallisation, minor disorder and H atoms omitted for clarity.

Table 2.17. Selected distances (Å) and angles (°) for {Yb(NacNac)(Fp)(THF)}₂(μ-YbFp₂) (**19**).

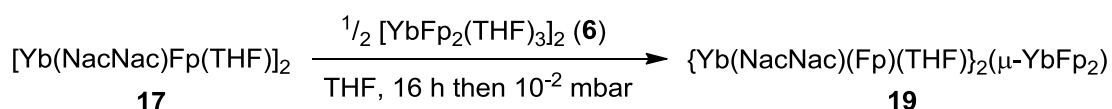
Yb(1)-Fe(1)	2.9961(5)	Yb(1)-Fe(2)	2.9758(5)
Yb(1)-Fe(3)	3.1702(5)	Yb(1)-Fe(4)	3.1498(5)
Yb(2)···Fe(1)	4.9541(5)	Yb(2)···Fe(3)	4.8284(5)
Yb(2)···Fe(4)	5.0949(5)	Yb(2)-O(1)	2.420(2)
Yb(2)-O(5)	2.457(2)	Yb(2)-O(7)	2.484(2)
Yb(2)-O(9)	2.400(2)	Yb(2)-N(1)	2.386(2)
Yb(2)-N(2)	2.387(2)	Fe(1)-C(1)	1.710(3)
Fe(1)-C(2)	1.739(4)	Fe(1)-Cp _{cent(1)}	1.725
Fe(3)-C(15)	1.721(3)	Fe(3)-C(16)	1.706(3)
Fe(3)-Cp _{cent(3)}	1.739	Fe(4)-Cp _{cent(4)}	1.721
Fe(4)-C(22)	1.702(3)	C(1)-O(1)	1.188(4)
C(2)-O(2)	1.164(5)	C(15)-O(5)	1.179(4)
C(16)-O(6)	1.188(4)	C(22)-O(7)	1.191(4)
Fe(1)-Yb(1)-Fe(2)	114.749(14)	Fe(1)-Yb(1)-Fe(3)	107.722(13)
Fe(1)-Yb(1)-Fe(4)	106.797(13)	Fe(2)-Yb(1)-Fe(4)	107.168(14)
Fe(3)-Yb(1)-Fe(4)	115.811(12)	O(1)-Yb(2)-O(5)	77.57(8)
O(1)-Yb(2)-O(7)	81.19(7)	O(1)-Yb(2)-O(9)	154.69(8)
O(5)-Yb(2)-O(7)	73.66(7)	O(5)-Yb(2)-N(2)	96.37(8)
O(7)-Yb(2)-N(1)	108.66(8)	N(1)-Yb(2)-N(2)	81.01(8)
Yb(1)-Fe(1)-C(1)	78.45(10)	Yb(1)-Fe(1)-C(2)	81.74(12)
Yb(1)-Fe(1)-Cp _{cent(1)}	116.86	Yb(1)-Fe(3)-C(15)	73.25(9)
Yb(1)-Fe(3)-C(16)	74.69(10)	Yb(1)-Fe(3)-Cp _{cent(3)}	127.80
C(1)-Fe(1)-C(2)	96.51(15)	C(1)-Fe(1)-Cp _{cent(1)}	132.33
C(2)-Fe(1)-Cp _{cent(1)}	129.00	C(15)-Fe(3)-C(16)	96.80(13)
C(15)-Fe(3)-Cp _{cent(3)}	133.22	C(16)-Fe(3)-Cp _{cent(3)}	127.26

Parameters associated with Cp rings averaged across both orientations.

Compound **19** may formally be viewed as a [Yb(NacNac)(THF)(μ-Fp)]₂ moiety (Yb(2), Yb(3), Fe(3) and Fe(4)) complexed by a YbFp₂ unit (Yb(1), Fe(1) and Fe(2)), thereby forming an Yb(1)Fe₄ centre in a tetrahedral arrangement. The Yb(1)-Fe

distances (Fe(1) = 2.9961(5), Fe(2) = 2.9758(5), Fe(3) = 3.1702(5), Fe(4) = 3.1498(5) Å) are consistent with direct interactions between these metal centres, where the sum of the respective covalent radii is 3.19(9) Å.¹⁵ Yb(2) is coordinated to a NacNac and THF ligand and three Yb(μ -OC)Fe groups (O(1), O(5), O(7)). The coordination geometry at Yb(3) is very similar and so only that at Yb(2) shall be focussed on. Compound **19** shares the same twelve-membered ring motif as observed for **18**. One THF is displaced at Yb(2) and Yb(3) to give an isocarbonyl bridged YbFp₂ group providing the interstitial Yb(1) which undergoes coordination to Fe(3) and Fe(4). Fe(1) and Fe(2) are singly isocarbonyl bridging whereas Fe(3) and Fe(4) are doubly bridging. This is reflected in the lengthened C-O distances for those carbonyl groups involved in isocarbonyl bridging. For example C(1)-O(1) = 1.188(4) compared to 1.164(5) Å for C(2)-O(2). Consistent with this the Fe(1)-C(1) distance (1.710(3) Å) is shorter than that for Fe(1)-C(2) (1.739(4) Å). Note also that the Yb(1)-Fe(3) and Fe(4) distances are longer than those to Fe(1) or Fe(2). The N(1)-Yb(2)-N(2) angle (81.01(8) °) in **19** is greater than the N(1)-Yb(1)-N(2) angle (77.97(7) °) in **18**. The Yb(2)-O(5) (2.457(2) Å) and O(7) (2.484(2) Å) distances in **19** can be considered equivalent to Yb(1)-O(1) (2.437(2) Å) and O(2A) (2.462(2) Å) in **18**. These distances are similar and are all longer than the Yb(2)-O(1) distance (2.420(2) Å) concerning the isocarbonyl interaction with the “YbFp₂” moiety. The Yb(2)-O(9) distance (2.400(2) Å) corresponding to the coordinated THF in **19** is shorter than for either of the THFs coordinated to Yb(1) in **18** (2.469(2) and 2.467(2) Å).

Compound **19** presumably forms by a redistribution reaction of **17** in the absence of stabilising THF. A rational synthesis was achieved by the reaction of [Yb(NacNac)Fp(THF)]₂ (**17**) with [YbFp₂(THF)₃]₂ (**6**) in THF to afford **19** as a brown solid in 74% isolated yield (Equation 2.14), based on ¹H NMR and in particular IR spectroscopy and elemental analysis.



Equation 2.14

2.6.5 Solid state and solution IR studies of NacNac supported M-Fp complexes

Table 2.18 lists the principal $\nu(\text{CO})$ bands in the IR spectra for the NacNac complexes Mg(NacNac)Fp(THF) (**12**), Mg(NacNac){(NTol)₂CFp} (**13**), [Ca(NacNac)Fp(THF)]₂

(**14**), $[\text{Yb}(\text{NacNac})\text{Fp}(\text{THF})]_2$ (**17**) and $\{\text{Yb}(\text{NacNac})(\text{Fp})(\text{THF})\}_2(\mu\text{-YbFp}_2)$ (**19**). Reassuringly none of these spectra correspond to those for $[\text{Mg}(\text{HMPA})_4][\text{Fp}]_2$ (**7**), consistent with a lack of separated ion pairs in these species.

The IR spectrum for **12** in Nujol shows two strong bands at 1926 and 1857 cm^{-1} corresponding to $\nu_{\text{sym}}(\text{CO})$ and $\nu_{\text{anti}}(\text{CO})$, respectively, consistent with that observed in THF (2015 and 1921 cm^{-1}) and that predicted by DFT (1926 and 1875 cm^{-1}). This compares with the two bands observed for $\text{Al}(\text{NacNac})\text{FpCl}$ (**2.19**, 1964 and 1908 cm^{-1} (CH_2Cl_2)),⁸⁷ $\text{Ge}(\text{NacNac})\text{Fp}$ (**2.20**, 1966 and 1910 cm^{-1} (KBr))⁸⁸ and $\text{In}(\text{NacNac})\text{FpI}$ (**2.21**, 2001 and 1954 cm^{-1} (KBr)).²⁷

The IR spectra for **13** in Nujol (2010 and 1956 cm^{-1}) and toluene (2015 and 1970 cm^{-1}) also exhibit two $\nu(\text{CO})$ bands, consistent with the proposed molecular structure (Figure 2.25) and the bands predicted by DFT (**13Q**) at 1987 and 1949 cm^{-1} for $\nu_{\text{sym}}(\text{CO})$ and $\nu_{\text{anti}}(\text{CO})$, respectively. These are higher than the Nujol, solution and DFT predicted bands corresponding to $\nu_{\text{sym}}(\text{CO})$ and $\nu_{\text{anti}}(\text{CO})$ for **12**, consistent with a decrease in the availability of electron density in the Fp^- anion. Two $\nu(\text{CO})$ bands are also observed in Aldridge's $[\text{Fp}(\text{BNR})_2][\text{BAR}^{\text{F}}_4]$, where $\text{R} = {}^i\text{Pr}$ (**2.28**, 2040 and 1993 cm^{-1}) or Cy (**2.29**, 2049 and 2003 cm^{-1}).⁹²

For **14** in Nujol two significant $\nu(\text{CO})$ bands are observed at 1823 and 1780 cm^{-1} , corresponding to $\nu_{\text{sym}}(\text{CO})$ and $\nu_{\text{anti}}(\text{CO})$, respectively. Two bands are also observed in THF at 1958 and 1810 cm^{-1} . Similarly the IR spectra for **17** in Nujol (1823 and 1780 cm^{-1}) and THF (1958 and 1810 cm^{-1}) exhibit two significant $\nu(\text{CO})$ bands. As evidenced by previous IR spectra (Table 2.6 and 2.12), the presence of bands below *ca.* 1790 cm^{-1} are indicative of $\text{M}(\mu\text{-OC})\text{Fe}$ isocarbonyl interactions. These are exhibited by **14** and **17** in Nujol and THF, consistent with the presence of these interactions in the bulk material.

Compound **19** in Nujol exhibits three significant $\nu(\text{CO})$ bands (1962, 1905 and 1761 cm^{-1}) which do not correspond to those for **6** or **17** from which **19** was synthesised. Compound **19** also exhibits two bands in THF at 1874 and 1782 cm^{-1} , the latter of which does not correspond to those for **14** or **17**. Likewise, the ${}^1\text{H}$ NMR spectrum of **19** in THF is not simply the sum of **6** and **17**.

Table 2.18. IR $\nu(\text{CO})$ (cm^{-1}) for $[\text{YbFp}_2(\text{THF})_3]_2$ (**6**), $[\text{Mg}(\text{HMPA})_4][\text{Fp}]_2$ (**7**), $\text{Mg}(\text{NacNac})\text{Fp}(\text{THF})$ (**12**), $\text{Mg}(\text{NacNac})\{(\text{NTol})_2\text{CFp}\}$ (**13**), $[\text{Ca}(\text{NacNac})\text{Fp}(\text{THF})]_2$ (**14**), $[\text{Yb}(\text{NacNac})\text{Fp}(\text{THF})]_2$ (**17**) and $\{\text{Yb}(\text{NacNac})(\text{Fp})(\text{THF})\}_2(\mu\text{-YbFp}_2)$ (**19**), in Nujol and THF.

Complex	$\nu(\text{CO})$ (cm^{-1}) in Nujol	$\nu(\text{CO})$ (cm^{-1}) in solution
6	1897 (s), 1823 (s), 1744 (s)	1875 (s), 1711 (s)
7	1863 (s), 1789 (s)	1865 (m), 1787 (m)
12	1926 (s), 1857 (s)	1926 (m), 1871 (s)
13	2010 (s), 1956 (s)	2015(s), 1970(m) ^a
14	1823 (s), 1780 (s)	1958 (s) 1810 (s)
17	1821(s), 1779 (s)	1873 (s), 1721 (s)
19	1962 (s), 1905 (m), 1761 (m, br)	1874 (s), 1782 (s)

^a Recorded in toluene. All other solution IR values recorded in THF.

2.7 Conclusions

The work contained in this Chapter has reported the first structurally authenticated Ca-TM bond, in $[\text{CaFp}_2(\text{THF})_3]_2$ (**3**), and the first direct comparison of Ae-TM with Ln-TM bonding through the synthesis and structural investigation of $[\text{YbFp}_2(\text{THF})_3]_2$ (**6**) alongside **3**. These materials were found to be isostructural and isomorphous. The Ca-Fe distance was longer than that for Yb-Fe, the opposite of that expected based on the sum of the respective covalent radii. Computational analysis of these structures was consistent with a stronger Yb-Fe interaction in **6Q** than Ca-Fe in **3Q**. This was further supported by the computational analysis of previously reported isostructural complexes $\text{M}\{\text{Ga}(\text{ArNCH})_2\}_2(\text{TMEDA})_2$ ($\text{M} = \text{Ca}$ (**1.55Q**) or Yb (**1.69Q**) with Ca-Ga and Yb-Ga bonds that were shorter for the latter.^{62, 63} Structural analysis of $[\text{MgFp}_2(\text{THF})]_2$ (**1**) confirmed the postulated existence of a direct Mg-Fe bond by McVicker.⁴² The behaviour of these species as sources of the Fp^- anion was confirmed by reaction with MeI. For the Sr analogue $[\text{SrFp}_2(\text{THF})_x]_y$ (**5**), spectroscopic data was consistent with the formation of a material similar in form to that of **1**, **3** and **6**. Given the lack of structural authentication it is not possible to conclude or dismiss the presence of a direct Sr-Fe interaction. Attempts to model **5** as dimeric $[\text{SrFp}_2(\text{THF})_3]_2$ (**5Q**) exhibited side-on (η^2 -) interactions between the carbonyl groups and Sr centres.

Addition of HMPA to **1**, **3** and **6** gave the corresponding HMPA adducts $[\text{Mg}(\text{HMPA})_4][\text{Fp}]_2$ (**7**), $\text{CaFp}_2(\text{HMPA})_4$ (**10**) and $\text{YbFp}_2(\text{HMPA})_4$ (**11**). In the case of **7** a separated ion pair was formed, the first such example confirmed to exist in solution and the solid state.

Reaction of KFp with $\text{M}(\text{NacNac})\text{I}(\text{THF})$ gave the corresponding $[\text{M}(\text{NacNac})\text{Fp}(\text{THF})]_x$ complexes where $\text{M} = \text{Mg}$ (**12**, $x = 1$), Ca (**14**, $x = 2$) or Yb (**17**, $x = 2$). Compound **12** was confirmed to contain a direct Mg-Fe interaction and could be reacted with $\text{TolN}=\text{C}=\text{NTol}$ to give $\text{Mg}(\text{NacNac})\{(\text{NTol})_2\text{CFp}\}$ (**13**). Compound **12** could also be reacted with MeI to return $\text{Mg}(\text{NacNac})\text{I}(\text{THF})$ and MeFp , confirming **12** to be a source of the Fp^- anion. Unlike **12**, **14** and **17** were found to be unstable in benzene, decomposing to give $\{\text{Ca}(\text{NacNac})(\text{THF})\}_2\{\text{Cp}_4\text{Fe}_5(\text{CO})_8\}$ (**16**) and $\{\text{Yb}(\text{NacNac})(\text{Fp})(\text{THF})\}_2(\mu\text{-YbFp}_2)$ (**19**), respectively. Compound **19** could also be synthesised rationally by reaction of **17** with **6**. The molecular structure of **19** bears four unsupported Yb-Fe interactions with an all-transition metal coordination sphere surrounding the interstitial Yb. Compounds **14** and **17** were recrystallised from THF to afford molecular structures of $[\text{Ca}(\text{NacNac})\text{Fp}(\text{THF})_2]_2$ (**15**) and $[\text{Yb}(\text{NacNac})\text{Fp}(\text{THF})_2]_2$ (**18**), respectively.

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Chapter Three

Activated Ca reduction of $\text{Fe}_3(\text{CO})_{12}$

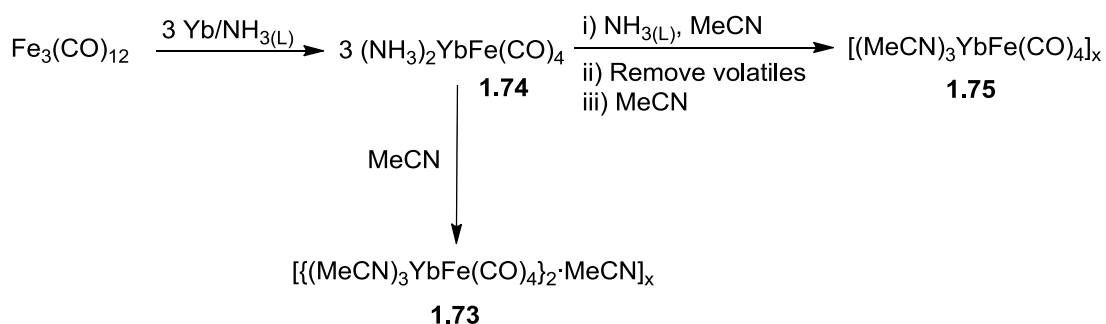
3.1 Overview

This Chapter describes the investigation of four complexes synthesised by the reduction of $\text{Fe}_3(\text{CO})_{12}$ with activated elemental Ca. Each of these complexes was structurally authenticated using single crystal X-ray diffraction. Analysis by $^{13}\text{C}\{^1\text{H}\}$ NMR and IR spectroscopy provided further information about the solution and solid state behaviour of these species. Related reports in the literature are also discussed. This research follows that reported by Shore *et al.* where Yb-Fe bonding was achieved *via* an analogous route.

3.2 Introduction

As discussed in Section 1.8, the first example of a structurally authenticated direct Ln-TM interaction was reported by Shore *et al.*^{1, 2} As illustrated in Scheme 3.1, this was achieved by the reduction of $\text{Fe}_3(\text{CO})_{12}$ with three equivalents of Yb in $\text{NH}_3(\text{L})$ to afford $(\text{NH}_3)_2\text{YbFe}(\text{CO})_4$ (**1.74**). To this was added MeCN. The solution was stirred for 10 minutes and the volume of the filtrate reduced until small crystals were observed. Crystallisation was continued for two weeks at $-40\text{ }^\circ\text{C}$ to give $[(\text{MeCN})_3\text{YbFe}(\text{CO})_4]_2 \cdot \text{MeCN}]_x$ (**1.73**, Figure 3.1) as orange needle-like crystals. The $[\text{Fe}(\text{CO})_4]^{2-}$ units have geometries intermediate of that for a tetrahedron and trigonal pyramid. Each Yb^{2+} is coordinated to two neighbouring $[\text{Fe}(\text{CO})_4]^{2-}$ units *via* isocarbonyl bridging and each $[\text{Fe}(\text{CO})_4]^{2-}$ to two neighbouring Yb^{2+} cations to give an isocarbonyl linked chain. Importantly, each Yb also has a direct interaction with an Fe centre on a neighbouring chain. The independent distances of 3.012(1) and 3.009(1) Å are shorter than the sum of the respective covalent radii (3.19(9) Å).³ Additionally each Yb is coordinated by three MeCN ligands to give a distorted octahedral geometry at each Yb centre. Together this gives a polymeric ladder where the direct Yb-Fe interactions form the rungs between the isocarbonyl bridged chains. The average C-O (1.154(9) Å) and Fe-C (1.768(11) Å) distances associated with the isocarbonyl linkages are consistent with a weakening and strengthening of these bonds, respectively, as a consequence of coordination to Yb. Quenching of the reaction mixture containing **1.74** with MeCN at $-78\text{ }^\circ\text{C}$, followed by removal of volatiles and crystallisation from a concentrated MeCN solution at $-40\text{ }^\circ\text{C}$ gave $[(\text{MeCN})_3\text{YbFe}(\text{CO})_4]_x$ (**1.75**).

This has a similar structure to that of **1.73**, with direct Yb-Fe interactions between the isocarbonyl linked chains to form a polymeric ladder. However, each Yb centre has an additional isocarbonyl interaction to a neighbouring ladder. This forms a polymeric sheet-like structure with repeating eight- and twelve-membered rings, with and without direct Yb-Fe interactions, respectively. Each Yb in **1.75** is also coordinated by three MeCN ligands to give a seven-coordinate centre with distorted pentagonal bipyramidal geometry. Consistent with the higher Yb coordination number for **1.75** compared to **1.73**, the Yb-Fe interactions are longer at 3.046(1) Å. The average Yb-O(isocarbonyl) distance is also increased from 2.374(7) for **1.73** to 2.45(5) Å for **1.75**. The very similar treatments of **1.74** that gave **1.73** or **1.75**, with similar but nonetheless different solid state structures, serves to highlight the delicate balance in this system with regard to the bonding and structural motifs observed.



Scheme 3.1. Reduction of Fe₃(CO)₁₂ with Yb/NH₃(L) and subsequent reactions with MeCN.^{1, 2}

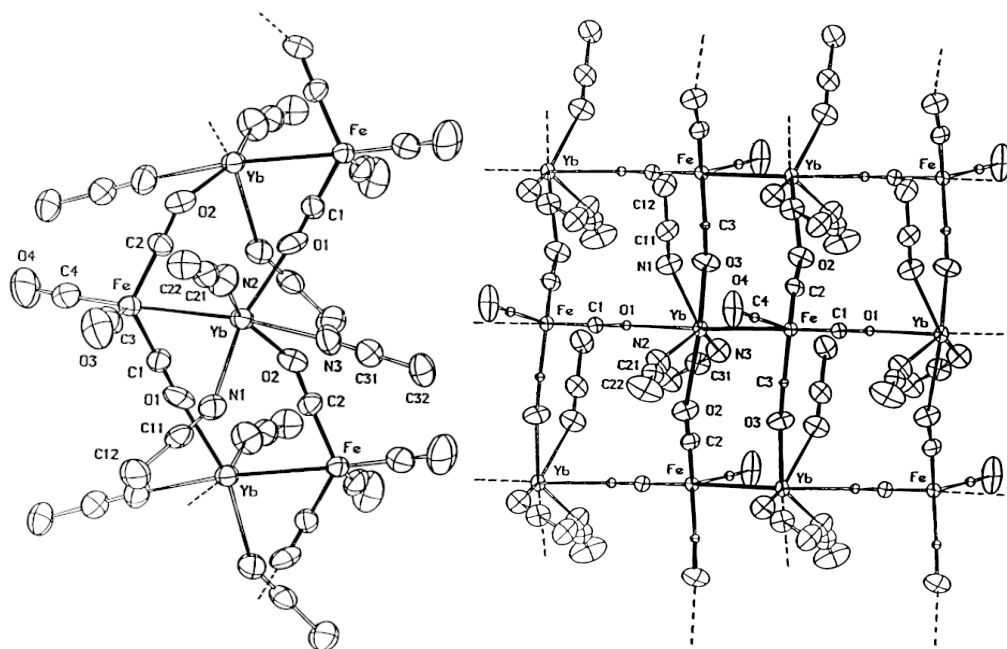
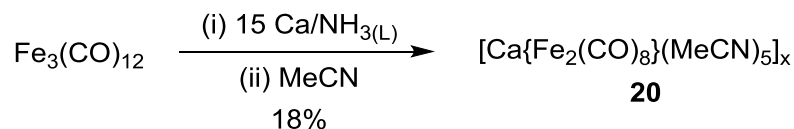


Figure 3.1. Displacement ellipsoid plots (50% probability) of $[\{(\text{MeCN})_3\text{YbFe}(\text{CO})_4\}_2 \cdot \text{MeCN}]_x$ (**1.73**, left) and $[(\text{MeCN})_3\text{YbFe}(\text{CO})_4]_x$ (**1.75**, right).^{1, 2}

Given the direct Yb-Fe interactions observed in **1.73** and **1.75** and the similar structural features of the Ca complexes to their Yb analogues in Chapter Two and those in the literature,⁴⁻⁹ the reduction of $\text{Fe}_3(\text{CO})_{12}$ with elemental Ca was investigated and is discussed in Section 3.3.

3.3 Reduction of $\text{Fe}_3(\text{CO})_{12}$ with Ca in liquid ammonia

$\text{Fe}_3(\text{CO})_{12}$ was reduced with an excess of $\text{Ca}/\text{NH}_3(\text{L})$ at -78°C to give a blue solution and formation of a yellow mirror on the wall of the vessel. Removal of volatiles under reduced pressure gave a grey solid. The material was dissolved in MeCN and stirred for 16 h at RT. The solution was filtered and volatiles removed under reduced pressure to give a yellow solid. This was washed with pentane and dried *in vacuo* to afford $[\text{Ca}\{\text{Fe}_2(\text{CO})_8\}(\text{MeCN})_5]_x$ (**20**) as a yellow solid in 18% yield (Equation 3.1). Elemental analysis of the bulk material was inconsistent with the molecular structure determined by X-ray crystallography, potentially a result of the labile MeCN ligands or the sensitivity of **20**.

**Equation 3.1**

Diffraction-quality crystals of **20** were grown from a saturated MeCN solution at RT. A portion of the infinite chain and selected distances and angles are shown in Figure 3.2 and Table 3.1. The coordination geometries at Ca(1) and Ca(2) are not substantially different and therefore Ca(1) will be focussed on. The geometry at the seven coordinate Ca(1) centre is distorted pentagonal bipyramidal, with five coordinated MeCN ligands and two isocarbonyl bridges to $[\text{Fe}_2(\text{CO})_8]^{2-}$ units. Each $[\text{Fe}_2(\text{CO})_8]^{2-}$ interacts with another $[\text{Ca}(\text{MeCN})_5]^{2+}$ and so forth to give an infinite chain. The $\text{Ca}\cdots\text{Fe}$ distances are considerably longer than the sum of the respective covalent radii (3.08(10) Å). For example $\text{Ca}(1)\cdots\text{Fe}(1) = 5.0171(10)$ Å.

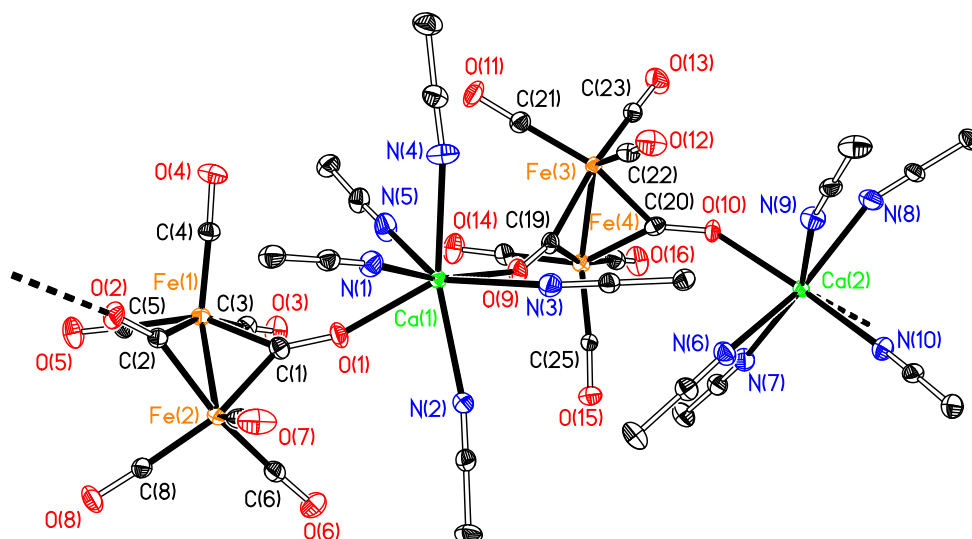


Figure 3.2. Displacement ellipsoid plot (20% probability) of the asymmetric unit of $[\text{Ca}\{\text{Fe}_2(\text{CO})_8\}(\text{MeCN})_5]_x$ (**20**). H atoms omitted for clarity. Ca(2) and O(2) connect to O(2A) and Ca(2B) in the neighbouring asymmetric units by the symmetry operators $x, y-1, z$ and $x, y+1, z$ respectively.

Table 3.1. Selected distances (Å) and angles (°) for [Ca{Fe₂(CO)₈}(MeCN)₅]_x (**20**).

Ca(1)···Fe(1)	5.0171(10)	Ca(1)···Fe(2)	5.1124(10)
Ca(1)···Fe(3)	4.8700(10)	Ca(1)···Fe(4)	5.2137(10)
Ca(1)-O(1)	2.301(3)	Ca(1)-O(9)	2.324(3)
Ca(2)-O(2A)	2.331(3)	Ca(2)-O(10)	2.303(3)
Ca(1)-N(1)	2.500(4)	Ca(1)-N(2)	2.509(4)
Ca(1)-N(3)	2.522(4)	Ca(1)-N(4)	2.503(4)
Ca(1)-N(5)	2.478(4)	Fe(1)-Fe(2)	2.5520(8)
Fe(1)-C(1)	1.946(5)	Fe(1)-C(2)	1.944(5)
Fe(1)-C(3)	1.763(5)	Fe(1)-C(4)	1.746(4)
Fe(1)-C(5)	1.785(5)	Fe(2)-C(1)	1.918(5)
Fe(2)-C(2)	1.957(5)	C(1)-O(1)	1.216(5)
C(2)-O(2)	1.198(5)	C(3)-O(3)	1.181(6)
C(4)-O(4)	1.176(5)	C(5)-O(5)	1.162(6)
C(19)-O(9)	1.210(5)	C(20)-O(10)	1.228(5)
Ca(1)-O(1)-C(1)	159.8(4)	Ca(1)-O(9)-C(19)	154.7(3)
Ca(2)-O(2B)-C(2B)	172.1(3)	Ca(2)-O(10)-C(20)	146.3(3)
O(1)-Ca(1)-O(9)	121.23(14)	O(1)-Ca(1)-N(1)	76.99(14)
O(2B)-Ca(2)-O(10)	121.50(13)	O(2B)-Ca(2)-N(6)	128.42(15)
N(1)-Ca(1)-N(5)	113.86(17)	N(1)-Ca(1)-N(5)	113.86(17)
N(2)-Ca(1)-N(3)	75.47(14)	N(3)-Ca(1)-N(4)	85.71(16)
N(4)-Ca(1)-N(5)	73.62(17)	Fe(1)-C(1)-Fe(2)	82.64(18)
Fe(1)-C(1)-O(1)	139.1(4)	Fe(1)-C(2)-Fe(2)	82.46(17)
Fe(1)-C(2)-O(2)	140.0(4)	Fe(1)-C(3)-O(3)	176.8(5)
Fe(1)-C(4)-O(4)	175.0(4)	Fe(1)-C(5)-O(5)	178.7(5)
Fe(2)-C(1)-O(1)	138.1(4)	Fe(2)-C(2)-O(2)	137.5(4)

Terminal C-O and Fe-C distances associated with Fe(2), Fe(3) and Fe(4) omitted. Average Fe-C terminal carbonyl distances: Fe(1) = 1.765(3), Fe(2) = 1.775(3), Fe(3) = 1.786(3), Fe(4) = 1.775(3) Å. Average terminal carbonyl C-O distances: Fe(1) = 1.173(3), Fe(2) = 1.166(3), Fe(3) = 1.156(3), Fe(4) = 1.162(3) Å. Average Ca(2)-N distance = 2.520(4) Å.

The C-O distances for the isocarbonyl bridged groups are longer than those for the terminal carbonyl groups. For example the C(1)-O(1) distance is 1.216(5) compared

to the average terminal carbonyl Fe(1) C-O distance of 1.173(3) Å. The Fe-C distances associated with the bridging carbonyls are also longer than the terminal carbonyl Fe-C distances. For example, Fe(1)-C(1) is 1.946(5) compared to the average terminal Fe(1)-C distance of 1.765(3) Å. As expected, the Fe-C-O angles associated with the bridging carbonyl groups are smaller than those for the terminal carbonyl groups. For example Fe(1)-C(1)-O(1) is 139.1(4) compared to the near-linear average Fe(1)-C-O value for the terminal carbonyl groups of 176.8(3)°.

The reaction is observed to give one Fe₂(CO)₈ unit per Ca with the formal loss of an equivalent of Fe(CO)₄, preserving one apparent Fe-Fe bond (2.5520(8) Å). This contrasts with the analogous reaction performed by Shore *et al.* where Fe₃(CO)₁₂ was reduced by Yb/NH₃ to give the polymeric structure **1.73** comprised of Fe(CO)₄ units. Crucially this also contained direct interactions between Yb and Fe, which are absent in **20**.

Structurally authenticated examples of any Ae²⁺ cation interacting with the [Fe₂(CO)₈]²⁻ anion are yet to be reported.¹⁰ However, the structure of Ca{Fe₂(CO)₆(μ-CO)(μ-PPh₂)}₂(THF)₄ (**2.16**, Figure 3.3) synthesised by the reaction of [Ca(PPh₂)₂(THF)₄] with Fe₃(CO)₁₂ or Fe₂(CO)₉ is comparable.¹¹ This contains a six-coordinate Ca centre with distorted octahedral geometry, with four THF ligands in the equatorial plane and *trans*-axial bridging carbonyl interactions to two [Fe₂(CO)₇(PPh₂)]²⁻ anions. The CO-Ca(1) and Fe(1)-Fe(2) distances are 2.298(4) and 2.579(2) Å, respectively. These compare with the Ca(1)-O carbonyl and Fe(1)-Fe(2) distances in **20** of 2.313(4) and 2.552(1) Å, respectively. Note again that the complexes featured in Chapter Two are the only other structurally authenticated examples of bridging carbonyl interactions between Ae and Fe. However, all of these contain μ₂- as opposed to μ₃-carbonyl interactions.

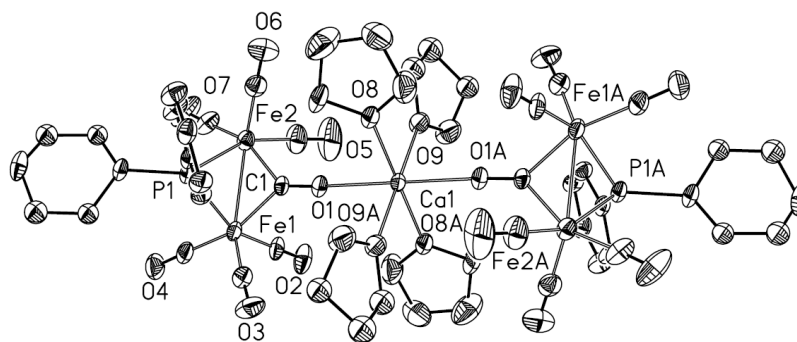


Figure 3.3. Displacement ellipsoid plot (40% probability) of $\text{Ca}\{\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)\}_2(\text{THF})_4$ (**2.16**).¹¹ H atoms omitted for clarity. Atoms carrying the suffix “A” are related to their counterparts by the symmetry operator $-x+2, -y+2, z$.

Despite established synthetic routes and its investigation as a catalyst for the synthesis of ammonia, the structure of $\text{K}_2[\text{Fe}_2(\text{CO})_8]$ (**3.1**) has not been reported.¹²⁻¹⁵ However, interaction of the $[\text{Fe}_2(\text{CO})_8]^{2-}$ anion with the Group one cations Li^+ and Na^+ have been studied and molecular structures reported.¹⁶ Reaction of $\text{Fe}_2(\text{CO})_9$ with elemental Li in THF gave the monomeric complex $\text{Li}_2\{\text{Fe}_2(\text{CO})_8\}(\text{THF})_6$ (**3.2**) when crystallised from THF. Conversion to polymeric $[\text{Li}_2\{\text{Fe}_2(\text{CO})_8\}(\text{THF})]_x$ **3.3** was achieved by crystallisation from toluene. Reaction of $\text{Fe}(\text{CO})_5$ with Collman’s reagent ($\text{Na}_2[\text{Fe}(\text{CO})_4]$, **3.4**) in THF gave polymeric $[\text{Na}_2\{\text{Fe}_2(\text{CO})_8(\text{THF})_4\}]_x$ (**3.5**) when crystallised from THF. Displacement ellipsoid plots of **3.2**, **3.3** and **3.5** are illustrated in Figure 3.4. Note the μ_3 -bridging carbonyl group between the Fe and Li centres in **3.2** and **3.3**, reminiscent of that observed in **20**. This is not observed in **3.5**, where terminal isocarbonyl interactions are observed instead between the Fe and Na centres exclusively.

The Fe(1)-Fe(2) distances in **3.2** (2.551(1) Å) and **3.3** (2.565(1) Å) are very similar to that in **20** (2.552(1) Å). The average Fe-C-Fe angles in **3.2**, **3.3** and **20** are identical within error at 83.0(4), 83.3(3) and 82.6(3) °, respectively.

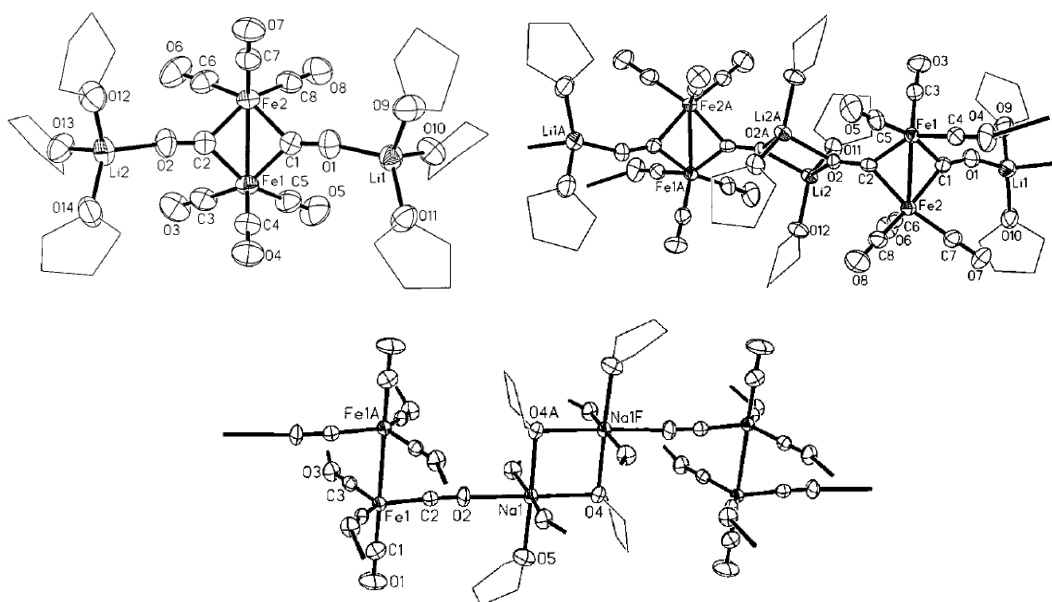
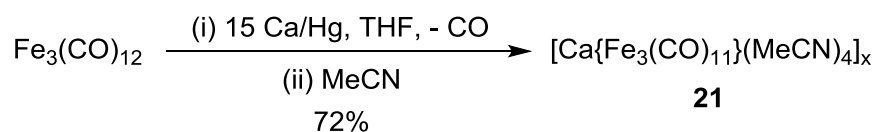


Figure 3.4. Displacement ellipsoid plots (40% probability) of $\text{Li}_2\{\text{Fe}_2(\text{CO})_8\}(\text{THF})_6$ (**3.2**, top left), $[\text{Li}_2\{\text{Fe}_2(\text{CO})_8\}(\text{THF})]_x$ (**3.3**, top right) and $[\text{Na}_2\{\text{Fe}_2(\text{CO})_8\}(\text{THF})_4]_x$ (**3.5**, bottom). Methylene groups of the THF ligands are given schematically.¹⁶

3.4 Reduction of $\text{Fe}_3(\text{CO})_{12}$ with Ca amalgam

Reduction of $\text{Fe}_3(\text{CO})_{12}$ in THF with an excess of Ca/Hg gave a red suspension. Isolation from the amalgam and removal of volatiles was followed by extraction into MeCN. Filtration and removal of volatiles gave $[\text{Ca}\{\text{Fe}_3(\text{CO})_{11}\}(\text{MeCN})_4]_x$ (**21**) as a black-dark red microcrystalline solid in 72% isolated yield (Equation 3.2). Elemental analysis of the bulk material was consistent with the molecular structure for **21** determined by X-ray crystallography.



Equation 3.2

Diffraction-quality crystals of **21** were grown from a saturated MeCN solution at RT. Sections of the polymeric structure and selected distances and angles are shown in Figure 3.5, 3.6 and Table 3.2.

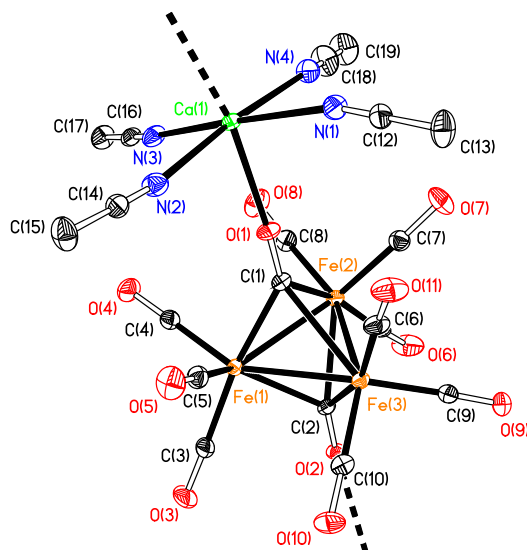


Figure 3.5. Displacement ellipsoid plot (20% probability) of the asymmetric unit of $[\text{Ca}\{\text{Fe}_3(\text{CO})_{11}\}(\text{MeCN})_4]_x$ (**21**). H atoms omitted for clarity. Ca(1) and O(2) connect to O(2B) and Ca(1A) in the neighbouring asymmetric units by the symmetry operators $-x+3/2, y+1/2, 3/2-z$ and $-x+3/2, y-1/2, 3/2-z$ respectively.

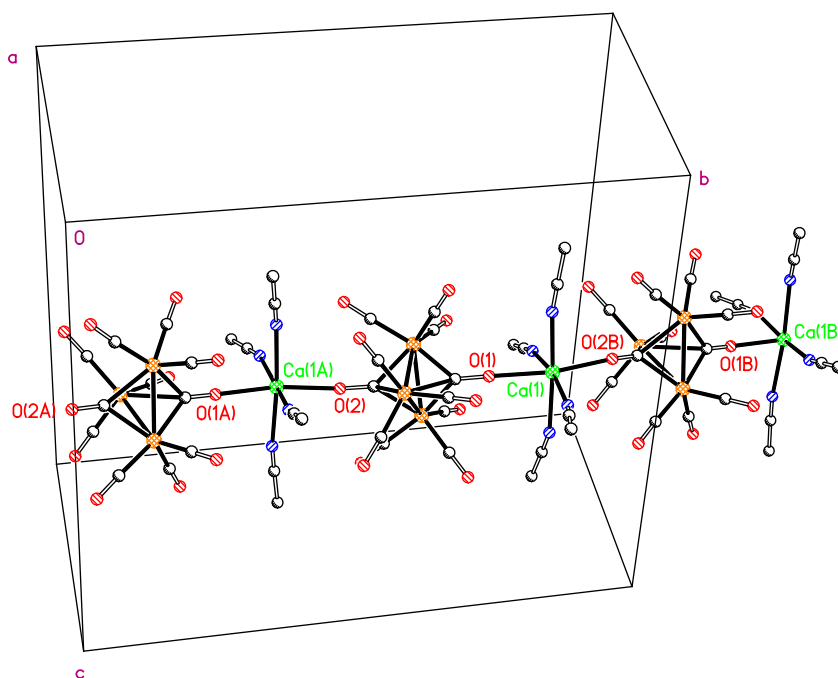


Figure 3.6. Ball and stick plot (arbitrary radius) of a portion of the $[\text{Ca}\{\text{Fe}_3(\text{CO})_{11}\}(\text{MeCN})_4]_x$ (**21**) extended chain structure. H atoms omitted for clarity. Symmetry related atoms correspond to their counterparts by the operators “A” = $-x+3/2, y-1/2, 3/2-z$; “B” = $-x+3/2, y+1/2, 3/2-z$.

Table 3.2. Selected distances (Å) and angles (°) for [Ca{Fe₃(CO)₁₁}(MeCN)₄]_x (**21**).

Ca(1)···Fe(1)	5.0230(5)	Ca(1)···Fe(2)	4.9491(5)
Ca(1)···Fe(3)	5.4492(5)	Ca(1)···Fe(1B)	5.0608(5)
Ca(1)···Fe(2B)	5.2952(5)	Ca(1)···Fe(3B)	4.6993(5)
Ca(1)-O(1)	2.2520(15)	Ca(1)-O(2B)	2.2514(14)
Ca(1)-N(1)	2.462(2)	Ca(1)-N(2)	2.454(2)
Ca(1)-N(3)	2.484(2)	Ca(1)-N(4)	2.456(2)
Fe(1)-Fe(2)	2.5927(4)	Fe(1)-Fe(3)	2.5654(4)
Fe(2)-Fe(3)	2.5666(4)	Fe(1)-C(1)	1.944(2)
Fe(1)-C(2)	2.081(2)	Fe(1)-C(3)	1.803(2)
Fe(1)-C(4)	1.775(2)	Fe(1)-C(5)	1.782(2)
Fe(2)-C(1)	2.081(2)	Fe(2)-C(2)	2.165(2)
Fe(3)-C(1)	1.803(2)	Fe(3)-C(2)	1.876(2)
C(1)-O(1)	1.221(3)	C(2)-O(2)	1.236(2)
C(3)-O(3)	1.144(3)	C(4)-O(4)	1.153(3)
C(5)-O(5)	1.149(3)		
Ca(1)-O(1)-C(1)	165.24(15)	Ca(1)-O(2B)-C(O2B)	153.62(14)
O(1)-Ca(1)-O(2B)	167.33(6)	O(1)-Ca(1)-N(1)	94.56(6)
N(1)-Ca(1)-N(2)	87.10(7)	N(1)-Ca(1)-N(4)	90.08(7)
N(2)-Ca(1)-N(3)	102.00(8)	N(3)-Ca(1)-N(4)	80.48(7)
Fe(1)-Fe(2)-Fe(3)	59.632(11)	Fe(1)-Fe(3)-Fe(2)	60.689(11)
Fe(1)-C(1)-Fe(2)	84.15(8)	Fe(1)-C(1)-Fe(3)	71.30(6)
Fe(1)-C(2)-Fe(2)	75.23(6)	Fe(1)-C(2)-Fe(3)	80.65(8)
Fe(1)-C(1)-O(1)	135.99(17)	Fe(1)-C(2)-O(2)	130.70(16)
Fe(1)-C(3)-O(3)	178.3(2)	Fe(1)-C(4)-O(4)	179.3(2)
Fe(1)-C(5)-O(5)	178.5(2)	Fe(2)-Fe(1)-Fe(3)	59.679(11)
Fe(2)-C(1)-Fe(3)	71.64(6)	Fe(2)-C(2)-Fe(3)	78.50(7)
Fe(2)-C(1)-O(1)	137.25(17)	Fe(2)-C(2)-O(2)	129.19(15)
Fe(3)-C(1)-O(1)	127.07(15)	Fe(3)-C(2)-O(2)	138.97(16)

Terminal C-O and Fe-C distances associated with Fe(2) and Fe(3) omitted. Average Fe-C terminal carbonyl distances: Fe(1) = 1.787(1), Fe(2) = 1.785(1), Fe(3) = 1.786(1) Å. Average terminal carbonyl C-O distances: Fe(1) = 1.149(2), Fe(2) = 1.150(2), Fe(3) = 1.152(2) Å. Average terminal Fe-C-O angles: Fe(1) = 178.7(1), Fe(2) = 177.2(1), Fe(3) = 176.9(1) Å.

In **21** the geometry at Ca(1) is approximately octahedral with four MeCN ligands coordinated in the equatorial plane and two $\text{Fe}_3(\text{CO})_{11}$ units *trans*-axially coordinated *via* isocarbonyl linkages. Each $\text{Fe}_3(\text{CO})_{11}$ unit is linked to another Ca centre and so forth to give an infinite chain. The Ca $\cdots$ Fe distances far exceed the sum of the respective covalent radii (3.08(10) Å). For example Ca(1) $\cdots$ Fe(1) = 5.0230(5) Å.

The C-O distances for the isocarbonyl bridged C(1)O(1) and C(2)O(2) groups of 1.211(3) and 1.236(3) Å, respectively, are longer than the average C-O distances for the terminal carbonyl groups (Fe(1) = 1.149(2), Fe(2) = 1.150(2), Fe(3) = 1.152(2) Å). The average Fe-C(1) (1.943(1) Å) and Fe-C(2) (2.041(1) Å) distances are also longer than the average Fe-C distances for the terminal carbonyl groups (Fe(1) = 1.787(1), Fe(2) = 1.785(1), Fe(3) = 1.786(1) Å). This is consistent with the μ_3 -coordination of the former compared to the μ_1 -coordination of the latter. As expected, the average Fe-C(1)-O(1) and Fe-C(2)-O(2) angles of 133.4(1) and 133.0(1) °, respectively, are shorter than the near-linear angles associated with the terminal carbonyl groups (Fe(1) = 178.7(1), Fe(2) = 177.2(1), Fe(3) = 176.9(1) °).

The Ca(1)-O distances in **21** (Ca(1)-O(1) = 2.252(2), Ca(1)-O(2B) = 2.251(2) Å) are shorter than those in **20** (Ca(1)-O(1) = 2.301(3), Ca(1)-O(9) = 2.324(3) Å) as are the average Ca(1)-N distances of 2.464(1) and 2.502(2) Å, respectively. This reflects the higher coordination number at Ca(1) in **20** than in **21**. There is a slight increase in the average Fe-C and decrease in the C-O distances associated with the terminal carbonyl groups in **21** compared to **20**. For example the average Fe(1)-C terminal carbonyl distance is 1.765(3) in **20** compared to 1.787(1) Å for **21**. The average Fe(1)C-O terminal carbonyl distance is 1.173(3) in **20** compared to 1.149(2) Å for **21**. This is consistent with the greater delocalisation of the 2- charge over the $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ anion than the $[\text{Fe}_2(\text{CO})_8]^{2-}$ anion. A formal oxidation state of $-2/3$ can be assigned to each Fe centre in **21** compared to -I in **20**. A lengthening of the Fe-Fe distances is observed in **20** compared to those in **21**. For example the Fe(1)-Fe(2) distance in **20** is 2.5520(8) compared to 2.5927(4) Å in **21**.

Considering the isocarbonyl linkages to Ca(1), the average C-O distance is little changed in **21** (1.229(2) Å) compared to **20** (1.213(4) Å). The average Fe-C distances associated with these bridging carbonyl groups are more differed at 1.990(1) and 1.933(2) Å for **21** and **20**, respectively. This is consistent with a change from μ_2 - to μ_3 -bridging carbonyls.

The Fe₃ core is preserved in **21** with the loss of one CO ligand per Ca, consistent with a two-electron reduction. This contrasts with the analogous reduction using Ca/NH₃(L) to give **20** where one equivalent of Fe(CO)₄ was formally lost per [Fe₂(CO)₈]²⁻ anion formed. The O(1)-C(1)-C(2)-O(2) vector in the Fe₃(CO)₁₁ cluster is not linear and therefore D_{3h} symmetry is not observed. There are several reports of the structure of Fe₃(CO)₁₂,¹⁷⁻²¹ where disorder is frequently observed. Taking the most recent report, the average Fe-Fe distance of 2.640(1) is longer than the average Fe-Fe distance in **21** of 2.575(2) Å.

Only one other structurally authenticated example of an [M{Fe₃(CO)₁₁}L_y]_x complex exists where M = any metal and L = any ligand. Namely, [{Li(THF)[HNC(NMe₂)₂]}₂{Fe₃(CO)₁₁}]_x (**3.6**, Figure 3.7).²² This was synthesised by the reduction of tetramethylguanidine (HNC(NMe₂)₂) with lithium powder in THF, followed by reaction with Fe(CO)₅. Crystals of **3.6** were grown from a toluene solution. A portion of the infinite chain is illustrated in Figure 3.7. The average Fe-Fe distance in **3.6** (2.561(1) Å) is shorter than that in **21** (2.575(2) Å). The Li(1)-O(1) distance (1.909(4) Å) is shorter than the Ca(1)-O(1) and C(1)-O(2B) distances of 2.252(2) and 2.251(1) Å, respectively, as expected given the smaller covalent radius of Li (1.28(7) Å) compared to that for Ca (1.76(10) Å).³ The C(1)-O(1) distance (1.226(2) Å) in **3.6** is identical within error to the C(1)-O(1) (1.221(3) Å), and slightly longer than the C(2)-O(2) (1.236(2) Å), distance in **21**. The average Fe-C(1) distance in **3.6** is 1.905(2), shorter than the average Fe-C(1) and Fe-C(2) distances in **21** of 1.943(1) and 2.041(1) Å, respectively.

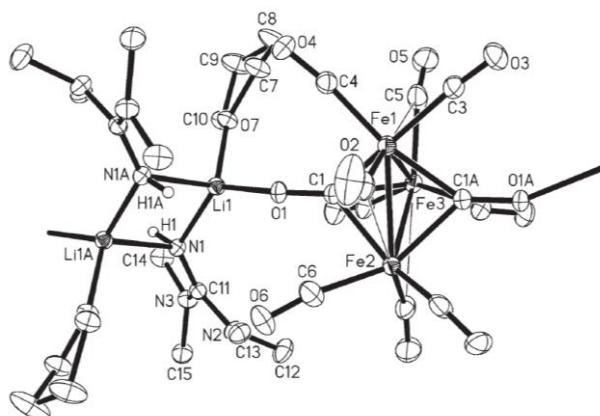
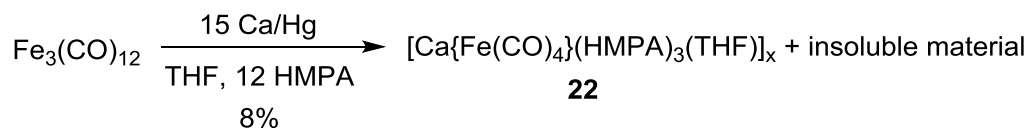


Figure 3.7 Displacement ellipsoid plot (20% probability) of a portion of the infinite chain of [Li(THF)[HNC(NMe₂)₂]₂{Fe₃(CO)₁₁}]_x (**3.6**). H atoms omitted for clarity.²²

Na and Yb mercury amalgams have been used successfully in the presence of MeCN.²³⁻²⁶ However, $\text{Fe}_3(\text{CO})_{12}$ is known to decompose in MeCN at a faster rate than in THF.²⁷ Indeed, addition of MeCN to $\text{Fe}_3(\text{CO})_{12}$ gave a rapid colour change from teal to red. Therefore it was necessary to carry out the reduction of $\text{Fe}_3(\text{CO})_{12}$ with Ca/Hg in THF, remove the volatiles and then dissolve the product in MeCN to afford **21**.

3.4.1 Reduction of $\text{Fe}_3(\text{CO})_{12}$ with Ca amalgam in the presence of HMPA

An analogous procedure was employed to that detailed for the synthesis of $[\text{Ca}\{\text{Fe}_3(\text{CO})_{11}\}(\text{MeCN})_4]_x$ (**21**), albeit with twelve equivalents of HMPA in THF present with an excess of Ca/Hg before the addition of $\text{Fe}_3(\text{CO})_{12}$. The mixture was stirred for 16 h at RT to give a brown suspension in a black solution. The mixture was decanted away from the amalgam and filtered to isolate the black solution. Volatiles were removed under reduced pressure to give a waxy green solid. Washing with pentane afforded **22** as a green solid in 8% yield (Equation 3.3). As for **20**, elemental analysis of the bulk material of **22** was inconsistent with the solid state structure. This may be a result of loss of the labile ligands or the sensitivity of the complex.



Equation 3.3

Diffraction-quality crystals of **22** were grown from a saturated THF solution. The molecular structure and selected distances and angles are shown in Figure 3.8 and Table 3.3. The geometry at the six-coordinate Ca(1) centre is approximately octahedral, with a *cis*-arrangement of isocarbonyl linkages to two $[\text{Fe}(\text{CO})_4]^{2-}$ units. These are accompanied by a THF ligand and three HMPA ligands. Each $[\text{Fe}(\text{CO})_4]^{2-}$ unit has a further isocarbonyl interaction with another Ca centre and so forth to give an infinite chain. The geometry at each Fe centre is approximately tetrahedral.

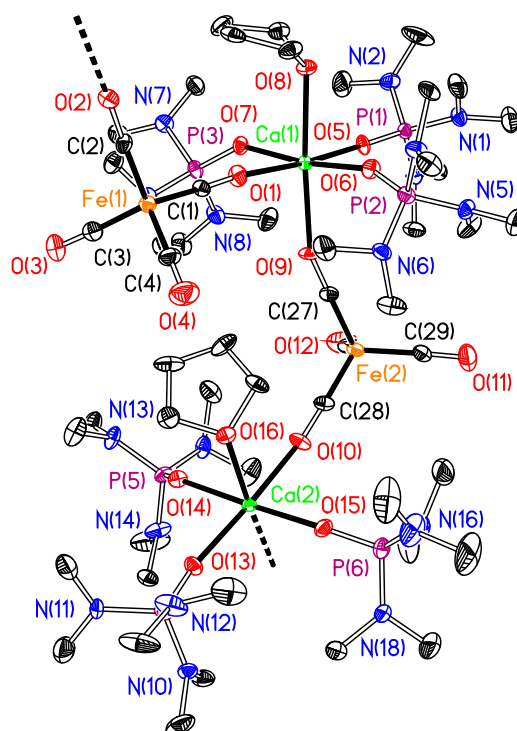


Figure 3.8. Displacement ellipsoid plot (20% probability) of the asymmetric unit of $[\text{Ca}\{\text{Fe}(\text{CO})_4\}(\text{HMPA})_3(\text{THF})]_x$ (**22**). H atoms omitted for clarity. Ca(2) and O(2) connect to O(2B) and Ca(2A) in the neighbouring asymmetric units by the symmetry operators $x, y-1, z$ and $x, y+1, z$ respectively.

Table 3.3. Selected distances (Å) and angles (°) for [Ca{Fe(CO)₄}(HMPA)₄(THF)]_x (**22**).

Ca(1)···Fe(1)	5.2782(15)	Ca(1)···Fe(2)	5.1468(15)
Ca(1)-O(1)	2.347(5)	Ca(1)-O(5)	2.274(4)
Ca(1)-O(6)	2.258(4)	Ca(1)-O(7)	2.297(4)
Ca(1)-O(8)	2.420(4)	Ca(1)-O(9)	2.318(4)
Ca(2B)-O(2)	2.303(5)	Fe(1)-C(1)	1.702(6)
Fe(1)-C(2)	1.715(7)	Fe(1)-C(3)	1.738(8)
Fe(1)-C(4)	1.740(8)	Fe(2)-C(27)	1.713(7)
Fe(2)-C(28)	1.704(7)	C(1)-O(1)	1.236(8)
C(2)-O(2)	1.234(8)	C(3)-O(3)	1.198(9)
C(4)-O(4)	1.186(9)	C(27)-O(9)	1.216(7)
C(28)-O(10)	1.217(8)	Ca(1)-O(1)-C(1)	174.1(4)
Ca(1)-O(9)-C(27)	157.9(5)	Ca(2B)-O(2)-C(2)	174.4(5)
Ca(2)-O(10)-C(28)	167.6(5)	O(1)-Ca(1)-O(5)	175.30(17)
O(1)-Ca(1)-O(9)	91.62(17)	O(6)-Ca(1)-O(7)	172.27(16)
O(6)-Ca(1)-O(9)	90.75(18)	O(7)-Ca(1)-O(8)	88.72(15)
O(8)-Ca(1)-O(9)	174.30(18)	C(1)-Fe(1)-C(2)	111.3(3)
C(1)-Fe(1)-C(3)	109.0(3)	C(1)-Fe(1)-C(4)	109.7(3)
C(2)-Fe(1)-C(3)	109.6(3)	C(2)-Fe(1)-C(4)	109.5(4)
C(3)-Fe(1)-C(4)	107.7(4)		

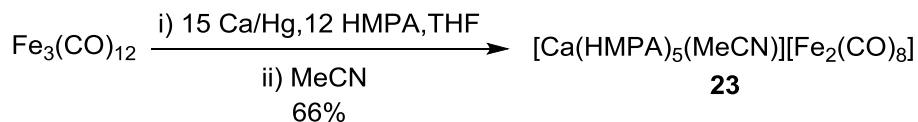
Whilst the parameters associated with Ca(1) and Ca(2), and Fe(1) and Fe(2), are not identical, they are not substantially different, therefore the focus shall be on those for Ca(1) and Fe(1). The Ca···Fe distances (Ca(1)···Fe(1) = 5.2782(15) Å) are considerably longer than the sum of the respective covalent radii (3.08(10) Å). The *trans*-influence of the HMPA ligand on the C(1)-O(1) (1.236(8) Å) and Fe(1)-C(1) (1.702(6) Å) distances is small given the similarities to the C(2)-O(2) (1.234(8) Å) and Fe(1)-C(2) (1.715(7) Å) distances for the carbonyl group *trans* to the THF ligand. These respective distances are identical within error. However, the Ca-O distances are different, where Ca(1)-O(1) = 2.347(5) and Ca(2B)-O(2) = 2.303(5) Å. Similar to that observed when comparing the distances associated with C(1)O(1) to those for

C(27)O(9). The Ca(1)-O-C angle associated with the isocarbonyl group C(1)O(1) ($174.1(4)^\circ$) is more linear than that for O(9)C(27) ($157.9(5)^\circ$). Although closer, the Ca(2B)-O(2)-C(2) angle ($174.4(5)^\circ$) remains greater than that for Ca(2)-O(10)-C(28) ($167.6(5)^\circ$). Therefore the isocarbonyl linkages to Fe(1) are more linear than those to Fe(2), contributing to the lack of symmetry between these components.

The solid state structure for **22** can be compared to Shore's [$\{(\text{MeCN})_3\text{YbFe}(\text{CO})_4\}_2 \cdot \text{MeCN}\}_x$ (**1.73**). Both possess an infinite chain composed of $[\text{Fe}(\text{CO})_4]^{2-}$ anions linked *via* isocarbonyl bridges to divalent cationic centres (Ca^{2+} or Yb^{2+}). However, in **1.73** additional Yb-Fe interactions occur between neighbouring chains to form a polymeric ladder. The analogous Ca-Fe interactions are not observed for **22** where the THF ligand can be considered as occupying the coordination site that would in theory be available for the analogous Ca-Fe interaction. The presence of sterically demanding HMPA ligands for **22**, which are absent for **1.73**, are also likely to inhibit these desired interactions between neighbouring chains.

As discussed in Chapter Two, the reaction of HMPA with $[\text{CaFp}_2(\text{THF})_3]_2$ (**3**) gave $\text{CaFp}_2(\text{HMPA})_4$ (**10**). In this process the Ca-Fe interactions between the Fp^- and Ca^{2+} ions were disrupted by the coordination of HMPA such that the dimeric complex was broken up to give monomers with isocarbonyl bridged interactions between the metal centres only. Due to data of insufficient quality associated with the molecular structure of **10** its bond lengths and angles cannot be compared with those in **22**. However, the fact that direct metal-metal interactivity was disrupted in the formation of **22** further demonstrates the inhibition of direct metal-metal interactions in these complexes as a consequence of strong Lewis base coordination.

As mentioned, a significant proportion of the material produced in the synthesis of **21** was insoluble in THF. To further investigate this, the insoluble brown solid was extracted into MeCN, filtered and volatiles were removed under reduced pressure to give a red solid. Washing with pentane afforded $[\text{Ca}(\text{HMPA})_5(\text{MeCN})][\text{Fe}_2(\text{CO})_8]$ (**23**) as a red solid in 66% yield (Equation 3.4). Elemental analysis of the bulk material was inconsistent with the solid state structure for **23**. This may be a consequence of the labile ligands or the sensitivity of the material.



Equation 3.4

Diffraction-quality crystals of **23** were grown from a saturated MeCN solution at RT. The structure and selected distances and angles are shown in Figure 3.9 and Table 3.4. In contrast to the polymeric structures observed for **20**, **21** and **22**, that for **23** is a separated ion pair consisting of a $[\text{Ca}(\text{HMPA})_5(\text{MeCN})]^{2+}$ cation and $[\text{Fe}_2(\text{CO})_8]^{2-}$ anion. There are two ion pairs per asymmetric unit. However, they are not substantially different, and therefore only one pair will be discussed.

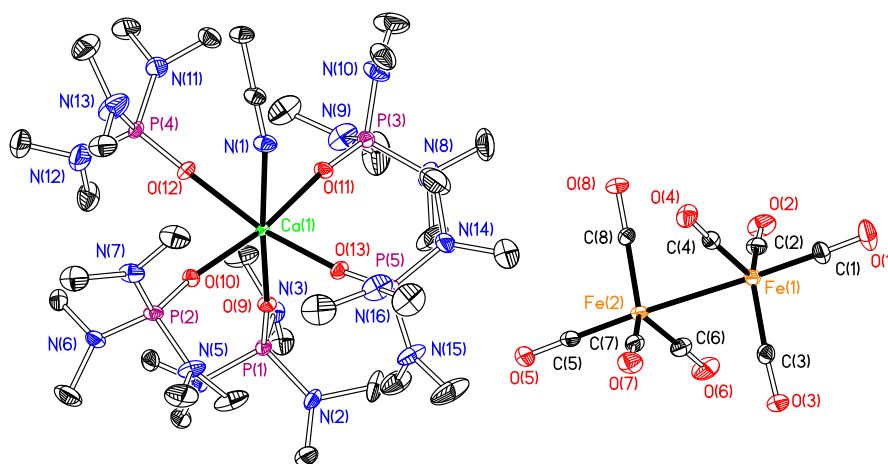


Figure 3.9. Displacement ellipsoid plot (20% probability) of $[\text{Ca}(\text{HMPA})_5(\text{MeCN})][\text{Fe}_2(\text{CO})_8]$ (**23**). H atoms and other ion pair omitted for clarity.

Table 3.4. Selected distances (Å) and angles (°) for [Ca(HMPA)₅(MeCN)][Fe₂(CO)₈] (**23**).

Ca(1)-N(1)	2.600(5)	Ca(1)-O(9)	2.322(4)
Ca(1)-O(10)	2.288(4)	Ca(1)-O(11)	2.274(4)
Ca(1)-O(12)	2.310(4)	Ca(1)-O(13)	2.319(4)
Fe(1)-Fe(2)	2.7951(13)	Fe(1)-C(1)	1.724(7)
Fe(1)-C(2)	1.789(7)	Fe(1)-C(3)	1.776(7)
Fe(1)-C(4)	1.782(7)	Fe(2)-C(5)	1.755(7)
Fe(2)-C(6)	1.773(7)	Fe(2)-C(7)	1.779(7)
Fe(2)-C(8)	1.764(6)	C(1)-O(1)	1.160(9)
C(2)-O(2)	1.151(8)	C(3)-O(3)	1.155(8)
C(4)-O(4)	1.163(8)	C(5)-O(5)	1.158(8)
C(6)-O(6)	1.167(9)	C(7)-O(7)	1.167(8)
C(8)-O(8)	1.169(7)	P(1)-O(9)	1.493(4)
P(2)-O(10)	1.477(4)	P(3)-O(11)	1.484(4)
P(4)-O(12)	1.469(4)	P(5)-O(13)	1.474(4)
N(1)-Ca(1)-O(9)	175.71(17)	N(1)-Ca(1)-O(10)	91.52(17)
O(10)-Ca(1)-O(11)	171.34(15)	O(10)-Ca(1)-O(13)	93.29(15)
O(11)-Ca(1)-O(12)	86.16(16)	O(12)-Ca(1)-O(13)	164.26(16)
Fe(1)-Fe(2)-C(5)	176.8(2)	Fe(2)-Fe(1)-C(1)	178.2(3)
C(1)-Fe(1)-C(2)	94.7(4)	C(1)-Fe(1)-C(3)	97.0(3)
C(1)-Fe(1)-C(4)	96.9(3)	C(2)-Fe(1)-C(3)	118.7(3)
C(2)-Fe(1)-C(4)	120.1(3)	C(3)-Fe(1)-C(4)	117.7(3)
C(5)-Fe(2)-C(6)	95.5(3)	C(5)-Fe(2)-C(7)	96.6(3)
C(5)-Fe(2)-C(8)	99.0(3)	C(6)-Fe(2)-C(7)	122.2(3)
C(6)-Fe(2)-C(8)	117.1(3)	C(7)-Fe(2)-C(8)	116.3(3)

In **23**, the [Ca(HMPA)₅(MeCN)]²⁺ cation contains an approximately octahedral Ca²⁺ centre, with one MeCN and five HMPA ligands. For the HMPA ligand (O(1)) located *trans* to the MeCN ligand, the Ca(1)-O(9) and P(1)-O(9) distances of 2.322(4) and 1.493(4) Å, respectively, are very similar to those associated with the HMPA ligands

arranged equatorially. Where the average equatorial Ca(1)-O distance is 2.298(1) and P-O distance is 1.476(1) Å.

The $[\text{Fe}_2(\text{CO})_8]^{2-}$ anion in **23** consists of two $\text{Fe}(\text{CO})_4$ units linked by a Fe-Fe bond ($\text{Fe}(1)\text{-Fe}(2) = 2.7951(13)$ Å). All four carbonyl groups per Fe are terminal, with three in the equatorial plane and one in the axial position *trans* to the Fe-Fe bond to give a trigonal bipyramidal geometry at Fe. The equatorial carbonyl groups bound to Fe(1) and Fe(2) have a *gauche* conformation. The *trans* carbonyl C(1)-Fe(1) and C(5)-Fe(2) distances are shorted relative to those in the equatorial positions. For example $\text{Fe}(1)\text{-C}(1) = 1.724(7)$ whereas the average Fe(1) equatorial carbonyl $\text{Fe}(1)\text{-C} = 1.782(4)$ Å. However, the C(1)-O(1) distance (1.160(9) Å) is identical within error to the average equatorial Fe(1)C-O distance (1.156(5) Å).

The $[\text{Fe}_2(\text{CO})_8]^{2-}$ anion in **23** contrasts with that in $[\text{Ca}\{\text{Fe}_2(\text{CO})_8\}(\text{MeCN})_5]_x$ (**20**), given the lack of isocarbonyl linkages to Ca or any bridging carbonyl groups between the Fe centres in **23**. This lack of isocarbonyl interaction is reminiscent of that observed for $[\text{Mg}(\text{HMPA})_4][\text{Fp}]_2$ (**7**). The presence of five HMPA ligands provides sufficient steric protection of the Ca centre such that interactivity through a μ_2 - or μ_3 -carbonyl interaction, as observed in **20** and **22**, respectively, is not achieved. Evidently, the strong Lewis basicity of HMPA is such that its displacement by $[\text{Fe}_2(\text{CO})_8]^{2-}$ is unachieved.²⁸⁻³²

The terminal carbonyl Fe-C and C-O distances in **23** are very similar to those in **20**. For example, the Fe(1)-C distances associated with Fe(1) in **23** (average $\text{Fe}(1)\text{-C} = 1.768(4)$ and $\text{Fe}(1)\text{C-O} = 1.157(4)$ Å) are actually identical within error to those in **20** (average terminal $\text{Fe}(1)\text{-C} = 1.765(3)$ and $\text{Fe}(1)\text{C-O} = 1.173(3)$ Å). However, the Fe(1)-Fe(2) distance in **23** (2.7951(13) Å) is significantly longer than that in **20** (2.5520(8) Å).

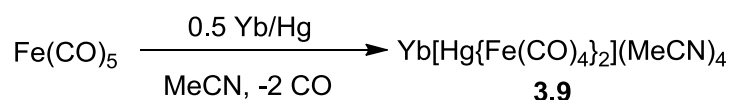
Structurally authenticated compounds containing the non-coordinated $[\text{Fe}_2(\text{CO})_8]^{2-}$ anion, that is without μ_2 -CO interactions, are known. Examples include $[\text{NEt}_4][\text{Fe}_2(\text{CO})_8]$ (**3.7**) and $[\text{K}(18\text{-crown-6})][\text{Fe}_2(\text{CO})_8]$ (**3.8**).^{33, 34} The average Fe-Fe (2.793(3) Å), Fe-C (1.76(1) Å) and C-O (1.16(1) Å) distances for non-coordinated $[\text{Fe}_2(\text{CO})_8]^{2-}$ anions in the literature are identical within error to the respective distances in **23**.¹⁰

Despite using a Ca/Hg reduction, as in the synthesis of **21**, the Fe₃ core in Fe₃(CO)₁₂ and maintained in **21** is not observed in **22** or **23**. Evidently the presence of an excess of HMPA has an influence on the reaction such that cleavage of Fe-Fe bonds is achieved. The yield for the synthesis of **23** (66%) is considerably greater than that for **22** (8%), therefore the “insoluble material” (Equation 3.3) produced in the synthesis of **22** actually represents the significantly greater proportion of the product mixture, which is converted to **23** upon extraction into MeCN.

Recall that **1.73** also contained the [Fe(CO)₄]²⁻ anion, with direct interactions between Yb and Fe. It is unsurprising that metal-metal bonding is not observed in **23** given the shielding of each Ca centre by the three sterically demanding Lewis basic HMPA ligands.²⁸⁻³²

3.5 Reduction of Fe(CO)₅

Shore *et al.* reported attempts to reduce Fe(CO)₅ with Yb/Hg. In ethers this gave an insoluble, intractable product. However, reduction in MeCN afforded Yb[Hg{(Fe(CO)₄)₂}(MeCN)₄] (**3.9**) as a yellow solid in 64% isolated yield (Equation 3.5).²³ Whilst analysis by single crystal X-ray diffraction was not reported for **3.9**, solution IR analysis was consistent with the maintenance of an association between the Yb²⁺ and [Hg{Fe(CO)₄}]²⁻ ions, likely through isocarbonyl bridging.



Equation 3.5²³

Given these observations, attempts were made to reduce Fe(CO)₅ with Ca/Hg in MeCN. As with Shore's Yb/Hg reduction, gas evolution was observed. However, a red-brown precipitate was formed that did not dissolve with continued stirring of the reaction mixture over 16 h. Given this insolubility in MeCN the reaction was not further investigated.

3.6 Solid state and solution IR studies

The complexes [Ca{Fe₂(CO)₈}(MeCN)₅]_x (**20**), [Ca{Fe₃(CO)₁₁}(MeCN)₄]_x (**21**), [Ca{Fe(CO)₄}(HMPA)₄(THF)]_x (**22**) and [Ca(HMPA)₅(MeCN)][Fe₂(CO)₈] (**23**) were analysed by IR spectroscopy, their ν(CO) bands are summarised in Table 3.5. It is important to recall that elemental analysis measurements of the bulk material for **20**,

22 and **23** were inconsistent with their respective solid state structures. This provides a caveat to the interpretation of these data. Reassuringly, the IR $\nu(\text{CO})$ bands reported for $\text{K}[\text{HFe}(\text{CO})_4]$ (**3.10**, 2017, 1928 and 1835 cm^{-1}) in Nujol do not correspond to those summarised in Table 3.5.³⁵

Table 3.5. IR $\nu(\text{CO})$, cm^{-1} for $[\text{Ca}\{\text{Fe}_2(\text{CO})_8\}(\text{MeCN})_5]_x$ (**20**), $[\text{Ca}\{\text{Fe}_3(\text{CO})_{11}\}(\text{MeCN})_4]_x$ (**21**), $[\text{Ca}\{\text{Fe}(\text{CO})_4\}(\text{HMPA})_3(\text{THF})]_x$ (**22**) and $[\text{Ca}(\text{HMPA})_5(\text{MeCN})][\text{Fe}_2(\text{CO})_8]$ (**23**) in Nujol.

Complex	$\nu(\text{CO})$ (cm^{-1}) in Nujol
20	2003 (sh), 1945 (s, br), 1881 (s, br)
21	2000 (sh), 1933 (s, br), 1879 (s, br)
22	1877 (s, br), 1745 (s), 1686 (s)
23	1905 (s, br), 1851 (s, br), 1801 (s, br) 1764 (s, br)

The IR spectrum of **20** in Nujol shows $\nu(\text{CO})$ bands at 2003, 1945 and 1881 cm^{-1} , similar to that for $\text{Li}_2\{\text{Fe}_2(\text{CO})_8\}(\text{THF})_6$ (**3.2**, 1991, 1937, 1885 and 1855 cm^{-1}).¹⁶ Elemental analysis of **21** was consistent with the composition of the solid state structure. The IR spectrum of **21** in Nujol contains broad bands in the $\nu(\text{CO})$ region at 2000, 1933 and 1879 cm^{-1} . The IR spectrum for $[\{\text{Li}(\text{THF})[\text{HNC}(\text{NMe}_2)_2]\}_2\{\text{Fe}_3(\text{CO})_{11}\}]_x$ (**3.6**) in Nujol,²² also containing the $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ anion, was reported to contain an unresolved strong broad band at 1921, amongst other strong bands including one at 1557 cm^{-1} assigned to the $\mu_3\text{-CO}$ group, absent at this position for **21**.

The IR spectrum of **22** in Nujol contains three $\nu(\text{CO})$ bands at 1877, 1745 and 1686 cm^{-1} . The IR spectrum of **22** in THF was also recorded, exhibiting one $\nu(\text{CO})$ band at 1875 cm^{-1} . This would suggest that the polymeric structure dissociates in THF solution to give non-coordinated $[\text{Fe}(\text{CO})_4]^{2-}$ anions and $[\text{Ca}(\text{HMPA})_x(\text{THF})_{6-x}]^{2+}$ cations. Shore's polymeric **1.73** ($\nu(\text{CO})$: 1890, 1781 and 1720 cm^{-1}) and **1.75** ($\nu(\text{CO})$: 1890, 1794 and 1715 cm^{-1}) also contain $[\text{Fe}(\text{CO})_4]^{2-}$ units.² Their IR spectra (Nujol) both contain three $\nu(\text{CO})$ bands, consistent with C_{3v} symmetry at the $[\text{Fe}(\text{CO})_4]^{2-}$ units resulting from an axial Yb-Fe interaction to give an approximately trigonal bipyramidal coordination geometry. As commented by Shore *et al.*, a single band

would be expected for a tetrahedral coordination geometry, as is observed for **22** in THF.

The IR spectrum of **23** in Nujol exhibits a series of overlapping bands from 2000 to 1600 with identifiable maxima at 1905, 1851, 1801 and 1764 cm^{-1} . Three of these maxima are similarly positioned to those in the IR $\nu(\text{CO})$ region of $[\text{PPN}]_2[\text{Fe}_2(\text{CO})_8]$ in Nujol, with bands at 1908, 1844 and 1831 cm^{-1} ($\text{PPN} = [\text{Ph}_3\text{PNPPH}_3]^+$).¹⁵

3.7 $^{13}\text{C}\{^1\text{H}\}$ NMR studies

The $^{13}\text{C}\{^1\text{H}\}$ $\delta(\text{CO})$ NMR data for **20-23** are summarised in Table 3.6. Compound **20** exhibits a single CO environment at 230.1 ppm, consistent with a lack of interaction between the $[\text{Fe}_2(\text{CO})_8]^{2-}$ anion and $[\text{Ca}(\text{MeCN})_x(\text{THF})_{6-x}]^{2+}$ cation in THF and CO scrambling within the $[\text{Fe}_2(\text{CO})_8]^{2-}$ anion on the NMR time-scale. Single $^{13}\text{C}\{^1\text{H}\}$ CO environments are also observed for $[\text{MeP}(\text{NMe}_2)_3]_2[\text{Fe}_2(\text{CO})_8]$ (**3.11**, 225.8 ppm, CD_3CN),³⁶ $\text{Li}_2\{\text{Fe}_2(\text{CO})_8\}(\text{THF})_6$ (**3.2**, 244 ppm, $\text{THF}-d_8$),¹⁶ and $[\text{PPN}]_2[\text{Fe}_2(\text{CO})_8]$ (**3.12**, 230.7 ppm, CD_2Cl_2).¹⁵

Three environments (236.4, 225.6, 225.4 ppm) are observed for **23**, contrasting with the single environments observed for each of the aforementioned complexes containing the $[\text{Fe}_2(\text{CO})_8]^{2-}$ anion. This could be the result of a maintained association between the $[\text{Fe}_2(\text{CO})_8]^{2-}$ anion and $[\text{Ca}(\text{HMPA})_x(\text{MeCN})_{6-x}]^{2+}$ cation in solution. However, this is unlikely given the solid state structure is that of a separated ion pair. The presence of other species in the bulk material provides a more plausible explanation for these multiple environments and lack of elemental analysis consistent with the solid state structure.

For **22** a single CO environment is observed at 250.2 ppm, consistent with the single $\nu(\text{CO})$ band recorded in THF solution and therefore its dissociation to give $[\text{Fe}(\text{CO})_4]^{2-}$ and $[\text{Ca}(\text{HMPA})_x(\text{THF})_{6-x}]^{2+}$ ions in solution.

As evidenced by the single environments for **20** and **22**, it is likely that **21** also dissociates in MeCN to afford free $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ anions and $[\text{Ca}(\text{MeCN})_6]^{2+}$ cations. Compound **21** exhibits singlets at 232.8 and 225.3 ppm, consistent with two CO environments in the $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ anion.

Table 3.6. $^{13}\text{C}\{^1\text{H}\}$ NMR $\delta(\text{CO})$ (ppm) data for **20**, **21**, **22**, and **23**.

Complex	$\delta(\text{CO})$ (ppm)
$[\text{Ca}\{\text{Fe}_2(\text{CO})_8\}(\text{MeCN})_5]_x$ (20)	230.1
$[\text{Ca}\{\text{Fe}_3(\text{CO})_{11}\}(\text{MeCN})_4]_x$ (21)	232.8, 225.3
$[\text{Ca}\{\text{Fe}(\text{CO})_4\}(\text{HMPA})_4(\text{THF})]_x$ (22)	250.2
$[\text{Ca}(\text{HMPA})_5(\text{MeCN})][\text{Fe}_2(\text{CO})_8]$ (23)	236.4, 225.6, 225.4

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz) data recorded in CD_3CN with the exception of **22** ($\text{THF}-d_8$).

3.8 Conclusions

This Chapter has demonstrated the synthesis of four new complexes by the reduction of $\text{Fe}_3(\text{CO})_{12}$ with activated Ca. This research was stimulated by Shore's $[(\text{MeCN})_3\text{YbFe}(\text{CO})_4]_2 \cdot \text{MeCN}]_x$ (**1.73**) and $[(\text{MeCN})_3\text{YbFe}(\text{CO})_4]_x$ (**1.75**) with direct Yb-Fe interactions. The analogous reduction of $\text{Fe}_3(\text{CO})_{12}$ with $\text{Ca}/\text{NH}_3(\text{L})$ did not afford a complex with direct Ca-Fe interactions but instead isocarbonyl bridged $[\text{Ca}\{\text{Fe}_2(\text{CO})_8\}(\text{MeCN})_5]_x$ (**20**), thus demonstrating the different reactivities of $\text{Yb}/\text{NH}_3(\text{L})$ and $\text{Ca}/\text{NH}_3(\text{L})$ with regard to the reduction of $\text{Fe}_3(\text{CO})_{12}$. Using Ca/Hg rather than $\text{Ca}/\text{NH}_3(\text{L})$ also failed to give a solid state structure with Ca-Fe bonding but instead $[\text{Ca}\{\text{Fe}_3(\text{CO})_{11}\}(\text{MeCN})_4]_x$ (**21**), with isocarbonyl interactions between the Ca and Fe centres. This demonstrates the different and perhaps milder reactivity of Ca/Hg vs. $\text{Ca}/\text{NH}_3(\text{L})$. In an attempt to improve the solubility of the reaction mixture in THF, HMPA was added. This resulted in the formation of a minor product, $[\text{Ca}\{\text{Fe}(\text{CO})_4\}(\text{HMPA})_4(\text{THF})]_x$ (**22**) with an insoluble material that was isolated and extracted into MeCN to afford $[\text{Ca}(\text{HMPA})_5(\text{MeCN})][\text{Fe}_2(\text{CO})_8]$ (**23**). Compound **22** contains $[\text{Fe}(\text{CO})_4]^{2-}$ rather than $[\text{Fe}_2(\text{CO})_8]^{2-}$ units (**20** and **23**), as featured in Shore's **1.73** and **1.75**. Again the Fe centres are linked to Ca *via* isocarbonyl bridging, rather than bonded directly. Unlike **20-22**, **23** contained separated ion pairs in the solid state. This series of complexes demonstrates the ability to readily modify the reactivity of elemental Ca as a reductant towards $\text{Fe}_3(\text{CO})_{12}$, resulting in the preservation (**21**) or cleavage of two (**20**) or all three (**21** and **23**) Fe-Fe bonds. This also shows that reductions with elemental Ca and Yb do not necessarily afford analogous complexes, contrasting with their reduction of Fp_2 in Chapter Two. To date, despite $[\text{Fe}(\text{CO})_4]^{2-}$ being referred to as a “supernucleophile”,³⁷ Shore's **1.73** and **1.75** represent the only

structurally authenticated examples with a direct bond between the Fe centre of the $[\text{Fe}(\text{CO})_4]^{2-}$ anion and a lanthanide,¹⁰ although many examples are known with direct bonds to main group metals.³⁸⁻⁴³ As expected, use of metal carbonyl anions that are considered less nucleophilic such as $[\text{Co}(\text{CO})_4]^-$ and $[\text{Mn}(\text{CO})_5]^-$ are yet to give any structurally authenticated complexes with TM-Ln bonds.^{23, 44, 45}

3.9 References

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Chapter Four

**Synthesis and study of Ae-Co and Ln-Co
complexes containing the $[\text{Co}(\text{CO})_3(\text{PR}_3)]^-$ anion**

4.1 Overview

This Chapter describes the reduction of $[\text{Co}(\text{CO})_3(\text{PR}_3)]_2$ ($\text{R} = \text{PPh}_3$ or PCy_3) with Ae (Mg, Ca, Sr, Ba) and Ln (Sm, Eu, Yb) metal amalgams to afford heterobimetallic complexes containing the $[\text{Co}(\text{CO})_3(\text{PR}_3)]^-$ anion. Use of the $[\text{Co}(\text{CO})_3(\text{PCy}_3)]^-$ anion allowed heterobimetallic complexes soluble in non-donor solvents to be obtained. Alternative routes to these complexes *via* reaction of $\text{K}[\text{Co}(\text{CO})_3(\text{PCy}_3)]$ with AeI_2 and LnI_2 were also investigated. New interactions between these metals and cobalt are structurally authenticated by single crystal X-ray diffraction and further supported by IR and diffusion (DOSY) NMR spectroscopy performed in collaboration with Dr Timothy Claridge of the University of Oxford's NMR service. Selected examples have also been studied computationally in collaboration with Prof. Nikolas Kaltsoyannis of University College London.

4.2 Introduction

The $[\text{Co}(\text{CO})_3(\text{L})]^-$ anion, where L is commonly CO or a phosphine, such as PPh_3 , has been studied regarding its interaction with cationic species. Brammer *et al.* have investigated its potential to act as a hydrogen-bond acceptor with cations such as $[(\text{DABCO})\text{H}]^+$ (DABCO = 1,4-diazabicyclooctane).¹ The $\text{Co}\cdots\text{N}$ distance was found to be considerably shortened in $[(\text{DABCO})\text{H}][\text{Co}(\text{CO})_3(\text{PPh}_3)]$ (**4.1**, 3.437(3) Å) relative to $[(\text{DABCO})\text{H}][\text{Co}(\text{CO})_4]$ (**4.2**, 3.294(6) Å). They also observed a change in the geometry at the Co centre, where the sum of the $\text{Ph}_3\text{P-Co-CO}$ angles ($\Sigma(\text{P-Co-CO})$) is 307.0(3) and the analogous sum of the $\text{OC}_{\text{ax}}\text{-Co-CO}$ angles ($\Sigma(\text{CO}_{\text{ax}}\text{-Co-CO})$) are 323.2(3) and 319.0(2) ° (two crystallographically independent molecules in the asymmetric unit). The use of other phosphines such as PTol_3 ($\text{Co}\cdots\text{N} = 3.372(2)$ Å, $\Sigma(\text{P-Co-CO}) = 314.3(1)$ °) also led to a perturbation of these values.²

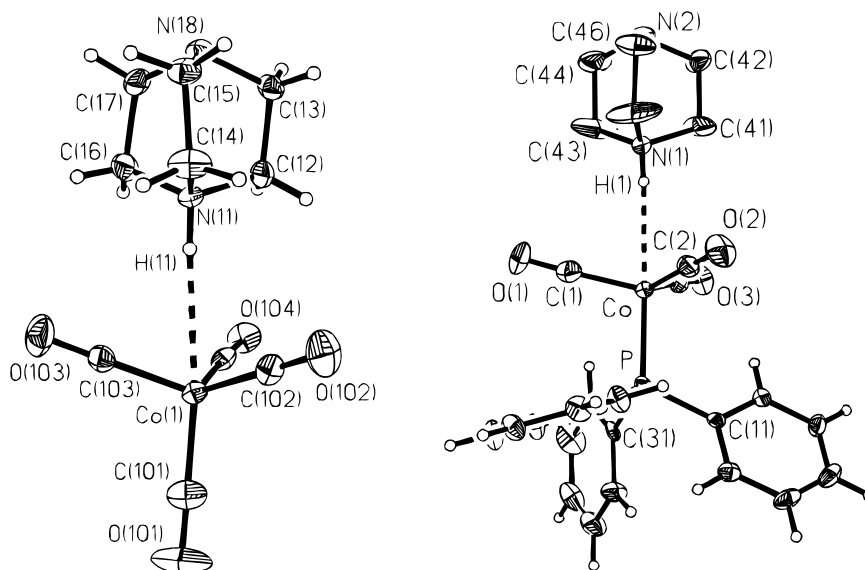


Figure 4.1. Displacement ellipsoid plots (50% probability) of $[(\text{DABCO})\text{H}][\text{Co}(\text{CO})_4]$ (**4.2**, left) and $[(\text{DABCO})\text{H}][\text{Co}(\text{CO})_3\text{PPh}_3]$ (**4.1**, right).^{1, 2}

As evidenced by the work of Brammer, interaction of the $[\text{Co}(\text{CO})_3(\text{L})]^-$ anion with a cationic acceptor has the potential to cause a significant alteration of the geometry at the Co centre. The sum of the $\text{R}_3\text{P}-\text{Co}-\text{CO}$ angles, $\Sigma(\text{P}-\text{Co}-\text{CO})$ (or $\Sigma(\text{C}_{\text{ax}}-\text{Co}-\text{CO})$ when $\text{L} = \text{CO}$) represents one way of measuring this (Figure 4.2). A greater strength of interaction is likely to cause a decrease in this value from that of the tetrahedral free anion towards that of a trigonal bipyramidal geometry.

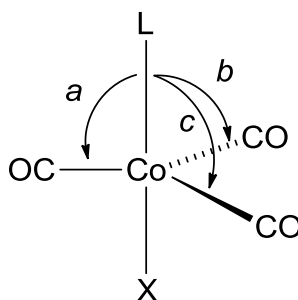


Figure 4.2. Perturbation of the sum of the $\text{L}-\text{Co}-\text{CO}$ angles (a , b and c) $\Sigma(\text{P}-\text{Co}-\text{CO})$ due to interaction with a cationic centre (X). $\text{L} = \text{CO}$ or a phosphine such as PPh_3 .

Importantly, use of the $[\text{Co}(\text{CO})_3(\text{L})]^-$ anion has enabled the synthesis of new species with direct bonds between Co and other transition metals (M). Akita *et al.* have achieved this for $\text{M} = \text{Mn}$, Fe and Ni through use of substituted Tp^{R} (tris(pyrazolyl)hydroborate) supporting ligands ($\text{R} = {}^i\text{Pr}_2$ and $\text{Me}_2,4\text{-Br}$), *via* reaction of $\text{K}[\text{Co}(\text{CO})_4]$ with $[\text{Tp}^{{}^i\text{Pr}_2}\text{M}][\text{PF}_6]$ or $\text{Tp}^{\text{Me}_2,4\text{-Br}}\text{MBr}$. For the case where $\text{R} = {}^i\text{Pr}_2$ and

M = Ni, substitution of the $[\text{Co}(\text{CO})_3(\text{PPh}_3)]^-$ anion for the $[\text{Co}(\text{CO})_4]^-$ anion to give $\text{Ni}(\text{Tp}^{\text{iPr}_2})\{\text{Co}(\text{CO})_3(\text{L})\}$, where L = PPh_3 (**4.4**) in place of CO (**4.5**), gave a shortening of the Co-Ni bond from 2.4640(8) to 2.4138(9) Å. The geometry at the Co centre was also altered such that the sum of the P-Co-CO angles (297.9(4) °) was reduced relative to the analogous sum of the C_{ax} -Co-CO angles (305.7(4) °).^{3, 4}

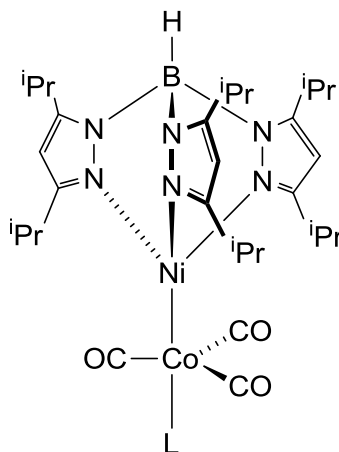


Figure 4.3. $\text{Ni}(\text{Tp}^{\text{iPr}_2})\{\text{Co}(\text{CO})_3(\text{L})\}$ where L = PPh_3 (**4.4**), CO (**4.5**) or PTol_3 .^{3, 4}

Gade *et al.* have studied unsupported Ti- and Zr-Co bonds in the heterobimetallic complexes $\text{M}\{\text{CH}_3\text{Si}(\text{SiMe}_2\text{NAr})_3\}_3\text{Co}(\text{CO})_3(\text{L})$ (M = Ti or Zr, L = CO, PPh_3 or PTol_3 and Ar = 4- $\text{CH}_3\text{C}_6\text{H}_4$; Figure 4.4). Synthesis of these complexes was achieved by reaction of the bromotitanium and chlorozirconium complexes with $\text{Na}[\text{Co}(\text{CO})_3(\text{L})]$. Where M = Ti, replacement of the axial CO (**4.6**) with PTol_3 (**4.7**) resulted in a shortening of the Ti-Co bond from 2.5542(10) to 2.471(4) Å and a decrease in the sum of the P-Co-CO angles relative to the analogous C_{ax} -Co-CO angles ($\Sigma(\text{P-Co-CO}) = 285.0(7)$ and $\Sigma(\text{CO}_{\text{ax}}\text{-Co-CO}) = 293.4(5)$ °). Similarly where M = Zr, substitution of PPh_3 (**4.8**) for CO (**4.9**) gave a shortening from 2.7051(11) to 2.6175(14) Å and $\Sigma(\text{P-Co-CO}) = 287.1(3)$ compared to $\Sigma(\text{CO}_{\text{ax}}\text{-Co-CO}) = 297.9(6)$ °. Computational analysis supported the conclusion that the geometrical constraints imposed by the tripodal ligand provides a significant contribution to the thermodynamic stability of these complexes.⁵

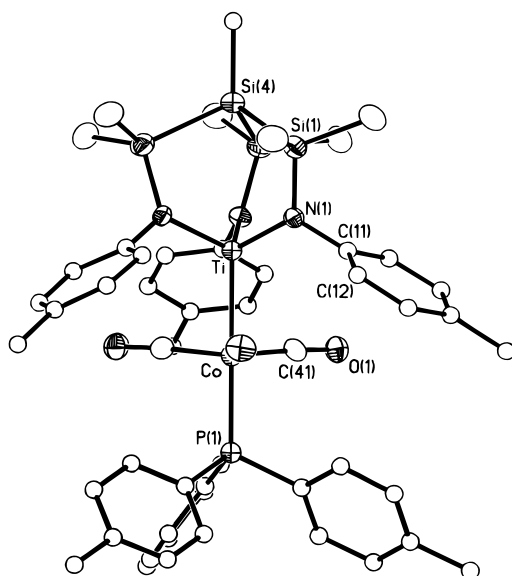


Figure 4.4. Displacement ellipsoid plot (30% probability) of $\text{Ti}\{\text{CH}_3\text{Si}(\text{SiMe}_2\text{NAr})_3\}_3\text{Co}(\text{CO})_3(\text{PTol})$ (**4.7**).⁵

As mentioned in Chapter One, Liddle *et al.* have utilised the $[\text{Co}(\text{CO})_3(\text{PPh}_3)]^-$ anion to afford the first structurally authenticated molecular U-Co bond in $\text{U}(\text{Ts}^{\text{Xy}})\text{Co}(\text{CO})_3(\text{PPh}_3)$ (**1.121**, Figure 4.5).⁶ This was synthesised by reaction of the inverse-sandwich diuranium complex $[\{\text{U}(\text{Ts}^{\text{Xy}})\}_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_6\text{H}_5\text{Me})]$ (**1.122**) with $[\text{Co}(\text{CO})_3(\text{PPh}_3)]_2$ (**1.123**), where $\text{Ts}^{\text{Xy}} = \text{HC}\{\text{SiMe}_2\text{N}(3,5\text{-Me}_2\text{C}_6\text{H}_3)\}_3$. The U-Co distance (2.9450(9) Å) is shorter than the sum of the respective covalent radii (3.22(4) Å).⁷ The sum of the P-Co-CO angles is 297.0(2) °. Attempts to synthesise **1.121** directly *via* the salt-metathesis reaction between $\text{U}(\text{Ts}^{\text{Xy}})\text{Cl}$ (**1.124**) and $\text{Na}[\text{Co}(\text{CO})_3(\text{PPh}_3)]$ (**1.125**) were unsuccessful.

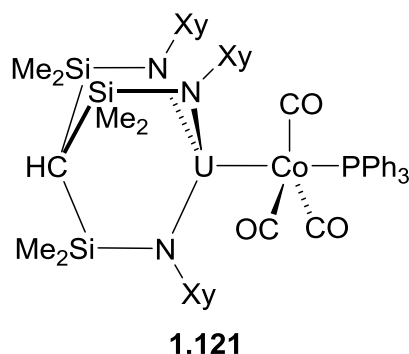


Figure 4.5. $\text{U}(\text{Ts}^{\text{Xy}})\text{Co}(\text{CO})_3(\text{PPh}_3)$ (**1.121**), where $\text{Ts}^{\text{Xy}} = \text{HC}\{\text{SiMe}_2\text{N}(3,5\text{-Me}_2\text{C}_6\text{H}_3)\}_3$.⁶

Structurally authenticated bonds between Co and main group metals (Ga,⁸ In,^{8,9} Tl,¹⁰

¹¹ Ge, ¹² Sn, ^{13, 14} Pb, ¹⁵ Sb, ^{16, 17} Bi¹⁸) have also been achieved using the $[\text{Co}(\text{CO})_3(\text{L})]^-$ anion. For example, Lotz *et al.* synthesised $(\text{Me}_3\text{Sn})\text{Co}(\text{CO})_3(\text{PPh}_3)$ (**4.10**) by Na/Hg reductive cleavage of **1.123** and subsequent reaction with Me_3SnCl . The Co-Sn distance (2.574(2) Å) is shorter than the sum of the respective covalent radii (2.65(3) Å).⁷ The sum of the P-Co-CO angles is 284.5 °.¹⁴ Reaction of Bi_2Ph_4 with $[\text{Co}(\text{CO})_4]_2$ gave $(\text{Ph}_2\text{Bi})\text{Co}(\text{CO})_4$ (**4.11**) which was isolated as the triphenylphosphine adduct $(\text{Ph}_2\text{Bi})\text{Co}(\text{CO})_3(\text{PPh}_3)$ (**4.12**). Analysis by single crystal X-ray diffraction showed this to have a Bi-Co distance of 2.692(5) Å and sum of P-Co-C angles of 286(2) °.¹⁸ $\text{In}\{\text{Co}(\text{CO})_4\}_3$ (**4.13**) was synthesised by Robinson and Schussler by reaction of $\text{Hg}\{\text{Co}(\text{CO})_4\}_2$ (**4.14**) in toluene with an excess of In/Hg. The In-Co distances (2.590(3)-2.597(3) Å) are consistent with the sum of the respective covalent radii (2.68(6) Å).⁷ The sums of the $\text{CO}_{\text{ax}}\text{-Co-CO}$ angles are 293(2), 289(2) and 289(2) °.⁹

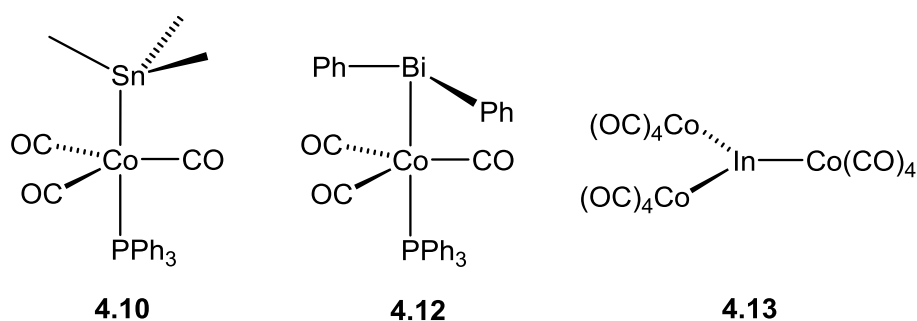


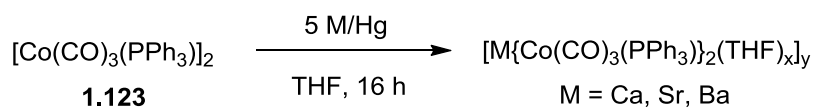
Figure 4.6. Complexes with cobalt-main group metal bonds.^{9, 14, 18}

4.3 Interaction of the $[\text{Co}(\text{CO})_3(\text{PPh}_3)]^-$ anion with Ae^{2+} cations

This Section will focus on the reduction of $[\text{Co}(\text{CO})_3(\text{PPh}_3)]_2$ (**1.123**) with Mg, Ca, Sr and Ba mercury amalgams in an attempt to afford new species with direct Ae-Co interactions. Attempts to reduce **1.123** in THF with an excess of Mg/Hg produced a green solid that was insoluble in THF and could not be isolated from the amalgam. Given the formation of isocarbonyl bridged, as opposed to metal-metal bonded, complexes that arose from the use of HMPA in Chapter Two, attempts to form a soluble adduct with a stronger Lewis base were not performed.

Following reduction of **1.123** in THF with Ca, Sr, and Ba amalgams (Equation 4.1), adequate solubility of the corresponding heterobimetallic products in THF was achieved allowing isolation and subsequent analysis. These complexes were found to be insoluble in non-donor solvents; consequently all crystals suitable for analysis by

single crystal X-ray diffraction were grown from THF. Elemental analysis supports these structures as being representative of the composition of the bulk material unless stated otherwise.



Equation 4.1

Reduction of **1.123** in THF with an excess of Ca/Hg at RT gave the heterobimetallic species $\text{Ca}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_4$ (**24**) as a pale green solid in 71% isolated yield. Diffraction-quality crystals of **24** were grown from a concentrated THF solution at RT. The molecular structure and selected distances and angles are shown in Figure 4.7 and Table 4.1.

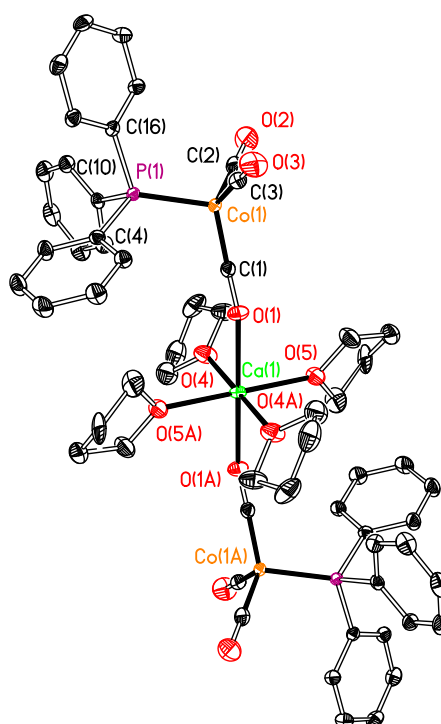


Figure 4.7. Displacement ellipsoid plot (20% probability) of $\text{Ca}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_4$ (**24**). H atoms omitted for clarity. Atoms carrying the suffix “A” are related to their counterparts by the operator $-x, 1-y, 1-z$.

Table 4.1. Selected distances (Å) and angles (°) for $\text{Ca}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_4$ (**24**).

Ca(1)···Co(1)	5.1375(2)	Ca(1)-O(1)	2.3161(12)
Ca(1)-O(4)	2.3262(13)	Ca(1)-O(5)	2.3309(13)
Ca(1)-O(5)	2.3309(13)	Co(1)-P(1)	2.1702(4)
Co(1)-C(1)	1.7125(16)	Co(1)-C(2)	1.7513(19)
Co(1)-C(3)	1.7542(19)	C(1)-O(1)	1.189(2)
C(2)-O(2)	1.164(2)	C(3)-O(3)	1.162(2)
O(1)-Ca(1)-O(1A)	179.99(5)	O(1)-Ca(1)-O(4)	86.82(5)
O(4)-Ca(1)-O(5)	88.95(5)	O(4)-Ca(1)-O(5A)	91.05(5)
O(4A)-Ca(1)-O(5)	91.05(5)	O(4A)-Ca(1)-O(5A)	88.95(5)
P(1)-Co(1)-C(1)	109.72(6)	P(1)-Co(1)-C(2)	105.15(6)
P(1)-Co(1)-C(3)	102.32(6)	C(1)-Co(1)-C(2)	117.55(9)
C(2)-Co(1)-C(3)	109.56(9)	C(3)-Co(1)-C(1)	111.27(8)

Compound **24** has a monomeric structure, where the geometry at the six-coordinate Ca(1) centre is approximately octahedral with four THF ligands in the equatorial plane and *trans*-axial Ca(μ -OC)Co isocarbonyl linkages. No direct Ca-Co interactions are observed, the Ca(1)···Co(1) separation is 5.1375(2) Å, considerably greater than the sum of the respective covalent radii (3.02(10) Å).⁷ The geometry at Co(1) is approximately tetrahedral and the sum of OC–Co(1)–P(1) angles is 317.2(1) °.

The Ca(μ -OC)Co isocarbonyl interaction is observed to cause an increase in the C(1)-O(1) distance (1.189(2) Å) relative to that for C(2)-O(2) (1.164(2) Å) and C(3)-O(3) (1.162(2) Å). Concomitantly the Co(1)-C(1) distance (1.7125(16) Å) is decreased relative to that for Co(1)-C(2) (1.7513(19) Å) and Co(1)-C(3) (1.7542(19) Å). This is analogous to that observed for the perturbation of Fe-C and C-O carbonyl distances associated with the Fp^- anion in Chapter Two. The Ca(μ -OC)Co Ca(1)-O(1) distance of 2.3161(12) Å is slightly shorter than the average Ca-O(THF) distance in **24** (2.3285(18) Å). This compares with the average literature Ca-O(THF) value of 2.39(4) Å (range: 2.30-2.55 Å).¹⁹ Compound **24** contains the first structurally authenticated example of a Ca(μ -OC)Co isocarbonyl interaction.¹⁹

Reduction of **1.123** in THF with an excess of Sr/Hg afforded $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_5]_2$ (**25**) as a yellow solid in 78% isolated yield. As with **24**, diffraction-quality crystals of **25** were grown from a concentrated THF solution at RT. The molecular structure and selected distances and angles are shown in Figure 4.8 and Table 4.2.

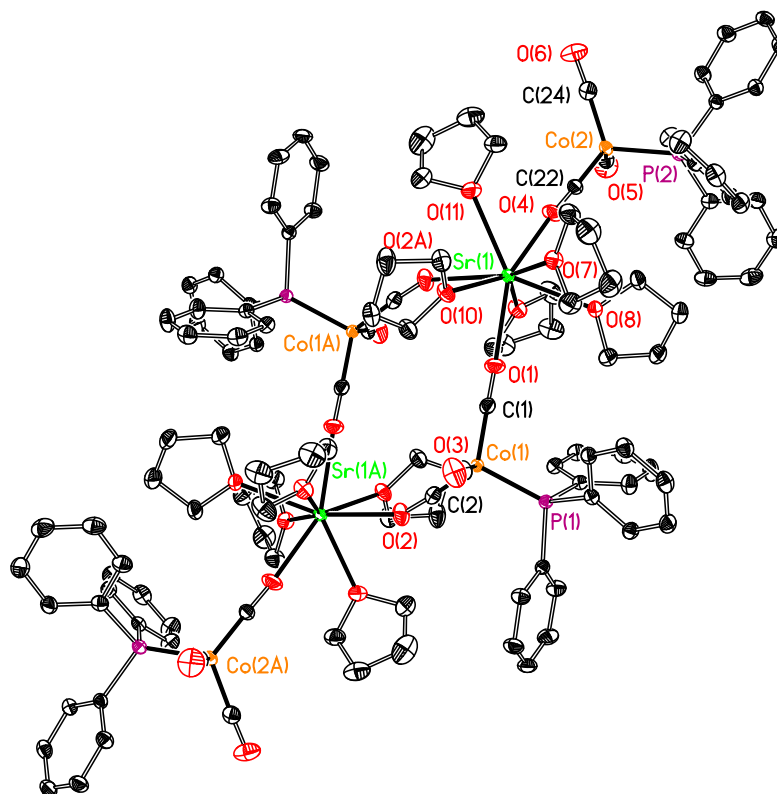


Figure 4.8. Displacement ellipsoid plot (20% probability) of $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_5]_2$ (**25**). H atoms, THF of crystallisation and minor disorder omitted for clarity. Atoms carrying the suffix “A” are related to their counterparts by the operator 2-*x*, 1-*y*, 2-*z*.

Table 4.2. Selected distances (Å) and angles (°) for [Sr{Co(CO)₃(PPh₃)₂(THF)₅]₂ (**25**).

Sr(1)···Co(1)	5.4104(3)	Sr(1)···Co(1A)	5.2967(3)
Sr(1)···Co(2)	5.4276(3)	Sr(1)-O(1)	2.5486(11)
Sr(1)-O(2A)	2.5724(10)	Sr(1)-O(4)	2.5280(10)
Sr(1)-O(7)	2.5928(10)	Sr(1)-O(8)	2.6048(10)
Sr(1)-O(9)	2.6375(10)	Sr(1)-O(10)	2.6401(10)
Sr(1)-O(11)	2.6422(12)	Co(1)-P(1)	2.1707(4)
Co(1)-C(1)	1.7281(14)	Co(1)-C(2)	1.7274(15)
Co(1)-C(3)	1.7510(14)	Co(2)-P(2)	2.1687(4)
Co(2)-C(22)	1.7197(14)	Co(2)-C(23)	1.7572(15)
Co(2)-C(24)	1.7475(16)	C(1)-O(1)	1.1773(18)
C(2)-O(2)	1.1732(18)	C(3)-O(3)	1.1614(19)
C(22)-O(4)	1.1828(19)	C(23)-O(5)	1.158(2)
C(24)-O(6)	1.1635(19)		
O(1)-Sr(1)-O(4)	143.93(4)	O(1)-Sr(1)-O(2A)	81.46(4)
O(1)-Sr(1)-O(7)	99.17(4)	O(2A)-Sr(1)-O(4)	107.00(4)
O(7)-Sr(1)-O(8)	70.90(3)	O(7)-Sr(1)-O(11)	80.64(4)
O(8)-Sr(1)-O(9)	73.94(3)	O(9)-Sr(1)-O(10)	133.89(3)
O(10)-Sr(1)-O(11)	74.37(4)	P(1)-Co(1)-C(1)	105.20(5)
P(1)-Co(1)-C(2)	109.60(5)	P(1)-Co(1)-C(3)	105.91(5)
P(2)-Co(2)-C(22)	107.30(5)	P(2)-Co(2)-C(23)	103.61(5)
P(2)-Co(2)-C(24)	109.25(5)	C(1)-Co(1)-C(2)	117.04(7)
C(1)-Co(1)-C(3)	110.87(7)	C(2)-Co(1)-C(3)	107.68(7)
C(22)-Co(2)-C(23)	116.12(7)	C(22)-Co(2)-C(24)	111.46(7)
C(23)-Co(2)-C(24)	108.66(7)		
^a Hinge angle	163		

^a Hinge angle = (Co(1), C(1), O(1), Co(1A), C(1A), O(1A))-(Co(1A), C(2A), O(2A), Sr(1), O(1)). Maximum deviation from plane = 0.11 Å (Sr(1)).

The geometry at each eight-coordinate Sr centre in **25** is approximately square antiprismatic, with five coordinated THFs and three Sr(μ-OC)Co isocarbonyl

linkages. Two of these linkages (Sr(1)···Co(1) and Sr(1)···Co(2)) form part of the monomeric unit while the third linkage (Sr(1)···Co(1A)) bridges the monomeric units. The structure has a twelve-membered ring motif in a chair conformation comprising four Sr(μ -OC)Co isocarbonyl linkages. Consequently, two distinct Co environments exist where Co(1) has two carbonyl groups (C(1) and C(2)) involved in isocarbonyl bridging and one terminal carbonyl group (C(3)). Co(2) has one carbonyl group interacting in an isocarbonyl fashion (C(22)) and two terminal carbonyl groups (C(23) and C(24)). The latter environment is reminiscent of that observed for monomeric **24**. The Sr···Co distances (Sr(1)···Co(1) = 5.4104(3), Sr(1)···Co(1A) = 5.2967(3) and Sr(1)···Co(2) = 5.4276(3) Å) are considerably greater than the sum of the respective covalent radii (3.21(10) Å).⁷ The shift from a monomeric to dimeric molecular structure reflects the greater covalent radius of Sr (1.95(10) Å) compared to Ca (1.76(10) Å).⁷ Consistent with the lack of direct Sr-Co interaction, the geometry at Co(1) and Co(2) is approximately tetrahedral where the sum of the OC–Co(1)–P(1) and OC–Co(2)–P(2) angles are 320.7(1) and 320.6(1) °, respectively.

As with **24**, the carbonyl groups bound to Co(1) involved in Sr(μ -OC)Co isocarbonyl bridging (C(1)–O(1) = 1.1773(18) and C(2)–O(2) = 1.732(18) Å) exhibit an increased C–O distance relative to that for terminal carbonyl C(3)O(3) (1.1614(19) Å). Additionally the Co(1)–C distances are shortened for Co(1)–C(1) (1.7281(14) Å) and Co(2)–C(2) (1.7274(15) Å) relative to that for Co(1)–C(3) (1.7510(14) Å). Considering the carbonyl groups bound to Co(2), the bridging carbonyl group C(22)O(4) has an increased C(22)–O(4) (1.1828(19) Å) distance relative to that for C(23)–O(5) (1.158(2) Å) or C(24)–O(6) (1.1635(19) Å). As expected, the Co(2)–C(22) (1.7197(14) Å) distance is shorter than that for Co(2)–C(23) (1.7572(15) Å) or Co(2)–C(24) (1.7475(16) Å). Reflective of the increase in covalent radius, the average Sr–O(THF) and Sr–O(isocarbonyl) distances of 2.624(1) and 2.550(1) are longer than the analogous distances for **24** of 2.329(1) and 2.316(1) Å, respectively. No structurally authenticated examples of Sr(μ -OC)TM interactions have been reported. The average Sr–O(THF) distance in **25** is comparable with that reported in the literature (2.56(4) (range: 2.47–2.71) Å).¹⁹

The atoms Co(1), C(1), O(1), Co(1A), C(1A) and O(1A) are co-planar and as such can be used to define a plane in the twelve-membered ring. Note that none of these atoms deviate from this plane by more than 0.01 Å (C(1)). The atoms Co(1A), C(2A),

O(2A), Sr(1) and O(1) can be used to define another plane, where the maximum deviation from this plane is 0.11 Å (Sr(1)). The hinge angle between these planes is 163 °. This is analogous to the hinge angle used in Chapter Two to analyse the geometry of the eight- and twelve-membered rings such as those for [MgFp₂(THF)]₂ (**1**) and [Ca(NacNac)Fp(THF)₂]₂ (**15**).

Reduction of **1.123** in THF with an excess of Ba/Hg afforded [Ba{Co(CO)₃(PPh₃)₂}(THF)₆]₂ (**26**) as a green solid in 89% isolated yield. Diffraction-quality crystals were grown from a concentrated THF solution at RT. Selected distances and angles are shown in Figure 4.9 and Table 4.3.

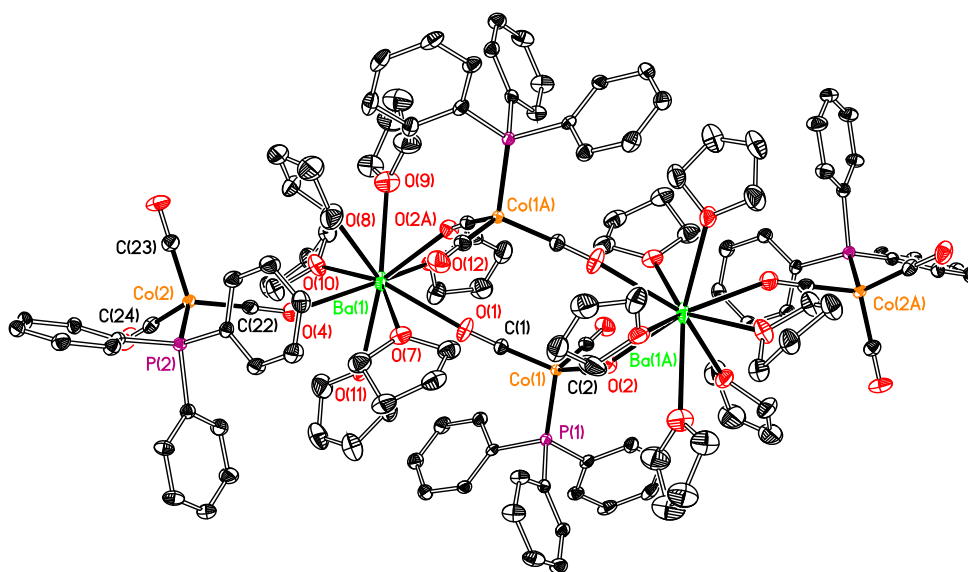


Figure 4.9. Displacement ellipsoid plot (20% probability) of [Ba{Co(CO)₃(PPh₃)₂}(THF)₆]₂ (**26**). H atoms and minor disorder omitted for clarity. Atoms carrying the suffix “A” are related to their counterparts by the operator -x, 1-y, 3-z.

Table 4.2. Selected distances (Å) and angles (°) for [Ba{Co(CO)₃(PPh₃)₂(THF)₆]₂ (**26**).

Ba(1)···Co(1)	5.6897(7)	Ba(1)···Co(1A)	5.3884(7)
Ba(1)···Co(2)	5.5569(8)	Ba(1)-O(1)	2.809(4)
Ba(1)-O(2A)	2.785(4)	Ba(1)-O(4)	2.793(4)
Ba(1)-O(7)	2.833(4)	Ba(1)-O(8)	2.702(4)
Ba(1)-O(9)	3.009(6)	Ba(1)-O(10)	2.728(5)
Ba(1)-O(11)	2.785(4)	Ba(1)-O(12)	2.764(5)
Co(1)-P(1)	2.1698(13)	Co(1)-C(1)	1.735(5)
Co(1)-C(2)	1.735(5)	Co(1)-C(3)	1.760(5)
Co(2)-P(2)	2.1659(13)	Co(2)-C(22)	1.724(5)
Co(2)-C(23)	1.747(5)	Co(2)-C(24)	1.748(5)
C(1)-O(1)	1.156(6)	C(2)-O(2)	1.163(6)
C(3)-O(3)	1.155(7)	C(22)-O(4)	1.171(6)
C(23)-O(5)	1.164(7)	C(24)-O(6)	1.155(7)
O(1)-Ba-(1)-O(2A)	74.90(14)	O(1)-Ba(1)-O(4)	129.75(15)
O(1)-Ba-(1)-O(7)	70.05(14)	O(2A)-Ba-(1)-O(4)	127.43(14)
O(7)-Ba-(1)-O(8)	92.07(14)	O(7)-Ba-(1)-O(12)	133.07(13)
O(8)-Ba-(1)-O(9)	60.59(16)	O(9)-Ba-(1)-O(10)	71.58(15)
O(10)-Ba-(1)-O(11)	79.73(14)	O(11)-Ba-(1)-O(12)	93.46(16)
P(1)-Co(1)-C(1)	107.15(18)	P(1)-Co(1)-C(2)	111.10(16)
P(1)-Co(1)-C(3)	105.05(18)	P(2)-Co(2)-C(22)	104.65(17)
P(2)-Co(2)-C(23)	104.39(17)	P(2)-Co(2)-C(24)	108.78(19)
C(1)-Co(1)-C(2)	108.3(2)	C(1)-Co(1)-C(3)	112.9(2)
C(2)-Co(1)-C(3)	112.2(2)	C(22)-Co(2)-C(23)	114.9(2)
C(22)-Co(2)-C(24)	112.4(2)	C(23)-Co(2)-C(24)	111.1(2)
^a Hinge angle	142		

^a Hinge angle = (Co(1), C(1), O(1), Co(1A), C(1A), O(1A))-(Co(1A), C(2A), O(2A), Ba(1), O(1)). Maximum deviation from plane = 0.03 Å (O(2A)).

The geometry at each nine-coordinate Ba centre in **26** is face-capped square antiprismatic. Analogous to **25**, there are three Ba(μ-OC)Co isocarbonyl linkages to

each Ba centre resulting in a dimeric molecular structure with a twelve-membered ring in a chair conformation. The hinge angle of 142° is smaller than that for **25** (163°). Consistent with a further increase in covalent radius (Sr = 1.95(10) and Ba = 2.15(11) Å),⁷ **26** has six coordinated THF ligands to Ba compared with five to Sr in **25**. As with **25**, there are three independent Ba...Co distances (Ba(1)...Co(1) = 5.6897(7), Ba(1)...Co(1A) = 5.3884(7) and Ba(1)...Co(2) = 5.5569(8) Å), all of which are greater than the sum of the respective covalent radii (3.41(11) Å).⁷ Similar to **25**, the Ba(1)...Co(1A) distance is shorter than the Co(1)...Ba(1) and Co(1)...Ba(2) distances of the monomeric unit. The geometry at Co(1) and Co(2) is approximately tetrahedral. The sum of the OC–Co(1)–P(1) and OC–Co(2)–P(2) angles are $323.3(3)$ and $317.8(3)^\circ$, respectively.

The three carbonyl groups bound to Co(1) have C–O distances (C(1)–O(1) = 1.156(6), C(2)–O(2) = 1.163(6) and C(3)–O(3) = 1.155(7) Å) that are identical within error. However, the Co(1)–C(3) (1.760(5) Å) distance for the terminal carbonyl group is longer than that for Co(1)–C(1) (1.735(5) Å) and Co(1)–C(2) (1.735(5) Å) involved in isocarbonyl bridging. For Co(2), the C–O distances (C(22)–O(4) = 1.171(6), C(23)–O(5) = 1.164(7) and C(24)–O(6) = 1.155(7) Å) are also identical within error. However, as observed with Co(1), the Co(2)–C(22) (1.724(5) Å) distance is shorter than that for Co(2)–C(23) (1.747(5) Å) or Co(2)–C(24) (1.748(5) Å). Analogous to that discussed when comparing **24** to **25**, the increase in covalent radius from Sr to Ba results in a further increase in the average Ae–O(THF) and Ae–O(isocarbonyl) distances to 2.804(2) and 2.796(2) Å, respectively. No structurally authenticated examples of Ba(μ -OC)TM interactions have been reported. The average Ba–O(THF) distance in **26** is comparable with that reported in the literature (2.77(5) (range: 2.67–2.94 Å)).¹⁹

4.4 Interaction of the [Co(CO)₃(PPh₃)][–] anion with Ln²⁺ cations

The reduction of **1.123** with an excess of Sm/Hg gave [Sm{Co(CO)₃(PPh₃)}₂(THF)₅]_x (**27**) as a purple-grey solid. Diffraction-quality crystals of **27** were grown from a concentrated THF solution at RT. A section of the polymeric structure is shown in Figure 4.10 and the asymmetric unit in 4.11 with selected distances and angles in Table 4.4.

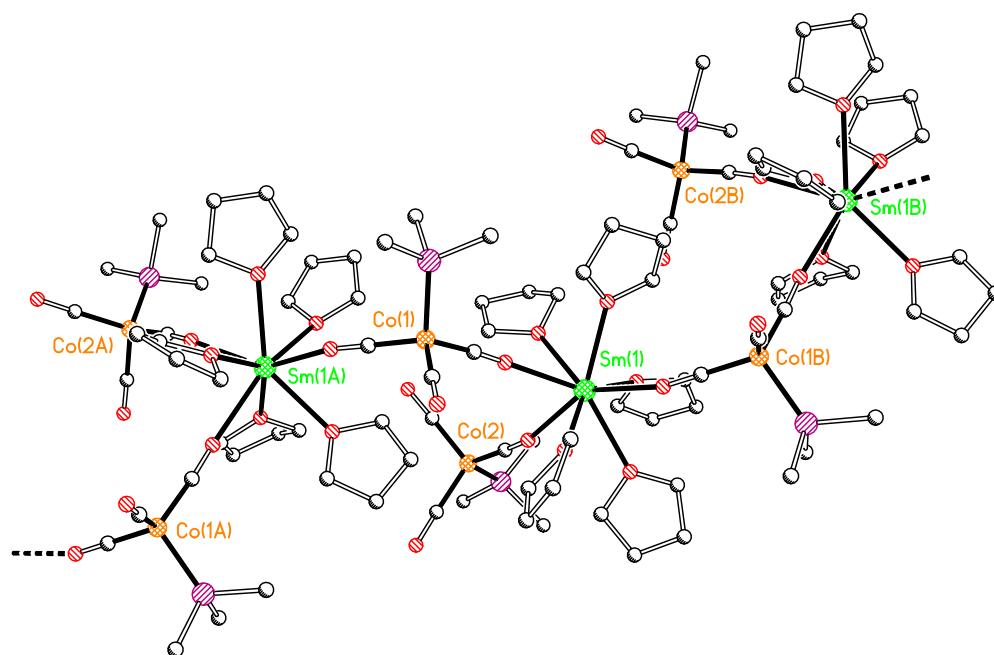


Figure 4.10. Ball and stick plot (arbitrary radius) of a Section of the $[\text{Sm}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_5]_x$ (**27**) infinite chain. H atoms and methine carbons omitted for clarity. Symmetry related atoms are related to their counterparts by the operators “A” = $x, -y+5/2, z-1/2$; “B” = $x, -y+5/2, z+1/2$

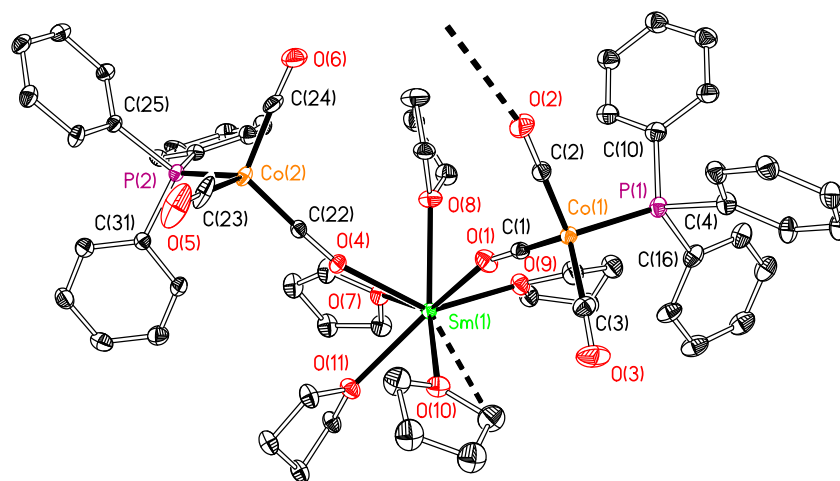


Figure 4.11. Displacement ellipsoid plot (25% probability) of the asymmetric unit of $[\text{Sm}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_5]_x$ (**27**). H atoms omitted for clarity.

Table 4.4. Selected distances (Å) and angles (°) for [Sm{Co(CO)₃(PPh₃)₂(THF)₅]_x (**27**).

Sm(1)···Co(1)	5.5128(13)	Sm(1)···Co(1A)	5.5098(16)
Sm(1)···Co(2)	5.4952(15)	Sm(1)-O(1)	2.624(3)
Sm(1)-O(2A)	2.654(3)	Sm(1)-O(4)	2.618(3)
Sm(1)-O(7)	2.669(3)	Sm(1)-O(8)	2.701(3)
Sm(1)-O(9)	2.598(3)	Sm(1)-O(10)	2.722(3)
Sm(1)-O(11)	2.639(3)	Co(1)-P(1)	2.1819(12)
Co(1)-C(1)	1.748(4)	Co(1)-C(2)	1.734(4)
Co(1)-C(3)	1.810(5)	Co(2)-P(2)	2.2324(12)
Co(2)-C(22)	1.755(4)	Co(2)-C(23)	1.747(5)
Co(2)-C(24)	1.772(5)	C(1)-O(1)	1.195(5)
C(2)-O(2)	1.182(5)	C(3)-O(3)	1.193(6)
C(22)-O(4)	1.210(5)	C(23)-O(5)	1.171(7)
C(24)-O(6)	1.152(6)		
O(1)-Sm(1)-O(2A)	111.71(13)	O(1)-Sm(1)-O(4)	84.84(11)
O(1)-Sm(1)-O(7)	145.56(11)	O(2A)-Sm(1)-O(4)	148.90(11)
O(7)-Sm(1)-O(8)	72.81(10)	O(7)-Sm(1)-O(10)	144.05(11)
O(8)-Sm(1)-O(9)	70.66(10)	O(9)-Sm(1)-O(10)	116.92(11)
P(1)-Co(1)-C(1)	110.15(13)	P(1)-Co(1)-C(2)	105.34(14)
P(1)-Co(1)-C(3)	104.51(16)	P(2)-Co(2)-C(22)	116.24(13)
P(2)-Co(2)-C(24)	105.16(15)	C(1)-Co(1)-C(2)	111.11(19)
C(1)-Co(1)-C(3)	111.13(19)	C(2)-Co(1)-C(3)	114.2(2)
C(22)-Co(2)-C(23)	109.4(2)	C(22)-Co(2)-C(24)	112.07(19)
C(23)-Co(2)-C(24)	110.5(3)		

The geometry at each eight-coordinate Sm centre in **27** is approximately square antiprismatic, coordinated to five THFs and three Sm(μ-OC)Co isocarbonyl linkages to form a polymeric chain. This contrasts with the dimeric structures observed for **25** and **26**. This occurs despite the covalent radius of Sm (1.98(8) Å) being intermediate between that of Sr (1.95(10) Å) and Ba (2.15(11) Å).⁷ Indeed, Sm and Sr have similar covalent radii and are ligated by five THFs in both **25** and **27**. Along with the other

complexes synthesised in this Chapter, this highlights the fine balance that exists in determining whether a monomeric, dimeric or polymeric structure is formed under analogous conditions. Despite this, for **27** the average Sm-O(THF) and Sm-O(isocarbonyl) distances of 2.666(1) and 2.632(2) Å, respectively, are intermediate of the analogous values for **25** (Sr-O(THF) = 2.624(1) and Sr-O(isocarbonyl) = 2.550(1) Å) and **26** (Ba-O(THF) = 2.804(2) and Ba-O(isocarbonyl) = 2.796(2) Å). This compares with the average literature Sm-O(THF) distance of 2.51(7) (range: 2.34–2.69) Å.¹⁹ No structurally authenticated Sm(μ -OC)Co isocarbonyl interactions have been reported, although interactions are known with Fe and Mo.^{20–24} As with **25** and **26**, two different Co environments are present in **27**, where Co(1) provides two isocarbonyl linkages, between Sm(1) and Sm(1A) centres to achieve a polymeric chain whilst Co(2) interacts *via* a single isocarbonyl linkage with Sm(1) only. The Sm $\cdots$ Co distances (Sm(1) $\cdots$ Co(1) = 5.5128(13) Å, Sm(1) $\cdots$ Co(1A) = 5.5098(16) Å and Sm(1) $\cdots$ Co(2) = 5.4952(15) Å) are greater than the sum of the respective covalent radii (3.24(9) Å).⁷ As with **25** and **26**, the Sm(1) $\cdots$ Co(1A) distance, the distance between monomeric units, is shorter than the Sm(1) $\cdots$ Co(1) and Sm(1) $\cdots$ Co(2) distances. The geometry at Co(1) and Co(2) is approximately tetrahedral. The sum of the OC–Co(1)–P(1) and OC–Co(2)–P(2) angles are 320.0(2) and 324.5(3) °, respectively.

For Co(1), there is little difference in the C–O distances of the Sm(μ -OC)Co isocarbonyl linkages relative to the distances associated with terminal C(3)O(3) (C(1)–O(1) = 1.195(5), C(2)–O(2) = 1.182(5) and C(3)–O(3) = 1.193(6) Å). However, there is a greater difference associated with the Co(1)–C distances (Co(1)–C(1) = 1.748(4), Co(1)–C(2) = 1.734(4) and Co(1)–C(3) = 1.810(5) Å). For Co(2) there is a greater difference in C–O distances (C(22)–O(4) = 1.210(5), C(23)–O(5) = 1.171(7) and C(24)–O(6) = 1.152(6) Å) but little correlation with the Co(2)–C distances (Co(2)–C(22) = 1.755(4), Co(2)–C(23) = 1.747(5), Co(2)–C(24) = 1.772(5) Å).

Unlike the other complexes in Section 4.3 and 4.4, an elemental analysis for the bulk material consistent with the structure of **27** (Figure 4.10) could not be obtained. Given this and the different colour of the crystals grown from THF (green) compared to that of the bulk material dried *in vacuo* (purple-grey), it is likely that the material readily loses THF under vacuum. It may also be the case that this material disproportionates to give a mixture of substances including a divalent Sm(II) complex. Given the lack

of solubility of this material in non-donor solvents it was not possible to grow diffraction-quality crystals from a suitable alternative solvent to investigate this further. However, the synthesis and analysis of the tricyclohexylphosphine analogues $[\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_6]$ (**28**) and $[\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_3(\text{THF})_3]$ (**29**) in Section 4.7 aid in substantiating this hypothesis. A further discussion of **27** is given with these complexes.

The reduction of **1.123** in THF with an excess of Yb/Hg gave monomeric $\text{Yb}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_5$ (**30**) as a yellow solid in 85% isolated yield. Diffraction-quality crystals of **30** were grown from a concentrated THF solution at RT. The molecular structure and selected distances and angles are shown in Figure 4.12 and Table 4.5.

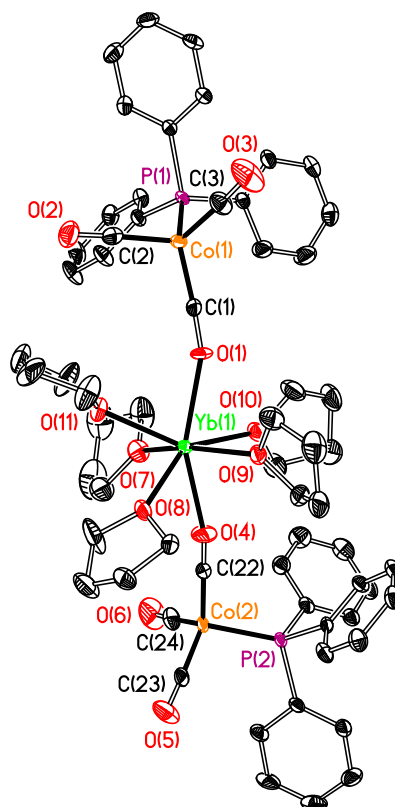


Figure 4.12. Displacement ellipsoid plot (20% probability) of $\text{Yb}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_5$ (**30**). H atoms and THF of crystallisation omitted for clarity.

Table 4.5. Selected distances (Å) and angles (°) for Yb{Co(CO)₃(PPh₃)₂}(THF)₅ (**30**).

Yb(1)···Co(1)	5.2441(6)	Yb(1)···Co(2)	5.2076(6)
Yb(1)-O(1)	2.437(3)	Yb(1)-O(4)	2.393(3)
Yb(1)-O(7)	2.447(3)	Yb(1)-O(8)	2.486(3)
Yb(1)-O(9)	2.415(3)	Yb(1)-O(10)	2.473(3)
Yb(1)-O(11)	2.446(3)	Co(1)-P(1)	2.1779(10)
Co(1)-C(1)	1.721(4)	Co(1)-C(2)	1.753(4)
Co(1)-C(3)	1.748(4)	Co(2)-P(2)	2.1726(10)
Co(2)-C(22)	1.711(4)	Co(2)-C(23)	1.739(5)
Co(2)-C(24)	1.749(5)	C(1)-O(1)	1.186(5)
C(2)-O(2)	1.146(6)	C(3)-O(3)	1.156(6)
C(22)-O(4)	1.181(6)	C(23)-O(5)	1.173(6)
C(24)-O(6)	1.162(7)		
O(1)-Yb(1)-O(4)	155.64(12)	O(1)-Yb(1)-O(7)	104.50(12)
O(7)-Yb(1)-O(8)	109.90(11)	O(7)-Yb(1)-O(11)	78.32(10)
O(8)-Yb(1)-O(9)	80.84(10)	O(9)-Yb(1)-O(10)	80.07(11)
O(10)-Yb(1)-O(11)	140.99(11)	P(1)-Co(1)-C(1)	112.99(14)
P(1)-Co(1)-C(2)	106.19(13)	P(1)-Co(1)-C(3)	101.83(16)
P(2)-Co(2)-C(22)	105.49(13)	P(2)-Co(2)-C(23)	105.76(13)
P(2)-Co(2)-C(24)	107.25(18)	C(1)-Co(1)-C(2)	108.77(18)
C(1)-Co(1)-C(3)	116.8(2)	C(2)-Co(1)-C(3)	109.7(2)
C(22)-Co(2)-C(23)	109.3(2)	C(22)-Co(2)-C(24)	116.0(2)
C(23)-Co(2)-C(24)	112.3(2)		

The geometry at the seven-coordinate Yb centre in **30** is face-capped octahedral, with five coordinated THFs and two Yb(μ-OC)Co isocarbonyl linkages. As expected, given the similar covalent radii for Ca (1.76(10) Å) and Yb (1.87(8) Å),⁷ this structure is similar to that observed for Ca{Co(CO)₃(PPh₃)₂}(THF)₄ (**24**). The Yb(1)···Co(1) (5.2441(6) Å) and Yb(1)···Co(2) (5.2076(6) Å) distances are considerably greater than the sum of the respective covalent radii (3.13(9) Å).⁷ They are also longer than the analogous Ca(1)···Co(1) distance (5.1375(2) Å) in **24**. The geometry at Co(1) and

Co(2) is approximately tetrahedral. The sum of the OC–Co(1)–P(1) and OC–Co(2)–P(2) angles are 321.0(2) and 318.5(3) °, respectively.

For Co(1), the carbonyl group involved in Yb(μ -OC)Co isocarbonyl bridging (C(1)–O(1) = 1.186(5) Å) exhibits an increased C–O distance relative to that for the terminal carbonyl groups (C(2)–O(2) = 1.146(6) and C(3)–O(3) = 1.156(6) Å). Consistent with this, the Co(1)–C(1) (1.721(4) Å) distance is shorter than that for Co(1)–C(2) (1.753(4) Å) or Co(1)–C(3) (1.748(4) Å). For the carbonyl groups bound to Co(2), the C(22)–O(4) (1.181(6) Å) distance is identical within error to that for C(23)–O(5) (1.173(6) Å) and C(24)–O(6) (1.162(7) Å). However, the Co(2)–C(22) (1.711(4) Å) distance is shortened relative to that for Co(2)–C(23) (1.739(5) Å) and Co(2)–C(24) (1.749(5) Å). The Co–C and C–O distances associated with the carbonyl groups bound to Co(1) in **30** are identical within error to those for Co(1) in **24**. However, both the average Yb–O(THF) (2.453(1) Å) and Yb–O(isocarbonyl) (2.415(2) Å) distances are longer than the analogous distances in **24** of 2.329(1) and 2.316(1) Å, respectively.

The average Yb–O(THF) distance in **30** is comparable with that for reported complexes of 2.38(6) (range: 2.21–2.56) Å.¹⁹ Literature examples of Yb(μ -OC)Co are known, including Shore's polymeric [Yb{Co(CO)₄}₂(py)₄]_x (**4.15**) and [Yb{Co(CO)₄}₂(THF)₂]_x (**4.16**) with average Yb–O(isocarbonyl) distances of 2.543(3) and 2.526(3) Å, respectively.²⁵ Compounds **4.15** and **4.16** are synthesised *via* the transmetallation reaction of Hg{Co(CO)₄}₂ (**4.14**) with elemental Yb in the presence of pyridine or THF, respectively. For **4.16**, crystallisation from toluene afforded the sheet-like structure illustrated in Figure 4.13, whilst crystallisation from THF gave the solvent-separated ion pair [Yb(THF)₆][Co(CO)₄]₂ (**4.17**).

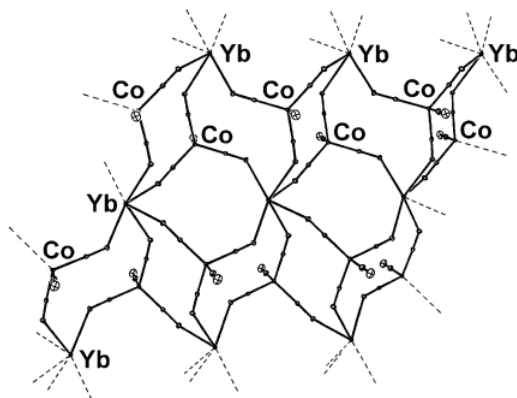


Figure 4.13. Section of the polymeric sheet structure of [Yb{Co(CO)₄}₂(THF)₂]_x (**4.16**).

4.5 Comparison of $[M\{Co(CO)_3(PPh_3)\}_2(THF)_x]_y$ structures

As discussed in Section 4.2, interaction of a $[Co(CO)_3(PR_3)]^-$ anion with a cationic acceptor has the potential to cause a significant perturbation of the geometry at the Co centre. One way to measure this is through the sum of the $R_3P-Co-CO$ angles, $\Sigma(P-Co-CO)$. A greater strength of interaction is likely to cause a reduction in this value from that of the free anion *towards* that expected for an ideal trigonal bipyramidal geometry (270°).

Considering the sum of the $Ph_3P-Co-CO$ angles as a probe of the strength of the interaction between the $[Co(CO)_3(PPh_3)]^-$ anion and the Ae/Ln^{2+} cations in the complexes **24–27** and **30**, the angles are observed to be similar throughout (Table 4.6). This is unsurprising given the lack of direct Co-Ae/Ln interaction in these complexes.

Table 4.6. $\Sigma(P-Co-CO)$ angles ($^\circ$) for **24–27** and **30**.

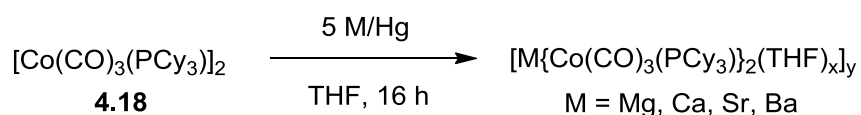
Complex		
$Ca\{Co(CO)_3(PPh_3)\}_2(THF)_4$ (24)	P(1)-Co(1)-CO	317.2(1)
$[Sr\{Co(CO)_3(PPh_3)\}_2(THF)_5]_2$ (25)	P(1)-Co(1)-CO	320.7(1)
	P(2)-Co(2)-CO	320.6(1)
$[Ba\{Co(CO)_3(PPh_3)\}_2(THF)_6]_2$ (26)	P(1)-Co(1)-CO	323.3(3)
	P(2)-Co(2)-CO	317.8(3)
$[Sm\{Co(CO)_3(PPh_3)\}_2(THF)_5]_x$ (27)	P(1)-Co(1)-CO	320.0(2)
	P(2)-Co(2)-CO	324.5(3)
$Yb\{Co(CO)_3(PPh_3)\}_2(THF)_5$ (30)	P(1)-Co(1)-CO	321.0(2)
	P(2)-Co(2)-CO	318.5(3)

As evidenced by the greater $Co\cdots Ae/Ln$ distances than the sum of the respective covalent radii and the lack of perturbation of the sum of the $P-Co-CO$ angles in the structures of **24–27** and **30**, it is apparent that these complexes lack any direct Co-Ae/Ln interaction. Any interaction takes place through isocarbonyl bridging. The lack of solubility in non-donor solvents required the manipulation of these complexes in THF thus promoting THF coordination at the metal centres and inhibition of direct metal-metal interactions as a result. Therefore, an increase in the solubility in non-

donor environments was sought and is discussed in Section 4.6-4.8. This conclusion is supported by the observation that metal-metal bonds to the $[\text{Co}(\text{CO})_4]^-$ anion are known (Section 4.2), critically these species were crystallised from non-donor solvents such as toluene to avoid disruption of the direct interaction between the metal centres. However, selection of the $[\text{Co}(\text{CO})_3(\text{PPh}_3)]^-$ anion over the $[\text{Co}(\text{CO})_4]^-$ anion did allow interaction between the metal centres in **24–27** and **30** to be maintained *via* isocarbonyl bridging when crystallised from THF, in contrast to that for Shore's $[\text{Yb}\{\text{Co}(\text{CO})_4\}_2(\text{THF})_2]_x$ (**4.16**) which crystallised as $[\text{Yb}(\text{THF})_6][\text{Co}(\text{CO})_4]$ (**4.17**) from THF.^{25, 26} The THF solution behaviour of this material and **24–27** and **30** are discussed in Section 4.10.

4.6 Interaction of the $[\text{Co}(\text{CO})_3(\text{PCy}_3)]^-$ anion with Ae^{2+} cations.

This Section will focus on the use of the $[\text{Co}(\text{CO})_3(\text{PCy}_3)]^-$ anion in an attempt to achieve metal-metal bonded species through improved solubility in non-donor solvents over those complexes investigated in Section 4.3-4.5. Additionally, substitution of the PPh_3 ligand for the PCy_3 ligand provides a more donating phosphine to increase electron density on the Co centre.^{27, 28} As with the $[\text{Co}(\text{CO})_3(\text{PPh}_3)]^-$ anion, the $[\text{Co}(\text{CO})_3(\text{PCy}_3)]^-$ anion could be accessed through reduction of $[\text{Co}(\text{CO})_3(\text{PCy}_3)]_2$ **4.18** with an Ae amalgam to afford new heterobimetallic species as depicted in Equation 4.2.



Equation 4.2

Reassuringly, the reduction of **4.18** in THF with an excess of Mg/Hg afforded $[\text{Mg}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_2]$ (**31**) as a toluene-soluble, white solid in 87% isolated yield. Diffraction-quality crystals of **31** were grown from a toluene solution layered with pentane at RT. The molecular structure and selected distances and angles are shown in Figure 4.14 and Table 4.7.

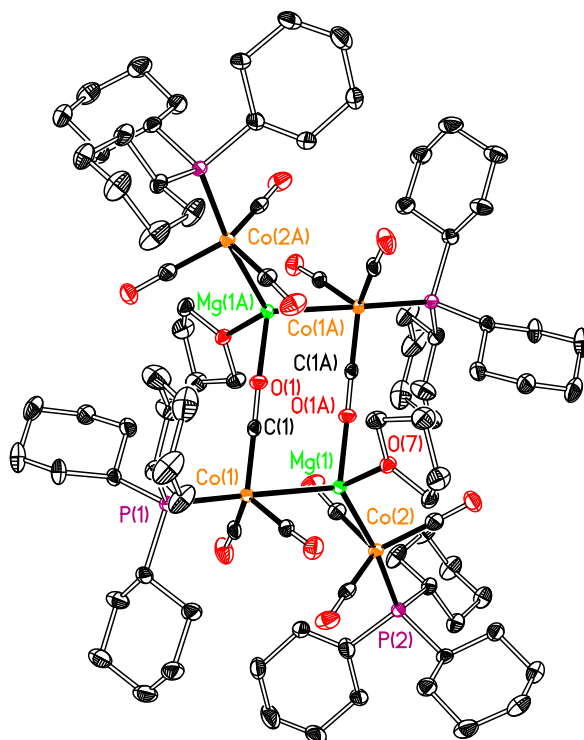


Figure 4.14. Displacement ellipsoid plot (20% probability) of $[\text{Mg}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})]_2$ (**31**). H atoms and minor disorder omitted for clarity. Atoms carrying the suffix “A” are related to their counterparts by the symmetry operator $-x+1, -y-1, -z+2$.

Table 4.7. Selected distances (Å) and angles (°) for [Mg{Co(CO)₃(PCy₃)₂(THF)}₂]₂ (**31**).

Mg(1)-Co(1)	2.6163(6)	Mg(1)-Co(2)	2.5427(6)
Mg(1)···Co(1A)	4.8538(7)	Mg(1)-O(1A)	2.0390(14)
Mg(1)-O(7)	2.0335(14)	Co(1)-P(1)	2.2062(5)
Co(1)-C(1)	1.7132(19)	Co(1)-C(2)	1.761(2)
Co(1)-C(3)	1.776(2)	Co(2)-P(2)	2.2183(5)
Co(2)-C(4)	1.757(2)	Co(2)-C(5)	1.763(2)
Co(2)-C(6)	1.760(2)	C(1)-O(1)	1.179(2)
C(2)-O(2)	1.161(2)	C(3)-O(3)	1.147(3)
C(4)-O(4)	1.161(3)	C(5)-O(5)	1.153(3)
C(6)-O(6)	1.158(3)		
Co(1)-Mg(1)-Co(2)	124.34(3)	Co(1)-Mg(1)-O(1A)	109.30(4)
Co(1)-Mg(1)-O(7)	104.67(4)	Co(2)-Mg(1)-O(1A)	107.92(4)
Co(2)-Mg(1)-O(7)	115.86(4)	O(1A)-Mg(1)-O(7)	89.02(6)
P(1)-Co(1)-Mg(1)	178.13(2)	P(1)-Co(1)-C(1)	102.58(6)
P(1)-Co(1)-C(2)	100.80(6)	P(1)-Co(1)-C(3)	97.48(6)
P(2)-Co(2)-C(4)	97.04(6)	P(2)-Co(2)-C(5)	104.44(6)
P(2)-Co(2)-C(6)	101.68(6)	C(1)-Co(1)-C(2)	115.76(9)
C(3)-Co(1)-C(1)	118.69(9)	C(2)-Co(1)-C(3)	116.19(9)
C(4)-Co(2)-C(5)	117.65(9)	C(6)-Co(2)-C(4)	119.76(10)
C(5)-Co(2)-C(6)	111.97(10)		
^a Hinge angle	155		

^a Hinge angle = (Co(1), C(1), O(1), Co(1A), C(1A), O(1A))-(Co(1), Mg(1), O(1A)). Maximum deviation from plane = 0.01 Å (C(1)).

The molecular structure of **31** is dimeric in the solid state with two four-coordinate tetrahedral Mg{Co(CO)₃(PCy₃)₂(THF)} units connected by Mg(μ-OC)Co isocarbonyl linkages. Each Mg is bonded to two Co atoms, a THF ligand and a μ-isocarbonyl group. The Mg–Co bond distances of 2.6163(6) and 2.5427(6) Å are consistent with significant interactions, based on the sum of the respective covalent radii (2.67(8) Å).⁷ The central moiety of **31** is a rectangular eight-membered ring comprised of two

Mg(μ -OC)Co linkages and two Mg–Co bonds. The internal Mg(1)–Co(1) distance of 2.6163(6) is longer than the external Mg(1)–Co(2) distance of 2.5427(6) Å. The Mg(1)⋯Co(1A) distance (4.8538(7) Å), that is the interaction *via* isocarbonyl linkage, is significantly greater than either of these distances and greater than the sum of the respective covalent radii.

The geometry at Co(1) and Co(2) is approximately trigonal bipyramidal, where the sum of the OC–Co(1)–P(1) and OC–Co(2)–P(2) angles are 300.9(1) and 303.2(1) °, respectively. These values are generally larger than previously found for Co-main group or metal complexes but substantially less than those in Brammer's N–H⋯Co hydrogen-bonded species (307.0(3)–314.3(1) °).^{1, 2} The only relevant structurally characterised previous examples feature PAr₃ ligands (Ar = Ph or Tol) which have a Tolman cone angle of 145 °,²⁸ whereas the PCy₃ ligand in **31** has a cone angle of 170 °. This justified the use of DFT to calculate the theoretical structures of [Co(CO)₃(PCy₃)][–] and Co(H)(CO)₃(PCy₃) (**4.19**) for which Σ (P–Co–CO) are 324.3 and 295.6 °, respectively.

The Mg(μ -OC)Co isocarbonyl linkage results in an increased C(1)–O(1) distance (1.179(2) Å) relative to the terminal carbonyl groups on Co(1) (C(2)–O(2) = 1.161(2) and C(3)–O(3) = 1.147(3) Å). The Co(1)–C(1) (1.7131(19) Å) distance is shortened relative to Co(2)–C(2) (1.761(2) Å) and C(3)–C(3) (1.776(2) Å). Reassuringly, the distances associated with the terminal C(2)O(2) and C(3)O(3) groups are similar to those for the three terminal carbonyl groups on Co(2) (C(4)–O(4) = 1.161(3), C(5)–O(5) = 1.153(3) and C(6)–O(6) = 1.158(3) Å) and (Co(2)–C(4) = 1.757(2), Co(2)–C(5) = 1.763(5) and Co(2)–C(6) = 1.760(2) Å). Note that the C–O distances associated with Co(2) are identical within error, as are the Co(2)–C distances.

NMR and Elemental analysis of the bulk material were consistent with the composition of the molecular structure of **31** (Figure 4.14) with an additional 1.5 THF molecules per dimer suggesting that crystallisation under the conditions described resulted in displacement of the additional THFs to achieve dimerisation. Nevertheless, the molecular structure demonstrates the ability of this material to form Mg–Co bonds in the solid state and studies by DOSY NMR (Section 4.9) support the existence of **31**, and therefore the ability to maintain Mg–Co interactions, in solution.

The Mg–Co interactions in **31** can be compared with the only known report of Ae–Co

bonding, namely $\text{Mg}\{\text{CpCo}(\eta^3\text{-C}_3\text{H}_5)\}(\text{Br})(\text{THF})_2$ (**1.20**, $\text{Mg-Co} = 2.480(4) \text{ \AA}$) and $\text{Mg}\{\text{CpCo}(\eta^2\text{-C}_2\text{H}_4)(\text{Ph})\}(\text{Br})(\text{TMEDA})$ (**1.21**, $\text{Mg-Co} = 2.565(3) \text{ \AA}$).²⁹ Other examples of structurally authenticated complexes containing Mg-TM bonds include $\text{Mg}(\text{NacNac})\text{Fp}(\text{THF})$ (**12**) ($\text{Mg-Fe} = 2.6326(4) \text{ \AA}$) and Felkin's $[\text{Cp}(\text{dppe})\text{FeMgBr}(\text{THF})_2]$ (**1.18**, $\text{Mg-Fe} = 2.593(7) \text{ \AA}$).³⁰ The eight-membered ring observed for **31**, with two $\text{Mg}(\mu\text{-OC})\text{Co}$ isocarbonyl bridges and two Mg-Co bonds, is reminiscent of that observed for the solid state structure of $[\text{MgFp}_2(\text{THF})]_2$ (**1**) (Chapter Two, Figure 2.6) which has two $\text{Mg}(\mu\text{-OC})\text{Fe}$ isocarbonyl bridges and two Mg-Fe bonds. Comparison of the distances associated with these rings shows the $\text{Mg}(1)\text{-Co}(1)$ distance ($2.6163(6) \text{ \AA}$) to be similar to the $\text{Mg}(1)\text{-Fe}(1)$ distance ($2.6112(5) \text{ \AA}$). The span of the isocarbonyl bridges within these rings are also similar ($\text{Mg}(1)\cdots\text{Co}(1\text{A}) = 4.8538(7)$ and $\text{Mg}(1)\cdots\text{Fe}(1\text{A}) = 4.7879(5) \text{ \AA}$). These structures also possess metal-metal bonds with similar distances ($\text{Mg}(1)\text{-Co}(2) = 2.5427(6)$ and $\text{Mg}(1)\text{-Fe}(2) = 2.5629(5) \text{ \AA}$) external to their eight-membered rings. The $\text{Mg-O}(\text{THF})$ distances of $2.034(1)$ and $2.048(1) \text{ \AA}$ in **31** and **1**, respectively, are near-identical and are comparable with the average literature $\text{Mg-O}(\text{THF})$ distance of $2.08(4)$ (range: $1.96\text{-}2.29$) $\text{ \AA}$.¹⁹ However, the $\text{Mg-O}(\text{isocarbonyl})$ distances are longer in **1** ($2.102(1) \text{ \AA}$) compared to those in **31** ($2.039(1) \text{ \AA}$). Only one structurally authenticated example of a $\text{Mg}(\mu\text{-OC})\text{Co}$ isocarbonyl interaction has been reported in the literature, namely $\{\text{Tp}^{\text{tBu,Me}}\text{Co}(\mu\text{-CO})\}_2\text{Mg}(\text{THF})_4$ (**2.10**, Figure 2.9) with an average $\text{Mg-O}(\text{isocarbonyl})$ distance of $2.068(1) \text{ \AA}$.³¹ Comparison of the hinge angles for these eight-membered rings shows that for **31** (155°) to be greater than that for **1** (138°) and is discussed in greater detail with that for **32**.

Reaction of **4.18** in THF with an excess of Ca/Hg afforded the toluene-soluble product $[\text{Ca}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_2]_x$ (**32**) in 84% isolated yield. Diffraction-quality crystals were grown from a toluene solution layered with pentane at RT. Sections of the polymeric structure and selected distances and angles are shown in Figures 4.15, 4.16 and Table 4.8.

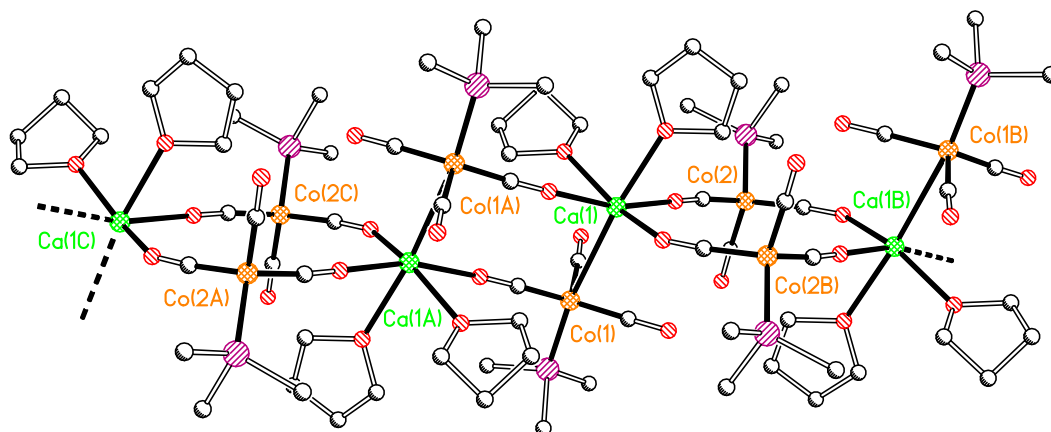


Figure 4.15. Ball and stick plot (arbitrary radius) of a portion of the $[\text{Ca}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_2]_x$ (**32**) infinite chain. H atoms and cyclohexyl methylene carbons omitted for clarity. Symmetry related atoms correspond to their counterparts by the operators “A” = $2-x, 1-y, 1-z$; “B” = $1-x, 1-y, 1-z$; “C” = $1+x, y, z$

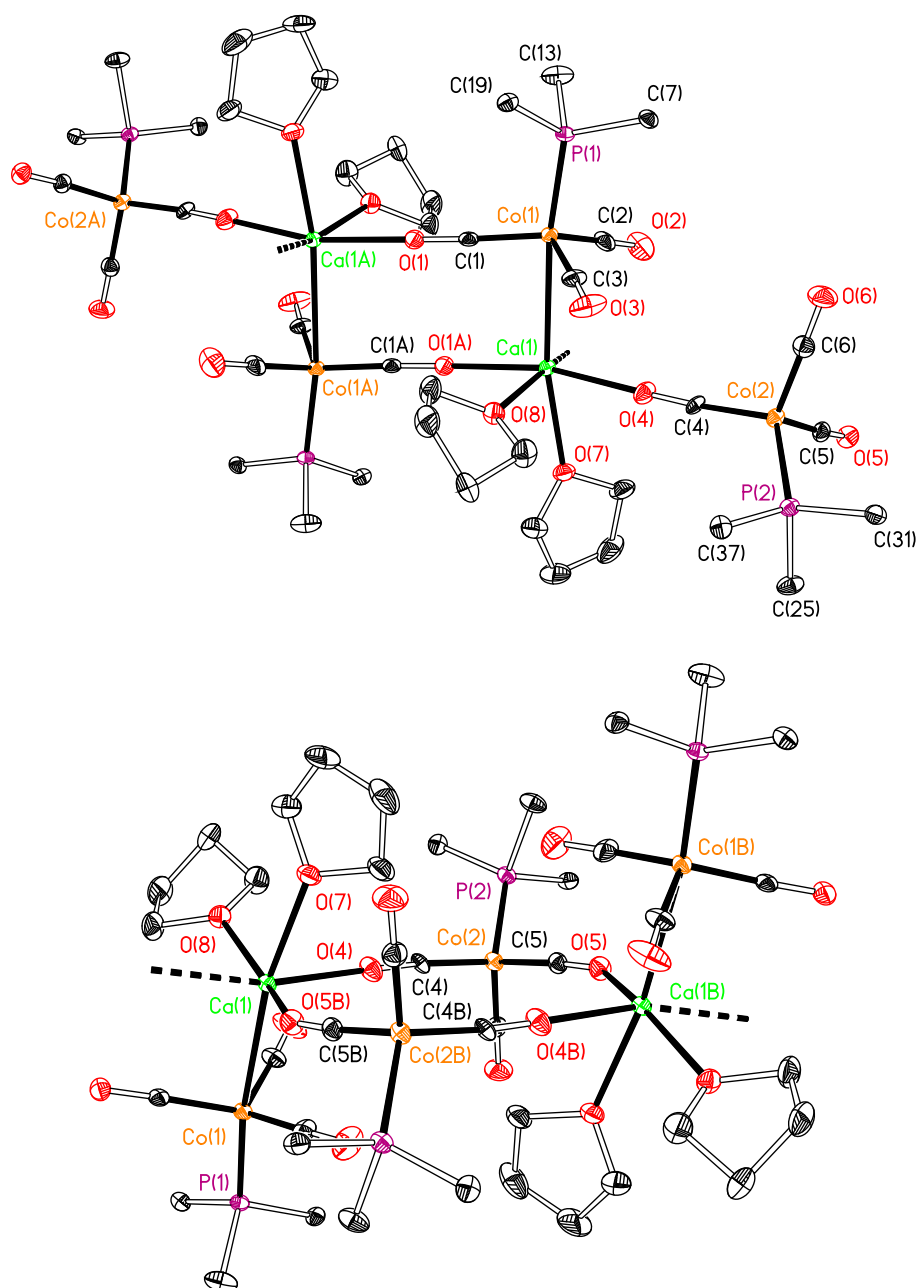


Figure 4.16. Displacement ellipsoid plots (20% probability) of eight- and twelve-membered ring components, top and bottom, respectively, of the $[\text{Ca}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_2]_x$ (**32**) infinite chain. H atoms and cyclohexyl methylene carbons omitted for clarity. Atoms carrying the suffix “A” are related to their counterparts by the symmetry operator $2-x, 1-y, 1-z$. Atoms carrying the suffix “B” are related to their counterparts by the symmetry operator $1-x, 1-y, 1-z$.

Table 4.8. Selected distances (Å) and angles (°) for [Ca{Co(CO)₃(PCy₃)₂(THF)₂]_x (**32**).

Ca(1)-Co(1)	3.0450(9)	Ca(1)···Co(1A)	5.2490(10)
Ca(1)···Co(2)	5.2266(10)	Ca(1)···Co(2B)	5.0919(9)
Ca(1)-O(1A)	2.347(3)	Ca(1)-O(4)	2.344(3)
Ca(1)-O(5B)	2.374(3)	Ca(1)-O(7)	2.400(3)
Ca(1)-O(8)	2.366(3)	Co(1)-P(1)	2.2113(10)
Co(1)-C(1)	1.741(4)	Co(1)-C(2)	1.742(4)
Co(1)-C(3)	1.785(4)	Co(2)-P(2)	2.2301(11)
Co(2)-C(4)	1.709(3)	Co(2)-C(5)	1.721(4)
Co(2)-C(6)	1.771(4)	C(1)-O(1)	1.173(5)
C(2)-O(2)	1.171(5)	C(3)-O(3)	1.120(5)
C(4)-O(4)	1.181(4)	C(5)-O(5)	1.198(5)
C(6)-O(6)	1.154(5)		
Co(1)-Ca(1)-O(1A)	97.29(7)	Co(1)-Ca(1)-O(4)	90.52(7)
Co(1)-Ca(1)-O(5B)	104.49(7)	Co(1)-Ca(1)-O(7)	167.61(8)
O(1A)-Ca(1)-O(4)	165.15(11)	O(1A)-Ca(1)-O(5B)	83.30(10)
O(1A)-Ca(1)-O(8)	79.60(10)	O(4)-Ca(1)-O(5B)	107.01(11)
O(4)-Ca(1)-O(8)	87.43(10)	P(1)-Co(1)-Ca(1)	172.65(4)
P(1)-Co(1)-C(1)	104.46(10)	P(1)-Co(1)-C(2)	101.83(13)
P(1)-Co(1)-C(3)	99.50(11)	P(2)-Co(2)-C(4)	113.52(13)
P(2)-Co(2)-C(5)	107.50(13)	P(2)-Co(2)-C(6)	106.35(14)
C(1)-Co(1)-C(2)	120.23(18)	C(3)-Co(1)-C(1)	114.84(19)
C(2)-Co(1)-C(3)	112.2(2)	C(4)-Co(2)-C(5)	108.46(17)
C(6)-Co(2)-C(4)	108.62(18)	C(5)-Co(2)-C(6)	112.46(18)
^a Hinge angle	170	^b Hinge angle	167
^c Inter-ring angle	61.5		

^a Hinge angle = (Co(1), C(1), O(1), Co(1A), C(1A), O(1A))-(Co(1), Ca(1), O(1A)). Maximum deviation from plane = 0.01 Å (Ca(1)). ^b Hinge angle = (Co(2), C(5), O(5), Co(2B), C(5B), O(5B))-(Co(2), C(4), O(4), Ca(1), O(5B)). Maximum deviation from plane = 0.04 Å (Co(2)). ^c Inter-ring angle = (Co(1), C(1), O(1), Co(1A), C(1A), O(1A))-(Co(2), C(5), O(5), Co(2B), C(5B), O(5B)).

In the solid state, **32** forms an infinite-chain comprised of eight- and twelve-

membered rings connected at their vertices by six-coordinate Ca atoms. Each Ca forms only one unsupported Ca–Co bond of length 3.0450(9) Å which, unlike in **31**, is identical within error to the sum of the respective covalent radii (3.02(10) Å).⁷ This represents the second structurally authenticated example of a Ca–TM bond following [CaFp₂(THF)₃]₂ (**3**, Figure 2.10) and the first between Ca and Co. The rectangular eight-membered ring containing Co(1), Ca(1), Co(1A), Ca(1A) is analogous to the corresponding motif in **31**. The Ca(1)⋯Co(1A) distance (5.2490(10) Å) spanned by C(1A)O(1A) is greater than the sum of the respective covalent radii. As expected, this is longer than the analogous Mg(1)⋯Co(1A) distance (4.8538(7) Å) in **31**. The twelve-membered ring containing Co(2), Ca(1), Co(2B), Ca(1B) does not possess a Ca–Co bond but instead contains four Ca(μ-OC)Co linkages. The Ca⋯Co distances (Ca(1)⋯Co(2) = 5.2266(10), Ca(1)⋯Co(2B) = 5.0919(9) Å) within this ring far exceed those expected for a direct interaction between metal centres. The Ca(1)⋯Co(2B) distance is notably shorter than for Ca(1)⋯Co(2). The sum of the OC–Co(1)–P(1) angles (305.8(2) °) is similar to those in **31** (300.9(1) and 303.2(1) °) and consistent with the Co(1)–Ca(1) bond, whereas for Co(2) the sum of the OC–Co(2)–P(2)) angles is 327.4(2) ° as expected.

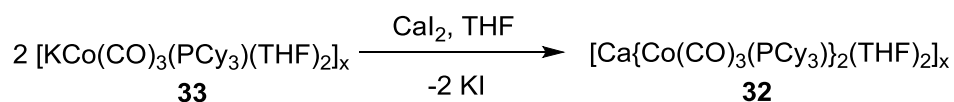
The C(1)–O(1) distance (1.173(5) Å) is identical within error to that for C(2)–O(2) (1.171(5) Å). This is perhaps unexpected given the former's involvement in Ca(μ-OC)Co isocarbonyl bridging whilst the latter is terminal. The respective Co–C distances are also similar (Co(1)–C(1) = 1.741(4) and Co(1)–C(2) = 1.742(4) Å). However, the distances associated with terminal C(3)O(3) are different, with shorter C(3)–O(3) (1.120(5)) and longer Co(1)–C(3) (1.785(4) Å) distances relative to those for C(1)O(1) as expected. For Co(2) the bridging C(4)–O(4) (1.181(4) and C(5)–O(5) (1.198(5) Å) distances are longer than the terminal C(6)–O(6) (1.154(5) Å) distance as expected. The Co(2)–C(4) (1.709(3) Å) and Co(2)–C(5) (1.721(4) Å) distances are shorter than the Co(2)–C(6) (1.771(4) Å) distance.

The average Ca–O(THF) distances of 2.383(2) and 2.363(1) Å are similar for **32** and **3**, respectively. These are comparable to the average Ca–O(THF) literature value of 2.39(4) (range: 2.30–2.55) Å.¹⁹ The respective Ca–O(isocarbonyl) distances of 2.346(2) and 2.335(1) Å are also similar. As expected these are longer than the analogous distances associated with **31** (Mg–O(THF) = 2.034(1) and Mg–O(isocarbonyl) = 2.039(1) Å). The eight-membered ring in **32**, with two Ca(μ-OC)Co

isocarbonyl bridges and two Ca-Co bonds, is reminiscent not only of that observed for **31** but also **3**. The internal metal-metal bond distances associated with these structures (Ca-Co = 3.0450(9) and Ca-Fe = 3.0185(6) Å) show the Ca-Co distance to be longer than the Ca-Fe distance. This is the opposite of that expected based on the respective covalent radii (Co = 1.26(3) and Fe = 1.32(3) Å). Whilst both of these complexes have six-coordinate octahedral Ca centres, **32** is polymeric whereas **3** is dimeric.

The hinge angle for the eight-membered ring in **32** (170 °) is greater than that for the eight-membered ring in **31** (155 °) or for those found in **1** (138 °), **3** (146 °) or [YbFp₂(THF)₃]₂ (**6**, 144 °). This may be a consequence of the geometric constraints that result from the polymeric nature of **32**. The hinge angle for the twelve-membered ring of 167 ° is similar to that for the eight-membered ring and that observed for the twelve-membered ring in **25** (163 °) but greater than that for **26** (142 °). The inter-ring angle (61.5 °) is a measure of the deviation of the eight- and twelve-membered rings from coplanarity and was found to be very similar for all the complexes in this section. This is only applicable for those structures that are polymeric with a repeating ring motif.

Elemental analysis of the bulk material of **32** was consistent with the structure illustrated in Figure 4.15 and 4.16. Compound **32** could also be synthesised by the salt metathesis reaction of [KCo(CO)₃(PCy₃)(THF)₂]_x (**33**) with CaI₂ in THF to afford **32** as a white solid in 53% isolated yield (Equation 4.3).



Equation 4.3

Crystallisation of **32** from a concentrated THF solution at RT gave the monomeric structure Ca{Co(CO)₃(PCy₃)}₂(THF)₅ (**34**) illustrated in Figure 4.17. Whilst the connectivity of **34** is unambiguous, the data are not of sufficient quality to allow an accurate analysis of bond lengths and angles. Ca(1) is seven-coordinate, ligated by five THF ligands and two Ca(μ-OC)Co linkages to give a monomeric structure, similar to the triphenylphosphine analogue Ca{Co(CO)₃(PPh₃)}₂(THF)₄ (**24**). The Ca centre in **24** is six-coordinate with four THF ligands in the equatorial plane. Compound **34** is also reminiscent of Yb{Co(CO)₃(PPh₃)}₂(THF)₅ (**30**) which features a seven-coordinate Yb centre with five coordinated THFs. Whilst an in-depth

comparison of the geometries cannot be carried out, this demonstrates the importance of crystallisation from a non-donor solvent. It is evident that in presence of excess THF the Ca-Co interactions are readily overcome by Ca-THF interactions, despite the increased donor strength of PCy_3 vs. PPh_3 .²⁷

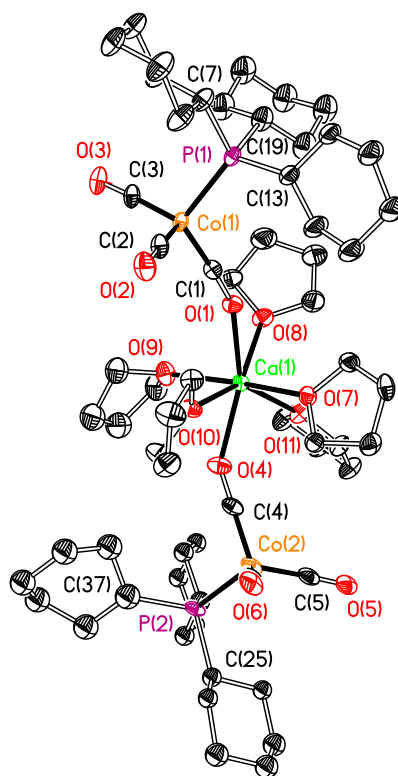


Figure 4.17. Displacement ellipsoid plot (15% probability) of $\text{Ca}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_5$ (**34**). H atoms and second disordered component of the $\text{Co}(2)(\text{CO})_2(\text{PCy}_3)$ fragment omitted for clarity. Carbons of the $\text{P}(2)\text{Cy}_3$ ligand were isotropically refined with a common $U[\text{iso}]$ parameter.

Reaction of **4.18** in THF with an excess of Sr/Hg afforded $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (**35**) as a toluene-soluble white solid in 70% isolated yield. Crystallisation from a concentrated pentane solution at RT gave diffraction-quality crystals. Sections of the polymeric structure and selected distances and angles are shown in Figures 4.18, 4.19 and Table 4.9.

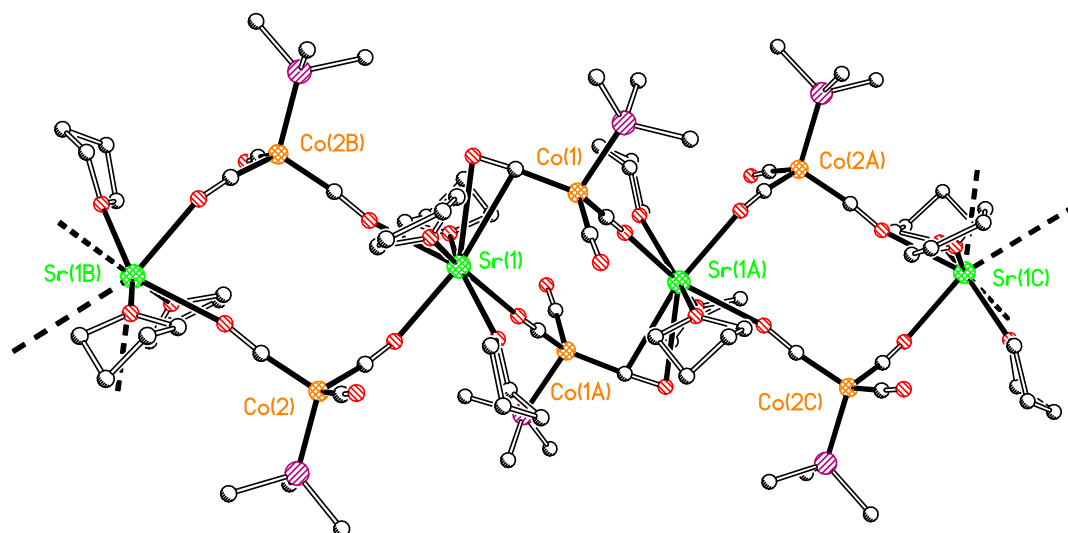


Figure 4.18. Ball and stick plot (arbitrary radius) of a portion of the $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (**35**) polymeric chain. H atoms and cyclohexyl methylene carbons omitted for clarity. Symmetry related atoms are related to their counterparts by the operators “A” = $1-x, 1-y, 1-z$; “B” = $1-x, 2-y, 1-z$; “C” = $x, y-1, z$.

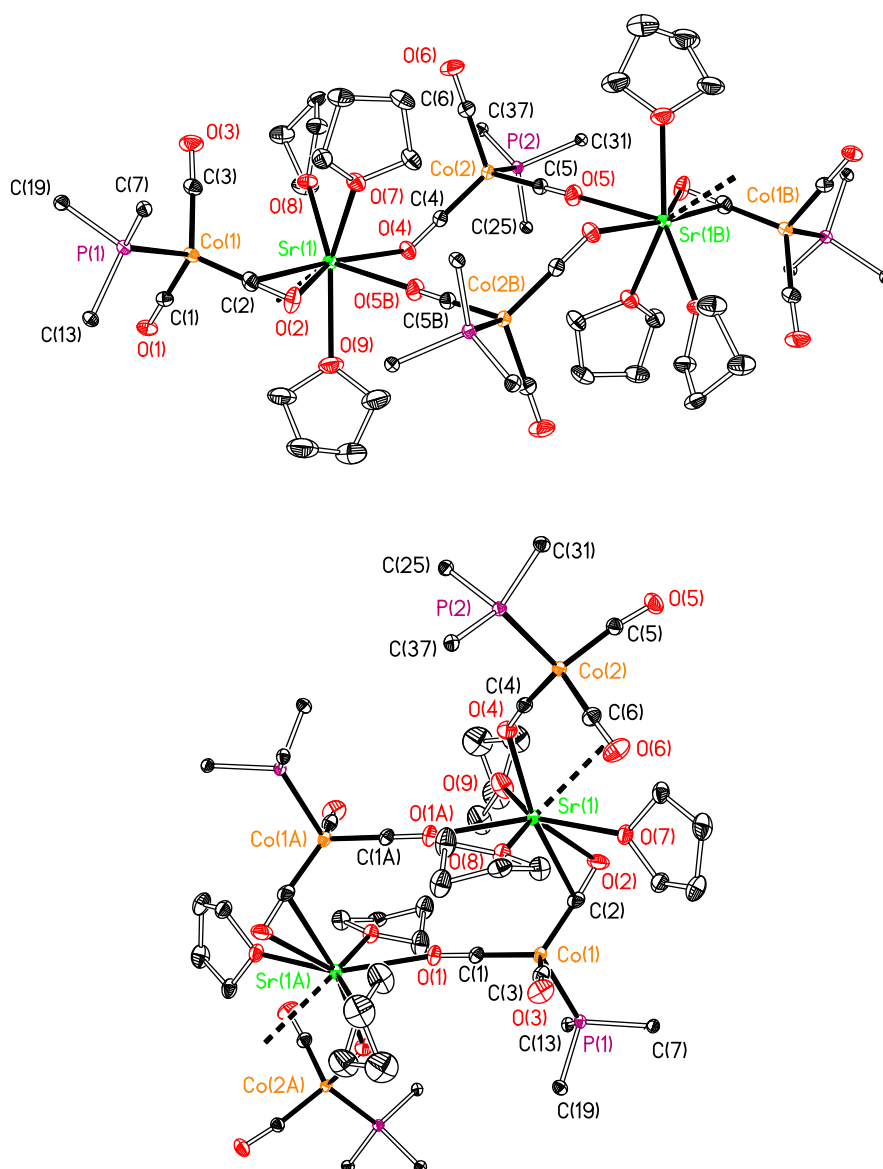


Figure 4.19. Displacement ellipsoid plots (25% probability) of twelve- and “eight”-membered ring components, top and bottom, respectively, of $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (**35**) polymeric chain. H atoms and cyclohexyl methylene carbons omitted for clarity. Atoms carrying the suffix “A” are related to their counterparts by the symmetry operator $1-x, 1-y, 1-z$. Atoms carrying the suffix “B” are related to their counterparts by the symmetry operator $1-x, 2-y, 1-z$.

Table 4.9. Selected distances (Å) and angles (°) for [Sr{Co(CO)₃(PCy₃)₂(THF)₃]_x (**35**).

Sr(1)···Co(1)	3.6263(4)	Sr(1)···Co(1A)	5.4697(4)
Sr(1)···Co(2)	5.0123(4)	Sr(1)···Co(2B)	5.4725(4)
Sr(1)-O(1A)	2.6197(18)	Sr(1)-O(4)	2.5639(18)
Sr(1)-O(5B)	2.5960(19)	Sr(1)-O(7)	2.5401(18)
Sr(1)-O(8)	2.5520(17)	Sr(1)-O(9)	2.559(2)
Sr(1)···O(2)	2.879(2)	Sr(1)···C(2)	2.909(2)
P(1)-Co(1)	2.2073(6)	Co(1)-C(1)	1.732(2)
Co(1)-C(2)	1.735(3)	Co(1)-C(3)	1.758(3)
P(2)-Co(2)	2.2152(6)	Co(2)-C(4)	1.728(3)
Co(2)-C(5)	1.732(2)	Co(2)-C(6)	1.752(3)
C(1)-O(1)	1.173(3)	C(2)-O(2)	1.173(3)
C(3)-O(3)	1.156(3)	C(4)-O(4)	1.185(3)
C(5)-O(5)	1.169(3)	C(6)-O(6)	1.156(3)
Co(1)···Sr(1)-O(4)	161.85(5)	O(1A)-Sr(1)-O(2)	114.64(6)
O(1A)-Sr(1)-O(4)	87.77(6)	O(1A)-Sr(1)-O(5B)	137.43(7)
O(1A)-Sr(1)-O(7)	151.52(6)	O(2)-Sr(1)-O(4)	146.51(6)
O(2)-Sr(1)-O(5B)	70.12(6)	O(4)-Sr(1)-O(5B)	76.56(6)
O(7)-Sr(1)-O(8)	77.48(6)	O(7)-Sr(1)-O(9)	137.26(7)
O(8)-Sr(1)-O(9)	145.26(7)	P(1)-Co(1)-C(1)	105.98(8)
P(1)-Co(1)-C(2)	104.34(8)	P(1)-Co(1)-C(3)	100.83(9)
P(2)-Co(2)-C(4)	113.01(8)	P(2)-Co(2)-C(5)	108.11(8)
P(2)-Co(2)-C(6)	105.79(8)	C(1)-Co(1)-C(2)	113.46(12)
C(3)-Co(1)-C(1)	110.78(12)	C(2)-Co(1)-C(3)	119.47(13)
C(4)-Co(2)-C(5)	109.80(11)	C(6)-Co(2)-C(4)	112.79(12)
C(5)-Co(2)-C(6)	107.04(12)		
^a Hinge angle	161	^b Hinge angle	136
^c Inter-ring angle	58.0		

^a Hinge angle = (Co(1), C(1), O(1), Co(1A), C(1A), O(1A))-(Co(1), Sr(1), O(1A)). ^b Hinge angle = (Co(2), C(4), O(4), Co(2A), C(4A), O(4A))-(Co(2B), C(5B), O(5B), Sr(1), O(4)). Maximum deviation from plane = 0.06 Å (O(5B)). ^c Inter-ring angle = (Co(1), C(1), O(1), Co(1A), C(1A), O(1A))-(Co(2), C(4), O(4), Co(2B), C(4B), O(4B)).

In the solid state, **35** forms an infinite chain comprised of twelve-membered rings

with $\text{Sr}(\mu\text{-OC})\text{Co}(\eta^1\text{-})$ isocarbonyl linkages that alternate at Sr vertices with rings that are intermediate between the twelve and eight-membered rings such as that observed for the metal-metal bond containing $[\text{Mg}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})]_2$ (**31**) and $[\text{Ca}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_2]_x$ (**32**). This results from an unusual side-on (η^2 -) interaction between Sr(1) and C(2)O(2) ($\text{Sr}(1)\cdots\text{C}(2) = 2.909(2)$, $\text{Sr}(1)\cdots\text{O}(2) = 2.879(2)$ Å), unprecedented between an Ae and a TM carbonyl. The $\text{Sr}\cdots\text{Co}$ distances ($\text{Sr}(1)\cdots\text{Co}(1\text{A}) = 5.4697(4)$, $\text{Sr}(1)\cdots\text{Co}(2) = 5.0123(4)$, $\text{Sr}(1)\cdots\text{Co}(2\text{B}) = 5.4725(4)$ Å) between the isocarbonyl linked metal centres exceed the sum of the respective covalent radii (3.21(10) Å).⁷ However, the $\text{Sr}(1)\cdots\text{Co}(1)$ distance (3.6263(4) Å) is considerably shorter. The sum of the $\text{OC-Co}(1)\text{-P}(1)$ angles is $311.2(1)^\circ$. Whereas for Co(2) the sum of the $\text{OC-Co}(2)\text{-P}(2)$ angles is $326.9(1)^\circ$, close to the tetrahedral value.

The carbonyl groups bound to Co(1) are involved in isocarbonyl (C(1)O(1)) and side-on (C(2)O(2)) bridging, whilst C(3)O(3), also bound to Co(1), is a terminal carbonyl group. The C(1)-O(1) (1.173(3) Å) and C(2)-O(2) (1.173(3) Å) distances are identical, whereas the C(3)-O(3) distance (1.156(3) Å) is shorter as expected. Consistent with this, the Co(1)-C(1) (1.732(2) Å) and Co(1)-C(2) (1.735(3) Å) distances are identical within error, whilst the Co(1)-C(3) (1.758(3) Å) distance is longer. Two of the carbonyl groups bound to Co(2), C(4)O(4) (C(4)-O(4) = 1.185(3) and Co(2)-C(4) = 1.728(3) Å) and C(5)O(5) (C(5)-O(5) = 1.169(3) and Co(2)-C(5) = 1.732(2) Å), are involved in isocarbonyl bridging, where the C-O distances are similar and the Co-C distances are identical within error. For C(6)O(6) (C(6)-O(6) = 1.156(3) and Co(2)-C(6) = 1.752(3) Å) the C-O and Co-C distances are observed to be shorter and longer than for C(4)O(4) and C(5)O(5), respectively, identical within error to those for terminal C(3)O(3). As expected, the average Sr-O(THF) (2.550(1) Å) distance is longer than that for Ca-O(THF) (2.383(2) Å) in **32**. This is also the case for the average Ae-O(isocarbonyl) distances (Ae = Sr: 2.550(1), Ca: 2.346(2) Å). The average Sr-O(THF) distance in $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (**35**) is comparable with literature values (2.56(4) (range: 2.47-2.71) Å) for structurally authenticated complexes.¹⁹ The hinge angle (136°) for the twelve-membered ring is considerably smaller than that for the eight-membered ring with η^2 -carbonyl interactions (161°). The inter-ring angle is 58.0° . A further discussion of this structure and its comparison with those of other complexes is given with that for $[\text{Eu}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$

(36, Section 4.7).

Reaction of **4.18** in THF with an excess of Ba/Hg afforded $\text{Ba}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_6$ (**37**) as a white solid in 53% isolated yield. The material was insoluble in toluene thus necessitating the growth of diffraction-quality crystals from a concentrated THF solution. The molecular structure and selected distances and angles are shown in Figure 4.20 and Table 4.10.

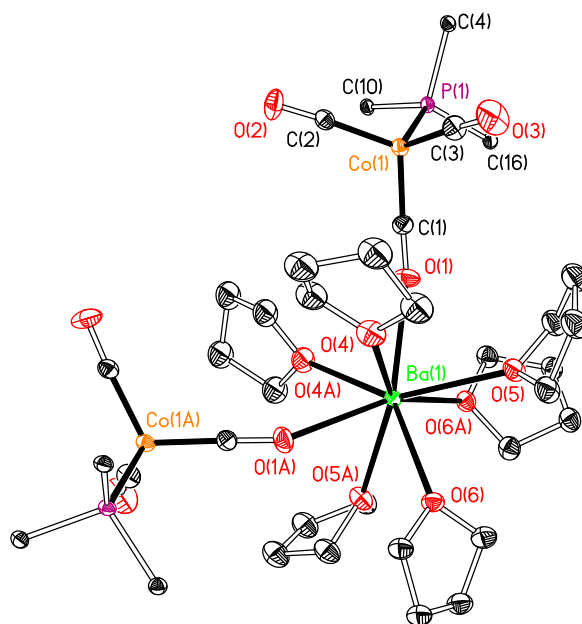


Figure 4.20. Displacement ellipsoid plot (20% probability) of $\text{Ba}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_6$ (**37**). H atoms and cyclohexyl methylene carbons omitted for clarity. Atoms carrying the suffix “A” are related to their counterparts by the symmetry operator $1-x, y, \frac{1}{2}-z$.

Table 4.10. Selected distances (Å) and angles (°) for Ba{Co(CO)₃(PCy₃)₂}(THF)₆ (**37**).

Ba(1)···Co(1)	5.4140(7)	Ba(1)-O(1)	2.723(4)
Ba(1)-O(4)	2.735(4)	Ba(1)-O(5)	2.806(4)
Ba(1)-O(6)	2.709(3)	Co(1)-P(1)	2.2021
Co(1)-C(1)	1.711(5)	Co(1)-C(2)	1.748(5)
Co(1)-C(3)	1.740(5)	C(1)-O(1)	1.186(6)
C(2)-O(2)	1.146(6)	C(3)-O(3)	1.159(7)
O(1)-Ba(1)-O(1A)	120.42(19)	O(1A)-Ba(1)-O(4)	69.22(15)
O(4)-Ba(1)-O(4A)	104.7(2)	O(4)-Ba(1)-O(6A)	142.18(13)
O(4A)-Ba(1)-O(5)	74.56(14)	O(5)-Ba(1)-O(5A)	126.35(17)
O(5A)-Ba(1)-O(6)	74.36(12)	O(6)-Ba(1)-O(6A)	101.74(14)
P(1)-Co(1)-C(1)	105.50(14)	P(1)-Co(1)-C(2)	105.28(14)
P(1)-Co(1)-C(3)	109.57(19)	C(1)-Co(1)-C(2)	113.5(2)
C(1)-Co(1)-C(3)	109.2(3)	C(2)-Co(1)-C(3)	113.3(3)

The geometry at the eight-coordinate Ba centre in **37** is face-capped trigonal prismatic, with six coordinated THFs and two Ba(μ-OC)Co isocarbonyl linkages to give a monomeric structure. The Ba(1)···Co(1) distance (5.4140(7) Å) is greater than the sum of the respective covalent radii (3.41(11) Å). The approximately tetrahedral geometry at the Co(1) centre and sum of the OC-Co(1)-P(1) angles (320.35(9) °) is consistent with this lack of direct interaction.

The C(1)-O(1) (1.186(6) Å) distance is longer than that for C(2)-O(2) (1.146(6) Å) or C(3)-O(3) (1.159(7) Å) as expected given the involvement of C(1)O(1) in Ba(μ-OC)Co isocarbonyl bridging. The Co(1)-C(1) (1.711(5) Å) distance is shorter than the Co(1)-C(2) (1.748(5) Å) or Co(1)-C(3) (1.740(5) Å) distances. As expected given the increase in the covalent radius, the average Ae-O(THF) distance is longer in **37** (2.750(2) Å) than in **35** (2.550(1) Å). Similarly, the average Ae-O(isocarbonyl) distance is longer in **37** (2.723(4) Å) than in **35** (2.608(1) Å). The average Ba-O(THF) distance in **37** is consistent with the average literature Ba-O(THF) distance of 2.77(5) (range: 2.67-2.94 Å).¹⁹

The monomeric structure for **37** contrasts with the dimeric structure for $[\text{Ba}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_6]_2$ (**26**), also crystallised from THF. However, the Ba $\cdots$ Co distances (Ba(1) $\cdots$ Co(1) = 5.6897(7), Ba(1) $\cdots$ Co(1A) = 5.3884(7) and Ba(1) $\cdots$ Co(2) = 5.5569(8) Å) and sum of the OC-Co-P angles (OC-Co(1)-P(1) = 323.3(3) and OC-Co(2)-P(2) = 317.8(3) °) in **26** are similar. This is expected given the lack of direct interaction between Ba and Co in either complex. Evidently, for the Ba²⁺ cation, use of the $[\text{Co}(\text{CO})_3(\text{PCy}_3)]^-$ anion over the $[\text{Co}(\text{CO})_3(\text{PPh}_3)]^-$ anion does not offer a great enough improvement in terms of solubility to permit manipulation in, and crystallisation from, a non-donor solvent.

Dissolving **37** in DME at 85 °C, followed by filtration and removal of volatiles under reduced pressure afforded $\text{Ba}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{DME})_4$ (**38**) as a white solid in 92% isolated yield. Slow cooling of a concentrated DME solution from 85 °C to RT gave diffraction-quality crystals. The molecular structure and selected distances and angles are illustrated in Figure 4.21 and Table 4.11.

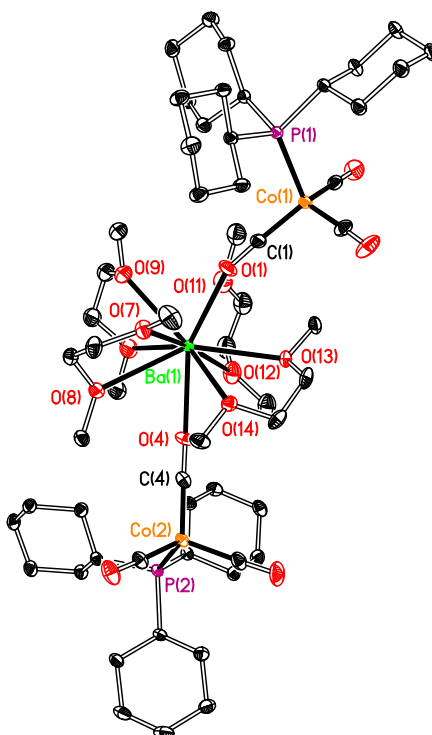


Figure 4.21. Displacement ellipsoid plot (20% probability) of $\text{Ba}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{DME})_4$ (**38**). H atoms omitted for clarity.

Table 4.11. Selected distances (Å) and angles (°) for Ba{Co(CO)₃(PCy₃)₂(DME)₄ (**38**).

Ba(1)···Co(1)	5.5273(7)	Ba(1)···Co(2)	5.5453(7)
Ba(1)-O(1)	2.750(3)	Ba(1)-O(4)	2.728(3)
Ba(1)-O(7)	2.911(3)	Ba(1)-O(8)	2.976(3)
Ba(1)-O(9)	2.789(4)	Ba(1)-O(10)	2.789(4)
Ba(1)-O(11)	2.997(4)	Ba(1)-O(12)	2.919(4)
Ba(1)-O(13)	2.802(3)	Ba(1)-O(14)	2.878(3)
Co(1)-P(1)	2.1942(11)	Co(1)-C(1)	1.718(5)
Co(1)-C(2)	1.748(4)	Co(1)-C(3)	1.760(5)
Co(2)-P(2)	2.1961(11)	Co(2)-C(4)	1.725(5)
Co(2)-C(5)	1.752(5)	Co(2)-C(6)	1.742(5)
C(1)-O(1)	1.180(6)	C(2)-O(2)	1.161(5)
C(3)-O(3)	1.164(7)	C(4)-O(4)	1.174(5)
C(5)-O(5)	1.157(6)	C(6)-O(6)	1.162(6)
O(1)-Ba(1)-O(4)	152.27(13)	O(1)-Ba(1)-O(7)	68.26(11)
O(7)-Ba(1)-O(8)	56.83(10)	O(8)-Ba(1)-O(9)	76.49(11)
O(14)-Co(1)-O(8)	84.66(9)	O(9)-Ba(1)-O(10)	59.89(13)
O(10)-Ba(1)-O(11)	71.73(12)	O(11)-Ba(1)-O(12)	54.51(13)
O(12)-Ba(1)-O(13)	67.10(11)	O(13)-Ba(1)-O(14)	57.85(9)
P(1)-Co(1)-C(1)	109.87(15)	P(1)-Co(1)-C(2)	102.15(14)
P(1)-Co(1)-C(3)	105.87(16)	P(2)-Co(2)-C(4)	111.46(14)
P(2)-Co(2)-C(5)	108.03(18)	P(2)-Co(2)-C(6)	102.03(15)
C(1)-Co(1)-C(2)	113.0(2)	C(1)-Co(1)-C(3)	110.1(3)
C(2)-Co(1)-C(3)	115.2(2)	C(4)-Co(1)-C(5)	109.1(2)
C(4)-Co(1)-C(6)	112.0(2)	C(5)-Co(1)-C(6)	114.0(2)

These confirm **38** to be a monomeric six-coordinate complex with two Ba(μ -OC)Co isocarbonyl linkages and four coordinated DME ligands. The Ba···Co distances (Ba(1)···Co(1) = 5.5273(7), Ba(1)···Co(2) = 5.5453(7) Å) are greater than the sum of the respective covalent radii (3.41(11) Å).⁷ The tetrahedral geometry at the Co centres and the sum of the OC–Co(1)–P(1) (317.9(3)°) and OC–Co(2)–P(2) (321.5(3)°) angles

are consistent with this.

The Co(1)-C(1) (1.718(5) Å) distance is longer than that for Co(1)-C(2) (1.748(4) Å) or Co(1)-C(3) (1.760(5) Å). However, the C-O distances are not significantly different (C(1)-O(1) = 1.180(6), C(2)-O(2) = 1.161(5) and C(3)-O(3) = 1.164(7) Å). For Co(2), the Co(2)-C(4) (1.725(5) Å) distance is longer than that for Co(2)-C(5) (1.752(5) Å) but not significantly different from that of Co(2)-C(6) (1.742(5) Å). The C-O distances associated with Co(2) are not significantly different from each other (C(4)-O(4) = 1.174(5), C(5)-O(5) = 1.157(6) and C(6)-O(6) = 1.162(6) Å). The average Ba-O(DME) distance (2.883(1) Å) is longer than the average Ba-O(THF) distance (2.750(2) Å) in **38** and is consistent with the average Ba-O(DME) distance (2.85(6) (range: 2.72-2.97) Å) for structurally authenticated examples in the literature.¹⁹ The average Ba-O(isocarbonyl) distance of 2.739(2) Å in **38** is increased relative to that in **37** (2.723(4) Å).

Evidently dissolving **37** in DME leads to complete substitution of the THF ligands for the bidentate DME ligands. Given the monomeric nature of **37** and the steric protection around the barium centre, it is unsurprising that dimerisation, let alone metal-metal bonding, is not observed for **38**. Indeed, the Ba...Co distances are increased compared to those for **37**. This is comparable with the transformation of [CaFp₂(THF)₃]₂ (**3**) to [CaFp₂(DME)₃]₂ (**4**) as discussed in Chapter Two.

4.7 Interaction of the [Co(CO)₃(PCy₃)]⁻ anion with Ln²⁺ and Ln³⁺ cations

Reaction of **4.18** in THF with an excess of Sm/Hg afforded Sm{Co(CO)₃(PCy₃)₂(THF)₆} (**28**) as a green solid. Green diffraction-quality crystals of **28** were grown from a concentrated THF solution at 5 °C. The molecular structure and selected distances and angles are shown in Figure 4.22 and Table 4.12.

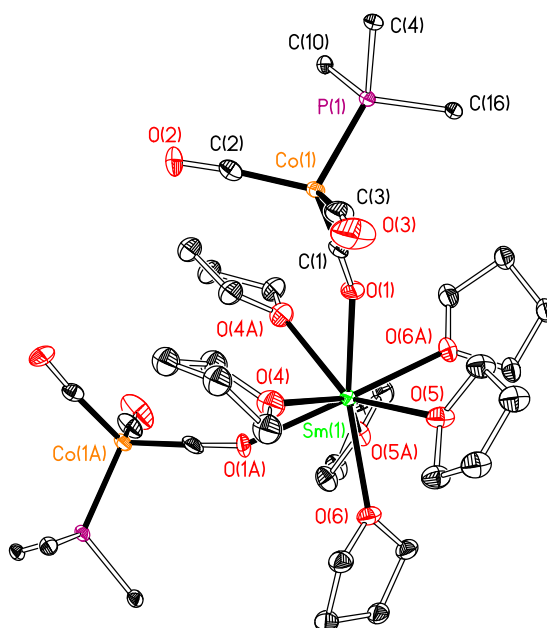


Figure 4.22. Displacement ellipsoid plot (20% probability) of $\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_6$ (**28**). H atoms and cyclohexyl methylene carbons omitted for clarity. Atoms carrying the suffix “A” are related to their counterparts by the symmetry operator $1-x, y, \frac{1}{2}-z$.

Table 4.12. Selected distances (Å) and angles (°) for $\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_6$ (**28**).

Sm(1)···Co(1)	5.3135(11)	Sm(1)-O(1)	2.543(5)
Sm(1)-O(4)	2.579(7)	Sm(1)-O(5)	2.702(6)
Sm(1)-O(6)	2.558(5)	P(1)-Co(1)	2.2016(18)
Co(1)-C(1)	1.700(10)	Co(1)-C(2)	1.739(8)
Co(1)-C(3)	1.750(10)	C(1)-O(1)	1.206(11)
C(2)-O(2)	1.157(10)	C(3)-O(3)	1.152(13)
O(4)-Sm(1)-O(4A)	91.1(4)	O(4)-Sm(1)-O(6A)	142.8(2)
O(4A)-Sm(1)-O(5)	142.8(2)	O(5)-Sm(1)-O(5A)	123.3(3)
O(5A)-Sm(1)-O(6)	72.0(2)	O(6)-Sm(1)-O(6A)	104.8(3)
P(1)-Co(1)-C(1)	106.0(3)	P(1)-Co(1)-C(2)	105.0(2)
P(1)-Co(1)-C(3)	110.8(3)	C(1)-Co(1)-C(2)	112.5(4)
C(1)-Co(1)-C(3)	110.3(5)	C(2)-Co(1)-C(3)	112.0(5)

The Sm(II) centre is eight-coordinate with face-capped trigonal prismatic geometry, with six coordinated THF molecules and two Sm(μ -OC)Co isocarbonyl linkages. The Sm(1)⋯Co(1) (5.3135(11) Å) distance exceeds the sum of the respective covalent radii (3.24(9) Å).⁷ Consistent with this, the geometry at the cobalt centres is approximately tetrahedral and the sum of the OC–Co(1)–P(1) angles is 321.8(5) °.

C(1)O(1) bound to Co(1) is involved in Sm(μ -OC)Co isocarbonyl bridging. The C(1)–O(1) (1.206(11) Å) and Co(1)–C(1) (1.700(10) Å) distances are longer and shorter, respectively, than the distances associated with C(2)O(2) (C(2)–O(2) = 1.157(10) and Co(1)–C(2) = 1.739(8) Å) and C(3)O(3) (C(3)–O(3) = 1.152(13) and Co(1)–C(3) = 1.750(10) Å), both of which are terminal. The values associated with C(2)O(2) and C(3)O(3) are identical within error. The average Sm–O(THF) distance (2.613(3) Å) is intermediate of that for **35** (2.550(1) Å) and **37** (2.750(2) Å) as expected given the intermediate covalent radius (Sr = 1.95(10), Sm = 1.98(8) and Ba = 2.15(11) Å).⁷ This is also observed with regard to the average M–O(isocarbonyl) distances (Sr: 2.608(1), Sm: 2.543(5), Ba: 2.723(4) Å), similar to that for [Sr{Co(CO)₃(PPh₃)₂}(THF)₅]₂ (**25**), [Sm{Co(CO)₃(PPh₃)₂}(THF)₅]₂ (**27**) and [Ba{Co(CO)₃(PPh₃)₂}(THF)₆]₂ (**26**). Both the average Sm–O(THF) and Sm–O(isocarbonyl) distances are longer in **28** than in **27** (Sm–O(THF) = 2.666(1) and Sm–O(isocarbonyl) = 2.796(2) Å). The Sm–O(THF) distance in **28** compares with the average literature Sm–O(THF) distance of 2.51(7) (range: 2.34–2.69) Å.¹⁹

The similar geometries of **28** and **37** are highly apparent. This is consistent with the similar covalent radii of Ba (2.15(11) Å) and Sm (1.98(8) Å).⁷ The longer Ba(1)⋯Co(1) distance compared to that for Sm(1)⋯Co(1) is expected given these radii. However, ¹H NMR analysis of **28** was consistent with three, as opposed to six, THFs per Sm. Elemental analysis was consistent with further loss of THF under exposure to vacuum.

Dissolving green **28** in benzene, filtering and removing volatiles under reduced pressure afforded Sm{Co(CO)₃(PCy₃)₃}(THF)₃ (**29**) as a red-black solid. Red diffraction-quality crystals of **29** were grown from a concentrated pentane solution at RT. The molecular structure and selected distances and angles are shown in Figure 4.23 and Table 4.13.

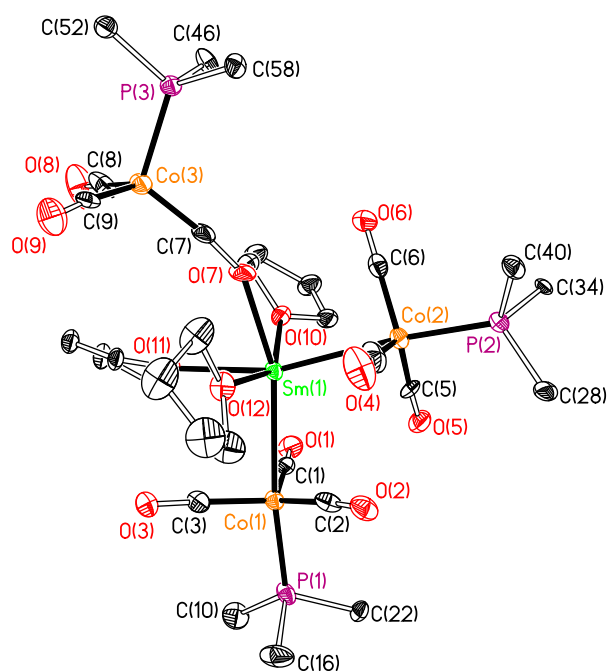


Figure 4.23. Displacement ellipsoid plot (20% probability) of $\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_3(\text{THF})_3$ (**29**). H atoms, pentane of crystallisation, minor disorder and cyclohexyl methylene carbons omitted for clarity.

Table 4.13. Selected distances (Å) and angles (°) for Sm{Co(CO)₃(PCy₃)₃}(THF)₃ (**29**).

Sm(1)-Co(1)	2.9541(10)	Sm(1)-Co(2)	2.8969(9)
Sm(1)···Co(3)	5.0582(11)	Sm(1)-O(7)	2.346(4)
Sm(1)-O(10)	2.450(4)	Sm(1)-O(11)	2.452(4)
Sm(1)-O(12)	2.445(4)	P(1)-Co(1)	2.2256(17)
Co(1)-C(2)	1.770(8)	Co(1)-C(2)	1.770(8)
Co(1)-C(3)	1.749(7)	P(2)-Co(2)	2.2231(18)
Co(2)-C(4)	1.755(10)	Co(2)-C(5)	1.732(7)
Co(2)-C(6)	1.770(8)	P(3)-Co(3)	2.2130(17)
Co(3)-C(7)	1.722(7)	Co(3)-C(8)	1.787(12)
Co(3)-C(9)	1.729(9)	C(1)-O(1)	1.174(8)
C(2)-O(2)	1.144(8)	C(3)-O(3)	1.151(8)
C(4)-O(4)	1.143(10)	C(5)-O(5)	1.157(8)
C(6)-O(6)	1.142(8)	C(7)-O(7)	1.203(8)
C(8)-O(8)	1.119(10)	C(9)-O(9)	1.170(9)
Co(1)-Sm(1)-Co(2)	106.10(3)	Co(1)-Sm(1)-O(7)	162.23(11)
Co(2)-Sm(1)-O(7)	89.44(12)	Co(2)-Sm(1)-O(10)	89.60(10)
O(12)-Sm(1)-Co(2)	104.77(11)	O(10)-Sm(1)-O(11)	75.50(13)
O(11)-Sm(1)-O(12)	84.68(14)	P(1)-Co(1)-C(1)	98.98(19)
P(1)-Co(1)-C(2)	97.4(2)	P(1)-Co(1)-C(3)	100.6(2)
P(2)-Co(2)-C(4)	97.8(3)	P(2)-Co(2)-C(5)	97.4(2)
P(2)-Co(2)-C(6)	100.6(2)	P(3)-Co(3)-C(7)	110.9(2)
P(3)-Co(3)-C(8)	104.1(3)	P(3)-Co(3)-C(9)	107.3(2)
C(1)-Co(1)-C(2)	124.1(3)	C(3)-Co(1)-C(1)	113.6(3)
C(2)-Co(1)-C(3)	115.2(3)	C(4)-Co(2)-C(5)	125.2(4)
C(6)-Co(2)-C(4)	114.8(4)	C(5)-Co(2)-C(6)	113.4(3)
C(7)-Co(3)-C(8)	112.1(4)	C(9)-Co(3)-C(7)	111.5(4)
C(8)-Co(3)-C(9)	110.6(4)		

The geometry at the six-coordinate Sm(1) centre is approximately octahedral, with three coordinated THFs, one Sm(μ -OC)Co(3) isocarbonyl linkage and direct bonds to Co(1) and Co(2) to give a monomeric structure. Analysis of the Sm $\cdots$ Co distances (Sm(1)-Co(1) = 2.9541(10), Sm(1)-Co(2) = 2.8969(9) and Sm $\cdots$ Co(3) = 5.0582(11) Å) shows that the isocarbonyl linked Co(1) $\cdots$ Sm(3) separation is considerably greater than the sum of the respective covalent radii (3.24(9) Å).⁷ However, the former distances are consistent with direct Co-Sm interactions. The geometries at Co(1) and Co(2) are approximately trigonal bipyramidal whereas the geometry at Co(3) is approximately tetrahedral. The sum of the OC-Co(1)-P(1) (297.0(4) °) and OC-Co(2)-P(2) (295.8(4) °) angles are smaller than those observed in **31** or **32** which also have direct metal-metal interactions. The sum of the OC-Co(3)-P(3) (322.3(4) °) angles is notably larger and is close to that for **28** (OC-Co(1)-P(1) = 321.8(5) °). There is a decrease in the Sm $\cdots$ Co distances going from **28** to **29**. Also, the average Sm-O(THF) (2.449(2) Å) and Sm-O(isocarbonyl) (2.346(4) Å) distances for **29** are shorter than those for **28** (Sm-O(THF) = 2.613(3) and Sm-O(isocarbonyl) = 2.543(5) Å). The structural change that comes about and subsequent decrease in these distances can be considered a consequence of the change from Sm²⁺ to Sm³⁺.³² As with **28**, ¹H NMR and elemental analysis of the bulk material was consistent with this material readily losing THF when manipulated in its absence or as a result of prolonged exposure to vacuum.

Given the lack of involvement of the carbonyl groups bound to Co(1) (C(1)-O(1) = 1.174(8), Co(1)-C(1) = 1.715(8), C(2)-O(2) = 1.144(8), Co(1)-C(2) = 1.770(8), C(3)-O(3) = 1.151(8) and Co(1)-C(3) = 1.749(7) Å) in Sm(μ -OC)Co isocarbonyl bridging, it is unsurprising that the C-O distances associated with C(1)O(1), C(2)O(2) and C(3)O(3) are identical within error. However, the Co(1)-C(1) distance is shorter than that for Co(1)-C(2). For Co(2) (C(4)-O(4) = 1.143(10), Co(2)-C(4) = 1.755(10), C(5)-O(5) = 1.157(8), Co(2)-C(5) = 1.732(7), C(6)-O(6) = 1.142(8) and Co(2)-C(6) = 1.770(8) Å), the C-O distances are also identical within error whilst the Co(2)-C(6) distance is shorter than that of Co(2)-C(5). Co(3) interacts with Sm(1) *via* a Sm(μ -OC)Co isocarbonyl linkage involving C(7)O(7) (C(7)-O(7) = 1.203(8) Å). As expected, this results in a longer C-O distance relative to that for the terminal C(8)O(8) (C(8)-O(8) = 1.119(10) Å) and C(9)O(9) (C(9)-O(9) = 1.170(9) Å) bound to Co(3) or compared to any of the C-O carbonyl distances associated with Co(1) or

Co(2). Whilst Co(3)-C(7) (1.722(7) Å) is shorter than Co(3)-C(8) (1.787(12) Å) as expected, it is the same as Co(3)-C(9) (1.729(9) Å) within error.

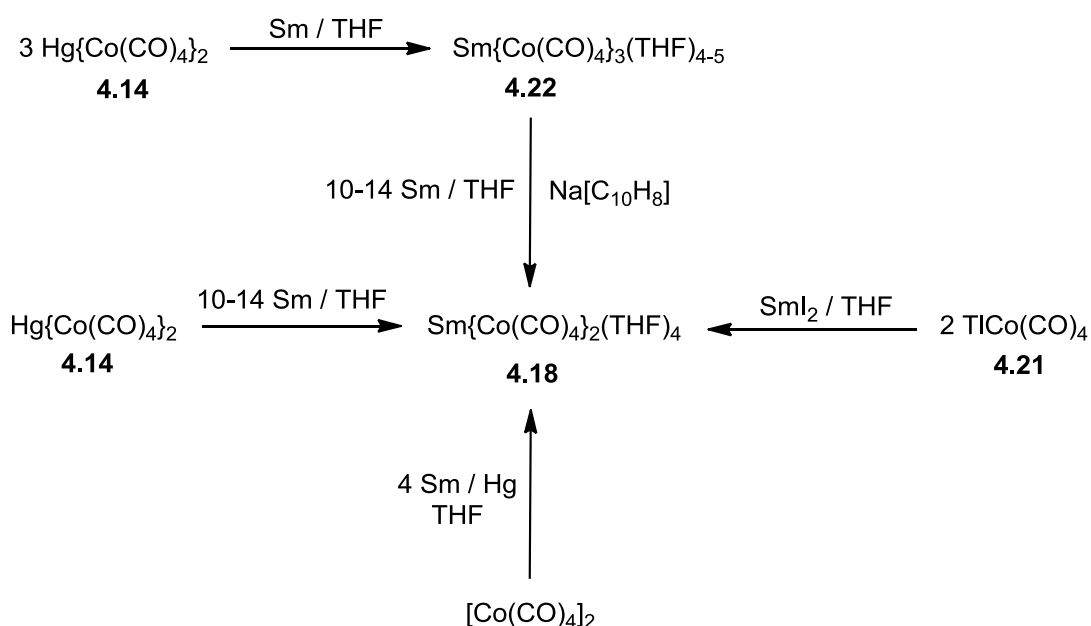
Compound **29** represents the first example of a structurally authenticated complex with a direct bond between Co and Sm. More substantially, it is the first example of a direct Co-Ln interaction, the only other *3d* element to do so being Fe. Only one other structurally authenticated complex is known with a direct bond between Sm and any of the transition metals, namely Kempe's Sm(Cp₂Re)₃.³³ The Sm-Re distances (2.9600(10)-2.9809(10) Å) are slightly longer than the Sm-Co distances in **29** (2.9541(10)-2.8969(9) Å) consistent with the larger covalent radius of Re (1.51(7) Å) *vs* Co (1.26(3) Å).⁷ However, one might have expected a greater difference in these distances given the covalent radius of Re is 0.25(8) Å greater than that of Co.⁷

Compound **28** apparently readily disproportionates to give **29** when manipulated in a non-donor solvent. The reduced co-product in the disproportionation reaction was not identified, this may be elemental Sm. Unfortunately, ³¹P{¹H} NMR spectroscopy was found to be unreliable as a consequence of the paramagnetic Sm(II) and Sm(III) centres. To further investigate the disproportionation of **28** to **29**, the reaction of SmI₂ with [K{Co(CO)₃(PCy₃)(THF)₂}]_x (**33**) in THF was performed. The blue solution, characteristic of SmI₂(THF)_x, was maintained after 24 h.³⁴ Removal of volatiles under reduced pressure gave a green solid. IR analysis of this material (Nujol mull) was consistent with a mixture of **28** and unreacted **33**. The material was dissolved in benzene to give a dark red-purple solution. Filtration of the solution and removal of volatiles under reduced pressure gave a dark red-black solid with an IR spectrum consistent with that for **29**. Importantly, this confirms that **29** can be derived from an unambiguous Sm(II) source as well as that of the **28**, for which elemental analysis of the bulk material consistent with the structure could not be obtained.

These observations serve to reinforce those for polymeric [Sm{Co(CO)₃(PCy₃)₂(THF)₅}]_x (**27**), which underwent a colour change under vacuum and elemental analysis of the bulk material was consistent with the loss of THF. As mentioned, this change may be the result of a switch from Sm(II) to Sm(III) with the formation of a co-product of disproportionation.

The observations for **27**, **28** and **29** are supported by the independent findings of Beletskaya and Evans for non-metal-metal bonded Sm...Co complexes. Beletskaya *et*

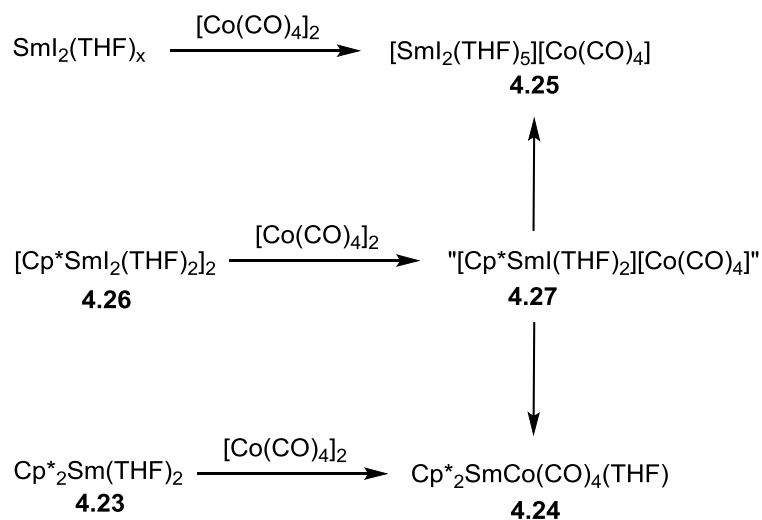
al. synthesised $\text{Ln}\{\text{Co}(\text{CO})_4\}_2(\text{THF})_{3-5}$ complexes, where $\text{Ln} = \text{Sm}$ (**4.18**), Eu (**4.19**) and Yb (**4.20**), *via* the reaction of $\text{Hg}[\text{Co}(\text{CO})_4]_2$ (**4.14**) with an excess of elemental Ln in THF. An alternative synthesis by reaction of the divalent LnI_2 with $\text{TiCo}(\text{CO})_4$ (**4.21**) was also successful. From both routes the products were afforded as solvates, where attempted removal of all coordinated THF led to decomposition. Solubility in aliphatic solvents was not achieved. Further studies showed that reaction of $[\text{Co}(\text{CO})_4]_2$ with Sm or Yb amalgam also afforded the heterobimetallic species **4.18** and **4.20**. Variation of the number of equivalents of Sm or Yb used in these reactions determined whether the divalent or trivalent Ln product was observed. The divalent complexes could also be formed through reduction of the corresponding trivalent complex, for example $\text{Sm}\{\text{Co}(\text{CO})_4\}_3(\text{THF})_{4-5}$ (**4.22**), with the respective elemental Ln or use of Na-naphthalene. These reactions are depicted in Scheme 4.1. The authors claimed the direct interaction of the Ln and Co metal centres in these species. However, no crystallographic evidence was provided, only IR and UV spectroscopy and the aforementioned redox behavior.^{35, 36}



Scheme 4.1. Synthesis of $\text{Sm}\{\text{Co}(\text{CO})_4\}_2(\text{THF})_4$ (**4.18**) *via* various routes.^{35, 36}

Evans *et al.* reacted $[\text{Co}(\text{CO})_4]_2$ with the divalent Sm complex $\text{Cp}^*_2\text{Sm}(\text{THF})_2$ (**4.23**) to form trivalent $\text{Cp}^*_2\text{SmCo}(\text{CO})_4(\text{THF})$ (**4.24**). Reaction of $[\text{Co}(\text{CO})_4]_2$ with $\text{SmI}_2(\text{THF})_x$ in THF gave $[\text{SmI}_2(\text{THF})_5][\text{Co}(\text{CO})_4]$ (**4.25**). Diffraction-quality crystals of **4.24** grown from THF confirmed the complex to exist as discrete $[\text{SmI}_2(\text{THF})_5]^+$ and $[\text{Co}(\text{CO})_4]^-$ ions with no $\text{Sm}(\mu\text{-OC})\text{Co}$ isocarbonyl linkage. Reaction of

$[\text{Co}(\text{CO})_4]_2$ with $[\text{Cp}^*\text{SmI}_2(\text{THF})_2]_2$ (**4.26**) resulted in the postulated formation of $[\text{Cp}^*\text{SmI}(\text{THF})_2][\text{Co}(\text{CO})_4]$ (**4.27**) and rapid disproportionation to **4.24** and **4.25**, as illustrated in Scheme 4.2.³⁴



Scheme 4.2. Reduction of $[\text{Co}(\text{CO})_4]_2$ by divalent Sm complexes.³⁴

Reaction of **4.18** in THF with an excess of Eu/Hg afforded $[\text{Eu}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (**36**) as a toluene-soluble white solid in 75% isolated yield. Diffraction-quality crystals were grown from a concentrated pentane solution. A section of the polymeric structure is shown in Figure 4.24, the asymmetric unit in Figure 4.25 and selected distances and angles in Table 4.14.

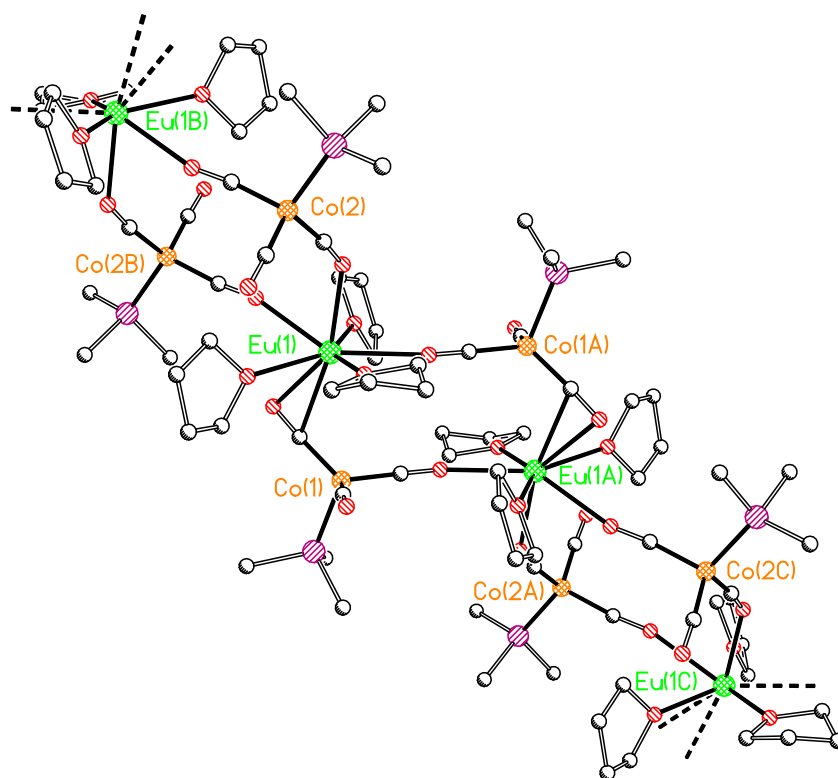


Figure 4.24. Ball and stick plot (arbitrary radius) of a section of the $[\text{Eu}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (**36**) infinite chain. H atoms and cyclohexyl methylene carbons omitted for clarity. Symmetry related atoms are related to their counterparts by the operators “A” = $1-x, 2-y, -z$; “B” = $1-x, 1-y, -z$; “C” = $x, 1+y, z$.

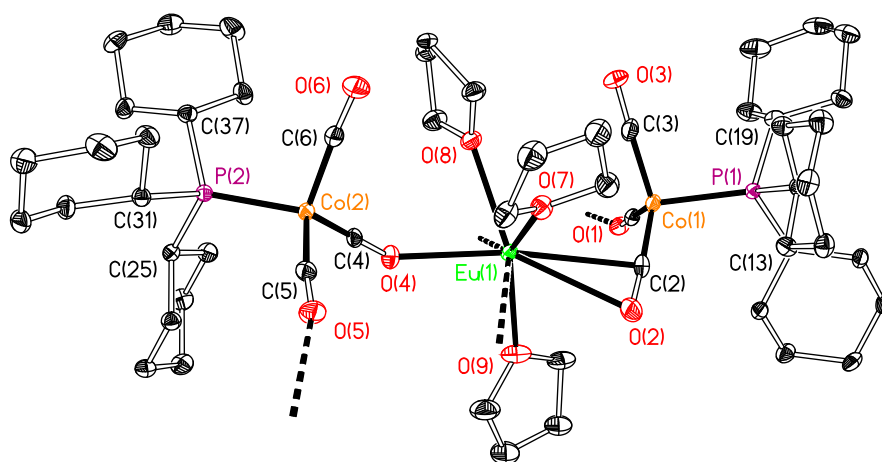


Figure 4.25. Displacement ellipsoid plot (25% probability) of the asymmetric unit of $[\text{Eu}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (**36**). H atoms omitted for clarity.

Table 4.14. Selected distances (Å) and angles (°) for [Eu{Co(CO)₃(PCy₃)₂(THF)₃]_x (**36**).

Eu(1)···Co(1)	3.5551(5)	Eu(1)···Co(1A)	5.4857(6)
Eu(1)···Co(2)	5.0264(5)	Eu(1)···Co(2B)	5.4798(5)
Eu(1)-O(1A)	2.635(3)	Eu(1)-O(4)	2.583(3)
Eu(1)-O(5B)	2.606(3)	Eu(1)-O(7)	2.544(3)
Eu(1)-O(8)	2.553(2)	Eu(1)-O(9)	2.576(3)
Eu(1)···O(2)	2.916(3)	Eu(1)···C(2)	2.885(3)
P(1)-Co(1)	2.2087(9)	Co(1)-C(1)	1.728(4)
Co(1)-C(2)	1.739(4)	Co(1)-C(3)	1.753(4)
P(2)-Co(2)	2.2164(9)	Co(2)-C(4)	1.728(4)
Co(2)-C(5)	1.724(4)	Co(2)-C(6)	1.747(4)
C(1)-O(1)	1.178(4)	C(2)-O(2)	1.171(5)
C(3)-O(3)	1.159(5)	C(4)-O(4)	1.184(4)
C(5)-O(5)	1.179(4)	C(6)-O(6)	1.162(5)
Co(1)···Eu(1)-O(4)	162.13(7)	O(1A)-Eu(1)-O(2)	115.86(9)
O(1A)-Eu(1)-O(4)	87.09(9)	O(1A)-Eu(1)-O(5B)	136.94(9)
O(1A)-Eu(1)-O(7)	151.89(9)	O(2)-Eu(1)-O(4)	145.49(9)
O(2)-Eu(1)-O(5B)	69.58(9)	O(4)-Eu(1)-O(5B)	76.08(10)
O(7)-Eu(1)-O(8)	77.63(9)	O(7)-Eu(1)-O(9)	137.33(10)
O(8)-Eu(1)-O(9)	145.03(10)	P(1)-Co(1)-C(1)	106.00(12)
P(1)-Co(1)-C(2)	104.11(12)	P(1)-Co(1)-C(3)	100.23(12)
P(2)-Co(2)-C(4)	112.91(11)	P(2)-Co(2)-C(5)	108.59(12)
P(2)-Co(2)-C(6)	105.33(12)	C(1)-Co(1)-C(2)	113.63(18)
C(3)-Co(1)-C(1)	110.97(17)	C(2)-Co(1)-C(3)	119.73(19)
C(4)-Co(2)-C(5)	109.57(17)	C(6)-Co(2)-C(4)	112.72(17)
C(5)-Co(2)-C(6)	107.46(18)		
^a Hinge angle	161	^b Hinge angle	136
^c Inter-ring angle	61.8		

^a Hinge = (Co(1), C(1), O(1), Co(1A), C(1A), O(1A))-(Co(1), Eu(1), O(1A)). ^b Hinge = (Co(2), C(4), O(4), Co(2B), C(4B), O(4B))-(Co(2B), C(5B), O(5B), Eu(1), O(4)). Maximum deviation from plane = 0.06 Å (O(5B)). ^c Inter-ring angle = (Co(1), C(1), O(1), Co(1A), C(1A), O(1A))-(Co(2), C(4), O(4), Co(2B), C(4B), O(4B)).

In the solid state **36** forms an infinite-chain comprised of twelve-membered rings with $\text{Eu}(\mu\text{-OC})\text{Co}(\eta^1\text{-})$ isocarbonyl linkages that alternate at Eu vertices with rings that are intermediate between the former and an eight-membered ring due to a side-on ($\eta^2\text{-}$) interaction between $\text{Eu}(1)$ and $\text{C}(2)\text{O}(2)$. This interaction was also observed for $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (**35**). In fact, the polymeric structure for **36** is very similar to that for **35**. In both complexes, Sr or Eu is coordinated to three THF ligands and the O-atoms of three terminally ($\eta^1\text{-}$) bound μ -isocarbonyl groups ($\text{OC-Co}(1\text{A}, 2, 2\text{B})$). The marginally different average M-O(THF) and M-O(isocarbonyl) distances for **35** (2.550(1) and 2.608(1) Å) compared to those for **36** (2.558(2) and 2.621(2) Å) are consistent with the slightly larger covalent radius of Eu (1.98(6) Å) compared to Sr (1.95(10) Å).⁷ The average Eu-O(THF) distance in **36** is consistent with the average literature Eu-O(THF) distance of 2.56(6) (range: 2.41–2.70) Å.¹⁹ The coordination spheres of both metals are completed by an unusual side-on ($\eta^2\text{-}$) carbonyl interaction where $\text{Eu}(1)\text{-O}(2) = 2.916(3)$ and $\text{Sr}(1)\cdots\text{O}(2) = 2.879(2)$ Å, and $\text{Sr}(1)\cdots\text{C}(2) = 2.909(2)$ and $\text{Eu}(1)\text{-C}(2) = 2.885(3)$ Å. As discussed, this is unprecedented in alkaline earth chemistry but it is also unknown for lanthanide chemistry. The shorter $\text{Eu}(1)\cdots\text{C}(2)$ and longer $\text{Eu}(1)\cdots\text{O}(1)$ distances appear to be associated with a $\text{Eu}(1)\cdots\text{Co}(1)$ distance (3.5551(5) Å) that is also shorter than that for $\text{Sr}(1)\cdots\text{Co}(1)$ (3.6263(4) Å). Both metal-metal distances are longer than the sum of the respective covalent radii for Co and Sr (3.21(10) Å) or Eu (3.24(7) Å).⁷ However, the sum of the $\text{OC-Co}(1)\text{-P}(1)$ angles is 311.2(1) and 310.3(2) ° for **35** and **36**, respectively, similar to those for the metal-metal bonded Co in $[\text{Yb}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_2$ (**39**, 309.1(2) °) but larger than that in $[\text{Mg}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})]_2$ (**31**, 300.9(1) and 303.2(1) °), $[\text{Ca}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_2]_2$ (**32**, 305.8(2) °) or $\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_3(\text{THF})_3$ (**29**, 297.0(4) and 295.8(4) °). For $\text{Co}(2)$ the sum of the $\text{OC-Co}(2)\text{-P}(2)$ angles is 326.8(2) °, close to the tetrahedral value and that for **35** (326.9(1) °). The slight shortening from $\text{Sr}(1)\cdots\text{Co}(1)$ to $\text{Eu}(1)\cdots\text{Co}(1)$ indicates some residual metal-metal bonding interactions in these complexes, as do the $\Sigma(\text{OC-Co}(1)\text{-P}(1))$ values.

The carbonyl groups bound to $\text{Co}(1)$ are involved in isocarbonyl (η^1) ($\text{C}(1)\text{O}(1)$) and side-on (η^2) ($\text{C}(2)\text{O}(2)$) bridging. $\text{C}(3)\text{O}(3)$, also bound to $\text{Co}(1)$, is a terminal carbonyl group. The $\text{C}(1)\text{-O}(1)$ (1.178(4), $\text{C}(2)\text{-O}(2)$ (1.171(5)) and $\text{C}(3)\text{-O}(3)$ (1.159(5) Å) distances are identical within error. Consistent with this, the $\text{Co}(1)\text{-C}(1)$

(1.728(4)), Co(1)-C(2) (1.739(4)) and Co(1)-C(3) (1.753(4) Å) distances are identical within error. This contrasts with **35** where the Co(1)-C(3) and C(3)-O(3) distances were different from those for the bridging C(2)O(2) and C(3)O(3). Two of the carbonyl groups bound to Co(2), C(4)O(4) (C(4)-O(4) = 1.184(4) and Co(2)-C(4) = 1.728(4) Å) and C(5)O(5) (C(5)-O(5) = 1.179(4) and Co(2)-C(5) = 1.724(4) Å), are involved in isocarbonyl bridging. The C-O distances and the Co-C distances are identical within error. For terminal C(6)O(6) (C(6)-O(6) = 1.162(5) and Co(2)-C(6) = 1.747(4) Å) the C-O distances are identical within error to those for C(4)-O(4) and C(5)-O(5) whereas the Co(2)-C(6) distance is slightly longer than that for Co(2)-C(4) or Co(2)-C(5). The values for C(6)O(6) are identical to those for terminal C(3)O(3) within error. The inability to differentiate between the terminal C(6)O(6) and bridging C(4)O(4) or C(5)O(5) based on these parameters contrasts with **35** where the respective C-O and Co-C distances are different.

Comparing the hinge angles for the twelve-membered rings, they are found to be identical for **35** and **36** (136 °). The hinge angle for the ring involving η^2 -isocarbonyl interactions is also found to be identical for **35** and **36** (161 °). The hinge angle for the eight-membered ring in **31** (155 °) is intermediate of these values. The difference between the hinge angles in **36** is much greater than that in **32** (167 ° and 170 °). The inter-ring angle for **36** (61.8 °) is similar to that for **32** (61.5 °) and greater than that for **35** (58.0 °) or [Eu{Co(CO)₃(PCy₃)₂}(THF)₄]_x (**40**, 56.8 °).

For these systems utilising the [Co(CO)₃PCy₃]⁻ anion, it would appear that the "tipping point" in Ae-TM and divalent Ln-TM occurs with the larger Sr and Eu, such that even the unique side-on (η^2 -) CO ligand bonding competes with direct Ae- or Ln-TM bonding, with Ln-TM bonding being slightly more favoured than for Ae-TM. No structurally authenticated complexes are known with a direct bond between Eu and a transition metal. However, there are examples of direct Eu-Al, Eu-Ga and Eu-Ge bonds.³⁷⁻⁴⁰ Due to the paramagnetic nature of **36** (*f*⁷) it was not possible to study this material by NMR spectroscopy. However, elemental analysis of the bulk material was consistent with the structure of **36** determined by single crystal X-ray diffraction.

This material is stable with respect to disproportionation in contrast to Sm{Co(CO)₃(PCy₃)₂}(THF)₆ (**28**). Indeed, the Eu(II) oxidation state is maintained whether the material is manipulated in a donor or non-donor solvent. Dissolving **36** in

THF and crystallising from a concentrated solution at RT gave the polymeric structure $[\text{Eu}\{\text{Co}(\text{CO})_3(\text{PCy}_3)_2(\text{THF})_4\}_x]$ (**40**), a section of which is shown in Figure 4.26 and the asymmetric unit in Figure 4.27 with selected distances and angles in Table 4.15.

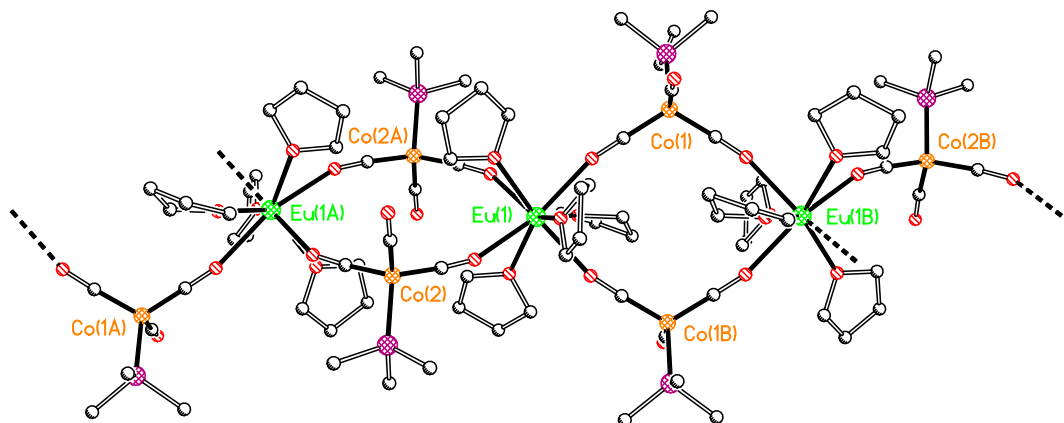


Figure 4.26. Ball and stick plot (arbitrary radius) of a section of the $[\text{Eu}\{\text{Co}(\text{CO})_3(\text{PCy}_3)_2(\text{THF})_3\}_x]$ (**40**) infinite chain. H atoms and cyclohexyl methylene carbons omitted for clarity. Symmetry related atoms are related to their counterparts by the operators “A” = 1-x, -y, 1-z; “B” = -x, 1-y, 1-z.

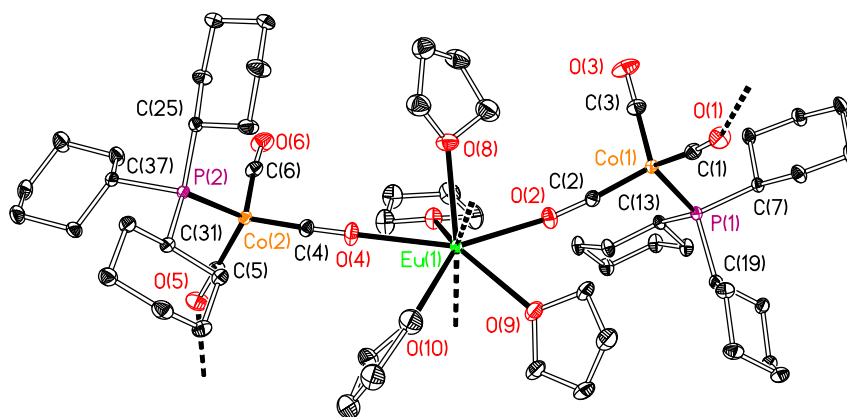


Figure 4.27. Displacement ellipsoid plot (25% probability) of the asymmetric unit of $[\text{Eu}\{\text{Co}(\text{CO})_3(\text{PCy}_3)_2(\text{THF})_4\}_x]$ (**40**). H atoms omitted for clarity.

Table 4.15. Selected distances (Å) and angles (°) for [Eu{Co(CO)₃(PCy₃)₂(THF)₄]_x (**40**).

Eu(1)···Co(1)	5.4198(5)	Eu(1)···Co(1A)	5.3505(5)
Eu(1)···Co(2)	5.3918(5)	Eu(1)···Co(2B)	5.2975(5)
Eu(1)-O(1A)	2.556(2)	Eu(1)-O(2)	2.562(2)
Eu(1)-O(4)	2.589(2)	Eu(1)-O(5B)	2.555(3)
Eu(1)-O(7)	2.623(2)	Eu(1)-O(8)	2.568(3)
Eu(1)-O(9)	2.618(2)	Eu(1)-O(10)	2.595(2)
P(1)-Co(1)	2.2068(8)	Co(1)-C(1)	1.725(3)
Co(1)-C(2)	1.719(3)	Co(1)-C(3)	1.757(3)
P(2)-Co(2)	2.2004(8)	Co(2)-C(4)	1.719(3)
Co(2)-C(5)	1.722(3)	Co(2)-C(6)	1.747(3)
C(1)-O(1)	1.180(4)	C(2)-O(2)	1.191(4)
C(3)-O(3)	1.155(4)	C(4)-O(4)	1.186(4)
C(5)-O(5)	1.184(4)	C(6)-O(6)	1.158(4)
O(1A)-Eu(1)-O(2)	93.70(9)	O(1A)-Eu(1)-O(4)	93.38(9)
O(1A)-Eu(1)-O(5B)	151.65(10)	O(1A)-Eu(1)-O(7)	140.27(9)
O(2)-Eu(1)-O(4)	151.00(9)	O(2)-Eu(1)-O(5B)	90.94(10)
O(4)-Eu(1)-O(5B)	95.99(10)	O(7)-Eu(1)-O(8)	70.70(9)
O(7)-Eu(1)-O(10)	130.18(9)	O(8)-Eu(1)-O(9)	132.02(9)
O(9)-Eu(1)-O(10)	70.14(9)	P(1)-Co(1)-C(1)	109.52(11)
P(1)-Co(1)-C(2)	109.25(11)	P(1)-Co(1)-C(3)	105.33(12)
P(2)-Co(2)-C(6)	111.09(11)	C(1)-Co(1)-C(2)	114.82(15)
C(1)-Co(1)-C(3)	108.51(16)	C(2)-Co(1)-C(3)	108.10(17)
C(4)-Co(2)-C(5)	119.20(16)	C(4)-Co(2)-C(6)	108.06(16)
C(5)-Co(2)-C(6)	104.66(17)		
^a Hinge angle	161	^b Hinge angle	159
^c Inter-ring angle	56.8		

^a Hinge angle = (Co(1), C(1), O(1), Co(1A), C(1A), O(1A))-(Co(1), C(2), O(2), Eu(1), O(1A)). Maximum deviation from plane = 0.06 Å (Co(1)). ^b Hinge angle = (Co(2), C(4), O(4), Co(2B), C(4B), O(4B))-(Co(2), C(5), O(5), Eu(1), O(4B)). Maximum deviation from plane = 0.07 Å (C(5)). ^c Inter-ring angle = (Co(1), C(1), O(1), Co(1A), C(1A), O(1A))-(Co(2), C(4), O(4), Co(2B), C(4B), O(4B)).

In the solid state, **40** forms an infinite chain comprised of twelve-membered rings with four Eu(μ-OC)Co isocarbonyl interactions per Eu. In addition, four THF

molecules are coordinated to each Eu to give a six-coordinate centre with square antiprismatic geometry. The additional THF at Eu(1) disrupts the coordination such that a side on (η^2 -) carbonyl interaction is no longer observed. The Eu(1)···Co distances (Eu(1)···Co(1) = 5.4198(5), Eu(1)···Co(1A) = 5.3505(5), Eu(1)···Co(2) = 5.3918(5) and Eu(1)···Co(2B) = 5.2975(5) Å) are all considerably greater than the sum of the respective covalent radii (3.24(7) Å).⁷ The additional THF of coordination results in increased average Eu–O(THF) distances of 2.601(1) Å for **40** relative to 2.558(2) Å for [Eu{Co(CO)₃(PCy₃)₂(THF)₄]_x (**36**). Both of these are consistent with the average literature Eu–O(THF) distance of 2.56(6) (range: 2.41–2.70) Å.¹⁹ However, the average Eu–O(isocarbonyl) distance is decreased from 2.621(2) for **36** to 2.566(1) Å for **40**. The geometry at Co(1) and Co(2) is approximately tetrahedral. The sum of the OC–Co(1)–P(1) and OC–Co(2)–P(2) angles are 325.1(2) and 324.8(2) °, respectively. These are expectedly similar to the sum of the OC–Co(2)–P(2) (326.8(2)), and somewhat smaller than the sum of the OC–Co(1)–P(1) (310.3(2) °) angles in **36** (326.8(2) °).

The carbonyl groups C(1)O(1) (C(1)–O(1) = 1.178(4), Co(1)–C(1) = 1.728(4) Å) and C(2)O(2) (C(2)–O(2) = 1.171(5) and Co(1)–C(2) = 1.739(4) Å) bound to Co(1) are involved in Eu(μ -OC)Co isocarbonyl bridging. As are C(4)O(4) (C(4)–O(4) = 1.184(4) and Co(2)–C(4) = 1.728(4) Å) and C(5)O(5) (C(5)–O(5) = 1.179(4) and Co(2)–C(5) = 1.724(4) Å) bound to Co(2). The C–O distances associated with these are identical within error. The Co–C distances are also identical within error. C(3)O(3) (C(3)–O(3) = 1.159(5) and Co(3)–C(3) = 1.753(4) Å) bound to Co(1) is a terminal carbonyl group. The C(3)–O(3) distance is slightly shorter than that for C(1)–O(1) and identical within error to that for C(2)–O(2). Consistent with this, the Co(1)–C(3) distance is longer than that for Co(1)–C(2) and identical to that for Co(1)–C(1) within error. C(6)O(6) (C(6)–O(6) = 1.162(5) and Co(2)–C(6) = 1.747(4) Å) bound to Co(2) is also a terminal carbonyl group. The C(6)–O(6) distance is shorter than that for C(4)–O(4) but identical within error to that for C(5)–O(5). The Co(2)–C(6) distance is longer than that for Co(2)–C(4) or Co(2)–C(5) as expected. The distances associated with C(3)O(3) and C(6)O(6) are identical within error.

The hinge angles for the twelve-membered rings in **40** are very similar (159 and 161 °). They are considerably closer to that for the ring in **36** that is formed through η^2 -carbonyl interactions (161 °), rather than comprised purely of Eu(μ -OC)Co

isocarbonyl linkages to give a twelve-membered ring (136 °). The inter-ring angle (56.8 °) is similar to those analysed for other structures in this section.

Reduction of **4.18** in THF with an excess of Yb/Hg afforded the toluene-soluble product $[\text{Yb}\{\text{Co}(\text{CO})_3\text{PCy}_3\}_2(\text{THF})_3]_2$ (**39**) in 51% isolated yield. Diffraction-quality crystals were grown from a concentrated pentane solution. The molecular structure and selected distances and angles are shown in Figure 4.28 and Table 4.16.

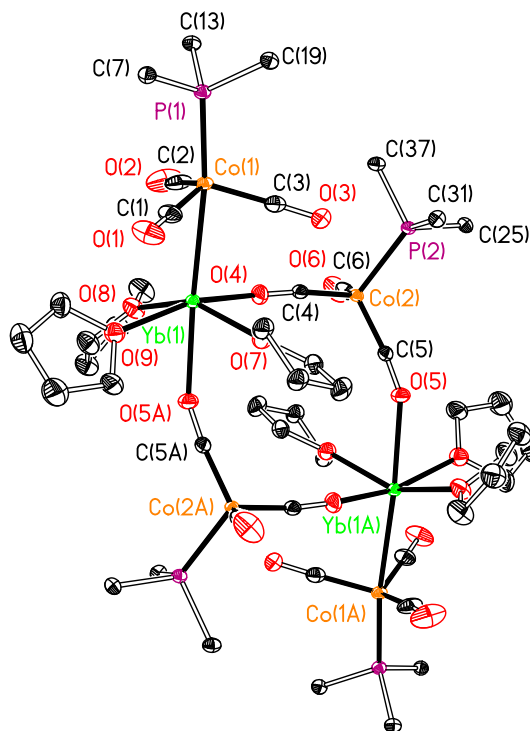


Figure 4.28. Displacement ellipsoid plot (20% probability) of $[\text{Yb}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_2$ (**39**). H atoms and cyclohexyl methylene carbons and minor disorder omitted for clarity. Atoms carrying the suffix “A” are related to their counterparts by the symmetry operator $2-x, -y, 1-z$.

Table 4.16. Selected distances (Å) and angles (°) for [Yb{Co(CO)₃(PCy₃)₃}₂(THF)₃]₂ (**39**).

Yb(1)-Co(1)	2.9893(4)	Yb(1)···Co(2)	5.2258(4)
Yb(1)···Co(2A)	5.1106(4)	Yb(1)-O(4)	2.3885(18)
Yb(1)-O(5A)	2.5005(17)	Yb(1)-O(7)	2.3912(17)
Yb(1)-O(8)	2.4128(17)	Yb(1)-O(9)	2.4258(18)
Co(1)-P(1)	2.2192(6)	Co(1)-C(1)	1.749(3)
Co(1)-C(2)	1.760(3)	Co(1)-C(3)	1.754(3)
Co(2)-P(2)	2.2222(6)	Co(2)-C(4)	1.719(2)
Co(2)-C(5)	1.725(2)	Co(2)-C(6)	1.761(3)
C(1)-O(1)	1.160(4)	C(2)-O(2)	1.152(4)
C(3)-O(3)	1.158(4)	C(4)-O(4)	1.183(3)
C(5)-O(5)	1.175(3)	C(6)-O(6)	1.153(4)
Co(1)-Yb(1)-O(4)	95.60(5)	Co(1)-Yb(1)-O(5A)	170.39(4)
O(4)-Yb(1)-O(5A)	88.81(7)	O(4)-Yb(1)-O(7)	88.54(7)
O(4)-Yb(1)-O(9)	163.91(7)	O(7)-Yb(1)-O(8)	152.13(7)
O(8)-Yb(1)-O(9)	86.85(7)	P(1)-Co(1)-Yb(1)	172.95(2)
P(1)-Co(1)-C(1)	99.62(9)	P(1)-Co(1)-C(2)	102.80(9)
P(1)-Co(1)-C(3)	106.63(9)	P(2)-Co(2)-C(4)	111.09(8)
P(2)-Co(2)-C(5)	111.40(8)	P(2)-Co(2)-C(6)	103.05(8)
C(1)-Co(1)-C(2)	124.97(15)	C(3)-Co(1)-C(1)	109.30(13)
C(2)-Co(1)-C(3)	111.15(15)	C(4)-Co(2)-C(5)	105.68(11)
C(6)-Co(2)-C(4)	112.48(12)	C(5)-Co(2)-C(6)	113.30(12)
^a Hinge angle	145		

^a Hinge angle = (Co(2), C(5), O(5), Co(2A), C(5A), O(5A))-(Co(2), C(4), O(4), Yb(1), O(5A)). Maximum deviation from plane = 0.232 Å (O(4)).

The structure of **39** is dimeric in the solid state with each six-coordinate Yb centre having distorted octahedral geometry. Each Yb is coordinated to three THF ligands and three [Co(CO)₃(PCy₃)₃][−] anions. Two of these interactions occur *via* Yb(μ-OC)Co isocarbonyl linkages and one by direct interaction of Yb(1)-Co(1) external to the ring. The Yb(1)-Co(1) distance (2.9893(4) Å) is consistent with that expected for a direct

interaction based on the sum of the respective covalent radii (3.13(9) Å).⁷ The distances associated with the isocarbonyl bridged interactions to Co(2) and Co(2A) are longer than that expected for a direct interaction (Yb(1)⋯Co(2) = 5.2258(4) and Yb(1)⋯Co(2A) = 5.1106(4) Å). The geometry at Co(1) is approximately trigonal bipyramidal whereas that at Co(2) is tetrahedral. As expected, the sum of the OC–Co(1)–P(1) angles (309.1(2) °) is somewhat lower than that for OC–Co(2)–P(2) (325.5(1) °).

For Co(1) the carbonyl group C–O distances (C(1)–O(1) = 1.160(4), C(2)–O(2) = 1.152(4) and C(3)–O(3) = 1.158(4) Å) are identical within error. Also the Co(1)–C distances (Co(1)–C(1) = 1.749(3), Co(1)–C(2) = 1.760(3) and Co(1)–C(3) = 1.754(3) Å) are identical within error. This is expected given all three carbonyl groups are terminal. This contrasts with the carbonyl groups bound to Co(2). C(4)O(4) and C(5)O(5) are bridging whereas C(6)O(6) is terminal. This leads to a lengthening of the C(4)–O(4) (1.183(3) and C(5)–O(5) (1.175(3) Å) bonds relative to C(6)–O(6) (1.153(4) Å). As expected the Co(2)–C(4) (1.719(2) Å) and Co(2)–C(5) (1.725(2) Å) distances are longer than for Co(2)–C(6) (1.761(3) Å). Indeed, the distances associated with C(6)O(6) are identical within error to those for the three terminal carbonyl groups bound to Co(1).

The solid state structure of **39** contains features reminiscent of both [Mg{Co(CO)₃(PCy₃)₂(THF)}₂] (31) and [Ca{Co(CO)₃(PCy₃)₂(THF)}₂]_x (32). Unsurprisingly the Mg–Co distances (Mg(1)–Co(1) = 2.6163(6) and Mg(1)–Co(2) = 2.5427(6) Å) are shorter than the Yb–Co distance (2.9893(4) Å). The average Yb–O(THF) and Yb–O(isocarbonyl) distances are longer for **39** (2.410(1) and 2.443(1) Å) than **32** (2.383(2) and 2.346(2) Å). However, the Yb–Co distance is shorter than the Ca–Co distance (3.0450(9) Å), despite the covalent radius of Yb (1.87(8) Å) being larger than that of Ca (1.76(10) Å). This is consistent with stronger Ln–TM bonding compared to Ae–TM in analogous complexes, as observed for [Eu{Co(CO)₃(PCy₃)₂(THF)}₃]_x (36) compared to [Sr{Co(CO)₃(PCy₃)₂(THF)}₃]_x (35) and [YbFp₂(THF)₃]₂ (6) compared to [CaFp₂(THF)₃]₂ (3). The average Yb–O(THF) distance in **39** is consistent with that for structurally authenticated complexes of 2.38(6) (range: 2.21–2.56) Å.¹⁹ As discussed for Yb{Co(CO)₃(PCy₃)₂(THF)}₅ (30), literature examples of Yb(μ-OC)Co are known, including Shore's polymeric [Yb{Co(CO)₄}₂(py)₄]_x (4.15) and [Yb{Co(CO)₄}₂(THF)₂]_x (4.16) with average Yb–

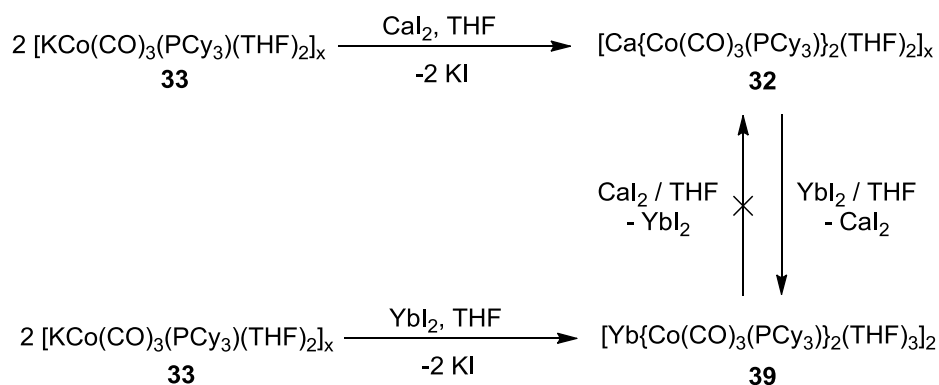
O(isocarbonyl) distances of 2.543(3) and 2.526(3) Å, respectively.^{25, 41} The hinge angle in **39** (144 °) is smaller than that measured for the twelve-membered ring in **32** and is therefore closer to that for the twelve-membered rings in **35** and **36**. It is also similar to that observed for the eight-membered ring in **6** (145 °, Chapter Two).

It is apparent that the solid state structure of **39** does not afford an isostructural structure with that of **32** when crystallised under comparable conditions, in contrast with the observations for **3** and **6**. Indeed **39** is dimeric whereas **32** is polymeric. One can consider the third THF to give coordinative saturation at the Yb centre inhibiting isocarbonyl bridging to a neighbouring Yb{Co(CO)₃(PCy₃)₂(THF)₂} unit. Despite these differences, both possess twelve-membered rings comprised exclusively of isocarbonyl bridging between the metal centres. Comparison of these shows their spans to be similar for Ca(1)⋯Co(2) (5.2266(10) Å) and Yb(1)⋯Co(2) (5.2258(4) Å). However, the Ca(1)⋯Co(2B) distance (5.0919(9) Å) is shorter than that for Yb(1)⋯Co(2A) (5.1106(4) Å).

Compound **39** bears the first structurally authenticated example of a Co-Yb bond, and following Sm{Co(CO)₃(PCy₃)₂(THF)₃} (29), the second example of a Co-Ln bond. However, as previously discussed, Yb-TM bonds are known in the literature, for example, Kempe's Cp₂YbReCp₂ (**1.81**, 2.897(2) Å), Yb(Cp₂Re)₂(THF)₂ (**1.90**, 3.0287(7) Å), [YbRp₂(THF)₂]_x (**1.91**, 3.1808(7) Å) and YbRp₂(^tBu₃py)₃ (**1.92**, 3.0626(4) Å) show a variation in Re- and Ru-Yb distances, where the metal-metal distance for [Cp₂YbReCp₂] is actually shorter than that for **39** (2.9892(4) Å). Shore's [{(MeCN)₃YbFe(CO)₄}]₂·MeCN]_x (**1.73**) and [(MeCN)₃YbFe(CO)₄]_x (**1.75**) have average Yb-Fe distances of 3.010(1) and 3.046(1) Å, respectively, longer than for the Yb-Co distance in **39** as expected. The Yb-Co distance in **39** is identical within error to that for **6** and is similar to that observed for two of the Yb-Fe interactions for {Yb(NacNac)(Fp)(THF)}₂(μ-YbFp₂) (**19**, Yb(1)-Fe(1) = 2.9961(5) and Yb(1)-Fe(2) = 2.9758(5) Å) but shorter than the remaining interactions (Yb(1)-Fe(3) = 3.1702(5) and Yb(1)-Fe(4) = 3.1498(5) Å).

The Yb-Co distance in **39** (2.9893(4) Å) is longer than the Sm-Co distances in **29** (Sm(1)-Co(1) = 2.9541(10) and Sm(1)-Co(2) = 2.8969(9) Å). This is consistent with the difference in the oxidation state of the lanthanide ions (Yb²⁺ vs. Sm³⁺), where the six-coordinate effective ionic radii for Yb²⁺ is 1.02 and that for Sm³⁺ is 0.958 Å.³²

Compound **39** was also synthesised *via* salt metathesis. Thus the reaction of $[\text{K}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}(\text{THF})_2]_x$ (**33**) with YbI_2 afforded **39** as a yellow solid in 58% isolated yield. Alternatively, it was found that reaction of $[\text{Ca}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_2]_x$ (**32**) with YbI_2 in THF also gave **39**, in 51% isolated yield. The attempted synthesis of **32** by the analogous reaction of **39** with CaI_2 was unsuccessful (Scheme 4.3).



Scheme 4.3. Synthesis of $[\text{Yb}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_2$ (**39**) *via* salt metathesis.

As with **36** and **40**, **39** was stable with respect to disproportionation in both THF and non-donor solvents. Compounds **30**, **36** and **39** contain Ln cations that are stable in the +2 oxidation state compared to their respective Sm counterparts **27** and **28** which readily disproportionate to give species containing Sm(III). This is unsurprising when one considers that Eu(II) and Yb(II) have half ($4f^7$) and full ($4f^{14}$) outer shell electronic configurations, respectively. The additional stability associated with these electronic configurations compared to that for Sm(II) ($4f^6$) results in a greater third ionisation energy for Eu and Yb compared to Sm (Eu = 2404, Sm = 2260, Yb = 2415 kJ mol^{-1}).⁴²

Following the synthesis of **28**, **29**, **36** and **39**, the formation and investigation of further Ln-Co complexes was sought. Numerous attempts to synthesise $[\text{La}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_3(\text{THF})_x]_y$ were unsuccessful, including the amalgam reduction of **4.18** that was successful for the Ae metals Mg to Ba and Ln metals Sm, Eu and Yb. Alternative attempts included the reaction of **33** with LaCl_3 in THF, which showed no reaction after 16 h at RT and exhibited decomposition on heating to 50 °C. This lack of reactivity at RT is likely to be a consequence of the poor solubility of LaCl_3 in THF. Attempts to dissolve elemental La in $\text{NH}_3(\text{L})$ were also unsuccessful and reactivity of this mixture with **4.18** was not observed, ruling out the use of ammonia

as an alternative to mercury for the activation of the metal.

Similarly, attempts to synthesise the Lu derivative $[\text{Lu}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_3(\text{THF})_x]_y$ were unsuccessful. As with attempts to synthesise the La analogue, use of an amalgam reduction of **4.18** was unsuccessful. This was unsurprising given the visible lack of interaction of elemental Lu with Hg. This is consistent with the high enthalpy change of fusion and melting point for elemental lutetium of $126 \text{ J g}^{-1} \text{ K}^{-1}$ and 1663°C , respectively, the highest for the lanthanides.⁴³ The combination of **33** with LuCl_3 in THF also gave no reaction and decomposition following heating of the mixture to 50°C . Insolubility of freshly cut elemental Lu in $\text{NH}_3(\text{L})$ was also observed.

Although scarce, structurally authenticated literature examples of heterobimetallic complexes with direct interactions between La or Lu and other metals do exist.^{33, 44} Kempe *et al.* have shown that Cp_2ReH reacts with $[\text{Ln}(\text{CH}\{\text{SiMe}_3\}_2)_3]$ (where Ln = La, Sm or Lu) to form $\text{Ln}(\text{ReCp}_2)_3$ (**1.83-1.85**) bearing the respective Ln-Re bonds. Note that both reactions and crystallisations were carried out in benzene. Evidently, the alkylated forms of La or Lu in these examples enabled effective reactivity to be achieved.

4.8 Interaction of the $[\text{Co}(\text{CO})_3(\text{PCy}_3)]^-$ anion with Group 1 cations

Whilst they do not exist in the divalent state, alkali metals form hard Lewis acidic cations,⁴⁵ as with the Ae and Ln metals, and structurally authenticated examples of their salts of TM complexes are prevalent in the literature.¹⁹ For this reason, the solid state structures of $\text{Na}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}(\text{THF})_5$ (**41**) and $[\text{K}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}]_x$ (**33**) were investigated.

Reaction of **4.18** in THF with an excess of Na/Hg afforded $\text{Na}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}(\text{THF})_5$ (**41**) as a white solid in 70% isolated yield. Prior to this research there was one literature report of $\text{Na}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}$ (**4.28**).⁴⁶ The material was neither fully characterised nor structurally authenticated and its preparation cited an analogous procedure for the synthesis of $\text{Na}\{\text{Co}(\text{CO})_3(\text{PR}_3)\}$ (R = PPh_3 (**4.29**) or POPh_3 (**4.30**)) using Na/Hg.⁴⁷ Diffraction-quality crystals of **41** were grown from a concentrated THF solution. The molecular structure and selected distances and angles are shown in Figure 4.29 and Table 4.17.

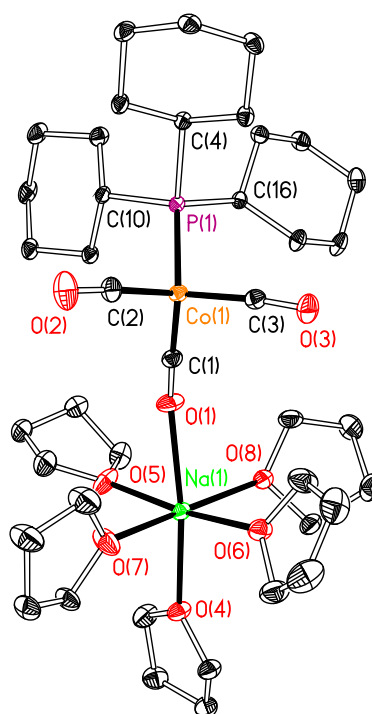


Figure 4.29. Displacement ellipsoid plot (20% probability) of $\text{Na}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}(\text{THF})_5$ (**41**). H atoms omitted for clarity.

Table 4.17. Selected distances (Å) and angles (°) for $\text{Na}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_5$ (**41**).

Na(1)···Co(1)	5.0931(9)	Na(1)-O(1)	2.360(2)
Na(1)-O(4)	2.3778(19)	Na(1)-O(5)	2.367(2)
Na(1)-O(6)	2.375(2)	Na(1)-O(7)	2.335(2)
Na(1)-O(8)	2.397(2)	P(1)-Co(1)	2.1995(6)
Co(1)-C(1)	1.728(3)	Co(1)-C(2)	1.743(3)
Co(1)-C(3)	1.744(2)	C(1)-O(1)	1.177(3)
C(2)-O(2)	1.169(3)	C(3)-O(3)	1.162(3)
O(1)-Na(1)-O(4)	168.17(8)	O(1)-Na(1)-O(5)	81.41(8)
O(5)-Na(1)-O(7)	93.51(9)	O(5)-Na(1)-O(8)	94.19(8)
O(5)-Na(1)-O(7)	93.51(9)	O(6)-Na(1)-O(7)	84.57(9)
O(6)-Na(1)-O(8)	87.28(8)	P(1)-Co(1)-C(1)	106.43(8)
C(1)-Co(1)-C(2)	113.14(12)	C(1)-Co(1)-C(3)	108.28(11)
C(2)-Co(1)-C(3)	110.62(11)		

The geometry at the six-coordinate Na(1) centre is approximately octahedral, with five THF ligands and one Na(μ -OC)Co isocarbonyl interaction, to give a monomeric complex. The Na(1)⋯Co(1) distance of 5.0931(9) Å is considerably greater than the sum of the respective covalent radii (2.92(9) Å).⁷ The geometry at Co(1) is approximately tetrahedral. The sum of the OC–Co(1)–P(1) angles is 324.7(1) °. C(1)O(1) (C(1)–O(1) = 1.177(3) and Co(1)–C(1) = 1.728(3) Å) involved in Na(μ -OC)Co isocarbonyl bridging has a C(1)–O(1) distance that is identical within error to that for C(2)O(2) (C(2)–O(2) = 1.169(3) and Co(1)–C(2) = 1.743(3) Å) but longer than that for C(3)O(3) (C(3)–O(3) = 1.162(3) and Co(1)–C(3) = 1.744(2) Å). As expected the Co(1)–C(1) distance is shorter than that for C(2)–O(2) or C(3)–O(3). Compound **41** is the first structurally authenticated example of a Na(μ -OC)Co isocarbonyl interaction. Only one other example of a monomeric structure with a Na(μ -OC)TM isocarbonyl interaction is known, namely Si(C₆H₄P^{iPr}₂)₃FeCONa(THF)₃ (**4.31**), with a Na–O(isocarbonyl) distance of 2.184(2) Å.⁴⁸ The average Na–O(THF) distance (2.370(4) Å) in **41** is consistent with the average literature distance of 2.33(6) (range: 2.19–2.56) Å.¹⁹

Reaction of **4.18** in THF with an excess of K/Hg afforded [KCo(CO)₃(PCy₃)(THF)₂]_x (**33**) as a white solid in 76% isolated yield. Diffraction-quality crystals were grown from a concentrated THF solution. In contrast to **41**, the structure is polymeric, a section of this is shown in Figure 4.30, the asymmetric unit in 4.31 and selected distances and angles in Table 4.18.

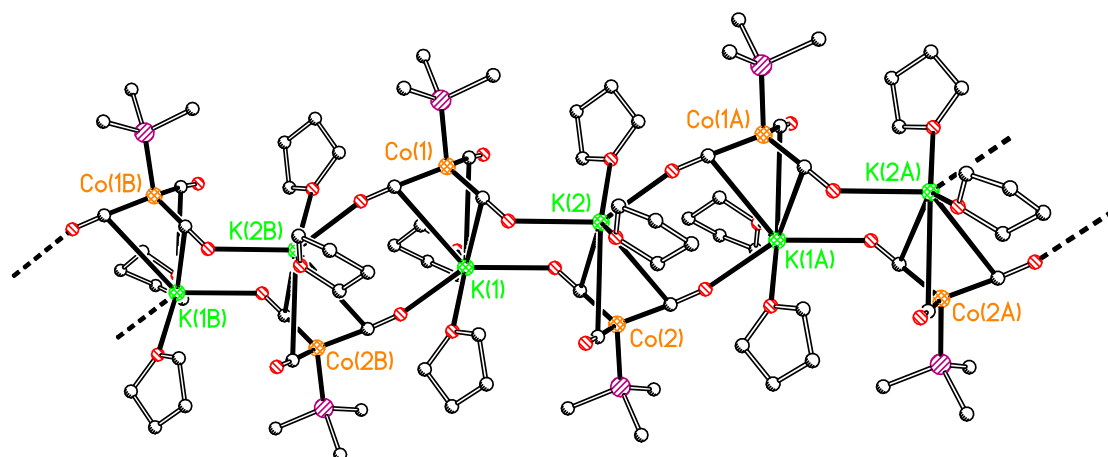


Figure 4.30. Ball and stick plot (arbitrary radius) of a portion of the $[\text{K}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}(\text{THF})_2]_x$ (**33**) infinite chain. H atoms and cyclohexyl methylene carbons omitted for clarity. Symmetry related atoms correspond to their counterparts by the operators “A” = $x+1, y, z$; “B” = $x-1, y, z$.

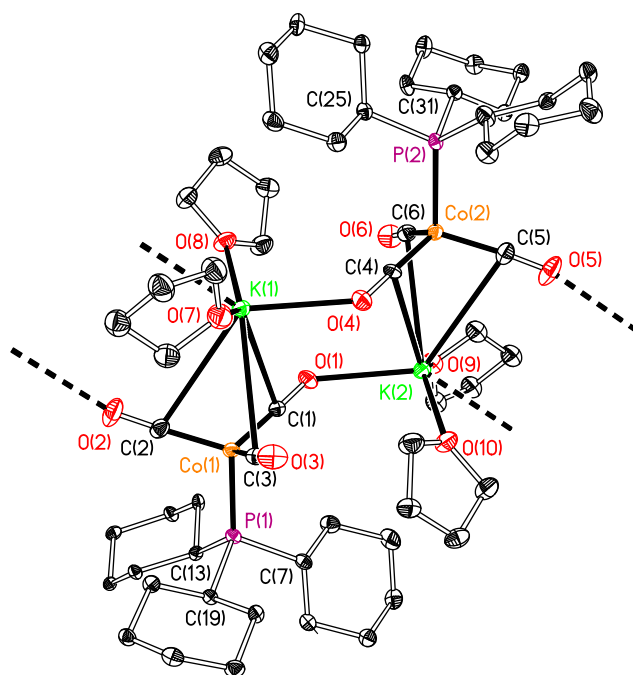


Figure 4.31. Displacement ellipsoid plot (20% probability) of the asymmetric unit of $[\text{K}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}(\text{THF})_2]_x$ (**33**). H atoms omitted for clarity.

Table 4.18. Selected distances (Å) and angles (°) for $[\text{K}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_2]_x$ (**33**).

K(1)···Co(1)	3.4373(13)	K1-Co(2)	5.2150(13)
K1-Co(2B)	5.5752(13)	K(2)···Co(2)	3.4443(14)
K2-Co(1)	5.2144(13)	K2-Co(1A)	5.5725(13)
K(1)-O(1)	3.467(4)	K(1)-O(2)	3.913(7)
K(1)-O(3)	3.779(5)	K(1)-O(4)	2.772(4)
K(1)-O(5B)	2.754(4)	K(1)-O(7)	2.704(5)
K(1)-O(8)	2.673(4)	K(2)-O(1)	2.768(4)
K(2)-O(2A)	2.767(4)	K(2)-O(4)	3.442(4)
K(2)-O(5)	3.906(7)	K(2)-O(6)	3.803(5)
K(2)-O(9)	2.708(5)	K(2)-O(10)	2.671(4)
K(1)-C(1)	3.192(5)	K(1)-C(2)	3.492(7)
K(1)-C(3)	3.406(5)	K(2)-C(4)	3.178(5)
K(2)-C(5)	3.497(7)	K(2)-C(6)	3.407(5)
P(1)-Co(1)	2.2094(13)	Co(1)-C(1)	1.728(5)
Co(1)-C(2)	1.739(5)	Co(1)-C(3)	1.744(6)
P(2)-Co(2)	2.2095(14)	Co(2)-C(4)	1.745(5)
Co(2)-C(5)	1.740(5)	Co(2)-C(6)	1.756(6)
C(1)-O(1)	1.174(6)	C(2)-O(2)	1.152(7)
C(3)-O(3)	1.169(7)	C(4)-O(4)	1.160(6)
C(5)-O(5)	1.162(7)	C(6)-O(6)	1.157(7)
Co(1)-K(1)-O(4)	97.06(9)	Co(2)-K(2)-O(1)	97.63(9)
O(4)-K(1)-O(5B)	141.25(18)	O(5B)-K(1)-O(7)	68.76(15)
O(4)-K(1)-O(8)	93.99(13)	O(7)-K(1)-O(8)	141.87(13)
O(1)-K(2)-O(2A)	140.44(17)	O(1)-K(2)-O(9)	102.40(13)
O(1)-K(1)-O(10)	94.00(13)	O(2A)-K(2)-O(9)	67.58(15)
O(9)-K(2)-O(10)	140.17(13)	P(1)-Co(1)-K(1)	174.43(5)
P(1)-Co(1)-C(1)	107.58(16)	P(1)-Co(1)-C(2)	107.4(2)
P(1)-Co(1)-C(3)	106.76(17)	P(2)-Co(2)-K(2)	174.01(5)
P(2)-Co(2)-C(4)	107.91(17)	P(2)-Co(2)-C(5)	107.7(2)
P(2)-Co(2)-C(6)	106.89(17)	C(1)-Co(1)-C(2)	116.8(2)
C(1)-Co(1)-C(3)	110.5(2)	C(2)-Co(1)-C(3)	107.3(3)
C(4)-Co(2)-C(5)	116.5(2)	C(4)-Co(2)-C(6)	110.8(2)
C(5)-Co(2)-C(6)	106.7(3)		
^a Hinge angle	113	^b Hinge angle	168
^c Inter-ring angle	69.9		

^a Hinge angle = (Co(1), C(1), O(1), Co(2), C(4), O(4))-(Co(1), K(1), O(4)). Maximum deviation from plane = 0.01 Å (Co(1)). ^b Hinge angle = (Co(1), C(2), O(2), Co(2B), C(5B), O(5B))-(Co(1), K(1), O(5B)). Maximum deviation from plane = 0.02 Å (C(2)). ^c Inter-ring angle = (Co(1), C(1), O(1), Co(2), C(4), O(4))-(Co(1), C(2), O(2), Co(2B), C(5B), O(5B)). Maximum deviation from plane = 0.02 Å (C(2)).

K(1) is coordinated to two THF ligands (O(7) and O(8)) and three $[\text{Co}(\text{CO})_3(\text{PCy}_3)]^-$ anions through carbonyl interactions. K(1) interacts side-on with the three carbonyl group C-atoms (C(1), C(2) and C(3)) on Co(1) and has $\text{K}(\mu\text{-OC})\text{Co}$ terminal isocarbonyl linkages to Co(2) and Co(2B) *via* O(4) and O(5B), respectively. The side-on interactions do not involve the O-atoms (O(1), O(2) and O(3)) bound to the respective C-atoms of the carbonyl groups.

Unlike the other ring motifs in this study, those observed in the solid state structure of **33** are not centrosymmetric. However, the interactions of K(2) are analogous to those of K(1) and all associated distances and angles are very similar. For both K(1) and K(2) all interactions with Co centres exist at a greater distance than the sum of the respective covalent radii (3.29(12) Å).⁷ The geometry at Co(1) and Co(2) is approximately tetrahedral where the sum of the OC–Co(1)–P(1) and OC–Co(2)–P(2) angles are 321.7(3) and 322.5(3) °, respectively. The carbonyl groups bound to Co(1) (C(1)–O(1) = 1.174(6), C(2)–O(2) = 1.152(7) and C(3)–O(3) = 1.169(7) Å) have C–O distances that are identical within error. The Co–C distances (Co(1)–C(1) = 1.728(5), Co(1)–C(2) = 1.739(5) and Co(1)–C(3) = 1.744(6) Å) are also identical within error. The analogous distances associated with Co(2) are also identical within error.

In **33**, Co(1), C(1), O(1), Co(2), C(4) and O(1) are co-planar. This allows one to calculate the hinge angle for the hypothetical eight-membered ring, that is, if a direct interaction were to exist between K and Co. The calculated hinge angle of 113 ° is considerably smaller than any of those measured for the other structures in this study, consistent with the lack of direct K–Co interaction. However, if one considers the twelve-membered ring, formed through the linkage of the dimeric units as depicted in Figure 4.30, a hinge angle of 168 ° is measured. This is similar to the hinge angle for the twelve-membered ring in $[\text{Ca}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_2]_x$ (**32**, 167 °) but greater than those for $[\text{Eu}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_4]_x$ (**40**, 159 and 161 °) or $[\text{Yb}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_2$ (**39**, 145 °). The inter-ring angle of 69.9 ° is the greatest observed for any complex in this study.

Consistent with the increase in covalent radius (Na = 1.66(9) and K = 2.03(12) Å), the average M–O(THF) and M–O(isocarbonyl) distances are longer for **33** (2.690(2) and 2.730(2) Å) than **41** (2.370(1) and 2.360(2) Å). The average M–O(THF) distance in **33** is consistent with the average literature value of 2.71(7) (range: 2.44–3.02) Å.¹⁹ Structurally authenticated complexes with $\text{K}(\mu\text{-OC})\text{Co}$ isocarbonyl (η^1) interactions in

monomeric and polymeric structures have been published.⁴⁹⁻⁵¹ Studies by Jones *et al.* have demonstrated the potential for K to undergo a side-on (η^2) interaction with the carbonyl groups bound to Co in $[\{K(\text{TMEDA})\}\{\text{CpCo}(\text{CO})\{\text{Ga}\{\text{N}(\text{Ar})\text{CH}_2\}_2\}_2]$ (**4.32**, Figure 4.32).⁵² The K(1)-C(32) distance (3.121(4) Å) is similar to the analogous distance in **33** (K(1)-C(1) = 3.192(5) Å), whilst the K(1)-O(1) distance (3.167(4) Å) is considerably shorter than that in **33** (3.467(4) Å), consistent with the absence of an η^2 -carbonyl interaction in **33**.

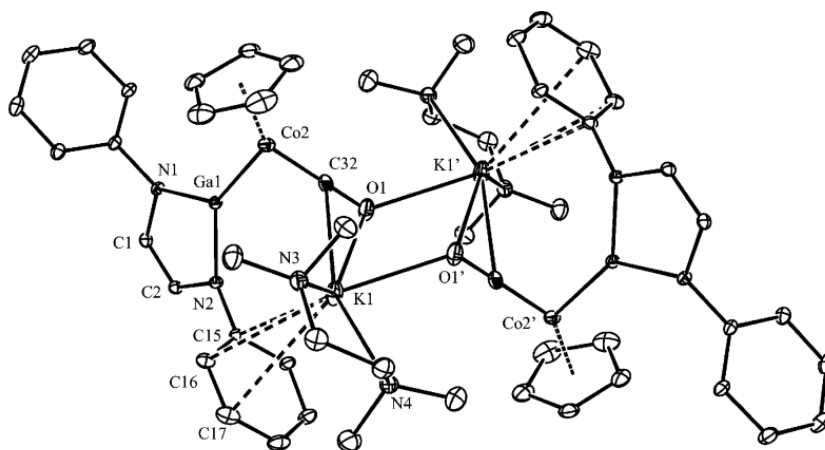


Figure 4.32. $[\{K(\text{TMEDA})\}\{\text{C}_5\text{H}_5\text{Co}(\text{CO})\{\text{Ga}\{\text{N}(\text{Ar})\text{CH}_2\}_2\}_2]$ (**4.32**).⁵²

The switch from a monomeric structure for **41** to a polymeric structure for **33** is comparable with the change from a monomeric structure for $\text{MgFp}_2(\text{THF})_4$ (**1**) to a dimeric structure for $[\text{CaFp}_2(\text{THF})_3]_2$ (**3**) when crystallised from THF, consistent with the increase in covalent and ionic radii.^{7, 32}

4.9 Diffusion NMR measurements

In collaboration with Dr Timothy Claridge of the University of Oxford's NMR service, DOSY (Diffusion Ordered Spectroscopy) NMR was carried out to analyse the solution behaviour of the complexes $[\text{Mg}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})]_2$ (**31**), $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (**35**) and $[\text{Yb}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_2$ (**39**). Through determination of the diffusion characteristics of these species, calculation of their molecular volumes and therefore structures could be inferred, to ascertain if direct metal-metal interactions are maintained. Samples of **4.18**, **31**, **35** and **39** were prepared with a concentration of 0.01 mol dm^{-3} in toluene- d_8 . For all samples the residual toluene solvent signal was used as an internal reference signal to monitor for possible viscosity differences between sample preparations. Diffusion coefficients (D)

were used to calculate hydrodynamic radii (r_s) according to the Stokes-Einstein Equation (Equation 4.4), where k is Boltzmann's constant, T is the temperature and η is the viscosity. Effective molecular volumes were then derived from these radii as spherical volumes. Molecular volumes derived from crystal structures were determined using Accelrys Discovery Studio Visualiser 2.5.5 based on a solvent accessible surface area determined using a 1.4 Å probe. These data are summarised in Table 4.19.

$$r_s = \frac{kT}{6\pi\eta D}$$

Equation 4.4⁵³

Table 4.19. Diffusion NMR measurements for $[\text{Co}(\text{CO})_3(\text{PCy}_3)]_2$ (**4.18**), $[\text{Mg}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})]_2$ (**31**), $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (**35**) and $[\text{Yb}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_2$ (**39**).

Compound	X-Ray volume (Å ³) ^a	NMR volume (Å ³) ^b	D(mean) x 10 ⁻¹⁰ (m ² s ⁻¹) ^c	D(Tol) x 10 ⁻¹⁰ (m ² s ⁻¹) ^c
4.18	749	869	6.58	23.41
31	1788	1178	5.95	23.16
35	2269	2008	4.98	23.73
39	2296	2072	4.93	22.90
Toluene	-	-	-	23.54

^a Molecular volume based on the caption formula and X-ray crystal structure (with $x = 2$ for **35**) measured using 1.4 Å probe radius; ^b molecular volume measured by DOSY; ^c Diffusion coefficient.

The solution effective molecular volume of **31** (1178 Å³) was found to be intermediate of that for dimeric $[\text{Mg}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})]_2$ (1788 Å³ based on the crystal structure) and the monomeric analogue $\text{Mg}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})$ (**31'**, 868 Å³). Assuming fast exchange between **31** and **31'** (as indicated by a single set of $\text{Co}(\text{CO})_3(\text{PCy}_3)$ NMR resonances) this suggests that **31** partially dissociates (*ca.* 50%) in solution under these conditions to afford a monomer-dimer equilibrium, where ΔG_{298} for **31** $\rightarrow$ **31'** is only *ca.* 10 kJ mol⁻¹. It was not possible to use diffusion NMR spectroscopy to reliably determine the solution effective molecular volume of **32** due to its solubility in toluene being lower than that required for accurate measurements.

Compound **35** was determined to have an effective molecular volume of 2008 Å³ in toluene-*d*₈. This is close to the value expected (2296 Å³) for a dimeric moiety [Sr{Co(CO)₃(PCy₃)₂(THF)₃]₂ based on the crystal structure and is therefore consistent with a change from polymeric to dimeric structure upon dissolving in toluene. Due to the paramagnetic nature of [Eu{Co(CO)₃(PCy₃)₂(THF)₃]_x (**36**, 4f⁷ configuration), its solution behaviour could not be studied by diffusion NMR spectroscopy. However, given the very similar solid state structures of **35** and **36** as determined by single crystal X-ray diffraction, one might expect **36** to have similar solution behaviour. The diamagnetic **39** (4f¹⁴ configuration) was determined to have an effective molecular volume (2072 Å³) close to that calculated (2296 Å³) for the solid state structure. This is consistent with a dimeric structure being maintained in solution. The diffusion coefficient for residual protio-toluene is similar for each of the samples tested and are close to that for the sample of pure toluene-*d*₈ without solute. Importantly, this shows that the presence of the materials under investigation do not significantly alter the viscosity of the solutions at 0.01 mol dm⁻³ concentration and therefore the rate of diffusion of the molecular species. It is important to consider the molecular volume of **4.18** derived from the crystal structure (749 Å³) reported by Bungu and Otto,⁵⁴ compared to that determined by NMR diffusion measurements (869 Å³), a difference of 120 Å³ or 14%, giving some indication of the error associated with these measurements.

4.10 Solid state and solution IR studies

Table 4.20 summarises the IR ν(CO) bands for Ca{Co(CO)₃(PPh₃)₂(THF)₄ (**24**), [Sr{Co(CO)₃(PPh₃)₂(THF)₅]₂ (**25**), [Ba{Co(CO)₃(PPh₃)₂(THF)₆]₂ (**26**), [Sm{Co(CO)₃(PPh₃)₂(THF)₅]_x (**27**) and Yb{Co(CO)₃(PPh₃)₂(THF)₅ (**30**).

As with the IR spectra for the complexes discussed in Chapter Two, the band of lowest wavenumber corresponds to the isocarbonyl bridged group, consistent with the weakening of the C-O bond as a result of increased antibonding character. For the series **24-26**, an increase in the wavenumber of the A' stretch associated with the bridging carbonyl group is observed, **24** (1729 cm⁻¹) < **25** (1746 cm⁻¹) < **26** (1780 cm⁻¹). This observation is supported by the decrease in average C-O isocarbonyl distances, **24** (1.189(2) Å) > **25** (1.175(1) Å) > **26** (1.160(4) Å) and increase in average Co-C isocarbonyl distances: **24** (1.713(2) Å) < **25** (1.725(1) Å) < **26** (1.731(3) Å) (Table 4.21) according to analysis of the corresponding solid state

structures. These observations are consistent with a decrease in the perturbation of the electron density associated with the C-O and Co-C bonds of the isocarbonyl group with increasing Ae^{2+} cation size. This trend contrasts with that observed for the series $[MgFp_2(THF)]_2$ (**1**), $[CaFp_2(THF)_3]_2$ (**3**) and $[SrFp_2(THF)_x]_y$ (**5**) in Chapter Two, where for the isocarbonyl bridged CO stretch **1** (1775 cm^{-1}) > **3** (1744 cm^{-1}) $\approx$ **5** (1749 cm^{-1}). Despite their similar molecular structures, three bands are observed for **24** compared to four for **30**. Considering the band associated with the isocarbonyl C-O stretch, this occurs at a greater wavenumber for **30** (1762 cm^{-1}) compared to **24** (1729 cm^{-1}). For the dimeric **25** and **26**, and polymeric **27**, a broadening of the bands is observed relative to monomeric **24** and **30**.

Considering the $\nu(CO)$ bands for **24-27** and **30** in THF, three are observed for each of these complexes. This is consistent with these materials existing as monomers in THF with localised C_s symmetry at the Co centres. Indeed, **24**, known to have a monomeric molecular structure when crystallised from THF, undergoes little change with regard to the position of its carbonyl bands in Nujol relative to those for **24** in THF. For **24** these bands can be assigned as follows: 1937 corresponds to the symmetric stretch of the terminal carbonyls; 1874 corresponds to the asymmetric stretch of the terminal carbonyls and 1721 cm^{-1} corresponds to the bridging carbonyl. IR bands for the other complexes can be assigned by analogy. As with the IR spectra for the series **24-26** in Nujol, an increasing wavenumber for the band associated with the bridging carbonyl group is observed. The bands for **24** are similar to those for **30**, consistent with their similar monomeric solid state structures and C-O and Co-C isocarbonyl distances as determined by single crystal X-ray diffraction. The bands associated with the terminal carbonyl groups in **27** and **30** are very similar and those for the isocarbonyl C-O stretch (1728 cm^{-1}) are identical.

Table 4.20. IR $\nu(\text{CO})$ (cm^{-1}) for $\text{Ca}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_4$ (**24**), $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_5]_2$ (**25**), $[\text{Ba}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_6]_2$ (**26**), $[\text{Sm}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_5]_x$ (**27**) and $\text{Yb}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_5$ (**30**) in Nujol and THF.

Compound	$\nu(\text{CO})$ (cm^{-1}) in Nujol	$\nu(\text{CO})$ (cm^{-1}) in THF
24	1935 (s), 1861 (s), 1729 (s)	1937 (m), 1874 (s), 1721 (s)
25	1930 (s), 1855 (m), 1816 (s, br), 1746 (s br)	1932 (m), 1874 (s), 1737 (s)
26	1924 (s), 1818 (s, br), 1780 (s, br)	1931 (m), 1872 (s), 1747(s)
27	1928 (s), 1856 (s), 1815 (s, br), 1774 (s, br)	1933 (m), 1874 (s), 1728 (s)
30	1952 (s), 1927 (s), 1854 (s), 1762 (s)	1939 (m), 1872 (s), 1728 (s)

Table 4.21. Average isocarbonyl (η^1) C-O and Co-C distances ($\text{\AA}$) for **24-33** & **35-40**.

Compound	C-O ($\text{\AA}$)	Co-C ($\text{\AA}$)
$\text{Ca}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_4$ (24)	1.189(2)	1.713(2)
$[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_5]_2$ (25)	1.175(1)	1.725(1)
$[\text{Ba}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_6]_2$ (26)	1.160(4)	1.731(3)
$[\text{Sm}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_5]_x$ (27)	1.196(3)	1.746(2)
$\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_6$ (28)	1.206(11)	1.700(1)
$\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_3(\text{THF})_3$ (29)	1.203(8)	1.722(7)
$\text{Yb}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_5$ (30)	1.184(4)	1.716(2)
$[\text{Mg}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})]_2$ (31)	1.179(2)	1.713(2)
$[\text{Ca}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_2]_x$ (32)	1.184(3)	1.724(2)
$[\text{K}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_2]_x$ (33)	1.162(3)	1.738(3)
$[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (35)	1.176(2)	1.731(1)
$[\text{Eu}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (36)	1.180(2)	1.727(2)
$\text{Ba}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_6$ (37)	1.186(6)	1.711(5)
$\text{Ba}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{DME})_4$ (38)	1.177(4)	1.722(4)
$[\text{Yb}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_2$ (39)	1.179(2)	1.722(1)
$[\text{Eu}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_4]_x$ (40)	1.186(2)	1.721(2)
$\text{Na}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}(\text{THF})_6$ (41)	2.360(2)	1.728(3)

Table 4.22 contains the IR $\nu(\text{CO})$ bands of $\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_6$ (**28**), $\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_3(\text{THF})_3$ (**29**), $[\text{Mg}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})]_2$ (**31**), $[\text{Ca}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_2]_x$ (**32**), $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (**35**), $[\text{K}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_2]_x$ (**33**), $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (**35**), $[\text{Eu}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (**36**), $\text{Ba}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_6$ (**37**), $\text{Ba}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{DME})_4$ (**38**), $[\text{Yb}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_2$ (**39**), $\text{Na}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}(\text{THF})_6$ (**41**) and in Nujol, toluene and THF.

For the complexes **31**, **32**, **35** and **37** in Nujol the isocarbonyl $\nu(\text{CO})$ band occurs at increasingly higher wavenumbers, as was observed for **24-26**. However, unlike the aforementioned series, this does not correspond to a decrease in average C-O isocarbonyl distances (Table 4.21) in the solid state. This poor correlation may result from the presence of Ae-Co direct interactions in these complexes as opposed to isocarbonyl interactions exclusively, as was the case for **24-26**. Consistent with their very similar solid state structures, **35** and **36** exhibit near-identical isocarbonyl absorption bands of 1743 and 1746 cm^{-1} , respectively. Importantly, the bands for **28** and **29** are different, enabling identification in the absence of solvent which, as discussed, has the potential to cause the disproportionation of **28** to **29**. Indeed, the carbonyl regions for “**28**” and **29** in toluene are indistinguishable.

Considering the IR spectra for the complexes in toluene solution (Table 4.22), four $\nu(\text{CO})$ bands are observed for all of the materials with the exception of **31**. There is little difference between the A' bands associated with the isocarbonyl interactions with the exception of that for **31**. There is also little difference between the respective A" bands throughout.

Three $\nu(\text{CO})$ bands are observed for each of the complexes in Table 4.22 in THF. As with **24-30**, this is consistent with these complexes existing as monomers in THF. Interestingly, the complexes that have monomeric molecular structures in the solid state (**28**, **37**, **38** and **41**) do not have corresponding $\nu(\text{CO})$ bands in Nujol or THF. This suggests that these complexes are susceptible to structural alterations with the change in environment despite having monomeric structures in the solid state. The THF solution IR bands for **41** and **33** are very similar. This contrasts with their different spectra in Nujol and suggests that they attain similar monomeric structures in THF, likely to be similar to that observed for the molecular structure of **41** (Figure 4.29) but not non-coordinated $[\text{Co}(\text{CO})_3(\text{PCy}_3)]^-$. For the series **31**, **32**, **35** and **37** an

increase in the wavenumber for the band corresponding to the isocarbonyl absorption occurs, as was observed in Nujol. Comparing **37** to **38**, these materials are indistinguishable based on their carbonyl bands in THF, unlike their spectra in Nujol.

Table 4.22. IR $\nu(\text{CO})$ (cm^{-1}) for $\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_6$ (**28**), $\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_3(\text{THF})_3$ (**29**), $[\text{Mg}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})]_2$ (**31**), $[\text{Ca}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_2]_x$ (**32**), $[\text{K}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_2]_x$ (**33**), $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (**35**), $[\text{Eu}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (**36**), $\text{Ba}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_6$ (**37**), $\text{Ba}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{DME})_4$ (**38**), $[\text{Yb}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_2$ (**39**) and $\text{Na}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}(\text{THF})_6$ (**41**) in Nujol, Toluene and THF.

Compound	$\nu(\text{CO})$ (cm^{-1}) in Nujol	$\nu(\text{CO})$ (cm^{-1}) in toluene	$\nu(\text{CO})$ (cm^{-1}) in THF
28	1917 (s), 1859 (m), 1801 (s), 1750 (s)	1893 (s), 1837 (s), 1755 (s), 1717 (m)	1921 (m), 1861 (m), 1712 (s)
29	1917 (s), 1861 (s, br), 1766 (s, br)	1893 (s), 1837 (s), 1755 (s), 1717 (m)	
31	1935 (s), 1861 (s), 1720 (s)	1905 (s), 1842 (m), 1701 (m)	1931(m), 1867(m), 1698(s)
32	1929 (s), 1844 (s), 1743 (s), 1718 (s)	1913 (s), 1838 (m), 1755 (s), 1718 (s)	1926(m), 1864(m), 1699(s)
33	1921 (s), 1822 (s, br), 1756 (s, br)		1914 (s), 1839 (s), 1788 (s)
35	1916 (m), 1821 (s), 1787 (s), 1743 (s)	1913 (s), 1837 (s), 1755 (s), 1717 (m)	1921(m), 1895(m), 1721(s)
36	1918 (s), 1797 (s), 1746 (s)	1892 (s), 1837 (s), 1755 (s), 1718 (m)	1922(m), 1860(m), 1720(s)
37	1953 (s), 1813 (s, br), 1755 (s, br)		1921 (s), 1857 (s), 1737 (s)
38	1928 (m), 1915 (s), 1827 (s), 1756 (s)		1921 (s), 1856 (s), 1737 (s)
39	1914 (s), 1853 (s), 1783 (s), 1757 (s)	1897 (s), 1838 (s), 1754 (s), 1718 (m)	1924(m), 1862(m), 1712(s)
41	1948 (s), 1922 (s), 1810 (s, br), 1781 (s, br)		1916 (s), 1849 (s), 1782 (s)

Comparing the triphenylphosphine complexes (**24**, **26**, **27**, **30**) to their tricyclohexylphosphine analogues (**32**, **37**, **28**, **39**), there is a decrease in the wavenumber for the respective $\nu(\text{CO})$ bands for the latter relative to the former in THF. For example the band associated with the isocarbonyl group in **32** (1699 cm^{-1}) has a lower wavenumber than that for **24** (1737 cm^{-1}). This is expected given the increased donating ability of PCy_3 relative to PPh_3 , which increases the availability of electron density on the Co centre and subsequently that in the C-O anti-bonding orbital.²⁷ However, an increased wavenumber is observed for the terminal carbonyl asymmetric stretch of **35** (1895 (s) cm^{-1}) relative to that for **25** (1874 (m) cm^{-1}).

As discussed, three $\nu(\text{CO})$ bands are observed in THF for each of the complexes listed in Table 4.20 and 4.22. This is consistent with the maintenance of an interaction between the respective Ae/Ln cation and $[\text{Co}(\text{CO})_3(\text{PR}_3)]^-$ anion through isocarbonyl bridging, that is, a contact ion pair, as opposed to the formation of a solvent separated ion pair. If the latter were formed, two bands would be observed, consistent with one symmetric stretch (A_1) and two degenerate asymmetric (E) carbonyl stretches at the Co centre with localised C_{3v} symmetry. Two bands are observed for $\text{Co}(\text{H})(\text{CO})_3(\text{PPh}_3)$ (**4.32**, 2041 (m) , 1952 (s)) and $\text{HCo}(\text{CO})_3\text{PCy}_3$ (**4.19**, 2038 (m) , 1953 (s)) in Nujol.⁵⁵ These observations serve to reinforce the importance of the selection of a phosphine substituted $[\text{Co}(\text{CO})_3(\text{L})]^-$ anion, $[\text{Co}(\text{CO})_3(\text{PR}_3)]^-$, as opposed to $[\text{Co}(\text{CO})_4]^-$. Recall that $[\text{Co}(\text{CO})_4]^-$ can be considered a weak nucleophile. Solvents such as THF and pyridine are stronger Lewis bases and will therefore readily displace interactions between the Ae/Ln cations and the $[\text{Co}(\text{CO})_4]^-$ anion. As discussed, $[\text{Yb}(\text{THF})_6][\text{Co}(\text{CO})_4]$ (**4.17**) exists as a solvent separated ion pair when crystallised from THF. An increase in the concentration of **4.17** led to the appearance of shoulders on the IR absorption band (1887 cm^{-1}) corresponding to carbonyl stretches of the unperturbed $[\text{Co}(\text{CO})_4]^-$ anion (T_d symmetry). These occurred as a result of weak isocarbonyl interactions between the Yb and Co centres, demonstrating the subtle equilibrium between THF coordination and isocarbonyl bridging that exists in this system. For **4.17** in pyridine, a single carbonyl band (1888 cm^{-1}) was observed, corresponding to the free $[\text{Co}(\text{CO})_4]^-$ anion.^{25, 26}

4.11 DFT computational analysis of $[\text{Ae}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_x]_y$ complexes

To gain further insight into the structures and bonding of the complexes detailed in this chapter, DFT analysis of model structures of $[\text{Mg}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})]_2$ (**31**), $[\text{Ca}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_2]_x$ (**32**) and $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (**35**) was carried out in collaboration with Professor Nikolas Kaltsoyannis of University College London. Selected data for these models are summarised in Table 4.23.

DFT calculations for dimeric $[\text{Mg}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}_2(\text{THF})]_2$ (**31Q**) and the monomeric $\text{Mg}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}_2(\text{THF})$ (**31'Q**, Figure 4.33) were used as models for $[\text{Mg}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}_2(\text{THF})]_2$ (**31**) and $\text{Mg}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})$ (**31'**), respectively. In addition, calculations were also performed for the hypothetical $[\text{Mg}\{\text{Co}(\text{CO})_4\}_2(\text{THF})]_2$ (**31aQ**) in which PR_3 was replaced by CO to probe the electronic effects of the two ligands.

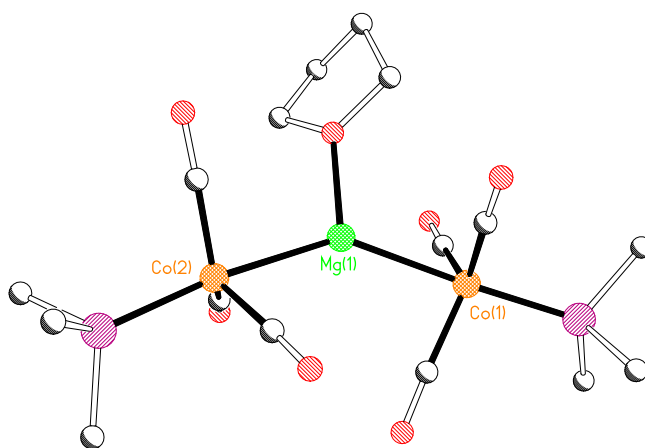


Figure 4.33. DFT calculated structure of $\text{Mg}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}(\text{THF})$ (**31'Q**).

Table 4.23. Selected computational results for $[\text{Mg}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}_2(\text{THF})]_2$ (**31Q**), $\text{Mg}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}(\text{THF})$ (**31'Q**), $[\text{Mg}\{\text{Co}(\text{CO})_4\}_2(\text{THF})]_2$ (**31aQ**), $[\text{Ca}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}_2(\text{THF})_2]_2$ (**32q**), $[\text{Ca}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}_2(\text{THF})_3]_2$ (**32Q**), $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}_2(\text{THF})_3]_2$ (**35q**) and $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}_2(\text{THF})_4]_2$ (**35Q**).

	31Q	31'Q	31aQ	32q	32Q	35q	35Q
$r(\text{Ae}\cdots\text{Co}(1))$ (Å) ^a	2.598	2.480	2.655	2.996	3.031	3.249	3.399
$r(\text{Ae}\cdots\text{Co}(2))$ (Å) ^a	2.528	2.486	2.547	3.168	4.753	3.204	4.880
Sum of OC–Co(1)–L(1) (°) ^a	295.9	298.0	303.1	297.1	298.7	303.3	281.7
Sum of OC–Co(2)–L(2) (°) ^a	301.1	298.9	307.4	314.6	323.1	301.7	321.6
Ae–Co(1) interaction energy ^b	-216.9	–	-192.5	-163.2	-147.3	-137.9	-129.9
orbital mixing energy ^b	-201.7	–	-167.0	-104.4	-91.9	-85.3	-99.6
electrostatic interaction energy ^b	-256.7	–	-211.9	-193.2	-175.4	-171.5	-153.85
Pauli repulsion energy ^b	241.5	–	186.4	134.4	119.9	118.9	108.37
Charge Ae	0.79	0.66	0.80	1.25	1.35	1.30	1.45
Charge Co(1)	-0.32	-0.35	-0.20	-0.26	-0.24	-0.24	-0.24
Charge Co(2)	-0.35	-0.35	-0.24	-0.28	-0.16	-0.30	–
ρ , ^c Ae–Co(1)	0.026	0.032	0.026	0.021	0.019	0.016	0.013
ρ , ^c Ae–Co(2)	0.030	0.032	0.030	–	–	0.016	–
$\nabla^2\rho$, ^d Ae–Co(1)	0.060	0.077	0.053	0.038	0.038	0.039	0.034
$\nabla^2\rho$, ^d Ae–Co(2)	0.072	0.077	0.068	–	–	0.042	–
H , ^e Ae–Co(1)	-0.003	-0.005	-0.003	-0.002	-0.001	-0.0002	0.0005
H , ^e Ae–Co(2)	-0.004	-0.005	-0.004	–	–	-0.0004	–

^a. L = PMe₃ or CO, Co(1) and Co(2) refer to the atoms within or external to the eight-membered ring, respectively; ^b. per Ae–Co bond in kJ mol⁻¹ (orbital mixing (and hence total interaction) energies corrected for basis set superposition error (**31Q** 6.7, **31aQ** 6.7, **32Q** 5.8, **35q** 6.6, **35Q** 7.6)); ^c. electron density; ^d. electron density Laplacian; ^e. energy density. All BCP data in atomic units.

As was observed experimentally for **31**, **31Q** contains an eight-membered ring comprised of two Mg-Co bonds and two Mg(μ -OC)Co isocarbonyl interactions. Similarly, two Mg-Co interactions exist external to ring. The internal distance (Mg-Co(1) = 2.598 Å) is longer than the external distance (Mg-Co(2) = 2.528 Å), as was observed for **31** (2.6163(6) and 2.5427(6) Å), where the calculated distances are shorter than the corresponding experimental distances. The sum of the OC-Co(1)-P(1) (295.9 °) and OC-Co(2)-P(2) (301.1 °) angles for **31Q** are similar to the corresponding angles for **31** (300.9(1) and 303.2(1) °). These angles for **31Q** are smaller than their counterparts in **31**, partially a consequence of the smaller cone angle of PMe₃ (118 °) vs PCy₃ (170 °).²⁸

For the DFT model structure of the monomeric form of **31**, **31'Q**, a shortening of the Mg-Co distances (2.480 and 2.486 Å) relative to **31Q** is observed, consistent with a decrease in the coordination number at the Mg centre. The sum of the OC-Co(1)-P(1) (298.0 °) and OC-Co(2)-P(2) (298.9 °) angles are near-identical as expected and are intermediate of those for **31Q** (295.9 ° and 301.1 °). The change from dimeric to monomeric structure results in a redistribution of charge such that the difference between the Mg(1) and Co(1) centres is lower in **31'Q** (1.01) than **31Q** (1.11). Consistent with this, the electron density (0.032 au) and its Laplacian (0.077 au) at the Mg-Co(1) BCP are increased in **31'Q** relative to that in **31Q** (0.026 and 0.060 au), suggesting a slight increase in the covalency of the Mg-Co interactions. However, these values and the associated energy densities are small, consistent with a predominantly ionic interaction between Mg and Co(1) in **31'Q** and **31Q**. Similar observations are made for the Mg-Co(2) interactions. With the caveat that these are calculated models in the gas phase, ΔG_{298} for **31Q** $\rightarrow$ **31'Q** is 22.0 kJ mol⁻¹, consistent with the small value determined experimentally by DOSY NMR measurements (*ca.* 10 kJ mol⁻¹) for **31** $\rightarrow$ **31'**, supporting the presence of a delicate monomer/dimer balance in this system.

To gain further insight into the influence of the phosphine donor on the structure and bonding in these molecules, the PMe₃ group in **31Q** was substituted for a CO to give **31aQ**. This change from a strong σ -donor to a weak σ -donor and strong π -acceptor is observed to bring about a significant increase in the Mg-Co distances (2.655 and 2.547 Å) relative to **31Q** (2.598 and 2.528 Å). The sum of the respective OC-Co(1)-Co_{ax} angles (303.1 and 307.4 °) are increased relative to the sum of the analogous OC-

Co(1)-P(1) (295.9°) and OC-Co(1)-P(2) (301.1°) angles. These parameters serve as an opportunity to reiterate the importance of the donating phosphine group in promoting direct Ae-Co interactions in these complexes. Consistent with these observations, the strength of internal Mg-Co interactions in **31Q** ($-192.5 \text{ kJ mol}^{-1}$) are decreased relative to those in **31aQ** ($-216.9 \text{ kJ mol}^{-1}$). Despite these changes in structure and the strength of the Mg-Co interactions, there is little change in the average charge difference between the Mg and Co centres (1.02) in **31aQ** relative to **31Q** (1.13). The electron density (0.026 au) and its Laplacian (0.060 au) at the Mg-Co(1) BCP in **31aQ** are also relatively unchanged compared to those for **31Q** (0.026 and 0.053 au) and the energy densities are also identical (-0.003 au). Comparison with the parameters for the Mg(1)-Co(2) interactions for these structures shows them to be very similar also.

DFT calculations for the model complexes $\text{Co(H)(CO)}_3(\text{L})$, where $\text{L} = \text{PPh}_3$, PCy_3 and CO were also performed. The geometry of these complexes were fixed and the H^+ cation removed. Analysis of the HOMO for each of the resulting anions (Figure 4.34.) shows that for $\text{L} = \text{PCy}_3$ (0.63 eV) to be slightly higher in energy than that for CO (0.24 eV) or PPh_3 (0.21 eV), consistent with the small changes observed at the Mg-Co BCPs as a result of substitution of the PCy_3 ligand in **31Q** for CO in **31aQ**.

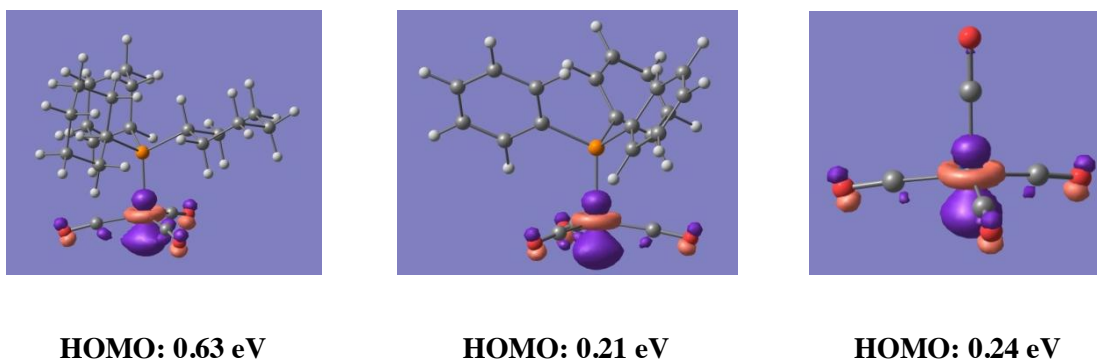


Figure 4.34. Isosurfaces and associated energies of the HOMO of the distorted $[\text{Co(CO)}_3(\text{L})]^-$ anion for $\text{L} = \text{PCy}_3$ (left), PPh_3 (middle) and CO (right).

As discussed, the form of **32** in a non-donor solvent could not be measured from DOSY NMR measurements due to inadequate solubility at the concentrations required. However, these measurements were consistent with $[\text{Yb}\{\text{Co(CO)}_3(\text{PCy}_3)\}_2(\text{THF})_3]_2$ (**39**) remaining as a dimer in solution. DFT calculations of the model structures $[\text{Ca}\{\text{Co(CO)}_3(\text{PMe}_3)\}_2(\text{THF})_2]_2$ (**32q**) and

$[\text{Ca}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}_2(\text{THF})_3]_2$ (**32Q**) were carried out in an attempt to provide some indication of the structure of **32** in dimeric and polymeric forms, respectively. These are illustrated in Figure 4.35.

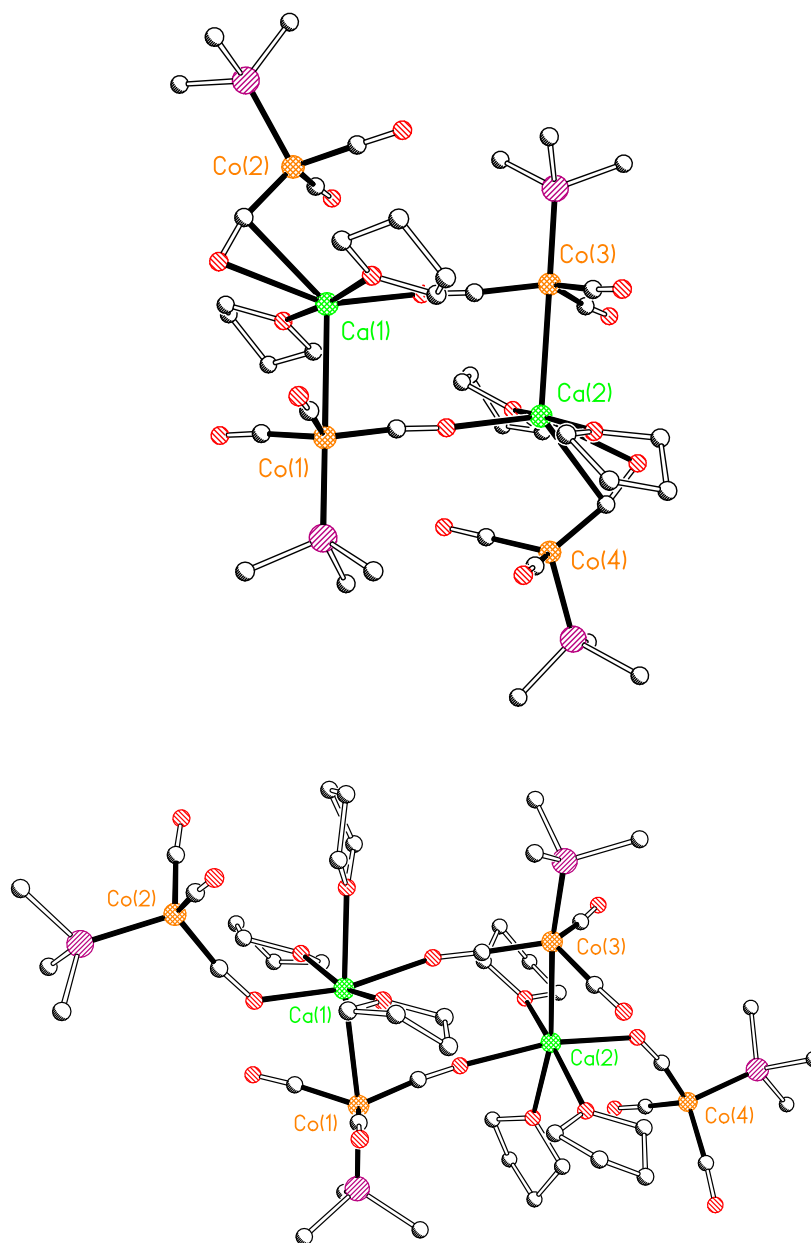


Figure 4.35. DFT calculated structures of $[\text{Ca}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}_2(\text{THF})_2]_2$ (**32q**, top) and $[\text{Ca}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}_2(\text{THF})_3]_2$ (**32Q**, bottom).

The structure of **32q** bears two THF ligands per Ca centre, as in **32**, and represents a possible form of **32** when dissolved in a non-donor solvent, that is, as a dimer. As is apparent from the minimised structure illustrated in Figure 4.35, the $\text{Co}(\text{CO})_3\text{PMe}_3$

groups external to the eight-membered ring exhibit side-on (η^2) carbonyl interactions with the Ca centres in an attempt to occupy the vacant coordination sites.

Addition of another THF ligand at each Ca centre gives **32Q**. These THF ligands serve to occupy the coordination site that would otherwise be involved in isocarbonyl bridging to neighbouring $\text{Co}\{\text{Co}(\text{CO})_3(\text{PR}_3)\}_2(\text{THF})_2$ units, therefore giving a simple model of the eight-membered ring component within the polymeric structure in **32**. Reassuringly, addition of a third THF ligand to each Ca centre gives an approximately octahedral coordination geometry with terminal $\text{Ca}(\mu\text{-OC})\text{Co}$ isocarbonyl interactions external to the ring, consistent with that observed for **32**.

In both **32q** and **32Q** direct Ca-Co interactions, along with $\text{Ca}(\mu\text{-OC})\text{Co}$, afford eight-membered rings, where the Ca-Co distance in **32q** (2.996 Å) is shorter than that in **32Q** (3.031 Å), consistent with the lower coordination number at the Ca centre in the former. Both of these are shorter than that observed for **32** (3.0450(9) Å). Consistent with the increased coordination number and transition from a side-on to terminal interaction, the $\text{Ca}(1)\cdots\text{Co}(2)$ distance is longer for **32Q** (4.753 Å) compared to **32q** (3.168 Å). Both of these are considerably shorter than the equivalent $\text{Ca}(1)\cdots\text{Co}(2)$ and $\text{Ca}(1)\cdots\text{Co}(2\text{B})$ distances in **32** of 5.2266(10) and 5.0919(9) Å, respectively. As expected, the sum of the $\text{OC-Co}(1)\text{-P}(1)$ angles in **32q** (297.1 °) and **32Q** (298.7 °) are near-identical. The sum of the $\text{OC-Co}(1)\text{-P}(2)$ angles in **32Q** (323.1 °) and **32q** (314.6 °) are considerably greater, consistent with the lack of direct Ca-Co interaction. Those for **32Q** are comparable to the corresponding angles for **32** (305.8(2) and 327.4(2) °). Indeed, for **32q** and **32Q** energy decomposition analysis finds no bond path between $\text{Ca}(1)$ and $\text{Co}(2)$. The electron density (0.021 au) and its Laplacian (0.038 au) at the Ca-Co(1) BCP in **32q** are very similar to those for **32Q** (0.019 and 0.038 au), being very small, consistent with a predominantly ionic interaction. The energy density at the Ca-Co(1) BCP in **32q** and **32Q** are also very small. This is supported by the charge difference of 1.50 and 1.59 between $\text{Ca}(1)$ and $\text{Co}(1)$ in **32q** and **32Q**, respectively. Consistent with the increase in coordination number at $\text{Ca}(1)$ in **32q** compared to **32Q**, the strength of the interaction between $\text{Ca}(1)$ and $\text{Co}(1)$ is greater in the former, as determined by the interaction energy of -163.2 vs. -147.3 kJ mol⁻¹.

Analogous to the model structures of **32** in dimeric (**32q**) and polymeric (**32Q**) forms, **35** was modelled as $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}_2(\text{THF})_3]_2$ (**35q**) and $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}_2(\text{THF})_4]_2$ (**35Q**), as illustrated in Figure 4.36.

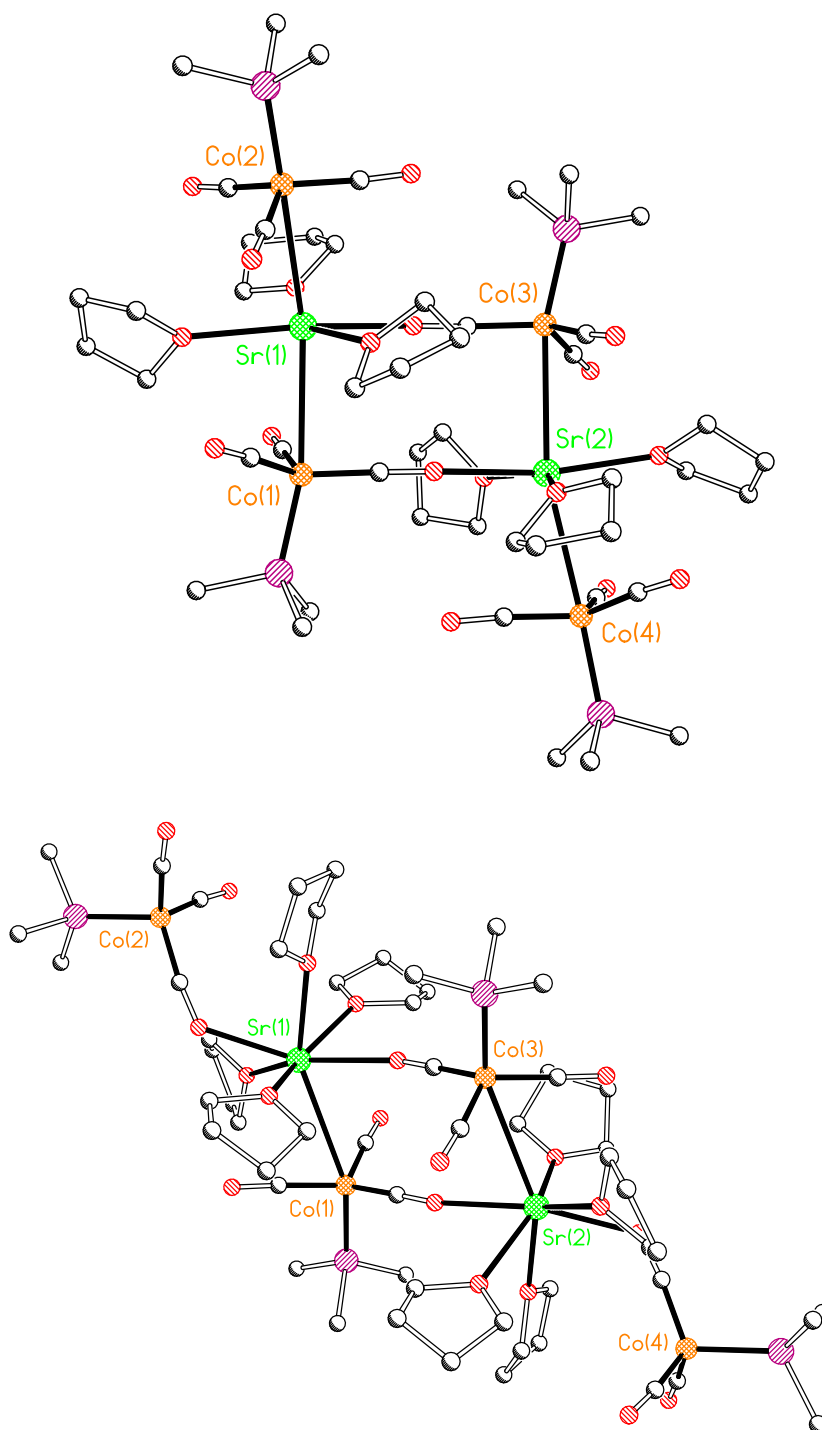


Figure 4.36. DFT structures of $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}_2(\text{THF})_3]_2$ (**35q**, top) and $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PMe}_3)\}_2(\text{THF})_4]_2$ (**35Q**, bottom).

Model complex **35q** has three THF ligands per Sr, representative of the postulated dimeric structural form of **35**. Unlike **35** this exhibits direct Sr-Co interactions both internal (3.249 Å) and external (3.204 Å) to the eight-membered ring, where side-on carbonyl interactions are absent. These distances are close to the sum of the respective covalent radii (3.21(10) Å). As with **31Q**, the Ae-Co(2) distance is shorter than the Ae-Co(1) distance. The presence of direct interactions between Sr(1) and Co(1) and Co(2) is supported by the sum of the OC–Co(1)–P(1) (303.3 °) and OC–Co(2)–P(2) (301.7 °) angles.

Addition of a fourth THF ligand to each Sr centre affords **35Q**, a model of the polymeric structure, where the additional THF occupies the coordination site otherwise used for isocarbonyl bridging to a neighbouring Sr{Co(CO)₃(PMe₃)₂(THF)₃ unit in **35q**. This increase in coordination number results in a geometric change such that the Co(CO)₃PMe₃ group external to the eight-membered ring interacts with Sr(1) *via* a Sr(μ-OC)Co isocarbonyl interaction. As a result the Sr(1)⋯Co(2) distance is increased to 4.880 Å, considerably greater than the sum of the respective covalent radii. Inspection of the eight-membered ring shows the two Sr{Co(CO)₃(PMe₃)₂(THF)₃ units to have shifted towards that of a side-on (η²) carbonyl interaction between Sr(1) and Co(1), as observed for **35**. However, the Sr(1)–Co(1) (3.204 Å) distance remains within the sum of the respective covalent radii within error. These observations are consistent with the sum of the OC–Co(1)–P(1) (281.7 °) and OC–Co(2)–P(2) (321.7 °) angles, consistent with direct and isocarbonyl interactions, respectively. These distances are considerably shorter than those for Sr(1)⋯Co(1) (3.6263 Å) and Sr(1)⋯Co(2) (5.0123 Å) in **35**. The OC–Co(1)–P(1) and OC–Co(2)–P(2) angles for **35Q** of 281.7 and 321.6 ° are smaller than those observed for **35**, 311.2(1) and 326.9(1), respectively. The charge difference between Sr(1) and Co(1) increases from **35q** (1.54) to **35Q** (1.69). Furthermore, the electron density and its Laplacian at the BCP are also decreased in **35Q** (0.013 and 0.034 au) compared to **35q** (0.016 and 0.039 au), consistent with the change from a Sr(1)–Co(1) direct interaction towards that of a side-on interaction. Analysis of the energy densities at the Sr(1)–Co(1) BCP for **35q** (–0.0002 au) and **35Q** (0.0005 au) shows these to be very small, as with the electron densities and associated Laplacians, consistent with predominantly ionic bonding between the Sr and Co centres in both models as expected. Calculation of the charge difference (1.60), the electron density (0.016 au),

its Laplacian (0.042 au) and the energy density (-0.0004 au) at the BCP for the Sr(1)-Co(2) interaction in **35q**, shows these to be very similar to those for the Sr(1)-Co(1) interaction, as expected given their similar distances and sum of OC-Co(1)-P(1) and of OC-Co(2)-P(2) angles.

Compared to **31Q** (2.598 and 2.528 Å) and **32Q** (3.031 and 4.753 Å), the respective Ae-Co(1) and Ae-Co(2) distances for **35Q** (3.399 and 4.880 Å) are longer, consistent with the larger covalent radius. Also as expected the strength of the Ae-Co(1) interaction decreases from Mg (-216.9 kJ mol⁻¹) < Ca (-147.3 kJ mol⁻¹) < Sr (-129.9 kJ mol⁻¹). For the Ae(1)-Co(1) BCP, the electron density and its Laplacian are observed to be similar for **32Q** and **35Q**, whereas the values for **31Q** are consistent with slightly greater covalency in this interaction. The charge difference between Ae and Co(1) in **31Q** (1.01), **32Q** (1.59) and **35Q** (1.69) reinforce this, as do the orbital mixing energies, where that for **31Q** (-201.7 kJ mol⁻¹) is considerably greater than that for **32Q** (-91.9 kJ mol⁻¹) or **35Q** (-99.6 kJ mol⁻¹).

Overall these DFT calculations show good agreement with that observed experimentally, with a weakening of the Ae-Co(1) interaction from Mg to Ca to Sr, with a tendency towards isocarbonyl and side-on interactions with increasing size of the Ae²⁺ cation. The addition or removal of THF ligands from these model complexes is observed to bring about significant structural changes, consistent with experimental observations by DOSY NMR spectroscopy.

4.12 Conclusions

Reduction of [Co(CO)₃(PCy₃)₃]₂ (**4.18**) with Ae and Ln amalgams has enabled the synthesis of toluene soluble heterobimetallic species [M{Co(CO)₃(PCy₃)₂(THF)_x]_y. The dimeric Mg complex [Mg{Co(CO)₃(PCy₃)₂(THF)}₂]₂ (**31**) contains direct Mg-Co interactions, the third structurally authenticated complex to do so following the work of Felkin *et al.*²⁹ The polymeric Ca complex [Ca{Co(CO)₃(PCy₃)₂(THF)₂]_x (**32**) possesses direct Ca-Co interactions, the first structurally authenticated example of such an interaction and the second example of a Ca-TM interaction following [CaFp₂(THF)₃]₂ (**3**) described in Chapter Two. Unlike **3** and [YbFp₂(THF)₃]₂ (**6**), [Yb{Co(CO)₃(PCy₃)₂(THF)₃]_x (**39**) is not isostructural with **32**, being dimeric in the solid state with two direct Yb-Co interactions, the first example of such an interaction and the only Yb-first row TM bond known other than to Fe. As with that observed for

3 and **6**, the Yb-Co interaction is shorter than the Ca-Co interaction, consistent with a stronger bond for the former. Reaction of $[\text{K}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}(\text{THF})_2]_x$ (**33**) with CaI_2 and YbI_2 afforded **32** and **39**, respectively. Conversion of **32** to **39** by reaction with YbI_2 in THF was also demonstrated.

Reduction of **4.18** with an excess of Sr or Eu/Hg gave isostructural polymeric complexes $[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (**35**) and $[\text{Eu}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3]_x$ (**36**) containing side-on (η^2) carbonyl interactions between the divalent metal centres and carbonyl group, unprecedented for Ae or Ln chemistry. Use of Sm/Hg gave $\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_6$ (**28**) which disproportionated in non-donor solvents to give $\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_3(\text{THF})_3$ (**29**) and an unidentified accompanying product, consistent with related literature reports.³⁴⁻³⁶ Compound **29** possesses two direct Sm-Co interactions, the first example of any structurally authenticated Sm-TM bond. Compound **29** could also be synthesised *via* reaction of SmI_2 with **33** in THF followed by extraction of the product into C_6H_6 . $\text{Ba}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_6$ (**37**) was insoluble in non-donor solvents and was crystallised from THF to afford a monomeric molecular structure lacking any direct Ba-Co interactions, very similar to that for **28**, consistent with the similar covalent radii of Ba and Sm. Dissolving **37** in DME gave $\text{Ba}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{DME})_3$ (**37**), also lacking direct Ba-Co interactions.

Attempts to reduce $[\text{Co}(\text{CO})_3(\text{PPh}_3)]_2$ (**1.123**) in THF with Ae and Ln amalgams gave Ae/Ln(μ -OC)Co isocarbonyl bridged complexes only, where the solubility of these complexes did not permit crystallisation from non-donor solvents. Many of these complexes possess eight- and twelve-membered Ae/Ln(μ -OC)Co isocarbonyl bridged rings, analogous to the motifs observed in Chapter Two. In particular **31** and **32** contain eight-membered rings with isocarbonyl bridged and Ae-TM interactions, analogous to that observed for the metal-metal bonded **1** and **3** in Chapter Two.

The behaviour of the complexes **31**, **35** and **39** in toluene solution was investigated by DOSY NMR spectroscopy. Measurements were consistent with a partial dissociation of dimeric **31** to afford monomeric $\text{Mg}\{\text{Co}(\text{CO})_3(\text{PCy}_3)_2(\text{THF})\}$ (**31'**), with ΔG_{298} for $\text{31} \rightarrow 2 \text{31'}$ of *ca.* 10 kJ mol⁻¹. DOSY NMR measurements for **35** were consistent with dissociation to a dimeric structure, similar in form to the solid state structure of **39**.

DFT calculations were performed for simplified model structures of **31**, **32** and **35**.

These showed good agreement with the solid state structures and supported the trend observed of a decreasing strength of direct Ae-Co interactions with increasing Ae²⁺ cation size. Analysis of the Ae-Co BCPs was also consistent with these interactions being predominantly ionic albeit with residual covalency in the Mg-Co interactions, greater than that for the Ca-Co or Sr-Co interactions. These observations are analogous to those for **1** and **3** in Chapter Two. Modelling of the aforementioned dissociation of **31** was consistent with a relatively small ΔG_{298} (22.0 kJ mol⁻¹), as with that calculated using experimental measurements. This, along with the relative ease with which the model structures were perturbed by the addition or removal of THF ligands, is consistent with the complexes containing direct Ae- or Ln-Co interactions in this Chapter readily undergoing structural changes in solution.

DFT analysis of the [Co(CO)₃(L)]⁻ anion shows the HOMO energy for L = PCy₃ to be slightly greater than that for L = PPh₃ or CO, consistent with the greater propensity for this anion to favour Ae-Co or Ln-Co interactions when L = PCy₃ rather than PPh₃ or CO. However, this relatively small energy difference shows that it is the improvement in solubility in non-donor solvents achieved through use of the PCy₃ ligand compared to PPh₃ or CO which plays a critical role in enabling these desired interactions to be achieved.

4.13 References

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Chapter Five

Experimental details and characterising data

5.1 General methods and instrumentation

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent (DME, benzene, pentane and hexanes).¹ Alternatively, solvents were predried over activated 4 Å molecular sieves and refluxed over sodium (toluene) or potassium (THF) and distilled. Deuterated solvents were dried over sodium (toluene-*d*₈), potassium (C₆D₆ and THF-*d*₈) or CaH₂ (CD₃CN), distilled under reduced pressure and stored under argon in Teflon valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ¹H and ¹³C{¹H} spectra were recorded on a Bruker AVC 500 spectrometer fitted with a ¹³C cryoprobe or Varian Mercury-VX 300. ³¹P{¹H} spectra were recorded on Varian Mercury-VX 300. ¹H and ¹³C{¹H} spectra are referenced internally to residual protio-solvent (¹H) or solvent (¹³C) resonances, and are reported relative to tetramethylsilane (δ = 0 ppm). ³¹P{¹H} spectra were referenced externally to an 85% H₃PO₄ solution. Assignments were confirmed as necessary with the use of two-dimensional ¹H-¹H and ¹³C-¹H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. IR spectra were recorded on a Perkin Elmer Paragon 1000 FTIR or Thermo Scientific Nicolet iS5 FTIR spectrometer and samples prepared in a dry-box as Nujol mulls between NaCl plates or as a solution (THF or toluene) in a NaCl cell. Mass spectra were recorded by the Mass Spectrometry Service of Oxford University's Department of Chemistry. Elemental analyses were carried out by the Elemental Analysis Service of London Metropolitan University or Elemental Analysis Ltd, Devon.

5.2 X-ray data collection and processing parameters

Crystals were mounted on glass fibres using perfluoropolyether oil and cooled rapidly in a stream of cold N₂ using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer or Agilent Technologies Supernova diffractometer using Mo-*κ*α or Cu-*κ*α, respectively. As appropriate, absorption and decay corrections were applied to the data and equivalent reflections merged.^{2, 3} The structures were solved using SIR92⁴ or Superflip⁵ and further refinements and all other crystallographic calculations were performed using

the CRYSTALS program suite.⁶ Other details of the structure solution and refinements are given in the CD Appendix.

5.3 Literature preparations

Unless stated, starting materials were purchased from Sigma Aldrich, Strem Chemicals or Alfa Aesar and used without further purification. HMPA was dried over CaH_2 and filtered. Hg was filtered, washed with $\text{HCl}_{(\text{aq})}$, distilled water, acetone then dried under reduced pressure. Anhydrous $\text{NH}_{3(\text{g})}$ was used from a pressurised cylinder without further purification. KFp ,⁷ $\text{Mg}(\text{NacNac})\text{I}(\text{THF})$,⁸ $[\text{Ca}(\text{NacNac})\text{I}(\text{THF})]_2$,⁹ $[\text{Yb}(\text{NacNac})\text{I}(\text{THF})]_2$,¹⁰ $[\text{Co}(\text{CO})_3(\text{PPh}_3)]_2$ and $[\text{Co}(\text{CO})_3(\text{PCy}_3)]_2$ were synthesised according to published procedures.^{11, 12}

5.4 Experimental details and characterising data for Chapter Two

$[\text{MgFp}_2(\text{THF})]_2$ (1). To a stirring Mg amalgam (0.343 g, 14.1 mmol Mg; 10 mL Hg) was added a solution of Fp_2 (1.00 g, 2.83 mmol) in THF (20 mL). The red solution was stirred over the amalgam for 16 h at RT. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was washed with pentane (2 x 10 mL) then dried *in vacuo* to afford **1**·1.3(THF) as a yellow solid. Yield: 1.18 g (84%). Diffraction-quality crystals of **1** were grown from a concentrated benzene solution layered with pentane at RT. Diffraction-quality crystals of $\text{MgFp}_2(\text{THF})_4$ (**2**) were grown from a concentrated THF solution at RT. ¹H NMR (THF-*d*₈, 299.9 MHz): δ 4.35 (20 H, s, Cp). ¹³C{¹H} NMR (THF-*d*₈, 75.5 MHz): δ 78.7 (Cp) ($\delta(\text{CO})$ not observed). EI-MS: m/z = 186 (100%) $[\text{Cp}_2\text{Fe}]^+$, 121 (100%) $[\text{CpFe}]^+$, 177 (75%) $[\text{Fp}]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 2021 (w), 1963 (w), 1912 (s, $\nu(\text{CO})$), 1855 (s, $\nu(\text{CO})$), 1775 (m, $\nu(\text{CO})$), 1261 (w), 1015 (m), 870 (m), 817 (w), 805 (w). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1875 (br, s), 1703 (s). Anal. found (calcd. for $\text{C}_{41.2}\text{H}_{46.4}\text{Fe}_4\text{Mg}_2\text{O}_{11.3}$): C, 49.97 (49.76); H, 4.49 (4.70)%.

$[\text{CaFp}_2(\text{THF})_3]_2$ (3). To a stirring Ca amalgam (0.566 g, 14.2 mmol Ca; 10 mL Hg) was added a solution of Fp_2 (1.00 g, 2.83 mmol) in THF (20 mL). The red solution was stirred over the amalgam for 16 h at RT. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was dried *in vacuo* to afford **3** as a red solid. Yield: 1.12 g (65%). Layering a solution of **3** (0.500 g) in THF (10 mL) with pentane (10 mL) and standing for 16 h gave **3** as a microcrystalline red solid (0.268 g) of analytical purity. Diffraction-quality crystals

were grown from a THF solution at RT. ^1H NMR (THF- d_8 , 299.9 MHz): δ 4.31 (20 H, s, Cp). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 229.5 (CO), 78.2 (Cp). EI-MS: m/z = 186 (100%) $[\text{Cp}_2\text{Fe}]^+$, 121 (60%) $[\text{CpFe}]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1899 (s, $\nu(\text{CO})$), 1828 (s, $\nu(\text{CO})$), 1780 (sh), 1744 (s, $\nu(\text{CO})$), 1260 (w), 1107 (w), 1029 (m), 875 (w), 802 (m), 671 (w). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1878 (s), 1703 (s). Anal. found (calcd. for $\text{C}_{52}\text{H}_{68}\text{Ca}_2\text{Fe}_4\text{O}_{14}$): C, 50.80 (51.17) ; H, 5.45 (5.62)%.

CaFp₂(DME)₃ (4). A stirring suspension of $[\text{CaFp}_2(\text{THF})_3]_2$ (**3**, 0.500 g, 0.410 mmol) in DME (30 mL) was heated at 60 °C for 1 h. The mixture was then filtered to give a red filtrate and red residue. The residue was extracted into DME (2 x 40 mL) at 60 °C and the solutions combined and allowed to cool to RT to afford a red solution with red suspension. Volatiles were removed under reduced pressure and the resulting solid was washed with pentane (2 x 10 mL) and dried *in vacuo* to afford **4** as a red solid. Yield: 0.481 g (88%). Diffraction-quality crystals were grown from a concentrated THF solution at RT. ^1H NMR (THF- d_8 , 299.9 MHz): δ 4.34 (10 H, s, Cp), 3.44 (12 H, s, CH_2), 3.28 (18 H, s, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 229.6 (CO), 78.2 (Cp), 72.8 (Me), 59.1 (CH_2). EI-MS: m/z = 186 (100%) $[\text{Cp}_2\text{Fe}]^+$, 121 (100%) $[\text{CpFe}]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 2020 (m), 1988 (w), 1963 (m), 1939 (w), 1869 (s, $\nu(\text{CO})$), 1733 (s, $\nu(\text{CO})$), 1595 (w), 1287 (w), 1243 (m), 1192 (m), 1160 (w), 1113 (m), 1060 (s), 1016 (m), 864 (s), 839 (m), 821 (w), 793 (m), 752 (w). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1875 (s), 1703 (s). Anal. found (calcd. for $\text{C}_{26}\text{H}_{40}\text{CaFe}_2\text{O}_{10}$): C, 46.81 (47.00); H, 8.83 (5.80)%.

[SrFp₂(THF)_x]_y (5). To a stirring Sr amalgam (1.24 g, 14.1 mmol Sr; 15 mL Hg) was added a solution of Fp₂ (1.00 g, 2.83 mmol) in THF (20 mL). The red solution was stirred over the amalgam for 16 h at RT. The solution was filtered away from the amalgam and volatiles removed under reduced pressure to give a brown solid. The solid was washed with pentane (2 x 10 mL) and dried *in vacuo* to afford **5** as a dark orange solid (1.20 g). ^1H NMR (THF- d_8 , 299.9 MHz): δ 4.29 (s, Cp). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 229.6 (CO), 78.0 (Cp). EI-MS: m/z = 186 (40%) $[\text{Cp}_2\text{Fe}]^+$, 121 (70%) $[\text{CpFe}]^+$, 72 (100%) $[\text{THF}]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1871 (s, br, $\nu(\text{CO})$), 1808 (m, $\nu(\text{CO})$), 1749 (m, $\nu(\text{CO})$), 1590 (w), 1260 (m), 1170 (w), 1107 (m), 1032 (m), 1011 (m), 797 (s), 673 (m). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1878 (s), 1712 (s). A sample of **5** apparently reacted with the elemental analysis capsule, inhibiting these measurements.

[YbFp₂(THF)₃]₂ (6). To a stirring Yb amalgam (2.44 g, 14.1 mmol Yb; 10 mL Hg) was added a solution of Fp₂ (1.00 g, 2.83 mmol) in THF (20 mL). The red solution was stirred over the amalgam for 16 h at RT. The solution was filtered away from the amalgam and volatiles were removed under reduced pressure. The resulting solid was dried *in vacuo* to afford **6** as a dark orange solid. Yield: 1.78 g (85%). Diffraction-quality crystals were grown from a concentrated THF solution at RT. ¹H NMR (THF-*d*₈, 299.9 MHz): δ 4.33 (20 H, s, Cp). ¹³C{¹H} NMR (THF-*d*₈, 75.5 MHz): δ 228.3 (CO), 78.2 (Cp). EI-MS: *m/z* = 186 (100%) [Cp₂Fe]⁺, 177 (25%) [Fp]⁺, 150 (60%) [CpFe(CO) + H]⁺, 121 (100%) [CpFe]⁺. IR (NaCl plates, Nujol mull, cm⁻¹): 2020 (w), 1962 (w), 1897 (s, ν(CO)), 1823 (s, (CO)), 1777 (sh), 1744 (s, ν(CO)), 1261 (w), 1106 (w), 1028 (m), 873 (w), 802 (w), 668 (w), 608 (w), 587 (w). IR (NaCl cell, THF, ν(CO), cm⁻¹): 1875 (s), 1711 (s). Anal. found (calcd. for C₅₂H₆₈Fe₄O₁₄Yb₂): C, 41.85 (42.01); H, 4.45 (4.61)%.

NMR tube-scale reaction of [CaFp₂(THF)₃]₂ (3) with MeI. To a solution of [CaFp₂(THF)₃]₂ (**3**, 10.0 mg, 8.19 μmol) in THF-*d*₈ (0.6 mL) was added MeI (2.6 μL, 41.0 μmol). The solution was analysed immediately by ¹H NMR spectroscopy. The spectrum was consistent with conversion to FpMe. Volatiles were removed under reduced pressure and the resulting brown solid was redissolved in CDCl₃ (0.6 mL). ¹H NMR analysis was consistent with literature values for FpMe.¹³ ¹H NMR (THF-*d*₈, 299.9 MHz): δ 4.80 (5 H, s, Cp), 0.07 (3 H, s, Me).

NMR tube-scale reaction of [MgFp₂(THF)]₂·1.3(THF) (1·1.3(THF)) with MeI. To a solution of [MgFp₂(THF)]₂·1.3(THF) (**1·1.3(THF)**), 10.0 mg, 10.1 μmol) in THF-*d*₈ (0.6 mL) was added MeI (3.1 μL, 50 μmol). The solution was analysed immediately by ¹H NMR spectroscopy. Observations were consistent with those for the analogous reaction using **1**.

[YbFp₂(THF)₃]₂ (6) with MeI. To a solution of [YbFp₂(THF)₃]₂ (**6**, 10.0 mg, 6.73 μmol) in THF-*d*₈ (0.6 mL) was added MeI (2.1 μL, 33.6 μmol). The solution was analysed immediately by ¹H NMR spectroscopy. Observations were consistent with those for the analogous reaction using **3**.

[Mg(HMPA)₄][Fp]₂ (7). To a stirring solution of [MgFp₂(THF)]₂·1.3(THF) (**1·1.3(THF)**), 0.300 g, 0.302 mmol) in THF (10 mL) was added HMPA (0.43 mL, 2.47 mmol). The red solution was stirred for 16 h at RT then volatiles were removed

under reduced pressure. The resulting solid was washed with pentane (2 x 10 mL) to afford **7** as a red solid. Yield: 0.451 g (68 %). Diffraction-quality crystals were grown from a concentrated THF solution at RT. ^1H NMR (THF- d_8 , 299.9 MHz): δ 4.20 (10 H, s, Cp), 2.65 (72 H, d, $^3J = 8.9$ Hz, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 76.8 (s, Cp), 37.1 (d, $^2J = 4.5$ Hz, Me), ($\delta(\text{CO})$ not observed). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8 , 121.6 MHz): δ 24.1 (s). EI-MS: $m/z = 186$ (100%) $[\text{Cp}_2\text{Fe}]^+$, 179 (100%) $[(\text{Me}_2\text{N})_3\text{PO}]^+$, 135 (100%) $[(\text{Me}_2\text{N})_2\text{PO}]^+$, 121 (95%) $[\text{CpFe}]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1863 (s, $\nu(\text{CO})$), 1789 (s, $\nu(\text{CO})$), 1304 (s), 1186 (s), 1165 (s), 1104 (w), 1068 (m), 994 (s), 801 (w), 759 (s), 672 (m). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1865 (m), 1787 (m). Anal. found (calcd. for $\text{C}_{38}\text{H}_{82}\text{Fe}_2\text{Mg}_1\text{N}_{12}\text{O}_8\text{P}_4$): C, 41.53 (41.68); H, 7.40 (7.55); N, 15.50 (15.35)%.

CaFp₂(HMPA)₄ (10). To a stirring Ca amalgam (0.283 g, 7.06 mmol Ca; 10 mL Hg) was added a solution of HMPA (1.03 mL, 5.93 mmol) in THF (10 mL). The colourless solution was stirred over the amalgam for 10 min at RT then a solution of Fp₂ (0.500 g, 1.41 mmol) in THF (10 mL) added. The red solution was stirred for 16 h at RT. The red solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting gummy red solid was washed with benzene (2 x 10 mL) and dried *in vacuo* to afford **10** as a red solid. Yield: 1.14 g (73%). Diffraction-quality crystals were grown from a concentrated THF solution at RT. ^1H NMR (THF- d_8 , 299.9 MHz): δ 4.16 (10 H, s, Cp), 2.67 (72 H, d, $^3J = 9.4$ Hz, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 229.7 (s, CO), 76.7 (s, Cp), 37.2 (d, $^2J = 4.4$ Hz, Me). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8 , 121.6 MHz): δ 23.7 (s). EI-MS: $m/z = 186$ (20%) $[\text{Cp}_2\text{Fe}]^+$, 179 (35%) $[(\text{Me}_2\text{N})_3\text{PO}]^+$, 147 (100%) $[\text{Fe}(\text{CO})(\text{C}_5\text{H}_3)]^+$, 135 (85%) $[(\text{Me}_2\text{N})_2\text{PO}]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1864 (s, $\nu(\text{CO})$), 1781 (s, $\nu(\text{CO})$), 1753 (s, $\nu(\text{CO})$), 1299 (s), 1196 (s), 1174 (s), 1105 (w), 1070 (s), 987 (s), 776 (m), 754 (s), 676 (w). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1787 (s), 1742 (s). Anal. found (calcd. for $\text{C}_{38}\text{H}_{82}\text{CaFe}_2\text{N}_{12}\text{O}_8\text{P}_4$): C, 40.92 (41.09); H, 7.28 (7.44); N, 14.72 (15.13)%.

Alternative NMR tube-scale synthesis of [CaFp₂(HMPA)₄] (10). To a solution of $[\text{CaFp}_2(\text{THF})_3]_2$ (**3**, 10.0 mg, 8.19 μmol) in THF- d_8 (0.6 mL) was added HMPA (11.4 μL , 65.3 μmol). The solution was analysed immediately by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The spectra were consistent with those reported for $\text{CaFp}_2(\text{HMPA})_4$ (**10**).

Alternative synthesis of $\text{CaFp}_2(\text{HMPA})_4$ (10**).** To elemental Ca (0.113 g, 2.83 mmol) in THF (10 mL) was added CH_2I_2 (5.0 μL , 0.609 μmol) and the mixture stirred for 2 h at RT. HMPA (1.97 mL, 11.3 mmol) was added drop-wise and the mixture stirred for 20 min. To the mixture was added a solution of benzophenone (1.03 g, 5.65 mmol) in THF (20 mL). After 10 min blue spots were observed on the surface of the Ca. After 5 h a dark blue solution was observed and the mixture was stirred for a further 16 h at RT then filtered. To the blue solution was added a solution of Fp_2 (1.00 g, 2.83 mmol) in THF (20 mL) drop-wise to give a dark green solution. The solution was stirred for 4 h at RT then volatiles were removed under reduced pressure. The resulting gummy red solid was washed with benzene (3 x 20 mL) then dried *in vacuo* to afford **10** as a red solid. Yield: 1.30 g (41%). Analysis by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy was consistent with that observed for the synthesis of **10** using Ca/Hg.

$\text{YbFp}_2(\text{HMPA})_4$ (11**).** To a stirring Yb amalgam (4.89 g, 28.3 mmol Yb; 20 mL Hg) was added a solution of HMPA (4.13 mL, 23.7 mmol) in THF (10 mL). The colourless solution was stirred over the amalgam for 10 min at RT then a solution of Fp_2 (2.00 g, 5.65 mmol) in THF (20 mL) added. The red solution was stirred over the amalgam for 16 h at RT. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting gummy red solid was washed with pentane (2 x 10 mL) then dried *in vacuo* to afford **11** as an orange solid. Yield: 6.93 g (99%). Diffraction-quality crystals were grown from a concentrated THF solution at RT. ^1H NMR (THF- d_8 , 299.9 MHz): δ 4.24 (10 H, s, Cp), 2.66 (72 H, d, $^3J = 8.2$ Hz, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 230.0 (s, CO), 76.7 (s, Cp), 37.2 (d, $^2J = 4.1$ Hz, Me). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8 , 121.6 MHz): δ 26.6 (s). EI-MS: $m/z = 186$ (100%) [Cp_2Fe] $^+$, 179 (100%) [$(\text{Me}_2\text{N})_3\text{PO}$] $^+$, 135 (80%) [$(\text{Me}_2\text{N})_2\text{PO}$] $^+$, 121 (80%) [CpFe] $^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1863 (s, $\nu(\text{CO})$), 1749 (s, br, $\nu(\text{CO})$), 1300 (s), 1194 (s), 1169 (s), 1104 (m), 1068 (m), 985 (s), 803 (w), 752 (s), 671 (m). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1790 (m), 1746 (m). Anal. found (calcd. for $\text{C}_{38}\text{H}_{82}\text{Fe}_2\text{N}_{12}\text{O}_8\text{P}_4\text{Yb}_1$): C, 36.51 (36.70); H, 6.47 (6.65); N, 13.39 (13.51)%.

$\text{Mg}(\text{NacNac})\text{Fp}(\text{THF})$ (12**).** To KFp (0.674 g, 3.12 mmol) and $\text{Mg}(\text{NacNac})\text{I}(\text{THF})$ (2.00 g, 3.12 mmol) was added THF (30 mL). The red-brown solution was stirred for 16 h at RT. Volatiles were removed under reduced pressure to give a brown solid. The solid was extracted into benzene (30 mL), filtered and volatiles were removed under reduced pressure. The resulting red solid was washed with pentane (2 x 10 mL) to

afford **12** as a pale yellow-green solid. Yield: 1.69 g (78%). Diffraction-quality crystals were grown from a concentrated benzene solution at RT. ^1H NMR (C_6D_6 , 299.9 MHz): δ 7.19 (6 H), *m*- & *p*- C_6H_3), 4.80 (1 H, s, $\text{NC}(\text{Me})\text{CH}$), 4.35 (5 H, s, Cp), 3.65 (4 H, m, OCH_2), 3.29 (4 H, sept, $^3J = 6.8$ Hz, CHMe_2), 1.67 (6 H, s, Me), 1.39 (12 H, d, $^3J = 6.8$ Hz, CHMe_2), 1.26 (12 H, d, $^3J = 6.8$ Hz, CHMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75.5 MHz): δ 221.3 (CO), 168.8 (CN), 146.9 (*i*- C_6H_3), 142.6 (*o*- C_6H_3), 125.7 (*p*- C_6H_3), 124.3 (*m*- C_6H_3), 96.1 ($\text{NC}(\text{Me})\text{CH}$), 78.1 Cp, 71.1 (OCH_2), 28.7 (CHMe_2), 25.5 (OCH_2CH_2), 25.3 (CHMe_2), 25.2 (Me), 24.8 (CHMe_2). EI-MS: $m/z = 441$ (100%) $[(\text{NacNac})\text{Mg}]^+$, 403 (30%) $[\text{NacNac-Me} + \text{H}]^+$, 202 (60%) $[\text{ArNC}_2\text{H}_3]^+$, 120 (45%) $[\text{C}_6\text{H}_5^i\text{Pr}]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 2020 (m), 1963 (m), 1926 (s, $\nu(\text{CO})$), 1857 (s, $\nu(\text{CO})$), 1519 (s), 1307 (m), 1261 (m), 1226 (w), 1172 (w), 1107 (m), 1055 (w), 1017 (s), 926 (m), 867 (m), 846 (m), 814 (m), 793 (s), 722 (m), 758 (m), 667 (s). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1926 (m), 1871 (s). IR (NaCl cell, toluene, $\nu(\text{CO})$, cm^{-1}): 2015 (s), 1921 (m). Anal. found (calcd. for $\text{C}_{40}\text{H}_{54}\text{Fe}_1\text{Mg}_1\text{N}_2\text{O}_3$): C, 69.31 (69.52); H, 7.66 (7.88); N, 4.17 (4.05)%.

NMR tube-scale reaction of $\text{Mg}(\text{NacNac})\text{Fp}(\text{THF})$ (12**) with MeI.** To a solution of $\text{Mg}(\text{NacNac})\text{Fp}(\text{THF})$ (**12**, 20.0 mg, 28.9 μmol) in C_6D_6 (0.6 mL) was added MeI (2.7 μL , 43 μmol). The ^1H NMR spectrum recorded after 10 min showed quantitative formation of FpMe and $\text{Mg}(\text{NacNac})\text{I}(\text{THF})$ as judged by comparison with the spectra for authentic samples.^{8, 13} ^1H NMR data for FpMe in C_6D_6 (299.9 MHz): 3.99 (5 H, s, Cp), 1.41 (3 H, s, Me).

$\text{Mg}(\text{NacNac})\{(\text{NTol})_2\text{CFp}\}$ (13**).** To $\text{Mg}(\text{NacNac})\text{Fp}(\text{THF})$ (**12**, 0.500 g, 0.724 mmol) and $\text{ToIN}=\text{C}=\text{NTol}$ (0.161 g, 0.724 mmol) was added C_6H_6 (10 mL). The resulting red solution was stirred for 16 h at RT, filtered and volatiles removed under reduced pressure to give a red solid. The solid was washed with pentane (2 x 5 mL) and dried *in vacuo* to afford **13** as a yellow solid. Yield: 0.404 g (66%). ^1H NMR (C_6D_6 , 299.9 MHz): δ 7.20 (6 H, s, *m*- & *p*- C_6H_3), 6.97 (4 H, d, $^3J = 8.2$ Hz, *o*- C_6H_4), 6.36 (4 H, d, $^3J = 8.2$ Hz, *m*- C_6H_4), 4.93 (1 H, s, $\text{NC}(\text{Me})\text{CH}$), 3.79 (5 H, s, Cp), 3.33 (4 H, sept, $^3J = 6.8$ Hz, CHMe_2), 2.24 (6 H, s, MeC_6H_4), 1.71 (6 H, s, NCMc), 1.20 (12 H, d, $^3J = 6.8$ Hz, CHMe_2), 1.12 (12 H, d, $^3J = 6.8$ Hz, CHMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75.5 MHz): δ 214.4 (CO), 200.7 (NCN), 168.8 (NCMe), 170 (*i*- C_6H_4), 146.3 (*i*- C_6H_3), 142.6 (*o*- C_6H_3), 130.5 (*p*- C_6H_4), 129.0 (*o*- C_6H_4), 128.0 (*m*- C_6H_4), 125.2 (*p*- C_6H_3), 124.1 (*m*- C_6H_3), 95.4 ($\text{NC}(\text{Me})\text{CH}$), 85.7 Cp, 28.7 (CHMe_2), 24.5 (CHMe_2),

24.4 (Me), 21.1 (C₆H₄Me). EI-MS: m/z = 441 (20%) [(NacNac)Mg]⁺, 403 (45%) [NacNac-Me + H]⁺, 202 (100%) [ArNC₂H₃]⁺, 121 (80%) [C₆H₅ⁱPr + H]⁺. IR (NaCl cell, Nujol mull, cm⁻¹): 2010 (s, ν(CO)), 1956 (s, ν(CO)), 1791 (w), 1600 (m), 1543 (m), 1522 (s), 1504 (s), 1406 (s), 1317 (m), 1262 (m), 1212 (w), 1179 (m), 1158 (m), 1018 (m), 951 (m), 933 (m), 848 (m), 821 (m), 759 (m). IR (NaCl cell, toluene, ν(CO), cm⁻¹): 2015 (s), 1970 (m). Anal. found (calcd. for C₅₁H₆₀Fe₁Mg₁N₄O₂): C, 72.64 (72.82); H, 7.32 (7.19); N, 6.79 (6.66)%.

[Ca(NacNac)Fp(THF)]₂ (14). To KFp (0.329 g, 1.52 mmol) and [Ca(NacNac)I(THF)]₂ (1.00 g, 0.760 mmol) was added THF (20 mL). The red solution was stirred for 5 h at RT. Volatiles were removed under reduced pressure. The orange solid was extracted into THF (15 mL) and the resulting solution filtered, layered with pentane (15 mL) and allowed to stand for 16 h at RT. The resulting orange microcrystalline solid was isolated by filtration, washed with pentane (2 x 5 mL) then dried *in vacuo* to afford **14** as an orange solid. Yield: 0.728 g (68%). Diffraction-quality crystals of [Ca(NacNac)Fp(THF)]₂ (**15**) were grown from a concentrated THF solution at RT. Diffraction-quality crystals of [{Ca(NacNac)(THF)}₂{Cp₄Fe₅(CO)₈}] (**16**) were grown from a concentrated C₆H₆ solution at RT. ¹H NMR (THF-*d*₈, 299.9 MHz): δ 7.09 (8 H, d, ³*J* = 6.4 Hz, *m*-C₆H₃), 7.02 (4 H, d, ³*J* = 6.4 Hz, *p*-C₆H₃), 4.73 (2 H, s, NC(Me)CH), 4.20 (10 H, s, Cp), 3.20 (8 H, sept, ³*J* = 6.8 Hz, CHMe₂), 1.58 (12 H, s, Me), 1.28 (24 H, d, ³*J* = 6.8 Hz, CHMe₂), 1.12 (24 H, d, ³*J* = 6.8 Hz, CHMe₂). ¹H NMR (C₆D₆, 299.9 MHz): δ 7.18 (12 H, s, *m*- & *p*-C₆H₃), 4.85 (2 H, s, NC(Me)CH), 4.04 (10 H, s, Cp), 3.92 (8 H, m, OCH₂), 3.32 (8 H, sept, ³*J* = 6.8 Hz, CHMe₂), 1.66 (12 H, s, Me), 1.42 (24 H, d, ³*J* = 6.8 Hz, CHMe₂), 1.39 (8 H, m, OCH₂CH₂), 1.19 (24 H, d, ³*J* = 6.8 Hz, CHMe₂). ¹³C{¹H} NMR (THF-*d*₈, 75.5 MHz): δ 231.0 (CO), 166.3 (CN), 149.9 (*i*-C₆H₃), 143.1 (*o*-C₆H₃), 124.9 (*p*-C₆H₃), 124.5 (*m*-C₆H₃), 95.0 (NC(Me)CH), 78.0 Cp, 29.0 (CHMe₂), 26.5 (Me), 25.7 (CHMe₂), 25.5 (CHMe₂). ¹³C{¹H} NMR (C₆D₆, 75.5 MHz): δ 166.2 (CN), 146.6 (*i*-C₆H₃), 142.0 (*o*-C₆H₃), 125.0 (*p*-C₆H₃), 124.1 (*m*-C₆H₃), 94.4 (NC(Me)CH), 79.5 Cp, 69.6 (OCH₂), 28.5 (CHMe₂), 25.4 (OCH₂CH₂), 25.3 (CHMe₂), 24.8 (Me), 25.5 (CHMe₂) (δ(CO) not observed). EI-MS: m/z = 457 (100%) [(NacNac)Ca]⁺, 403 (100%) [Nacnac-Me + H]⁺, 186 (70%) [Cp₂Fe]⁺. IR (NaCl plates, Nujol mull, cm⁻¹): 1905 (w), 1823 (s, ν(CO)), 1780 (s, ν(CO)), 1721 (m), 1540 (m), 1513 (m), 1408 (s), 1313 (m), 1253 (w), 1225 (w), 1167 (m), 1105

(w), 1032 (m), 922 (m), 892 (w), 787 (m), 759 (w). IR (NaCl cell, THF, $\nu(\text{CO}) \text{ cm}^{-1}$): 1958 (s), 1810 (s). Anal. found (calcd. for $\text{C}_{80}\text{H}_{108}\text{Ca}_2\text{Fe}_2\text{N}_4\text{O}_6$): C, 67.91 (67.97) ; H, 7.70 (7.70) ; N, 3.97 (3.96)%.

[Yb(NacNac)Fp(THF)]₂ (17). To KFp (0.137 g, 0.633 mmol) and [Yb(NacNac)I(THF)]₂ (0.500 g, 0.317 mmol) was added THF (20 mL). The red solution was stirred for 16 h at RT. Volatiles were removed under reduced pressure. The red solid was dissolved in THF (20 mL) and the resulting solution filtered and volatiles removed under reduced pressure. The resulting solid was dried *in vacuo* to afford **17** as a red solid. Yield: 0.471 g (88%). Layering a THF solution (20 mL) of crude **17** (0.471 g) with pentane (20 mL) and standing for 16 h gave **17** as a microcrystalline red solid (201 mg) of analytical purity. Diffraction-quality crystals of [Yb(NacNac)Fp(THF)]₂ (**18**) were grown from a concentrated THF solution at RT. Diffraction-quality crystals of {Yb(NacNac)(Fp)(THF)}₂(μ -YbFp₂) (**19**) were grown from a dilute pentane solution at -30 °C. ¹H NMR (THF-*d*₈, 299.9 MHz): δ 7.13 (8 H, d, ³*J* = 6.4 Hz, *m*-C₆H₃), 7.06 (4 H, d, ³*J* = 6.4 Hz, *p*-C₆H₃), 4.75 (2 H, s, NC(Me)CH), 4.20 (10 H, s, Cp), 3.22 (8 H, sept, ³*J* = 6.8 Hz, CHMe₂), 1.59 (12 H, s, Me), 1.30 (24 H, d, ³*J* = 6.8 Hz, CHMe₂), 1.16 (24 H, d, ³*J* = 6.8 Hz, CHMe₂). ¹H NMR (C₆D₆, 299.9 MHz): δ 7.20 (12 H, s, *m*- & *p*-C₆H₃), 4.74 (2 H, s, NC(Me)CH), 4.24 (10 H, s, Cp), 3.76 (8 H, s, OCH₂), 3.29 (8 H, s, CHMe₂), 1.61 (12 H, s, Me), 1.41 (32 H, s, CHMe₂ & OCH₂CH₂), 1.23 (24 H, s, CHMe₂). ¹³C{¹H} NMR (THF-*d*₈, 75.5 MHz): δ 230.6 (CO), 165.7 (CN), 149.2 (*i*-C₆H₃), 142.9 (*o*-C₆H₃), 124.8 (*p*-C₆H₃), 124.4 (*m*-C₆H₃), 95.4 (NC(Me)CH), 77.7 Cp, 28.9 (CHMe₂), 26.5 (Me), 25.3 (CHMe₂ coincident with THF multiplet). ¹³C{¹H} NMR (C₆D₆, 75.5 MHz): δ 165.7 (CN), 146.0 (*i*-C₆H₃), 141.7 (*o*-C₆H₃), 125.1 (*p*-C₆H₃), 124.2 (*m*-C₆H₃), 93.9 (NC(Me)CH), 78.9 Cp, 69.7 (OCH₂), 28.7 (CHMe₂), 25.4 (OCH₂CH₂), 25.1 (CHMe₂), 24.8 (Me & CHMe₂) ($\delta(\text{CO})$ not observed). EI-MS: *m/z* = 403 (100%) [NacNac-Me + H]⁺, 186 (70%) [Cp₂Fe]⁺. IR (NaCl plates, Nujol mull, cm^{-1}): 1908 (m), 1837 (s), 1821 (s, $\nu(\text{CO})$), 1779 (s, $\nu(\text{CO})$), 1737 (s), 1717 (m), 1541 (m), 1514 (m), 1406 (s), 1314 (m), 1260 (w), 1228 (w), 1170 (w), 1107 (w), 1027 (m), 923 (w), 875 (w). IR (NaCl cell, THF, $\nu(\text{CO}) \text{ cm}^{-1}$): 1873 (s), 1721 (s). Anal. found (calcd. for $\text{C}_{80}\text{H}_{108}\text{Fe}_2\text{N}_4\text{O}_6\text{Yb}_2$): C, 57.59 (57.21) ; H, 6.93 (6.48) ; N, 2.93 (3.34)%.

{Yb(NacNac)(Fp)(THF)}₂(μ -YbFp₂) (19). To [Yb(NacNac)Fp(THF)]₂ (0.200 g, 0.238 mmol) and [YbFp₂(THF)₃]₂ (0.177 mg, 0.199 mmol) was added THF (15 mL).

The resulting red-brown solution was stirred for 16 h at RT then volatiles were removed under reduced pressure. To the resulting solid was added pentane (10 mL) and the suspension stirred for 15 min. Volatiles were removed under reduced pressure and the resulting solid was dried *in vacuo* to afford **19** as a brown solid. Yield 0.194 g (74 %). ^1H NMR (THF- d_8 , 299.9 MHz): δ 7.13 (8 H, m, $m\text{-C}_6\text{H}_3$), 7.07 (4 H, d, $^3J = 6.7$ Hz, $p\text{-C}_6\text{H}_3$), 4.86 (2 H, s, $\text{NC}(\text{Me})\text{CH}$), 4.31 (20 H, s, Cp), 3.21 (8 H, m, CHMe_2), 1.58 (12 H, s, Me), 1.32 (24 H, m, CHMe_2), 1.16 (24 H, d, $^3J = 6.4$ Hz, CHMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8): Not obtained due to poor solubility. EI-MS: $m/z = 403$ (50%) $[\text{NacNac-Me} + \text{H}]^+$, 202 (100%) $[\text{ArNC}_2\text{H}_3]^+$, 186 (70%) $[\text{Cp}_2\text{Fe}]^+$, 66 (20%) $[\text{CpH}]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 2019 (s), 1962 (s, $\nu(\text{CO})$), 1905 (m, $\nu(\text{CO})$), 1761 (m, br $\nu(\text{CO})$), 1623 (w), 1576 (m), 1552 (m), 1314 (m), 1260 (m), 1099 (m), 1017 (m), 754 (w). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1874 (m), 1782 (s). Anal. found (calcd. for $\text{C}_{94}\text{H}_{118}\text{Fe}_4\text{N}_4\text{O}_{10}\text{Yb}_3$): C, 50.88 (51.17); H, 5.23 (5.39); N, 2.67 (2.54)%.

5.5 Experimental details and characterising data for Chapter Three

$[\text{Ca}\{\text{Fe}_2(\text{CO})_8\}(\text{MeCN})_5]_x$ (20**).** $\text{NH}_{3(\text{g})}$ was condensed (20 ml) onto elemental Ca (0.637 g, 0.16 mmol) and $\text{Fe}_3(\text{CO})_{12}$ (2.00 g, 3.97 mmol) at -78°C to give a blue solution and formation of a yellow mirror on the wall of the vessel. The material was stirred at -78°C for 5 h then allowed to gradually warm to RT, allowing evaporation of NH_3 , then was then dried *in vacuo*. To the resultant grey solid was added MeCN (40 ml) and the resulting red mixture was stirred for 16 h at RT. The solution was filtered and volatiles removed under reduced pressure. The resulting solid was washed with pentane (2 x 5 mL) then dried *in vacuo* to afford **20** as a yellow solid. Yield: 0.644 g (18%). Diffraction-quality crystals were grown from a concentrated MeCN solution at RT. $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 230.1 (CO). EI-MS: $m/z = 196$ (70%) $[\text{Fe}(\text{CO})_5]^+$, 168 (100%) $[\text{Fe}(\text{CO})_4]^+$, 140 (70%) $[\text{Fe}(\text{CO})_3]^+$, 112 (80%) $[\text{Fe}(\text{CO})_2]^+$, 84 (100%) $[\text{Fe}(\text{CO})]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 2304 (m), 2279 (s), 2208 (w), 2003 (sh, $\nu(\text{CO})$), 1945 (s, br, $\nu(\text{CO})$), 1881 (s, br, $\nu(\text{CO})$), 1580 (s, br), 1261 (m), 1092 (w), 1035 (m), 931 (w), 799 (w), 695 (m), 650 (m), 620 (m), 578 (m). A satisfactory elemental analysis could not be obtained.

$[\text{Ca}\{\text{Fe}_3(\text{CO})_{11}\}(\text{MeCN})_4]_x$ (21**).** To a stirring Ca amalgam (2.39 g, 59.6 mmol; 20 mL Hg) was added a suspension of $\text{Fe}_3(\text{CO})_{12}$ (2.00 g, 3.97 mmol) in THF (30 mL). An immediate colour change from teal to red was observed. The mixture was stirred

over the amalgam for 16 h at RT. The red suspension was decanted away from the amalgam. The amalgam was washed with THF (20 mL) and the washings combined with the red suspension. Volatiles were removed under reduced pressure. To the resulting brown solid was added MeCN (20 mL) and the resulting red solution was stirred for 16 h at RT. The solution was filtered and volatiles were removed under reduced. The resulting solid was dried *in vacuo* to afford **21** as a dark red-black microcrystalline solid. Yield: 1.94 g (72%). Diffraction-quality crystals were grown from a concentrated MeCN solution at RT. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 75.5 MHz): δ 232.8 (CO), 225.3 (CO). EI-MS: m/z = 204 (15%) $[\text{Ca}(\text{MeCN})_4]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 2303 (m), 2272 (s), 2203 (w), 2000 (sh, $\nu(\text{CO})$), 1933 (s, br, $\nu(\text{CO})$), 1879 (s, br, $\nu(\text{CO})$), 1619 (w), 1562 (w), 1302 (w), 1261 (w), 1155 (w), 1080 (w), 1029 (m), 929 (w), 798 (m), 722 (m), 684 (m), 619 (m). Anal. found (calcd. for $\text{C}_{19}\text{H}_{12}\text{CaFe}_3\text{N}_4\text{O}_{11}$): C, 33.36 (33.56); H, 1.67 (1.78); N, 8.05 (8.24)%.

$[\text{Ca}\{\text{Fe}(\text{CO})_4\}(\text{HMPA})_3(\text{THF})]_x$ (22). Following filtration, the THF solution produced in the synthesis of **23** (see below) was concentrated under reduced pressure to give a black viscous oil. Reduced pressure (to 10^{-2} mbar) was maintained for a further 5 h to afford a waxy green solid. The material was washed with pentane (2 x 10 mL) and dried *in vacuo* to afford **22** as a green solid. Yield: 0.458 g (8%). Diffraction-quality crystals were grown from a concentrated THF solution at RT. ^1H NMR ($\text{THF}-d_8$, 299.9 MHz): δ 2.63 (s, 72 H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF}-d_8$, 75.5 MHz): δ 250.2 (CO), 37.4 (Me). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{THF}-d_8$, 121.6 MHz): δ 25.5 (s). EI-MS: m/z = 179 (100%) $[(\text{Me}_2\text{N})_3\text{PO}]^+$, 135 (100%) $[(\text{Me}_2\text{N})_2\text{PO}]^+$, 92 (80%) $[\text{H}(\text{Me}_2\text{N})\text{PO}]^+$. IR (NaCl plates, Nujol, cm^{-1}): 1877 (s, br, $\nu(\text{CO})$), 1745 (s, $\nu(\text{CO})$), 1686 (s, $\nu(\text{CO})$), 1300 (s), 1261 (m), 1194 (s), 1068 (m), 987 (s), 890 (w), 801 (m), 747 (s). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1875 (s). A satisfactory elemental analysis could not be obtained.

$[\text{Ca}(\text{HMPA})_5(\text{MeCN})][\text{Fe}_2(\text{CO})_8]$ (23). To a stirring Ca amalgam (1.19 g, 29.8 mmol; 20 mL Hg) was added a solution of HMPA (4.15 mL, 23.8 mmol) in THF (10 mL). The colourless solution was stirred over the amalgam for 10 min at RT then a suspension of $\text{Fe}_3(\text{CO})_{12}$ (1.00 g, 1.99 mmol) in THF (20 mL) was added. An immediate colour change from teal to purple was observed followed by a gradual transition to brown. The suspension was stirred over the amalgam for 16 h at RT. The suspension was decanted away from the amalgam and filtered, isolating a brown

solid. To the solid was added MeCN (40 mL) and the resulting red solution was stirred for 16 h at RT. The solution was filtered and volatiles removed under reduced pressure. The resulting solid was washed with pentane (2 x 10 mL) and dried *in vacuo* to afford **23** as a red solid. Yield: 2.68 g (66%). Diffraction-quality crystals were grown from a concentrated MeCN solution at RT. ^1H NMR (CD_3CN , 299.9 MHz): δ 2.60 (d, $^3J = 9.5$ Hz, 90 H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 75.5 MHz): δ 236.4 (CO), 225.6 (CO), 225.4 (CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN , 121.6 MHz): δ 23.8 (s). EI-MS: $m/z = 179$ (70%) $[(\text{Me}_2\text{N})_3\text{PO}]^+$, 135 (100%) $[(\text{Me}_2\text{N})_2\text{PO}]^+$, 92 (95%) $[\text{H}(\text{Me}_2\text{N})\text{PO}]^+$. IR (NaCl plates, Nujol, cm^{-1}): Broad band from 2000-1600 with maxima at 1905 (s, br, $\nu(\text{CO})$), 1851 (s, br, $\nu(\text{CO})$), 1801 (s, br, $\nu(\text{CO})$) 1764 (s, br, $\nu(\text{CO})$). Other bands at 1300 (s), 1193 (s), 1165 (s), 1067 (m), 986 (s), 799 (w), 749 (s), 698 (m). A satisfactory elemental analysis could not be obtained.

5.6 Experimental details and characterising data for Chapter Four

$\text{Ca}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_4$ (24**).** To a stirring Ca amalgam (0.124 g, 3.08 mmol Ca; 10 mL Hg) was added a red suspension of $[\text{Co}(\text{CO})_3(\text{PPh}_3)]_2$ (0.500 g, 0.617 mmol) in THF (30 mL). The suspension was stirred over the amalgam for 16 h at RT to give a green solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was washed with hexanes (2 x 10 mL) and dried *in vacuo* to afford **24** as a pale green solid. Yield: 0.501 g (71%). Diffraction-quality crystals were grown from a concentrated THF solution at RT. ^1H NMR ($\text{THF}-d_8$, 299.9 MHz): δ 7.49 (24 H, s, *o*- C_6H_5), 7.19 (32 H, s, *m*- & *p*- C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF}-d_8$, 75.5 MHz): δ 142.9 (d, $^1J = 29.4$ Hz, *i*- C_6H_5), 134.3 (d, $^2J = 13.8$ Hz, *o*- C_6H_5), 128.8 (s, *p*- C_6H_5), 128.2 (d, $^4J = 8.8$ Hz, *m*- C_6H_5) ($\delta(\text{CO})$ not observed). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{THF}-d_8$, 121.4 MHz): δ 63.6 (br s). EI-MS: $m/z = 277$ (10%) $[\text{OPPh}_3 - \text{H}]^+$, 262 (20%) $[\text{PPh}_3]^+$, 183 (20%) $[\text{PPh}_2 - 2 \text{H}]^+$, 154 (100%) $[\text{C}_{12}\text{H}_{10}]^+$, 78 (100%) $[\text{C}_6\text{H}_6]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1935 (s, $\nu(\text{CO})$), 1861 (s, $\nu(\text{CO})$), 1729 (s, $\nu(\text{CO})$), 1584 (w), 1297 (w), 1261 (w), 1180 (w), 1090 (m), 1026 (m), 918 (w), 872 (m), 801 (w), 746 (m), 696 (m). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1937 (m), 1874 (s), 1721 (s). Anal. found (calcd. for $\text{C}_{58}\text{H}_{62}\text{CaCo}_2\text{O}_{10}\text{P}_2$): C, 61.29 (61.16); H, 5.69 (5.49)%.

$[\text{Sr}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_5]_2$ (25**).** To a stirring Sr amalgam (0.270 g, 3.08 mmol Sr; 10 mL Hg) was added a red suspension of $[\text{Co}(\text{CO})_3(\text{PPh}_3)]_2$ (0.500 g, 0.617 mmol) in THF (30 mL). The suspension was stirred over the amalgam for 16 h at RT

to give a yellow solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was washed with hexanes (2 x 10 mL) and dried *in vacuo* to afford **25** as a yellow solid. Yield: 0.604 g (78%). Diffraction-quality crystals were grown from a concentrated THF solution at RT. ^1H NMR (THF- d_8 , 299.9 MHz): δ 7.54 (24 H, s, *o*-C₆H₅), 7.21 (32 H, s, *m*- & *p*-C₆H₅). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 143.3 (d, $^1J = 28.7$ Hz, *i*-C₆H₅), 134.3 (d, $^2J = 14.1$ Hz, *o*-C₆H₅), 128.8 (s, *p*-C₆H₅), 128.2 (d, $^4J = 8.8$ Hz, *m*-C₆H₅) ($\delta(\text{CO})$ not observed). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8 , 121.4 MHz): δ 64.1 (br s). El-MS: $m/z = 277$ (95%) $[\text{OPPh}_3 - \text{H}]^+$, 262 (100%) $[\text{PPh}_3]^+$, 183 (100%) $[\text{PPh}_2 - 2 \text{H}]^+$, 154 (100%) $[\text{C}_{12}\text{H}_{10}]^+$, 108 (90%) $[\text{PPh}]^+$, 77 (90%) $[\text{C}_6\text{H}_5]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1930 (s, $\nu(\text{CO})$), 1855 (m, $\nu(\text{CO})$), 1816 (s, br, $\nu(\text{CO})$), 1746 (s, br, $\nu(\text{CO})$), 1585 (w), 1261 (m), 1179 (w), 1089 (m), 1029 (s), 918 (w), 875 (w), 801 (w), 744 (m), 696 (s). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1932 (m), 1874 (s), 1737 (s). Anal. found (calcd. for $\text{C}_{124}\text{H}_{140}\text{Co}_4\text{O}_{22}\text{P}_4\text{Sr}_2$): C, 58.91 (59.16); H, 5.48 (5.61)%.

[Ba{Co(CO)₃(PPh₃)₂(THF)₆]₂ (26). To a stirring Ba amalgam (0.847 g, 6.17 mmol Ba; 20 mL Hg) was added a red suspension of $[\text{Co}(\text{CO})_3(\text{PPh}_3)]_2$ (1.00 g, 1.24 mmol) in THF (50 mL). The suspension was stirred over the amalgam for 16 h at RT to give a green solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was washed with hexanes (2 x 10 mL) and dried *in vacuo* to afford **26** as a dark green solid. Yield: 1.51 g (89%). Diffraction-quality crystals were grown from a concentrated THF solution at RT. ^1H NMR (THF- d_8 , 299.9 MHz): δ 7.50 (24 H, s, *o*-C₆H₅), 7.18 (32 H, s, *m*- & *p*-C₆H₅). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 143.3 (d, $^1J = 28.6$ Hz, *i*-C₆H₅), 134.3 (d, $^2J = 13.9$ Hz, *o*-C₆H₅), 128.8 (s, *p*-C₆H₅), 128.2 (d, $^4J = 8.8$ Hz, *m*-C₆H₅) ($\delta(\text{CO})$ not observed). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8 , 121.4 MHz): δ 64.3 (br s). El-MS: $m/z = 262$ (100%) $[\text{PPh}_3]^+$, 183 (85%) $[\text{PPh}_2 - 2 \text{H}]^+$, 154 (100%) $[\text{C}_{12}\text{H}_{10}]^+$, 108 (85%) $[\text{PPh}]^+$, 78 (100%) $[\text{C}_6\text{H}_6]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1924 (s, $\nu(\text{CO})$), 1818 (s, br, $\nu(\text{CO})$), 1780 (s, br, $\nu(\text{CO})$), 1260 (m), 1168 (w), 1087 (m), 1026 (m), 875 (w), 800 (m), 694 (m). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1931 (m), 1872 (s), 1747 (s). Anal. found (calcd. for $\text{C}_{132}\text{H}_{156}\text{Ba}_2\text{Co}_4\text{O}_{24}\text{P}_4$): C, 57.31 (57.42); H, 5.60 (5.70)%.

[Sm{Co(CO)₃(PPh₃)₂(THF)₅]_x (27). To a stirring Sm amalgam (0.464 g, 3.08 mmol Sm; 10 mL Hg) was added a red suspension of $[\text{Co}(\text{CO})_3(\text{PPh}_3)]_2$ (0.500 g, 0.617 mmol) in THF (30 mL). The solution was stirred over the amalgam for 16 h at RT to

give a dark green solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was washed with pentane (2 x 10 mL) and dried *in vacuo* to afford **27** as a purple-grey solid. Yield: 0.561 g (69%). Diffraction-quality crystals were grown from a concentrated THF solution at RT. ^1H NMR (THF- d_8 , 299.9 MHz): δ 7.93 (12 H, s, *o*-C₆H₅), 7.26 (16 H, s, *m*-C₆H₅ & *p*-C₆H₅). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 142.1 (d, $^1J = 28.5$ Hz, *i*-C₆H₅), 133.9 (d, $^2J = 14.0$ Hz, *o*-C₆H₅), 128.3 (s, *p*-C₆H₅), 127.8 (d, $^4J = 8.9$ Hz, *m*-C₆H₅) ($\delta(\text{CO})$ not observed). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8 , 121.4 MHz): δ 65.7 (br s). EI-MS: $m/z = 262$ (85%) $[\text{PPh}_3]^+$, 183 (80%) $[\text{PPh}_2 - 2\text{H}]^+$, 154 (100%) $[\text{C}_{12}\text{H}_{10}]^+$, 108 (40%) $[\text{PPh}]^+$, 78 (90%) $[\text{C}_6\text{H}_6]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1928 (s, $\nu(\text{CO})$), 1856 (s, $\nu(\text{CO})$), 1815 (s, br, $\nu(\text{CO})$), 1774 (s, br, $\nu(\text{CO})$), 1584 (w), 1295 (w), 1263 (w), 1181 (m), 1157 (w), 1090 (m), 1031 (s), 876 (m), 749 (m), 697 (s). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1933 (m), 1874 (s), 1728 (s). Anal. found (calcd. for C₆₂H₇₀Co₂O₁₁P₂Sm): C, 52.50 (56.35); H, 3.15 (5.34)%.

Sm{Co(CO)₃(PCy₃)₂(THF)₆ (28). To a stirring Sm amalgam (0.887 g, 5.90 mmol Sm; 20 mL Hg) was added a red solution of [Co(CO)₃(PCy₃)₂] (1.00 g, 1.18 mmol) in THF (40 mL). The solution was stirred over the amalgam for 16 h at RT to give a black solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was dried *in vacuo* to afford **28** as a green solid. Yield: 1.19 g (83%) NMR interpretation shows that **28** loses three THF molecules per formula unit upon drying *in vacuo*. The yield and elemental analysis take this into account. Diffraction-quality crystals were grown from a concentrated THF solution at 5 °C. ^1H NMR (C₆D₆, 500.3 MHz): δ 3.61 (12 H, br s, OCH₂), 1.87 (12 H, br s, 2,6-C₆H₁₁), 2.05-1.54 (18 H, br s centred at 1.73 & 1.67, overlapping 3,5- & 4-C₆H₁₁) 1.41 (12 H, br s, 2,6-C₆H₁₁), 1.22 (18 H, br s, 4- & 3,5-C₆H₁₁), 0.25 (6H, br s, 1-C₆H₁₁), -0.33 (12 H, br s, OCH₂CH₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (C₆D₆, 125.8 MHz): δ 31.1 (d, $^1J = 14.7$ Hz, 1-C₆H₁₁), 28.1 (d, $^3J = 9.8$ Hz, 3,5-C₆H₁₁), 27.7 (s, 2,6-C₆H₁₁ & OCH₂), 22.3 (s, 4-C₆H₁₁), 22.2 (s, OCH₂CH₂) ($\delta(\text{CO})$ not observed). ^1H NMR (THF- d_8 , 500.3 MHz): δ 2.49 (12 H, br s, 2,6-C₆H₁₁), 2.06-1.59 (m centred at 1.89 & 1.72, overlapping 2,6-, 3,5- & 4-C₆H₁₁ overlapping with THF resonance) 1.51-1.13 (18 H, m centred at 1.42 & 1.35, overlapping 3,5- & 4-C₆H₁₁) br s, 2,6-C₆H₁₁). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 125.8 MHz): δ 30.5 (s, 2,6-C₆H₁₁), 28.8 (d, $^1J = 10.0$ Hz, 1-C₆H₁₁), 27.8 (s, 3,5-C₆H₁₁), 26.2 (s, 2,6-C₆H₁₁) ($\delta(\text{CO})$ not observed). EI-MS:

$m/z = 280$ (40%) $[\text{PCy}_3]^+$, 198 (100%) $[\text{HPCy}_2]^+$, 143 (35%) $[\text{Co}(\text{CO})_3]^+$, 117 (100%) $[\text{H}_3\text{PCy}]^+$, 83 (80%) $[\text{C}_6\text{H}_{11}]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1917 (s, $\nu(\text{CO})$), 1859 (m, $\nu(\text{CO})$), 1801 (s, $\nu(\text{CO})$), 1750 (s, $\nu(\text{CO})$), 1340 (w), 1293 (w), 1261 (w), 1196 (w), 1171 (w), 1109 (w), 1041 (m), 915 (w), 888 (m), 851 (m), 817 (w), 727 (w). IR (NaCl cell, toluene, $\nu(\text{CO})$, cm^{-1}): 1893 (s), 1837 (s), 1755 (s), 1717 (m). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1921 (m), 1861 (m), 1712 (s). Anal. found (calcd. for $\text{C}_{54}\text{H}_{90}\text{Co}_2\text{O}_9\text{P}_2\text{Sm}$): C, 54.10 (53.45); H, 9.77 (7.48)% (for 3 THF per Sm).

$\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_3(\text{THF})_3$ (29). $\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_3$ (**28**, 450 mg, 0.371 mmol, based on three THF per formula unit) was dissolved in benzene (10 mL) to give a dark red-black solution. The solution was filtered and the residue further extracted with benzene (10 mL). Volatiles were removed from the combined solution under reduced pressure. The solid was dried *in vacuo* to afford the product as a dark red-black solid. Yield: 348 mg (92%). Diffraction-quality crystals were grown from a concentrated pentane solution at RT. NMR interpretation shows that **29** loses 1.5 THF molecules per formula unit upon drying *in vacuo*. The yield and elemental analysis take this into account. ^1H NMR (C_6D_6): Identical to NMR before benzene extraction but with 1.5 THF per Sm. EI-MS: $m/z = 280$ (40%) $[\text{PCy}_3]^+$, 198 (100%) $[\text{HPCy}_2]^+$, 143 (30%) $[\text{Co}(\text{CO})_3]^+$, 117 (100%) $[\text{H}_3\text{PCy}]^+$, 83 (80%) $[\text{C}_6\text{H}_{11}]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1917 (s, $\nu(\text{CO})$), 1861 (s, br, $\nu(\text{CO})$), 1766 (s, br, $\nu(\text{CO})$), 1342 (w), 1295 (w), 1262 (m), 1198 (w), 1172 (m), 1111 (m), 1035 (m), 1006 (m), 916 (w), 887 (m), 851 (m), 818 (m), 728 (m). IR (NaCl cell, toluene, $\nu(\text{CO})$, cm^{-1}): IR data consistent with that observed for $[\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_6]_2$ (**28**). Anal. found (calcd. for $\text{C}_{75}\text{H}_{123}\text{Co}_3\text{O}_{12}\text{P}_3\text{Sm}$): C, 48.71 (55.03); H, 6.85 (7.57)%.

Alternative synthesis of $\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_3(\text{THF})_3$ (29). To SmI_2 (167 mg, 0.412 mmol) and $[\text{K}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}(\text{THF})_2]_x$ (**33**, 0.500 g, 0.824 mmol) was added THF (20 mL). The resulting blue solution was stirred for 24 h at RT. The blue solution was filtered and volatiles were removed under reduced pressure to give a green solid (561 mg). The material was extracted into benzene (20 mL), filtered to give a dark red-purple solution and volatiles were removed under reduced pressure to afford **33** as a dark red-black solid. Yield: 298 mg (71%). IR (NaCl plates, Nujol mull, cm^{-1}): Consistent with that for $[\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_3(\text{THF})_3]$ (**29**) synthesised *via* $[\text{Sm}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_6]_2$ (**28**).

$\text{Yb}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2(\text{THF})_5$ (30). To a stirring Yb amalgam (0.534 g, 3.08 mmol

Yb; 10 mL Hg) was added a red suspension of $[\text{Co}(\text{CO})_3(\text{PPh}_3)]_2$ (0.500 g, 0.617 mmol) in THF (30 mL). The suspension was stirred over the amalgam for 16 h at RT to give a yellow solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was washed with hexanes (2 x 10 mL) and dried *in vacuo* to afford **28** as a yellow solid. Yield: 0.684 g (83%). Diffraction-quality crystals were grown from a concentrated THF solution at RT. ^1H NMR (THF- d_8 , 299.9 MHz): δ 7.51 (24 H, s, *o*-C₆H₅), 7.20 (32 H, s, *m*- & *p*-C₆H₅). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 75.5 MHz): δ 142.9 (d, $^1J = 29.1$ Hz, *i*-C₆H₅), 134.3 (d, $^2J = 14.0$ Hz, *o*-C₆H₅), 129.0 (s, *p*-C₆H₅), 128.3 (d, $^4J = 8.9$ Hz, *m*-C₆H₅) ($\delta(\text{CO})$ not observed). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8 , 121.4 MHz): δ 63.8 (br s). EI-MS: $m/z = 277$ (70%) $[\text{OPPh}_3 - \text{H}]^+$, 262 (80%) $[\text{PPh}_3]^+$, 183 (80%) $[\text{PPh}_2 - 2 \text{ H}]^+$, 154 (100%) $[\text{C}_{12}\text{H}_{10}]^+$, 108 (60%) $[\text{PPh}]^+$, 77 (35%) $[\text{C}_6\text{H}_5]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1952 (s, $\nu(\text{CO})$), 1927 (s, $\nu(\text{CO})$), 1854 (s, $\nu(\text{CO})$), 1762 (s, $\nu(\text{CO})$), 1584 (w), 1260 (m), 1182 (w), 1091 (s), 1026 (s), 914 (w), 871 (m), 800 (m), 744 (m), 695 (s). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1939 (m), 1872 (s), 1728 (s). Anal. found (calcd. for $\text{C}_{62}\text{H}_{70}\text{Co}_2\text{O}_{11}\text{P}_2\text{Yb}$): C, 55.57 (55.40); H, 5.36 (5.25)%.

$[\text{Mg}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})]_2$ (31). To a stirring Mg amalgam (0.0574 g, 2.36 mmol Mg; 10 mL Hg) was added a red solution of $[\text{Co}(\text{CO})_3(\text{PCy}_3)]_2$ (0.400 g, 0.472 mmol) in THF (30 mL). The solution was stirred over the amalgam for 16 h at RT to give a dark dichroic red-green solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was washed with hexanes (2 x 10 mL) and dried *in vacuo* to afford **31**·1.5(THF) as a white solid. Yield: 0.410 g (87%). Diffraction-quality crystals were grown from a toluene solution layered with pentane at RT. ^1H NMR (C_6D_6 , 500.3 MHz): δ 3.91 (14 H, br s, OCH_2), 2.26 (24 H, m, 2,6-C₆H₁₁), 2.10 (12 H, m, 1-C₆H₁₁), 1.82 (24 H, m, 3,5-C₆H₁₁), 1.77-1.58 (36 H, m centred at 1.71 & 1.64, overlapping 4- & 2,6-C₆H₁₁), 1.44 (14 H, br s, OCH_2CH_2), 1.28 (36 H, m, 4- & 3,5-C₆H₁₁). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz): δ 210.4 (s, CO), 69.2 (s, OCH_2), 37.7 (d, $^1J = 16.6$ Hz, 1-C₆H₁₁), 30.4 (s, 2,6-C₆H₁₁), 28.2 (d, $^3J = 10.2$ Hz, 3,5-C₆H₁₁), 27.0 (s, 4-C₆H₁₁), 25.5 (s, OCH_2CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.4 MHz): δ 68.6 (br s). EI-MS: $m/z = 280$ (70%) $[\text{PCy}_3]^+$, 198 (100%) $[\text{HPCy}_2]^+$, 143 (50%) $[\text{Co}(\text{CO})_3]^+$, 117 (100%) $[\text{H}_3\text{PCy}]^+$, 83 (70%) $[\text{C}_6\text{H}_{11}]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1935 (s, $\nu(\text{CO})$), 1861 (s, $\nu(\text{CO})$), 1720 (s, $\nu(\text{CO})$), 1261 (w), 1171 (w), 1026 (m), 918 (w), 882 (w), 850 (w), 801 (w). IR

(NaCl cell, toluene, $\nu(\text{CO})$, cm^{-1}): 1905 (s), 1842 (m), 1701 (m). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1931 (m), 1867 (m), 1698 (s). Anal. found (calcd. for $\text{C}_{98}\text{H}_{160}\text{Co}_4\text{Mg}_2\text{O}_{15.5}\text{P}_4$ (**31**·1.5(THF)): C, 58.75 (59.01); H, 7.93 (8.09)%.

[Ca{Co(CO)₃(PCy₃)₂(THF)₂}]_x (32**).** To a stirring Ca amalgam (0.118 g, 2.95 mmol Ca; 10 mL Hg) was added a red solution of $[\text{Co}(\text{CO})_3(\text{PCy}_3)]_2$ (0.500 g, 0.590 mmol) in THF (30 mL). The solution was stirred over the amalgam for 16 h at RT to give a dark dichroic red-green solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was dried *in vacuo* to afford **32** as a white solid. Yield: 0.512 g (84%). Diffraction-quality crystals of **32** were grown from a concentrated toluene solution layered with pentane at RT. Diffraction-quality crystals of $\text{Ca}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}_2(\text{THF})_5$ (**34**) were grown from a concentrated THF solution of **32** in THF at RT. ^1H NMR (C_6D_6 , 500.3 MHz): δ 4.00 (8 H, br s, OCH_2), 2.21 (12 H, m, 2,6- C_6H_{11}), 1.97 (6 H, m, 1- C_6H_{11}), 1.86 (12 H, m, 3,5- C_6H_{11}), 1.76-1.53 (26 H, m centred at 1.71 & 1.65 and br s at 1.59, overlapping 4- & 2,6- C_6H_{11} and OCH_2CH_2), 1.33 (18 H, m, 4- & 3,5- C_6H_{11}). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz): δ 217.4 (s, CO), 69.2 (s, OCH_2), 37.4 (d, $^1J = 14.9$ Hz, 1- C_6H_{11}), 30.5 (s, 2,6- C_6H_{11}), 28.3 (d, $^3J = 10.0$ Hz, 3,5- C_6H_{11}), 27.2 (s, 4- C_6H_{11}), 25.7 (s, OCH_2CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.4 MHz): δ 71.2 (br s). EI-MS: $m/z = 280$ (20%) $[\text{PCy}_3]^+$, 198 (70%) $[\text{HPCy}_2]^+$, 143 (15%) $[\text{Co}(\text{CO})_3]^+$, 117 (80%) $[\text{H}_3\text{PCy}]^+$, 83 (95%) $[\text{C}_6\text{H}_{11}]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1929 (s, $\nu(\text{CO})$), 1844 (s, $\nu(\text{CO})$), 1743 (s, $\nu(\text{CO})$), 1718 (s, $\nu(\text{CO})$), 1261 (w), 1028 (m), 876 (w), 803 (w). IR (NaCl cell, toluene, $\nu(\text{CO})$, cm^{-1}): 1913 (s), 1838 (m), 1755 (s), 1718 (s). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1931 (m), 1867 (m), 1698 (s). Anal. found (calcd. for $\text{C}_{50}\text{H}_{82}\text{CaCo}_2\text{O}_8\text{P}_2$): C, 58.08 (58.24); H, 7.92 (8.02)%.

Alternative synthesis of [Ca{Co(CO)₃(PCy₃)₂(THF)₂}]_x (32**).** To $[\text{K}\{\text{Co}(\text{CO})_3(\text{PCy}_3)\}(\text{THF})_2]_x$ (**33**, 0.400 g, 0.659 mmol) and CaI_2 (0.0791 g, 0.330 mmol) was added THF (20 mL) to give a yellow-green solution and white suspension. The mixture was stirred for 16 h at RT. Volatiles were removed under reduced pressure to give an off-white solid. The solid was extracted into THF (10 mL), filtered and volatiles removed under reduced pressure to give an off-white solid. The solid was washed with pentane (2 x 5 mL) and dried *in vacuo* to afford **32** as a white solid. Yield: 0.361 g (53%).

[K{Co(CO)₃(PCy₃)}(THF)₂]_x (33**).** To a stirring K amalgam (0.231 g, 5.90 mmol K; 10 mL Hg) was added a red solution of [Co(CO)₃(PCy₃)₂] (1.00 g, 1.18 mmol) in THF (40 mL). The solution was stirred over the amalgam for 16 h at RT to give a pale-yellow solution. The solution was filtered and volatiles were removed under reduced pressure. The resulting solid was washed with pentane (2 x 10 mL) and dried *in vacuo* to afford **33** as a white solid. Yield: 1.09 g (76%). Diffraction-quality crystals were grown from a concentrated THF solution at RT. ¹H NMR (THF-*d*₈, 500.3 MHz): δ 1.98 (6 H, m, 2,6-C₆H₁₁), 1.73 (overlapping with THF resonance, m, 3,5-C₆H₁₁), 1.64 (6 H, m, overlapping 1- & 4-C₆H₁₁), 1.39 (6 H, m, 2,6-C₆H₁₁), 1.22 (9 H, m, overlapping 4- & 3,5-C₆H₁₁). ¹³C{¹H} NMR (THF-*d*₈, 125.8 MHz): δ 38.4 (d, ¹J = 11.7 Hz, 1-C₆H₁₁), 31.1 (d, ²J = 3.4 Hz, 2,6-C₆H₁₁), 29.1 (d, ³J = 9.9 Hz, 3,5-C₆H₁₁), 28.0 (s, 4-C₆H₁₁) (δ(CO) not observed). ³¹P{¹H} NMR (THF-*d*₈, 121.4 MHz): δ 74.7 (br s). EI-MS: *m/z* = 280 (10%) [PCy₃]⁺, 198 (60%) [HPCy₂]⁺, 143 (15%) [Co(CO)₃]⁺, 117 (100%) [H₃PCy]⁺, 83 (40%) [C₆H₁₁]⁺. IR (NaCl plates, Nujol mull, cm⁻¹): 1921 (s, ν(CO)), 1822 (s, br, ν(CO)), 1756 (s, br, ν(CO)), 1264 (w), 1198 (w), 1173 (w), 1111 (w), 1040 (w), 1005 (w), 916 (w), 851 (w). IR (NaCl cell, 0.33 mmol dm⁻³ [**33**], THF, ν(CO), cm⁻¹): 1914 (s), 1839 (s), 1788 (s). Anal. found (calcd. for C₂₉H₄₉CoKO₅P): C, 56.95 (57.41); H, 7.96 (8.14)%.

[Sr{Co(CO)₃(PCy₃)}₂(THF)₃]_x (35**).** To a stirring Sr amalgam (0.207 g, 2.36 mmol Sr; 10 mL Hg) was added a red solution of [Co(CO)₃(PCy₃)₂] (0.400 g, 0.472 mmol) in THF (30 mL). The solution was stirred over the amalgam for 16 h at RT to give a dark dichroic red-green solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was washed with hexanes (2 x 10 mL) and dried *in vacuo* to afford **35** as a white solid. Yield: 0.381 g (70%). Diffraction-quality crystals were grown from a concentrated pentane solution at RT. ¹H NMR (C₆D₆, 500.3 MHz): δ 4.05 (12 H, br s, OCH₂), 2.21 (12 H, m, 2,6-C₆H₁₁), 2.05-1.81 (18 H, m centred at 1.96 & 1.89, 1- & 3,5-C₆H₁₁), 1.79-1.52 (30 H, m centred at 1.73 & 1.67 and br s at 1.60, overlapping 4- & 2,6-C₆H₁₁ and OCH₂CH₂), 1.34 (18 H, m, 4- & 3,5-C₆H₁₁). ¹³C{¹H} NMR (C₆D₆, 125.8 MHz): δ 217.8 (s, CO), 69.0 (s, OCH₂), 37.5 (d, ¹J = 14.9 Hz, 1-C₆H₁₁), 30.5 (s, 2,6-C₆H₁₁), 28.4 (d, ³J = 10.1 Hz, 3,5-C₆H₁₁), 27.2 (s, 4-C₆H₁₁), 25.7 (s, OCH₂CH₂). ³¹P{¹H} NMR (C₆D₆, 121.4 MHz): δ 71.7 (br s). EI-MS: *m/z* = 280 (80%) [PCy₃]⁺, 198 (100%) [HPCy₂]⁺, 143 (50%) [Co(CO)₃]⁺, 117 (100%) [H₃PCy]⁺, 83 (80%) [C₆H₁₁]⁺.

IR (NaCl plates, Nujol mull, cm^{-1}): 1916 (m, $\nu(\text{CO})$), 1821 (s, $\nu(\text{CO})$), 1787 (s, $\nu(\text{CO})$), 1743 $\nu(\text{CO})$), 1260 (w), 1036 (m), 886 (w), 851 (w), 800 (w). IR (NaCl cell, toluene, $\nu(\text{CO})$, cm^{-1}): 1913 (s), 1837 (s), 1755 (s), 1717 (m). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1921 (m), 1895 (m), 1721 (s). Anal. found (calcd. for $\text{C}_{54}\text{H}_{90}\text{Co}_2\text{O}_9\text{P}_2\text{Sr}$): C, 56.13 (56.36); H, 8.08 (7.88)%.

[Eu{Co(CO)₃(PCy₃)₂(THF)₃]_x (36). To a stirring Eu amalgam (1.40 g, 9.21 mmol Eu; 20 mL Hg) was added a red solution of $[\text{Co}(\text{CO})_3(\text{PCy}_3)_2]$ (1.56 g, 1.84 mmol) in THF (40 mL). The solution was stirred over the amalgam for 16 h at RT to give a dark dichroic red-green solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was dried *in vacuo* to afford **36** as a light green-grey solid. Yield: 1.67 g (75%). Diffraction-quality crystals of **36** were grown from a concentrated pentane solution at RT. Diffraction-quality crystals of $[\text{Eu}\{\text{Co}(\text{CO})_3(\text{PCy}_3)_2(\text{THF})_4\}]_x$ (**40**) were grown from a concentrated THF solution at RT. EI-MS: $m/z = 280$ (30%) $[\text{PCy}_3]^+$, 198 (95%) $[\text{HPCy}_2]^+$, 143 (20%) $[\text{Co}(\text{CO})_3]^+$, 117 (100%) $[\text{H}_3\text{PCy}]^+$, 83 (70%) $[\text{C}_6\text{H}_{11}]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1918 (s, $\nu(\text{CO})$), 1797 (s, br $\nu(\text{CO})$), 1746 (s, br, $\nu(\text{CO})$), 1293 (w), 1261 (w), 1172 (w), 1109 (w), 1040 (m), 915 (w), 887 (m), 850 (m), 801 (w). IR (NaCl cell, toluene, $\nu(\text{CO})$, cm^{-1}): 1892 (s), 1837 (s), 1755 (s), 1718 (m). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1922 (m), 1860 (m), 1720 (s). Anal. found (calcd. for $\text{C}_{54}\text{H}_{90}\text{Co}_2\text{EuO}_9\text{P}_2$): C, 53.19 (53.38); H, 7.31 (7.47)%.

Ba{Co(CO)₃(PCy₃)₂(THF)₆ (37). To a stirring Ba amalgam (0.407 g, 2.95 mmol Ba; 20 mL Hg) was added a red solution of $[\text{Co}(\text{CO})_3(\text{PCy}_3)_2]$ (0.500 g, 0.590 mmol) in THF (40 mL). The solution was stirred over the amalgam for 16 h at RT to give a dark dichroic red-green solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting off-white solid was washed with pentane (2 x 10 mL) and dried *in vacuo* to afford **37** as a white solid. Yield: 0.444 g (53%). Diffraction-quality crystals were grown from a concentrated THF solution at RT. ^1H NMR (THF- d_8 , 500.3 MHz): δ 1.97 (12 H, m, 2,6- C_6H_{11}), 1.75 (overlapping with THF resonance, m, 3,5- C_6H_{11}), 1.66 (12 H, m, overlapping 1- & 4- C_6H_{11}), 1.38 (12 H, m, 2,6- C_6H_{11}), 1.23 (18 H, m, overlapping 4- & 3,5- C_6H_{11}). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 125.8 MHz): δ 220.9 (s, CO), 38.10 (d, $^1J = 12.8$ Hz, 1- C_6H_{11}), 31.1 (s, 2,6- C_6H_{11}), 29.0 (d, $^3J = 10.0$ Hz, 3,5- C_6H_{11}), 27.9 (s, 4- C_6H_{11}). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8 , 121.4 MHz): δ 76.6 (br s). EI-MS: $m/z = 280$ (15%) $[\text{PCy}_3]^+$,

198 (65%) $[\text{HPCy}_2]^+$, 117 (100%) $[\text{H}_3\text{PCy}]^+$, 83 (80%) $[\text{C}_6\text{H}_{11}]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1953 (s, $\nu(\text{CO})$), 1813 (s, br, $\nu(\text{CO})$), 1755 (s, br, $\nu(\text{CO})$), 1294 (w), 1261 (w), 1194 (w), 1172 (w), 1107 (w), 1039 (m), 1005 (w), 917 (w), 886 (m), 851 (m), 818 (w). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1921 (s), 1857 (s), 1737 (s). Anal. found (calcd. for $\text{C}_{66}\text{H}_{114}\text{BaCo}_2\text{O}_{12}\text{P}_2$): C, 55.69 (55.95); H, 7.89 (8.11)%.

Ba{Co(CO)₃(PCy₃)₂(DME)₄ (38). To Ba{Co(CO)₃(PCy₃)₂(THF)₆ (**37**, 0.250 g, 0.176 mmol) was added DME (30 mL) to give a white suspension. The suspension was heated to 85 °C to give a yellow solution. The solution was stirred for 20 min, filtered and allowed to cool to RT to return a white suspension. Volatiles were removed under reduced pressure and the resulting solid dried *in vacuo* to afford Ba{Co(CO)₃(PCy₃)₂(DME)₄ as a white solid. Yield: 219 mg (92%). Diffraction-quality crystals were grown by slow cooling of a DME solution from 85 °C to RT. ¹H NMR (THF-*d*₈, 500.3 MHz): δ 3.43 (16 H, s, OCH₂), 3.27 (24 H, s, OMe), 1.97 (12 H, m, 2,6-C₆H₁₁), 1.76 (overlapping with THF resonance, m, 3,5-C₆H₁₁), 1.66 (12 H, m, overlapping 1 & 4-C₆H₁₁), 1.38 (12 H, m, 2,6-C₆H₁₁), 1.24 (18 H, m, overlapping 4- & 3,5-C₆H₁₁). ¹³C{¹H} NMR (THF-*d*₈, 125.8 MHz): δ 72.9 (s, OCH₂), 59.1 (s, OMe), 38.1 (d, ¹J = 12.7 Hz, 1-C₆H₁₁), 31.2 (s, 2,6-C₆H₁₁), 29.0 (d, ³J = 9.9 Hz, 3,5-C₆H₁₁), 28.0 (s, 4-C₆H₁₁) ($\delta(\text{CO})$ not observed). ³¹P{¹H} NMR (THF-*d*₈, 121.4 MHz): δ 76.6 (br s). EI-MS: *m/z* = 280 (85%) $[\text{PCy}_3]^+$, 198 (100%) $[\text{HPCy}_2]^+$, 143 (80%) $[\text{Co(CO)}_3]^+$, 117 (100%) $[\text{H}_3\text{PCy}]^+$, 83 (100%) $[\text{C}_6\text{H}_{11}]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1928 (m, $\nu(\text{CO})$), 1915 (s, $\nu(\text{CO})$), 1827 (s, $\nu(\text{CO})$), 1756 (s, $\nu(\text{CO})$), 1292 (w), 1261 (w), 1193 (w), 1171 (w), 1117 (m), 1068 (s), 1027 (m), 887 (w), 857 (m), 802 (w). IR (NaCl cell, THF, $\nu(\text{CO})$, cm^{-1}): 1921 (s), 1856 (s), 1737 (s). Anal. found (calcd. for $\text{C}_{58}\text{H}_{106}\text{Ba}_1\text{Co}_2\text{O}_{14}\text{P}_2$): C, 51.52 (51.81); H, 7.81 (7.95)%.

[Yb{Co(CO)₃(PCy₃)₂(THF)₃]₂ (39). To a stirring Yb amalgam (0.409 g, 2.36 mmol Yb; 10 mL Hg) was added a red solution of [Co(CO)₃(PCy₃)₂] (0.400 g, 0.472 mmol) in THF (30 mL). The solution was stirred over the amalgam for 16 h at RT to give a yellow solution. The solution was filtered away from the amalgam and volatiles removed under reduced pressure. The resulting solid was washed with pentane (2 x 10 mL) and dried *in vacuo* to afford **39** as a yellow solid. Yield: 0.360 g (62%). Diffraction-quality crystals were grown from a concentrated pentane solution at RT. ¹H NMR (C₆D₆, 500.3 MHz): δ 3.84 (24 H, br s, OCH₂), 2.20 (24 H, m, 2,6-C₆H₁₁), 1.98 (12 H, m, 1-C₆H₁₁), 1.82 (24 H, m, 3,5-C₆H₁₁), 1.66 (36 H, m, overlapping 4- &

2,6-C₆H₁₁, 1.50 (24 H, br s, OCH₂CH₂), 1.30 (36 H, m, 4- & 3,5-C₆H₁₁). ¹³C{¹H} NMR (C₆D₆, 125.8 MHz): δ 217.0 (s, CO), 68.7 (s, OCH₂), 37.5 (d, ¹J = 15.3 Hz, 1-C₆H₁₁), 30.5 (s, 2,6-C₆H₁₁), 28.3 (d, ³J = 10.1 Hz, 3,5-C₆H₁₁), 27.2 (s, 4-C₆H₁₁), 25.7 (s, OCH₂CH₂). ³¹P{¹H} NMR (C₆D₆, 121.4 MHz): δ 71.6 (br s). EI-MS: *m/z* = 280 (85%) [PCy₃]⁺, 198 (100%) [HPCy₂]⁺, 143 (75%) [Co(CO)₃]⁺, 117 (100%) [H₃PCy]⁺, 83 (90%) [C₆H₁₁]⁺. IR (NaCl plates, Nujol mull, cm⁻¹): 1914 (s, ν(CO)), 1853 (s, ν(CO)), 1783 (s, ν(CO)), 1757 (s, ν(CO)), 1295 (w), 1262 (w), 1171 (w), 1109 (w), 1028 (s), 915 (w), 884 (m), 850 (w). IR (NaCl cell, toluene, ν(CO), cm⁻¹): 1897 (s), 1838 (s), 1754 (s), 1718 (m ν(CO)). IR (NaCl cell, THF, ν(CO), cm⁻¹): 1924 (m), 1862 (m), 1712 (s). Anal. found (calcd. for C₁₀₈H₁₈₀Co₄O₁₈P₄Yb₂): C, 52.21 (52.47); H, 7.13 (7.34)%.

First alternative synthesis of [Yb{Co(CO)₃(PCy₃)₂(THF)₃]₂ (39). To [K{Co(CO)₃(PCy₃)}(THF)₂]_x (**33**, 0.400 g, 0.659 mmol) and YbI₂ (0.141 g, 0.330 mmol) was added THF (20 mL) to give a yellow solution with white suspension. The mixture was stirred for 16 h at RT. Volatiles were removed under reduced pressure to give a yellow solid. The solid was extracted into toluene (20 mL), filtered and volatiles were removed under reduced pressure to afford **39** as a yellow solid. Yield: 0.278 g (58%).

Second alternative synthesis of [Yb{Co(CO)₃(PCy₃)₂(THF)₃]₂ (39). To [Ca{Co(CO)₃(PCy₃)₂(THF)₂]_x (**32**, 400 mg, 0.388 mmol) and YbI₂ (0.167 mg, 0.388 mmol) was added THF (20 mL). The resulting yellow solution with white suspension was stirred for 16 h at RT. Volatiles were removed under reduced pressure to give a yellow solid. The solid was extracted into toluene (30 mL), filtered and volatiles were removed under reduced pressure. The resulting solid was washed with pentane (2 x 5 mL) to afford **39** as a yellow solid. Yield: 246 mg (51%).

[Na{Co(CO)₃(PCy₃)}(THF)₅] (41). To a stirring Na amalgam (0.679 g, 2.95 mmol Na; 10 mL Hg) was added a red solution of [Co(CO)₃(PCy₃)]₂ (0.500 g, 0.590 mmol) in THF (30 mL). The solution was stirred over the amalgam for 16 h at RT to give a pale-yellow solution. The solution was filtered and volatiles were removed under reduced pressure. The resulting solid was washed with pentane (2 x 10 mL) and dried *in vacuo* to afford **41** as a white solid. Yield: 0.671 g (70%). Diffraction-quality crystals were grown from a concentrated THF solution at RT. ¹H NMR (THF-*d*₈, 500.3 MHz): δ 1.95 (6 H, m, 2,6-C₆H₁₁), 1.73 (overlapping with THF resonance, m,

3,5-C₆H₁₁), 1.61 (6 H, m, overlapping 1- & 4-C₆H₁₁), 1.31 (6 H, m, 2,6-C₆H₁₁), 1.19 (9 H, m, overlapping 4- & 3,5-C₆H₁₁). ¹³C{¹H} NMR (THF-*d*₈, 125.8 MHz): δ 219.2 (s, CO) 38.4 (d, ¹J = 12.3 Hz, 1-C₆H₁₁), 31.0 (d, ²J = 3.0 Hz, 2,6-C₆H₁₁), 29.1 (d, ³J = 9.9 Hz, 3,5-C₆H₁₁), 28.0 (s, 4-C₆H₁₁). ³¹P{¹H} NMR (THF-*d*₈, 121.4 MHz): δ 74.8 (br s). EI-MS: *m/z* = 280 (40%) [PCy₃]⁺, 198 (100%) [HPCy₂]⁺, 143 (30%) [Co(CO)₃]⁺, 117 (100%) [H₃PCy]⁺, 83 (40%) [C₆H₁₁]⁺. IR (NaCl plates, Nujol mull, cm⁻¹): 1948 (s, ν(CO)), 1922 (s, ν(CO)), 1810 (s, br, ν(CO)), 1781 (s, br ν(CO)), 1267 (w), 1197 (w), 1110 (w), 1023 (w), 1005 (w), 916 (w), 850 (w), 812 (w). IR (NaCl cell, 0.33 mmol dm⁻³ [**41**], THF, ν(CO), cm⁻¹): 1916 (s), 1849 (s), 1782 (s). Anal. found (calcd. for C₄₁H₇₃CoNaO₈P): C, 60.80 (61.03); H, 8.84 (9.12)%.

5.7 References

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Appendix

A.1 Attempted synthesis of $[\text{CaRp}_2(\text{THF})_x]_y$ (**42**)

In an attempt to expand the chemistry discussed in Chapter Two to the second row of the transition metals, Rp_2 was synthesised according to literature procedures and reacted in THF with an excess of Ca/Hg in THF in an attempt to synthesise $[\text{CaRp}_2(\text{THF})_y]_x$ (**42**).¹ The ^1H NMR ($\text{THF}-d_8$) spectrum featured two singlet resonances at 5.78 and 4.89 ppm, attributed to Cp ligands. The corresponding resonance for Rp_2 comes at 5.34 ppm. A concentrated THF solution afforded diffraction-quality crystals of $\text{Ca}\{\text{CpRu}(\text{CO})_2\}(\text{OH})_4$ (**43**). The molecular structure and selected distances and angles are shown in Figure A.1 and Table A.1.

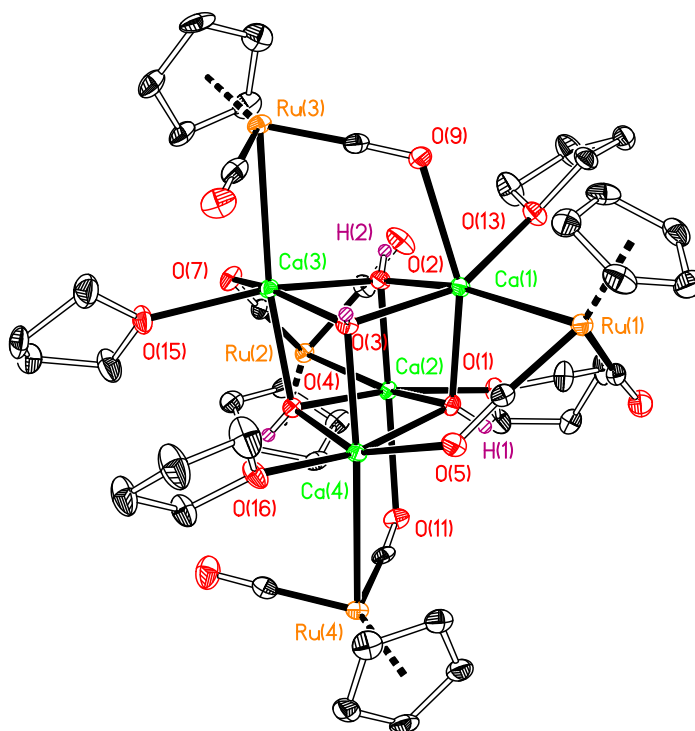


Figure A1. Displacement ellipsoid plot (25% probability) of $\text{Ca}\{\text{CpRu}(\text{CO})_2\}(\text{OH})_4$ (**43**). H atoms omitted for clarity with the exception of hydroxyl groups where H atoms are drawn as spheres of arbitrary radius.

Table A1. Selected distances (Å) and angles (°) for Ca{CpRu(CO)₂}(OH)₄ (**43**).

Ca(1)-Ru(1)	3.1728(10)	Ca(1)-O(1)	2.312(3)
Ca(1)-O(2)	2.331(3)	Ca(1)-O(3)	2.346(4)
Ca(1)-O(9)	2.522(4)	Ca(1)-O(13)	2.451(3)
Ru(1)-C(1)	1.818(5)	Ru(1)-C(2)	1.827(5)
C(1)-O(5)	1.198(6)	C(2)-O(6)	1.181(6)
Ru(1)-Cp _{cent} (1)	1.940		
Ca(1)-O(1)-Ca(2)	103.18(13)	Ru(1)-Ca(1)-O(2)	171.27(10)
Ru(1)-Ca(1)-O(9)	99.87(9)	O(1)-Ca(1)-O(2)	76.60(12)
O(1)-Ca(1)-O(3)	79.35(12)	O(1)-Ca(1)-O(13)	111.96(12)
O(2)-Ca(1)-O(3)	77.95(13)	O(3)-Ca(1)-O(9)	83.93(12)
O(9)-Ca(1)-O(13)	79.46(13)	Ca(1)-Ru(1)-C(1)	71.12(14)
Ca(1)-Ru(1)-C(2)	6.96(15)	Ca(1)-Ru(1)-Cp _{cent} (1)	121.57
C(1)-Ru(1)-C(2)	88.7(2)	C(1)-Ru(1)-Cp _{cent} (1)	138.65
C(2)-Ru(1)-Cp _{cent} (1)	131.26		

Given the similar environments at each Ca and Ru centre, parameters associated with Ca(1) and Ru(1) will be focussed on. Compound **43** consists of a distorted heterocubane core with alternating Ca atoms and OH groups at the vertices. Each six-coordinate Ca centre has distorted octahedral geometry and is bound to three OH groups, a THF ligand and two R_p[−] anions. For the latter, one of these interactions occurs *via* a direct Ca-Ru bond whilst the other involves an isocarbonyl bridge to a R_p[−] anion that undergoes Ca-Ru bonding with a neighbouring Ca atom. The Ca(1)-Ru(1) distance of 3.1728(10) Å is consistent with the sum of the respective covalent radii (3.22(12) Å).² This is the first example of a structurally authenticated direct interaction between Ca and Ru or any of the 2nd row transition metals. The Ca(1)-Ru(1) distance is comparable with the Yb-Ru distances in Kempe's [YbR_p2(THF)₂]_x (**1.91**, 3.1808(7) and 3.1391(8) Å) but considerably longer than those in YbR_p2(^tBu₃py)₃ (**1.92**, 3.0626(4) and 3.0129(4) Å).³ The Ca(1)-O(9) distance (2.522(4) Å), corresponding to the isocarbonyl interaction with Ru(2), is longer than the bonds to the hydroxyl groups (O(1) = 2.312(3), O(2) = 2.331(3), O(3) = 2.346(4) Å) or the coordinated THF (O(13) = 2.451(3) Å). The influence of the isocarbonyl bridged interaction on the R_p[−] anion

carbonyl C-O and Ru-C distances is minimal. For example Ru(1)-C(1) = 1.818(5) and Ru(1)-C(2) = 1.827(5) Å, identical within error. As mentioned the heterocubane core is distorted from an ideal geometry, the Ca-O-Ca angles are obtuse and the O-Ca-O angles are acute. For example Ca(1)-O(1)-Ca(2) = 103.18(13) and O(1)-Ca(1)-O(2) = 76.60(12)°.

Whilst lacking metal-metal interactions, structurally authenticated examples of the Ca₄O₄ heterocubane core have been reported.⁴⁻⁷ For example, [Ca(TMHD)(OEt)(EtOH)]₄ (**A.1**) illustrated in Figure A.2 comprises a Ca₄O₄ distorted cube with each Ca coordinated to a bidentate TMHD (H-TMHD = ^tBuCOCH₂CO^tBu) ligand, three OEt groups at the vertices of the cube and one EtOH. As with **43**, acute O-Ca-O (78.0(2)-82.6(2)°) and obtuse Ca-O-Ca (96.1(2)-101.8(2)°) angles are observed within the distorted cube motif.

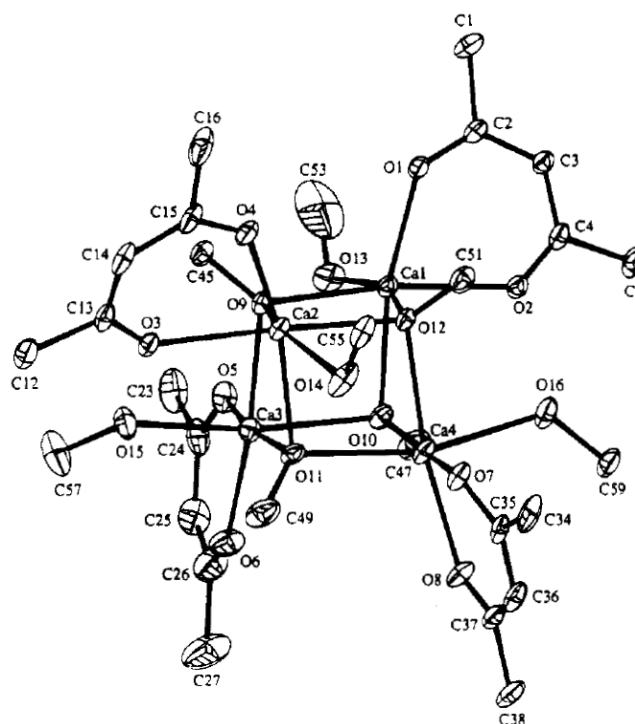


Figure A.2. Displacement ellipsoid plot of [Ca(TMHD)(OEt)(EtOH)]₄ (**A.1**). H atoms and terminal Me groups omitted on EtOH ligands and ^tBu groups for clarity.⁶

Given Kempe's successful synthesis of **1.91** using NaRp(THF),³ CaI₂ was reacted with NaRp(THF) in THF in an attempt to obtain **42**. This gave a mixture of products by ¹H NMR spectroscopy. KRp(THF) was also synthesised and reacted with CaI₂ on the NMR tube-scale to afford a mixture of products by ¹H NMR. Attempts to react Rp₂ with Ca/NH₃(L) were also unsuccessful, affording a brown solid, insoluble in THF or pyridine. Other routes to **42** were not investigated.

A.2 DFT Computational analysis of $[\text{CaRp}_2(\text{THF})_2]_2$ (**42Q**)

To gain an insight into the possible Ca-Ru interactions in **42**, the model structure $[\text{CaRp}_2(\text{THF})_3]_2$ **42Q** (Figure A.3) was analysed by DFT. Structure **42Q** bears two Ca-Ru interactions per dimer with an average distance of 3.063 Å, consistent with the sum of the respective covalent radii (3.22(12) Å) and the average Ca-Ru distance in **42** (3.1180(5) Å).² As with $[\text{CaFp}_2(\text{THF})_3]_2$ (**3**) the minimised structure also contains two isocarbonyl interactions per Ca centre, one is a component in the familiar eight-membered ring and the other linkage is to a Rp^- anion external to the ring. Consistent with the larger covalent radius of Ru compared to Fe, the span of these linkages is longer in **42Q** (4.965 Å) than in **3Q** (4.945 Å). As with the DFT calculated structures **3Q** and $[\text{YbFp}_2(\text{THF})_3]_2$ (**6Q**) (and their experimentally determined analogues **3** and **6**) the minimised structure of **42Q** has an eight-membered ring in a chair-conformation.

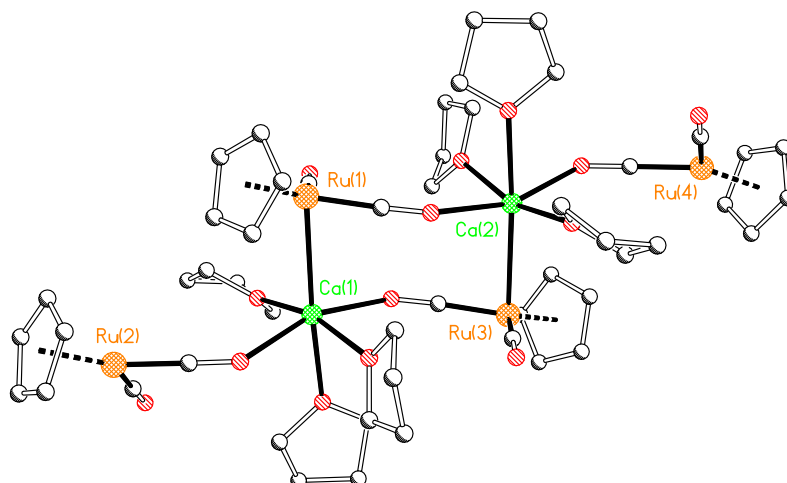


Figure A.3. DFT calculated structure of $[\text{CaRp}_2(\text{THF})_3]_2$ (**42Q**).

Table A.1 contains a summary of the relevant calculated parameters for **42Q** accompanied by those for **3Q** and **6Q**. The interaction energy per M-TM bond is consistent with a stronger interaction for **42Q** ($-144.8 \text{ kJ mol}^{-1}$) than **3Q** ($-134.9 \text{ kJ mol}^{-1}$) and is closer to that calculated for **6Q** ($-143.3 \text{ kJ mol}^{-1}$). Analysing the charge difference between the M and TM centres in the hypothetical monomeric structure $\text{M}\{\text{CpTM}(\text{CO})_2\}_2(\text{THF})_3$ shows this to be smaller for **42Q** (0.93) than **3Q** (1.37) or **6Q** (1.17). The analogous charge differences in the dimer $[\text{M}\{\text{CpTM}(\text{CO})_2\}_2(\text{THF})_3]_2$ are also smaller for **42Q** (1.12) than in **3Q** (1.43) but larger than **6Q** (1.02). Comparing these charge differences there is observed to be an increase in the charge difference on bringing these fragments together for **42Q** (0.19 au) as for **3Q** (0.06), contrasting with that for **6Q** (-0.15) where a decrease in the charge difference was observed. The overall

change in the charge difference is greatest for **42Q**, consistent with a greater perturbation of electron density on bringing these fragments together. Calculation of the electron density at the BCPs in these structures shows that for **42Q** (0.024 au) to be intermediate of that for **3Q** (0.022 au) or **6Q** (0.029 au). The low values for the electron density and its Laplacian are consistent with an ionic interaction between these metal centres.

Whilst the calculated structure of **42Q** offers the opportunity to compare the nature of the Ca-Ru bond with the Ca-Fe and Yb-Fe bonds in **3Q** and **6Q**, respectively, it is important to point out that this may not be the solid state form of the molecular structure of **42** if it were to be isolated. However, based on the structure of **3**, **6** and the polymeric structure of Kempe's $[\text{YbRp}_2(\text{THF})_2]_x$ (**1.91**), it is plausible that **42** bears an eight-membered ring motif supported by direct Ca-Ru and $\text{Ca}(\mu\text{-OC})\text{Ru}$ isocarbonyl interactions to give a dimeric or perhaps polymeric structure.

Table A1. Selected parameters for [CaFp₂(THF)₃]₂ (**3Q**), [YbFp₂(THF)₃]₂ (**6Q**) and [CaRp₂(THF)₃]₂ (**42Q**).

	3Q	6Q	42Q
$r(\text{M-TM})$ (Å)	2.984	2.965	3.067
	2.978	2.956	3.059
M-TM interaction energy (per M-TM bond)	-134.9	-143.3	-144.8
orbital mixing energy	-91.1	-107.4	-101.1
electrostatic interaction energy	-191.2	-249.5	-208.1
Pauli repulsion energy	147.4	213.5	164.4
charge M ([M{CpTM(CO) ₂ } ₂ (THF) ₃] fragment)	1.51	1.32	1.52
charge TM(1) ([M{CpTM(CO) ₂ } ₂ (THF) ₃] fragment)	0.14	0.15	0.59
charge M	1.38	1.01	1.46
charge TM(1)	-0.05	-0.01	0.34
Δ (charge M – charge TM(1)) (fragment)	1.37	1.17	0.93
Δ (charge M – charge TM(1)) (in complex)	1.43	1.02	1.12
$\Delta\Delta$ (charge M – charge TM(1))	+0.06	-0.15	+0.19
ρ (electron density)	0.022	0.029	0.024
$\nabla^2\rho$ (electron density Laplacian)	0.041	0.040	0.048

M = Ca or Yb. TM = Fe or Ru. All energies in kJ mol⁻¹. Orbital mixing (and hence total interaction) energies corrected for basis set superposition error (**3Q** 7.2, **6Q** 10.2, **42Q** 7.32). AIM data (atomic units) obtained at the bond critical point. Charges obtained from Mulliken analyses.

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