Synthesis, characterisation and structural studies of amidinate and guanidinate alkaline earth–transition metal bonded complexes

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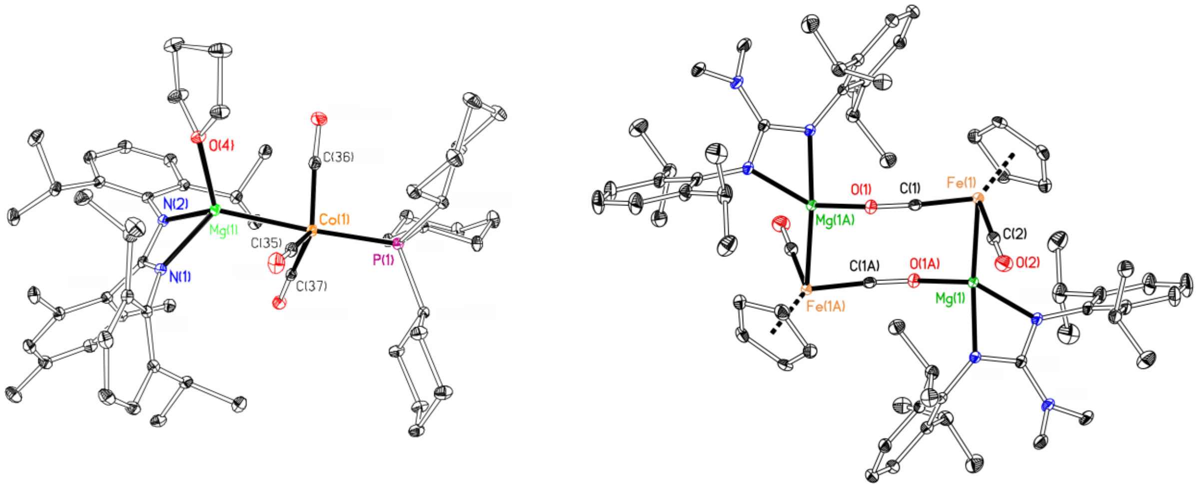
Abstract

Reaction of magnesium amidinate complexes of the form $[\{MesC(NR)_2\}MgBr(OEt_2)]_2$ (R = ^{i}Pr, Dipp, Mes) with the potassium salts of transition metal anions $K[CpFe(CO)_2]$ (K[Fp]) and $K[Co(CO)_3(PCy_3)](THF)_2$ gave the complexes $\{MesC(NR)_2\}MgFp(THF)$ and $\{MesC(NR)_2\}Mg\{Co(CO)_3(PCy_3)\}(THF)$. Single crystal X-ray diffraction studies of $\{MesC(NR)_2\}Mg\{Co(CO)_3(PCy_3)\}(THF)$ for R = ^{i}Pr and Dipp confirm these to have Mg−Co bonds in the solid state. Reaction of the structurally similar magnesium guanidinate complex $\{Me_2NC(NDipp)_2\}MgI(OEt_2)$ with the aforementioned transition metal anions and additional $K[Co(CO)_3(PPh_3)](THF)$ gave the series of complexes $[\{Me_2NC(NDipp)_2\}MgFp]_2$, $\{Me_2NC(NDipp)_2\}Mg\{Co(CO)_3(PCy_3)\}(OEt_2)$ and $\{Me_2NC(NDipp)_2\}Mg\{Co(CO)_3(PPh_3)\}(OEt_2)$. Structural authentication by X-ray crystallography showed $[\{Me_2NC(NDipp)_2\}MgFp]_2$ to be a very rare example of a base-free alkaline earth−transition bonded complex, having two Mg−Fe bonds. IR and diffusion NMR spectroscopy were carried out to gain further insight into the solid state and solution phase structures.

Graphical abstract

The first amidinate and guanidinate magnesium complexes with bonds to transition metals have been synthesised and structurally authenticated. IR and diffusion NMR spectroscopy provide further evidence for their structural forms in the solid state and solution.



Keywords

Metal–metal bonding; Alkaline earth; Transition metal; Magnesium; Amidinate; Guanidinate.

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1. Introduction

Compounds containing metal–metal bonds have been the focus of renewed attention for over a decade.[1] Reports of Zn–Zn[2] and Mg–Mg[3] single bonds, transition metal quintuple bonds,[4] Group 12 homo- and hetero-trimetallic[5] species and myriad 4*f* element– and 5*f* element–main group and transition metal bonded complexes[6] have piqued interest in the synthesis, structure, bonding and reactivity of such compounds. One area that has received little attention until very recently is that of Ae–TM (alkaline earth–transition metal) bonding. Since the first report of $Cp(DPPE)FeMgBr(THF)_2$ (**1**)[7] by Felkin in 1974 there have been few examples of structurally authenticated Ae–TM bonded complexes, most of which feature Ae = Mg. These include Green's Mg–Mo species $Cp_2Mo(H)\{MgBr(THF)_2\}$,[8] the Mg–Ir species $[Cp^*Ir(PMe_3)(H)MgPh]_2$,[9] and the two Mg–Co species $CpCo(\eta^3\text{-}C_3H_5)MgBr(THF)_2$ (**2**) and $CpCo(\eta^2\text{-}C_2H_4)(Ph)MgBr(TMEDA)$ (**3**).[10] The first Be–TM bonded compounds, $(Cy_3P)_2Pt\{Be(Cl)X\}$ (X = Cl or Me), were only characterised and structurally authenticated as recently as 2009.[11] Ca–TM bonds are even more elusive; $[CaFp_2(THF)_3]_2$ (**4**)[12] and $[Ca\{Co(CO)_3(PCy_3\}_2(THF)_3]_x$ (**5**)[13] remain the only examples reported to date.

Group 2 contains some of the most electropositive elements and as a consequence Ae–TM bonds are considerably ionic. Any potential TM bond partner must therefore be able to accommodate significant anionic charge. Investigation of the literature[14] for similarly polar M–TM bonded species (e.g. where M = lanthanide (Ln) or actinide (An))[15] or early-late heterobimetallics[16] reveals only a handful of metal anions that are routinely exploited for these purposes. These "privileged anions" are $[CpM(CO)_2]^-$ (M = Fe ("Fp") or Ru ("Rp")), $[Cp_2Re]^-$, $[Co(CO)_4]^-$ and its monophosphine analogue

$[Co(CO)_3(PR_3)]^-$. Shore *et al.* have also utilised the "supernucleophile" $[Fe(CO)_4]^{2-}$ successfully to form Yb– Fe bonded structures.[17] However attempts to extend this to achieve Ae– TM bonds were unsuccessful.[13] Carbonylate anions stabilise the build-up of negative charge on the TM moiety through π back-donation from TM(d_π) to C–O(π*) orbitals. However, their presence introduces the possibility of Ae– (μ-OC)– TM isocarbonyl bonding, which can often occur in preference to Ae– TM bonding. This dilemma has been referred to by Kempe as "the isocarbonyl problem"[15] and has been similarly observed by Marks for the highly oxophilic 5*f* elements in the pursuit of An– TM bonds.[18]

Work in our laboratories has recently led to the report of several structurally authenticated Ae– TM bonded species, including $[MgFp_2(THF)]_2$ (**6**)[12] and $[Mg\{Co(CO)_3(PCy_3)\}_2(THF)]_2$ (**7**),[13] synthesised from the reductive cleavage of Fp_2 and $[Co(CO)_3(PCy_3)]_2$ by a Mg/Hg amalgam. These were found to undergo significant structural changes in solution, with loss of the Mg– Fe interaction for the latter. This gave us significant impetus to synthesise (^{Dipp}NacNac)MgFp(THF) (**8**, Dipp = 2,6-diisopropylphenyl, ^{R}NacNac = HC{C(Me)NR}$_2$), isolated from the salt-elimination reaction of (^{Dipp}NacNac)MgI(THF) and K[Fp].[19] Complex **8** is soluble in non-donor solvents and contains a Mg– Fe bond in both the solid state and solution. Complex **8** features a β-diketiminate (NacNac) ligand, ubiquitous in Ae chemistry for having stabilising and solubilising properties.[20] Tuning of these properties can be accomplished through variation of substituents on the N-atoms. A complex featuring a larger Ae for instance, may be kinetically stabilised *via* increased steric protection from bulky N-aryl groups.

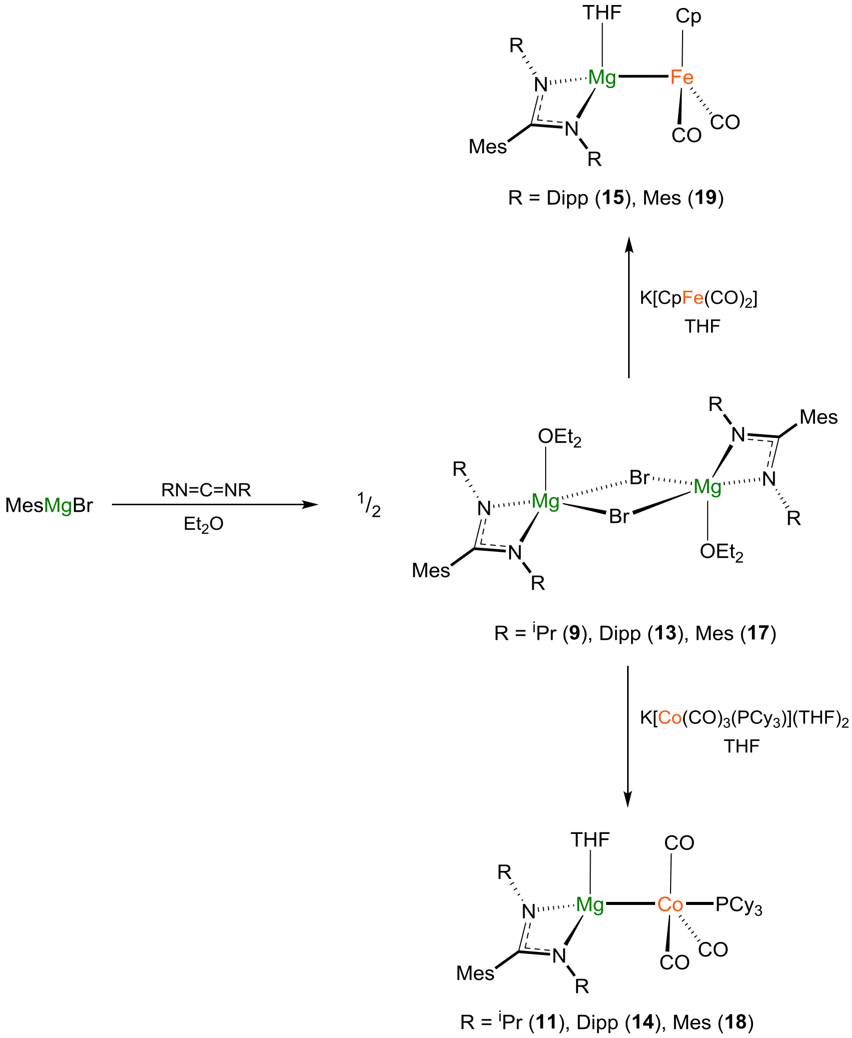
Amidinates ($R'C(NR)_2$) and guanidinates ($R'_2NC(NR)_2$) are similar classes of bidentate mono-anionic ligand that have been successfully deployed in Ae chemistry.[21] However, they are yet to be successfully exploited for Ae– TM bonding. As with β-diketiminates, these ligands can be readily modified at their N-substituents to allow the properties of the complex to be tuned as required. Amidinates and guanidinates differ from β-diketiminates in having only one, rather than three, backbone carbons. This results in formation of a four-membered, rather than six-membered ring, when complexed to the metal and a more acute N– Ae– N bite-angle (typically between 63 - 65°[21a]), giving a potentially more accessible metal centre to participate in metal-metal bonding with a suitable anion. We were therefore interested to see if our initial success with **8** could be extended to complexes with amidinate and guanidinate supporting ligands with a view to increasing the breadth of Ae– TM bonded systems, particularly those where metal-metal bonding is maintained in solution.

2. Results and discussion

2.1 Magnesium amidinate complexes

$[\{MesC(N^iPr)_2\}Mg(\mu\text{-}Br)(OEt_2)]_2$ (**9**) was prepared in 88% yield from $^iPrNCN^iPr$ and MesMgBr in

Et_2O using an analogous procedure to that reported by Coles *et al.*[21c] Diffraction quality crystals of **9** were grown from an Et_2O solution at 5 °C. The structure is shown in Fig. 1. Complex **9** is dimeric in the sold state with two μ-Br bridging the Mg centres. Each Mg centre is five-coordinate with distorted trigonal bipyramidal geometry. Distances and angles are as expected and similar to that for reported by Coles for the analogous $[\{MesC(NCy)_2\}Mg(\mu\text{-}Br)(OEt_2)]_2$ (**10**). In particular the bite angle of the amidinate in **9** (N(1)– Mg(1)– N(2) = 64.29(6)°) is comparable to that for **10** (64.76(8)°).



Scheme 1. Synthetic routes to Mg– Fe (**15**, **19**) and Mg– Co (**11**, **14**, **18**) bonded amidinate complexes.

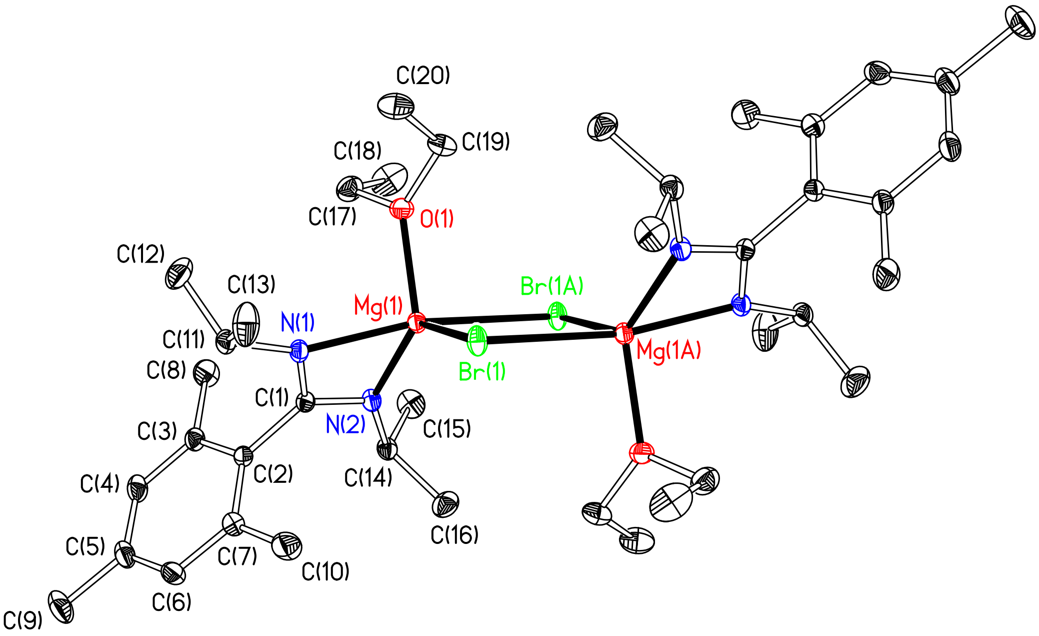


Figure 1. Displacement ellipsoid plot (20% probability) of $[\{MesC(N^{i}Pr)_2\}Mg(\mu\text{-}Br)(OEt_2)]_2$ (**9**). H atoms omitted. Atoms carrying the suffix ‘A’ are related to their counterparts by the symmetry operator 1-x, 1-y, 1-z. Selected distances (Å) and angles (°): Mg(1)–Br(1) 2.6677(8), Mg(1)–Br(1A) 2.5560(8), Mg(1)–N(1) 2.1144(17), Mg(1)–N(2) 2.0757(17), Mg(1)–O(1) 2.0398(16), N(1)–Mg(1)–N(2) 64.29(6), N(1)–Mg(1)–Br(1) 164.69(5), N(1)–Mg(1)–Br(1A) 101.55(6), N(1)–Mg(1)–O(1) 97.40(7), N(1)–C(1)–N(2) 114.02(17), Br(1)–Mg(1)–Br(1A) 87.36(3).

The salt-elimination reaction of **9** with $K[Co(CO)_3(PCy_3)](THF)_2$ in THF gave $\{MesC(N^{i}Pr)_2\}Mg\{Co(CO)_3(PCy_3)\}(THF)$ (**11**) in 58% isolated yield as illustrated in Scheme 1. Diffraction quality crystals of **11** were grown from pentane at room temperature. The structure is shown in Fig. 2 and selected distances and angles in Table 1. The heterobimetallic species is monomeric in the solid state. The geometry at the four-coordinate Mg centre is approximately tetrahedral with two bonds to the bidentate amidinate ligand and one to each of the THF and $Co(CO)_3(PCy_3)$ groups. The Mg–Co distance (2.5310(7) Å) is comparable with our previously reported **7** (*endo* Mg–Co 2.6163(6) and *exo* Mg–Co 2.5427(6) Å)[13] and Jonas’ complexes **2** (2.480(4) Å) and **3** (2.593(7) Å).[10] The amidinate bite-angle (N(1)-Mg(1)-N(2) = 65.28(7)°) is little changed from **9**.

The geometry at the five-coordinate Co centre is approximately trigonal bipyramidal with the three carbonyl groups lying in the equatorial plane and the Mg and P atoms occupying the axial positions with a near-linear arrangement (Mg–Co–P = 174.58(2)°). Interaction of the $[Co(CO)_3(PR_3)]^-$ anion with a cationic acceptor is known to bring about a significant geometric change in the anion.[22] The sum of the three P–Co–CO angles (∑(P–Co–CO)) represents one measure of this geometric change and a way in which the strength of interaction can be quantified. A greater strength of interaction is expected to cause a deviation in this value away from that of the tetrahedral free anion towards that of trigonal bipyramidal geometry. In the case of **11** $\sum$(P–Co–CO) = 302.27(12)° consistent with a significant interaction between the Mg and Co centres and very similar to that measured for our recently reported Mg–Co bonded **7** (300.9(2) and 303.2(2)°) and Ca–Co bonded **5** (305.8(3)°).[13]

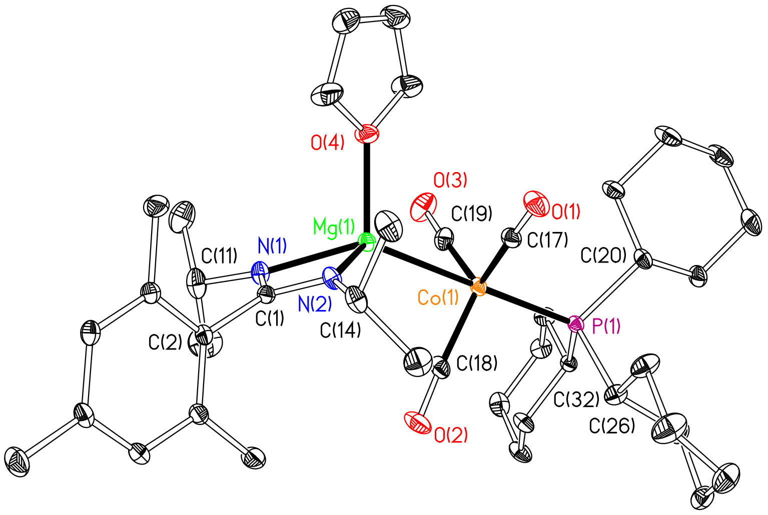


Figure 2. Displacement ellipsoid plot (25% probability) of {MesC(N^{i}Pr)$_2$}Mg{Co(CO)$_3$(PCy$_3$)}(THF) (**11**). H atoms omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for {MesC(N^{i}Pr)$_2$}Mg{Co(CO)$_3$(PCy$_3$)}(THF) (**11**).

Mg(1)–Co(1)	2.5310(7)	Mg(1)–N(1)	2.0777(18)
Mg(1)–N(2)	2.0498(17)	Mg(1)–O(4)	2.0312(16)
Co(1)–P(1)	2.2071(5)	Co(1)–C(17)	1.745(2)
Co(1)–C(18)	1.759(2)	Co(1)–C(19)	1.745(2)
C(1)–N(1)	1.332(3)	C(1)–N(2)	1.327(3)
Co(1)–Mg(1)–N(1)	137.70(6)	Co(1)–Mg(1)–N(2)	120.64(6)
Co(1)–Mg(1)–O(4)	109.92(5)	N(1)–Mg(1)–N(2)	65.28(7)
N(1)–Mg(1)–O(4)	106.23(7)	N(2)–Mg(1)–O(4)	108.22(7)
Mg(1)–Co(1)–P(1)	174.58(2)	Mg(1)–Co(1)–C(17)	76.45(7)
Mg(1)–Co(1)–C(18)	80.87(7)	Mg(1)–Co(1)–C(19)	80.20(7)
P(1)–Co(1)–C(17)	99.02(7)	P(1)–Co(1)–C(18)	98.62(7)
P(1)–Co(1)–C(19)	104.63(7)	C(17)–Co(1)–C(18)	115.17(10)
C(17)–Co(1)–C(19)	115.48(11)	C(18)–Co(1)–C(19)	119.07(11)
N(1)–C(1)–N(2)	113.75(17)		

The solid state IR spectrum of **11** shows three main higher frequency ν(CO) bands at 1963, 1922 and 1879 cm^{-1} and no significant lower frequency ν(CO) bands, consistent with a Mg–Co bonded structure without Mg(μ-OC)Co isocarbonyl bridging. The solution IR spectrum of **11** in toluene is more complicated with three ν(CO) bands at 1969, 1904 and 1895 cm^{-1}, attributed to a Mg–Co bonded species, and lower frequency bands at 1839 and 1755 cm^{-1}, possibly indicative of more complex behaviour in solution.

Reaction of **9** with K[Fp] in THF-d_8 on the NMR tube-scale showed quantitative formation of $\{MesC(N^iPr)_2\}MgFp(THF)$ by ^{1}H NMR spectroscopy. However, benzene extraction during the preparative scale reaction resulted in a complex mixture of products, evidenced by the presence of multiple ligand environments and Fp_2 in the ^{1}H NMR spectrum, the latter being a common decomposition product in the chemistry of the $[Fp]^-$ anion.[23] Given the stability of **11** in a non-donor solvent, the apparent decomposition of the desired Mg–Fe bonded species was somewhat unexpected. Of note is that the related **8** is also successfully isolated *via* a benzene extraction. It was postulated that substituting the N-bound ^{i}Pr groups for more sterically demanding Dipp or Mes (Mes = 2,4,6-trimethylphenyl) groups would improve the overall complex stability and allow isolation of an amidinate Mg–Fe, alongside Mg–Co, bonded complex.

The synthesis of the required carbodiimide, DippNCNDipp (**12**), has been reported in the literature previously, albeit on a relatively small scale, from the reaction of Dipp(H)NC(S)N(H)Dipp with $HgO/MgSO_4$.[24] A report by Patel *et al.* details the conversion of arylthioureas to carbodiimides *via* reaction with I_2 in the presence of NEt_3.[25] Using this general procedure Dipp(H)NC(S)N(H)Dipp was converted to **12**. However, the carbodiimide was contaminated with residual elemental sulfur. A modified procedure was therefore developed based on a report by Blumer[26] in which the contaminated hydrocarbon solution of carbodiimide was treated with an excess of activated Cu, thereby removing the elemental sulfur as insoluble CuS and giving **12** in 65% isolated yield.

Reaction of **12** with MesMgBr in Et_2O gave $[\{MesC(NDipp)_2\}Mg(\mu\text{-}Br)(OEt_2)]_2$ (**13**) in 67% isolated yield. Whilst crystalline samples of **13** could be isolated these were not suitable for analysis by single crystal X-ray diffraction. Reaction of **13** with $K[Co(CO)_3(PCy_3)](THF)_2$ in THF followed by pentane extraction gave $\{MesC(NDipp)_2\}Mg\{Co(CO)_3(PCy_3)\}(THF)$ (**14**) as a grey solid in 39% isolated yield. Diffraction quality crystals of **14** were grown from a benzene solution at room temperature. The structure of **14** is monomeric in the solid state (Fig. 3) containing a four-coordinate magnesium centre with approximately tetrahedral geometry. Somewhat surprisingly the Mg–Co distance (2.5193(5) Å) in **14** is shorter than that observed in **11** which features less bulky N-^{i}Pr substituents on the amidinate ligand. This can be attributed to one or two different effects. First, the orientation of the Dipp groups in **14** away from the metal anion. In the case of **11** the ^{i}Pr substituents orient themselves such that the Me groups are pointing away from the Mes group and towards the Co centre, potentially increasing the Mg–Co distance as a result. This effect may be viewed as an extension of that reported by Jordan *et al.* for steric repulsion within sterically demanding amidinate aluminium systems.[27] In addition, the N-aryl substituted ligand in **14** gives a more electrophilic Mg centre than the N-alkyl functionalised ligand in **11**. Consistent with this, the Mg–N distances are shorter in **11** (2.0498(17) and 2.0777(18) Å) than **14** (2.0590(12) and 2.0983(13) Å), and hence the N(1)–Mg(1)–N(2) bite-angle in **14** (64.51(5)°) is slightly more acute than in **11** (65.28(7)°). For **14** ∑(P–Co–CO) = 301.37(9)°, very similar to that for **11** (302.27(12)°), indicative of a significant interaction between the metal centres.

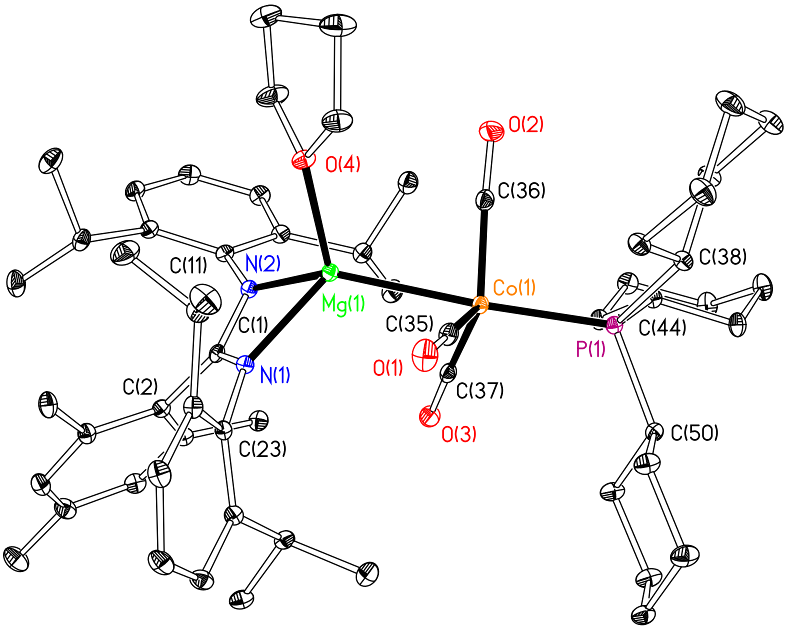


Figure 3. Displacement ellipsoid plot (25% probability) of {MesC(NDipp)$_2$}{MgCo(CO)$_3$(PCy$_3$)}(THF) (**14**). H atoms and independent molecule of protio-ligand omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for {MesC(Dipp)$_2$}Mg{Co(CO)$_3$(PCy$_3$)}(THF) (**14**).

Mg(1)–Co(1)	2.5193(5)	Mg(1)–N(1)	2.0590(12)
Mg(1)–N(2)	2.0983(13)	Mg(1)–O(4)	2.0317(11)
Co(1)–P(1)	2.2026(4)	Co(1)–C(35)	1.7580(16)
Co(1)–C(36)	1.7494(16)	Co(1)–C(37)	1.7605(16)
C(1)–N(1)	1.3356(17)	C(1)–N(2)	1.3531(18)
Co(1)–Mg(1)–N(1)	118.74(4)	Co(1)–Mg(1)–N(2)	134.60(4)
Co(1)–Mg(1)–O(4)	109.46(4)	N(1)–Mg(1)–N(2)	64.51(5)
N(1)–Mg(1)–O(4)	116.86(5)	N(2)–Mg(1)–O(4)	106.64(5)
Mg(1)–Co(1)–P(1)	174.780(18)	Mg(1)–Co(1)–C(35)	80.37(5)
Mg(1)–Co(1)–C(36)	80.13(5)	Mg(1)–Co(1)–C(37)	78.54(5)
P(1)–Co(1)–C(35)	104.51(5)	P(1)–Co(1)–C(36)	95.89(5)
P(1)–Co(1)–C(37)	100.97(5)	C(35)–Co(1)–C(36)	116.22(7)

C(35)–Co(1)–C(37)	112.35(7)	C(36)-Co(1)-C(37)	121.96(7)
N(1)–C(1)–N(2)	111.23(12)		

The solid state IR spectrum of **14** shows two strong ν(CO) bands at 1965 and 1873 cm^{-1}, the latter of which is broad and may comprise two overlapping bands. There are no ν(CO) bands at lower frequencies, indicating an absence of isocarbonyl interactions in the solid state. The solution IR of **14** in toluene shows only three ν(CO) bands at 1968, 1891 and 1840 cm^{-1}, consistent with preservation of the Mg– Co bond in solution.

Reaction of **13** with K[Fp] in THF followed by benzene extraction gave {MesC(NDipp)$_2$}MgFp(THF) (**15**) as a light brown solid in 74% yield. This is in contrast to the attempted reaction of **9** with K[Fp] to form {MesC(N^{i}Pr)$_2$}MgFp(THF) which was unstable in non-donor solvent. Although diffraction quality crystals of **15** could not be grown, ^{1}H and ^{13}C{^{1}H} NMR spectroscopic data are consistent with formation of the desired species. A diffusion NMR spectroscopic study of **15** (see below) suggests that it is monomeric in toluene. The solid state IR spectrum of **15** shows four ν(CO) bands; two strong bands at 1930 and 1866 and medium intensity bands at 1961 and 1791 cm^{-1}. The solution IR spectrum of **15** in toluene shows two ν(CO) bands at 2017 and 1925 cm^{-1} consistent with a non-isocarbonyl bridged species in the solution phase. For comparison, the solution IR spectrum of structurally authenticated Mg– Fe bonded **8** in toluene was recorded and showed two ν(CO) bands at 2017 and 1925 cm^{-1}. The similar position of the ν(CO) bands in **8** and **15** strongly support the latter as being Mg– Fe bonded in solution.

MesNCNMes (**16**) was synthesised from Mes(H)NC(S)N(H)Mes using an analogous procedure to that employed for Dipp(H)NC(S)N(H)Dipp. Reaction of **16** with MesMgBr in Et$_2$O gave [{MesC(NMes)$_2$}Mg(μ-Br)(OEt$_2$)]$_2$ (**17**) in 93% isolated yield. Diffraction quality crystals of **17** were grown from an Et$_2$O solution at 5 °C. X-ray crystallographic studies confirmed **17** as having a dimeric structure in the solid state, very similar to that observed for **9**. The solid state structure of **17** and a table containing selected distances and angles for **9** and **17** is presented in the SI. ^{1}H NMR analysis of crystals of **17** grown from Et$_2$O shows one equivalent of Et$_2$O per ligand. However, prolonged drying of the bulk material *in vacuo* leads to loss of Et$_2$O and two distinct ligand environments when observed in C$_6$D$_6$. In contrast, the ^{1}H NMR spectrum recorded for **17** in THF-d_8 shows only one set of ligand environments consistent with a monomeric structure with equivalent N-Mes environments.

Reaction of **17** with K[Co(CO)$_3$(PCy$_3$)](THF)$_2$ in THF followed by benzene extraction gave {MesC(NMes)$_2$}Mg{Co(CO)$_3$(PCy$_3$)}(THF) (**18**) as a white solid in 84% isolated yield. The solid state IR spectrum of **18** shows a large number of ν(CO) bands at 1964, 1937, 1885, 1865 and 1720 cm^{-1}. Comparison with the IR data for **14** suggests that those at 1964, 1885 and 1865 cm^{-1} are attributable to the A$_1$- and two E-type ν(CO) stretching modes of the monomeric Mg– Co complex. The peaks at 1937 and 1720 cm^{-1} are likely the result of a secondary species which exhibits Mg(μ-

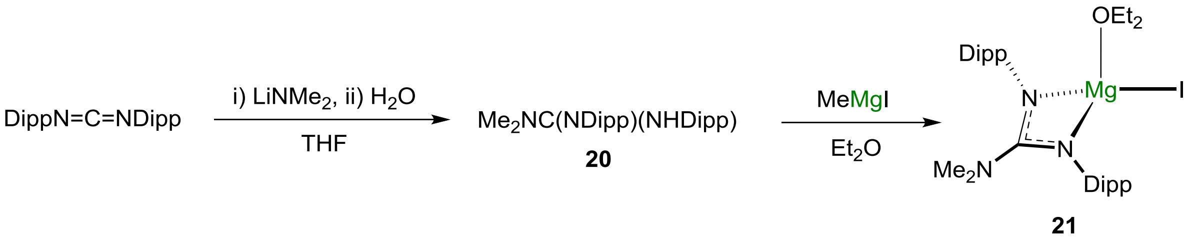
OC)Co isocarbonyl interactions. The solution IR spectrum of **18** in toluene shows ν(CO) bands at 1970, 1910, 1890, 1836 and 1755 cm^{-1}, again consistent with two species with at least one band in the range indicating an isocarbonyl interaction. These data are in contrast to that of **14**, which showed no significant low frequency ν(CO) bands in solution or the solid state, and was confirmed to be Mg– Co bonded by X-ray crystallography.

The reaction of **17** with K[Fp] in THF followed by benzene extraction gave {MesC(NMes)$_2$}MgFp(THF) (**19**) by ^{1}H NMR spectroscopy, albeit accompanied by other ligand environments. This susceptibility to decomposition in non-donor solvents was also observed for the product of the reaction between **9** and K[Fp]. To combat this decomposition the procedure was modified to use THF as the only solvent. This allowed isolation of {MesC(NMes)$_2$}MgFp(THF) (**19**) as a light brown solid in 68% isolated yield. The solid state IR spectrum of **19** showed two main ν(CO) bands at 1923 and 1858 cm^{-1}, notably absent are lower frequency ν(CO) bands that would indicate the presence of isocarbonyl interactions. The solution IR spectrum of **19** in THF is more complicated but nonetheless dominated by ν(CO) bands at 1921 and 1861 cm^{-1}. Reassuringly, the previously reported solution IR spectrum of Mg– Fe bonded **8** in THF similarly shows bands at 1926 and 1871 cm^{-1}.[19]

2.2 Magnesium guanidinate complexes

Guanidinate ligands (R′$_2$NC(NR)$_2$) are structurally and geometrically very similar to amidinate ligands but have subtly different electronic properties as a result of the distal nitrogen. Donation of electron density from this nitrogen has the ultimate effect of increasing the overall ligand Lewis basicity, potentially increasing the strength of interaction with the Lewis acidic Ae centre and overall complex stability as a result.[28] Given our successful synthesis of Mg–TM complexes using the Dipp substituents in both our NacNac and aforementioned amidinate systems we selected this for the R-group in these complexes. Whilst a range of bulky R′ groups for the distal nitrogen have been reported,[21a] these offer little steric protection at the Mg centre and primarily have a solubilising effect. Therefore, given the solubilising R-groups already selected, we opted for a simple NMe$_2$ group.

Reaction of LiNMe$_2$ with DippNCNDipp, followed by an aqueous workup gave the protio-ligand Me$_2$NC(NDipp)(NHDipp) (**20**) as a white solid in 69% isolated yield. Crystals of **20** suitable for analysis by X-ray diffraction were grown from a hexane solution at RT. The structure of **20** and selected distances and angles are presented in the SI.



Scheme 2. Synthesis of {Me$_2$NC(NDipp)$_2$}MgI(OEt$_2$) (**21**).

Reaction of **20** with MeMgI afforded {Me$_2$NC(NDipp)$_2$}MgI(OEt$_2$) (**21**) as a white solid in 95% isolated yield. Crystals of **21** suitable for analysis by X-ray diffraction were grown from benzene at room temperature. The structure of **21**, shown in Fig. 4, has a four-coordinate Mg centre with approximately tetrahedral coordination geometry, with two Mg–N bonds to the bidentate guanidinate ligand and one bond to each of the iodine and ether ligand. The N(1)–Mg(1)–N(2) bite-angle (66.86(13)°) is similar to that for the structurally similar (Priso)Mg(μ-I)$_2$Mg(OEt$_2$)(Priso) (66.47(8)°, Priso = ^{i}Pr$_2$NC(NDipp)$_2$) reported by Jones *et al.*[3] It is also similar to the aforementioned Mg–Br (**9**: 64.29(6), **17**: 63.44(6)°) and Mg–Co (**11**: 65.28(7), **14**: 64.51(5)°) bonded amidinate complexes consistent with the concept of a similar geometry despite substitution of a mesityl for the more electron-donating NMe$_2$ group.

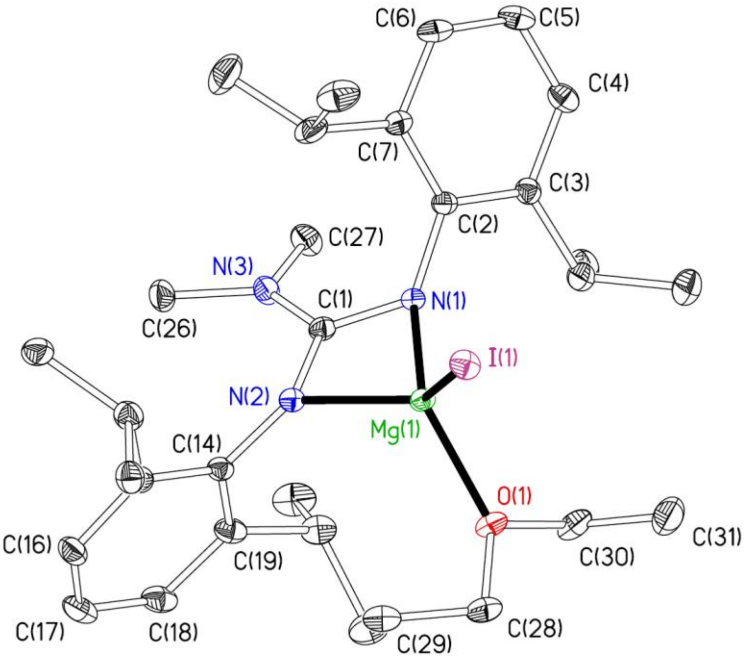
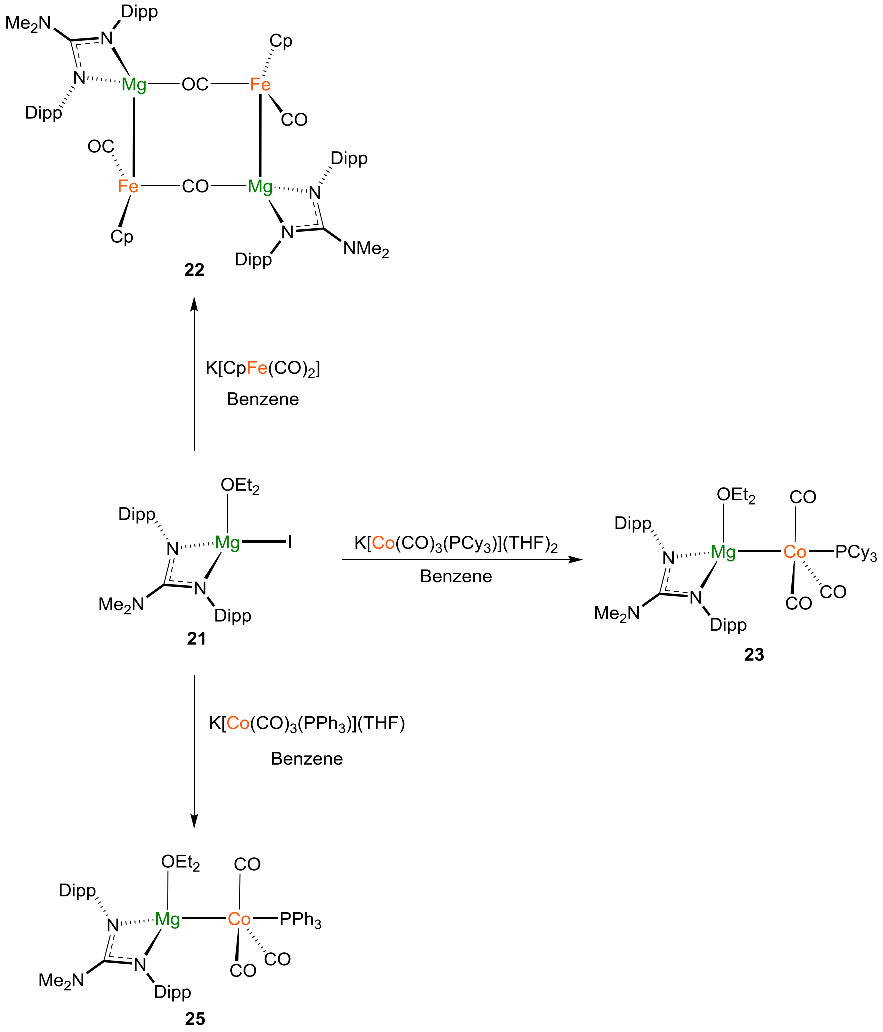


Figure 4. Displacement ellipsoid plot (20% probability) of {Me$_2$NC(NDipp)$_2$}MgI(OEt$_2$) (**21**). H atoms omitted for clarity. Selected distances (Å) and angles (°): Mg(1)–I(1) 2.6500(13), Mg(1)–N(1) 2.052(3), Mg(1)–N(2) 2.040(3), Mg(1)–O(1) 2.029(3), N(1)–Mg(1)–N(2) 66.86(13), N(1)–C(1)–N(2) 112.8(3).

Initial attempts to synthesise [{Me$_2$NC(NDipp)$_2$}MgFp(THF)$_x$]$_n$ by reacting **21** with K[Fp] in THF were unsuccessful. Analysis of this reaction on the NMR-tube scale showed there to be no conversion to the desired product, contrasting with the syntheses of **8** and **15**, which proceeded under ambient conditions. Gratifyingly however, repeating the reaction on the NMR tube-scale in C_6D_6 gave quantitative conversion to $[\{Me_2NC(NDipp)_2\}MgFp]_2$ (**22**) by ^{1}H NMR. The reaction was scaled-up, affording **22** as a yellow solid in 64% isolated yield (Scheme 3).



Scheme 3. Synthesis of guanidinate Mg–Fe bonded **22** and Mg–Co bonded **23** and **25** from **21**.

Crystals of **22** suitable for analysis by X-ray diffraction were grown from a benzene solution at 5 °C. The structure is shown in Fig. 5 and selected distances and angles in Table 3. Complex **22** crystallises as a dimer in the solid state with two Mg–Fe bonds and two Mg(μ-OC)Fe linkages. Each Mg centre is four-coordinate with an approximately tetrahedral geometry. The Mg–Fe bond distances (2.5279(4) Å) are shorter than those in monomeric **8** (2.6326(4) Å),[19] which also features a considerably larger bite-angle compared to **22** (90.97(4) *vs*. 66.00(4)°). The Mg–Fe distances are also shorter than those in dimeric **6** (2.6112(5) & 2.5629(5) Å), which does not feature a sterically demanding supporting ligand. Being shorter than those in Felkin's **1** (2.593(7) Å),[7] the Mg–Fe distances in **22** are the shortest reported to date.[14]

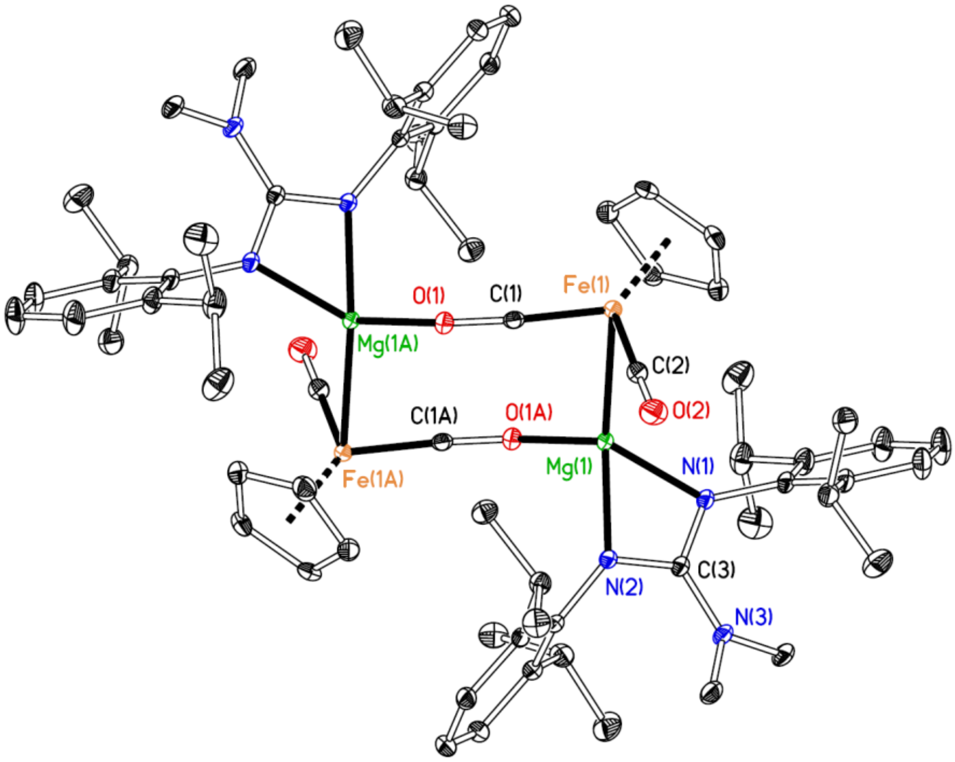


Figure 5. Displacement ellipsoid plot (20% probability) of [{$Me_2NC(NDipp)_2$}MgFp]$_2$ (**22**). H atoms and solvent of crystallisation omitted for clarity. Atoms carrying the suffix ‘A’ are related to their counterparts by the symmetry operator 1-x, 1-y, 1-z.

Table 3. Selected bond lengths (Å) and angles (°) for [{$Me_2NC(NDipp)_2$}MgFp]$_2$ (**22**).

Mg(1)–Fe(1)	2.5279(4)	Mg(1)–O(1A)	2.0552(10)
Mg(1)–N(1)	2.0620(10)	Mg(1)–N(2)	2.0627(10)
Fe(1)–C(1)	1.6985(12)	Fe(1)–C(2)	1.7469(14)
Fe(1)–Mg(1)–O(1A)	108.46(3)	Fe(1)–Mg(1)–N(1)	121.23(3)
Fe(1)–Mg(1)–N(2)	137.58(3)	N(1)–Mg(1)–N(2)	66.00(4)
N(1)–C(3)–N(2)	113.05(10)		

The absence of a coordinated donor solvent in **22**, that is, it is isolated “base-free”, is notable. All reported Mg–Fe bonded complexes to date have THF bonded by virtue of their syntheses. Indeed the only structurally authenticated base-free Ae–TM bonded complex reported to date is Jones’ Mg–Mn bonded (^{Mes}NacNac)MgMnN(Ar*)Si^{i}Pr$_3$ (Ar* = $C_6H_2\{C(H)Ph_2\}_2{}^iPr$-2,6,4) synthesised by the reaction of [(^{Mes}NacNac)Mg]$_2$ with [(^{Mes}NacNac)Mn(μ-Br)(THF)]$_2$ in cyclohexane.[29] The lack of coordinated Et_2O in the bulk sample of **22** is confirmed by the absence of signals attributable to Et_2O in the ^{1}H or ^{13}C{^{1}H} NMR spectra. Our recent findings have shown the presence of coordinated donor groups to be potentially very disruptive to Ae–TM bonding, favouring the formation of isocarbonyl linkages and in extreme cases separated ion pairs.[13] Therefore, to isolate a base-free

Ae–TM bonded complex is significant and may enable enhanced reactivity in future studies. To investigate the potential interaction of **22** with THF, a sample of **22** was dissolved in THF then volatiles removed under reduced pressure and the solid dried *in vacuo*. ^{1}H NMR analysis showed there to be no THF present. This lack of coordination and therefore maintenance of the dimeric structure is somewhat remarkable but would appear to be the exception rather than rule for the series of guanidinate complexes investigated in this study (see below). The solid state IR spectrum of **22** shows two main ν(CO) bands at 1944 and 1778 cm^{-1}. The former is attributed to the terminal carbonyl and latter to the isocarbonyl groups, consistent with the structure determined by X-ray crystallography. The solution IR spectrum of **22** in toluene also shows a low frequency ν(CO) band at 1781 cm^{-1}, consistent with isocarbonyl interactions in solution. The solution IR spectrum in THF was dominated by two major ν(CO) bands (2014 and 1946 cm^{-1}) consistent with dissociation to a monomeric structure without isocarbonyl bridging, most probably a THF adduct.

Given the successful synthesis of **22** in benzene, this was also attempted for the reaction between **21** and $K[Co(CO)_3(PCy_3)](THF)_2$, giving $\{Me_2NC(NDipp)_2\}Mg\{Co(CO)_3(PCy_3)\}(OEt_2)$ (**23**) as a red solid in 68% isolated yield. Crystals of **23** suitable for analysis by X-ray crystallography could not be obtained. However, unlike **22**, the presence of one coordinated Et_2O per set of ligand environments is apparent by ^{1}H NMR spectroscopy. Low frequency ν(CO) bands are absent in the solid state IR spectrum, consistent with no isocarbonyl bridging, suggesting a monomeric Mg–Co bonded structure. The solution IR spectrum of **23** in toluene also supports this, having only three ν(CO) bands (1962, 1858, 1804 cm^{-1}), all at comparatively high frequency. These observations are consistent with that for the structurally authenticated monomeric Mg–Co bonded complex **14** which also exhibits three ν(CO) bands (1968, 1891 and 1840 cm^{-1}) at high frequency only. It is notable that the bands in **23** are at a lower frequency than the respective bands in **14**. This is consistent with the greater electron donating effect of the guanidinate *vs*. amidinate ligand and ultimately increased back-donation of electron density from the $Co(d_\pi)$ to C–O(π*) orbitals.

The $[Co(CO)_3(PPh_3)]^-$ anion has been shown to be a viable anion for metal-metal bonding, with a range of structurally authenticated examples[14] featuring bonds to transition metals, main group metals and also electropositive metals such as in Liddle's U–Co bonded $(Ts^{Xyl})U\{Co(CO)_3(PPh_3)\}$ (Ts^{Xyl} = $HC(SiMe_2NXyl)_3$; Xyl = 3,5-dimethylphenyl).[30] However, our recent studies with this anion in combination with unsupported alkaline earth systems such as $Ca\{Co(CO)_3(PPh_3)\}_2(THF)_4$ showed these complexes to have poor solubility in non-donor solvents ($Mg\{Co(CO)_3(PPh_3)\}_2(THF)_x$ was insoluble in THF) necessitating manipulations and crystallisations from THF, giving complexes with isocarbonyl bridging between the metal centres only.[13] Therefore we were interested to see if use of a supporting, solubilising ligand could enable the isolation of a complex with the $[Co(CO)_3(PPh_3)]^-$ anion that could be crystallised in the absence of a donor-solvent thus favouring a Mg–Co over Mg(μ-OC)Co interaction. Complex **21** was reacted with $K[Co(CO)_3(PPh_3)](THF)$ (**24**, structure in the SI) in benzene to afford $\{Me_2NC(NDipp)_2\}Mg\{Co(CO)_3(PPh_3)\}(OEt_2)$ (**25**) as a red solid in 58% isolated yield. As with **23**, crystals suitable for analysis by X-ray crystallography could not be obtained. NMR spectroscopic analysis confirms there is one Et_2O per set of guanidinate ligand environments, consistent with that for **23**. The solid state IR spectrum for **25** shows no significant low frequency ν(CO) bands. Also the solution IR spectrum for **25** in toluene shows only three principal ν(CO) bands (2049, 1976, 1896 cm^{-1}), all at high frequency, consistent with a monomeric Mg–Co bonded structure as with **23**. The higher frequency A_1 stretch for **25** compared to **23** is consistent with the lower σ-donating ability of the PPh_3 compared to PCy_3 group and resultant decreased $Co(d_{\pi})$ to $C–O(\pi^*)$ back bonding.

2.3 Diffusion NMR spectroscopy

We used diffusion NMR spectroscopy to further investigate the solution phase structures of complexes **14**, **15**, **18**, **22** and **23**. The results are shown in Table 4, together with comparative reference data for **8**.

Table 4. Diffusion NMR data for $(^{Dipp}NacNac)MgFp(THF)$ (**8**), $\{MesC(NDipp)_2\}Mg\{Co(CO)_3(PCy_3)\}(THF)$ (**14**), $\{MesC(NDipp)_2\}MgFp(THF)$ (**15**), $\{MesC(NMes)_2\}Mg\{Co(CO)_3(PCy_3)\}(THF)$ (**18**), $[\{Me_2NC(NDipp)_2\}MgFp]_2$ (**22**), and $\{Me_2NC(NDipp)_2\}Mg\{Co(CO)_3(PCy_3)\}(OEt_2)$ (**23**).

Compound	Solvent	X-Ray volume (Å^3) [a]	NMR volume (Å^3) [b]	D (mean) × 10^{-10} (m^2 s^{-1}) [c]	D (Solvent) × 10^{-10} (m^2 s^{-1}) [c]
8	toluene-d_8	698	519	7.96	22.02
14	toluene-d_8	1034	1209	6.01	21.21
15	toluene-d_8	936*	812	6.87	17.72
18	toluene-d_8	1116*	1224	5.98	18.45
22	toluene-d_8	1239	1139	6.12	20.19
23	toluene-d_8	1116*	849	6.75	19.63
8	THF-d_8	698	536	9.94	27.43
22	THF-d_8	1239	663	8.84	26.76

[a] Molecular volume based on the caption formula and X-ray crystal structures measured using 1.4 Å probe radius. Volumes denoted with * are instead based on that expected for a monomeric structure using the 18 Å^3 rule. [b] Molecular volume measured by diffusion NMR spectroscopy in toluene-d_8 or THF-d_8. [c] Diffusion coefficient of the compound and the residual protio solvent in the sample under consideration (for comparison the diffusion coefficients for the protio solvents were 23.54 × 10^{-10} m^2 s^{-1} in pure toluene-d_8 and 27.0154 × 10^{-10} m^2 s^{-1} in pure THF-d_8). Further details are provided in the SI.

The structure of **8** is known to be monomeric in the solid state and solution. It is also structurally similar to the amidinate and guanidinate complexes studied in this investigation making it a suitable reference molecule. Indeed the solution effective molecular volume in toluene (519 Å^3) and THF (536 Å^3) are similar to that expected (698 Å^3) based on the solid state structure. There is good agreement between the effective volume for **14** in the solid state (1034 Å^3) and solution (1209 Å^3) supporting this as being a monomer in both environments. It was not possible to obtain a solid state structure for **15**, making the diffusion NMR measurement for this particularly insightful. The solution effective volume (812 Å^3) is similar to that for a monomeric structure (936 Å^3) based on that predicted using the 18 Å^3 rule.[31] As with **15**, the solid state structure for **18** could not be determined but its effective monomeric volume based on the 18 Å^3 rule (1116 Å^3) is similar to that determined by NMR (1224 Å^3). Therefore based on diffusion NMR measurements the amidinate complexes **14**, **15** and **18** are monomeric in solution.

Turning to the guanidinate complexes, **22** has a solution effective volume (1139 Å^3) very similar to that for the dimeric solid state structure (1239 Å^3). The close match in effective volume suggests very little, if any, dissociation in toluene at this concentration. This is consistent with the IR spectroscopic data where a low frequency band, indicative of an isocarbonyl bridging interaction, is present in both the solid state and toluene. Diffusion NMR measurements were also made in THF-d_8. These showed a solution effective volume (663 Å^3) very close to half of that for the dimeric solid state structure, consistent with dissociation to monomeric units in the donor solvent environment as supported by IR spectroscopy in THF solution. Although a solid state structure could not be obtained, diffusion NMR measurements for **23** were carried out. There is a significant disparity (*ca*. 33%) between the solution effective volume (849 Å^3) and that expected for a dimeric solid state structure (1116 Å^3) based on the 18 Å^3 rule. Whilst it may be the case that solid state volume is overestimated, the fact that the measured solution effective volume is significantly below this is strongly indicative of a monomeric structure in solution.

3. Conclusion

We have reported the first examples of amidinate and guanidinate supported Ae–TM bonded complexes ultimately synthesised from reduction of their corresponding carbodiimides. In order to achieve this on a suitable scale we developed an improved synthetic procedure *via* the corresponding thiourea. Structurally authenticated examples of Ae–TM bonded species have been achieved featuring Mg bonded to the $[Fp]^-$ and $[Co(CO)_3(PCy_3)]^-$ anions. A guanidinate magnesium complex using the $[Co(CO)_3(PPh_3)]^-$ anion was also synthesised. IR analysis is consistent with this being Mg–Co rather than Mg(μ-OC)Co bonded in both the solid state and solution. Crucially this introduces another anion to the limited number shown to be capable of bonding with the alkaline earth metals without suffering from the “isocarbonyl problem”. Diffusion NMR spectroscopy measurements on a series of these complexes are consistent with them existing as monomers in toluene-d_8 with the exception of [{$Me_2NC(NDipp)_2$}MgFp]$_2$ (**22**) where a dimeric structure is maintained. However, measurements in THF-d_8 were consistent with dissociation of **22** to monomeric units. Complex **22** was also shown to be a very rare example of a "base-free" Ae–TM complex and as having the shortest Mg–Fe bond reported to date.

4. Experimental

4.1 General

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were either degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent (benzene, pentane and hexane).[32] Alternatively solvents were predried over activated 4 Å molecular sieves and refluxed over sodium (toluene), potassium (THF) or sodium-potassium alloy (Et_2O) and distilled. Deuterated solvents were dried over sodium (toluene-d_8) or potassium (C_6D_6, THF-d_8), 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, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra were recorded on a Bruker Ascend 400 or Varian Mercury-VX 300 at ambient temperature. ^1H and $^{13}C\{^1H\}$ spectra are referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances, and are reported relative to tetramethylsilane ($\delta = 0$ ppm). $^{31}P\{^1H\}$ spectra were referenced externally to an 85% H_3PO_4 solution. Assignments were confirmed as necessary with the use of two-dimensional ^1H-^1H and ^{13}C-^1H NMR correlation experiments. Diffusion NMR spectroscopic studies were performed on a Bruker Avance III 500 spectrometer (further details are contained in the SI). IR spectra were recorded on a 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 at London Metropolitan University.

4.2 Starting materials

K[Fp],[33] [$Co(CO)_3(PPh_3)$]$_2$,[34] K[$Co(CO)_3(PCy_3)$](THF)$_2$,[13] DippN(H)C(S)N(H)Dipp, MesN(H)C(S)N(H)Mes[24] and activated Cu[26] were synthesised according to published procedures. Metals and other reagents were purchased from Strem Chemicals, Sigma Aldrich or Alfa Aesar and either used as received or purified according to standard procedures.

*4.3 [{MesC(N^{i}Pr)$_2$}Mg(μ-Br)(OEt$_2$)]$_2$ (**9**)*

To a stirring solution of MesMgBr in Et_2O (60.0 mL, 0.5 M, 30.0 mmol) was added ^{i}PrNCN^{i}Pr (4.50 mL, 29.0 mmol) dropwise. The solution was stirred for 18 h at room temperature to give a white precipitate. The solid was isolated by filtration then washed with cold Et_2O (2 x 20 mL, −78 °C) before drying *in vacuo* to afford **9** as a white solid. Yield: 10.8 g (88%). Diffraction-quality crystals were grown from an Et_2O solution at 5 °C. ^1H NMR (C_6D_6, 400.2 MHz): δ 6.82 (s, 4 H, C_6H_2), 3.73 (8 H, quart, ^3J = 7.0 Hz, OCH_2), 3.24 (4 H, sept, ^3J = 5.9 Hz, $C\underline{H}Me_2$), 2.38 (12 H, s, 2,6-$C_6H_2\underline{Me}_3$), 2.16 (6 H, s, 4-$C_6H_2\underline{Me}_3$), 1.27 (24 H, d, ^3J = 5.9 Hz, $CH\underline{Me}_2$), 1.17 (12 H, t, ^3J = 7.0 Hz, $OCH_2\underline{Me}$). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δ 173.9 (CN_2), 136.8 (4-C_6H_2), 134.5 (2,6-C_6H_2), 133.6 (1-C_6H_2), 128.4 (3,5-C_6H_2), 65.5 (OCH_2), 47.2 ($\underline{C}HMe_2$), 26.9 ($CH\underline{Me}_2$), 21.2 (4-$C_6H_2\underline{Me}_3$), 20.5 (2,6-$C_6H_2\underline{Me}_3$), 14.5 ($OCH_2\underline{Me}$). IR (NaCl plates, Nujol mull, cm^{-1}): 1355 (m), 1340 (m), 1233 (m), 1181 (m), 1166 (m), 1119 (m), 1090 (m), 1051 (m), 998 (m), 902 (w), 860 (m), 836 (w), 824 (w), 783 (m), 767 (m), 693 (w). EI-MS *m/z* = 499 (95%) $[\{MesC(N^iPr)_2\}Mg\{(N^iPr)_2C(C_6H_2Me_2)\}]^+$. It was not possible to obtain a satisfactory elemental analysis for **9**.

*4.4 $\{MesC(N^iPr)_2\}Mg\{Co(CO)_3(PCy_3)\}(THF)$ (**11**)*

To $[\{MesC(N^iPr)_2\}Mg(\mu\text{-}Br)(OEt_2)]_2$ (400 mg, 0.472 mmol) and $K[Co(CO)_3(PCy_3)](THF)_2$ (572 mg, 0.944 mmol) was added THF (20 mL). The brown solution was stirred for 3 h before removal of volatiles under reduced pressure. The dark brown solid was extracted with benzene (3 x 5 mL) and volatiles removed under reduced pressure. The residue was washed with cold pentane (10 mL, −78 °C) and dried *in vacuo* to afford **11** as a grey-brown solid. Yield: 418 mg (58%). ^1H NMR (C_6D_6, 400.2 MHz): δ 6.79 (2 H, s, C_6H_2), 4.13 (4 H, s, OCH_2), 3.19 (2 H, br sept, ^3J = 5.3 Hz, $C\underline{H}Me_2$), 2.43 (6 H, s, 2,6-$C_6H_2\underline{Me}_3$), 2.15 (3 H, s, 4-$C_6H_2\underline{Me}_3$), 2.04 (3 H, m, 1-C_6H_{11}), 1.79 (6 H, m, 4-C_6H_{11}), 1.64 (12 H, m, 2,6-C_6H_{11}), 1.35 (4 H, s, $OCH_2C\underline{H}_2$), 1.24 (24 H, d & m overlapping, ^3J = 5.3 Hz, $CH\underline{Me}_2$ & 3,5-C_6H_{11}). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δ 210.2 (s, CO), 173.9 (s, CN_2), 136.9 (s, 4-C_6H_2), 134.6 (s, 2,6-C_6H_2), 133.0 (s, 1-C_6H_2), 128.5 (s, 4-C_6H_2), 70.0 (s, OCH_2), 46.8 (s, $\underline{C}HMe_2$), 37.6 (d, ^1J = 16.8 Hz, 1-C_6H_{11}), 30.5 (s, 2,6-C_6H_{11}), 28.2 (d, ^3J = 10.2 Hz, 3,5-C_6H_{11}), 27.0 (m, overlapping $CH\underline{Me}_2$ & 4-C_6H_{11}), 25.3 (s, $OCH_2\underline{C}H_2$), 21.2 (s, 4-$C_6H_2\underline{Me}_3$), 20.6 (s, 2,6-$C_6H_2\underline{Me}_3$). $^{31}P\{^1H\}$ (C_6D_6, 162.0 MHz): δ 70.0 (s). IR (NaCl plates, Nujol mull, cm^{-1}): 3818 (w), 3438 (w), 1963 (m), 1922 (m), 1879 (s), 1864 (s), 1821 (m), 1756 (w), 1611 (w), 1582 (w), 1335 (m), 1240 (w), 1168 (w), 1143 (w), 1110 (m), 917 (w), 876 (w) 853 (m), 766 (w). IR (NaCl cell, toluene, ν(CO), cm^{-1}): 2038 (w), 1969 (m), 1904 (s), 1895 (s), 1839 (m). It was not possible to obtain a satisfactory elemental analysis for **11**.

*4.5 DippNCNDipp (**12**)*

To a stirring solution of DippN(H)C(S)N(H)Dipp (7.93 g, 20.0 mmol) and NEt_3 (5.58 mL, 40.0 mmol) in ethyl acetate (100 mL) was added I_2 (5.58 g, 22.0 mmol) in portions over 30 min. The mixture was stirred for 2 h at room temperature then filtered to give a brown solution. Volatiles were removed under reduced pressure to give a brown solid. The solid was extracted with pentane (4 x 50 mL), filtered through a silica plug and the resultant brown solution added to activated Cu (3.00 g, 48.0 mmol). The mixture was stirred for 16 h at room temperature to give a black suspension. The suspension was filtered through silica to give a colourless solution. Volatiles were removed under reduced pressure and the resultant solid was dried *in vacuo* to afford **12** as a colourless crystalline solid. Yield: 4.74 g (65%). The ^1H NMR spectrum was consistent with that reported by Cowley *et al.*[24]

4.6 $[\{MesC(NDipp)_2\}Mg(\mu\text{-}Br)(OEt_2)]_2$ *(**13**)*

To a stirring solution of MesMgBr in Et_2O (43.0 mL, 0.3 M, 12.9 mmol) was added a solution of DippNCNDipp (**12**, 4.50 g, 12.4 mmol) in Et_2O (30 mL) dropwise. The solution was stirred for 18 h to give a white precipitate. The solid was isolated by filtration and washed with cold Et_2O (2 x 50 mL, −78 °C) before drying *in vacuo* to afford (**13**) as a white solid. Yield: 5.05 g (67%). ^1H NMR (C_6D_6, 400.2 MHz): δ 7.02 (12 H, s, $C_6\underline{H}_3{}^iPr_2$), 6.34 (4 H, s, $C_6\underline{H}_2Me_3$), 3.60 (8 H, s, OCH_2), 3.33 (8 H, br s, $C\underline{H}Me_2$), 2.04 (12 H, s, 2,6-$C_6H_2\underline{Me}_3$), 1.81 (6 H, s, 4-$C_6H_2\underline{Me}_3$), 1.38 (24 H, s, $CH\underline{Me}_2$), 1.07 (24 H, s, $CH\underline{Me}_2$), 0.91 (12 H, s, $OCH_2\underline{Me}$). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δ 175.0 (CN_2), 142.9 (2-$\underline{C}_6H_3{}^iPr_2$), 141.7 (6-$\underline{C}_6H_3{}^iPr_2$), 141.2 (1-$\underline{C}_6H_3{}^iPr_2$), 137.9 (4-$\underline{C}_6H_2Me_3$), 137.0 (2,6-$\underline{C}_6H_2Me_3$), 130.5 (1-$\underline{C}_6H_2Me_3$), 129.6 (3,5-$\underline{C}_6H_2Me_3$), 124.1 (4-$\underline{C}_6H_3{}^iPr_2$), 123.6 (3-$\underline{C}_6H_3{}^iPr_2$), 123.4 (5-$\underline{C}_6H_3{}^iPr_2$), 65.7 ($OCH_2$), 28.8 ($\underline{C}HMe_2$), 27.0 ($CH\underline{Me}_2$), 22.1 ($CH\underline{Me}_2$), 21.6 (2,6-$C_6H_2\underline{Me}_3$), 20.6 (4-$C_6H_2\underline{Me}_3$), 13.6 ($OCH_2\underline{Me}$). IR (NaCl plates, Nujol mull, cm^{-1}): 1437 (s), 1412 (sh), 1392 (s), 1319 (m), 1231 (w), 1189 (w), 1177 (m), 1051 (m), 996 (m), 967 (m), 949 (w), 936 (w), 889 (w), 853 (m), 834 (w), 779 (m), 762 (m), 754 (m), 672 (w), 659 (w). Anal. found (calcd for $C_{76}H_{110}Mg_2Br_2N_4O_2$): C, 68.92 (69.15); H, 8.52 (8.40); N, 4.28 (4.24)%.

4.7 $\{MesC(NDipp)_2\}Mg\{Co(CO)_3(PCy_3)\}(THF)$ *(**14**)*

To $[\{MesC(NDipp)_2\}Mg(\mu\text{-}Br)(OEt_2)]_2$ (**13**, 500 mg, 0.379 mmol) and $K[Co(CO)_3(PCy_3)](THF)_2$ (460 mg, 0.757 mmol) was added THF (20 mL). The brown solution was stirred for 18 h before removal of volatiles under reduced pressure. The grey solid was extracted with pentane (3 x 10 mL) and volatiles removed under reduced pressure. Drying *in vacuo* afforded **14** as a grey solid. Yield: 298 mg (39%). ^1H NMR (C_6D_6, 400.2 MHz): δ 7.03 (6 H, s, 4- & 3,5-$C_6\underline{H}_3{}^iPr_3$), 6.40 (1 H, s, 3-$C_6\underline{H}_2Me_3$), 6.36 (1 H, s, 5-$C_6\underline{H}_2Me_3$), 4.16 (4 H, s, OCH_2), 3.42 (4 H, br s, $C\underline{H}Me_2$) 2.38 (3 H, s, 2-$C_6H_2\underline{Me}_3$), 2.02 (3 H, m, 1-C_6H_{11}), 1.95 (3 H, s, 6-$C_6H_2\underline{Me}_3$), 1.83 (3 H, s, 4-$C_6H_2\underline{Me}_3$), 1.78 (6 H, m, 4-C_6H_{11}), 1.62 (12 H, m, 2,6-C_6H_{11}), 1.51 (12 H, s, $CH\underline{Me}_2$), 1.35 (s, 4 H, $OCH_2C\underline{H}_2$), 1.26 (12 H, s, $CH\underline{Me}_2$), 1.21 (12 H, m, 3,5-C_6H_{11}). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δ 209.4 (s, CO), 174.7 (s, CN_2), 143.3 (s, 2-$\underline{C}_6H_3{}^iPr_2$), 142.5 (s, 6-$\underline{C}_6H_3{}^iPr_2$), 138.3 (s, 2-$\underline{C}_6H_2Me_3$), 137.6 (s, 6-$\underline{C}_6H_2Me_3$), 137.5 (s, 4-$\underline{C}_6H_2Me_3$), 131.0 (s, 1-$\underline{C}_6H_2Me_3$), 130.0 (s, 3-$\underline{C}_6H_2Me_3$), 129.3 (s, 5-$\underline{C}_6H_2Me_3$), 127.9 (s, 1-$\underline{C}_6H_3{}^iPr_2$), 123.9 (s, 4-$\underline{C}_6H_3{}^iPr_2$), 123.7 (s, 3-$\underline{C}_6H_3{}^iPr_2$), 123.6 (s, 5-$\underline{C}_6H_3{}^iPr_2$), 71.0 (s, OCH_2), 37.7 (d, ^1J = 17.3 Hz, 1-C_6H_{11}), 30.3 (s, 2,6-C_6H_{11}), 28.9 (s, $CH\underline{Me}_2$), 28.5 (s, $\underline{C}HMe_2$) 28.1 (d, ^3J = 10.3 Hz, 3,5-C_6H_{11}), 26.9 (s, 4-C_6H_{11}), 25.0 ($OCH_2\underline{C}H_2$), 23.8 (2-$C_6H_2\underline{Me}_3$), 22.7 (6-$C_6H_2\underline{Me}_3$), 20.6 (4-

$C_6H_2\underline{Me}_3$). $^{31}P\{^1H\}$ (C_6D_6, 162.0 MHz): δ 68.6 (s). IR (NaCl plates, Nujol mull, cm^{-1}): 3827 (w), 3747 (w), 2040 (w), 1965 (s), 1873 (s), 1612 (m), 1586 (w), 1569 (w), 1433 (s), 1413 (m), 1316 (m), 1230 (w), 1198 (w), 1174 (m), 1079 (m), 1041 (m), 963 (w), 947 (w), 935 (w), 916 (w), 875 (m), 851 (m), 777 (m), 758 (m), 700 (w), 659 (w), 585 (m), 562 (m). IR (NaCl cell, toluene, ν(CO), cm^{-1}): 1968 (m), 1891 (s), 1840 (w). Anal. found (calcd for $C_{59}H_{86}CoMgN_2O_4P$): C, 70.54 (70.75); H, 8.50 (8.66); N, 2.88 (2.80)%.

*4.8 {MesC(NDipp)$_2$}MgFp(THF) (**15**)*

To a stirring solution of {MesC(NDipp)$_2$}Mg(μ-Br)(OEt_2) (**13**, 1.00 g, 1.51 mmol) in THF (10 mL) was added a solution of K[Fp] (326 mg, 1.51 mmol) in THF (10 mL) dropwise. The reaction mixture was stirred for 2 h before removal of volatiles under reduced pressure. The dark brown solid was extracted with benzene (2 x 10 mL) and volatiles removed under reduced pressure. The solid was triturated with pentane (5 mL) before removal of volatiles under reduced pressure and drying *in vacuo* to afford **15** as a light brown solid. Yield: 0.89 g (74%). ^1H NMR (C_6D_6, 400.2 MHz): δ 7.01 (6 H, s, $C_6\underline{H}_3{}^iPr_2$), 6.36 (2 H, s, $C_6\underline{H}_2Me_3$), 4.51 (5 H, s, Cp), 4.00 (4 H, s, OCH_2), 2.96 (2 H, br s, $C\underline{H}Me_2$), 2.12 (3 H, s, 2-$C_6H_2\underline{Me}_3$), 1.96 (3 H, s, 6-$C_6H_2\underline{Me}_3$), 1.87 (3 H, s, 4-$C_6H_2\underline{Me}_3$), 1.50 (12 H, br s, $CH\underline{Me}_2$), 1.26 (4 H, s, $OCH_2C\underline{H}_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δ 221.7 (CO), 173.6 (CN_2), 142.4 (2,6-$\underline{C}_6H_3{}^iPr_2$), 137.8 (2-$\underline{C}_6H_2Me_3$), 137.7 (4-$\underline{C}_6H_2Me_3$), 137.3 (6-$\underline{C}_6H_2Me_3$), 131.2 (1-$\underline{C}_6H_2Me_3$), 130.0 (3-$\underline{C}_6H_2Me_3$), 129.8 (5-$\underline{C}_6H_2Me_3$), 128.6 (1-$\underline{C}_6H_3{}^iPr_2$), 124.0 (3-$\underline{C}_6H_3{}^iPr_2$), 123.8 (4-$\underline{C}_6H_3{}^iPr_2$), 123.6 (5-$\underline{C}_6H_3{}^iPr_2$), 78.7 (Cp), 71.0 ($O\underline{C}H_2CH_2$), 28.9 ($\underline{C}HMe_2$), 27.0 ($CH\underline{Me}_2$), 25.2 ($OCH_2\underline{C}H_2$), 23.6 ($CH\underline{Me}_2$), 22.8 (2,6-$C_6H_2\underline{Me}_3$), 20.6 (4-$C_6H_2\underline{Me}_3$). IR (NaCl plates, Nujol mull, cm^{-1}): 2020 (m), 2003 (m), 1961 (sh), 1930 (s), 1866 (s), 1791 (sh), 1609 (m), 1567 (m), 1433 (s), 1412 (s), 1311 (m), 1228 (m), 1178 (m), 1078 (m), 1052 (m), 962 (w), 945 (w), 934 (w), 872 (m), 861 (m), 852 (m), 815 (m), 800 (m), 779 (m), 760 (s), 698 (w), 664 (m). IR (NaCl cell, toluene, ν(CO), cm^{-1}): 2017 (s), 1925 (m). It was not possible to obtain a satisfactory elemental analysis for **15**.

*4.9 MesNCNMes (**16**)*

To a stirring solution of MesN(H)C(S)N(H)Mes (12.5 g, 40.0 mmol) and NEt_3 (11.2 mL, 80.0 mmol) in ethyl acetate (300 mL) was added I_2 (10.2 g, 40.0 mmol) in portions over 30 min. The mixture was stirred for 2 h at room temperature then filtered to give a brown solution. Volatiles were removed under reduced pressure to give a brown solid. The solid was extracted with pentane (4 x 50 mL), filtered through a silica plug and the resultant brown solution added to activated Cu (6.10 g, 96.0 mmol). The mixture was stirred for 16 h at room temperature to give a black suspension. The suspension was filtered through silica to give a colourless solution. Volatiles were removed under reduced pressure and the resultant solid was dried *in vacuo* to afford **16** as a colourless crystalline solid. Yield: 6.97 g (63%). The ^1H NMR spectrum was consistent with that reported by Cowley *et al.*[24]

4.10 $[Mg\{MesC(NMes)_2\}(\mu\text{-}Br)(OEt_2)]_2$ *(**17**)*

To a stirring solution of MesMgBr in Et_2O (43.0 mL, 0.3 M, 12.9 mmol) was added a solution of MesNCNMes (**16**, 3.48 g, 12.5 mmol) in Et_2O (30 mL) dropwise. The solution was stirred for 18 h to give a white precipitate. The solid was isolated by filtration and washed with cold Et_2O (2 x 20 mL, −78 °C) before drying *in vacuo* to afford **17** as a white solid. Yield: 6.66 g (93%). ^1H NMR (THF-d_8, 400.2 MHz): δ 6.54 (8 H, s, N-$C_6\underline{H}_2Me_3$), 6.42 (4 H, s, C-$C_6\underline{H}_2Me_3$), 3.38 (8 H, quart, ^3J = 7.0 Hz, OCH_2), 2.18 (24 H, s, N-(2,6-$C_6H_2\underline{Me}_3$)), 2.09 (12 H, s, C-(2,6-$C_6H_2\underline{Me}_3$)), 2.06 (12 H, s, N-(4-$C_6H_2\underline{Me}_3$)), 2.02 (6 H, s, C-(4-$C_6H_2\underline{Me}_3$)), 1.11 (12 H, t, ^3J = 7.0 Hz, $OCH_2\underline{Me}$). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δ 173.5 (CN_2), 144.9 (N-(2,6-C_6H_2)), 137.9 (C-(2,6-C_6H_2)), 137.7 (C-(4-C_6H_2)), 134.7 (C-(1-C_6H_2)), 132.8 (N-(1-C_6H_2)), 130.7 (N-(4-C_6H_2)), 129.5 (N-(3,5-C_6H_2)), 129.3 (C-(3,5-C_6H_2)), 66.5 (OCH_2), 23.3 (C-(2,6-$C_6H_2\underline{Me}_3$)), 21.3 (N-(2,6-$C_6H_2\underline{Me}_3$)), 21.0 (C-(4-$C_6H_2\underline{Me}_3$)), 20.9 (N-(4-$C_6H_2\underline{Me}_3$)), 15.8 ($OCH_2\underline{Me}$). IR (NaCl plates, Nujol mull, cm^{-1}): 1733 (w), 1396 (s), 1205 (m), 1181 (w), 1148 (m), 1086 (m), 1048 (m), 968 (w), 936 (w), 919 (w), 909 (w), 853 (s), 834 (w), 787 (m), 749 (w), 740 (w), 659 (w). It was not possible to obtain a satisfactory elemental analysis for **17**.

4.11 $\{MesC(NMes)_2\}Mg\{Co(CO)_3(PCy_3)\}(THF)$ *(**18**)*

To a stirring solution of $[\{MesC(NMes)_2\}Mg(\mu\text{-}Br)(OEt_2)]_2$ (**17**, 500 mg, 0.434 mmol) in THF (10 mL) was added a solution of $K[Co(CO)_3(PCy_3)](THF)_2$ (527 mg, 0.868 mmol) in THF (10 mL) dropwise. The reaction mixture was stirred for 2 h before removal of volatiles under reduced pressure. The brown residue was extracted with benzene (2 x 10 mL), volatiles were removed under reduced pressure and the solid dried *in vacuo* to afford **18** as a pale brown solid. Yield: 668 mg (84%). ^1H NMR (C_6D_6, 400.2 MHz): δ 6.71 (4 H, s, N-(3,5-C_6H_2)), 6.42 (2 H, s, C-(3,5-C_6H_2)), 3.98 (4 H, s, OCH_2), 2.46 (12 H, s, N-(2,6-$C_6H_2\underline{Me}_3$), 2.26 (6 H, s, C-(2,6-$C_6H_2\underline{Me}_3$), 2.15 (12 H, br s, 2,6-C_6H_{11}), 2.06 (6 H, s, N-(4-$C_6H_2\underline{Me}_3$), 2.01 (3 H, br s, 1-C_6H_{11}), 1.86 (3 H, s, C-(4-$C_6H_2\underline{Me}_3$), 1.77 (12 H, br s, 3,5-C_6H_{11}), 1.62 (12 H, br s, 4-C_6H_{11}), 1.32 (4 H, br s, $OCH_2C\underline{H}_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δ 211.1 (s, CO), 172.7 (CN_2), 143.3 (s, N-(2,6-C_6H_2)), 138.0 (s, C-(4-C_6H_2)), 137.3 (s, C-(1-C_6H_2)), 133.4 (s, C-(2,6-C_6H_2)), 131.5 (s, N-(4-C_6H_2)), 130.8 (s, N-(1-C_6H_2)), 129.9 (s, N-(3,5-C_6H_2)), 129.3 (s, C-(3,5-C_6H_2)), 70.0 (s, OCH_2), 37.5 (d, ^1J = 16.6 Hz, 1-C_6H_{11}), 30.4 (s, 2,6-C_6H_{11}), 28.2 (d, ^3J = 10.2 Hz, 3,5-C_6H_{11}), 27.0 (s, 4-C_6H_{11}), 25.3 (s, $OCH_2\underline{C}H_2$), 22.0 (s, C-(2,6-$C_6H_2\underline{Me}$)), 20.8 (s, C-(4-$C_6H_2\underline{Me}$)), 20.7 (s, N-(4-$C_6H_2\underline{Me}$)), 20.5 (s, N-(2,6-$C_6H_2\underline{Me}$)). $^{31}P\{^1H\}$ (C_6D_6, 162.0 MHz): δ 70.0 (s). IR (NaCl plates, Nujol mull, cm^{-1}): 2040 (w), 1964 (sh), 1937 (s), 1885 (sh), 1865 (s), 1784 (w), 1720 (s), 1569 (w), 1425 (s), 1396 (s), 1207 (m), 1172 (w), 1148 (w), 972 (w), 919 (w), 886 (m), 851 (s), 818 (w), 741 (m), 675 (w). IR (NaCl cell, toluene, ν(CO), cm^{-1}): 1970 (m), 1910 (m), 1890 (m), 1836 (m), 1755 (m). Anal. found (calcd for $C_{53}H_{73}CoMgN_2O_4P$): C, 69.53 (69.39); H, 8.18 (8.13); N, 2.99 (3.05)%.

4.12 {MesC(NMes)$_2$}MgFp(THF) (***19***)

To a stirring solution of [{MesC(NMes)$_2$}Mg(μ-Br)(OEt$_2$)]$_2$ (**17**, 300 mg, 0.260 mmol) in THF (15 mL) was added a solution of K[Fp] (113 mg, 0.520 mmol) in THF (10 mL) dropwise. The reaction mixture was stirred for 3 h before removal of volatiles under reduced pressure. The dark brown solid was extracted with THF (2 x 10 mL) and filtered before removal of volatiles under reduced pressure. The solid was triturated with pentane before removal of volatiles under reduced pressure and drying *in vacuo* to afford **19** as a light brown solid. Yield: 236 mg (68%). ^{1}H NMR (THF-d_8, 400.2 MHz): δ 6.61 (4 H, s, N-$C_6\underline{H_2}Me_3$), 6.52 (2 H, s, C-$C_6\underline{H_2}Me_3$), 4.40 (5 H, s, Cp), 2.10 (6 H, s, C-(2,6-$C_6H_2\underline{Me_3}$)), 2.09 (15 H, s, N-(2,6-$C_6H_2\underline{Me_3}$) & C-(4-$C_6H_2\underline{Me_3}$)), 1.98 (6 H, s, N-(4-$C_6H_2\underline{Me_3}$)). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz): δ 223.1 (CO), 172.1 (CN_2), 143.9 (N-(2,6-C_6H_2)), 138.6 (C-(4-C_6H_2)), 137.8 (C-(2,6-C_6H_2)), 134.0 ((C-(1-C_6H_2))), 131.4 (N-(1-C_6H_2)), 131.0 (N-(4-C_6H_2)), 130.0 (N-(3,5-C_6H_2)), 129.7 (C-(3,5-C_6H_2)), 78.8 (Cp), 22.2 (N-(4-$C_6H_2\underline{Me_3}$)), 21.0 (C-(2,6-$C_6H_2\underline{Me_3}$)), 20.8 (N-(2,6-$C_6H_2\underline{Me_3}$) & C-(4-$C_6H_2\underline{Me_3}$)). IR (NaCl plates, Nujol mull, cm^{-1}): 2019 (m), 1961 (sh), 1923 (s), 1858 (s), 1790 (sh), 1678 (w), 1610 (m), 1168 (w), 1147 (w), 969 (m), 955 (w), 935 (w), 920 (m), 852 (s), 676 (m), 634 (m), 606 (m), 592 (m). IR (NaCl cell, THF ν(CO), cm^{-1}): 2013 (s), 1992 (sh), 1950 (sh), 1921 (s), 1879 (sh), 1861 (s). It was not possible to obtain a satisfactory elemental analysis for **19**.

4.13 Me$_2$NC(NDipp)(NHDipp) (***20***)

To a stirring solution of LiNMe$_2$ (0.561 g, 11.0 mmol) in THF (10 mL) was added DippNCNDipp (**12**, 4.00 g, 11.0 mmol) over 5 min in THF (10 mL) at −78 °C. The colourless solution was allowed to warm to room temperature then stirred for a further 2 h at room temperature, quenched with deionised water (10 mL) and extracted into Et$_2$O (3 x 10 mL). Volatiles were removed under reduced pressure and the resultant white solid dried *in vacuo* to afford **20**. Yield: 4.13 g (92%). Diffraction-quality crystals were grown from a hexane solution at room temperature. ^{1}H NMR (C_6D_6, 400.2 MHz): δ 7.26 (2 H, app. d, ^3J = 8.0 Hz, 4-C_6H_3), 7.00 (4 H, d, ^3J = 7.0 Hz, 3,5-C_6H_3), 5.25 (1 H, s, NH), 3.45 (2 H, br m, $C\underline{H}Me_2$), 3.28 (2 H, br m, $C\underline{H}Me_2$), 2.48 (6 H, s, NMe$_2$), 1.23 (24 H, d, ^3J = 6.9 Hz, $CH\underline{Me_2}$). ^{13}C{^{1}H} NMR (C_6D_6, 101.6 MHz): δ 151.3 ($\underline{C}NMe_2$), 145.0 (1-C_6H_3), 140.1 (2,6-C_6H_3), 124.1 (3,5-C_6H_3), 123.5 (4-C_6H_3), 39.5 (NMe$_2$), 29.0 ($\underline{C}HMe_2$), 28.8 ($\underline{C}HMe_2$), 25.0 ($CH\underline{Me_2}$), 24.7 ($CH\underline{Me_2}$), 23.4 ($CH\underline{Me_2}$), 22.5 ($CH\underline{Me_2}$). EI-HRMS: m/z found (calc. for $C_{27}H_{41}N_3$, [Me$_2$NC(NDipp)(NHDipp)]$^+$) 407.3303 (407.3300). IR (NaCl plates, Nujol mull, cm^{-1}): 3391 (w, ν(NH)), 1625 (s), 1260 (s), 1019 (m), 761 (w). Anal. found (calcd. for $C_{27}H_{41}N_3$): C, 79.46 (79.55); H, 10.30 (10.14); N, 10.25 (10.31)%.

4.14 {Me$_2$NC(NDipp)$_2$}MgI(OEt$_2$) (***21***)

To a stirring solution of MeMgI in Et$_2$O (11.64 mL, 0.4 M, 4.91 mmol) was added a solution of Me$_2$NC(NDipp)(NHDipp) (**20**, 2.00 g, 4.91 mmol) in Et$_2$O (10 mL) dropwise at −20 °C. The colourless solution was allowed to warm to room temperature and stirred for a further 2 h. The volatiles were removed under reduced pressure to give a white solid, which was washed with hexane (3 x 5 mL) and dried *in vacuo* to afford **21** as a white solid. Yield: 2.94 g (95%). Diffraction-quality crystals were grown from an Et_2O solution at room temperature. ^{1}H NMR (C_6D_6, 400.2 MHz): δ 7.20 (2 H, br m, 4-C_6H_3), 7.14 (4 H, br m, 3,5-C_6H_3), 3.71 (4 H, sept, ^3J = 6.8 Hz, C$\underline{H}$$Me_2$), 3.34 (4 H, q, ^3J = 7.0 Hz, OCH_2), 2.14 (6 H, s, NMe_2), 1.38 (12 H, d, ^3J = 6.8 Hz, CH$\underline{Me_2}$), 1.31 (12 H, d, ^3J = 6.8 Hz, CH$\underline{Me_2}$), 0.93 (6 H, t, ^3J = 7.0 Hz, $OCH_2$$\underline{Me}$). ^{13}C{^{1}H} NMR ($C_6D_6$, 101.6 MHz): δ 167.0 ($\underline{C}$$NMe_2$), 143.4 (1-$\underline{C_6}H_3$), 142.9 (2,6-$\underline{C_6}H_3$), 123.8 (3,5-$\underline{C_6}H_3$), 123.6 (4-$\underline{C_6}H_3$), 66.9 ($OCH_2$), 39.6 ($NMe_2$), 27.9 ($\underline{C}$$HMe_2$), 26.2 (CH$\underline{Me_2}$), 23.7 (CH$\underline{Me_2}$), 14.1 ($OCH_2$$\underline{Me}$). IR (NaCl plates, Nujol mull, cm^{-1}): 1522 (s), 1315 (m), 1250 (m), 1203 (m), 1100 (m), 1042 (s), 934 (w), 835 (w), 904 (m), 835 (w), 771 (s). Anal. found (calcd. for $C_{31}H_{50}IMgN_3O$): C, 58.79 (58.92); H, 7.89 (7.98); N, 6.52 (6.65)%.

*4.15 [{$Me_2NC(NDipp)_2$}MgFp]$_2$ (**22**)*

To a stirring suspension of K[Fp] (171 mg, 0.791 mmol) in C_6H_6 (10 mL) was added a solution of {$Me_2NC(NDipp)_2$}MgI(Et_2O) (**21**, 500 mg, 0.791 mmol) in C_6H_6 (10 mL) dropwise at room temperature. The mixture was stirred for 1 h at room temperature then filtered. Volatiles were removed from the filtrate under reduced pressure to give a red solid, which was washed with cold hexane (3 x 5 mL, −78 °C) and dried *in vacuo* to afford **22** as a yellow solid. Yield: 308 mg (64%). Diffraction-quality crystals were grown from a benzene solution at 5 °C. ^{1}H NMR (C_6D_6, 400.2 MHz): δ 7.10 (4 H, br m, 4-C_6H_3), 6.81 (8 H, br m, 3,5-C_6H_3), 4.15 (10 H, s, Cp), 3.64 (8 H, br s, C$\underline{H}$$Me_2$), 2.12 (12 H, s, NMe_2), 1.35 (24 H, d, ^3J = 7.1 Hz, CH$\underline{Me_2}$), 1.25 (24 H, d, ^3J = 7.1 Hz, CH$\underline{Me_2}$). ^{13}C{^{1}H} NMR (C_6D_6, 101.6 MHz): δ 166.0 ($\underline{C}$$NMe_2$), 144.0 (1-$C_6H_3$), 142.6 (2,6-$C_6H_3$), 123.8 (3,5-$C_6H_3$), 123.5 (4-$C_6H_3$), 80.5 (Cp), 39.5 ($NMe_2$), 28.1 ($\underline{C}$$HMe_2$), 25.7 (CH$\underline{Me_2}$), 23.7 (CH$\underline{Me_2}$), (δ (CO) not observed). IR (NaCl plates, Nujol mull, cm^{-1}): 2020 (m), 1962 (s), 1944 (s), 1778 (s), 1626 (m), 1410 (w), 1018 (m), 800 (m), 770 (w). IR (NaCl cell, toluene, ν(CO), cm^{-1}): 2016 (s), 1921 (m), 1781 (m). IR (NaCl cell, THF, ν(CO), cm^{-1}): 2014 (s), 1946 (m). Anal. found (calcd. for $C_{68}H_{90}Fe_2Mg_2N_6O_4$): C, 66.89 (67.18); H, 7.34 (7.46); N, 6.91 (6.76)%.

*4.16 {$Me_2NC(NDipp)_2$}Mg{$Co(CO)_3(PCy_3)$}(OEt_2) (**23**)*

To a stirring suspension of K[$Co(CO)_3(PCy_3)$]$(THF)_2$ (480 mg, 0.791 mmol) in C_6H_6 (10 mL) was added a solution of {$Me_2NC(NDipp)_2$}MgI(Et_2O) (**21**, 500 mg, 0.791 mmol) in C_6H_6 (10 mL) dropwise at room temperature. The mixture was stirred for 1 h then filtered. Volatiles were removed from the filtrate under reduced pressure and the resultant red solid (**11**) dried *in vacuo*. Yield: 410 mg (56%). ^{1}H NMR (C_6D_6, 400.2 MHz): δ 7.20 (4 H, br m, 3,5-C_6H_3), 7.11 (2 H, m, ^3J = 7.4 Hz, 4-C_6H_3), 3.91 (8 H, br m, C$\underline{H}$$Me_2$ & OCH_2), 2.22 (6 H, s, NMe_2), 1.97 (3 H, br m, 1-C_6H_{11}), 1.77 (6 H, br m, 4-C_6H_{11}), 1.56 (12 H, br m, 2,6-C_6H_{11}), 1.32 (27 H, br m, CH$\underline{Me_2}$ & $OCH_2$$\underline{Me}$), 1.21 (12 H, br m, 3,5-C_6H_{11}). $^{13}C\{^1H\}$ NMR (C_6D_6, 101.6 MHz): δ 209.4 (s, CO), 165.9 (s, $\underline{C}NMe_2$), 144.0 (s, 1-C_6H_3), 142.9 (s, 2,6-C_6H_3), 123.6 (s, 3,5-C_6H_3), 123.1 (s, 4-C_6H_3), 70.2 (s, $O\underline{C}H_2$), 39.9 (s, NMe_2), 37.6 (d, ^1J = 17.1 Hz, 1-C_6H_{11}), 30.3 (s, 2,6-C_6H_{11}), 28.1 (d, ^1J = 10.6 Hz, 3,5-C_6H_{11}), 28.0 (s, $\underline{C}HMe_2$) 26.9 (s, 4-C_6H_{11}), 25.1 (s, $OCH_2\underline{Me}$), 24.0 (s, $CH\underline{Me}_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 162.0 MHz): δ 69.2 (br s). IR (NaCl plates, Nujol mull, cm^{-1}): 1960 (s), 1944 (s), 1879 (s), 1849 (s), 1517 (w), 769 (w). IR (NaCl cell, toluene, ν(CO), cm^{-1}): 1962 (s), 1858 (m), 1804 (m). It was not possible to obtain a satisfactory elemental analysis for **23**.

*4.17 K[Co(CO)$_3$(PPh$_3$)](THF) (**24**)*

To a stirring K amalgam (121 mg, 3.08 mmol; 10 mL Hg) was added a red suspension of $[Co(CO)_3(PPh_3)]_2$ (500 mg, 0.617 mmol) in THF (20 mL). The suspension was stirred over the amalgam for 16 h at room temperature to give a green-yellow solution, which was filtered and volatiles removed under reduced pressure. The resulting green-yellow solid was washed with pentane (2 x 10 mL) and dried in *vacuo* to afford **24**. Yield: 562 mg (88%). Diffraction quality crystals were grown from a THF solution at room temperature. ^1H NMR (THF-d_8, 299.9 MHz): δ 7.53 (6 H, s, 2,6-C_6H_3), 7.14 (9 H, s, 3,4,5-C_6H_3). $^{13}C\{^1H\}$ NMR (THF-d_8, 75.5 MHz): δ 144.0 (d, ^1J = 27.1 Hz, 1-C_6H_3), 134.3 (d, ^2J = 14.0 Hz, 2,6-C_6H_3), 128.3 (s, 4-C_6H_3), 127.9 (d, ^3J = 8.7 Hz, 3,5-C_6H_3) (δ(CO) not observed). $^{31}P\{^1H\}$ NMR (THF-d_8, 121.4 MHz): δ 64.0 (br s). IR (NaCl plates, Nujol mull, cm^{-1}): 1932 (s), 1855 (s), 1804 (s), 1583 (w), 1435 (s), 1305 (w), 1261 (w), 1177 (w), 1084 (m), 1056 (s), 1029 (m), 914 (w), 801 (w), 750 (m), 736 (m), 697 (s), 591 (m), 575 (s). IR (NaCl cell, THF, ν(CO), cm^{-1}): 1925 (m), 1859 (s), 1806 (sh). Anal. found (calcd for $C_{25}H_{23}CoKO_4P$): C, 57.88 (58.14); H, 4.37 (4.49)%.

*4.18 {Me$_2$NC(NDipp)$_2$}Mg{Co(CO)$_3$(PPh$_3$)}(OEt$_2$) (**25**)*

To a stirring solution of $K[Co(CO)_3(PPh_3)](THF)$ (**24**, 401 mg, 0.791 mmol) in C_6H_6 (10 mL) was added a solution of $\{Me_2NC(NDipp)_2\}MgI(OEt_2)$ (**21**, 500 mg, 0.791 mmol) in C_6H_6 (10 mL) dropwise at room temperature. The mixture was stirred for 1 h at room temperature then filtered. Volatiles were removed from the filtrate and the resultant red solid (**25**) dried *in vacuo*. Yield: 380 mg (53%). ^1H NMR (C_6D_6, 400.2 MHz): δ 7.76 (3 H, t, ^3J = 8.5 Hz, 2,6-C_6H_5), 7.18 (2 H, br m, 4-$C_6\underline{H}_3{}^iPr_2$), 7.08 (4 H, dd, ^3J = 8.5, 6.5 Hz, 3,5-C_6H_5), 7.06 (2 H, br m, 2,6-C_6H_5), 7.02 (4 H, d, ^3J = 6.8 Hz, 3,5-$C_6\underline{H}_3{}^iPr_2$), 3.83 (8 H, br m, $C\underline{H}Me_2$ & OCH_2), 2.20 (6 H, s, NMe_2), 1.32 (24 H, br m, $CH\underline{Me}_2$), 1.22 (6 H, br s, $OCH_2\underline{Me}$). $^{13}C\{^1H\}$ NMR (C_6D_6, 101.6 MHz): δ 208.0 (s, CO), 165.9 (s, $\underline{C}NMe_2$), 144.0 (s, 1-$\underline{C}_6H_3{}^iPr_2$), 142.8 (s, 2,6-$\underline{C}_6H_3{}^iPr_2$), 138.5 (d, ^1J = 38.0 Hz, 1-C_6H_5), 133.6 (d, ^2J = 12.0 Hz, 2,6-C_6H_5), 129.5 (s, 4-C_6H_5), 128.1 (3,5-C_6H_5 overlapping with solvent), 123.7 (3,5-$\underline{C}_6H_3{}^iPr_2$), 123.2 (4-$\underline{C}_6H_3{}^iPr_2$), 70.2 ($O\underline{C}H_2$), 39.8 ($NMe_2$), 28.0 ($\underline{C}HMe_2$), 25.05 ($OCH_2\underline{Me}$), 23.9 ($CH\underline{Me}_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 162.0 MHz): δ 62.0 (br s). IR (NaCl plates, Nujol mull, cm^{-1}): 1973 (s, ν(CO)), 1887 (s, ν(CO)), 1807 (m, br ν(CO)), 1520, (m), 1200 (w), 1016 (w), 865 (m), 771 (m), 674 (m). IR (NaCl cell, toluene, ν(CO), cm^{-1}): 2049 (s), 1976 (s), 1896 (m). It was not possible to obtain a satisfactory elemental analysis for **25**.

4.19 X-ray crystallography

Crystals were mounted on glass fibres using perfluoropolyether oil and cooled rapidly in a stream of cold N_2 using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (**9**, **11**, **17**, **20**, **21**, **24**) or Agilent Technologies Supernova diffractometer (**14**, **22**) using Mo-κα or Cu-κα, respectively. As appropriate, absorption and decay corrections were applied to the data and equivalent reflections merged.[35] The structures were solved using SIR92[36] or Superflip[37] and further refinements and all other crystallographic calculations were performed using the CRYSTALS program suite.[38]

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Appendix A. Supplementary data

Supplementary crystallographic data for the structures of **9**, **11**, **14**, **17**, **20**, **21**, **22** and **24** are provided in the Supporting Information. The structures of **17**, **20** and **24** with selected distances and angles are also provided. CCDC 1448329–1448336 contain the supplementary crystallographic data for the structurally characterised compounds. Supplementary diffusion NMR spectroscopy parameters are also provided.

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