



Synthesis of Heavy Cyanide Analogs for the Design of Novel Prussian Blue Analogs

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Abstract

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This thesis describes the chemistry of metal complexes of the cyaphide ion ($\text{C}\equiv\text{P}^-$) and some of its derivatives, including their syntheses, properties, and reactivity.

Chapter 1. The chemistry of the cyaphide ion is introduced, starting with a cursory overview of its more common lighter congener, the cyanide ion, and its application in Prussian blue analogs. Next, the use of the isolobal analogy in describing fragments that are related to the cyanide and cyaphide ions is outlined. Finally, reported examples of the cyaphide ion in the chemical literature are surveyed, and their syntheses and characterization are discussed.

Chapter 2. Magnesium(II) cyaphide complexes are accessed by the reductive deoxygenation of siloxyphosphaalkynes using magnesium(I) reducing agents. The synthesis of these ionic cyaphide complexes is detailed, as is their characterization by multinuclear NMR spectroscopy, infrared and Raman spectroscopy, and single crystal X-ray crystallography. Theoretical insights into the properties of these complexes and the mechanism of their formation are also discussed.

Chapter 3. By analogy with classic Grignard reagents, magnesium(II) cyaphide complexes can be used to transfer the cyaphide ion to other metal centers. The synthesis of cyaphide-containing main group and transition metal complexes by cyaphide transfer is detailed. Where possible, these compounds are characterized by multinuclear NMR spectroscopy, infrared and Raman vibrational spectroscopy, and single crystal X-ray crystallography.

Chapter 4. The ligand properties of the cyaphide ion in the terminal, end-on κC coordination mode are determined in a comparative study of gold(I) IDipp complexes and group 9 D^{ipp} PDI complexes. Using this approach, the σ donor and π acceptor properties of the cyaphido ligand are deconvoluted. In order to provide illustrative points of comparison, analogous metal complexes bearing various strong-field ligands are also synthesized and analyzed using the same approach.

Chapter 5. Hetero-multimetallic complexes of the cyaphide ion are synthesized by the reaction of a gold(I) cyaphide complex with electron-rich metal centers. These reactions are driven by the low-lying $C\equiv P \pi^*$ orbitals and result in side-on bridging cyaphide complexes, though reactivity at the Au–C bond can also occur for especially nucleophilic metals. These complexes are fully characterized, and the unusual chemical bonding in these species is discussed with the aid of theoretical calculations.

Chapter 6. Metal cyaphide complexes undergo 1,3-dipolar cycloaddition reactions with organic azides to afford metallo-triazaphospholes. These reactions proceed straightforwardly and regioselectively in high yields under mild conditions, reminiscent of the archetypal “click” reaction between alkynes and azides. The resulting metallo-triazaphospholes remain reactive and can be carbon-functionalized to give otherwise difficult to access protio- and iodo- species.

Chapter 7. Metal cyaphide complexes are susceptible to oligomerization by formal cycloaddition reactions involving the reactive cyaphide $C\equiv P \pi$ bonds to give highly charged, conjugated organophosphorus anions. The synthesis, characterization, and bonding of the oligomers and their monomer precursors are discussed herein. The factors that favor oligomerization are elucidated, providing a framework for understanding the stabilization of metal cyaphide complexes.

Chapter 8. The synthesis of highly stable iron(II) mono- and dicyaphide complexes is described. These are used as precursors to multimetallic iron complexes containing the cyaphide ion in end-on bridging coordination modes, structurally related to fragments of Prussian blue. The properties of these complexes are investigated using NMR and vibrational spectroscopy, X-ray crystallography, and cyclic voltammetry. Theoretical calculations provide insight into their electronic structures.

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To my supervisor, Prof. Jose Goicoechea: Thank you for your mentorship, your enthusiasm, and your unwavering support. It's been an incredible four years – I've learned so much.

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致我的家人：我非常感谢你们所做的一切，没有你们就没有现在的我。虽然我们相距很远，我时时刻刻都感受到你们的爱和支持。

List of Abbreviations

18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane
2.2.2-crypt	4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane
Ad	1-adamantyl
anal.	analysis
approx.	approximately
Ar	aryl
Ar ^F	3,5-bis(trifluoromethyl)phenyl
ATR	attenuated total reflectance
a.u.	atomic units
Bn	benzyl
Bu	butyl
calcd.	calculated
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl
Cp*	1,2,3,4,5-pentamethylcyclopentadienyl
CPCM	conductor-like polarized continuum model
CV	cyclic voltammetry
Cy	cyclohexyl
depe	1,2-bis(diethylphosphino)ethane
DCM	dichloromethane
dcype	1,2-bis(dicyclohexylphosphino)ethane
1,2-DFB	1,2-difluorobenzene
DFT	density functional theory
diox	1,4-dioxane
Dipp	2,6-diisopropylphenyl
dippe	1,2-bis(diisopropylphosphino)ethane
^{Dipp} NacNac	Dipp substituted β -diketimate N,N-bis(2,6-diisopropylphenyl)-pentane-2,4-diimine

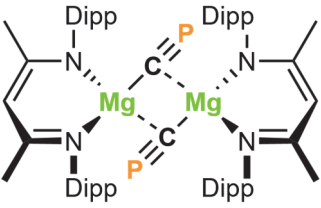
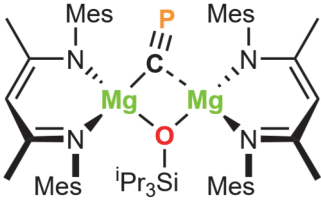
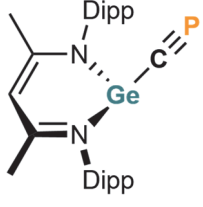
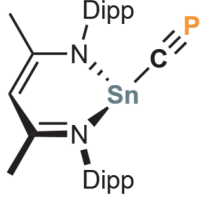
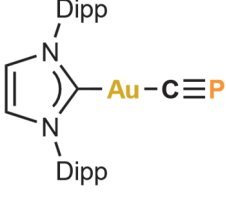
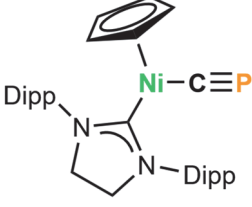
^{Dipp} PDI	Dipp substituted PDI 1,1'-(pyridine-2,6-diyl)bis(<i>N</i> -(2,6-diisopropylphenyl)ethan-1-imine)
^{Dipp} PIEA	Dipp substituted PIEA 1,1'-(pyridine-2,6-diyl)(<i>N</i> -(2,6-diisopropylphenyl)ethan-1-imine)(<i>N</i> -(2,6-diisopropylphenyl)vinylamine)
DMAP	4-dimethylaminopyridine
DME	1,2-dimethoxyethane
DMSO	dimethylsulfoxide
DOSY	diffusion-ordered spectroscopy
dppe	1,2-bis(diphenylphosphino)ethane
DZ	double-zeta
ECP	effective core potential
EDA	energy decomposition analysis
Et	ethyl
ETS	extended transition state
Fc	ferrocene $\text{Fe}(\text{C}_5\text{H}_5)_2$
FT	Fourier-transform
gCP	geometric counterpoise
GIAO	gauge-independent atomic orbital
HEP	Huynh electronic parameter
hex	hexane
HOMO	highest occupied molecular orbital
IDipp	Dipp substituted unsaturated NHC 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
ipc	isopinocampheyl 2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl
ⁱ Pr	isopropyl
IR	infrared
IVCT	intervalence charge transfer
LUMO	lowest unoccupied molecular orbital
Me	methyl

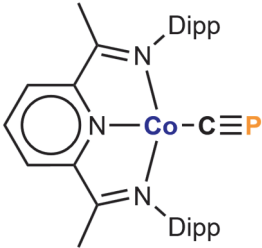
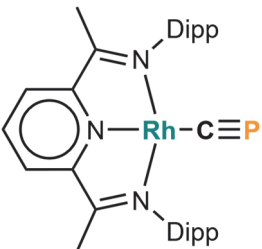
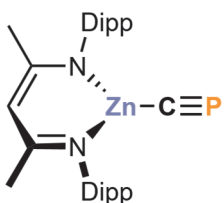
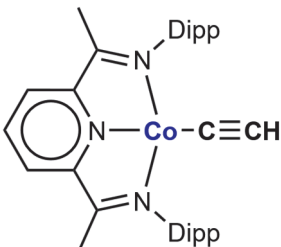
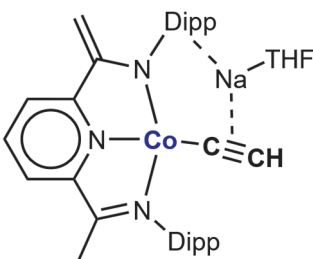
$^{\text{Me}}\text{iPr}_2$	methylated and isopropyl substituted unsaturated NHC 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene)
Mes	mesityl 2,4,6-trimethylphenyl
Mes*	supermesityl 2,4,6-tri- <i>tert</i> -butylphenyl
$^{\text{Mes}}\text{NacNac}$	Mes substituted β -diketiminato <i>N,N</i> -bis(2,4,6-trimethylphenyl)-pentane-2,4-diimine
MO	molecular orbital
NacNac	β -diketiminato
$\text{N}(\text{Ad}^{\text{Me}}\text{ArO})_3^{3-}$	tris(2-hydroxy-3-(1-adamantyl)-5-methylbenzyl)amine-triide
NBO	natural bond orbital
^nBu	butyl
NHC	<i>N</i> -heterocyclic carbene
NICS	nucleus independent chemical shift
NLMO	natural localized molecular orbital
NMR	nuclear magnetic resonance
NOCV	natural orbitals for chemical valence
NPA	natural population analysis
PBE	Perdew-Burke-Ernzerhof
PDI	pyridine-2,6-diimine
pent	pentane
Ph	phenyl
PIEA	pyridine-2-imine-6-enamine
ppm	parts per million
py	pyridine
QRO	quasi-restricted orbital
QTAIM	quantum theory of atoms-in-molecules
RMS	root-mean-square
RT	room temperature
SARC	segmented all-electron relativistically contracted

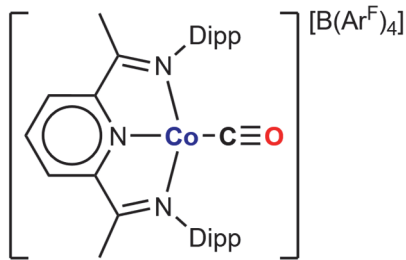
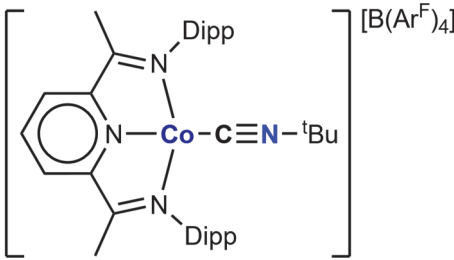
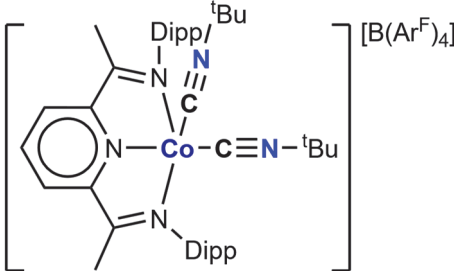
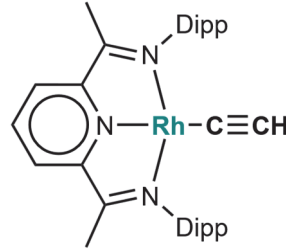
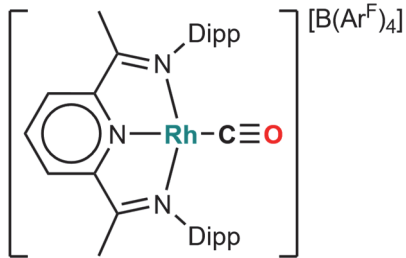
SIDipp	Dipp substituted saturated NHC 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene
SOMO	singly occupied molecular orbital
SQUID	superconducting quantum interference device
SVP	split valence with polarization
^t Bu	<i>tert</i> -butyl
TEP	Tolman electronic parameter
Tf	triflyl
THF	tetrahydrofuran
tol	toluene
TPP	5,10,15,20-tetraphenyl-21 <i>H</i> ,23 <i>H</i> -porphine
TZVP	triple-zeta valence with polarization
UV	ultraviolet
vis	visible
WBI	Wiberg bond index
XRD	X-ray diffraction
ZORA	zeroth-order regular approximation

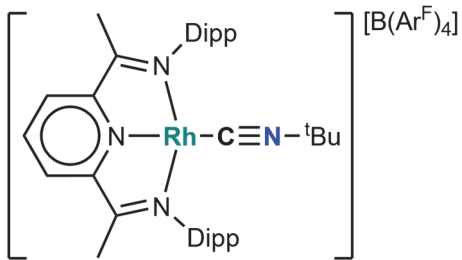
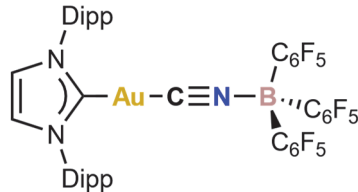
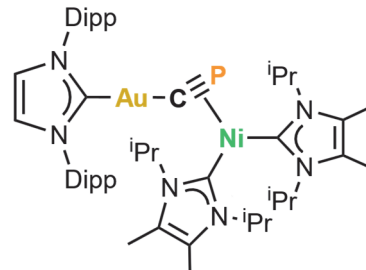
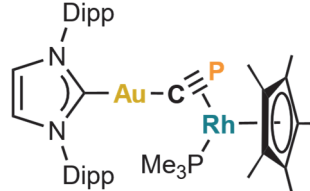
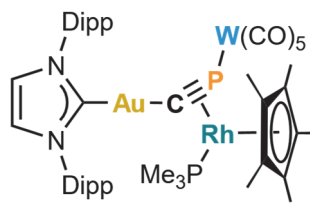
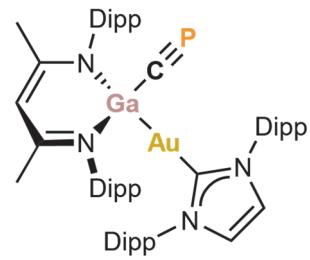
List of Compounds

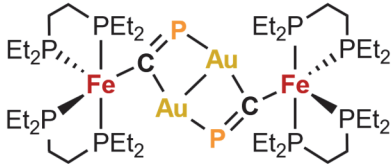
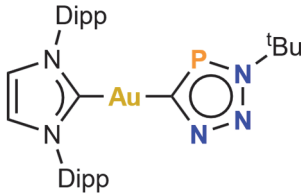
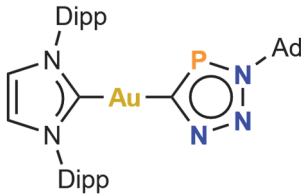
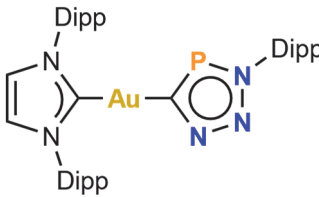
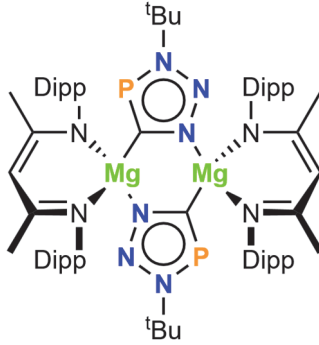
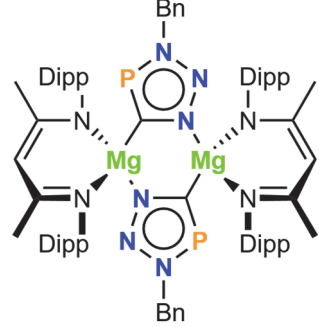
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1_{THF} $\text{Mg}(\text{DippNacNac})(\text{CP})(\text{THF})$	
1_{Et2O} $\text{Mg}(\text{DippNacNac})(\text{CP})(\text{OEt}_2)$	
1_{MeCN} $\text{Mg}(\text{DippNacNac})(\text{CP})(\text{NCMe})$	
1_{DMAP} $\text{Mg}(\text{DippNacNac})(\text{CP})(\text{DMAP})$	
2_{diox} $\text{Mg}(\text{DippNacNac})(\text{OSi}^i\text{Pr}_3)(\text{diox})$	

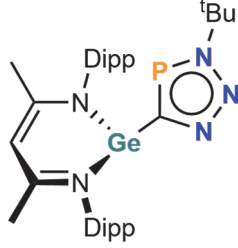
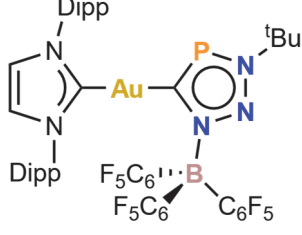
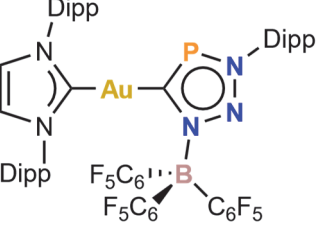
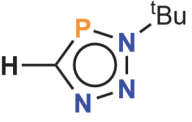
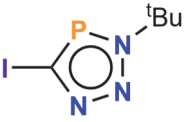
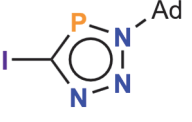
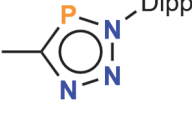
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5 $\text{Ge}(\text{DippNacNac})(\text{CP})$	
6 $\text{Sn}(\text{DippNacNac})(\text{CP})$	
7 $\text{Au}(\text{IDipp})(\text{CP})$	
8 $\text{Ni}(\text{SIDipp})(\text{Cp})(\text{CP})$	

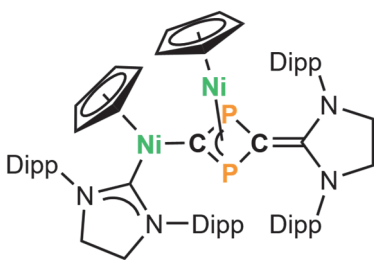
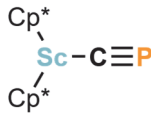
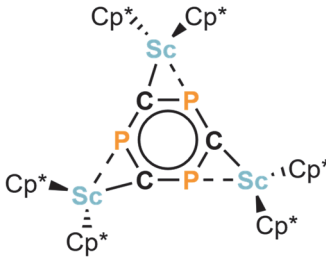
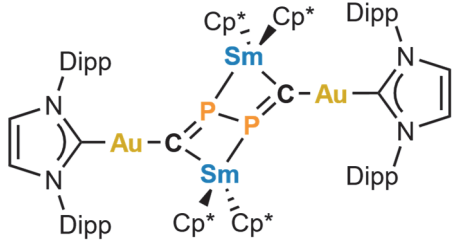
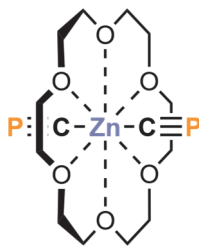
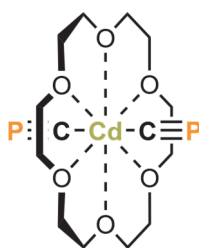
9 $\text{Co}(\text{DippPDI})(\text{CP})$	
10 $\text{Rh}(\text{DippPDI})(\text{CP})$	
11 $\text{Zn}(\text{DippNacNac})(\text{CP})$	
12 $\text{Co}(\text{DippPDI})(\text{CCH})$	
13 $\text{Na}(\text{THF})\text{Co}(\text{DippPIEA})(\text{CCH})$	

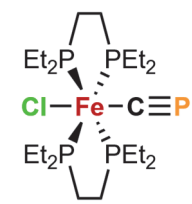
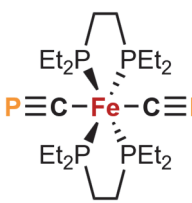
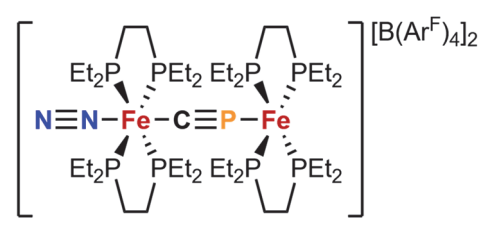
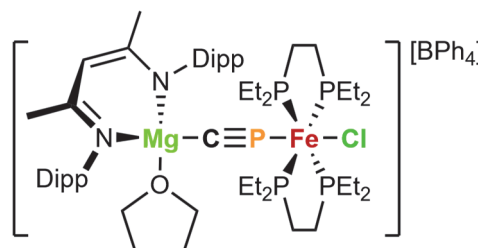
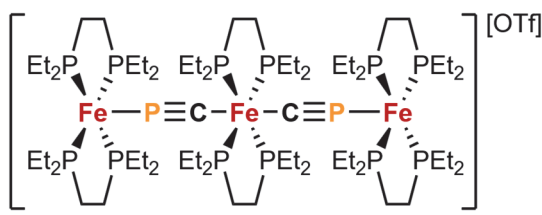
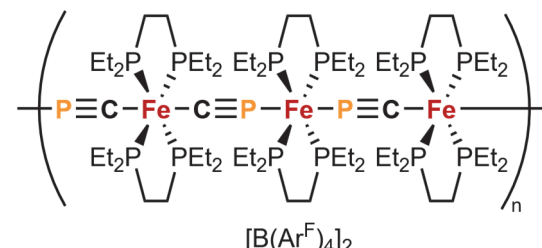
14 $[\text{Co}(\text{DippPDI})(\text{CO})][\text{B}(\text{Ar}^{\text{F}})_4]$	
15 $[\text{Co}(\text{DippPDI})(\text{CN}^t\text{Bu})][\text{B}(\text{Ar}^{\text{F}})_4]$	
16 $[\text{Co}(\text{DippPDI})(\text{CN}^t\text{Bu})_2][\text{B}(\text{Ar}^{\text{F}})_4]$	
17 $\text{Rh}(\text{DippPDI})(\text{CCH})$	
18 $[\text{Rh}(\text{DippPDI})(\text{CO})][\text{B}(\text{Ar}^{\text{F}})_4]$	

19 $[\text{Rh}(\text{DippPDI})(\text{CN}^t\text{Bu})][\text{B}(\text{Ar}^{\text{F}})_4]$	
20 $\{\text{Au}(\text{IDipp})\}(\mu\text{-CN})\{\text{B}(\text{C}_6\text{F}_5)_3\}$	
21 $\{\text{Au}(\text{IDipp})\}(\mu\text{-CP})\{\text{Ni}(\text{Me}^i\text{IPr}_2)_2\}$	
22 $\{\text{Au}(\text{IDipp})\}(\mu\text{-CP})\{\text{Rh}(\text{Cp}^*)(\text{PMe}_3)\}$	
23 $\{\text{Au}(\text{IDipp})\}(\mu_3\text{-CP})\{\text{Rh}(\text{Cp}^*)(\text{PMe}_3)\}\{\text{W}(\text{CO})_5\}$	
24 $\text{Au}(\text{IDipp})\{\text{Ga}(\text{DippNacNac})(\text{CP})\}$	

25 $\{\text{Fe}(\text{depe})_2\}_2(\mu\text{-C}_2\text{P}_2\text{Au}_2)$	
26a $\text{Au}(\text{IDipp})(\text{CPN}_3^t\text{Bu})$	
26b $\text{Au}(\text{IDipp})(\text{CPN}_3\text{Ad})$	
26c $\text{Au}(\text{IDipp})(\text{CPN}_3\text{Dipp})$	
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27b $\{\text{Mg}^{(\text{Dipp})\text{NacNac}}(\mu\text{-CPN}_3\text{Bn})\}_2$	

28 $\text{Ge}^{(\text{Dipp})}\text{NacNac}(\text{CPN}_3^t\text{Bu})$	
29a $\{\text{Au}(\text{IDipp})\}(\mu\text{-CPN}_3^t\text{Bu})\{\text{B}(\text{C}_6\text{F}_5)_3\}$	
29c $\{\text{Au}(\text{IDipp})\}(\mu\text{-CPN}_3\text{Dipp})\{\text{B}(\text{C}_6\text{F}_5)_3\}$	
30 HCPN_3^tBu	
31a ICPN_3^tBu	
31b ICPN_3Ad	
31c ICPN_3Dipp	

32 $\{\text{Ni}(\text{SIDipp})(\text{Cp})\}\{\text{Ni}(\text{Cp})\}\{\mu\text{-(SIDipp)}\text{C}_2\text{P}_2\}$	
33 $\text{Sc}(\text{Cp}^*)_2(\text{CP})$	
34 $\{\text{Sc}(\text{Cp}^*)_2\}_3(\mu_3\text{-C}_3\text{P}_3)$	
35 $\{\text{Au}(\text{IDipp})\}_2\{\text{Sm}(\text{Cp}^*)_2\}_2(\mu_4\text{-C}_2\text{P}_2)$	
36 $\text{Zn}(\text{18-crown-6})(\text{CP})_2$	
37 $\text{Cd}(\text{18-crown-6})(\text{CP})_2$	

38 $\text{Fe}(\text{depe})_2(\text{Cl})(\text{CP})$	
39 $\text{Fe}(\text{depe})_2(\text{Cl})(\text{CP})$	
40 $[\{\text{Fe}(\text{depe})_2\}_2(\text{N}_2)(\mu\text{-CP})][\text{BAr}^{\text{F}}_4]_2$	
41 $[\{\text{Mg}^{\text{(Dipp)}}\text{NacNac}(\text{THF})\}(\mu\text{-CP})$ $\{\text{Fe}(\text{depe})_2\text{Cl}\}][\text{BPh}_4]$	
42 $[\{\text{Fe}(\text{depe})_2\}_3(\mu\text{-CP})_2][\text{OTf}]_2$	
43 $([\{\text{Fe}(\text{depe})_2\}_3(\mu\text{-CP})_{3-x}(\text{Cl})_x][\text{B}(\text{Ar}^{\text{F}})_4]_2)_n$	

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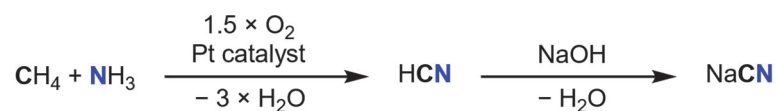
Introduction

Abstract. The chemistry of the cyaphide ion is introduced, starting with a cursory overview of its more common lighter congener, the cyanide ion, and its application in Prussian blue analogs. Next, the use of the isolobal analogy in describing fragments that are related to the cyanide and cyaphide ions is outlined. Finally, reported examples of the cyaphide ion in the chemical literature are surveyed, and their syntheses and characterization are discussed.

1.1 The cyanide ion

1.1.1 Synthesis, structure, and bonding

The cyanide ion ($\text{C}\equiv\text{N}^-$) is a diatomic anion containing a carbon atom and a nitrogen atom bonded *via* a triple bond. Compounds containing the cyanide ion are naturally occurring (e.g. in enzyme cofactors), and are produced by biosynthetic pathways in plants, fungi, and microorganisms. Industrially, cyanide is most commonly produced as hydrocyanic acid (HCN) from methane and ammonia *via* the Andrussow process, which can then be deprotonated to afford cyanide salts (Scheme 1.1).^[1,2]



Scheme 1.1. Synthesis of hydrocyanic acid *via* the Andrussow process, and subsequent deprotonation.

Despite the higher electronegativity of nitrogen than carbon, the dipole moment of the cyanide ion points towards the carbon atom. This is due to the polarized electron distribution of its highest occupied molecular orbital (HOMO), which is σ symmetric and can be approximated as a carbon-centered lone pair (Figure 1.1). The two degenerate lowest unoccupied molecular orbitals (LUMOs) are the orthogonal $\text{C}\equiv\text{N} \pi^*$ antibonding orbitals, which are significantly polarized toward the carbon atom.

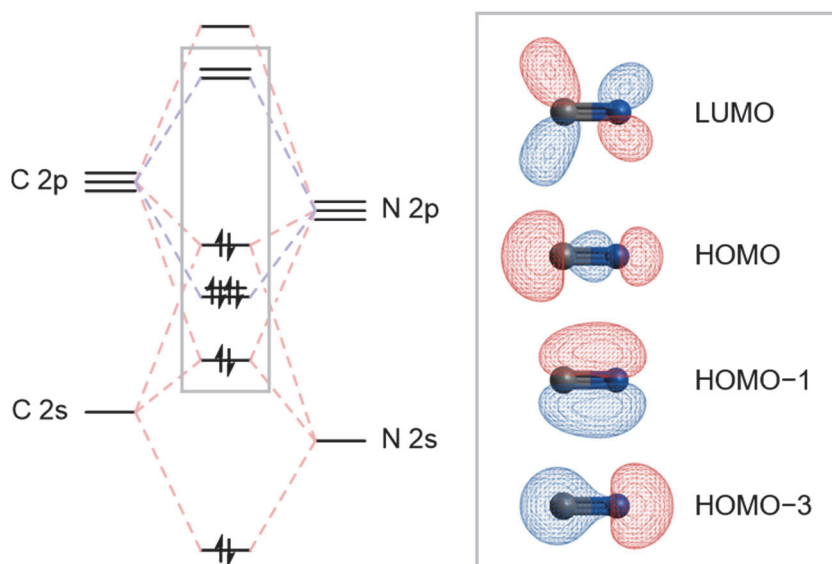


Figure 1.1. Qualitative molecular orbital (MO) diagram of the cyanide ion.

1.1.2 Properties and applications

In inorganic metal coordination complexes, the cyanide ion is an archetypal strong-field ligand (Figure 1.2). The κC -cyanido ligand is a strong σ donor due to its high-energy σ lone pair HOMO, and is also a moderate π acceptor due to its energetically accessible $\text{C}\equiv\text{N} \pi^*$ LUMOs. The cyanide ion can also bond to transition metal centers *via* its nitrogen atom, and commonly does this as a bridging ligand. In the κN coordination mode, the cyanido ligand is a much weaker σ donor and π acceptor due to the polarized electron distributions of its frontier molecular orbitals.



Figure 1.2. Molecular orbital (MO) diagram of the cyanide ion.

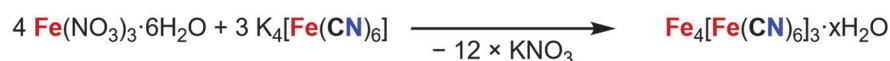
The ligand properties of the cyanide ion enable it to strongly bind metal centers, affording metal cyanide complexes; its ability to do this in biological settings gives rise to its well-known high toxicity. The strong affinity for metal cyanide complexation is also used extensively in the mining industry for the extractive metallurgy of silver and gold, as their cyanide salts can be dissolved and separated from unrefined ores.^[1]

One of the most important applications of the cyanide ion is in metal cyanide coordination compounds, exemplified by Prussian blue.

1.2 Prussian blue analogs

1.2.1 Prussian blue

Prussian blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$) is one of the oldest synthetic coordination compounds, and was likely first synthesized by Diesbach in 1706.^[3] It can be produced from alkali metal ferrocyanides and iron(III) salts (Scheme 1.2).



Scheme 1.2. Synthesis of Prussian blue.

The structure of Prussian blue contains iron atoms bridged by cyanide ions in an extended cubic 3D framework (Figure 1.3).^[4] The cyanido ligands adopt a linear bridging coordination mode, and are bonded $\eta^1, \kappa\text{C}$ to the low-spin iron(II) centers, and $\eta^1, \kappa\text{N}$ to the high-spin iron(III) centers. The simple formulation belies substantial structural complexity.^[5] Prussian blue is intrinsically defect-rich. In the solid-state, one quarter of the ferrocyanide $[\text{Fe}(\text{CN})_6]^{4-}$ subunits are absent, and the vacant iron(III) coordination sites are occupied by coordinated water molecules.^[4] The cubic framework structure makes Prussian blue a nanoporous material, with interstices capable of incorporating guest molecules, including alkali metal cations in ferrocyanide-rich formulations.

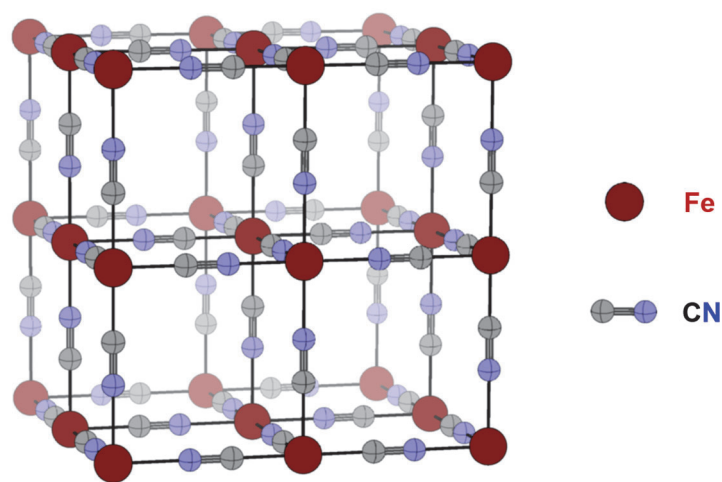


Figure 1.3. Idealized structure of Prussian blue (vacancies not shown).

Prussian blue is most commonly used as a pigment, with its characteristic blue color arising from intervalence charge transfer (IVCT) between its iron(II) and iron(III) centers, mediated by the bridging cyanido ligands. In addition, Prussian blue is also an essential medicine and is used as an antidote for metal poisoning, as its nanoporosity enables the sequestration of toxic metal cations.^[6]

1.2.2 Prussian blue analogs containing other metal ions

Transition metals other than iron can also be used to construct related metal cyanide frameworks. These Prussian blue analogs (PBAs) have emerged as an important family of materials with a broad range of applications (Figure 1.4). PBAs show promise as catalysts,^[7,8] ion conductors,^[9] battery cathodes,^[10,11] hydrogen storage materials,^[12] and stimuli-responsive magnetic materials.^[13–15]

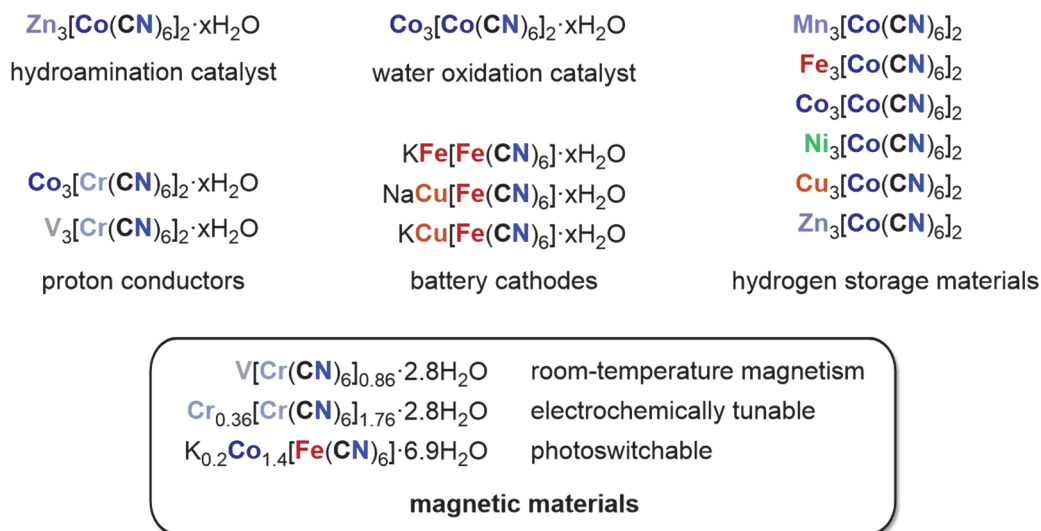


Figure 1.4. Applications of Prussian blue analogs.

The magnetic properties of PBAs have attracted considerable attention for the development of switchable nanomaterials. For these applications, the electronic and magnetic structures of PBAs are critical. These are dependent on not only the identity of the metal cations used, but also their stoichiometries, which has a large effect on the quantity and nature of defects and vacancies.^[5,15]

While it has been postulated that PBAs based on 4d or 5d metals are likely to have advantageous magnetic properties, such PBAs are uncommon and often involve the use of heavier cyanometallates (e.g. $\text{Ru}(\text{CN})_6^{4-}$ or $\text{Os}(\text{CN})_6^{3-}$) in conjunction with 3d metals.^[16–18] The incorporation of 4d or 5d metals in the nitrogen-bound sites is even less common due to the mismatch between the heavier transition metal centers and the κN -cyanido ligands, which are weak σ donors and poor π acceptors. Moreover, this leads to ineffective electronic communication between the metal ions in these materials and results in poor magnetic properties.^[19]

This represents a more general constraint to the design of PBAs; the reliance on bridging cyanide ligands fundamentally limits their performance. As such, the possibility for PBAs containing other bridging ligands is an attractive proposition.

1.3 The isolobal analogy

1.3.1 Fragments isolobal to the cyanide ion

The isolobal analogy is a powerful concept for relating the structures and reactivities of molecular fragments. This principle was introduced by Hoffmann, who described fragments as being isolobal if “the number, symmetry properties, approximate energy, and shape of the frontier orbitals and the number of electrons in them are similar.”^[20]

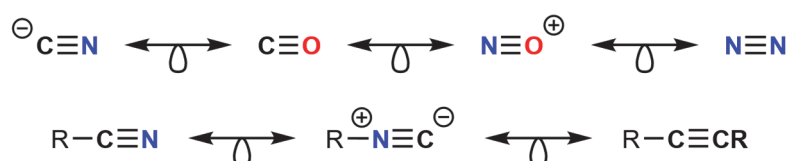


Figure 1.5. Fragments that are isolobal to the cyanide ion and its organic derivatives.

Many fragments can be likened to cyanide ion in this manner (Figure 1.5). Diatomic molecules that are isolobal to the cyanide ion include dinitrogen ($\text{N} \equiv \text{N}$), carbon monoxide ($\text{C} \equiv \text{O}$), and the nitrosonium cation ($\text{N} \equiv \text{O}^+$). It is worth noting that the nitrosonium cation is capable of substituting for the cyanide ion in nitroprussides ($[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$),^[21] which have been used to synthesize PBAs containing terminal nitrosyl ligands for water oxidation catalysis and photoswitchable superionic conduction.^[22,23] Organic cyanide derivatives exist as two isolobal isomers, nitriles ($\text{R}-\text{C} \equiv \text{N}$) and isocyanides ($\text{R}-\text{N} \equiv \text{C}$), which are also isolobal to alkynes.

The isolobal analogy is remarkably effective for organophosphorus chemistry, as phosphorus centers can be isolobal to both nitrogen- and carbon-containing organic fragments. Low-coordinate phosphorus compounds are particularly well-suited to comparisons with unsaturated molecules, including the cyanide ion and its organic derivatives.

The cyaphide ion ($\text{C} \equiv \text{P}^-$) is a phosphorus-containing heavy analog of the cyanide ion. Its organic derivatives, phosphalkynes ($\text{R}-\text{C} \equiv \text{P}$), are heavy analogs of nitriles (Figure 1.6).

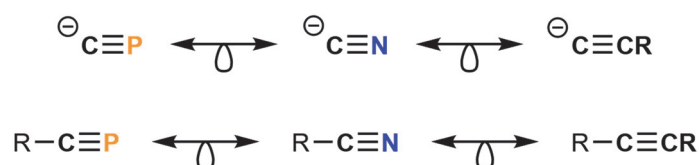


Figure 1.6. Fragments that are isolobal to the cyaphide ion and its organic derivatives.

1.3.2 The cyaphide ion

The cyaphide ion is isolobal and valence isoelectronic to the cyanide ion (Figure 1.7). As with the cyanide ion, the HOMO of the cyaphide ion is polarized toward the carbon atom and can be described as a carbon-centered lone pair. The degenerate LUMO and LUMO+1 of the cyaphide ion correspond to the $\text{C}\equiv\text{P } \pi^*$ orbitals, which are significantly less polarized than the $\text{C}\equiv\text{N } \pi^*$ orbitals in the cyanide ion. Its π bonds are the product of relatively inefficient 2p–3p orbital overlap, in violation of Pitzer’s classic “double bond rule”,^[24,25] and as a result the cyaphide ion has a relatively small π – π^* orbital energy gap. These properties should in principle allow for more effective metal–ligand π bonding than the cyanide ion in both the κC and κP coordination modes and enable efficient intermetallic electronic communication in multimetallic species, for example heavy analogs of Prussian blue.

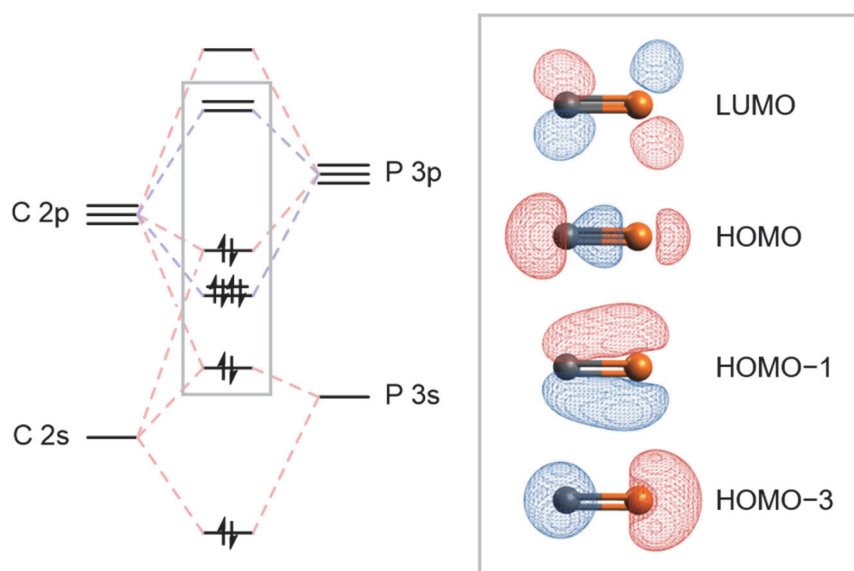


Figure 1.7. Qualitative MO diagram of the cyaphide ion.

In the cyanide ion, the electronegativity of carbon is less than that of nitrogen. In the cyaphide ion, this situation is reversed, with carbon being slightly more electronegative than phosphorus. This results in a situation where the negative charge of the cyaphide ion is even more carbon-centered than in the cyanide ion. Consequently, the dipole moment of the cyaphide ion (calcd. 2.95 D) is higher than that of the cyanide ion (calcd. 0.66 D).

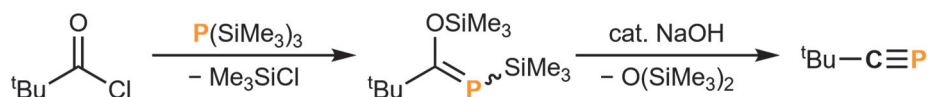
Coordination of the cyanide ion to an electropositive center results in a reversal of polarity towards the nitrogen atom and a greater overall dipole moment (e.g. for $\text{H}-\text{C}^{\delta+}\equiv\text{N}^{\delta-}$: calcd. 3.08 D; exp. 3.00 D). Conversely, coordination of the cyaphide ion to an electropositive center results only in a reduction in polarity, and a lower overall dipole moment (e.g. for $\text{H}-\text{C}^{\delta-}\equiv\text{P}^{\delta+}$: calcd. 0.39 D; exp. 0.39 D).

1.4 Cyaphide-containing molecules

1.4.1 Phosphaalkynes

The cyaphide ion is rare, and only a handful of examples have been reported in the chemical literature. Its organic derivatives, phosphaalkynes, are much more well-studied.^[26]

The simplest phosphaalkyne is phosphaethyne (HCP), the conjugate acid of the cyaphide ion. It was first synthesized in 1961 by Gier, who passed phosphine gas (PH₃) through an arc between two carbon electrodes, producing phosphaethyne in addition to other products such as acetylene and ethylene.^[27] This finding was corroborated in 1976 by Nixon and co-workers, who synthesized phosphaethyne *via* the flash vacuum pyrolysis of methyldichlorophosphine (CH₃PCl₂).^[28] This laid the foundations for the synthesis of other phosphaalkynes using similar β -elimination strategies, including the first kinetically stable phosphaalkyne, *tert*-butyl phosphaalkyne (tBuCP), in 1981 (Scheme 1.3).^[29]



Scheme 1.3. Synthesis of *tert*-butyl phosphaalkyne.

Like the cyaphide ion, phosphaalkynes also contain relatively weak carbon–phosphorus π bonds, which has important consequences for their reactivity. Phosphaalkynes are capable of forming complexes with transition metals, and in this regard behave much more similarly to alkynes than nitriles. The reactive C $\equiv$ P π manifold results in a preference for side-on η^2 coordination modes, first demonstrated by Nixon and co-workers for a platinum(0) complex (Figure 1.8).^[30]

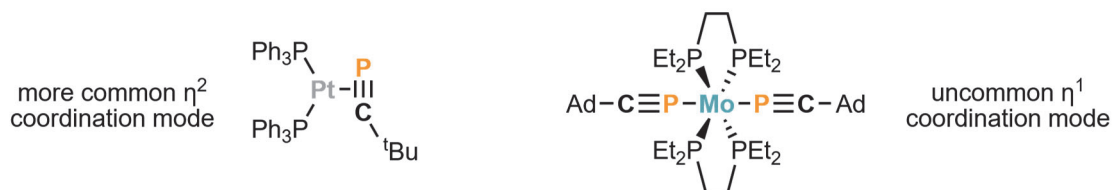


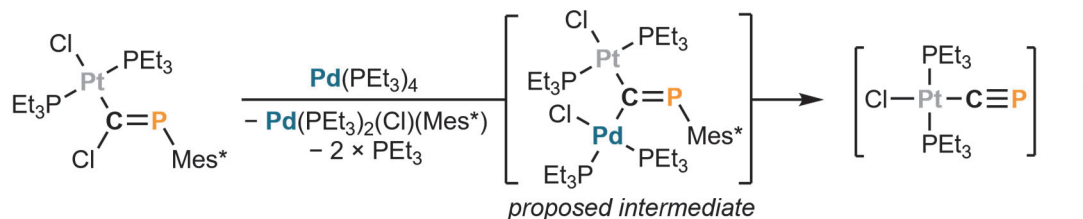
Figure 1.8. Coordination behavior of phosphaalkynes.

The coordination of phosphaalkynes to transition metal centers in an end-on $\eta^1:\kappa P$ mode is disfavored due to the low basicity of the phosphorus atom (*vide supra*), and only occurs in situations where η^2 binding is sterically precluded, first demonstrated by Nixon and co-workers for a molybdenum(0) complex (Figure 1.8). The only crystallographically characterized examples of $\eta^1:\kappa P$ -phosphaalkyne coordination are in molybdenum(0),^[31] iron(II),^[32] and ruthenium(II)^[33–36] bisphosphine complexes.

1.4.2 $\{\text{Pt}(\text{PEt}_3)_2(\text{Cl})\}(\mu\text{-CP})\{\text{Pt}(\text{PEt}_3)_2\}$

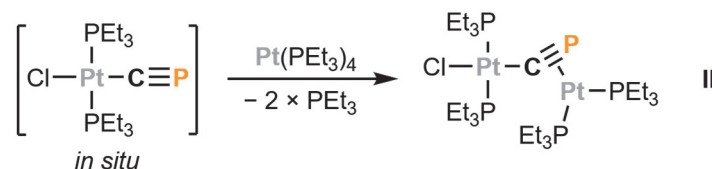
The cyaphide ion was first synthesized in 1992, generated in the coordination sphere of platinum(II) by Angelici and co-workers.^[37]

The reduction of the platinum(II) phosphavinyl complex $\text{Pt}(\text{PEt}_3)_2(\text{Cl})\{\text{C}(\text{Cl})=\text{PMes}^*\}$ ($\text{Mes}^* = 2,4,6\text{-tri-}t\text{-butylphenyl}$) with $\text{Pd}(\text{PEt}_3)_4$ results in the elimination of $\text{Pd}(\text{PEt}_3)_2(\text{Cl})(\text{Mes}^*)$ and the formation of a platinum(II) cyaphide complex, $\text{Pt}(\text{PEt}_3)_2(\text{Cl})(\text{CP})$ (**I**, Scheme 1.4).



Scheme 1.4. Synthesis of the kinetically unstable platinum(II) cyaphide complex **I**.

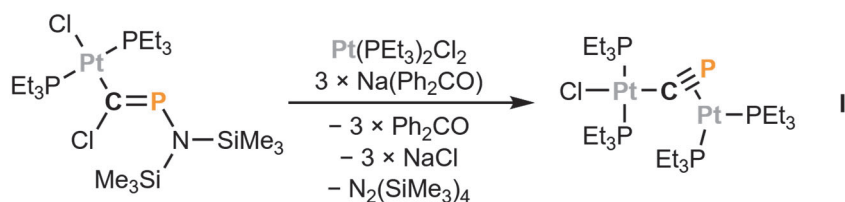
I was found to be unstable, and could only be transiently observed by $^{31}\text{P}\{^1\text{H}\}$ nuclear magnetic resonance (NMR) spectroscopy, which showed a triplet with ^{195}Pt satellites at 68.0 ppm ($^3J_{\text{P-P}} = 9.2$ Hz, $^2J_{\text{P-Pt}} = 303$ Hz) corresponding to the cyaphide phosphorus atom. However, once generated, **I** could be reacted *in situ* with $\text{Pt}(\text{PEt}_3)_4$ to afford a stable bimetallic complex containing a bridging $\eta^1:\eta^2$ -cyaphido ligand, $\{\text{Pt}(\text{PEt}_3)_2\text{Cl}\}(\mu\text{-CP})\{\text{Pt}(\text{PEt}_3)_2\}$ (**II**, Scheme 1.5).



Scheme 1.5. Synthesis of the stable platinum(II)/platinum(0) bridging cyaphide complex **II**.

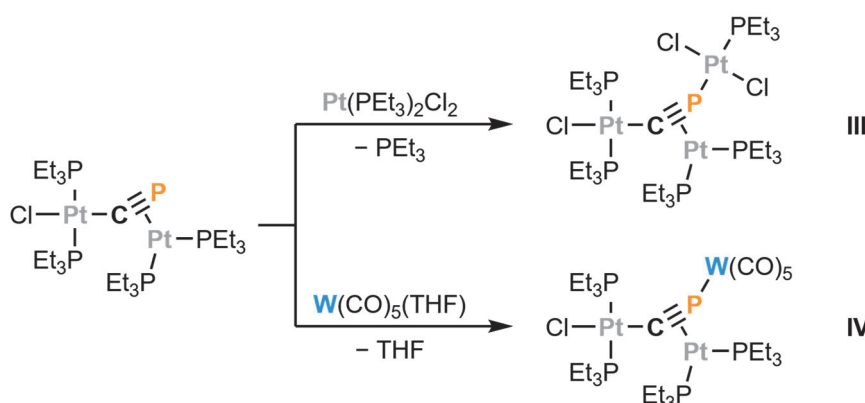
The bridging cyaphido ligand in **II** appears in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum as a multiplet with two sets of ^{195}Pt satellites at 107.0 ppm ($^2J_{\text{P-P}} = 10.7$ Hz; $^3J_{\text{P-P}} = 10.7, 13.7$ Hz; $^1J_{\text{P-Pt}} = 255$ Hz; $^2J_{\text{P-Pt}} = 58$ Hz). The solid-state structure of **II** was determined by single crystal X-ray diffraction, confirming the $\eta^1:\eta^2$ bridging coordination mode of the cyaphide ion, and showing a C–P bond length of 1.666(6) Å.

In 1999, Angelici and co-workers reported an improved synthesis for **II**, starting instead from the amide substituted phosphavinyl complex $\text{Pt}(\text{PEt}_3)_2(\text{Cl})\{\text{C}(\text{Cl})=\text{PN}(\text{SiMe}_3)_2\}$.^[38] This reacts with the platinum(II) complex $\text{Pt}(\text{PEt}_3)_2\text{Cl}_2$ in the presence of three equivalents of sodium benzophenone ketyl (NaPh_2CO) to give **II** (Scheme 1.6).



Scheme 1.6. Synthesis of the stable platinum(II)/platinum(0) bridging cyaphide complex **II**.

The functionalization of **II** was also investigated. Reactions with $\text{Pt}(\text{PEt}_3)_2\text{Cl}_2$ and $\text{W}(\text{CO})_5(\text{THF})$ (THF = tetrahydrofuran) yielded the trimetallic cyaphide complexes $\{\text{Pt}(\text{PEt}_3)_2\text{Cl}\}(\mu_3\text{-CP})\{\text{Pt}(\text{PEt}_3)_2\}\{\text{Pt}(\text{PEt}_3)_2\text{Cl}_2\}$ (**III**) and $\{\text{Pt}(\text{PEt}_3)_2\text{Cl}\}(\mu_3\text{-CP})\{\text{Pt}(\text{PEt}_3)_2\}\{\text{W}(\text{CO})_5\}$ (**IV**), respectively (Scheme 1.7).



Scheme 1.7. Synthesis of the trimetallic bridging cyaphide complexes **III** and **IV**.

III has a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum with a complex multiplet at 111.2 ppm ($^2J_{\text{P-P}} = 148.0, 42.5$ Hz; $^3J_{\text{P-P}} = 21.4$ Hz) corresponding to the cyaphide phosphorus atom, though no ^{195}Pt satellites were observed. The corresponding signal in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **IV** appears as a multiplet at 41.4 ppm ($^2J_{\text{P-P}} = 152.9, 38.7$ Hz; $^3J_{\text{P-P}} = 18.9$ Hz; $^2J_{\text{P-Pt}} = 507$ Hz), though no ^{183}W satellites were observed. The structure of **IV** was confirmed by X-ray crystallography, revealing a C–P bond length of 1.663(9) Å.

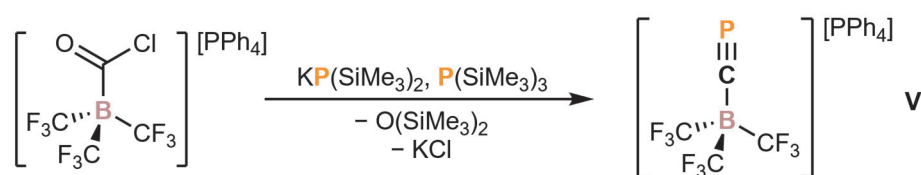
The reaction of **II** with organic electrophiles (e.g. excess MeI) was also investigated, and was proposed to result in the formation of bridging isocyaphide complexes (e.g. $\{\text{Pt}_2(\text{PEt}_3)\text{Cl}\}(\mu\text{-CPMe})\{\text{Pt}(\text{PEt}_3)_2\text{I}\}$), though this remained unconfirmed by single crystal X-ray crystallography.

These results were a major breakthrough, demonstrating that the cyaphide ion is synthetically accessible in the coordination sphere of a transition metal. For over two decades, the bimetallic complex **II** and trimetallic complexes **III** and **IV** remained the only examples of bridging cyaphide complexes (see Chapter 5).

1.4.3 [PPh₄][B(CF₃)₃(CP)]

In 2004, Willner and co-workers reported a cyaphidoborate salt, [PPh₄][B(CF₃)₃(CP)] (**V**), in which the cyaphide ion is stabilized by coordination to a highly electrophilic borane.^[39]

V was synthesized *via* a very similar route to that commonly used for the synthesis of phosphalkynes. The chlorocarbonyl borate [PPh₄][B(CF₃)₃(COCl)] was treated with KP(SiMe₃)₂ in the presence of P(SiMe₃)₃, resulting in the elimination of trimethylsilyl ether (O(SiMe₃)₂) and potassium chloride (KCl), forming **V** (Scheme 1.8). It is worth noting that the cyarside (C≡As[−]) analog of **V** is accessible by the same method using the analogous arsenic reagents KAs(SiMe₃)₂ and As(SiMe₃)₃.



Scheme 1.8. Synthesis of the cyaphidoborate salt **V**.

V exhibits complex multiplets corresponding to the cyaphide phosphorus and carbon atoms in its ³¹P and ¹³C NMR spectra at 39.6 ppm (²J_{31P–11B} = 3.0 Hz, ⁴J_{P–F} = 1.3 Hz) and 202.3 ppm (¹J_{C–P} = 27.6 Hz, ¹J_{13C–11B} = 59.5 Hz, ³J_{C–F} = 2.9 Hz), respectively. Raman spectroscopy shows a band at 1468 cm^{−1}, assigned to the C≡P bond stretching mode. Single crystal X-ray diffraction corroborates the structure of the cyaphidoborate anion, though significant crystallographic disorder prevents the reliable discussion of its bond metrics.

The negative charge of the cyaphidoborate anion in **V** affords it a surprising degree of stability, allowing it to be handled in wet acetonitrile solutions. Slow hydrolysis over several days leads to the formation of the phosphinic acid derivative [B(CF₃)₃{CH₂P(O)(OH)H}][−].

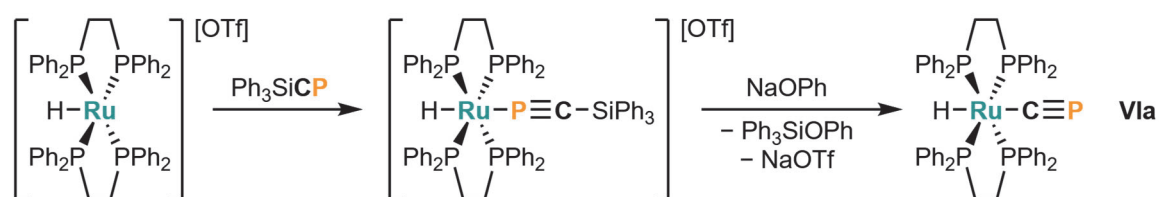
V once again showed the viability of accessing cyaphide-containing molecules by using a conventional β-elimination strategy to construct the C≡P triple bond.

1.4.4 Ru(dppe)₂(H)(CP)

An important milestone in the synthesis of metal cyaphide complexes was the synthesis of Ru(dppe)₂(H)(CP) (**VIa**; dppe = 1,2-bis(diphenylphosphino)ethane) by Grützmacher and co-workers

in 2006, the first example of a terminal transition metal cyaphide complex, and the first synthesized using a phosphaaalkyne precursor.^[33]

The reaction of the octahedral ruthenium(II) bisphosphine complex $[\text{Ru}(\text{dppe})_2(\text{H})][\text{OTf}]$ with triphenylsilyl phosphaaalkyne affords an η^1 -phosphaaalkyne complex $[\text{Ru}(\text{dppe})_2(\text{H})(\text{PCSiPh}_3)][\text{OTf}]$. Treatment of this complex with conventional desilylating reagents such as fluorides or alkoxides results in uncontrolled reactivity due to irreversible deleterious side reactions with the electrophilic phosphaaalkyne ligand. However when sodium phenoxide (NaOPh) is used, the desilylation is successful and results in the ruthenium(II) cyaphide complex **VIa** (Scheme 1.9).



Scheme 1.9. Synthesis of the ruthenium(II) cyaphide complex **VIa**.

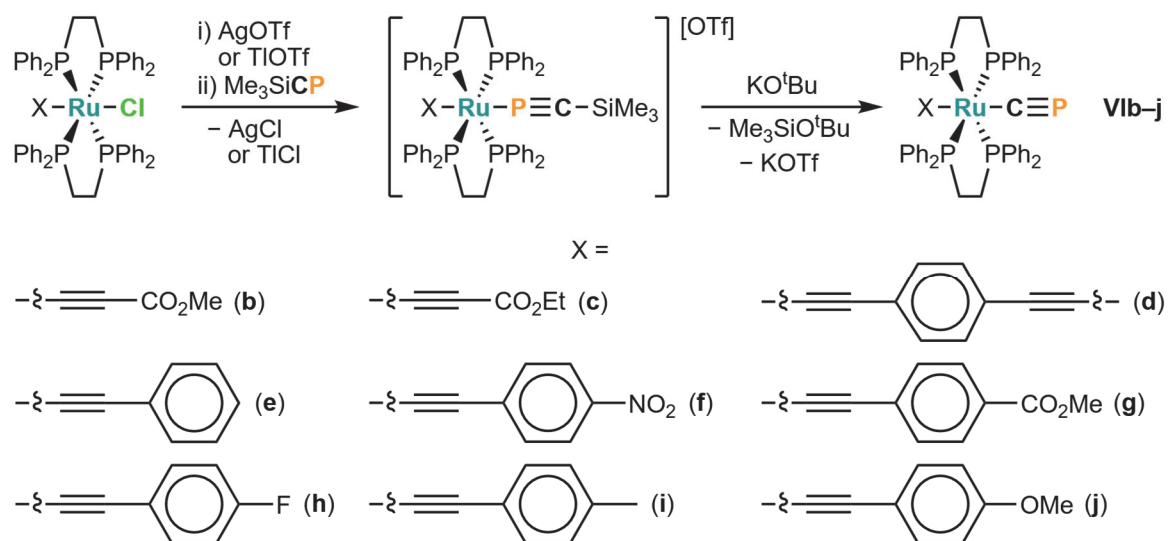
VIa has a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum containing a broad peak at 165.0 ppm corresponding to the cyaphide phosphorus atom, and a $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum containing a multiplet at 287.1 ppm ($^1J_{\text{C-P}} = 90$ Hz) corresponding to the cyaphide carbon atom. Raman spectroscopy shows a $\text{C}\equiv\text{P}$ vibrational stretching mode at 1229 cm^{-1} . The structure of **VIa** was confirmed by single crystal X-ray diffraction, and the C–P bond length was determined to be $1.573(2)\text{ \AA}$.

The formation of **VIa** was later investigated computationally by Ehlers, Grützmacher, and co-workers.^[40] They found that nucleophilic attack of phenoxide at the phosphaaalkyne phosphorus atom can occur (consistent with ^{31}P NMR spectroscopy of the reaction mixtures), though is reversible. Nucleophilic attack at the silicon center leads to irreversible desilylation and formation of **VIa** via a side-on η^2 -cyaphido intermediate. Notably, the isocyaphide structure $\text{Ru}(\text{dppe})_2(\text{H})(\text{PC})$ was found to be a transition state and not a local minimum.

These results established, in principle, a more general route to metal cyaphide complexes via the desilylation of silyl phosphaaalkynes. However, the apparent requirement for the uncommon end-on η^1 -phosphaaalkyne coordination mode led to the rather narrow applicability of this route. Nevertheless, this enabled the synthesis of numerous cyaphide complexes based on the $\text{Ru}(\text{dppe})_2$ scaffold by Crossley and co-workers.

1.4.5 Ru(dppe)₂(X)(CP)

Between 2014 and 2019, Crossley and co-workers reported a series of analogous ruthenium(II) cyaphide complexes with *trans*-acetylido ligands, Ru(dppe)₂(X)(CP) [X = C₂(CO₂Me) (**VIb**), C₂(CO₂Et) (**VIc**), μ -C₂(C₆H₄)C₂ (**VIId**), C₂(C₆H₅) (**VIe**), C₂(C₆H₄NO₂) (**VIIf**), C₂(C₆H₄CO₂Me) (**VIg**), C₂(C₆H₄F) (**VIh**), C₂(C₆H₄Me) (**VIi**), C₂(C₆H₄OMe) (**VIj**)].^[34–36] These were synthesized by the desilylation of their respective η^1 trimethylsilyl phosphaaalkyne (Me₃SiCP) complexes using potassium *tert*-butoxide (Scheme 1.10).



Scheme 1.10. Synthesis of the ruthenium(II) cyaphide complexes **VIb–j**.

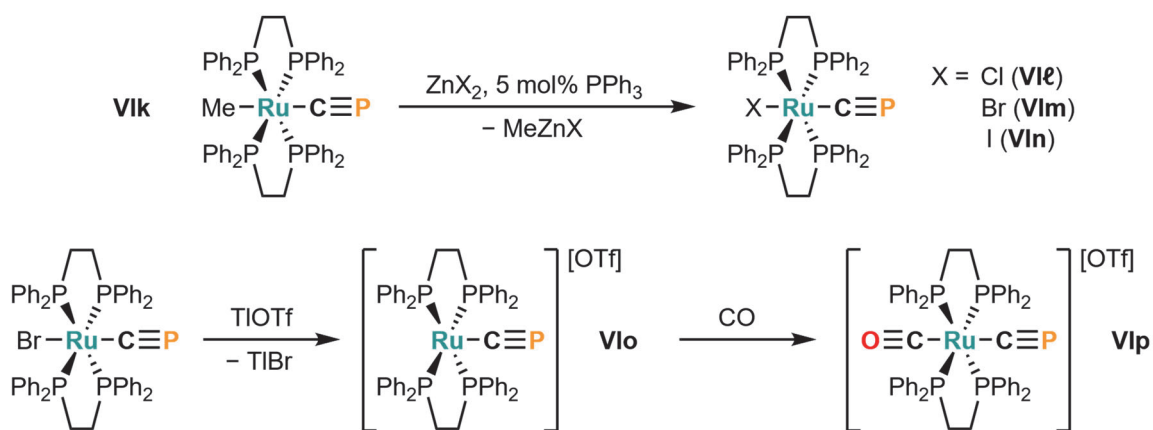
Single crystal X-ray crystallography allowed the solid-state structures of **VIb**, **VIg**, **VIh**, and **VIj** to be determined, and also revealed structures and bond metrics in line with expectation.

Complexes **VIb–j** were characterized by NMR and infrared (IR) spectroscopy, showing similar spectral characteristics to **VIa**, though with some variation due to the nature of the *trans* substituents. Cyclic voltammetry (CV) was also used to study the phenylacetylido complexes **VIe–j** and show a shift of the Ru^{II}/Ru^{III} oxidation events to more anodic potentials relative to the corresponding chloride complexes, suggesting electron-withdrawing character for the cyaphido ligand.

From these data, Hammett correlations could be drawn for the cyaphide ³¹P{¹H} and ¹³C{¹H} NMR chemical shifts, as well as the Ru^{II}/Ru^{III} oxidation potentials for **VIe–j**. These studies show that the cyaphido ligand is strongly affected by remote substituents, indicating its involvement in metal-mediated π conjugation with the *trans*-acetylides.

In 2019, Crossley and co-workers further expanded the range of accessible $\text{Ru}(\text{dppe})_2(\text{X})(\text{CP})$ complexes by demonstrating the possibility for their synthetic modification.^[41]

The ruthenium(II) *trans*-methyl cyaphide complex $\text{Ru}(\text{dppe})_2(\text{Me})(\text{CP})$ (**Vlk**) was accessible in the same manner as **Vlb–j**. Reaction of this complex with zinc(II) halides (ZnX_2) in the presence of substoichiometric triphenylphosphine (PPh_3) results in unexpected methyl/halide exchange, giving the *trans*-halide cyaphide complexes $\text{Ru}(\text{dppe})_2(\text{X})(\text{CP})$ [$\text{X} = \text{Cl}$ (**Vle**), Br (**Vlm**), I (**Vln**)]. For the bromide complex **Vlm**, halide abstraction using thallium(I) triflate (TlOTf) affords a cationic five-coordinate cyaphide complex $[\text{Ru}(\text{dppe})_2(\text{CP})][\text{OTf}]$ (**Vlo**). **Vlo** has a vacant coordination site capable of ligand association, demonstrated by the synthesis of the carbonyl complex $[\text{Ru}(\text{dppe})_2(\text{CO})(\text{CP})][\text{OTf}]$ (**Vlp**; Scheme 1.11).



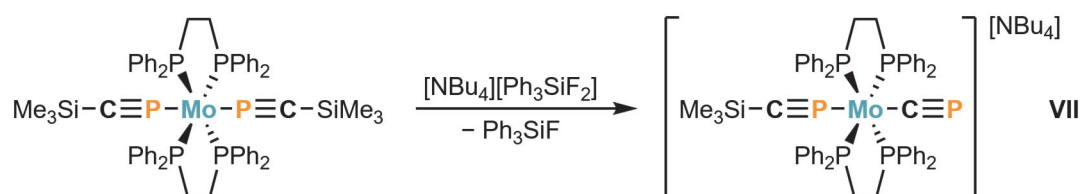
Scheme 1.11. Synthetic modification of the ruthenium(II) cyaphide complex **Vlk**.

These transformations showcase the potential for the synthetic modification of cyaphide complexes. **Vlk–p** were characterized by NMR and IR spectroscopy. Single crystal X-ray crystallography confirmed the structures of **Vlk**, **Vlm**, **Vlo**, and **Vlp**, though significant disorder prevents full anisotropic refinement for **Vlp**. For **Vlp**, the carbonyl IR stretching frequency of 1980 cm^{-1} once again suggests electron-withdrawing character for the cyaphido ligand.

1.4.6 $[\text{NBu}_4][\text{Mo}(\text{dppe})_2(\text{PCSiMe}_3)(\text{CP})]$

There is only one example of silyl phosphalkyne desilylation to afford a cyaphide complex on a transition metal other than ruthenium(II).

In 2012, Russell and co-workers investigated the coordination chemistry of trimethylsilyl phosphalkyne, and synthesized the molybdenum(0) complex $\text{Mo}(\text{dppe})_2(\text{PCSiMe}_3)_2$, bearing two η^1 -phosphalkyne ligands. Treatment of this complex with one equivalent of the fluoride source $[\text{NBu}_4][\text{Ph}_3\text{SiF}_2]$ resulted in the formation of fluoro(triphenyl)silane (Ph_3SiF), as well as a product with a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum containing a doublet of doublets at 65.5 ppm for the dppe ligands, and two other multiplets at 197.8 and 183.0 ppm. This product was assigned as the anionic molybdenum(0) cyaphide complex $[\text{NBu}_4][\text{Mo}(\text{dppe})_2(\text{PCSiMe}_3)(\text{CP})]$ (**VII**; Scheme 1.12).^[42]



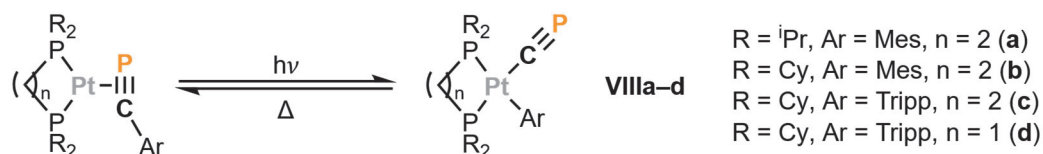
Scheme 1.12. Synthesis of the molybdenum(0) cyaphide complex **VII**.

Unfortunately, the isolation and further characterization of **VII** was not forthcoming.

1.4.7 Pt(bisphosphine)(Ar)(CP)

In 2021, Jones, Müller, and co-workers were able to generate platinum(II) cyaphide complexes *via* the photolysis of platinum(0) precursors containing aryl phosphalkynes in the more common η^2 coordination mode.^[43]

Under ultraviolet (UV) irradiation, the platinum(0) phosphalkyne complexes $\text{Pt}(\text{dippe})(\text{MesCP})$ (dippe = 1,2-bis(diisopropylphosphino)ethane; Mes = 2,4,6-trimethylphenyl), $\text{Pt}(\text{dcype})(\text{MesCP})$ (dcype = 1,2-bis(dicyclohexylphosphino)ethane), $\text{Pt}(\text{dcype})(\text{TrippCP})$ (Tripp = 2,4,6-triisopropylphenyl), and $\text{Pt}(\text{dcypm})(\text{TrippCP})$ (dcypm = 1,2-bis(dicyclohexylphosphino)methane) undergo photolytic $\text{C}(\text{sp}^2)\text{--C}(\text{sp})$ bond cleavage reactions to afford the platinum(II) cyaphide complexes $\text{Pt}(\text{dippe})(\text{Mes})(\text{CP})$ (**VIIIa**), $\text{Pt}(\text{dcype})(\text{Mes})(\text{CP})$ (**VIIIb**), $\text{Pt}(\text{dcype})(\text{Tripp})(\text{CP})$ (**VIIIc**), and $\text{Pt}(\text{dcypm})(\text{Tripp})(\text{CP})$ (**VIIId**; Scheme 1.13).



Scheme 1.13. Synthesis of the platinum(II) cyaphide complexes **VIIIa-d**.

These reactions are thermally reversible. For **VIIIa** and **VIIIb**, maximum conversions of 70% and 80%, respectively, are achievable, and they rapidly undergo reductive elimination reactions to the phosphalkyne precursors above room temperature. For **VIIIc** and **VIId**, full conversions are achieved, and reversion to the phosphalkyne precursors occurs slowly at room temperature and 60 °C, respectively. Photolytic bond cleavage was not observed for the nickel(0) phosphalkyne complexes Ni(dippe)(MesCP) and Ni(dippe)(Mes*CP), nor the platinum(0) complex Pt(dippe)(Mes*CP).

VIIIa–d were characterized by NMR spectroscopy following *in situ* photolysis, and exhibit multiplets in their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra between 96.6 and 110.5 ppm for the cyaphide phosphorus atoms. IR spectroscopy showed that the $\text{C}\equiv\text{P}$ vibrational stretching frequencies in **VIIIa–d** are between 1242 and 1262 cm^{-1} . The structures of **VIIIb** and **VIId** were confirmed by single crystal X-ray crystallography, and have C–P bond lengths of 1.563(2) and 1.555(1) Å, respectively.

The 1,3-dipolar cycloaddition reaction between **VIIIb** and an aryl azide DippN₃ (Dipp = 2,6-diisopropylphenyl) was also reported, and leads to the formation of a platinum(II) triazaphosphole complex, Pt(dcype)(Mes)(CPN₃Dipp) (see Chapter 6).

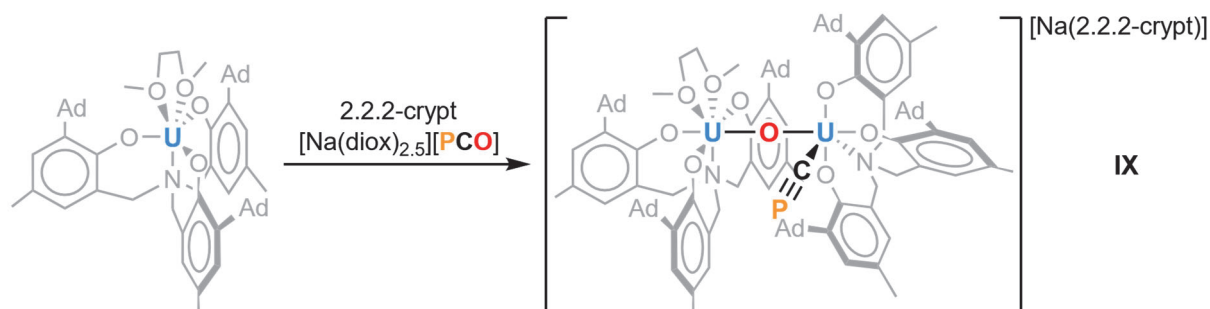
These results offered an alternative route to the synthesis of cyaphide complexes, and also show that thermal reductive elimination of the cyaphido ligand with *cis*-coordinated $\text{C}(\text{sp}^2)$ centers is possible. This mode of reactivity has significant consequences for the stability of group 10 metal cyaphide complexes (see Chapter 7).

1.4.8 [Na(2.2.2-crypt)][{U(N^{(Ad,Me)ArO})₃(DME)}(μ-O){U(N^{(Ad,Me)ArO})₃(CP)}]

In 2016, Meyer and co-workers demonstrated another possible method for the generation of the cyaphide ion: the reductive deoxygenation of the 2-phosphaethynolate (PCO^-) ion.^[44]

The reaction between the highly reducing uranium(III) complex $\text{U}(\text{N}^{(\text{Ad,Me})\text{ArO}})_3(\text{DME})$ ($\text{N}^{(\text{Ad,Me})\text{ArO}}_3^{3-}$ = tris(2-hydroxy-3-(1-adamantyl)-5-methylbenzyl)amine-triide; DME = 1,2-dimethoxyethane) and an excess of sodium 2-phosphaethynolate ($[\text{Na}(\text{diox})_{2.5}][\text{PCO}]$; diox = 1,4-dioxane) in the presence of 2.2.2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane) results in the formation of an asymmetric bimetallic uranium(IV) cyaphide complex, $[\text{Na}(2.2.2\text{-crypt})][\{\text{U}(\text{N}^{(\text{Ad,Me})\text{ArO}})_3(\text{DME})\}(\mu\text{-O})\{\text{U}(\text{N}^{(\text{Ad,Me})\text{ArO}})_3(\text{CP})\}]$ (**IX**; Scheme 1.14).

It is worth noting that the same uranium(III) reductant can also be used to deoxygenate the 2-arsaethynolate ion (AsCO^-), affording an analogous uranium(IV) cyarside complex.^[45]



Scheme 1.14. Synthesis of the bimetallic uranium(IV) cyaphide complex **IX**.

Single crystal X-ray crystallography revealed the molecular structure of **IX**, which contains a terminal cyaphido ligand with a C–P bond length of 1.523(8) Å. While **IX** is paramagnetic, its ^{31}P NMR spectrum contains a broad resonance at 265.8 ppm corresponding to the cyaphide phosphorus atom. Its magnetic behavior was also investigated by superconducting quantum interference device (SQUID) magnetometry, and found to be similar to other bimetallic uranium(IV) complexes.

1.4.9 Summary of known synthesis methods

Aside from the work presented in this thesis, **I–IX** are the only reported examples of the cyaphide ion in the chemical literature. This stands in stark contrast to the ubiquity of the cyanide ion, and stems from the lack of a general synthetic protocol for the preparation of cyaphide-containing molecules.

Whereas metal cyanides are readily accessible from ionic cyanide salts (e.g. NaCN), no such species exist for the cyaphide ion. Instead, the cyaphide moieties in **I–IX** were either constructed in the coordination sphere of the target complex (**I–V**), installed by way of elusive η^1 -phosphaalkyne intermediates (**VI** and **VII**), generated by reversible photolysis reactions (**VIII**), or in the coordination sphere of a strong reductant (**IX**).

1.5 Aims

For decades, the dearth of accessible cyaphide complexes has severely hampered the systematic study of the cyaphide ion. The limited understanding of its chemistry has thus far prevented the cyaphide ion from being incorporated in materials and investigated for practical applications, including as a bridging ligand in heavy analogs of Prussian blue.

This project aimed to develop an improved understanding of the synthesis, properties, reactivity, and stability of the cyaphide ion and its metal complexes, with a particular focus on multimetallic systems.

To this end, the first aim was to develop a general synthesis method for cyaphide-containing molecules. The synthesis of ionic magnesium(II) cyaphide complexes to serve as organometallic cyaphide transfer reagents is the subject of Chapter 2. These reagents were applied to the synthesis of novel main-group and transition metal cyaphide complexes, and is detailed in Chapter 3.

The next aim was to use the newly accessible cyaphide complexes to study the properties of the cyaphide ion. A systematic study of the coordination chemistry of the κ C-cyaphido ligand is detailed in Chapter 4.

A broad aim of this project was to investigate the reactivity of metal cyaphide complexes. The reactivity of a gold(I) cyaphide complex toward electron-rich metals is the subject of Chapter 5. The reactivity of a variety of cyaphide complexes with organic azides is the subject of Chapter 6.

Demystifying the stability of metal cyaphide complexes was a major aim throughout this project. The study of metal-mediated cyaphide oligomerization reactions was highly informative to this end, and is discussed in Chapter 7.

Finally, the broader aim of using the cyaphide ion as a bridging ligand in heavy analogs of Prussian blue was probed for molecular systems, which are presented in Chapter 8.

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Ionic Cyaphide Transfer Reagents

Abstract. Magnesium(II) cyaphide complexes are accessed by the reductive deoxygenation of siloxyphosphaalkynes using magnesium(I) reducing agents. The synthesis of these ionic cyaphide complexes is detailed, as is their characterization by multinuclear NMR spectroscopy, infrared and Raman spectroscopy, and single crystal X-ray crystallography. Theoretical insights into the properties of these complexes and the mechanism of their formation are also discussed.

2.1 O-functionalization of the 2-phosphaethynolate ion

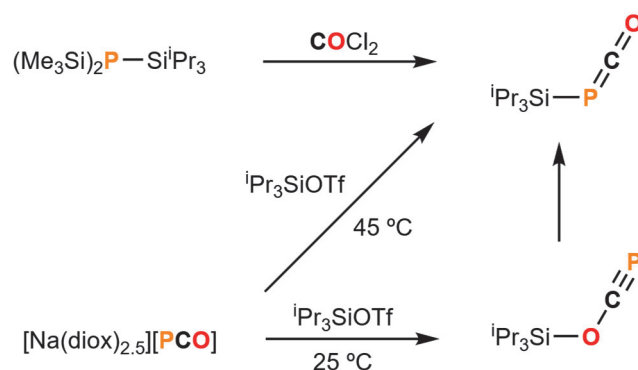
2.1.1 Ambident reactivity of the 2-phosphaethynolate ion

The cyaphide ion can be generated by the reductive deoxygenation of the 2-phosphaethynolate ion, as demonstrated by Meyer (see Section 1.4.8),^[1] although this necessitated the use of a strong uranium(III) reductant. O-functionalization of the 2-phosphaethynolate ion to a neutral phosphaehtynyl compound may enable more facile C–O bond cleavage by other reducing agents.

Like its more common congener the cyanate ion (NCO^-), the 2-phosphaethynolate ion is an ambident nucleophile; it can undergo substitution reactions with electrophiles (R-X) to form phosphaehtynyl (R-OCP) and phosphaketynyl (R-PCO) linkage isomers. While examples of both isomers are known, the number of *P*-functionalized phosphaketenes far outnumbers *O*-functionalized species.^[2] This is due to the intrinsic thermodynamic stability of the phosphaketynyl isomer for most systems.^[3] The only exceptions to this are in highly ionic complexes of hard, oxophilic metal centers (e.g. s-block,^[4–6] early d-block,^[7–9] and f-block metals^[1,10,11]), in which κO -phosphaethynolato coordination is favored. For the p-block elements, neutral phosphaehtynyl compounds are only known as kinetically metastable isomers when bonded to silyl or boryl functionalities.

2.1.2 Siloxyphosphaalkynes ([Si]–OCP)

In 1999, Heckmann and co-workers proposed that the siloxyphosphaalkyne ${}^i\text{Pr}_3\text{SiOCP}$ was generated in the reaction of ${}^i\text{Pr}_3\text{SiP}(\text{SiMe}_3)_2$ with phosgene, based on ${}^{31}\text{P}$, ${}^{13}\text{C}$, ${}^{17}\text{O}$, ${}^{29}\text{Si}$ and ${}^1\text{H}$ NMR spectroscopy.^[12] This claim was reexamined in 2014 by Heift, Benkő, and Grützmacher.^[13] They found that the reaction of $[\text{Na}(\text{diox})_{2.5}][\text{PCO}]$ with ${}^i\text{Pr}_3\text{SiOTf}$ in THF at 25 °C resulted in the formation of a different kinetic product, which over time (or at 45 °C) converted to a thermodynamic product with similar spectroscopic signatures to those reported by Heckmann and co-workers. By means of NMR and IR spectroscopy, as well as theoretical investigations, the thermodynamic product was identified as being the silyl phosphaketene ${}^i\text{Pr}_3\text{SiPCO}$, whereas the siloxyphosphaalkyne ${}^i\text{Pr}_3\text{SiOCP}$ was reassigned as being the identity of the intermediate kinetic product (Scheme 2.1).

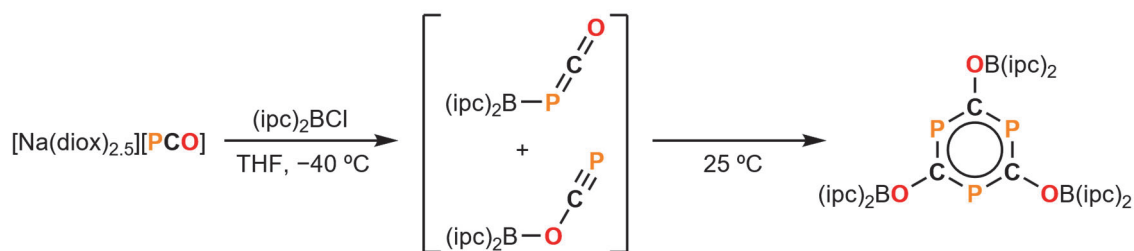


Scheme 2.1. Generation of the silyl phosphaketene ${}^i\text{Pr}_3\text{SiPCO}$ and the siloxyphosphaalkyne ${}^i\text{Pr}_3\text{SiOCP}$.

${}^i\text{Pr}_3\text{SiOCP}$ remains the only known example of a siloxyphosphaalkyne. Attempts to target phosphaehtynyl compounds with arylsilyl or heavier tetryl substituents resulted only in the observation of phosphaketenes.^[13]

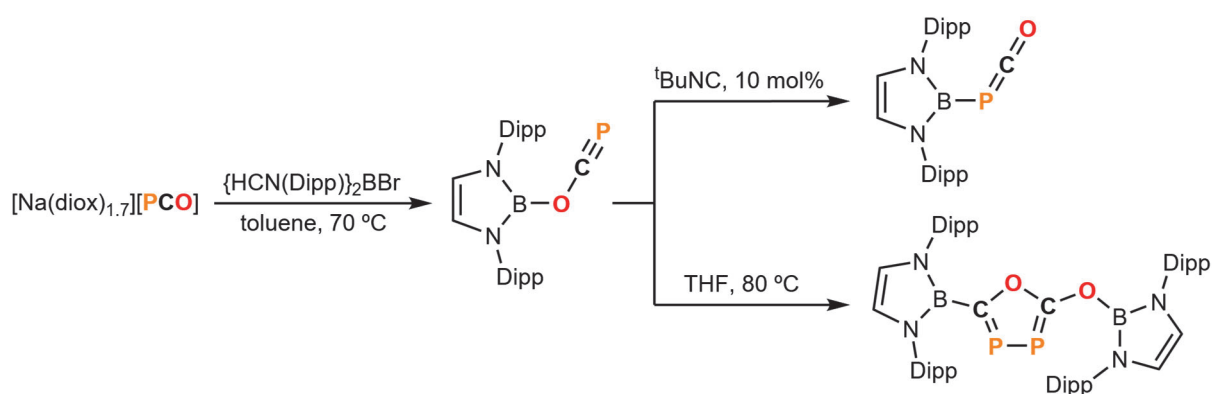
2.1.3 Boryloxyphosphaalkynes ([B]–OCP)

In 2016, Suter, Benkő, Grützmacher, and co-workers found that $[\text{Na}(\text{diox})_{2.5}][\text{PCO}]$ reacts with the dialkylchloroborane $(\text{ipc})_2\text{BCl}$ (ipc = isopinocampheyl) in THF at –40 °C to form a mixture of isomers, including both the boryl phosphaketene $(\text{ipc})_2\text{BPCO}$ and the boryloxyphosphaalkyne $(\text{ipc})_2\text{BOCP}$.^[14] These compounds are not thermally stable in THF solution; upon warming to room temperature, the mixture converts to one major product, the trimeric [2+2+2] cycloaddition product $\{(\text{ipc})_2\text{B}\}_3(\text{C}_3\text{P}_3)$, a phosphorus-containing analog of cyanuric acid (Scheme 2.2).



Scheme 2.2. Synthesis of $\{(\text{ipc})_2\text{BO}\}_3(\text{C}_3\text{P}_3)$ by *in situ* generation of the boryloxyphosphaalkyne $(\text{ipc})_2\text{BOCP}$.

Goicoechea and co-workers were able to prevent an analogous oligomerization from occurring by employing a more sterically bulky borane. Reaction of $[\text{Na}(\text{diox})_{1.7}][\text{PCO}]$ with $\{\text{HCN}(\text{Dipp})\}_2\text{BBr}$ in toluene at 70°C resulted in the formation of the boryloxyphosphaalkyne $\{\text{HCN}(\text{Dipp})\}_2\text{BOCP}$ (Scheme 2.3).^[15]



Scheme 2.3. Synthesis of the isolable boryloxyphosphaalkyne $\{\text{HCN}(\text{Dipp})\}_2\text{BOCP}$ and its reactivity toward Lewis bases.

$\{\text{HCN}(\text{Dipp})\}_2\text{BOCP}$ was found to be thermally stable toward isomerization, though only in the absence of donor solvents such as THF, or indeed excess dioxane from $[\text{Na}(\text{diox})_x][\text{PCO}]$ during its synthesis.^[16] In THF solution, $\{\text{HCN}(\text{Dipp})\}_2\text{BOCP}$ dimerizes to form a 1,3,4-oxadiphosphole, suggesting a base-assisted isomerization or boryl-migration pathway. Catalytic amounts of a stronger donor, *tert*-butyl isocyanide, result in isomerization to the boryl phosphaketene $\{\text{HCN}(\text{Dipp})\}_2\text{BPCO}$.^[17]

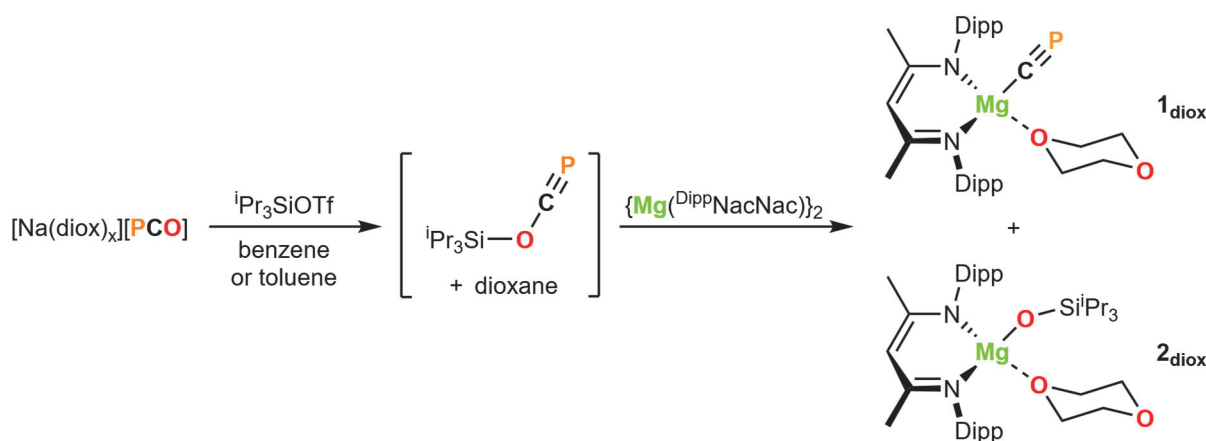
$^i\text{Pr}_3\text{SiOCP}$ and $\{\text{HCN}(\text{Dipp})\}_2\text{BOCP}$ show that *O*-functionalization of the 2-phosphaethynolate ion to generate neutral siloxy- and boryloxyphosphaalkynes is possible, and represent good targets for reductive C–O bond cleavage. Preliminary results showed that the reduction of $\{\text{HCN}(\text{Dipp})\}_2\text{BOCP}$ results in intractable product mixtures, possibly due to the reactivity of the boryloxy byproducts.^[16] As such, the reductive deoxygenation of the siloxyphosphaalkyne $^i\text{Pr}_3\text{SiOCP}$ was investigated.

2.2 Synthesis of magnesium(II) cyaphide complexes

2.2.1 Synthesis of $\text{Mg}(\text{DippNacNac})(\text{CP})(\text{diox})$

Given the ability for Lewis base-assisted isomerization and dimerization of $\{\text{HCN}(\text{Dipp})\}_2\text{BOCP}$, the generation of ${}^i\text{Pr}_3\text{SiOCP}$ was conducted in arene solvents instead of in THF as previously reported. While $[\text{Na}(\text{diox})_x][\text{PCO}]$ is poorly soluble in benzene or toluene, with a high enough dioxane content (approx. $x > 3$) the reaction proceeds smoothly in 4 h at room temperature, resulting in benzene or toluene solutions of ${}^i\text{Pr}_3\text{SiOCP}$ containing approximately x equivalents of dioxane.

Dimeric magnesium(I) reducing agents have been shown to be highly effective as hydrocarbon-soluble, two-electron reductants, including in reductive C–E bond cleavage reactions.^[18,19] The reaction of an *in situ* generated benzene solution of ${}^i\text{Pr}_3\text{SiOCP}$ with the mesityl substituted magnesium(I) dimer $\{\text{Mg}(\text{MesNacNac})\}_2$ ($\text{MesNacNac} = N,N\text{-bis}(2,4,6\text{-trimethylphenyl})\text{-pentane-2,4-diimine}$) results in the formation of a bright red solution containing an intractable mixture of products by ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. However, when the bulkier 2,6-diisopropylphenyl substituted magnesium(I) dimer $\{\text{Mg}(\text{DippNacNac})\}_2$ ($\text{DippNacNac} = N,N\text{-bis}(2,6\text{-diisopropylphenyl})\text{-pentane-2,4-diimine}$) is used, the reaction is much more controlled. In this case, the sole products are a magnesium(II) cyaphide complex $\text{Mg}(\text{DippNacNac})(\text{CP})(\text{diox})$ (**1_{diox}**), as well as a magnesium(II) siloxide complex $\text{Mg}(\text{DippNacNac})(\text{OSi}^i\text{Pr}_3)(\text{diox})$ (**2_{diox}**). The reaction was found to proceed quantitatively by NMR spectroscopy (Scheme 2.4).



Scheme 2.4. Synthesis of the magnesium(II) cyaphide complex **1_{diox}** and siloxide byproduct **2_{diox}** ($x = 2.8 - 5.2$).

1_{diox} has a ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectrum containing one resonance at 177.2 ppm corresponding to the cyaphide phosphorus atom; the cyaphide carbon atom appears as a doublet in its ${}^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 270.97

ppm ($^1J_{\text{C-P}} = 34.0$ Hz). The $\text{C}\equiv\text{P}$ bond stretching vibrational mode could not be assigned in its IR spectrum due to overlap with aromatic aryl stretches from the DippNacNac ligand, though was calculated to have a frequency of 1327 cm^{-1} . **1_{diox}** and **2_{diox}** were crystallized from hexane, allowing their structures to be determined by single crystal X-ray diffraction (Figure 2.1).

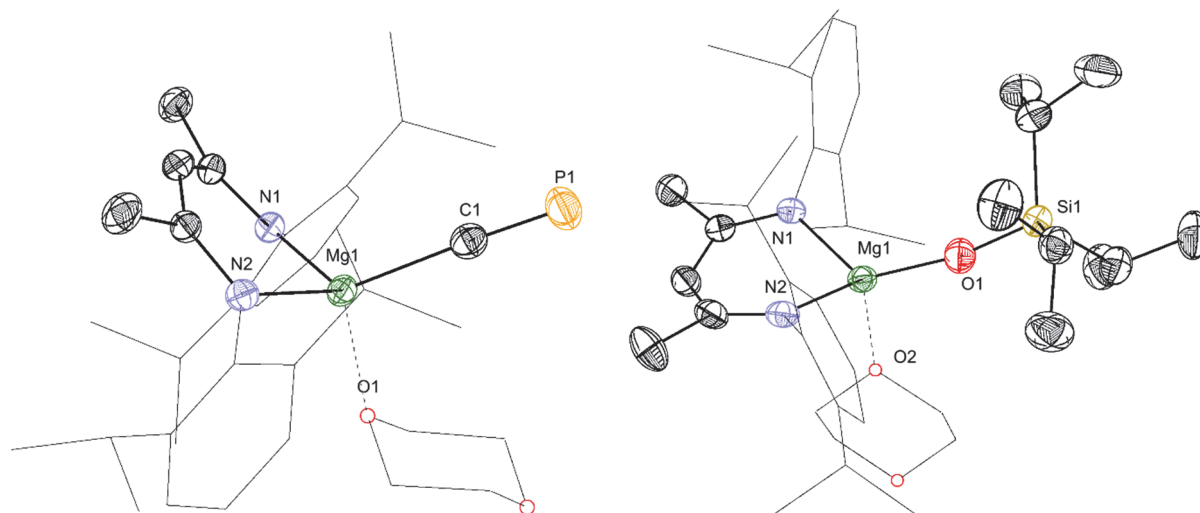


Figure 2.1. Solid-state structures of **1_{diox}** (left) and **2_{diox}** (right). Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Dipp and dioxane groups are depicted as wireframes.

The solid-state structure of **1_{diox}** contains a tetrahedral magnesium center bonded κC to the cyaphide ion in a linear geometry, with a Mg1-C1-P1 bond angle of $177.4(2)^\circ$. The Mg1-C1 bond length is $2.118(2)\text{ \AA}$ and the cyaphide C1-P1 bond length is $1.553(2)\text{ \AA}$, similar to other metal cyaphide complexes and in agreement with the sum of covalent radii for C–P triple bonds ($1.54\text{ \AA}$).^[20]

The isolation of **1_{diox}** is challenging. As a consequence of their similar solubilities, the separation of **1_{diox}** and **2_{diox}** by fractional crystallization is laborious, low yielding ($\sim 20\%$), and impractical on larger scales. Moreover, the isolation of even crude mixtures of **1_{diox}** and **2_{diox}** as solid material is prevented by the instability of the former to vacuum, as indicated by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of samples subjected to repeated solvent removal and redissolution. This includes the appearance of a new minor species in $^{31}\text{P}\{^1\text{H}\}$ spectra at 246.7 ppm , likely to be a solvent-free magnesium(II) cyaphide complex, though its isolation *via* the desolvation of **1_{diox}** was unsuccessful due to its vacuum sensitivity.

Nevertheless, due to the quantitative production of **1_{diox}** and **2_{diox}** from $^i\text{Pr}_3\text{SiOCP}$, *in situ* generated mixtures can be used as a source of **1_{diox}** for further reactions. Because of the strong oxophilicity of magnesium(II), **2_{diox}** is relatively inert and in most cases does not interfere in metathesis reactions between **1_{diox}** and other substrates.

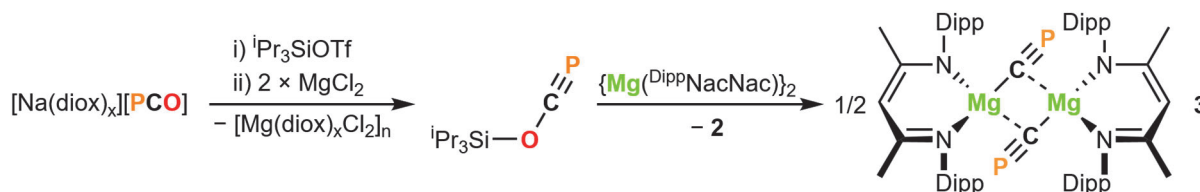
2.2.2 Synthesis of $\{\text{Mg}(\text{DippNacNac})(\mu\text{-CP})\}_2$

The use of $\mathbf{1}_{\text{diox}}$ in *in situ* generated mixtures often renders subsequent reaction procedures operationally difficult. While the siloxymagnesium byproduct $\mathbf{2}_{\text{diox}}$ is usually inert, its separation from reaction products is often challenging. Moreover, the necessity of generating $^i\text{Pr}_3\text{SiOCP}$ in benzene or toluene solutions severely limits solvent choice for procedures involving the use of $\mathbf{1}_{\text{diox}}$.

Reacting $^i\text{Pr}_3\text{SiOCP}$ with the magnesium(I) reagent $\{\text{Mg}(\text{DippNacNac})\}_2$ in the absence of coordinating Lewis bases should allow for the isolation of the previously-observed desolvated species. However, the removal of dioxane from *in situ* generated solutions of $^i\text{Pr}_3\text{SiOCP}$ is non-trivial. Attempts to do so by fractional distillation, either at elevated temperatures or under reduced pressure, invariably resulted in isomerization to the silyl phosphaketene $^i\text{Pr}_3\text{Si-PCO}$. Generating $^i\text{Pr}_3\text{SiOCP}$ from dioxane-free sodium 2-phosphaethynolate (NaPCO) is precluded by the complete insolubility of the latter in non-coordinating solvents. A chemical method for dioxane sequestration was employed instead.

Treatment of *in situ* generated solutions of $^i\text{Pr}_3\text{SiOCP}$ and dioxane with anhydrous magnesium(II) chloride results in the formation of a viscous slurry, in which dioxane has been removed from solution as the insoluble polymer $[\text{Mg}(\text{diox})_x\text{Cl}_2]_n$. While this method for dioxane sequestration is unknown in the literature, the production of $[\text{Mg}(\text{diox})_x\text{Cl}_2]_n$ by adding dioxane to Grignard reagents is a commonplace textbook method for affecting Schlenk equilibria. Notably, once the dioxane has been removed, $^i\text{Pr}_3\text{SiOCP}$ appears to be reasonably stable in benzene solution at room temperature, showing very little isomerization to the phosphaketene.

In the absence of dioxane, $^i\text{Pr}_3\text{SiOCP}$ is indeed reduced by $\{\text{Mg}(\text{DippNacNac})\}_2$ to generate the solvent-free dimeric complex $\{\text{Mg}(\text{DippNacNac})(\mu\text{-CP})\}_2$ (**3**; Scheme 2.5). Gratifyingly, the solubility of **3** is drastically reduced in non-polar solvents; if the reaction is performed using a saturated benzene solution of $\{\text{Mg}(\text{DippNacNac})\}_2$ at 80 °C, **3** crystallizes from the reaction mixture on standing. While **3** remains sensitive to vacuum, its crystallinity allows it to be isolated in good yield (~70%) on gram scale.



Scheme 2.5. Synthesis of the dimeric magnesium(II) cyaphide complex **3** from dioxane-free $^i\text{Pr}_3\text{SiOCP}$ ($x = 2.8 - 3.6$).

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** shows one singlet resonance at 246.7 ppm, matching the chemical shift of the species observed upon desolvation of **1_{diox}**. The symmetric $\text{C}\equiv\text{P}$ vibrational stretching mode appears in its Raman spectrum at 1262 cm^{-1} , substantially lower than the calculated value for **1_{diox}**, likely because the cyaphide ions adopt a bridging coordination mode. This was confirmed by single crystal X-ray crystallography (Figure 2.2).

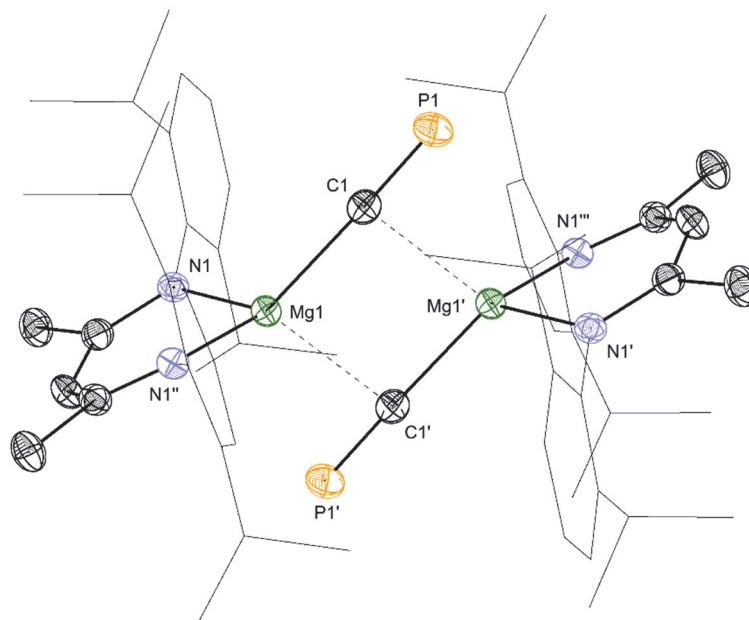
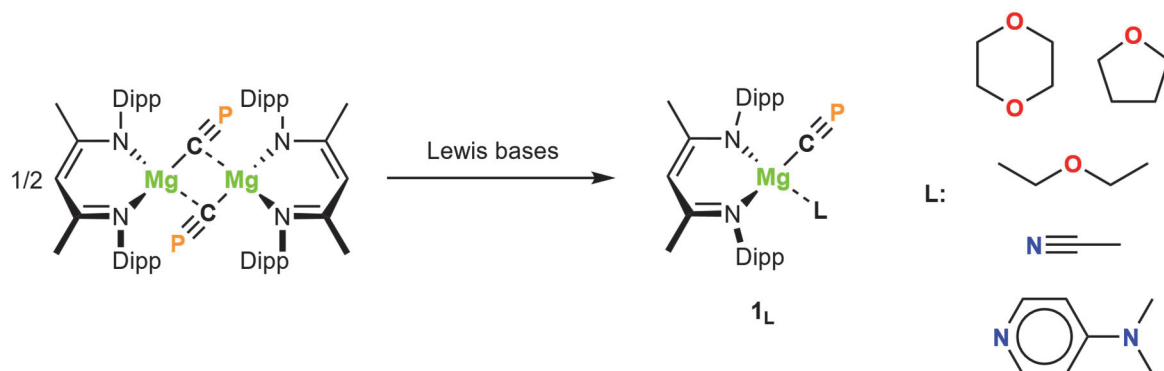


Figure 2.2. Solid-state structure of **3**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms and co-crystallized benzene are omitted for clarity. Dipp groups are depicted as wireframes.

The solid-state structure of **3** shows a dimeric structure wherein two symmetry-related magnesium(II) centers are bridged by “semi-bridging” $\mu\text{-}1\kappa\text{C}:2\kappa\text{C}$ cyaphide ligands. The Mg1-C1-P1 angle is near linear at $178.5(2)^\circ$, whereas the Mg1'-C1-P1 angle is $89.38(9)^\circ$. The Mg1-C1 bond length is $2.170(2)\text{ \AA}$, similar to the value for **1_{diox}**; the Mg1'-C1 distance is substantially longer at $2.421(2)\text{ \AA}$. The cyaphide C1-P1 bond length is $1.559(2)\text{ \AA}$, essentially unchanged from in **1_{diox}**.

2.2.3 Solubilizing $\{\text{Mg}(\text{DippNacNac})(\mu\text{-CP})\}_2$ using Lewis bases

The magnesium(II) cyaphide dimer **3** has very poor solubility in non-coordinating solvents, even those with substantial polarity (e.g. 1,2-difluorobenzene). While this enables its facile isolation, poor solubility may also have deleterious consequences for its reactivity. Fortunately, in the presence of Lewis bases (including common coordinating solvents), **3** readily deaggregates into monomeric base-adducts (Scheme 2.6).



Scheme 2.6. Deaggregation of **3** into Lewis base adducts **1_L**.

The cyaphide phosphorus atoms in these Lewis base-adducts have similar $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts (**1_{diox}**: 177.6 ppm, **1_{THF}**: 175.0 ppm, **1_{Et2O}**: 172.1 ppm, **1_{MeCN}**: 172.5 ppm, **1_{DMAP}**: 178.1 ppm; DMAP = 4-dimethylaminopyridine). For **1_{DMAP}**, the ^1H NMR spectrum shows broadened signals for a pseudo C_{2v} symmetric $^{\text{Dipp}}\text{NacNac}$ ligand at room temperature, likely indicating the reversible dissociation of DMAP in solution.

These conversions are quantitative by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, and can be conducted stoichiometrically or with the Lewis bases in excess. Importantly, **1_L** are highly soluble, and can be generated cleanly even in aliphatic hydrocarbon solvents.

2.2.4 Computed mechanism of C–O bond cleavage by $\{\text{Mg}(\text{DippNacNac})\}_2$

Density functional theory (DFT) calculations suggest a two-step mechanism for the reduction of $^i\text{Pr}_3\text{SiOCP}$ (Figure 2.3). The first step is the reduction of phosphalkyne triple bond. The siloxyphosphalkyne initially approaches the Mg–Mg σ bond end-on to form a three-membered cyclic transition state (TS1), then inserts to form a dimagnesiated phosphalkene intermediate (Int1). A structurally analogous dimagnesiated phosphalkene was recently isolated in the reaction of $\{\text{Mg}(\text{DippNacNac})\}_2$ with *tert*-butyl phosphalkyne.^[21]

The second step in which the C–O bond cleavage occurs is a 1,3-migration of the siloxy group from carbon to magnesium, proceeding *via* a low-barrier four membered cyclic transition state (TS2). Following C–O bond cleavage, the resulting magnesium cyaphide fragment either associates dioxane to form **1_{diox}** or dimerizes to form **3**. Overall, the reaction is calculated to be exergonic ($\Delta G = -52.19 \text{ kcal mol}^{-1}$) with a barrier of $12.47 \text{ kcal mol}^{-1}$, in agreement with the rapid rate of reaction at room temperature.

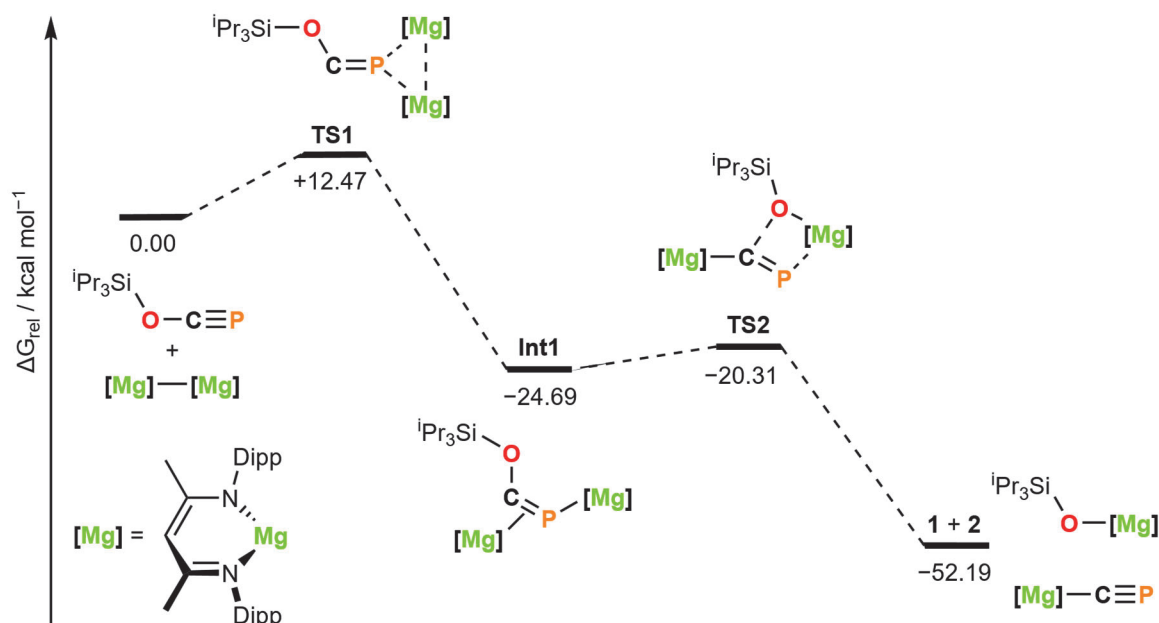
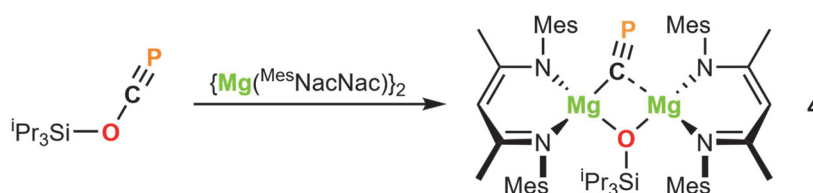


Figure 2.3. Computed mechanism for the reduction of $i\text{Pr}_3\text{SiOCP}$.

2.2.5 Synthesis of $\{\text{Mg}^{(\text{Mes}\text{NacNac})}\}_2(\mu\text{-CP})(\mu\text{-OSi}(i\text{Pr})_3)$

Previously, reactions of *in situ* generated solutions of $i\text{Pr}_3\text{SiOCP}$ with the less bulky mesityl substituted magnesium(I) dimer $\{\text{Mg}^{(\text{Mes}\text{NacNac})}\}_2$ resulted in a mixture of products. When the same reaction is instead performed using dioxane-free solutions of $i\text{Pr}_3\text{SiOCP}$, the reaction results in one major product, a dinuclear magnesium(II) cyaphide complex $\{\text{Mg}^{(\text{Mes}\text{NacNac})}\}_2(\mu\text{-CP})(\mu\text{-OSi}(i\text{Pr})_3)$ (**4**; Scheme 2.7).



Scheme 2.7. Synthesis of the dinuclear magnesium(II) cyaphide complex **4** from dioxane-free $i\text{Pr}_3\text{SiOCP}$ ($x = 2.8 - 3.6$).

4 exhibits a complex ^1H NMR spectrum due to the asymmetry of its molecular structure. The cyaphide phosphorus atom appears in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum as a singlet at 259.0 ppm. While its dinuclear structure is similar to that of **3**, the presence of the non-polar silyl group leads to much higher solubility in non-polar solvents. Crystals were obtained from benzene solution by slow evaporation, allowing its structure to be confirmed by single crystal X-ray crystallography (Figure 2.4).

The molecular structure of **4** consists of two inequivalent $\text{Mg}^{(\text{Mes}\text{NacNac})}$ fragments bridged by a siloxide ligand as well as a semi-bridging cyaphide ligand. As in **3**, the cyaphide ion adopts an asymmetric semi-

bridging coordination mode. The Mg1-C1-P1 angle is off-linear at $162.7(1)^\circ$, and the Mg2-C1-P1 bond angle is $114.0(1)^\circ$. The Mg–C bond lengths are more similar than in **3**, with a Mg1–C1 distance of $2.192(2)$ Å and a Mg2–C1 distance of $2.280(2)$ Å. The siloxide ligand bridges the magnesium centers more symmetrically, with Mg–O–Si bond angles of $128.10(7)^\circ$ and $136.56(7)^\circ$ and Mg–O bond lengths of $2.027(1)$ Å and $2.005(1)$ Å.

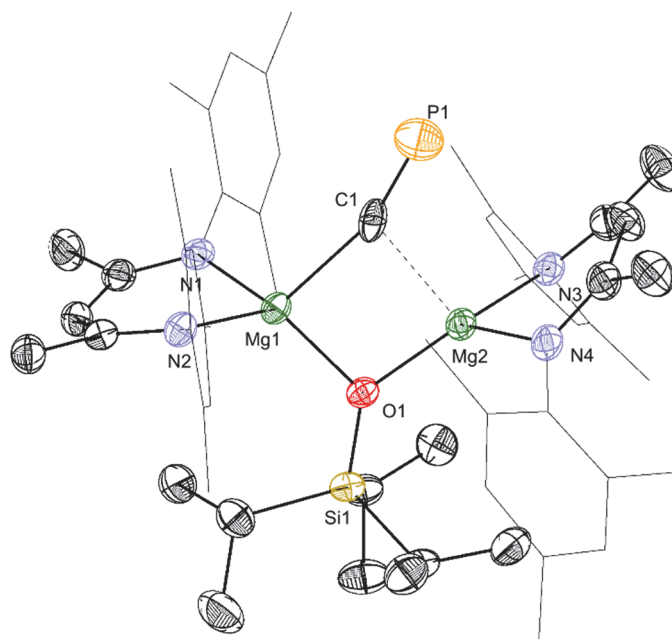
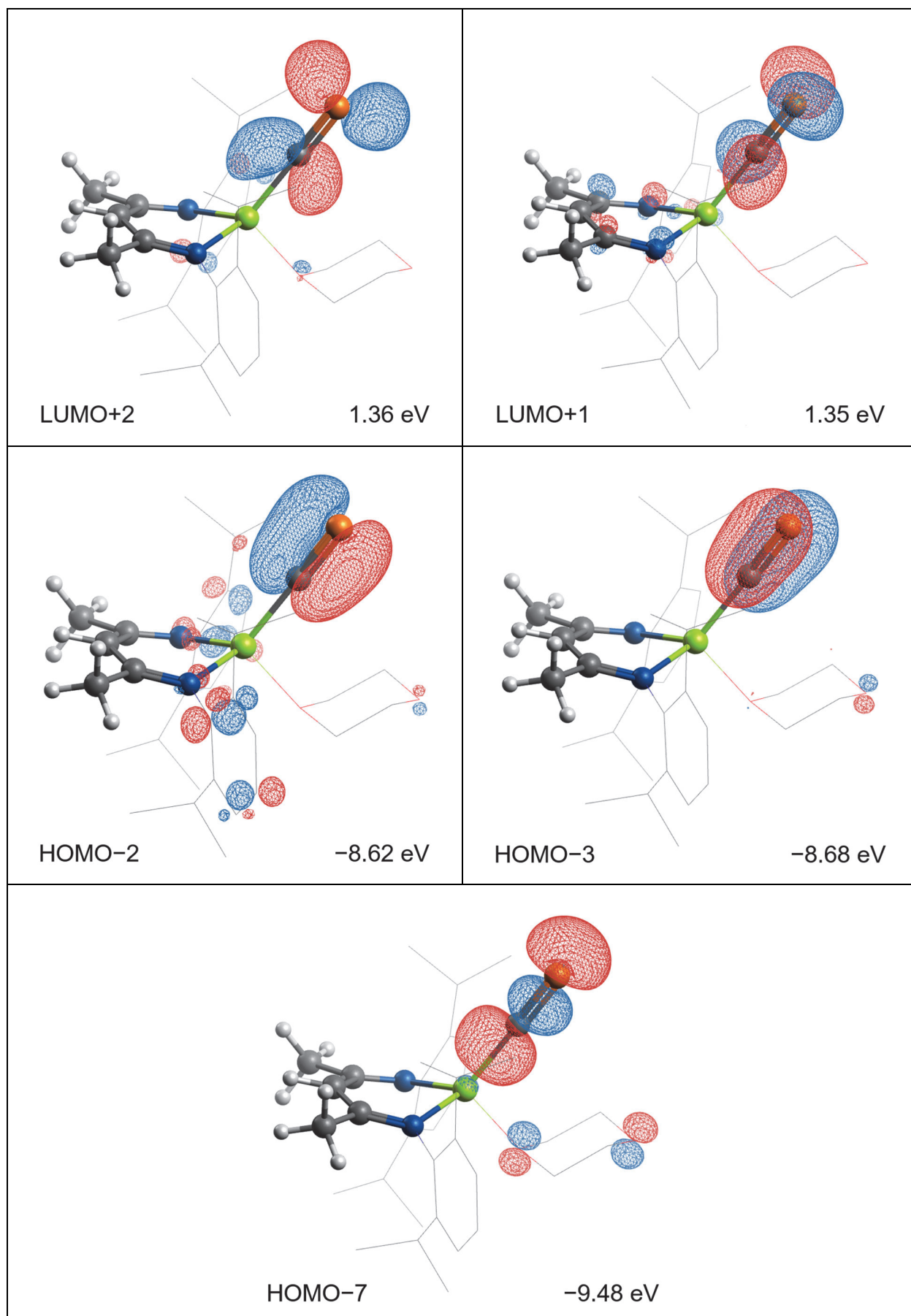


Figure 2.4. Solid-state structure of **4**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Mes groups are depicted as wireframes.

The outcome of this reaction is different to that which afforded **3** (*vide supra*). When the bulkier diisopropylphenyl substituted magnesium(I) dimer is used, the formation of an analogous asymmetric dinuclear species is likely disfavored due to the large steric demand of the triisopropylsilyl group.

2.2.6 Electronic structure of magnesium(II) cyaphide complexes

The electronic structure of **1_{diox}** and **3** were investigated using density functional theory. The Kohn-Sham molecular orbitals were calculated for **1_{diox}**, and show well-localized frontier orbitals corresponding to the cyaphide C–P π -bonding ($E = -8.62, -8.68$ eV), π^* antibonding ($E = 1.35$ eV, 1.36 eV), and Mg–C σ bonding ($E = -9.48$ eV) orbitals (Table 2.1). Natural Population Analysis (NPA) was used to calculate localized atomic charges. In **1_{diox}**, the NPA charge at magnesium is +1.75, in line with expectation. The charges at carbon and phosphorus are -1.22 and $+0.33$ respectively, showing significant polarization of the cyaphide C $\equiv$ P bond toward the carbon atom.

Table 2.1. Kohn-Sham molecular orbitals of **1_{diox}**.

Quantum Theory of Atoms-In-Molecules (QTAIM) topological analysis of the DFT calculated electron density was employed as a complementary theoretical approach (Figure 2.5). In **1**_{diox}, (3, -1) bond critical points corresponding to the Mg–C and C≡P bonds were located. At the Mg–C bond critical point, the electron density (ρ) and the Laplacian of the electron density ($\nabla^2\rho$) are low ($\rho = 0.05$ a.u., $\nabla^2\rho = 0.26$ a.u.), as is the delocalization index ($\delta(\text{Mg–C}) = 0.21$). The energy density (H/ρ) is small and positive ($H/\rho = 0.05$ a.u.), with a potential energy density (V/ρ) of -1.19 a.u. and kinetic energy density (G/ρ) of 1.24 a.u.; the kinetic energy density is larger in magnitude than the potential energy density ($-G/V = 1.04$). Collectively these parameters indicate an ionic Mg–C bond. For the C≡P bond, the QTAIM parameters indicate a polar covalent bond (in agreement with the population analysis). The electron density and the Laplacian of the electron density are relatively high ($\rho = 0.21$ a.u., $\nabla^2\rho = 0.67$ a.u.), and the delocalization index is 2.59 , in good agreement with a C≡P triple bond. The energy density is negative ($H/\rho = -0.91$ a.u.), and the ratio of the kinetic and potential energy densities is between 0.5 and 1 ($-G/V = 0.65$), in line with a polar covalent bond.

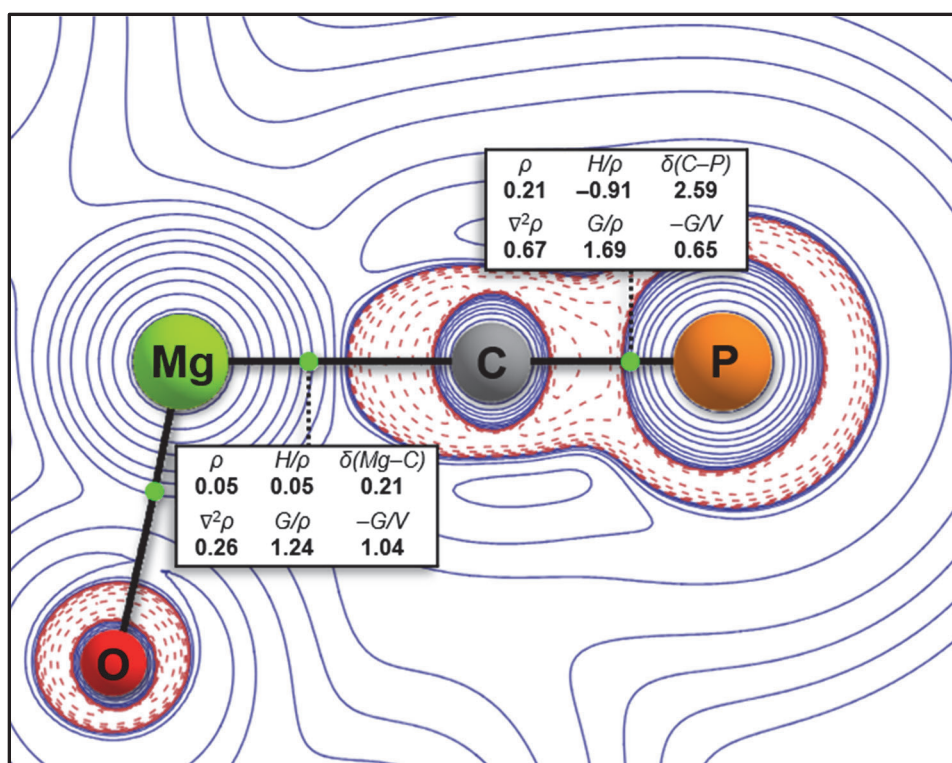
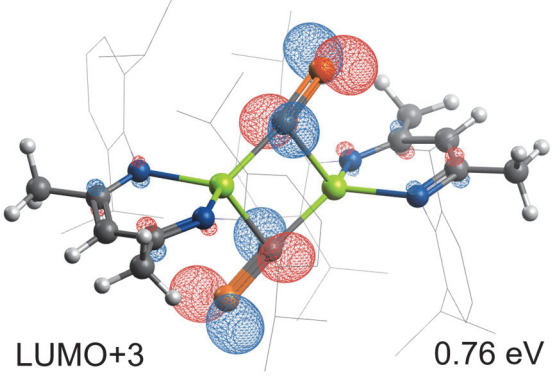
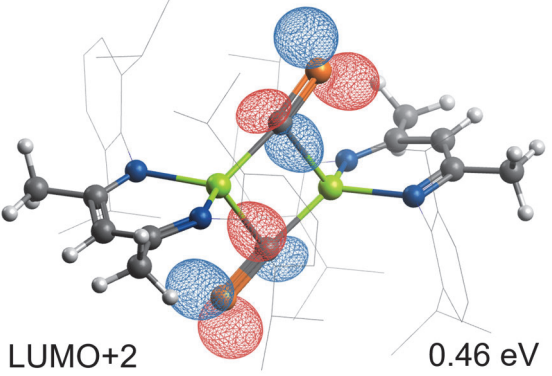
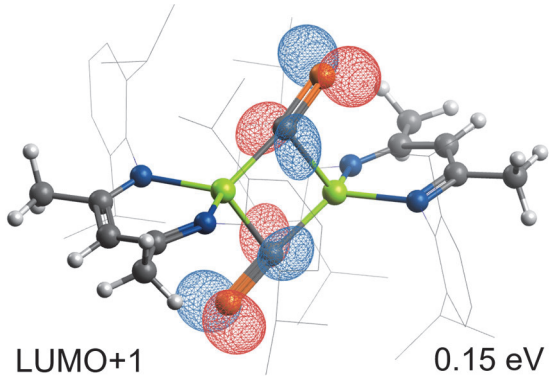
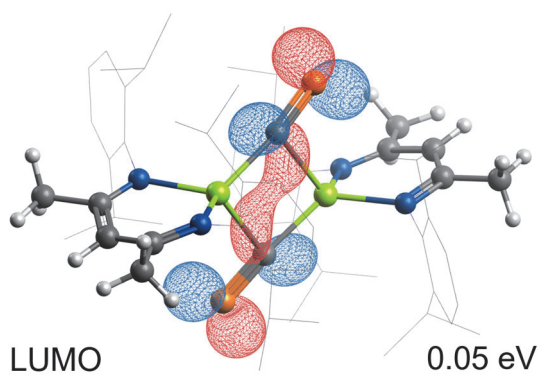
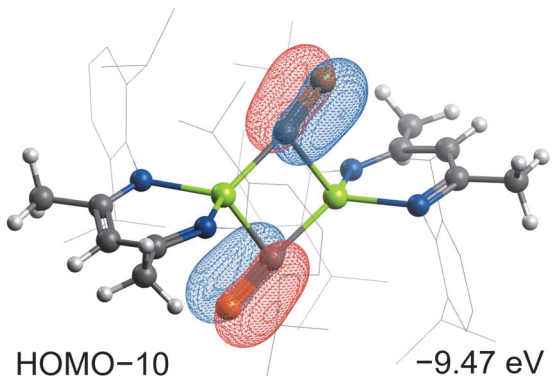
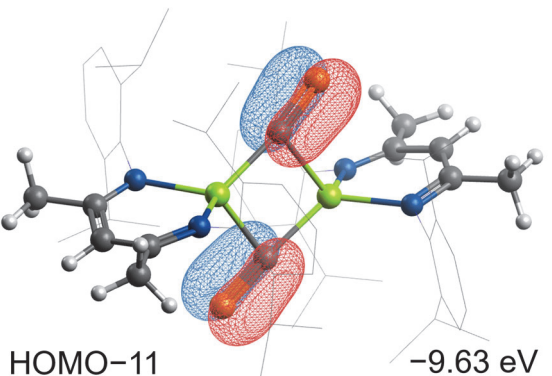
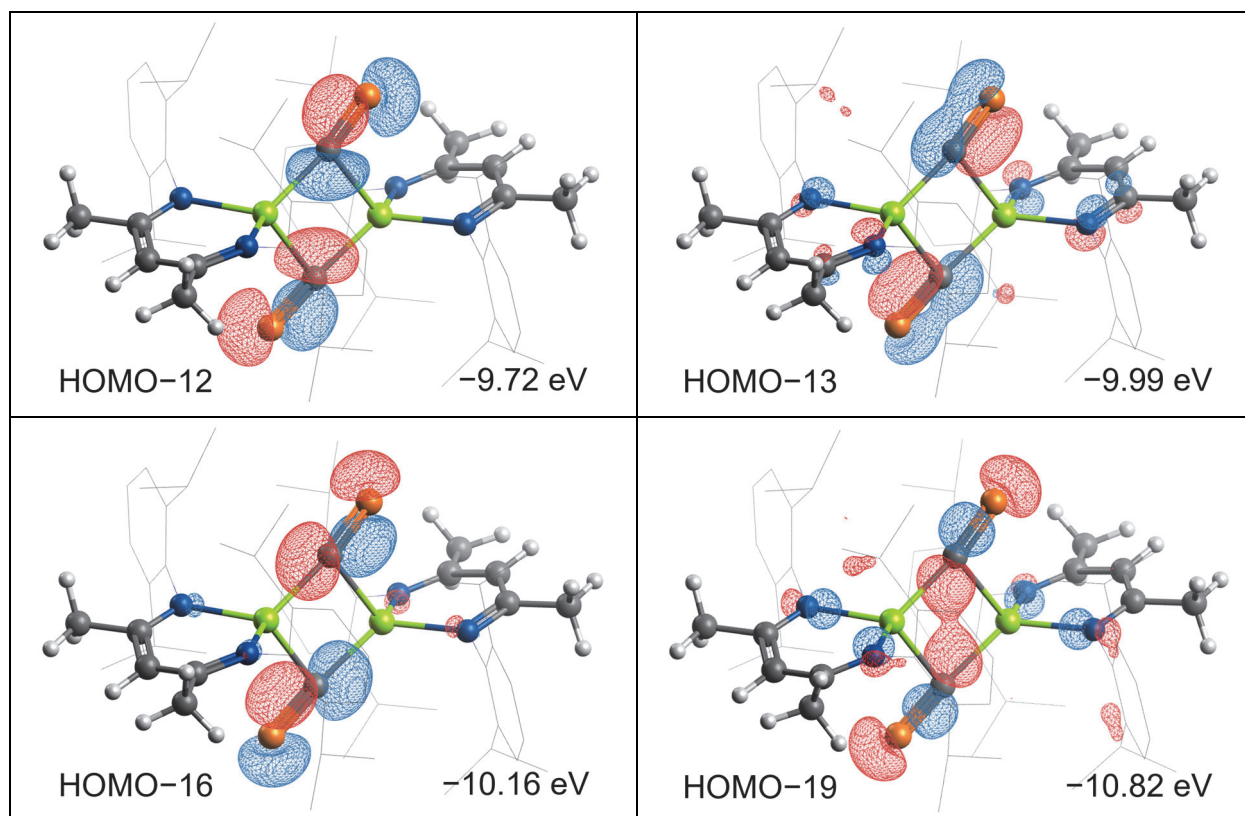


Figure 2.5. 2D QTAIM topological analysis of **1**_{diox}. Parameters at bond critical points are specified in a.u.

In **3**, the molecular orbital picture is slightly different due to the semi-bridging coordination mode of the cyaphide ions (Table 2.2). The $\text{C}\equiv\text{P}$ π orbitals in the plane of the $\text{Mg}-\text{C}-\text{Mg}'-\text{C}'$ ring ($E = -9.99, -10.16$ eV) are distorted due to side-on $\text{Mg}'-\text{C}$ bonding, as are the $\text{Mg}-\text{C}$ σ bonding orbitals ($E = -9.72, -10.82$ eV). This is less the case for the out-of-plane $\text{C}\equiv\text{P}$ π bonding orbitals ($E = -9.47, -9.63$ eV) as well as both the in-plane ($E = 0.05$ eV, 0.46 eV) and out-of-plane ($E = 0.15, 0.76$ eV) $\text{C}\equiv\text{P}$ π^* antibonding orbitals.

Table 2.2. Kohn-Sham molecular orbitals of **3**.

 LUMO+3 0.76 eV	 LUMO+2 0.46 eV
 LUMO+1 0.15 eV	 LUMO 0.05 eV
 HOMO-10 -9.47 eV	 HOMO-11 -9.63 eV



The slightly lower energies of the cyaphide molecular orbitals in **3** compared to **1_{diox}** may be due to a lower overall charge on the cyaphide fragments; NPA indicates a total charge of -0.85 for each cyaphide (cf. -0.89 for **1_{diox}**). This also suggests that in addition to improving solubility, the addition of Lewis bases to **3** to afford monomeric solvent-adducts may enable increased nucleophilic reactivity. This effect is well studied in conventional organolithium and organomagnesium chemistry.^[22–25]

QTAIM analysis of **3** show Mg–C and C≡P bond critical points with similar parameters to **1_{diox}** (Figure 2.6). At the side-on Mg'–C bond critical point, the electron density ($\rho = 0.02$ a.u.), the Laplacian of the electron density ($\nabla^2\rho = 0.08$ a.u.), the total energy density ($H/\rho = -0.03$ a.u.), and the delocalization index ($\delta(\text{Mg}'\text{--C}) = 0.19$) are all low, and the ratio of the kinetic and potential energy densities is 1.09, indicating a weak, largely ionic bond. This is consistent with the ease of Mg'–C bond displacement by Lewis bases.

Interestingly, a (3, -1) critical point is also found between the two cyaphide carbon atoms. While the parameters for the C–C' bond critical point are very low and indicate a very weak C–C' interaction, some degree of C–C' orbital overlap can nevertheless be seen in the Kohn-Sham molecular orbitals (LUMO+1 & HOMO-19), suggesting the possibility for oxidative or reductive C–C coupling (this pattern of reactivity is discussed in Chapter 7).

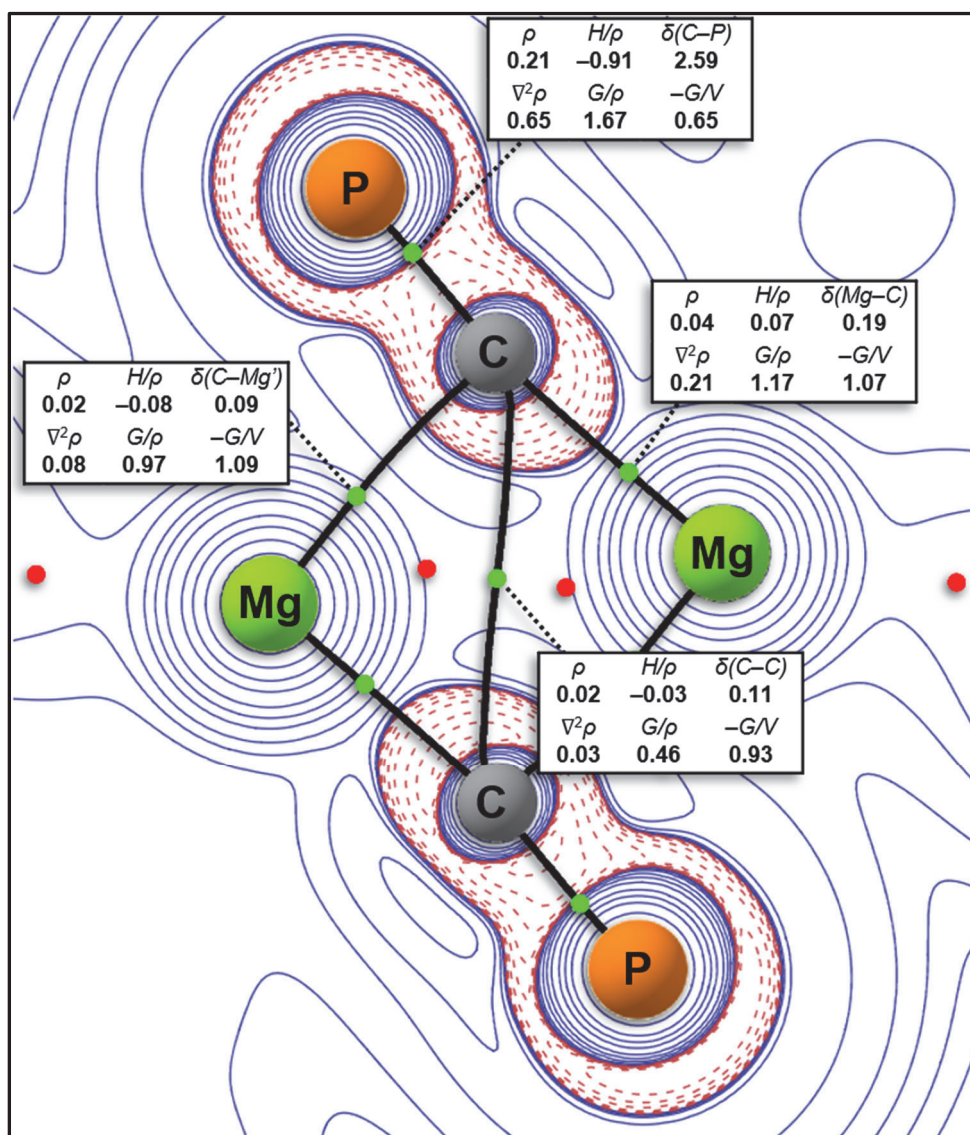


Figure 2.6. 2D QTAIM topological analysis of **3**. Parameters at bond critical points are specified in a.u.

2.3 Conclusions

The cyaphide ion can be generated at magnesium(II) centers from the 2-phosphaethynolate ion in a two-step procedure. Silylation of $[\text{Na}(\text{diox})_x][\text{PCO}]$ by $^i\text{Pr}_3\text{SiOTf}$ affords the siloxyphosphaalkyne $^i\text{Pr}_3\text{SiOCP}$; this can then be reacted with magnesium(I) reducing agents to cleave the C–O bond.

Several cyaphide complexes can be synthesized in this manner. Using the 2,6-diisopropylphenyl substituted magnesium(I) dimer $\{\text{Mg}(\text{DippNacNac})_2$, the magnesium(II) cyaphide complex **1_{diox}** forms in an equimolar mixture with a siloxymagnesium byproduct **2_{diox}**. **1_{diox}** is unstable to vacuum and similar in solubility to **2_{diox}**, preventing its isolation in practical quantities. In the absence of dioxane, the poorly soluble solvent-free dimer **3** is formed instead, allowing for its facile isolation on gram scale. **3** can be solubilized in nonpolar solvents by *in situ* conversion to the Lewis base-adducts **1_L**. When the reduction is performed using the less sterically bulky mesityl substituted magnesium(I) dimer, the molecule remains intact after C–O bond cleavage, resulting in an asymmetric dinuclear complex **4**.

DFT calculations show that these magnesium(II) cyaphide complexes are ionic in nature, with energetically high-lying Mg–C bonds typical of organomagnesium chemistry. In these complexes the cyaphide ion retains an intact $\text{C}\equiv\text{P}$ triple bond and is significantly polarized toward the carbon atom, signaling its reactivity as a carbon-centered nucleophile.

By analogy to Grignard reagents, these magnesium(II) cyaphide complexes behave as nucleophilic synthons for transferring the cyaphide ion to electrophiles. This is applied to the synthesis of metal cyaphide complexes in the following chapter.

Some of the work in this chapter has been published in *The Journal of the American Chemical Society*:

D. W. N. Wilson, S. J. Urwin, E. S. Yang, J. M. Goicoechea, *J. Am. Chem. Soc.* **2021**, 143, 10367–10373.

Dr. D. W. N. Wilson and Dr. S. J. Urwin contributed experimentally to the work in Section 2.2.1.

2.4 Experimental section

2.4.1 Synthesis of $\text{Mg}(\text{DippNacNac})(\text{CP})(\text{diox})$ (**1_{diox}**) and $\text{Mg}(\text{DippNacNac})(\text{OSi}^i\text{Pr}_3)(\text{diox})$ (**2_{diox}**)

$[\text{Na}(\text{diox})_{5.6}][\text{PCO}]$ (167 mg, 0.29 mmol) was added to a solution of $^i\text{Pr}_3\text{SiOTf}$ (90 mg, 0.29 mmol) in toluene (0.5 mL). This suspension was stirred for 4 hours, then filtered to obtain a yellow solution, washing through with an additional 0.5 mL of toluene. $\{\text{Mg}(\text{DippNacNac})\}_2$ (195 mg, 0.22 mmol) was added, resulting in an immediate color change to orange-red upon dissolution. At this stage, the solution can be used *in situ* as a source of **1_{diox}**. Crystals were obtained by gentle concentration of the reaction mixture to an oil, then extraction with hexane (1 mL) and storage at -35°C overnight. Yield: 29 mg, 0.05 mmol 22%. Anal. Calcd. (%) for $\text{C}_{34}\text{H}_{49}\text{MgN}_2\text{O}_2\text{P}$: C, 71.26; H, 8.62; N, 4.89. Found: 71.35; H, 9.15; N, 4.82. Anal. Calcd. (%) for $\text{C}_{42}\text{H}_{70}\text{MgN}_2\text{O}_3\text{Si}$: C, 71.72; H, 10.03; N, 3.98. Found: 71.99; H, 10.50; N, 4.01.

$\text{Mg}(\text{DippNacNac})(\text{CP})(\text{diox})$ (**1_{diox}**):

^1H NMR (500 MHz, C_6D_6): δ (ppm) 7.11–7.09 (m, 6H, Dipp **CH**), 4.78 (s, 1H; NacNac **CH**), 3.34–3.16 (br m, 12H, Dipp **CH**(CH_3)₂ and dioxane **CH**₂), 1.63 (s, 6H, NacNac **CH**₃), 1.38 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 6H, Dipp **CH**(CH_3)₂), 1.24–1.17 (m, Dipp **CH**(CH_3)₂)*, 0.88 (d, $^3J_{\text{H-H}} = 7.9$ Hz, 6H, Dipp **CH**(CH_3)₂).

*Peaks could not be integrated due to overlap with broad dioxane solvent resonances.

^{13}C NMR (126 MHz, C_6D_6): δ (ppm) 270.97 (d, $^1J_{\text{C-P}} = 34.0$ Hz, **CP**), 169.19 (NacNac **CNDipp**), 145.21 (Dipp *ipso*-**C**), 142.81 (Dipp *ortho*-**C**), 142.11 (Dipp *ortho*-**C**), 136.43 (Dipp *para*-**C**), 125.63 (Dipp *meta*-**C**), 124.17 (Dipp *meta*-**C**), 94.85 (NacNac **CH**), 67.26 (Dipp **CH**(CH_3)₂), 27.98 (NacNac **CH**₃), 25.98 (diox **CH**₂), 24.67 (Dipp **CH**(CH_3)₂), 24.13 (Dipp **CH**(CH_3)₂).

^{31}P NMR (162 MHz, C_6D_6): δ (ppm) 177.2 (s, **CP**).

$\text{Mg}(\text{DippNacNac})(\text{OSi}^i\text{Pr}_3)(\text{diox})$ (**2_{diox}**):

^1H NMR (500 MHz, C_6D_6): δ (ppm) 7.15 (m, 6H, Dipp **CH**), 4.73 (s, 1H, NacNac **CH**), 3.83 (s, 6H, diox **CH**₂), 3.21 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 4H, Dipp **CH**(CH_3)₂), 1.59 (s, 6H, NacNac **CH**₃), 1.38 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp **CH**(CH_3)₂), 1.21 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 12H, Dipp **CH**(CH_3)₂), 0.90 (m, 18H, **Si**(**CH**(CH_3)₂)₃), 0.80 (m, 3H, **Si**(**CH**(CH_3)₂)₃).

^{13}C NMR (126 MHz, C_6D_6): δ (ppm) 170.08 (NacNac CNDipp), 145.28 (Dipp *ortho*-C), 142.04 (Dipp *ipso*-C), 125.72 (Dipp *para*-C), 124.19 (Dipp *meta*-C), 94.91 (NacNac CH), 67.95 (diox CH_2), 31.97 (Dipp $\text{CH}(\text{CH}_3)_2$), 28.35 (Dipp $\text{CH}(\text{CH}_3)_2$), 25.31 (NacNac CH_3), 24.43 (NacNac CH_3), 18.96 $\text{Si}(\text{CH}(\text{CH}_3)_2)_3$, 14.65 $\text{Si}(\text{CH}(\text{CH}_3)_2)_3$.

2.4.2 Synthesis of $\{\text{Mg}(\text{DippNacNac})(\mu\text{-CP})\}_2$ (3)

$[\text{Na}(\text{diox})_{3.4}][\text{PCO}]$ (1.25 g, 3.3 mmol) was added to a solution of $^i\text{Pr}_3\text{SiOTf}$ (1.00 g, 3.3 mmol) in benzene (10 mL), and the resulting suspension was stirred vigorously for 4 h. The reaction mixture was filtered *via* cannula filtration, and the filtrant was extracted with a further 5 mL of benzene. The bright yellow filtrate was collected in a flask containing anhydrous MgCl_2 (2.12 g, 22.3 mmol). The mixture was sonicated for 3 h with periodic agitation, then stirred for 16 h to afford a viscous pale-yellow suspension. The suspension was then filtered through Celite, washing through with additional benzene (2×5 mL) to afford a bright yellow solution of dioxane-free $^i\text{Pr}_3\text{SiOCP}$.

In a J-Young flask, a suspension of $\{\text{Mg}(\text{DippNacNac})\}_2$ (2.50 g, 2.8 mmol) in benzene (20 mL) was heated to 80 °C, and stirred until completely dissolved. Once fully dissolved, the stirring was ceased, and the freshly-prepared benzene solution of dioxane-free $^i\text{Pr}_3\text{SiOCP}$ was added. The resulting deep red solution was allowed to cool to room temperature without stirring. The solution was allowed to stand undisturbed for 2 h, during which $\{\text{Mg}(\text{DippNacNac})(\mu\text{-CP})\}_2 \cdot \text{C}_6\text{H}_6$ crystallizes as off-white crystals suitable for single crystal X-ray diffraction. The crystals were isolated by cannula filtration and washed with pentane (3×15 mL), then transferred under argon into a glovebox where they were dried under a dinitrogen atmosphere to obtain $\{\text{Mg}(\text{DippNacNac})(\mu\text{-CP})\}_2$ as an amorphous off-white powder. Yield: 1.01 g, 1.1 mmol, 74%. Anal. Calcd. (%) for $\text{C}_{60}\text{H}_{82}\text{Mg}_2\text{N}_4\text{P}_2$: C, 74.30; H, 8.52; N, 5.78. Found: C, 73.99; H, 8.46; N, 5.69. The poor solubility of $\{\text{Mg}(\text{DippNacNac})(\mu\text{-CP})\}_2$ in non-coordinating solvents precludes meaningful analysis by ^{13}C NMR spectroscopy.

^1H NMR (400 MHz, C_6D_6): δ (ppm) 7.24–7.05 (m, Dipp CH)*, 4.73 (s, 2H, NacNac CH), 3.34 (br, 8H, Dipp $\text{CH}(\text{CH}_3)_2$), 1.49 (s, 12H, NacNac CH_3), 1.18 (d, 24H, $^3J_{\text{H-H}} = 6.8$ Hz, Dipp $\text{CH}(\text{CH}_3)_2$).

*Peaks could not be integrated due to overlap with the residual solvent resonance.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): δ (ppm) 246.7 (s, CP).

Raman: 1262 cm^{-1} (s, $\nu(\text{C}\equiv\text{P})$).

2.4.3 Synthesis of $\{\text{Mg}(\text{Mes}^{\text{NacNac}})\}_2(\mu\text{-CP})(\mu\text{-OSi}^{\text{iPr}}\text{Pr})$ (4)

A benzene solution of dioxane-free iPr_3SiOCP (0.13 M) was prepared as above. To 1.0 mL of this solution was added $\{\text{Mg}(\text{Mes}^{\text{NacNac}})\}_2$ (90 mg, 0.13 mmol), resulting in a color change to bright red on dissolution. The reaction mixture was stirred for 1 h, then filtered to remove particulates. Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation from benzene. The supernatant was decanted, and the crystals washed with cold pentane then dried under a dinitrogen atmosphere. Yield: 29 mg, 0.03 mmol, 25%. Anal. Calcd. (%) for $\text{C}_{56}\text{H}_{79}\text{Mg}_2\text{N}_4\text{OPSi}$: C, 72.17; H, 8.54; N, 6.01. Found: C, 73.12; H, 8.51; N, 5.50.

^1H NMR (400 MHz, C_6D_6): δ (ppm) 7.23–7.18 (m, 1H, Mes **CH**), 6.83–6.61 (m, 7H, Mes **CH**), 5.19 (s, 1H, NacNac **CH**), 4.94 (s, 1H, NacNac **CH**), 3.34 (br, 8H, Dipp **CH**(CH_3)₂), 2.27 (s, 3H, Mes **CH**₃), 2.24 (s, 3H, Mes **CH**₃), 2.21 (s, 3H, Mes **CH**₃), 2.15 (s, 6H, NacNac **CH**₃), 2.14 (s, 3H, Mes **CH**₃), 2.13 (s, 3H, Mes **CH**₃), 2.10 (s, 3H, Mes **CH**₃), 2.08 (s, 3H, Mes **CH**₃), 1.82 (d, $^6J_{\text{H-P}} = 2.2$ Hz, 6H, NacNac **CH**₃), 1.67 (s, 3H, Mes **CH**₃), 1.64 (s, 3H, Mes **CH**₃), 1.43 (s, 3H, Mes **CH**₃), 0.87 (d, $^3J_{\text{H-H}} = 7.5$ Hz, 9H, $\text{OSi}^{\text{iPr}}\text{Pr}_3$ **CH**(CH_3)₂), 0.63 (d, $^3J_{\text{H-H}} = 7.5$ Hz, 9H, $\text{OSi}^{\text{iPr}}\text{Pr}_3$ **CH**(CH_3)₂), -0.23 (d, $^3J_{\text{H-H}} = 7.5$ Hz, 3H, $\text{OSi}^{\text{iPr}}\text{Pr}_3$ **CH**(CH_3)₂).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): δ (ppm) 170.17 (NacNac **CN**Mes), 169.70 (NacNac **CN**Mes), 168.37 (d, $^4J_{\text{C-P}} = 5.4$ Hz, NacNac **CN**Mes), 146.42 (Mes *ipso/ortho*-**C**), 146.14 (d, $^5J_{\text{C-P}} = 14.8$ Hz, Mes *ortho*-**C**), 143.18 (Mes *ipso/ortho*-**C**), 141.90 (Mes *ipso/ortho*-**C**), 133.26 (d, $^5J_{\text{C-P}} = 11.5$ Hz, (Mes *ortho*-**C**)), 133.16 (d, $^4J_{\text{C-P}} = 2.9$ Hz Mes *ipso*-**C**), 132.99 (Mes *ipso/ortho/para*-**C**), 132.88 (Mes *ipso/ortho/para*-**C**), 132.76 (Mes *ipso/ortho/para*-**C**), 131.52 (d, $^7J_{\text{C-P}} = 11.9$ Hz, Mes *para*-**C**), 131.09 (Mes *ipso/ortho/para*-**C**), 129.68 (d, $^6J_{\text{C-P}} = 10.6$ Hz, Mes *meta*-**C**), 129.53 (Mes *meta*-**C**), 129.30 (d, $^6J_{\text{C-P}} = 11.7$ Hz, Mes *meta*-**C**), 128.84 (Mes *meta*-**C**), 125.94 (Mes *meta*-**C**), 124.41 (Mes *meta*-**C**), 96.30 (NacNac **CH**), 24.27 (Mes **CH**₃), 23.19 (Mes **CH**₃), 22.91 (NacNac **CH**₃), 21.56 (Mes **CH**₃), 21.14 (Mes **CH**₃), 20.87 (Mes **CH**₃), 20.72 (Mes **CH**₃), 20.68 (Mes **CH**₃), 19.40 (Mes **CH**₃), 19.12 ($\text{OSi}^{\text{iPr}}\text{Pr}_3$ **CH**(CH_3)₂), 18.76 (Mes **CH**₃), 18.59 (NacNac **CH**₃), 18.40 (Mes **CH**₃), 16.08 ($\text{OSi}^{\text{iPr}}\text{Pr}_3$ **CH**(CH_3)₂). Some peaks corresponding to aromatic carbons could not be assigned due to peak overlap.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): δ (ppm) 259.0 (s, **CP**).

2.4.4 Synthesis of $\text{Mg}(\text{DippNacNac})(\text{CP})(\text{L})$ (**1_L**)

Dioxane: Generated *in situ* by the addition of dioxane (1 eq.) to a suspension of **3** in C_6D_6 . NMR characterization matched those described above.

THF: Generated *in situ* by the dissolution of **3** in d_8 -THF or by the addition of d_8 -THF to a solution of **1_{diox}** in C_6D_6 .

^1H NMR (500 MHz, C_6D_6): $\delta(\text{ppm})$ 7.16–7.12 (m, 6H, Dipp CH), 4.79 (s, 1H, NacNac CH), 3.53 (m, THF), 3.46 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 4H, Dipp CH(CH_3)₂), 3.36 (s, 8H, free dioxane), 1.64 (s, 6H, NacNac CH_3), 1.37 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp CH(CH_3)₂), 1.21 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp CH(CH_3)₂).

^{31}P NMR (162 MHz, C_6D_6): $\delta(\text{ppm})$ 175.0 (s, CP).

Ether: Generated *in situ* by the dissolution of **3** in diethyl ether.

^{31}P NMR (162 MHz, $\text{O}(\text{CH}_2\text{CH}_3)_2$): $\delta(\text{ppm})$ 172.1 (s, CP).

Acetonitrile: Generated *in situ* by the addition of acetonitrile (1 eq.) to a suspension of **3** in C_6D_6 .

^1H NMR (400 MHz, C_6D_6): $\delta(\text{ppm})$ 7.23–7.18 (m, 6H, Dipp CH), 4.83 (s, 1H, NacNac CH), 3.52 (sept, $^3J_{\text{H-H}} = 6.4$ Hz, 4H, Dipp CH(CH_3)₂), 1.68 (s, 6H, NacNac CH_3), 1.43 (d, $^3J_{\text{H-H}} = 6.4$ Hz, 12H, Dipp CH(CH_3)₂), 1.26 (d, 12H, $^3J_{\text{H-H}} = 6.4$ Hz, Dipp CH(CH_3)₂), 0.69 (s, 3H, NCCCH_3).

^{31}P NMR (162 MHz, C_6D_6): $\delta(\text{ppm})$ 172.5 (s, CP).

DMAP: Generated *in situ* by the addition of DMAP (1 eq.) to a suspension of **3** in C_6D_6 .

^1H NMR (400 MHz, C_6D_6): $\delta(\text{ppm})$ 8.34 (d, 2H, $^3J_{\text{H-H}} = 6.2$ Hz, DMAP *ortho*-CH), 7.22–7.16 (m, 6H, Dipp CH), 5.78–5.72 (m, 2H, DMAP *meta*-CH), 4.97 (s, 1H, NacNac CH), 3.43 (br, Dipp CH(CH_3)₂)*, 2.01 (s, 6H, DMAP N(CH_3)₂), 1.79 (s, 6H, NacNac CH_3), 1.27 (br d, $^3J_{\text{H-H}} = 6.3$ Hz, Dipp CH(CH_3)₂)*.

*Peaks could not be integrated due to significant broadening.

^{31}P NMR (162 MHz, C_6D_6): $\delta(\text{ppm})$ 178.1 (s, CP).

2.5 References

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Cyaphide Transfer Chemistry

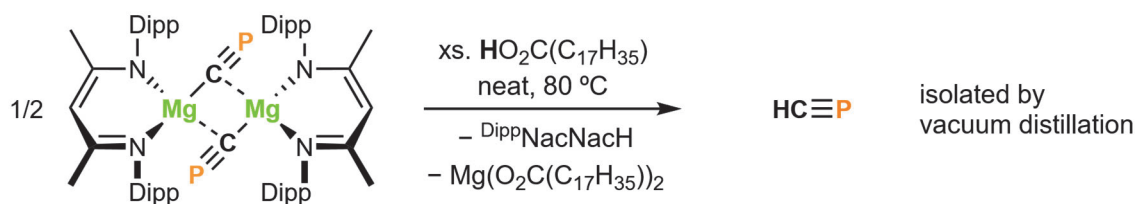
Abstract. By analogy with classic Grignard reagents, magnesium(II) cyaphide complexes can be used to transfer the cyaphide ion to other metal centers. The synthesis of cyaphide-containing main group and transition metal complexes by cyaphide transfer is detailed. Where possible, these compounds are characterized by multinuclear NMR spectroscopy, infrared and Raman vibrational spectroscopy, and single crystal X-ray crystallography.

3.1 Cyaphide transfer to main group centers

3.1.1 Protonation of $\{\text{Mg}(\text{DippNacNac})(\mu\text{-CP})\}_2$

The magnesium(II) cyaphide complexes **1_L**, **3**, and **4** contain highly polar Mg–C bonds that are largely ionic in character, and can be thought of analogously to traditional s-block organometallic reagents, particularly Grignard reagents. Like Grignard reagents, **1_L**, **3**, and **4** are carbanionic synthons capable of being protonated.

In the presence of adventitious water, **3** hydrolyzes to form phosphaethyne gas (HCP) and a magnesium(II) hydroxide byproduct. The protonation of the cyaphide ion in **3** can be performed under more controlled conditions in molten stearic acid. Melting stearic acid over solid **3** under vacuum transfer conditions allows for the isolation of HCP in benzene solutions (Scheme 3.1).



Scheme 3.1. Protonation of **3** by stearic acid to afford phosphaethyne gas (HCP).

Following the discovery of phosphaethyne in 1961 (see Section 1.4.1), other methods for its synthesis have been developed, including the use of molecular precursors.^[1–3] The NMR characterization of HCP generated from **3** matches closely with these previous reports (Figure 3.1).

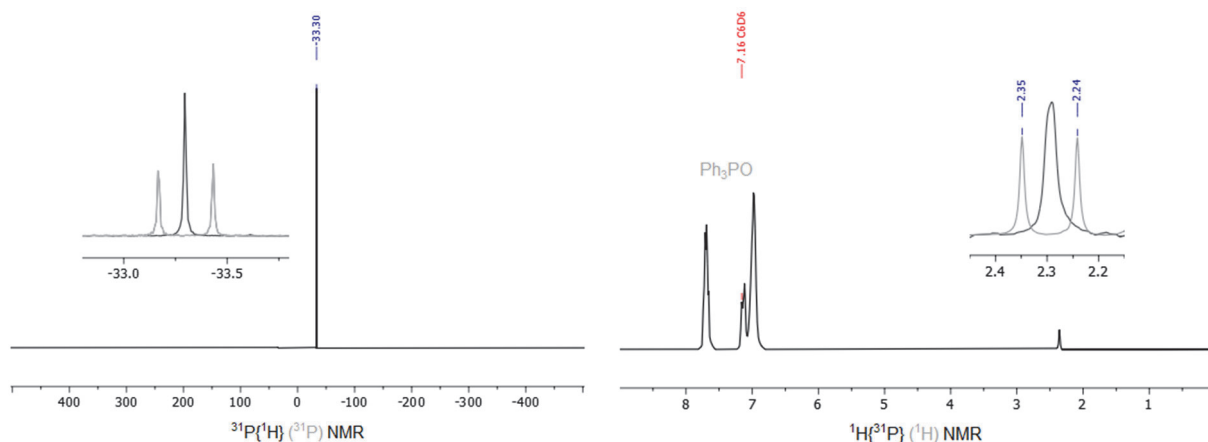


Figure 3.1. ^{31}P and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of HCP generated from **3** (left). ^1H and $^1\text{H}\{^{31}\text{P}\}$ NMR spectra of HCP generated from **3** with Ph_3PO as an internal standard (right).

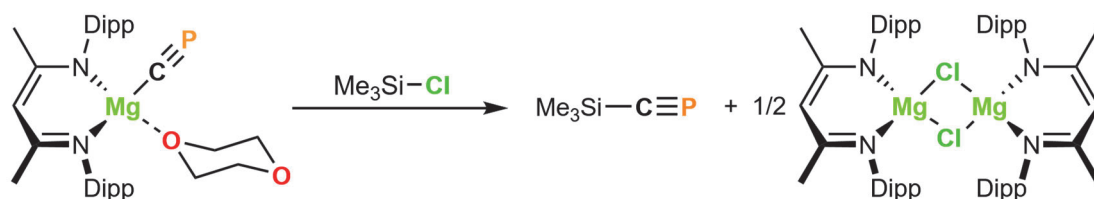
Its ^{31}P NMR spectrum appears as a doublet at -33.3 ppm ($^2J_{\text{P-H}} = 43.4$ Hz) that collapses to a singlet upon proton decoupling (cf. neat: -32.0 ppm, d, $^2J_{\text{P-H}} = 43.9$ Hz;^[4] Et_2O : -32.1 ppm, d, $^2J_{\text{P-H}} = 46.0$ Hz; THF: -23.8 ppm, d, $^2J_{\text{P-H}} = 45.9$ Hz^[3]). Curiously, the ^1H NMR spectrum of phosphaethyne has not previously been reported; in C_6D_6 , HCP generated by this method has a ^1H NMR spectrum containing a doublet at 2.30 ppm ($^2J_{\text{H-P}} = 43.1$ Hz) which collapses to a singlet upon proton decoupling.

The overall yield for the protonation and subsequent vacuum transfer was found to be $\sim 16\%$, as determined by both ^1H NMR and inverse-gated $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy using a sealed capillary containing a known quantity of Ph_3PO in C_6D_6 as an internal standard.

Contrary to previous reports, which describe rapid polymerization of HCP upon warming past approx. -78 °C (neat) or -60 °C (in THF), dilute solutions of HCP in benzene generated by this method are at least somewhat stable at room temperature, with a half-life of approx. 2 hours. This stability can likely be attributed to its dilute concentration as well as its high purity. Indeed, the condensation of HCP into THF solutions or solutions containing Lewis bases (e.g. PPh_3) results in rapid polymerization.

3.1.2 Silylation of $\text{Mg}^{\text{(DippNacNac)}}(\text{CP})(\text{diox})$

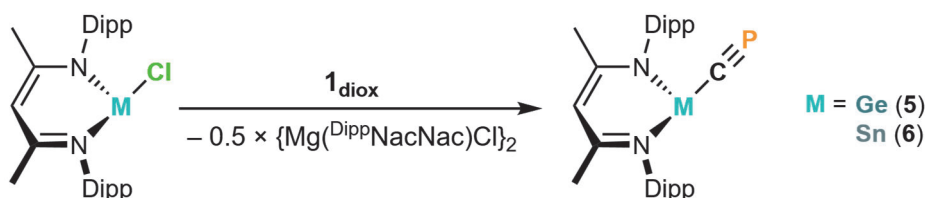
The Grignard-like reactivity of $\mathbf{1}_{\text{diox}}$ was also explored by targeting the known silyl phosphalkyne Me_3SiCP . An *in situ* generated mixture of $\mathbf{1}_{\text{diox}}$ and $\mathbf{2}_{\text{diox}}$ in benzene was reacted with Me_3SiCl , resulting in clean, quantitative conversion to Me_3SiCP , with the concomitant elimination of a magnesium(II) chloride salt-metathesis byproduct (Scheme 3.2). This magnesium(II) chloride complex is known in the literature, and exists as a solvent-free dimeric form, $\{\text{Mg}^{\text{(DippNacNac)}}(\mu\text{-Cl})\}_2$, or as monomeric adducts of easily displaced donor-solvents (e.g. THF).^[5] This finding encouraged the investigation of other salt-metathesis reactions with heavier group 14 element halides.



Scheme 3.2. Silylation of $\mathbf{1}_{\text{diox}}$ by Me_3SiCl to afford the known phosphalkyne Me_3SiCP and salt-metathesis byproduct $\{\text{Mg}^{\text{(DippNacNac)}}(\mu\text{-Cl})\}_2$.

3.1.3 Synthesis of group 14 metal cyaphide complexes $\text{M}^{\text{(DippNacNac)}}(\text{CP})$ ($\text{M} = \text{Ge}, \text{Sn}$)

An *in situ* generated solution of $\mathbf{1}_{\text{diox}}$ and $\mathbf{2}_{\text{diox}}$ reacts rapidly with $\text{Ge}^{\text{(DippNacNac)}}\text{Cl}$ in toluene to afford a new phosphorus-containing compound with a chemical shift of 106.4 ppm by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, proposed to be the germanium(II) cyaphide complex $\text{Ge}^{\text{(DippNacNac)}}(\text{CP})$ ($\mathbf{5}$; Scheme 3.3). $\mathbf{5}$ is thermally unstable, and could not be isolated or crystallized. However, its identity could be confirmed by its further reactivity (see Section 6.2.3).



Scheme 3.3. Synthesis of the group 14 metal cyaphide complexes $\mathbf{5}$ and $\mathbf{6}$.

Due to the instability of $\mathbf{5}$, the heavier tin(II) analog was also targeted. The reaction of $\text{Sn}^{\text{(DippNacNac)}}\text{Cl}$ with an *in situ* generated solution of $\mathbf{1}_{\text{diox}}$ and $\mathbf{2}_{\text{diox}}$ in toluene results in the formation of the tin(II) cyaphide

complex $\text{Sn}(\text{Dipp}(\text{NacNac}))(\text{CP})$ (**6**), which was isolated in modest yield by fractional crystallization from hexane (Scheme 3.3).

6 has a similar $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift to **5** at 122.4 ppm, though with satellites due to $^{117}\text{Sn}/^{119}\text{Sn}$ ($^2J_{\text{P-Sn}} = 69.8$ Hz). Its ^{119}Sn NMR spectrum contains a resonance at -245.6 ppm corresponding to the tin(II) center. Infrared spectroscopy shows a cyaphide $\text{C}\equiv\text{P}$ vibrational stretching frequency of 1321 cm^{-1} . The molecular structure of **6** was confirmed by single crystal X-ray diffraction (Figure 3.2).

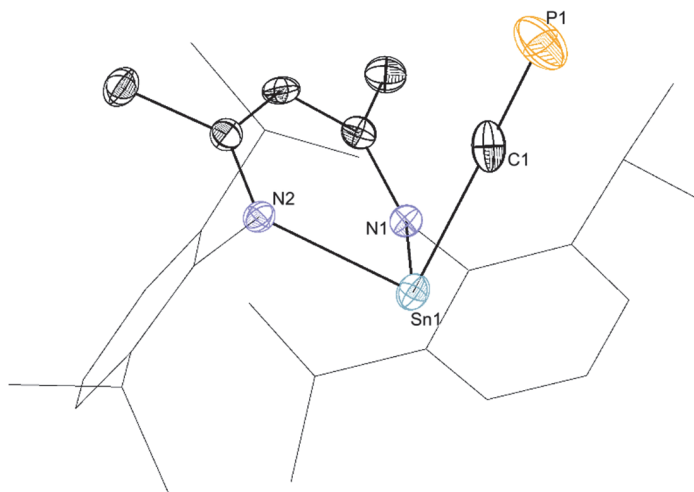


Figure 3.2. Solid-state structure of **6**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Dipp groups are depicted as wireframes.

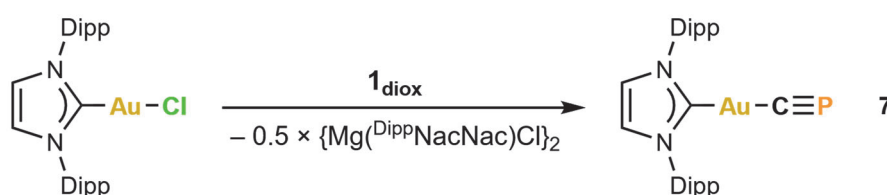
The solid-state structure of **6** contains a trigonal-pyramidal tin center due to the presence of a stereochemically active tin-centered lone pair. The Sn1-C1-P1 bond angle is linear at $179.2(2)^\circ$, and the C1-Sn1-N angles are $89.26(9)^\circ$ and $89.3(1)^\circ$. The Sn1-C1 bond length is $2.216(3)\text{ \AA}$, and the cyaphide C1-P1 bond length is $1.542(4)\text{ \AA}$, comparable to other reported cyaphide complexes.

5 and **6** are the first examples of cyaphide complexes of germanium and tin, as well as the first cyaphide complexes with trigonal pyramidal geometries. They demonstrate the feasibility of using ionic magnesium(II) cyaphide complexes to transfer the cyaphide ion to main group centers. The viability of using cyaphide transfer reactivity to incorporate the cyaphide ion in the coordination sphere of transition metal complexes was investigated next.

3.2 Cyaphide transfer to transition metal centers

3.2.1 Synthesis of Au(IDipp)(CP)

Attempts to target gold(I) cyaphide complexes by salt-metathesis from Au(PPh₃)Cl and Au(SMe₂)Cl resulted in the precipitation of purple solid, presumed to be colloiddally unstable gold(0) species. A gold(I) precursor with a more stabilizing ligand was selected instead. Au(IDipp)Cl (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), with a strongly σ donating *N*-heterocyclic carbene (NHC) ligand, reacts with **1**_{diox} in toluene (either generated *in situ* from ¹Pr₃SiOCP or from **3**) to afford the gold(I) cyaphide complex Au(IDipp)(CP) (**7**; Scheme 3.4).



Scheme 3.4. Synthesis of the gold(I) cyaphide complex **7**.

The cyaphide phosphorus atom in **7** has a chemical shift of 84.1 ppm in its ³¹P{¹H} NMR spectrum, and the cyaphide carbon atom appears as a doublet (¹J_{C-P} = 6.1 Hz) at 247.70 ppm in its ¹³C{¹H} NMR spectrum. The Raman and IR spectra of **7** each show an intense band at 1350 and 1342 cm⁻¹, respectively, corresponding to coupled vibrational modes involving the C≡P bond stretch as well as a NHC imidazole ring stretch.

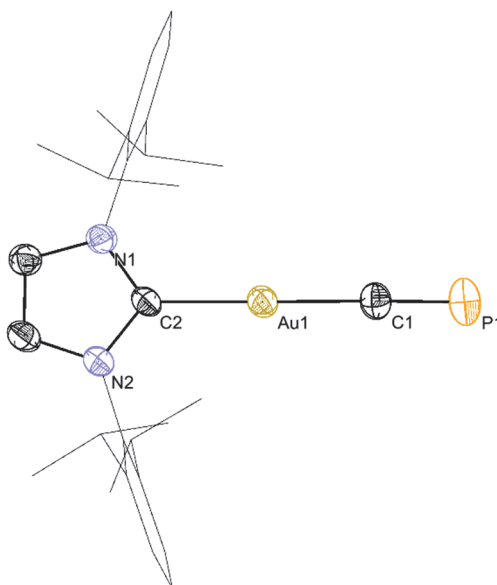


Figure 3.3. Solid-state structure of **7**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Dipp groups are depicted as wireframes.

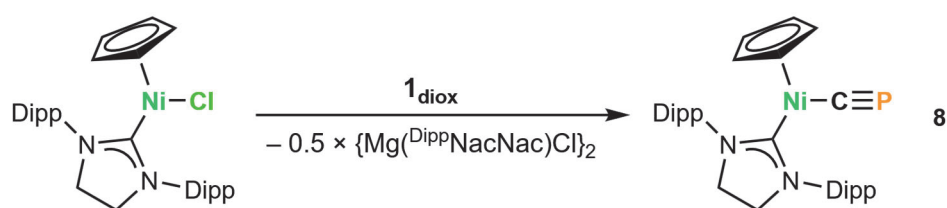
The structure of **7** was determined by single crystal X-ray diffraction, revealing a linear gold center ligated by one IDipp and one cyaphido ligand (Figure 3.3). The C1–Au1–C2 angle is essentially linear at $178.2(2)^\circ$, as is the Au1–C1–P1 angle of $178.0(5)^\circ$. The gold IDipp Au1–C2 bond length is $2.034(6)$ Å and the gold cyaphide Au1–C1 bond length is $1.972(6)$ Å. The cyaphide C1–P1 bond length is $1.552(6)$ Å.

7 is the first example of a gold cyaphide complex, and the first metal complex with a linear coordination geometry. As cyaphide complexes of 3d transition metals were unknown in the literature, species of this type were targeted by cyaphide transfer.

3.2.2 Synthesis of Ni(SIDipp)(Cp)(CP)

The stabilization of **7** using a *N*-heterocyclic carbene ligand prompted whether a lighter group 11 congener Cu(IDipp)(CP) would be possible. Attempts to synthesize this species were unsuccessful, resulting only in metallic precipitates and no well-defined phosphorus-containing products. A different late 3d metal cyaphide complex with a supporting NHC ligand was attempted instead.

The nickel(II) complex Ni(SIDipp)(Cp)Cl (SIDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene) reacts with **1_{diox}** (generated *in situ* as a mixture with **2_{diox}**) to form a nickel(II) cyaphide complex, Ni(SIDipp)(Cp)(CP) (**8**; Scheme 3.5). **8** has a resonance at 181.2 ppm in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum as well as a doublet in its $^{13}\text{C}\{^1\text{H}\}$ spectrum at 224.02 ppm ($J_{\text{C-P}} = 10.4$ Hz), corresponding to the cyaphide phosphorus and carbon atoms, respectively. In its infrared spectrum, the cyaphide $\text{C}\equiv\text{P}$ stretching frequency appears at 1307 cm^{-1} .

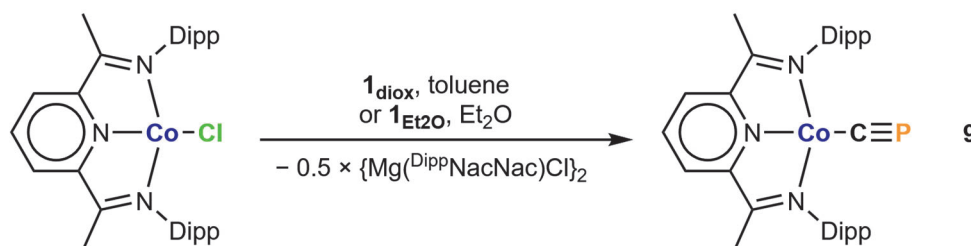


Scheme 3.5. Synthesis of the nickel(II) cyaphide complex **8**.

While isolable, **8** slowly converts to a different product in concentrated solution *via* a rearrangement involving the NHC ligand (see Section 7.2.2), preventing the growth of single crystals suitable for X-ray crystallography. As such, the synthesis of another 3d metal cyaphide complex without C-donor ligands was targeted.

3.2.3 Synthesis of $\text{Co}(\text{DippPDI})(\text{CP})$

The reaction of the square planar, formally cobalt(I) complex $\text{Co}(\text{DippPDI})\text{Cl}$ ($\text{DippPDI} = 1,1'$ (pyridine-2,6-diyl)bis(N -(2,6-diisopropylphenyl)ethan-1-imine), featuring a sterically bulky pyridine-2,6-diimine pincer ligand, with either $\mathbf{1}_{\text{diox}}$ in toluene (generated *in situ* as a mixture with $\mathbf{2}_{\text{diox}}$) or $\mathbf{1}_{\text{Et}_2\text{O}}$ in diethyl ether (generated from $\mathbf{3}$) results in cyaphide transfer to give the cobalt(I) cyaphide complex $\text{Co}(\text{DippPDI})(\text{CP})$ ($\mathbf{9}$; Scheme 3.6).



Scheme 3.6. Synthesis of the cobalt(I) cyaphide complex **9**.

9 has a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum containing a conspicuously downfield-shifted resonance corresponding to the cyaphide ion at 345.4 ppm; this is in line with its ^1H NMR spectrum, which contains upfield- and downfield-shifted resonances for the DippPDI backbone. The origin of this behavior is discussed further in Section 4.3.3. The cyaphide $\text{C}\equiv\text{P}$ stretching frequency was measured to be 1306 cm^{-1} by infrared spectroscopy.

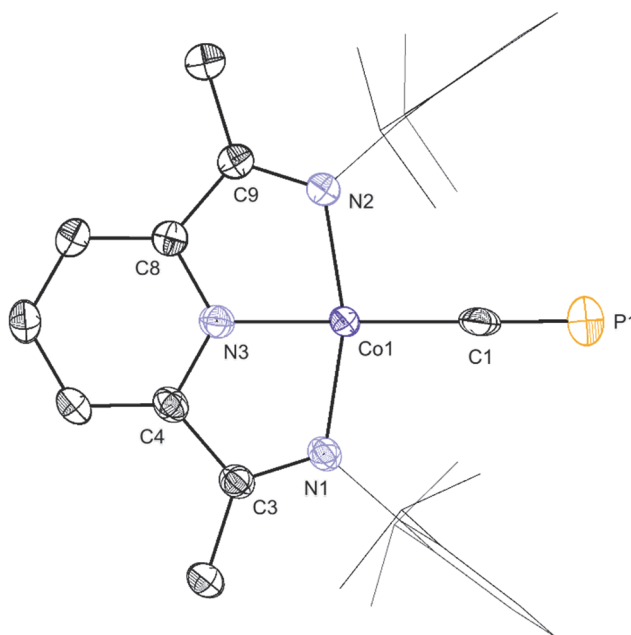


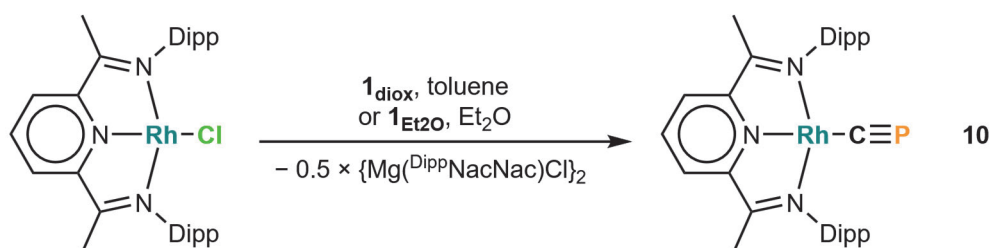
Figure 3.4. Solid-state structure of **9**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Dipp groups are depicted as wireframes.

The solid-state structure of **9** was determined by single crystal X-ray diffraction (Figure 3.4). The cobalt center is in a pseudo-square planar geometry, ligated $\kappa^3\text{N}$ to the ^{Dipp}PDI pincer ligand, and κC to the cyaphido ligand. The Co1-C1-P1 angle is linear at $178.3(3)^\circ$, with a Co1-C1 bond length of $1.927(4)$ Å and C1-P1 bond length of $1.506(4)$ Å.

9 is the first structurally-authenticated cyaphide complex of a 3d metal, and the first with a square-planar geometry. To aid in the experimental determination of the properties of the cyaphido ligand (see Chapter 4), the isostructural rhodium(I) cyaphide complex was also synthesized.

3.2.4 Synthesis of Rh(^{Dipp}PDI)(CP)

In an analogous manner to the synthesis of **9**, Rh(^{Dipp}PDI)Cl reacts with either **1_{diox}** in toluene (generated *in situ* as a mixture with **2_{diox}**) or **1_{Et2O}** in diethyl ether (generated *in situ* from **3**) to afford the rhodium(I) cyaphide complex Rh(^{Dipp}PDI)(CP) (**10**), the first example of a rhodium cyaphide complex (Scheme 3.7).



Scheme 3.7. Synthesis of the rhodium(I) cyaphide complex **10**.

Similar to its lighter congener, **10** also exhibits somewhat shifted resonances in its NMR spectra, though to a lesser magnitude. The cyaphide phosphorus resonance appears as a doublet at 251.4 ppm ($^2J_{\text{P-Rh}} = 6.0$ Hz) in its $^{31}\text{P}\{^1\text{H}\}$ spectrum. The cyaphide carbon appears as a doublet of doublets at 264.15 ppm ($^1J_{\text{C-Rh}} = 54.8$ Hz, $^1J_{\text{C-P}} = 22.9$ Hz). The Raman spectrum of **9** shows a band at 1334 cm^{-1} corresponding to the $\text{C}\equiv\text{P}$ stretching mode, somewhat higher than in **9**.

Single crystal X-ray diffraction of **10** reveals a square-planar rhodium center in a complex isostructural to **9** (Figure 3.5). The Rh1-C1-P1 angle is $178.6(3)^\circ$, the Rh1-C1 bond length is $1.969(3)$ Å, and the cyaphide C1-P1 bond length is $1.542(4)$ Å.

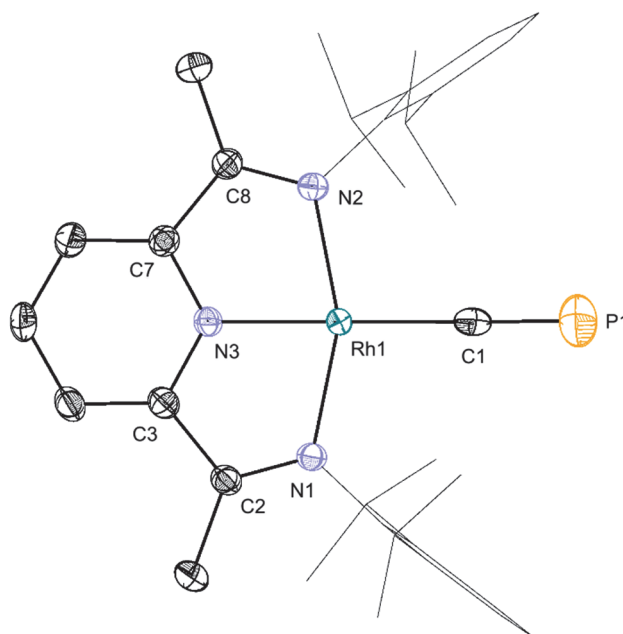
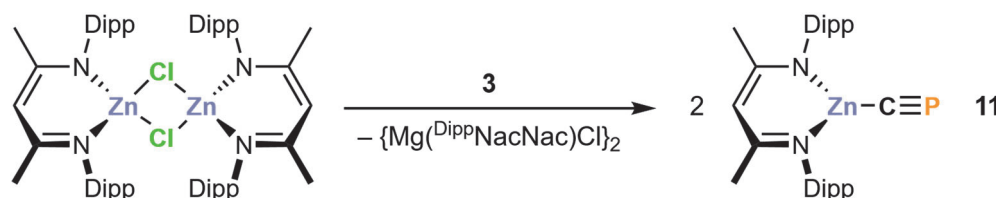


Figure 3.5. Solid-state structure of **10**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Dipp groups are depicted as wireframes.

3.2.5 Synthesis of $\text{Zn}(\text{DippNacNac})(\text{CP})$

5–10 demonstrate that cyaphide transfer is a broadly applicable route to synthesize covalent transition metal coordination complexes of the cyaphido ligand. The transfer of the cyaphide ion to a more ionic d-block metal center was also investigated.

The reaction of **3** with $\{\text{Zn}(\text{DippNacNac})(\mu\text{-Cl})\}_2$ in toluene results in the formation of a new phosphorus-containing product with a $^{31}\text{P}\{^1\text{H}\}$ chemical shift of 140.7 ppm and a $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum containing a doublet at 222.23 ppm ($^1J_{\text{C-P}} = 5.9$ Hz) corresponding to the cyaphide carbon atom. This is proposed to be the zinc(II) cyaphide complex $\text{Zn}(\text{DippNacNac})(\text{CP})$ (**11**; Scheme 3.8).



Scheme 3.8. Synthesis of the zinc(II) cyaphide complex **11**.

Attempts to grow single crystals of **11** for X-ray crystallography were unsuccessful, so it cannot be discounted that the structure of **11** is dimeric, similar to **3**. Both three-coordinate and four-coordinate $\text{Zn}(\text{DippNacNac})$ compounds are known in the literature, and give rise to similar NMR spectra.^[6,7]

3.3 Cyaphide ^{31}P chemical shifts

^{31}P NMR spectroscopy is of critical importance in the characterization of cyaphide-containing molecules, and is incredibly helpful in guiding the exploration of cyaphide chemistry. However, due to the limited number of known cyaphide complexes in the literature, the ^{31}P chemical shift of the cyaphide ion in novel compounds is difficult to predict. Moreover, while the cyaphide ^{31}P chemical shifts should in principle be greatly informative of the nature of metal–cyaphide bonding, it is difficult to infer meaningful information from the extrapolation of scant literature-known data.

DFT can be used to calculate NMR shielding tensors for various nuclei using the gauge-independent atomic orbital (GIAO) method. While this works well for ^1H NMR chemical shift prediction, its application to other nuclei can be problematic and often requires the use of prohibitively costly methods.^[8] The accurate prediction of ^{31}P chemical shifts is a well-known challenge, in particular for unusual phosphorus-containing molecules and metal complexes.^[9] As such, even well-performing methods for more conventional organophosphorus compounds perform poorly for cyaphide-containing molecules. The use of “locally-dense” composite basis sets to model the electron density in DFT calculations has been proposed as a method for improving accuracy in chemical shielding calculations.^[10] This has recently found success when applied to DFT ^{31}P chemical shift prediction for 3d transition metal tertiary phosphine complexes.^[11]

Several computationally economic methods were screened for predicting the ^{31}P chemical shifts of cyaphide-containing molecules and metal complexes. A method employing a similar “locally-dense” basis set was found to perform the best, predicting ^{31}P chemical shifts with a root-mean-square (RMS) error of ~ 10 ppm, after correction using empirical linear regression (Figure 3.6).

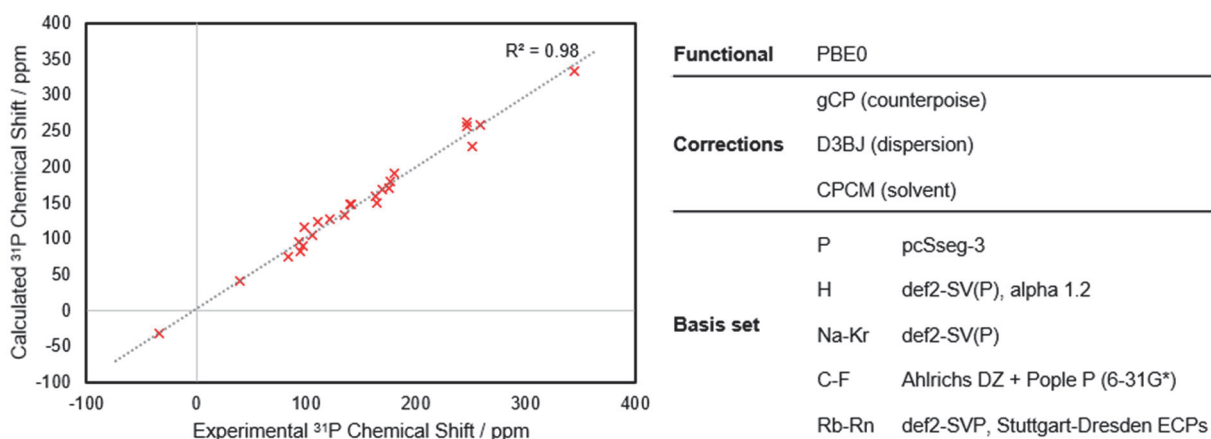


Figure 3.6. Experimental vs. calculated ^{31}P chemical shifts (left). DFT method used to calculate chemical shielding (right).

This method uses optimized geometries obtained using the PBEh-3c semi-empirical method.^[12] For the chemical shielding calculation, the method uses the PBE0 global hybrid functional,^[13] and is corrected for geometric counterpoise (gCP) and for dispersion using Grimme's D3 method with Becke-Johnson damping (D3BJ).^[14,15] Solvent-correction is applied using the polarized continuum model (CPCM), using gaussian charges and a van der Waals cavity.^[16,17] The chemical-shielding-optimized triple-zeta basis set pcSseg-3 is used for phosphorus;^[18] for all other atoms, a composite split-valence basis set def2-mSVP is used.^[12] The obtained chemical shielding values were directly fitted to the corresponding experimental ³¹P chemical shifts by linear regression ($y = -0.9236x + 266.85$), which was then used to convert the calculated shielding values to predicted chemical shifts.

In general, cyaphide complexes of metals without partially filled d-subshells have ³¹P chemical shifts that depend on M–C covalency. Even without accounting for the effect of varying metal oxidation states, geometries, and coordination spheres, the ³¹P chemical shift of the cyaphide ion (in a terminal κ C coordination mode) correlates surprisingly well with the electronegativity of the metal to which it is coordinated (Figure 3.7).

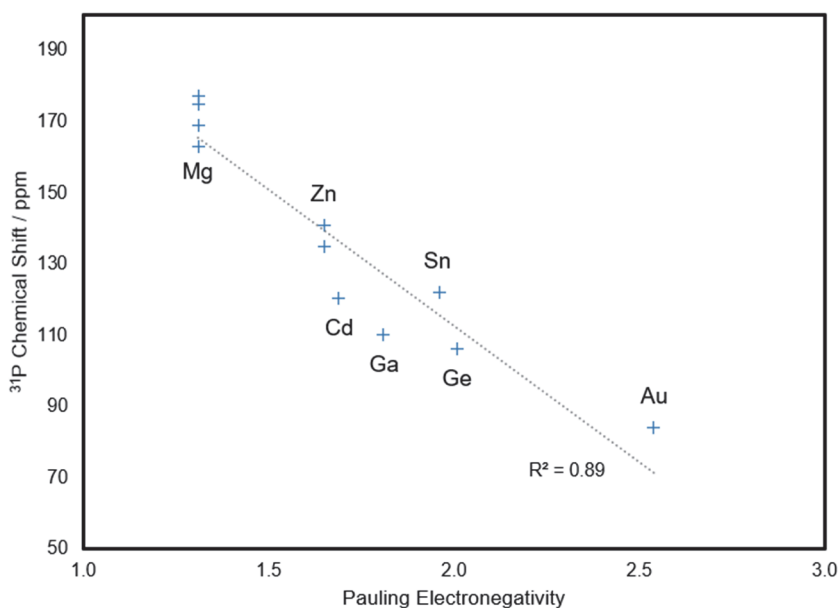


Figure 3.7. Cyaphide ³¹P chemical shifts in metal cyaphide complexes ([M]–CP) plotted against the Pauling electronegativity of the metal M (includes cyaphide complexes discussed in Chapters 2, 5, and 8).

Metal cyaphide complexes with partially filled d-subshells do not follow this simple trend. The reason is likely two-fold: 1) a greater significance of π -bonding contributions to the M–C bond; and 2) an increase in the paramagnetic contribution to the chemical shielding constant. These are discussed in more detail for **9** and **10** in the next chapter.

3.4 Conclusions

Ionic magnesium(II) cyaphide complexes can be used to access cyaphide-containing molecules by cyaphide transfer. The reaction of **1_L** and **3** with metal chlorides results in the salt elimination of a magnesium(II) chloride byproduct and the formation of metal cyaphide complexes.

This was demonstrated first for main group elements *via* the synthesis of the known cyaphide-containing molecules HCP and Me₃SiCP, and applied to the preparation of novel cyaphide complexes of germanium(II) (**5**) and tin(II) (**6**).

The broad applicability of cyaphide transfer chemistry was then extended to 3d, 4d, and 5d transition metals. Using this general synthesis route, novel cyaphide complexes of gold(I) (**7**), nickel(II) (**8**), cobalt(I) (**9**), rhodium(I) (**10**), and zinc(II) (**11**) were isolated and characterized.

To aid experimental efforts to target novel cyaphide complexes, a computational method was developed for predicting the ³¹P NMR chemical shifts of cyaphide-containing molecules. Analysis of the data for a range of metal cyaphide complexes show that the ³¹P chemical shift of the cyaphide ion is highly dependent on the covalency of the M–C bond.

The nature of metal–cyaphide bonding is investigated from a coordination chemistry perspective in the next chapter, in which the donor/acceptor properties of the κC-cyaphido ligand are determined.

Some of the work in this chapter has been published in *the Journal of the American Chemical Society*, *Angewandte Chemie*, and *Chemical Science*:

D. W. N. Wilson, S. J. Urwin, E. S. Yang, J. M. Goicoechea, *J. Am. Chem. Soc.* **2021**, 143, 10367–10373.

E. S. Yang, D. W. N. Wilson, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2023**, 62, e202218047.

E. S. Yang, E. Combey, J. M. Goicoechea, *Chem. Sci.* **2023**, 14, 4627–4632.

Dr. D. W. N. Wilson and Dr. S. J. Urwin contributed experimentally to the work in Sections 3.1.2–3.2.2.

3.5 Experimental section

3.5.1 HCP generation from $\{\text{Mg}(\text{DippNacNac})(\mu\text{-CP})\}_2$

$\{\text{Mg}(\text{DippNacNac})(\mu\text{-CP})\}_2$ (20 mg, 0.02 mmol) and stearic acid (200 mg, 0.70 mmol) were added as a homogeneous solid mixture to a J-Young NMR tube (tube A). Tube A was attached to a greaseless vacuum transfer bridge, along with a second J-Young NMR tube containing 0.5 mL of C_6D_6 (tube B). The two NMR tubes were evacuated, and tube B was degassed by three freeze-pump-thaw cycles. The entire vacuum transfer apparatus was left open under a static vacuum, and tube B was cooled to -196°C using liquid nitrogen. Tube A was gently heated to approx. 80°C using a temperature-adjustable heat gun, resulting in the melting of the stearic acid. Tube A was heated with gentle agitation for 10 minutes, after which both tubes were sealed under vacuum and removed from the vacuum transfer apparatus. Tube B was thawed at room temperature, giving a colorless C_6D_6 solution of HCP. Yield (by NMR): approx. 0.3 mg, 0.01 mmol, 16%.

^1H NMR (400 MHz, C_6D_6): $\delta(\text{ppm})$ 2.30 (d, $^1J_{\text{H-P}} = 43.1$ Hz, 1H, HCP).

^{31}P NMR (162 MHz, C_6D_6): $\delta(\text{ppm})$ -33.3 (d, $^1J_{\text{P-H}} = 43.4$ Hz, HCP).

3.5.2 Me_3SiCP generation from $\text{Mg}(\text{DippNacNac})(\text{CP})(\text{diox})$

A solution of $\text{Mg}(\text{DippNacNac})(\text{CP})(\text{diox})$ (approx. 19 mg, 0.03 mmol) in C_6D_6 was generated *in situ*, as in Section 2.4.1. Me_3SiCl (5 μL , 0.04 mmol) was added *via* syringe, and the reaction mixture was stirred for 30 minutes. $^{31}\text{P}\{^1\text{H}\}$ NMR of the reaction mixture shows complete conversion to Me_3SiCP .

^1H NMR (400 MHz, C_6D_6): $\delta(\text{ppm})$ 0.09 (s, 9H, CH_3).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): $\delta(\text{ppm})$ -97.9 (s, Me_3SiCP).

3.5.3 *In situ* generation of $\text{Ge}(\text{DippNacNac})(\text{CP})$ (5)

A solution of $\text{Mg}(\text{DippNacNac})(\text{CP})(\text{diox})$ (approx. 86 mg, 0.15 mmol) in toluene (1 mL) was generated *in situ*, as in Section 2.4.1. To this toluene solution, $\text{Ge}(\text{DippNacNac})\text{Cl}$ (40 mg, 0.08 mmol) was added as a solid with stirring. NMR spectroscopy showed immediate formation of a single major product, $\text{Ge}(\text{DippNacNac})(\text{CP})$, which was not isolable due to its thermal instability.

¹H NMR (400 MHz, C₆D₆): δ (ppm) 5.08 (s, 1H, NacNac CH), 4.15 (sept, $^3J_{\text{H-H}} = 6.7$ Hz, 2H, Dipp CH(CH₃)₂), 3.42 (sept, Dipp CH(CH₃)₂)*, 1.56 (s, NacNac CH₃)*, 1.44 (d, $^3J_{\text{H-H}} = 6.7$ Hz, Dipp CH(CH₃)₂)*, 1.28 (d, $^3J_{\text{H-H}} = 6.8$ Hz, Dipp CH(CH₃)₂)*, 1.23 (d, $^3J_{\text{H-H}} = 6.9$ Hz, Dipp CH(CH₃)₂)*, 1.07 (d, $^3J_{\text{H-H}} = 6.8$ Hz, Dipp CH(CH₃)₂)*. * Some proton signals, include those in the aromatic region, could not be identified due to overlap with resonances arising from **2**.

³¹P{¹H} NMR (162 MHz, C₆D₆): δ (ppm) 106.4 (s, CP).

3.5.4 Synthesis of Sn(^{Dipp}NacNac)(CP) (**6**)

A solution of Mg(^{Dipp}NacNac)(CP)(diox) (approx. 92 mg, 0.16 mmol) in toluene (1 mL) was generated *in situ*, as in Section 2.4.1. To this toluene solution, Sn(^{Dipp}NacNac)Cl (82 mg, 0.14 mmol) was added as a solid, then stirred for 2 h. The solvent was removed, and the residue was extracted with hexane (5 mL) and filtered. The solution was concentrated and cooled to -35 °C for 18 h to form yellow crystals of Sn(^{Dipp}NacNac)(CP). Yield: 28 mg, 0.05 mmol, 34%. Anal. Calcd (%) for C₃₀H₄₁N₂SnP: C, 62.19; H, 7.13; N, 4.84. Found: C, 60.87; H, 7.35; N, 4.70.

¹H NMR (400 MHz, C₆D₆): δ (ppm) 7.18–7.09 (m, Dipp CH)*, 7.07 (d, $^3J_{\text{H-H}} = 2.1$ Hz, 1H, Dipp CH), 7.06 (d, $^3J_{\text{H-H}} = 2.1$ Hz, 1H, Dipp CH), 5.04 (s, 1H, NacNac CH), 4.12 (sept, $^3J_{\text{H-H}} = 6.7$ Hz, 2H, Dipp CH(CH₃)₂), 3.28 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 2H, Dipp CH(CH₃)₂), 1.60 (s, 6H, NacNac CH₃), 1.44 (d, $^3J_{\text{H-H}} = 6.7$ Hz, 6H, Dipp CH(CH₃)₂), 1.31 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, Dipp CH(CH₃)₂), 1.22 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 6H, Dipp CH(CH₃)₂), 1.11 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, Dipp CH(CH₃)₂).

¹³C{¹H} NMR (126 MHz, C₆D₆): δ (ppm) 166.34 (NacNac CNDipp), 145.49 (Dipp *ortho*-C), 142.65 (Dipp *ortho*-C), 142.31 (Dipp *ipso*-C), 136.07 (Dipp *ipso*-C), 126.80 (Dipp *para*-C), 124.67 (Dipp *meta*-C), 123.78 (Dipp *meta*-C), 100.59 (NacNac CH), 28.89 (Dipp C(CH₃)₂), 28.74 (Dipp C(CH₃)₂), 27.76 (Dipp C(CH₃)₂), 24.51 (Dipp C(CH₃)₂), 24.15 (Dipp C(CH₃)₂), 23.64 (NacNac CH₃) 23.18 (Dipp C(CH₃)₂).

³¹P{¹H} NMR (162 MHz, C₆D₆): δ (ppm) 122.4 (s, $^2J_{\text{P-Sn}} = 69.8$ Hz, CP).

¹¹⁹Sn NMR (186 MHz, C₆D₆): δ (ppm) -245.6 .

ATR-FTIR: 1321 cm⁻¹ (w, $\nu(\text{C}\equiv\text{P})$).

3.5.5 Synthesis of Au(IDipp)(CP) (7)

From $i\text{Pr}_3\text{SiOCP}$:

A solution of $\text{Mg}(\text{DippNacNac})(\text{CP})(\text{diox})$ (approx. 126 mg, 0.22 mmol) in toluene (1 mL) was generated *in situ*, as in Section 2.4.1. This toluene solution was added dropwise to a stirred solution of $\text{Au}(\text{IDipp})\text{Cl}$ (75 mg, 0.12 mmol) in toluene (1 mL). The reaction was stirred for 2 h and filtered through a glass paper filter. The solvent was removed to dryness, and the yellow solids were washed with hexane (3×2 mL). The resulting off-white solid was taken into toluene (2 mL), then layered with hexane at -35°C to afford off-white needles of $\text{Au}(\text{IDipp})(\text{CP})$. Yield: 41 mg, 0.07 mmol, 54%.

From **3**:

Dioxane (approx. 0.03 mL) was added to a suspension of $\{\text{Mg}(\text{DippNacNac})(\mu\text{-CP})\}_2$ (200 mg, 0.20 mmol) in toluene (2 mL). This was added dropwise to a suspension of $\text{Au}(\text{IDipp})\text{Cl}$ (250 mg, 0.40 mmol) in toluene (2 mL), and the resulting red suspension was stirred overnight at room temperature. The reaction mixture was filtered into a flask containing 30 mL of pentane. On standing for 2 h, $\text{Au}(\text{IDipp})(\text{CP})$ crystallizes as off-white needles. The supernatant can be evaporated and recrystallized from diethyl ether at -35°C to obtain a second crop as yellow blocks. (Occasionally an unidentified red impurity precipitates, this can be removed by recrystallization.) Yield: 191 mg, 0.30 mmol, 75%.

Anal. Calcd (%) for $\text{C}_{28}\text{H}_{36}\text{AuN}_2\text{P}$: C, 53.51; H, 5.77; N, 4.46. Found: 54.14; H, 5.87; N, 4.32.

^1H NMR (500 MHz, C_6D_6): $\delta(\text{ppm})$ 7.15 (m, 2H, Dipp *para*-CH), 7.01 (d, $^3J_{\text{H-H}} = 7.7$ Hz, 4H, Dipp *meta*-CH), 6.21 (s, 2H, IDipp CH), 2.49 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 4H, Dipp CH(CH₃)₂), 1.40 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 12H, Dipp CH(CH₃)₂), 1.04 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 12H, Dipp CH(CH₃)₂).

^{13}C NMR (126 MHz, C_6D_6): $\delta(\text{ppm})$ 247.70 (d, $^1J_{\text{C-P}} = 6.1$ Hz, CP), 193.02 (d, $^3J_{\text{C-P}} = 5.0$ Hz, IDipp CAu), 145.29 (Dipp *ortho*-C), 144.72 (Dipp *ortho*-C), 134.02 (Dipp *ipso*-C), 130.49 (Dipp *para*-C), 123.94 (Dipp *meta*-C), 122.57 (IDipp CH), 28.65 (Dipp CH(CH₃)₂), 24.45 (Dipp CH(CH₃)₂), 23.53 (Dipp CH(CH₃)₂).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): $\delta(\text{ppm})$ 84.1 (s, CP).

ATR-FTIR: 1342 cm^{-1} (m, $\nu(\text{C}\equiv\text{P})$).

Raman: 1350 cm^{-1} (s, $\nu(\text{C}\equiv\text{P})$).

3.5.6 Synthesis of Ni(SIDipp)(Cp)(CP) (8)

A solution of $\text{Mg}(\text{DippNacNac})(\text{CP})(\text{diox})$ (approx. 130 mg, 0.23 mmol) in toluene (1 mL) was generated *in situ*, as in Section 2.4.1. $\text{Ni}(\text{SIDipp})(\text{Cp})\text{Cl}$ (105 mg, 0.19 mmol) was added as a solid, and the mixture was stirred at room temperature for 4 hours. The mixture was filtered, and the solvent removed from the filtrate *in vacuo*. The residue was extracted with hexane (2 mL), which was then concentrated and stored at $-35\text{ }^{\circ}\text{C}$ for 1 day, yielding $\text{Ni}(\text{SIDipp})(\text{Cp})(\text{CP})$ as an off-white, microcrystalline solid. The crystals were isolated by filtration, and washed with cold hexane ($2 \times 0.5\text{ mL}$). Yield: 72 mg, 0.13 mmol, 68%. Anal. Calcd. (%) for $\text{C}_{33}\text{H}_{43}\text{N}_2\text{NiP}$: C, 71.11; H, 7.78; N, 5.03. Found: C, 71.53; H, 8.47; N, 4.77.

^1H NMR (400 MHz, C_6D_6): $\delta(\text{ppm})$ 7.26 (dd, $^3J_{\text{H-H}} = 8.6, 6.7\text{ Hz}$, 2H, Dipp *para*-CH), 7.20–7.16 (m, 4H, Dipp *meta*-CH), 4.75 (s, 5H, Cp C_5H_5), 3.55 (sept, $^3J_{\text{H-H}} = 6.7\text{ Hz}$, 4H, Dipp CH(CH₃)₂), 3.55 (s, 4H, SIDipp C_2H_4), 1.53 (d, $^3J_{\text{H-H}} = 6.7\text{ Hz}$, 12H, Dipp CH(CH₃)(CH₃)), 1.09 (d, $^3J_{\text{H-H}} = 6.7\text{ Hz}$, 12H, Dipp CH(CH₃)(CH₃)).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): $\delta(\text{ppm})$ 224.02 (d, $^1J_{\text{C-P}} = 10.0\text{ Hz}$, NiCP), 211.39 (s, SIDipp CNi), 147.91 (s, Dipp *para*-C), 138.03 (s, Dipp *ipso*-C), 129.56 (s, Dipp *ortho*-C), 124.67 (s, *meta*-C), 92.07 (s, Cp C_5H_5), 53.64 (s, SIDipp CH₂), 28.70 (s, Dipp CH(CH₃)₂), 26.83 (s, Dipp CH(CH₃)₂), 24.42 (s, Dipp CH(CH₃)₂).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): $\delta(\text{ppm})$ 181.2 (s, CP).

ATR-FTIR: 1307 cm^{-1} (m, $\nu(\text{C}\equiv\text{P})$).

3.5.7 Synthesis of Co(^{Dipp}PDI)(CP) (9)

From $^i\text{Pr}_3\text{SiOCP}$:

A solution of $\text{Mg}(\text{DippNacNac})(\text{CP})(\text{diox})$ (approx. 65 mg, 0.11 mmol) in toluene (1 mL) was generated *in situ*, as in Section 2.4.1. $\text{Co}(\text{DippPDI})\text{Cl}$ (33 mg, 0.06 mmol) was added as a solid, and the reaction mixture was stirred for 4 days. The solvent was removed, and the residue was washed with hexane ($2 \times 5\text{ mL}$) and then extracted with toluene (1.5 mL). After filtration, the resulting deep blue solution was concentrated and stored at $-35\text{ }^{\circ}\text{C}$ for 1 week to form blue crystals of $\text{Co}(\text{DippPDI})(\text{CP})$. The supernatant solution was concentrated and stored at $-35\text{ }^{\circ}\text{C}$ to yield a second crop of crystals. Yield: 17 mg, 0.03 mmol, 51%.

From **3**:

$\{\text{Mg}(\text{DippNacNac})(\mu\text{-CP})\}_2$ (150 mg, 0.15 mmol) and $\text{Co}(\text{DippPDI})\text{Cl}$ (178 mg, 0.31 mmol) were suspended in diethyl ether (10 mL). The dark blue mixture was stirred for 5 days, then filtered and washed with an additional 5 mL of ether. The dark residue was extracted with toluene (100 mL) into a glass-tapped J-Young ampoule (Schlenk flasks sealed with silicon grease do not provide a good enough seal for this extremely air sensitive compound), then stored at -80°C for 2 days to afford dark blue crystals of $\text{Co}(\text{DippPDI})(\text{CP})$. The supernatant was filtered off at -78°C , then concentrated at room temperature and stored at -80°C for 2 days to obtain a second crop. Yield: 123 mg, 0.21 mmol, 68%.

Due to its extreme air sensitivity, satisfactory elemental microanalysis of $\text{Co}(\text{DippPDI})(\text{CP})$ could not be obtained despite numerous attempts. In the presence of oxygen gas, $\text{Co}(\text{DippPDI})(\text{CP})$ immediately changes color in the solid state or in solution, affording a deep red metastable product that decomposes in air or under inert atmospheres. A single crystal X-ray diffraction experiment on poor-quality crystals of this oxidized product tentatively suggests it is a cobalt(III) peroxo cyaphido compound.

^1H NMR (400 MHz, C_6D_6): $\delta(\text{ppm})$ 9.76 (t, $^3J_{\text{H-H}} = 7.7$ Hz, 1H, pyridine *para*-CH), 7.51 (t, $^3J_{\text{H-H}} = 7.7$ Hz, 2H, Dipp *para*-CH), 7.36 (d, $^3J_{\text{H-H}} = 7.7$ Hz, 4H, Dipp *meta*-CH), 7.03 (d, $^3J_{\text{H-H}} = 7.7$ Hz, 2H, pyridine *meta*-CH), 3.10 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 4H, Dipp CH(CH₃)₂), 1.21 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 11H, Dipp CH(CH₃)₂), 1.04 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp CH(CH₃)₂), -0.23 (s, 6H, NCCH₃).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): $\delta(\text{ppm})$ 169.06 (imine CNDipp), 155.03 (Dipp *ipso*-C), 153.78 (Dipp *ortho*-C), 140.95 (Dipp *para*-C), 123.75 (Dipp *meta*-C), 123.60 (pyridine *meta*-C), 120.07 (pyridine *para*-C), 28.96 (Dipp CH(CH₃)₂), 24.11 (Dipp CH(CH₃)₂), 23.75 (Dipp CH(CH₃)₂), 22.22 (NCCH₃).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): $\delta(\text{ppm})$ 345.4 (s, CP).

ATR-FTIR: 1307 cm^{-1} (w, $\nu(\text{C}\equiv\text{P})$).

3.5.8 Synthesis of $\text{Rh}(\text{DippPDI})(\text{CP})$ (**10**)

From $^i\text{Pr}_3\text{SiOCP}$:

A solution of $\text{Mg}(\text{DippNacNac})(\text{CP})(\text{diox})$ (approx. 65 mg, 0.11 mmol) in toluene (1 mL) was generated *in situ*, as in Section 2.4.1. $\text{Rh}(\text{DippPDI})\text{Cl}$ (62 mg, 0.10 mmol) was added as a solid, and the reaction

mixture was stirred at room temperature for 3 days. The mixture was filtered, and the solvent removed from the filtrate *in vacuo*. The residue was washed with hexane (3×1 mL), then extracted with toluene (1 mL). The dark green solution was concentrated *in vacuo*, then layered with hexane and stored at -35 °C for 3 days, yielding $\text{Rh}(\text{DippPDI})(\text{CP})$ as green-black crystals. The crystals were isolated by filtration, and washed with cold hexane (2×0.5 mL). Yield: 14 mg, 0.02 mmol, 22%.

From **3**:

$\{\text{Mg}(\text{DippNacNac})(\mu\text{-CP})\}_2$ (50 mg, 0.05 mmol) and $\text{Rh}(\text{DippPDI})\text{Cl}$ (62 mg, 0.10 mmol) were suspended in diethyl ether (5 mL). The dark green mixture was stirred for 3 days, then filtered and washed with an additional 1 mL of ether. The dark residue was extracted with toluene (10 mL), then layered with hexane (30 mL) and stored at -80 °C for 7 days to afford dark green crystals of $\text{Rh}(\text{DippPDI})(\text{CP})$. The crystals were isolated by filtration at -78 °C. Yield: 36 mg, 0.06 mmol, 57%.

Anal. Calcd. (%) for $\text{C}_{34}\text{H}_{43}\text{N}_3\text{PRh}$: C, 65.07; H, 6.91; N, 6.70. Found: C, 63.69; H, 5.91; N, 5.65.

^1H NMR (400 MHz, C_6D_6): δ (ppm) 7.48 (t, $^3J_{\text{H-H}} = 7.9$, 1H, pyridine *para*-CH), 7.26–7.22 (m, 6H, Dipp *para/meta*-CH), 6.85 (d, $^3J_{\text{H-H}} = 7.9$, 2H, pyridine *meta*-CH), 3.28 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 4H, Dipp CH(CH₃)₂), 1.53 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp CH(CH₃)₂), 1.09 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp CH(CH₃)₂), 1.09 (s, 6H, imine NCCH₃).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): δ (ppm) 264.15 (dd, $^1J_{\text{C-Rh}} = 54.8$ Hz, $^1J_{\text{C-P}} = 22.9$ Hz, RhCP), 166.98 (imine NCCH₃), 156.34 (Dipp *ipso*-C), 146.30 (Dipp *ortho*-C), 140.63 (Dipp *para*-C), 127.01 (Dipp *meta*-C), 124.61 (pyridine *meta*-C), 123.59 (pyridine *ortho*-C), 121.61 (pyridine *para*-C), 28.68 (Dipp CH(CH₃)₂), 24.05 (Dipp CH(CH₃)₂), 23.88 (Dipp CH(CH₃)₂), 17.41 (imine NCCH₃).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): δ (ppm) 251.4 (d, $^2J_{\text{P-Rh}} = 6.0$ Hz, CP).

Raman: 1334 cm^{-1} (m, $\nu(\text{C}\equiv\text{P})$).

3.5.9 Synthesis of $\text{Zn}(\text{DippNacNac})(\text{CP})$ (**11**)

A suspension of $\{\text{Mg}(\text{DippNacNac})(\mu\text{-CP})\}_2$ (20 mg, 0.02 mmol) in benzene (0.5 mL) was added dropwise to a stirred suspension of $\{\text{Zn}(\text{DippNacNac})(\mu\text{-Cl})\}_2$ (19 mg, 0.02 mmol) in benzene (0.5 mL). The off-white suspension was stirred overnight, then filtered. The solvent was removed *in vacuo*, and the residue

was extracted with toluene (0.5 mL). Layering with hexane (3 mL) at $-35\text{ }^{\circ}\text{C}$ results in the precipitation of $\text{Zn}(\text{DippNacNac})(\text{CP})$ as an off-white powder after 2 days. Yield: 6 mg, 0.01 mmol, 29%.

^1H NMR (400 MHz, C_6D_6): $\delta(\text{ppm})$ 7.14–7.12 (m, 6H, Dipp **CH**), 4.95 (s, 1H, NacNac **CH**), 3.10 (sept, $^3J_{\text{H-H}} = 6.9\text{ Hz}$, 4H, Dipp **CH**(CH_3)₂), 1.63 (s, 6H, NacNac **CH**₃), 1.41 (d, $^3J_{\text{H-H}} = 6.9\text{ Hz}$, 12H, Dipp **CH**(CH_3)₂), 1.16 (d, $^3J_{\text{H-H}} = 6.9\text{ Hz}$, 12H, Dipp **CH**(CH_3)₂).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): $\delta(\text{ppm})$ 222.23 (d, $^1J_{\text{C-P}} = 5.9\text{ Hz}$, **CP**), 169.03 (NacNac **CNDipp**), 143.62 (Dipp *ortho*-**C**), 141.70 (Dipp *ipso*-**C**), 126.65 (Dipp *para*-**C**), 123.99 (Dipp *meta*-**C**), 95.80 (NacNac **CH**), 28.57 (Dipp **CH**(CH_3)₂), 24.93 (Dipp **CH**(CH_3)₂), 23.31 (Dipp **CH**(CH_3)₂).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): $\delta(\text{ppm})$ 140.7 (s, **CP**).

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Properties of the κ C-Cyaphido Ligand

Abstract. The ligand properties of the cyaphide ion in the terminal, end-on κ C coordination mode are determined in a comparative study of gold(I) IDipp complexes and group 9 ^{Dipp}PDI complexes. Using this approach, the σ donor and π acceptor properties of the cyaphido ligand are deconvoluted. In order to provide illustrative points of comparison, analogous metal complexes bearing various strong-field ligands are also synthesized and analyzed using the same approach.

4.1 Evaluating ligand donor/acceptor abilities

4.1.1 The Tolman Electronic Parameter

In metal carbonyls, backdonation of electron density from a metal center into the $\text{C}\equiv\text{O}$ π^* orbitals results in a reduction in the frequency of the $\text{C}\equiv\text{O}$ vibrational stretching modes, the magnitude of which depends on the donor/acceptor abilities of the metal and of other coordinated ligands. This effect is used to quantify the electron releasing and withdrawing abilities of ligands (most notably phosphines) by the A_1 -symmetric carbonyl stretching frequency of their nickel(0) tricarbonyl complexes, the well-known Tolman Electronic Parameter (TEP; Figure 4.1).^[1]

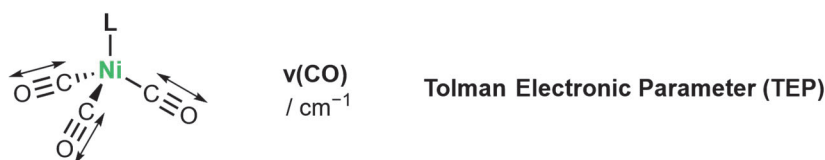


Figure 4.1. The Tolman Electronic Parameter, based on carbonyl vibrational stretching frequencies.

While this has been broadly applied to a large number of ligands, it is intrinsically limited by the synthetic accessibility of their nickel(0) tricarbonyl complexes. Alternative metrics for quantifying ligand donor/acceptor abilities have been developed based on other ancillary reporter ligands.

4.1.2 The Huynh Electronic Parameter

N-heterocyclic carbenes are strong σ donor and moderate to weak π acceptor ligands. The ^{13}C chemical shift of the carbenoid carbon atom is sensitive to the strength of the $\text{M}-\text{C}$ σ bond, and consequently to the σ donor strength of *trans*-coordinated co-ligands. This concept was introduced as the Huynh Electronic Parameter (HEP) for quantifying ligand σ donor abilities on square planar palladium(II) bromide NHC complexes (Figure 4.2).^[2] Importantly, the dominance of σ bonding in these palladium(II) NHC complexes results in the HEP being insensitive to π donor/acceptor effects.

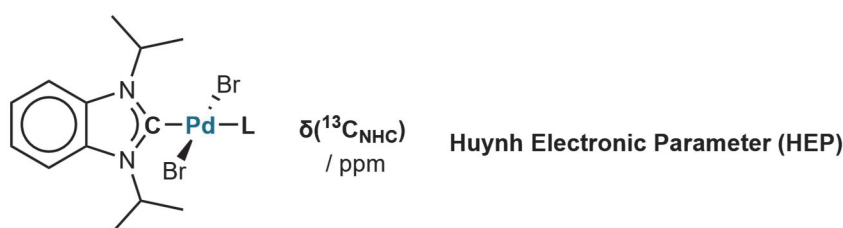


Figure 4.2. The Huynh Electronic Parameter, based on NHC ^{13}C NMR chemical shifts.

4.1.3 Pyridine-2,6-diimine ligands

Pincer ligands based on pyridine-2,6-diimine (PDI) scaffolds have been used extensively to stabilize transition metal complexes in formally low oxidation states. This is not just due to the steric bulk of *N*-substituents; in many cases the redox non-innocence of the PDI ligand backbone plays a crucial role. The PDI backbone is easily chemically reduced by the population of its low-lying π^* orbitals, which also give rise to substantial π accepting ligand character. These π^* orbitals are antibonding with respect to the pyridine and imine $\text{C}=\text{N}$ π bonds, but bonding with respect to the $\text{C}=\text{C}$ π bonds. This results in measurable changes to the solid-state bond metrics of the PDI backbone upon ligand reduction or π backdonation, which is summarized in a parameter, $\delta(\text{PDI})$, defined as the difference in average $\text{C}-\text{C}$ and $\text{C}-\text{N}$ bond lengths (Figure 4.3).^[3]

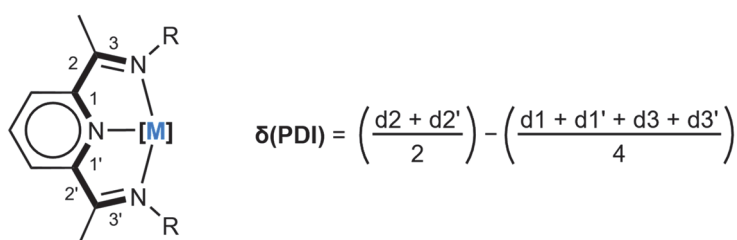


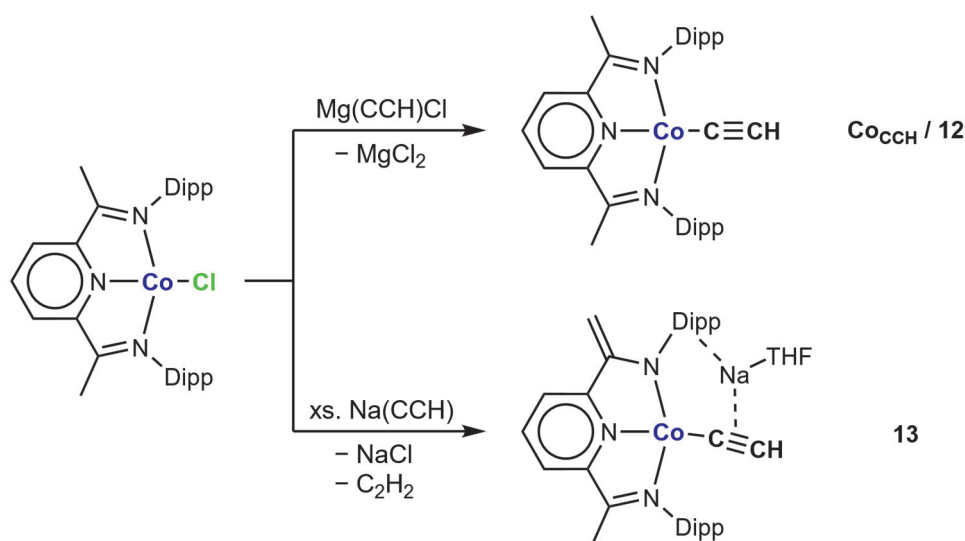
Figure 4.3. The $\delta(\text{PDI})$ structural parameter, based on solid-state bond metrics of the PDI backbone.

4.2 Synthesis of group 9 Dip^{PDI} complexes with strong field ligands

4.2.1 Synthesis of $\text{Co}(\text{Dip}^{\text{PDI}})\text{X}$ and $[\text{Co}(\text{Dip}^{\text{PDI}})\text{L}]^+$ complexes

The $\delta(\text{PDI})$ value of $\text{Co}(\text{Dip}^{\text{PDI}})(\text{CP})$ ($\text{Co}_{\text{CP}}/\mathbf{9}$)* should be sensitive to the π accepting ability of the cyaphido ligand, though it is uninformative on its own without meaningful points of comparison. Therefore, $\text{Co}(\text{Dip}^{\text{PDI}})\text{X}$ and $[\text{Co}(\text{Dip}^{\text{PDI}})\text{L}]^+$ complexes (Co_{X} and Co_{L}^+) bearing X and L ligands of varying π accepting ability were synthesized and characterized.

The acetylide complex $\text{Co}(\text{Dip}^{\text{PDI}})(\text{CCH})$ ($\text{Co}_{\text{CCH}}/\mathbf{12}$) was prepared by the reaction of Co_{Cl} with one equivalent of ethynylmagnesium chloride. Co_{CCH} is purple, and has a signals corresponding to the acetylide ligand in its ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra at 2.27 ppm and 132.24 ppm respectively. A different product, the sodium cobaltate complex $\text{Na}(\text{THF})\text{Co}(\text{Dip}^{\text{PIEA}})(\text{CCH})$ ($\mathbf{13}$; PIEA = pyridine-2-imine-6-enamine), forms when an excess of sodium acetylide is used instead of a Grignard reagent due to the deprotonation of the Dip^{PDI} ligand backbone (Scheme 4.1).



Scheme 4.1. Synthesis of the cobalt acetylide complex Co_{CCH} and sodium cobaltate complex $\mathbf{13}$.

The solid-state structure of Co_{CCH} is as expected, with a C1–C2 bond length of 1.192(4) Å, a pyridine–cobalt $\text{N}_{\text{py}}\text{–Co}$ bond length of 1.812(2) Å and Dip^{PDI} C–C and C–N bond lengths that give a $\delta(\text{PDI})$ value of 0.098(7). The structure of $\mathbf{13}$ has an asymmetric Dip^{PIEA} ligand, and a sodium atom coordinated by a THF molecule and by acetylide and arene π interactions (Figure 4.4).

* In this chapter, complexes of the type $\text{M}(\text{Dip}^{\text{PDI}})(\text{X})$ and $[\text{M}(\text{Dip}^{\text{PDI}})(\text{L})]^+$ are denoted as M_{X} and M_{L}^+ , respectively, in addition to assigned compound numbers.

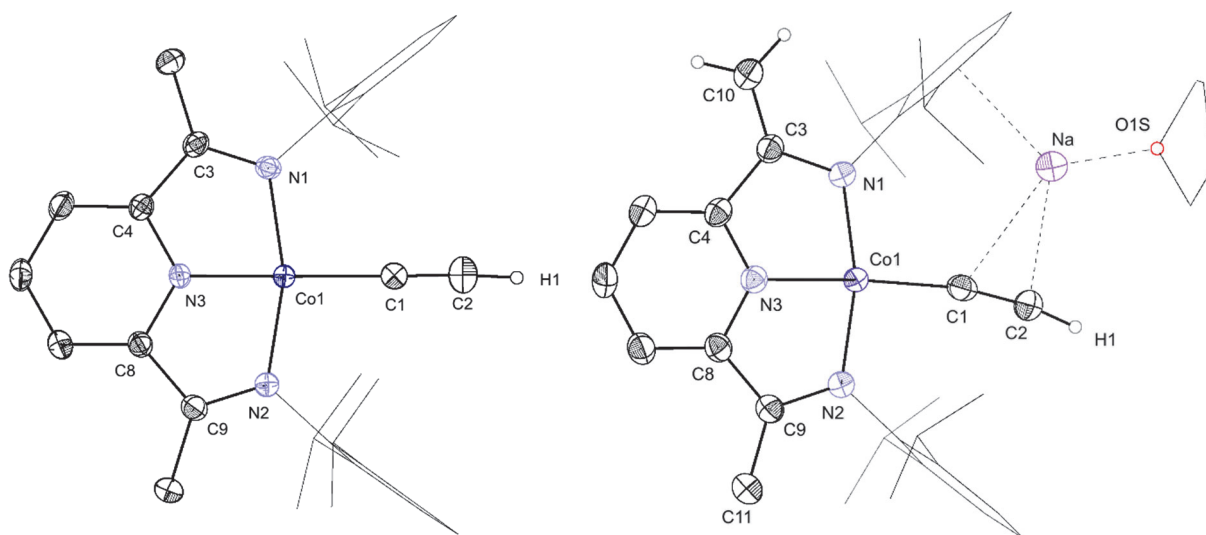
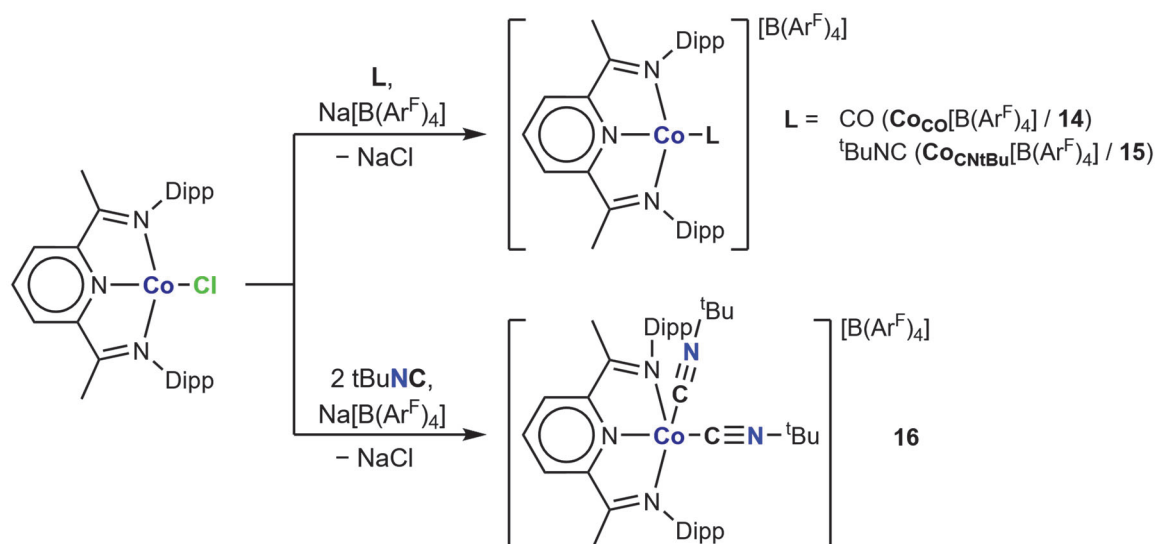


Figure 4.4. Solid-state structures of **Co_{CCH}** (left) and **13** (right). Anisotropic displacement ellipsoids set at 50% probability. Some hydrogen atoms are omitted for clarity. Dipp and THF groups are depicted as wireframes.

Cationic cobalt complexes of L ligands can be synthesized from **Co_{Cl}** by halide abstraction. The reaction of **Co_{Cl}** with $\text{Na}[\text{B}(\text{Ar}^{\text{F}})_4]$ ($\text{Ar}^{\text{F}} = 3,5\text{-bis(trifluoromethyl)phenyl}$) in 1,2-difluorobenzene (1,2-DFB) under a carbon monoxide atmosphere affords the carbonyl complex $[\text{Co}^{\text{(DippPDI)}}(\text{CO})][\text{B}(\text{Ar}^{\text{F}})_4]$ (**Co_{Co}** $[\text{B}(\text{Ar}^{\text{F}})_4]$ / **14**). **Co_{Co}⁺** is blue, and has a $\text{C}\equiv\text{O}$ stretching frequency of 2000 cm^{-1} . The blue *tert*-butyl isocyanide complex $[\text{Co}^{\text{(DippPDI)}}(\text{CN}^t\text{Bu})][\text{B}(\text{Ar}^{\text{F}})_4]$ (**Co_{CNTBu}** $[\text{B}(\text{Ar}^{\text{F}})_4]$ / **15**) can be synthesized in a similar way, by treating a mixture of **Co_{Cl}** and $\text{Na}[\text{B}(\text{Ar}^{\text{F}})_4]$ with $^t\text{BuNC}$, though if two equivalents are used, the diisocyanide complex $[\text{Co}^{\text{(DippPDI)}}(\text{CN}^t\text{Bu})_2][\text{B}(\text{Ar}^{\text{F}})_4]$ (**16**) results instead (Scheme 4.2).



Scheme 4.2. Synthesis of the cobalt complexes **Co_{Co}** $[\text{B}(\text{Ar}^{\text{F}})_4]$, **Co_{CNTBu}** $[\text{B}(\text{Ar}^{\text{F}})_4]$, and **16**.

The structures of **14**–**16** were determined by X-ray diffraction. **Co**_{Co}[B(Ar^F)₄] has a C1–O1 bond length of 1.129(4) Å, a N_{py}–Co bond length of 1.847(2) Å, and a δ (PDI) value of 0.144(7). **Co**_{CNTBu}[B(Ar^F)₄] has a isocyanide C1–N4 bond length of 1.154(3) Å, a N_{py}–Co bond length of 1.876(2) Å, and a δ (PDI) value of 0.121(4). **16** has isocyanide C–N bond lengths of 1.145(3) and 1.147(3) Å (Figure 4.5).

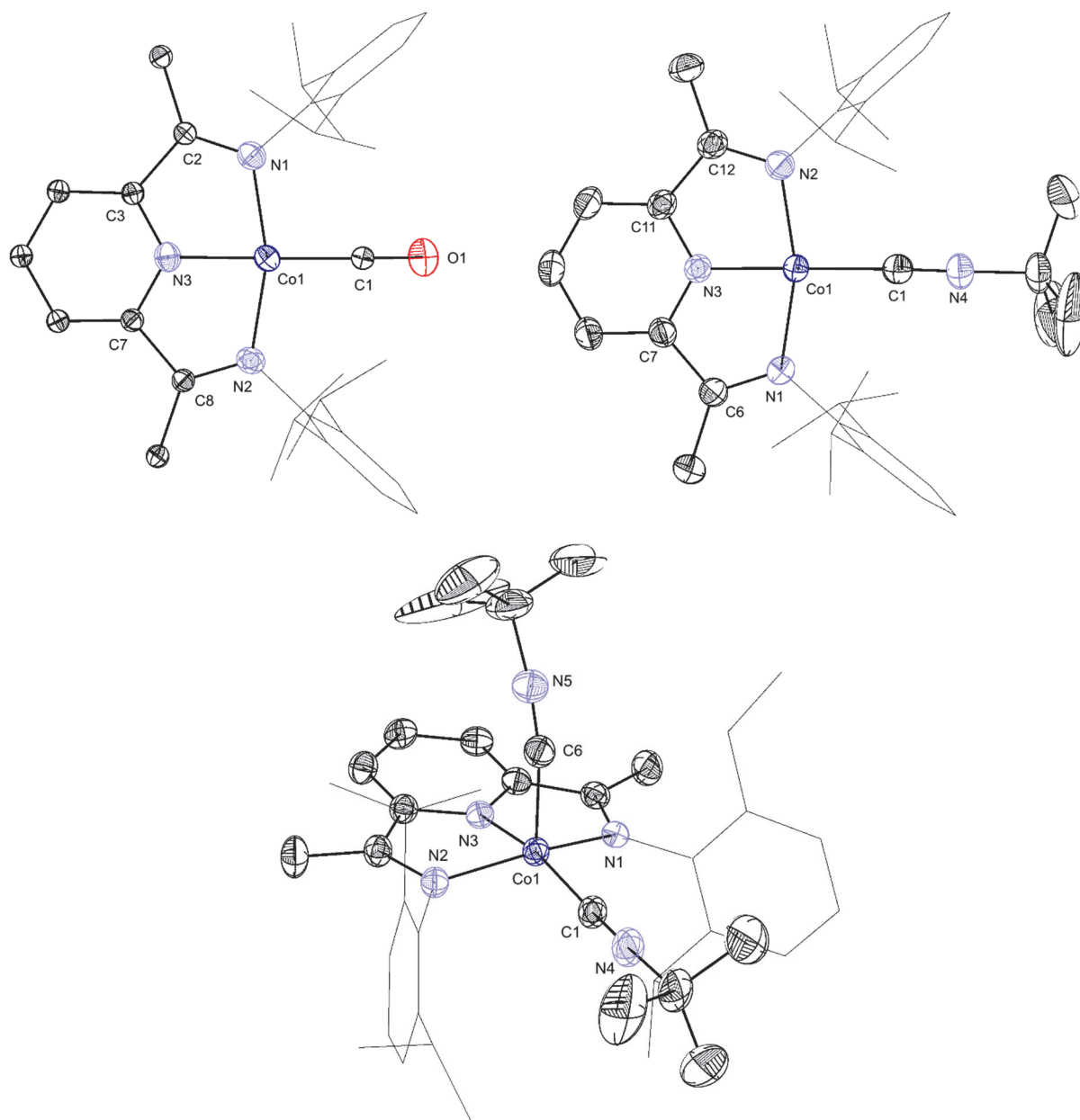


Figure 4.5. Solid-state structures of **Co**_{Co}[B(Ar^F)₄] (top left), **Co**_{CNTBu}[B(Ar^F)₄] (top right), and **16** (bottom). Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms and [B(Ar^F)₄][−] counterions are omitted for clarity. Dipp groups are depicted as wireframes.

Attempts to target the cyanide complex Co(^{Dipp}PDI)(CN) (**Co**_{CN}) were unsuccessful. The reaction of Co(^{Dipp}PDI)Cl₂ with NaCN was previously shown to result in the cobalt(III) cyanide complex

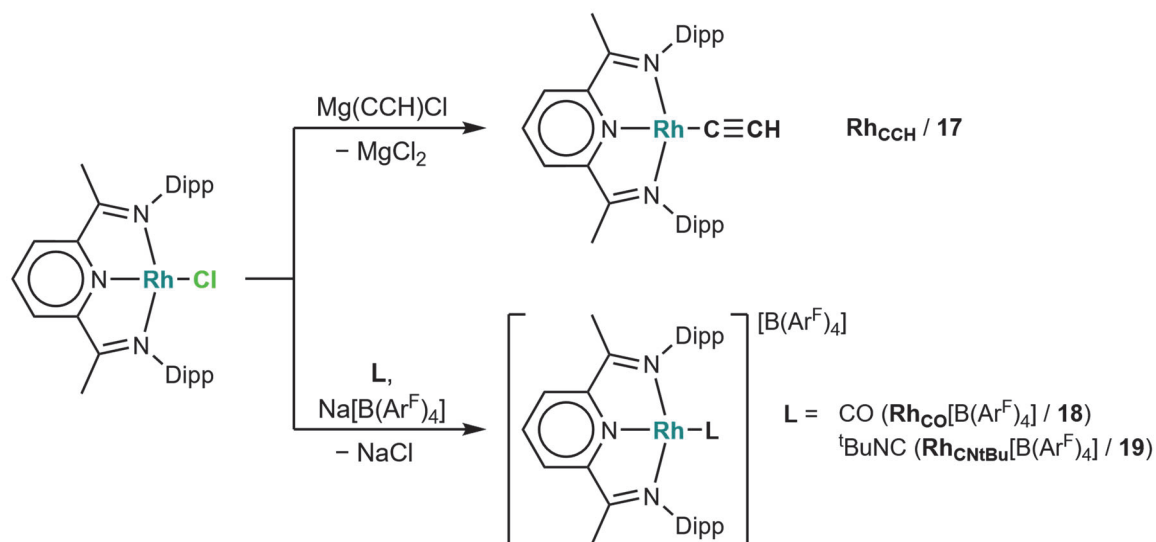
$\text{Co}(\text{DippPDI})(\text{CN})_3$ due to redox disproportionation; a similar disproportionation reaction may be occurring here. Alternatively, the basicity of the cyanide ion may lead to deprotonation of the DippPDI backbone (as seen for **13**), opening up another decomposition pathway.

4.2.2 Synthesis of $\text{Rh}(\text{DippPDI})\text{X}$ and $[\text{Rh}(\text{DippPDI})\text{L}]^+$ complexes

Rhodium(I) complexes Rh_X and Rh_L^+ with π accepting X or L ligands were synthesized using the same methods as for the lighter cobalt analogs.

The rhodium(I) acetylide complex $\text{Rh}(\text{DippPDI})(\text{CCH})$ (Rh_{CCH} / **17**) was prepared by salt metathesis from Rh_{Cl} and ethynylmagnesium chloride (Scheme 4.3). The acetylido ligand appears in its ^1H NMR spectrum as a doublet at 3.03 ppm ($^3J_{\text{H-Rh}} = 1.3$ Hz), and in its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum as doublets at 123.49 ppm ($^2J_{\text{C-Rh}} = 11.3$ Hz) and 114.28 ppm ($^1J_{\text{C-Rh}} = 60.6$ Hz).

Carbonyl ($\text{Rh}_{\text{CO}}[\text{B}(\text{Ar}^{\text{F}})_4]$ / **18**), and isocyanide ($\text{Rh}_{\text{CNtBu}}[\text{B}(\text{Ar}^{\text{F}})_4]$ / **19**) complexes were also prepared from Rh_{Cl} , using $\text{Na}[\text{B}(\text{Ar}^{\text{F}})_4]$ as a halide abstraction reagent (Scheme 4.3). Rh_{CO}^+ has a $^{13}\text{C}\{^1\text{H}\}$ signal at 187.42 ppm ($^1J_{\text{C-Rh}} = 77.2$ Hz) corresponding to the carbonyl carbon atom, and a band at 2026 cm^{-1} for the $\text{C}\equiv\text{O}$ vibrational stretching mode. The isocyanide ligand in $\text{Rh}_{\text{CNtBu}}^+$ appears in its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum as a doublet at 178.60 ppm ($^1J_{\text{C-Rh}} = 43.8$ Hz).



Scheme 4.3. Synthesis of rhodium(I) acetylide (Rh_{CCH}), carbonyl ($\text{Rh}_{\text{CO}}[\text{B}(\text{Ar}^{\text{F}})_4]$), and isocyanide ($\text{Rh}_{\text{CNtBu}}[\text{B}(\text{Ar}^{\text{F}})_4]$) complexes.

As with the cobalt system, the rhodium(I) cyanide complex $\text{Rh}^{(\text{DippPDI})}(\text{CN})$ (**Rh_{CN}**) could not be obtained. Both metathesis reactions of **Rh_{Cl}** or **Rh_{OMe}** with cyanide salts or Me_3SiCN , and ligand substitution reactions of **Rh_{C₂H₄}** $[\text{B}(\text{Ar}^{\text{F}})_4]$ or **Rh_{CO}** $[\text{B}(\text{Ar}^{\text{F}})_4]$ with $[\text{NBu}_4]\text{CN}$ resulted in intractable mixtures of products including free ^{Dipp}PDI ligand.

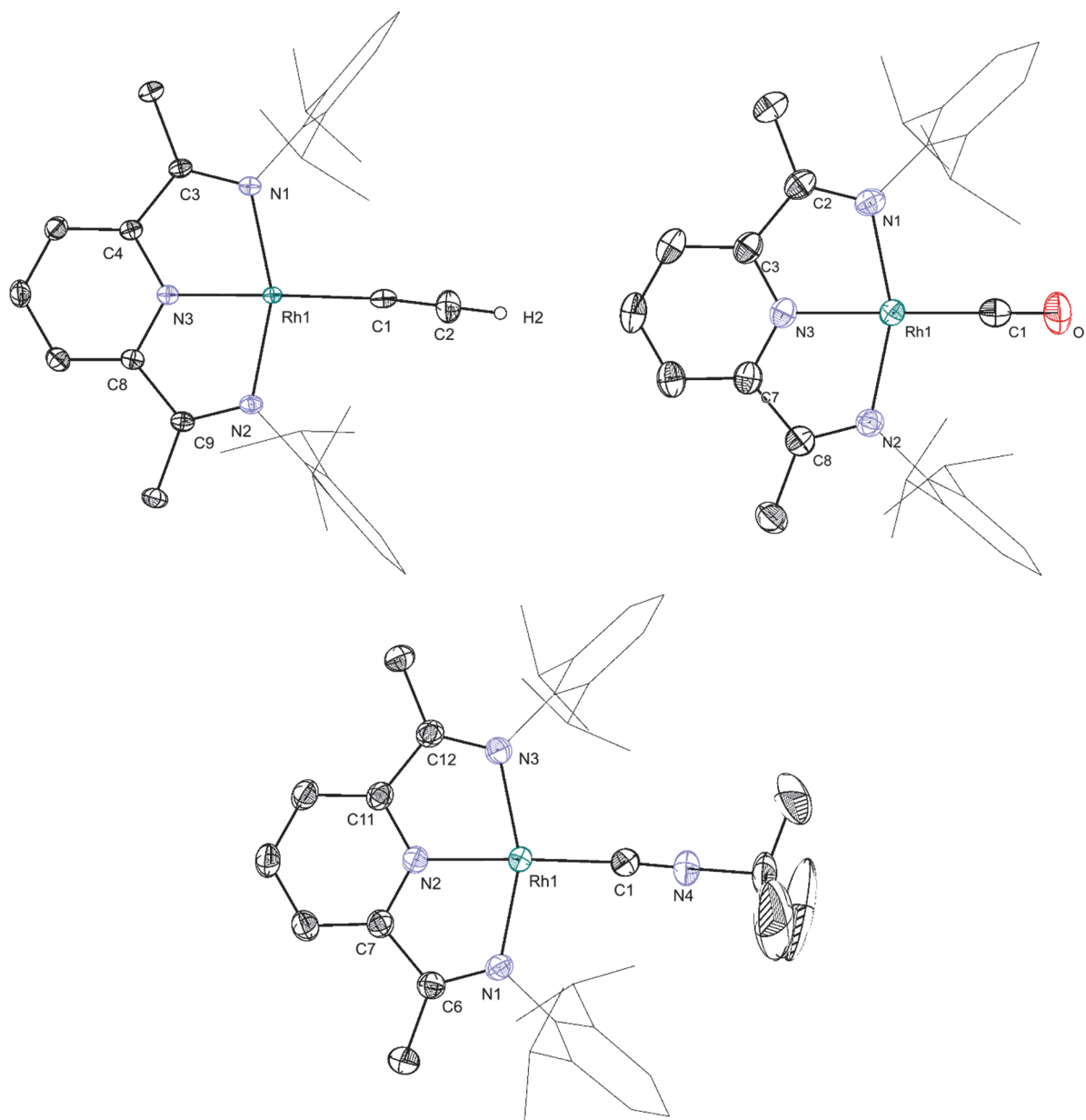


Figure 4.6. Solid state structures of **Rh_{CCH}** (top left), **Rh_{CO}** $[\text{B}(\text{Ar}^{\text{F}})_4]$ (top right), and **Rh_{CNtBu}** $[\text{B}(\text{Ar}^{\text{F}})_4]$ (bottom). Anisotropic displacement ellipsoids set at 50% probability. Some hydrogen atoms and $[\text{B}(\text{Ar}^{\text{F}})_4]^-$ counterions are omitted for clarity. Dipp groups are depicted as wireframes.

The solid-state structures of **Rh_{CCH}**, **Rh_{CO}** $[\text{B}(\text{Ar}^{\text{F}})_4]$, and **Rh_{CNtBu}** $[\text{B}(\text{Ar}^{\text{F}})_4]$ were determined by X-ray crystallography (Figure 4.6). **Rh_{CCH}** has an acetylide C1–C2 bond length of 1.188(3) Å, a $\text{N}_{\text{py}}\text{--Rh}$ bond length of 1.926(2) Å and a $\delta(\text{PDI})$ value of 0.124(2). **Rh_{CO}⁺** has a carbonyl C1–O1 bond length of

1.135(3) Å, a N_{py} –Rh bond length of 1.969(2) Å and a $\delta(PDI)$ value of 0.161(3). $\mathbf{Rh}_{CNEtBu}^+$ has a isocyanide C1–N4 bond length of 1.150(3) Å, N_{py} –Rh bond length of 1.942(3) Å and a $\delta(PDI)$ value of 0.152(3).

In addition, the structures of several literature-known complexes ($\mathbf{Rh}_{Cl}$,^[4] $\mathbf{Rh}_{Me}$,^[5] and $\mathbf{Rh}_{C_2H_4}[B(Ar^F)_4]$ ^[6]) were measured by X-ray crystallography (Figure 4.7). $\mathbf{Rh}_{Cl}$ has a N_{py} –Rh bond length of 1.898(4) Å and a $\delta(PDI)$ value of 0.108(6), $\mathbf{Rh}_{Me}$ has a N_{py} –Rh bond length of 1.936(3) Å and a $\delta(PDI)$ value of 0.110(6), and $\mathbf{Rh}_{C_2H_4}^+$ has a N_{py} –Rh bond length of 1.960(2) Å, and a $\delta(PDI)$ value of 0.152(3).

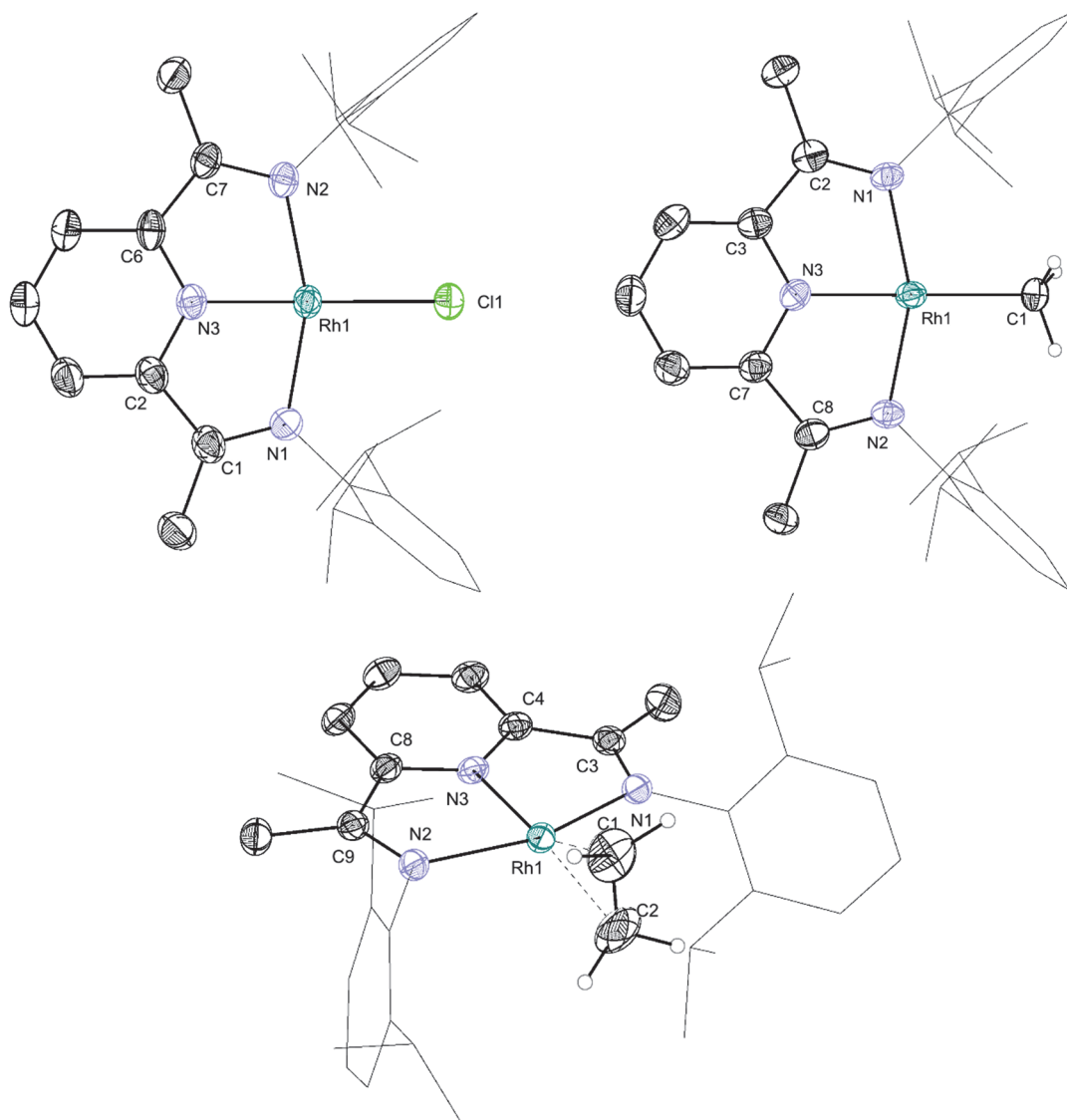


Figure 4.7. Solid-state structures of $\mathbf{Rh}_{Cl}$ (top left), $\mathbf{Rh}_{Me}$ (top right), and $\mathbf{Rh}_{C_2H_4}[B(Ar^F)_4]$ (bottom). $\mathbf{Rh}_{Cl}$ and $\mathbf{Rh}_{Me}$ crystallize with two distinct molecules per asymmetric unit, only one of which is shown for clarity. Anisotropic displacement ellipsoids set at 50% probability. Some hydrogen atoms, $[B(Ar^F)_4]^-$ counterions, and co-crystallized solvent molecules are omitted for clarity. Dipp groups are depicted as wireframes.

4.3 Determining the donor/acceptor properties of the κ C-cyaphido ligand

4.3.1 Theoretical comparison to isolobal congeners

The cyaphide ion (CP^-), the cyanide ion (CN^-) and the acetylide ion (CCH^-) are conceptually related by the isolobal analogy (see Section 1.3). While these sp -hybridized carbanions are indeed isolobal, the relative energies of their frontier orbitals differ (Figure 4.8).

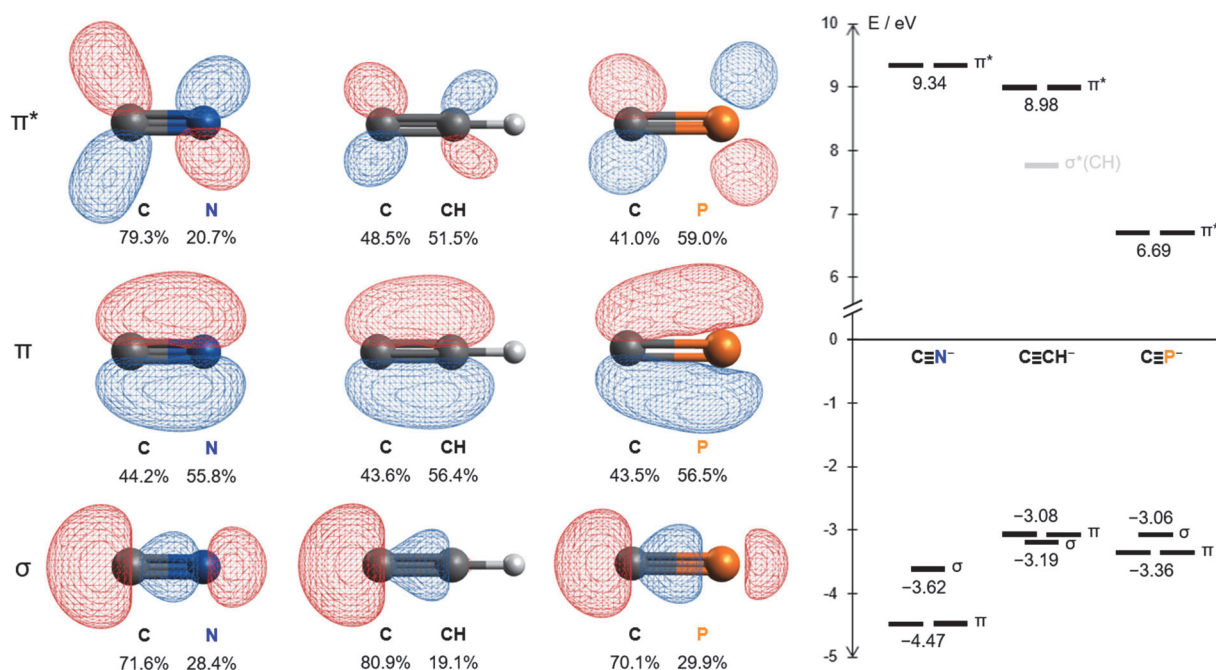


Figure 4.8. Frontier orbitals of the cyanide, acetylide, and cyaphide ions, and their Löwdin reduced populations.

The cyanido ligand is an archetypical strong field ligand due to its π accepting ability, though acetylide ligands are considered borderline π donors or acceptors. This can be rationalized by considering the relative energies of their π orbitals. While their π^* antibonding orbitals are similar in energy (CN^- : 9.34 eV; CCH^- : 8.98 eV), the $\text{C}\equiv\text{C}$ π orbitals of the acetylide ion are appreciably higher in energy when compared to the $\text{C}\equiv\text{N}$ π orbitals of the cyanide ion (CN^- : -4.47 eV; CCH^- : -3.19 eV). The relatively poor interatomic p-orbital overlap in the $2\text{p}-3\text{p}$ π bonds of the cyaphide ion result in π^* antibonding orbitals that are very low in energy (CP^- : 6.69 eV), though the $\text{C}\equiv\text{P}$ π bonding orbitals are similar in energy to those of the acetylide ion (CP^- : -3.36 eV). The cyaphide σ orbital is similar in energy to the corresponding σ orbitals of the acetylide and cyanide ions (CN^- : -3.62 eV; CCH^- : -3.19 eV; CP^- : -3.06 eV). Calculated HOMO energies for the three ions are in agreement with experimental and/or calculated electron affinities for their neutral radicals, $\text{CN}^\bullet$, $\text{CCH}^\bullet$, and $\text{CP}^\bullet$.^[7-9]

The other major difference in the frontier orbitals of these ions is their polarization. The significant polarization of the cyanide $C\equiv N$ π^* orbitals toward the carbon atom results in much better overlap with metal d-orbitals in the κC coordination mode than in the κN coordination mode, explaining the higher field strength of the cyanido ligand in the former (see Section 1.1.2). Due to the lower electronegativity of phosphorus relative to carbon, the $C\equiv P$ π^* antibonding orbitals have smaller carbon-centered lobes than for the cyanide ion.

4.3.2 Determining σ donor ability: gold(I) NHC complexes

While the Huynh Electronic Parameter is defined for square planar platinum(II) complexes, the carbenoid ^{13}C chemical shifts ($^{13}C_{NHC}$) in linear gold(I) NHC complexes also follow a similar trend. Many $Au(IDipp)X$ ($\mathbf{Au}_X$) and $[Au(IDipp)L]^+$ ($\mathbf{Au}_L^+$) complexes are known in the literature. When X or L is a weaker σ donor, the IDipp carbenoid ^{13}C chemical shifts are relatively low (e.g. $\mathbf{Au}_{NCMe}^+$: $^{13}C_{NHC} = 166.0$ ppm); conversely if X or L is a strong σ donor, the chemical shift is high (e.g. $\mathbf{Au}_{BPin}^-$: $^{13}C_{NHC} = 216.7$ ppm). This trend is also reflected in the solid-state $C_{NHC}-Au$ bond lengths, albeit with larger errors associated with crystallographically determined bond metrics (Table 4.1).

Table 4.1. $^{13}C_{NHC}$ NMR shifts and $C_{NHC}-Au$ bond lengths for $\mathbf{Au}_X$ and $\mathbf{Au}_L^+$ complexes.

L	$^{13}C_{NHC}$ / ppm	$C_{NHC}-Au$ / Å	Ref.
CP^-	193.0	2.035(6)	10 / Section 3.2.1
$(\mu-CP)\{Ni(^{Me}IPr)_2\}^-$	198.5	2.024(3)	11 / Section 5.2.2
$(\mu-CP)\{Rh(Cp^*)(PMe_3)\}^-$	195.6	2.026(4)	11 / Section 5.2.3
$(\mu_3-CP)\{Rh(Cp^*)(PMe_3)\}\{W(CO)_5\}^-$	193.9	2.025(4)	11 / Section 5.2.4
CN^-	186.2	2.00(2)	12
$(\mu-CN)(BCF)^-$	183.1	2.005(3)	11 / Section 5.2.1
$CCPh^-$	190.9	2.018(7)	12
$BPin^-$	216.7	2.084(4)	13
H^-	204.9	2.045(3)	14
Me^-	201.4	2.038(5)	15
OH^-	171.9	1.935(9)	12
Cl^-	175.1	1.9394(1)	16, 17

CO	174.6	1.971(5)	18
CNXyl	178.6	–	19
IDipp	184.2	2.025(7)	20
P ^t Bu ₃	191.9	2.045(7)	20
PPh ₃	188.2	2.039(5)	20
Py	167.1	1.961(7)	21
MeCN	166.0	1.974(2)	21

Energy Decomposition Analysis using Natural Orbitals for Chemical Valence (EDA-NOCV) was used to examine Au–X bonding for several **Au_x** complexes, using the Extended Transition State (ETS) method to determine the σ and π contributions to the total orbital interaction energy (Table 4.2).

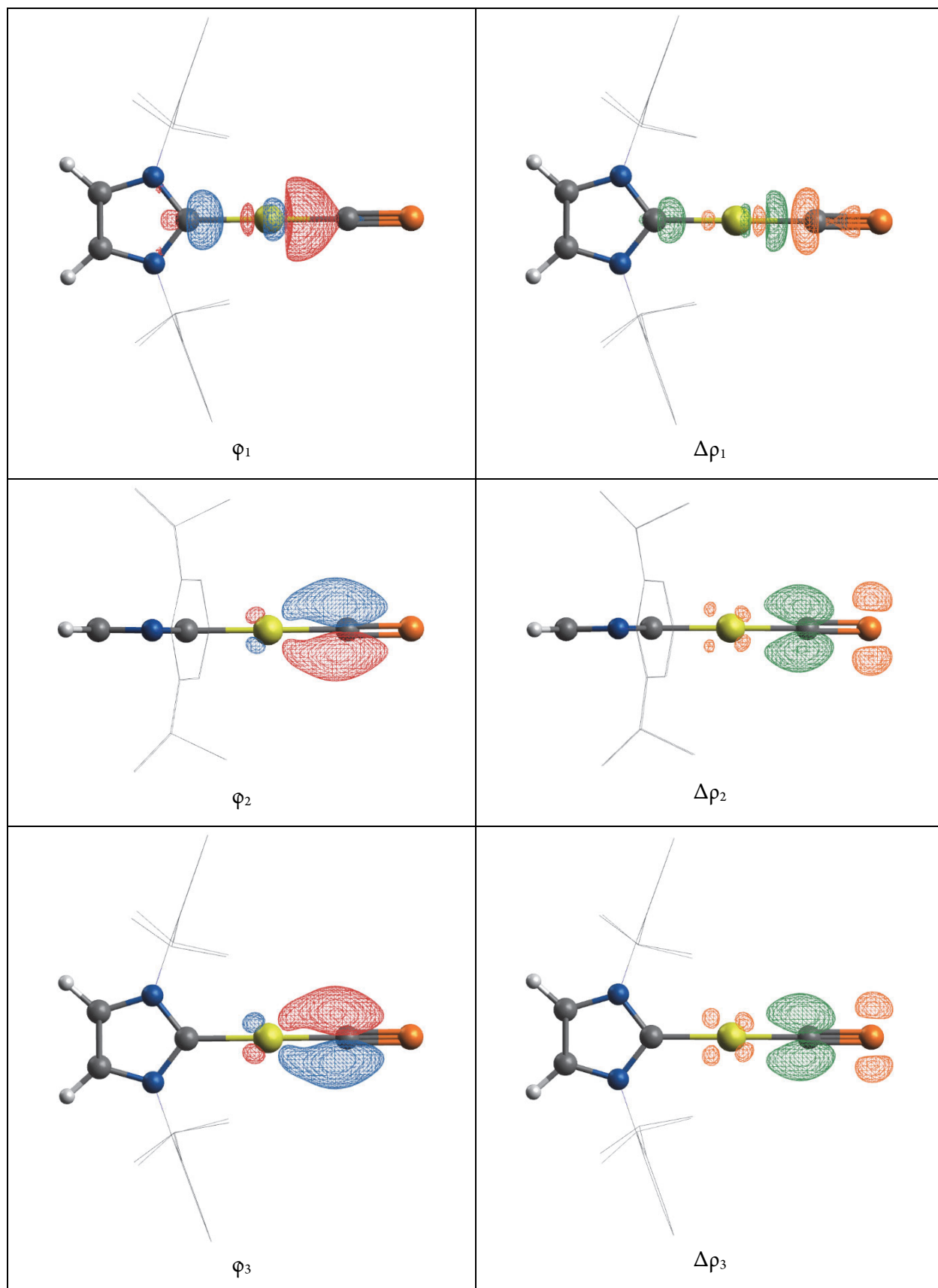
Table 4.2. Summary of EDA-NOCV analysis of the Au–X bond in **Au_x**, including ETS-NOCV energies from orbital contributions due to σ donation ($\Delta E_{\text{orb}}^{\sigma}$) and π backdonation ($\Delta E_{\text{orb}}^{\pi}$), in kcal mol^{–1}.

X =	ΔE_{tot}	ΔE_{steric}	ΔE_{disp}	ΔE_{oi}	$\Delta E_{\text{orb}}^{\sigma}$	$\Delta E_{\text{orb}}^{\pi}$
CP [–]	–111.6	5.4	–31.4	–85.6	–44.5	–18.0
(μ -CP){Ni(^{Me} IPr) ₂ } [–]	–126.3	54.3	–77.8	–102.8	–51.0	–17.5
(μ -CP){Rh(Cp*)(PMe ₃)} [–]	–101.5	51.7	–59.5	–93.7	–46.9	–17.2
(μ_3 -CP){Rh(Cp*)(PMe ₃)}{W(CO) ₅ } [–]	–109.2	54.9	–71.4	–92.7	–47.0	–18.4
CN [–]	–101.0	2.9	–31.0	–72.8	–40.8	–12.3
(μ -CN)(B(C ₆ F ₅) ₃) [–]	–73.9	50.1	–54.1	–69.8	–35.1	–19.1
CCH [–]	–107.7	4.2	–31.1	–80.8	–42.5	–12.8
Me [–]	–107.7	4.9	–30.7	–81.9	–50.5	–8.3
Cl [–]	–91.1	7.4	–31.0	–67.5	–38.4	–5.6
OH [–]	–113.9	1.9	–30.5	–85.3	–46.0	–6.5

$$\Delta E_{\text{tot}} = \Delta E_{\text{steric}} + \Delta E_{\text{disp}} + \Delta E_{\text{oi}} = \Delta E_{\text{steric}} + \Delta E_{\text{disp}} + \Sigma \Delta E_{\text{orb}}^{\text{n}}$$

For the Au–CP bond in the gold(I) cyaphide complex **Au_{CP}/7**, this analysis shows orbital contributions from C–Au σ donation as well as Au–C π backdonation (Table 4.3). In line with previous theoretical studies on Au–C bonds,^[22,23] σ donor effects are dominant over π backdonation, with an almost three-fold greater contribution to the orbital interaction energy.

Table 4.3. Contours of NOCVs φ_1 , φ_2 , and φ_3 , ($v > 0$), as well as their contributions to the deformation density, $\Delta\rho_1$, $\Delta\rho_2$, and $\Delta\rho_3$, (green: $\Delta\rho > 0$, orange: $\Delta\rho < 0$), for the Au–CP interaction in **Au_{CP}**. φ_1 corresponds to σ donation, whereas φ_2 and φ_3 correspond to π backdonation.



The ETS-NOCV energies for X–Au σ donation correlate very well with experimental $^{13}\text{C}_{\text{NHC}}$ chemical shifts, and those for π backdonation exhibit no correlation (Figure 4.9). This demonstrates that the $^{13}\text{C}_{\text{NHC}}$ chemical shift can be interpreted as a measure of the deconvoluted σ donor ability of X.

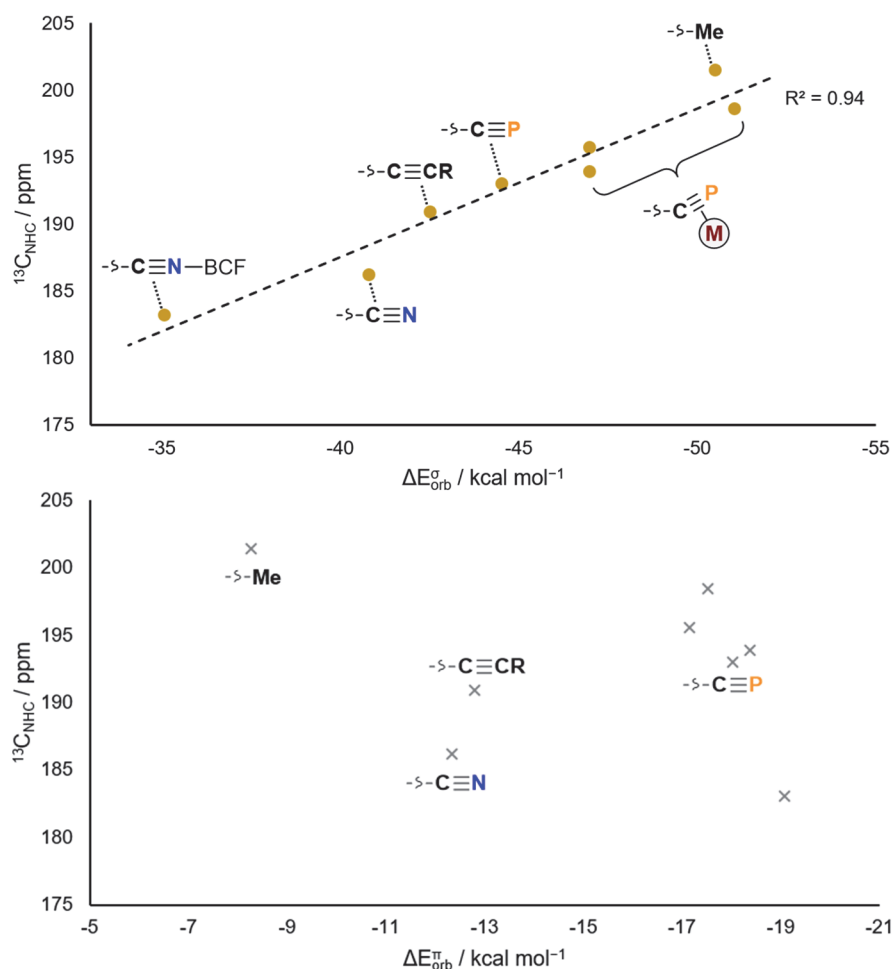


Figure 4.9. Calculated X–Au σ donation energies ($\Delta E_{\text{orb}}^{\sigma}$, top) and π backdonation energies ($\Delta E_{\text{orb}}^{\pi}$, bottom) plotted against experimental $^{13}\text{C}_{\text{NHC}}$ NMR shifts for selected Au_x complexes (includes complexes discussed in Chapter 5).

The carbenoid $^{13}\text{C}_{\text{NHC}}$ chemical shift of the gold(I) complex of the cyaphido ligand Au_{CP} is 193.0 ppm, very similar to the values for the cyanido (Au_{CN} : $^{13}\text{C}_{\text{NHC}} = 186.2$ ppm) and phenylacetylido (Au_{CCPh} : $^{13}\text{C}_{\text{NHC}} = 190.0$) ligands. These correspond to ETS-NOCV σ donation energies ($\Delta E_{\text{orb}}^{\sigma}$) of -44.5 , -40.8 , and -42.5 kcal mol $^{-1}$ respectively. The higher σ donor ability of the cyaphide ion is consistent with its somewhat higher energy HOMO. While it is a similarly strong σ donor to other sp -hybridized carbanions, the cyaphido ligand is a poorer σ donor than the sp^3 hybridized methylido ligand (Au_{Me} : $^{13}\text{C}_{\text{NHC}} = 201.4$ ppm, $\Delta E_{\text{orb}}^{\sigma} = -50.5$ kcal mol $^{-1}$).

Au(IDipp)X complexes have $^{13}\text{C}_{\text{NHC}}$ chemical shifts that depend on X–Au σ donor ability and are insensitive to π donor/acceptor effects, allowing the σ donor ability of the κ C-cyaphido ligand to be determined experimentally *via* ^{13}C NMR spectroscopy of **Au_{CP}**. In order to probe the π donor/acceptor ability of the κ C-cyaphido ligand, **Co_{CP}** (**9**) and **Rh_{CP}** (**10**) were examined using a similar comparative approach.

4.3.3 Determining π acceptor ability: cobalt(I)/(II) ^{Dipp}PDI complexes

The cobalt ^{Dipp}PDI complexes **Co_X** and **Co_L⁺** can be categorized into two distinct groups based on their $\delta(\text{PDI})$ values and color.

The purple complexes **Co_{CCH}**, **Co_{Me}**,^[24] and **Co_{Cl}**^[25] have low $\delta(\text{PDI})$ values (0.090(9)–0.98(7)), and are open-shell singlets, with cobalt(II) centers and radical anion ^{Dipp}PDI^{•−} ligands (**Co²⁺(^{Dipp}PDI)^{•−}X[−]**). This was previously determined experimentally for the literature-known chloride and methyl complexes *via* a ^1H NMR study.^[5]

The blue complexes, including **Co_{N₂}⁺**,^[25] **Co_{CO}⁺**, and **Co_{CNtBu}⁺**, have higher $\delta(\text{PDI})$ values (0.121(4)–0.144(7)), and a closed-shell electronic structure (**Co⁺(^{Dipp}PDI)X[−]**). The blue cyaphide complex **Co_{CP}** fits into this latter category, with a $\delta(\text{PDI})$ value of 0.131(9).

The distinct difference in color between the two groups was quantified by UV-vis spectroscopy. The purple complexes exhibit absorption maxima (λ_{max}) between 533–577 nm, whereas the blue complexes have maxima between 587–606 nm. These absorption features likely heavily involve both the cobalt center as well as the ^{Dipp}PDI ligand, and relate discontinuously with the $\delta(\text{PDI})$ parameter (Figure 4.10).

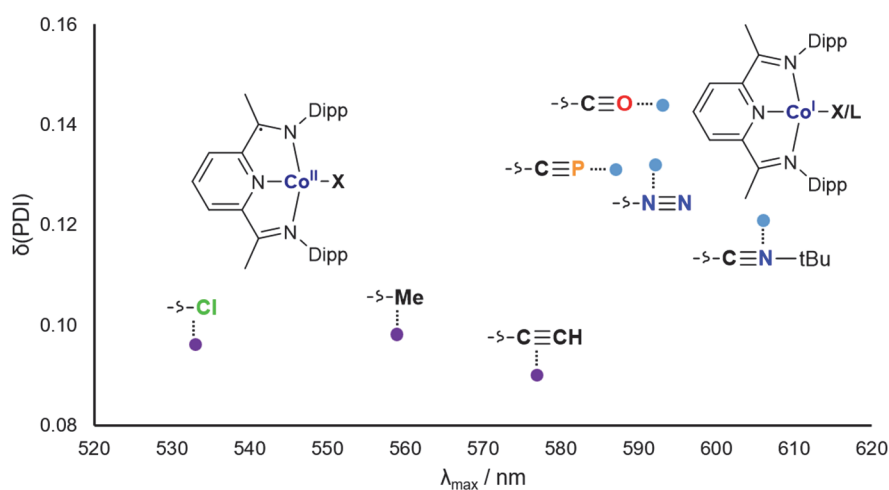


Figure 4.10. UV-vis absorption maxima (λ_{max}) plotted against $\delta(\text{PDI})$ values for **Co_X** and **Co_L⁺** complexes.

These data clearly show that the cyaphido ligand is a π acceptor ligand, though the occurrence of two different electronic structures in Co_X and Co_L^+ complexes makes quantitative analyses non-trivial.

4.3.4 Determining π acceptor ability: rhodium(I) $^{\text{DippPDI}}$ complexes

Unlike the cobalt complexes Co_X and Co_L^+ , the rhodium $^{\text{DippPDI}}$ complexes Rh_X and Rh_L^+ all exhibit closed-shell ground-state electronic structures with rhodium(I) centers and neutral $^{\text{DippPDI}}$ ligands, likely due to the relative unfavorability of the rhodium +2 oxidation state. Consequently, the $\delta(\text{PDI})$ values of Rh_X and Rh_L^+ vary continuously between 0.108(6)–0.161(3).

Energy decomposition analysis using the ETS-NOCV method was used to determine the σ and π contributions to the Rh–X and Rh–L bonds (Table 4.4). The σ donor contribution is the largest for most complexes, with the exception of the ethylene ligand, which has σ donation and π backdonation in approximately equal magnitudes. A NOCV corresponding to π donation to a π^* orbital of the $^{\text{DippPDI}}$ ligand is present for all complexes in varying magnitudes, and is countered by a purely Rh–X or Rh–L π backdonation component ($\Delta E_{\text{orb}}^\pi$).

Table 4.4. Summary of EDA-NOCV analysis of the Rh–X or Rh–L bond in Rh_X or Rh_L^+ complexes, including ETS-NOCV energies from orbital contributions due to σ donation ($\Delta E_{\text{orb}}^\sigma$) and π backdonation ($\Delta E_{\text{orb}}^\pi$), in kcal mol $^{-1}$.

X or L =	ΔE_{tot}	ΔE_{steric}	ΔE_{disp}	ΔE_{oi}	$\Delta E_{\text{orb}}^\sigma$	$\Delta E_{\text{orb}}^\pi$
CP^-	–108.1	28.8	–39.4	–97.4	–46.5	–21.5
CN^-	–98.4	15.5	–38.1	–75.8	–38.3	–11.1
CCH^-	–113.2	12.5	–38.4	–87.3	–41.6	–13.5
Me^-	–106.8	13.7	–38.6	–81.9	–50.5	–8.3
CO	–50.2	67.5	–37.6	–80.1	–31.1	–42.2
CN^tBu	–62.7	50.0	–46.9	–65.8	–32.2	–25.5
C_2H_4	–43.6	53.6	–39.8	–57.4	–22.3	–25.0
Cl^-	–92.4	10.7	–38.0	–65.1	–28.2	–5.5

$$\Delta E_{\text{tot}} = \Delta E_{\text{steric}} + \Delta E_{\text{disp}} + \Delta E_{\text{oi}} = \Delta E_{\text{steric}} + \Delta E_{\text{disp}} + \Sigma \Delta E_{\text{orb}}^n$$

For the Rh–CP bond in the rhodium(I) cyaphide complex Rh_{CP} , energy decomposition analysis shows the dominant orbital interaction contributions are from C–Rh σ donation and secondarily from Rh–C π backdonation (Table 4.5).

Table 4.5. Contours of NOCVs φ_1 , φ_3 , and φ_4 , ($v > 0$), as well as their contributions to the deformation density, $\Delta\rho_1$, $\Delta\rho_3$, and $\Delta\rho_4$, (green: $\Delta\rho > 0$, orange: $\Delta\rho < 0$), for the Rh–CP interaction in **Rh_{CP}**. φ_1 corresponds to σ donation, whereas φ_3 and φ_4 correspond to π backdonation.

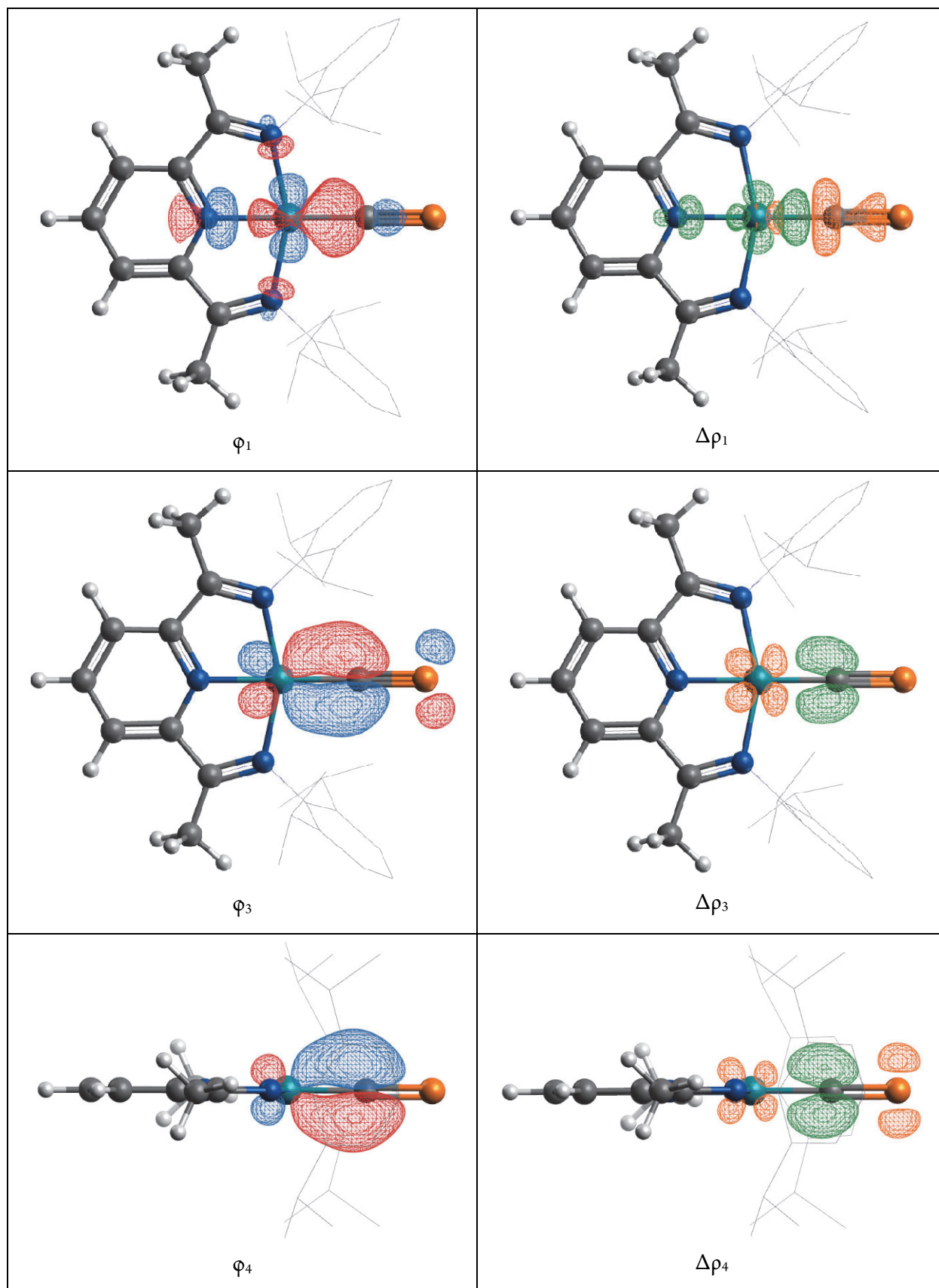


Figure 1 consists of two scatter plots showing the relationship between the chemical shift of the propargylidene carbon ($\delta(\text{CPD})$) and the energy of the propargylidene lone pair orbital ($\Delta E_{\pi_{\text{orb}}}$) and the propargylidene σ orbital ($\Delta E_{\sigma_{\text{orb}}}$).

The top plot shows $\delta(\text{CPD})$ (y-axis, 0.10 to 0.17) versus $\Delta E_{\pi_{\text{orb}}}$ (x-axis, 0 to -45 kcal mol⁻¹). A dashed regression line is shown with $R^2 = 0.92$. Data points are labeled with their corresponding substituents: -Cl, -Me, -CH, -C≡CH, -C≡N-tBu, -C≡P, -C≡O, and -C≡C≡C.

The bottom plot shows $\delta(\text{CPD})$ (y-axis, 0.10 to 0.17) versus $\Delta E_{\sigma_{\text{orb}}}$ (x-axis, -20 to -55 kcal mol⁻¹). Data points are labeled with their corresponding substituents: -Cl, -Me, -CH, -C≡CH, -C≡N-tBu, -C≡P, -C≡O, and -C≡C≡C.

The π donor chlorido ligand results in the lowest $\Delta E_{\text{orb}}^{\pi}$ of $-5.5 \text{ kcal mol}^{-1}$ and lowest $\delta(\text{PDI})$ value of 0.108(6). The strongly π accepting carbonyl ligand gives rise to the highest $\Delta E_{\text{orb}}^{\pi}$ value of $-42.2 \text{ kcal mol}^{-1}$ as well as the highest $\delta(\text{PDI})$ value of 0.161(3). **Rh_{CP}** has a $\delta(\text{PDI})$ value of 0.134(3) and a calculated $\Delta E_{\text{orb}}^{\pi}$ of $-21.5 \text{ kcal mol}^{-1}$. This indicates that the κC -cyaphido ligand is a very strong π acceptor, especially when compared to other anions.

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Unlike $\delta(\text{PDI})$, $N_{\text{py}}\text{-Rh}$ is affected by σ donor effects, and can be interpreted as a direct measure of the *trans* influence of X or L. As a result, the correlation between $N_{\text{py}}\text{-Rh}$ bond lengths and $\Delta E_{\text{orb}}^{\pi}$ values is poorer, with notable outliers due to varying σ donor abilities (e.g. **Rh_{Me}**) (Figure 4.12).

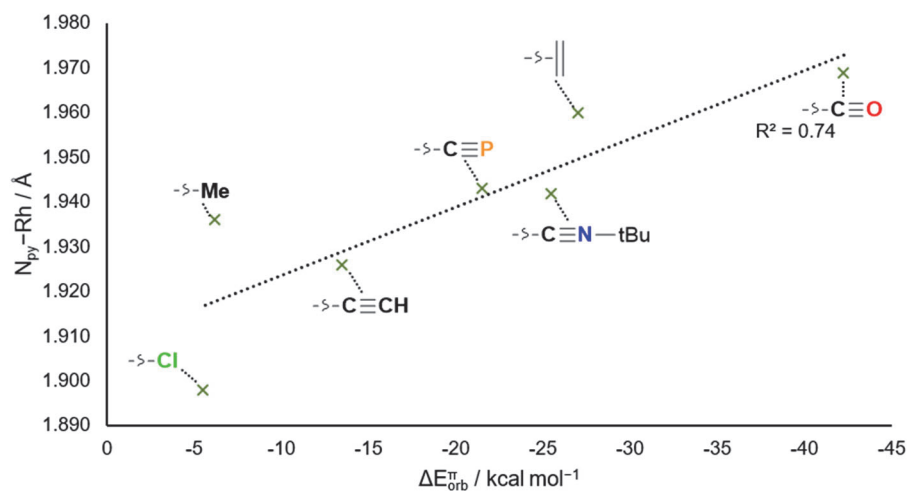


Figure 4.12. Calculated X–Rh or L–Rh π backdonation energies ($\Delta E_{\text{orb}}^{\pi}$) plotted against experimental $N_{\text{py}}\text{-Rh}$ bond lengths for selected **Rh_x** and **Rh_L⁺** complexes.

4.4 Conclusions

The donor/acceptor properties of the κ C-cyaphido ligand were determined in comparison to more conventional ligands through a combined experimental and theoretical study.

By studying **Au_{CP}** (**7**) and other gold(I) NHC complexes **Au_x** and **Au_L⁺**, the cyaphido ligand was determined to be a slightly stronger σ donor than the acetylide and cyanido ligands, though somewhat weaker than the methylido ligand. Analysis of the cobalt(I) and rhodium(I) cyaphide complexes **Co_{CP}** (**9**) and **Rh_{CP}** (**10**) show that the cyaphido ligand is a strong π acceptor in spite of its negative charge.

Overall, this suggests a position for the cyaphido ligand on the spectrochemical series – it is a strong field ligand, with a *trans* influence on par with neutral isocyanides.

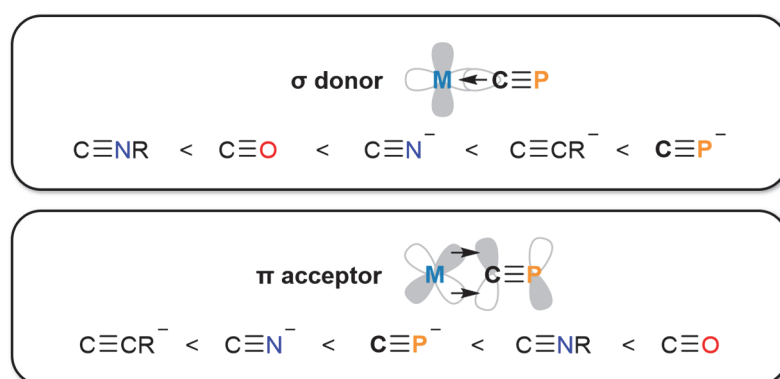


Figure 4.13. The σ donating and π accepting properties of the cyaphido ligand in comparison to other strong field ligands.

Some of the work in this chapter has been published in *Chemical Science*:

E. S. Yang, E. Combey, J. M. Goicoechea, *Chem. Sci.* **2023**, *14*, 4627–4632.

E. Combey contributed experimentally to the work in Section 4.2 under my supervision, and submitted a thesis on her work in fulfilment of Part II of the degree of *Master of Chemistry*.

4.5 Experimental section

4.5.1 Synthesis of $\text{Co}(\text{DippPDI})(\text{CCH})$ (**12**)

$\text{Co}(\text{DippPDI})\text{Cl}$ (100 mg, 0.17 mmol) was dissolved in THF (10 mL). Ethynylmagnesium chloride (0.7 mL, 0.25 M in THF, 0.18 mmol) was added dropwise, and stirred for 3 days. This was then filtered, and the solvent removed under reduced pressure. The product was crystallized from a 3:1 mixture of pentane/toluene at -20°C for 3 days, then isolated by filtration to give $\text{Co}(\text{DippPDI})(\text{CCH})$ as dark purple crystals. Yield: 33 mg, 0.06 mmol, 34%. Anal. Calcd. (%) for $\text{C}_{35}\text{H}_{44}\text{N}_3\text{Co}$: C, 74.31; H, 7.84; N, 7.43. Found: C, 72.86; H, 7.17; N, 6.75.

^1H NMR (600 MHz, C_6D_6): $\delta(\text{ppm})$ 10.05 (t, $^3J_{\text{H-H}} = 7.7$, 1H, pyridine *para*-CH), 7.50 (t, $^3J_{\text{H-H}} = 7.8$, 2H, Dipp *para*-CH), 7.37 (d, $^3J_{\text{H-H}} = 7.8$, 4H, Dipp *meta*-CH), 7.08 (d, $^3J_{\text{H-H}} = 7.7$, 2H, pyridine *meta*-CH), 3.27 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 4H, Dipp CH(CH₃)₂), 2.27 (s, 1H, CCH), 1.25 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp CH(CH₃)₂), 0.94 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp CH(CH₃)₂), -0.33 (s, 6H, imine NCCH₃).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): $\delta(\text{ppm})$ 169.05 (imine NCCH₃), 154.83 (Dipp *ipso*-C), 154.25 (Dipp *ortho*-C), 140.84 (pyridine *ortho*-C), 132.24 (CCH), 126.65 (Dipp *para*-C), 124.42 (pyridine *meta*-C), 123.72 (Dipp *meta*-C), 117.57 (pyridine *para*-C), 29.01 (Dipp CH(CH₃)₂), 24.04 (Dipp CH(CH₃)₂), 23.53 (Dipp CH(CH₃)₂), 22.54 (imine NCCH₃).

UV-vis: $\lambda_{\text{max}}(\text{nm})$ 559.

4.5.2 Synthesis of $\text{Na}(\text{THF})\text{Co}(\text{DippPIEA})(\text{CCH})$ (**13**)

$\text{Co}(\text{DippPDI})\text{Cl}$ (120 mg, 0.21 mmol) and sodium acetylide (20 mg, 0.42 mmol) were dissolved in THF (15 mL), then stirred overnight. The solvent was removed under reduced pressure, then extracted with hexane (3×10 mL). This solution was concentrated, then crystallized at -20°C for 3 days, yielding dark red crystals of $\text{Na}(\text{THF})\text{Co}(\text{PIEA})(\text{CCH})$ that were isolated by filtration. Yield: 28 mg, 0.04 mmol, 20%. Anal. Calcd. (%) for $\text{C}_{39}\text{H}_{51}\text{N}_3\text{CoNaO}$: C, 71.00; H, 7.79; N, 6.37. Found: C, 69.99; H, 7.42; N, 6.24. In solution, $\text{Na}(\text{THF})\text{Co}(\text{DippPIEA})(\text{CCH})$ (**13a**) appears to be in equilibrium with the separated ion pair $[\text{Na}(\text{THF})_n][\text{Co}(\text{DippPIEA})(\text{CCH})]$ (**13b**).

^1H NMR (400 MHz, $\text{d}_8\text{-THF}$): $\delta(\text{ppm})$ 11.00 (d, $^3J_{\text{H-H}} = 7.3$ Hz, 1H, **13a** *o*-imine pyridine *meta*-CH), 10.51 (t, $^3J_{\text{H-H}} = 7.8$ Hz, 1H, **13b** pyridine *para*-CH), 8.35 (d, $^3J_{\text{H-H}} = 8.1$ Hz, 1H, **13a** *o*-imine pyridine *meta*-CH), 8.22–8.15 (m, 1H, **13a** pyridine *para*-CH), 7.75 (t, $^3J_{\text{H-H}} = 7.8$ Hz, 2H, **13b** pyridine *meta*-CH), 7.43–7.37 (m, 1H, **13a** enamine Dipp *para*-CH), 7.34 (t, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, **13b** Dipp *para*-CH), 7.27 (d, $^3J_{\text{H-H}} = 7.7$ Hz, 2H, **13a** enamine Dipp *meta*-CH), 7.07 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, **13b** Dipp *meta*-CH), 6.78 (dd, $^3J_{\text{H-H}} = 8.3, 6.6$ Hz, 1H, **13a** imine Dipp *para*-CH), 6.72–6.67 (m, 2H, **13a** imine Dipp *meta*-CH), 5.25 (s, 1H, **13a** enamine NCCH_2), 3.47 (s, 1H, **13a** enamine NCCH_2), 3.11 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 2H, **13a** enamine Dipp $\text{CH}(\text{CH}_3)_2$), 2.76 (s, 1H, **13a** CCH), 2.40 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 2H, **13a** imine Dipp $\text{CH}(\text{CH}_3)_2$), 2.27 (s, 1H, **13b** CCH), 2.03 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 4H, **13b** Dipp $\text{CH}(\text{CH}_3)_2$), 1.54 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, **13b** Dipp $\text{CH}(\text{CH}_3)_2$), 1.25 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, **13a** enamine Dipp $\text{CH}(\text{CH}_3)_2$), 0.94 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, **13a** imine Dipp $\text{CH}(\text{CH}_3)_2$), 0.66 (d, $^3J_{\text{H-H}} = 7.0$ Hz, 12H, **13b** Dipp $\text{CH}(\text{CH}_3)_2$), 0.64 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, **13a** enamine Dipp $\text{CH}(\text{CH}_3)_2$), 0.43 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, **13a** imine Dipp $\text{CH}(\text{CH}_3)_2$), 0.03 (bs, 5H, **13b** imine/enamine $\text{NCCH}_3/\text{NCCH}_2$), –4.20 (s, 3H, **13a** imine NCCH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, $\text{d}_8\text{-THF}$): $\delta(\text{ppm})$ 174.87 (**13a** enamine NCCH_2), 164.26 (**13b** enamine/imine $\text{NCCH}_3/\text{NCCH}_2$), 158.43 (**13b** Dipp *ipso*-C), 156.34 (**13a** imine NCCH_3), 155.17 (**13a** enamine Dipp *ipso*-C), 152.01 (**13a** imine Dipp *ipso*-C), 146.80 (**13a** imine Dipp *ortho*-C), 141.15 (**13a** enamine Dipp *para*-C), 135.82 (**13b** Dipp *ortho*-C), 132.18 (**13a** pyridine *para* C), 131.65 (**13b** pyridine *ortho*-C), 126.42 (**13a** enamine Dipp *ortho*-C), 125.08 (**13b** pyridine *meta*-C), 124.39 (**13b** Dipp *para*-C), 123.62 (**13a** enamine Dipp *meta*-C), 122.55 (**13a** imine Dipp *meta*-C), 121.75 (**13b** Dipp *meta*-C), 121.60 (**13a** imine Dipp *para*-C), 114.66 (**13a** *o*-imine pyridine *meta*-C), 102.20 (**13a** *o*-enamine pyridine *meta*-C), 97.72 (**13a** CCH), 81.63 (**13a** enamine NCCH_2), 68.03 (**13b** CCH), 29.15 (**13a** enamine Dipp $\text{CH}(\text{CH}_3)_2$), 27.87 (**13b** Dipp $\text{CH}(\text{CH}_3)_2$), 26.94 (**13a** imine Dipp $\text{CH}(\text{CH}_3)_2$), 26.19 (**13a** imine NCCH_3), 24.59 (**13a** imine Dipp $\text{CH}(\text{CH}_3)_2$), 24.39 (**13b** Dipp $\text{CH}(\text{CH}_3)_2$), 23.94 (**13a** enamine Dipp $\text{CH}(\text{CH}_3)_2$), 23.56 (**13a** imine Dipp $\text{CH}(\text{CH}_3)_2$), 23.43 (**13a** enamine Dipp $\text{CH}(\text{CH}_3)_2$), 23.24 (**13b** Dipp $\text{CH}(\text{CH}_3)_2$).

4.5.3 Synthesis of $[\text{Co}(\text{DippPDI})(\text{CO})][\text{B}(\text{Ar}^{\text{F}})_4]$ (**14**)

$\text{Co}(\text{DippPDI})\text{Cl}$ (100 mg, 0.17 mmol) and $\text{Na}(\text{BAr}^{\text{F}}_4)$ (154 mg, 0.17 mmol) were dissolved in 1,2-DFB (3 mL). The solution was degassed, then placed under CO gas (1 bar). The dark blue solution was degassed then filtered. The filtrate was concentrated, then layered with pentane (30 mL) for one week. After filtration, $[\text{Co}(\text{DippPDI})(\text{CO})][\text{BAr}^{\text{F}}_4]$ was obtained as large dark blue crystals. Yield: 145 mg, 0.10 mmol, 58%. Anal. Calcd. (%) for $\text{C}_{66}\text{H}_{55}\text{N}_3\text{BCoF}_{24}\text{O}$: C, 55.36; H, 3.87; N, 2.93. Found: C, 54.92; H, 2.85; N, 2.87.

^1H NMR (400 MHz, 1,2-DFB/ C_6D_6): δ (ppm) 8.17–8.09 (m, 8H, BAr^{F}_4 *ortho*-CH) 7.69 (t, $^3J_{\text{H-H}} = 8.0$, 1H, pyridine *para*-CH), 7.49 (bs, 4H, BAr^{F}_4 *para*-CH), 7.42 (d, $^3J_{\text{H-H}} = 8.0$, 2H, pyridine *meta*-CH), 3.01 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 4H, Dipp CH(CH_3)₂), 1.59 (s, 6H, imine NCCH_3), 1.30 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp CH(CH_3)₂), 1.04 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp CH(CH_3)₂). The signals for some aromatic protons could not be located due to overlap with the 1,2-DFB solvent peaks.

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 1,2-DFB/ C_6D_6): δ (ppm) 175.64 (s, imine NCCH_3), 162.60 (q, $^1J_{\text{C-B}} = 49.7$ Hz, BAr^{F}_4 *ipso*-C), 157.07 (s, Dipp *ipso*-C), 144.91 (s, Dipp *ortho*-C), 141.80 (s, pyridine *para*-C), 138.29 (s, Ar-C), 135.16 (bs, BAr^{F}_4 *ortho*-C), 129.76 (qq, $^2J_{\text{C-F}} = 31.5$ Hz, $^2J_{\text{C-B}} = 3.0$ Hz, BAr^{F}_4 *meta*-C), 128.86 (s, Ar-C), 125.86 (s, pyridine *meta*-C), 124.06 (s, Ar-C), 117.73–117.56 (m, BAr^{F}_4 *para*-C), 29.15 (s, Dipp CH(CH_3)₂), 23.01 (s, CH(CH_3)₂), 22.83 (s, Dipp CH(CH_3)₂), 16.48 (s, imine NCCH_3). The signals for some aromatic carbons could not be assigned due to overlap with the 1,2-DFB solvent peaks.

ATR-FTIR: 2000 cm^{-1} (s, $\nu(\text{C}\equiv\text{O})$)

UV-vis: λ_{max} (nm) 593.

4.5.4 Synthesis of $[\text{Co}(\text{DippPDI})(\text{CN}^t\text{Bu})][\text{B}(\text{Ar}^{\text{F}})_4]$ (**15**)

$\text{Co}(\text{DippPDI})\text{Cl}$ (100 mg, 0.17 mmol) and $\text{Na}(\text{BAr}^{\text{F}}_4)$ (154 mg, 0.17 mmol) were dissolved in 1,2-DFB (3 mL). The solution was degassed, then placed under CO gas (1 bar). The dark blue solution was degassed then filtered. The filtrate was concentrated, then layered with pentane (30 mL) for one week. After filtration, $[\text{Co}(\text{DippPDI})(\text{CO})][\text{BAr}^{\text{F}}_4]$ was obtained as large dark blue crystals. Yield: 145 mg, 0.10 mmol, 58%. Anal. Calcd. (%) for $\text{C}_{66}\text{H}_{55}\text{N}_3\text{BCoF}_{24}\text{O}$: C, 55.36; H, 3.87; N, 2.93. Found: C, 54.92; H, 2.85; N, 2.87.

^1H NMR (400 MHz, 1,2-DFB/ C_6D_6): δ (ppm) 8.17–8.09 (m, 8H, BAr^{F_4} *ortho*-CH), 7.69 (t, $^3J_{\text{H-H}} = 8.0$, 1H, pyridine *para*-CH), 7.49 (bs, 4H, BAr^{F_4} *para*-CH), 7.42 (d, $^3J_{\text{H-H}} = 8.0$, 2H, pyridine *meta*-CH), 3.01 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 4H, Dipp CH(CH₃)₂), 1.59 (s, 6H, imine NCCH₃), 1.30 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp CH(CH₃)₂), 1.04 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp CH(CH₃)₂). The signals for some aromatic protons could not be located due to overlap with the 1,2-DFB solvent peaks.

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 1,2-DFB/ C_6D_6): δ (ppm) 175.64 (s, imine NCCH₃), 162.60 (q, $^1J_{\text{C-B}} = 49.7$ Hz, BAr^{F_4} *ipso*-C), 157.07 (s, Dipp *ipso*-C), 144.91 (s, Dipp *ortho*-C), 141.80 (s, pyridine *para*-C), 138.29 (s, ArC), 135.16 (bs, BAr^{F_4} *ortho*-C), 129.76 (qq, $^2J_{\text{C-F}} = 31.5$ Hz, $^2J_{\text{C-B}} = 3.0$ Hz, BAr^{F_4} *meta*-C), 128.86 (s, ArC), 125.86 (s, pyridine *meta*-C), 124.06 (s, ArC), 117.73–117.56 (m, BAr^{F_4} *para*-C), 29.15 (s, Dipp CH(CH₃)₂), 23.01 (s, CH(CH₃)₂), 22.83 (s, Dipp CH(CH₃)₂), 16.48 (s, imine NCCH₃). The signals for some aromatic carbons could not be assigned due to overlap with the 1,2-DFB solvent peaks.

UV-vis: λ_{max} (nm) 593.

4.5.5 Synthesis of $[\text{Co}(\text{DippPDI})(\text{CN}^t\text{Bu})_2][\text{B}(\text{Ar}^{\text{F}})_4]$ (16)

$\text{Co}(\text{DippPDI})\text{Cl}$ (50 mg, 0.09 mmol) and $\text{Na}(\text{BAr}^{\text{F}_4})$ (77 mg, 0.09 mmol) were dissolved in 1,2-DFB (3 mL). $^t\text{BuNC}$ (17 mg, 0.2 mmol) was added, and the dark blue-green reaction mixture was stirred for 1 h, then filtered. The filtrate was concentrated, then layered with pentane (30 mL) for one week. After filtration, $[\text{Co}(\text{DippPDI})(\text{CN}^t\text{Bu})_2][\text{BAr}^{\text{F}_4}]$ was obtained as dark blue-green crystals. Yield: 140 mg, 0.08 mmol, 84%. Anal. Calcd. (%) for $\text{C}_{75}\text{H}_{73}\text{N}_5\text{BCoF}_{24}$: C, 57.37; H, 4.69; N, 4.46. Found: C, 57.59; H, 4.91; N, 4.25.

^1H NMR (400 MHz, 1,2-DFB/ C_6D_6): δ (ppm) 8.17–8.11 (m, 8H, BAr^{F_4} *ortho*-CH), 7.84–7.75 (m, 3H, pyridine *para/meta*-CH), 7.50 (bs, 4H, BAr^{F_4} *para*-CH), 2.67 (sept, $^3J_{\text{H-H}} = 6.7$ Hz, 2H, Dipp CH(CH₃)₂), 2.23 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 2H, Dipp CH(CH₃)₂), 1.66 (s, 6H, imine NCCH₃), 1.30 (d, $^3J_{\text{H-H}} = 6.7$ Hz, 6H, Dipp CH(CH₃)₂), 1.11 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 6H, Dipp CH(CH₃)₂), 0.93 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 6H, Dipp CH(CH₃)₂), 0.90 (s, 9H, CNC(CH₃)₃), 0.80 (d, $^3J_{\text{H-H}} = 6.7$ Hz, 6H, Dipp CH(CH₃)₂), 0.66 (s, 9H, CNC(CH₃)₃). The signals for some aromatic protons could not be located due to overlap with the 1,2-DFB solvent peaks.

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 1,2-DFB/ C_6D_6): δ (ppm) 184.29 (s, imine NCCH_3), 162.58 (q, $^1J_{\text{C-B}} = 49.8$ Hz, BAr^{F}_4 *ipso*-C), 162.37 (s pyridine ArC), 148.99 (s, pyridine *ortho*-C), 141.10 (s, Dipp ArC), 138.25 (s, Dipp ArC), 135.13 (bs, BAr^{F}_4 *ortho*-C), 130.57 (s, Dipp ArC), 129.77 (qq, $^2J_{\text{C-F}} = 31.3$ Hz, $^2J_{\text{C-B}} = 3.2$ Hz, BAr^{F}_4 *meta*-C), 127.40 (s, Dipp ArC), 125.84 (s, ArC), 125.20 (s, ArC), 123.48 (s, ArC), 117.73–117.56 (m, BAr^{F}_4 *para*-C), 57.97 (s, $\text{CNC}(\text{CH}_3)_3$), 57.84 (s, $\text{CNC}(\text{CH}_3)_3$), 29.16 (s, $\text{CNC}(\text{CH}_3)_3$), 29.08 (s, $\text{CNC}(\text{CH}_3)_3$), 27.91 (s, Dipp $\text{CH}(\text{CH}_3)_2$), 27.83 (s, Dipp $\text{CH}(\text{CH}_3)_2$), 25.49 (s, Dipp $\text{CH}(\text{CH}_3)_2$), 23.65 (s, Dipp $\text{CH}(\text{CH}_3)_2$), 23.64 (s, Dipp $\text{CH}(\text{CH}_3)_2$), 22.71 (s, Dipp $\text{CH}(\text{CH}_3)_2$), 16.21 (s, imine NCCH_3). The signals for some aromatic carbons were not assigned due to overlap with the 1,2-DFB solvent peaks.

4.5.6 Synthesis of $\text{Rh}(\text{DippPDI})(\text{CCH})$ (17)

$\text{Rh}(\text{DippPDI})\text{Cl}$ (100 mg, 0.16 mmol) was dissolved in THF (10 mL). Ethynylmagnesium chloride (0.7 mL, 0.25 M in THF, 0.18 mmol) was added dropwise, and stirred for 3 days. This was then filtered, and the solvent removed under reduced pressure to give $\text{Rh}(\text{DippPDI})(\text{CCH})$ as a green solid. Yield: 60 mg, 0.10 mmol, 61%. Anal. Calcd. (%) for $\text{C}_{35}\text{H}_{44}\text{N}_3\text{Rh}$: C, 68.95; H, 7.27; N, 6.89. Found: C, 66.89; H, 6.37; N, 6.10. Crystals suitable for X-ray diffraction were obtained from toluene/pentane by vapor diffusion.

^1H NMR (600 MHz, C_6D_6): δ (ppm) 7.78 (t, $^3J_{\text{H-H}} = 7.9$, 1H, pyridine *para*-CH), 7.25–7.22 (m, 6H, Dipp *para/meta*-CH), 6.97 (d, $^3J_{\text{H-H}} = 7.9$, 2H, pyridine *meta*-CH), 3.27 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 4H, Dipp $\text{CH}(\text{CH}_3)_2$), 3.03 (d, $^3J_{\text{H-Rh}} = 1.3$ Hz, 1H, CCH), 1.42 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp $\text{CH}(\text{CH}_3)_2$), 1.12 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp $\text{CH}(\text{CH}_3)_2$), 1.04 (s, 6H, imine NCCH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): δ (ppm) 166.35 (s, imine NCCH_3), 156.41 (d, $^2J_{\text{C-Rh}} = 2.8$ Hz, Dipp *ipso*-C), 148.37 (s, Dipp *ortho*-C), 140.41 (s, Dipp *para*-C), 126.52 (s, Dipp *meta* C), 125.00 (s, pyridine *meta*-C), 123.50 (s, pyridine *ortho*-C), 123.49 (d, $^2J_{\text{C-Rh}} = 11.3$ Hz, CCH), 122.94 (s, pyridine *para*-C), 114.28 (d, $^1J_{\text{C-Rh}} = 60.6$ Hz, CCH), 28.57 (s, Dipp $\text{CH}(\text{CH}_3)_2$), 23.96 (s, Dipp $\text{CH}(\text{CH}_3)_2$), 23.81 (s, Dipp $\text{CH}(\text{CH}_3)_2$), 17.58 (d, $^3J_{\text{C-Rh}} = 1.5$ Hz imine NCCH_3).

4.5.7 Synthesis of $[\text{Rh}(\text{DippPDI})(\text{CO})][\text{B}(\text{Ar}^{\text{F}})_4]$ (18)

$\text{Rh}(\text{DippPDI})\text{Cl}$ (100 mg, 0.16 mmol) and $\text{Na}(\text{BAr}^{\text{F}}_4)$ (144 mg, 0.16 mmol) were dissolved in 1,2-DFB (3 mL). The solution was degassed, then placed under CO gas (1 bar). After stirring for 1 hour, the solution

was degassed then filtered. The solution was concentrated, then layered with pentane (30 mL) for one week. After filtration, $[\text{Rh}(\text{DippPDI})(\text{CO})][\text{BAr}^{\text{F}}_4]$ was obtained as large dark green crystals. Yield: 181 mg, 0.12 mmol, 76%. Anal. Calcd. (%) for $\text{C}_{66}\text{H}_{55}\text{N}_3\text{BF}_{24}\text{ORh}$: C, 53.71; H, 3.76; N, 2.85. Found: C, 53.39; H, 3.68; N, 2.74.

^1H NMR (600 MHz, 1,2-DFB/ C_6D_6): δ (ppm) 8.17–8.09 (m, 8H, BAr^{F}_4 *ortho*-CH) 7.86 (t, $^3J_{\text{H-H}} = 8.1$, 1H, pyridine *para*-CH), 7.63 (d, $^3J_{\text{H-H}} = 8.1$, 2H, pyridine *meta*-CH), 7.49 (bs, 4H, BAr^{F}_4 *para*-CH), 3.16 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 4H, Dipp CH(CH₃)₂), 1.97 (s, 6H, imine NCCH₃), 1.26 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp CH(CH₃)₂), 1.08 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp CH(CH₃)₂). The signals for some aromatic protons could not be located due to overlap with the 1,2-DFB solvent peaks.

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 1,2-DFB/ C_6D_6): δ (ppm) 187.42 (d, $^1J_{\text{C-Rh}} = 77.2$ Hz, CO), 176.19 (s, imine NCCH₃), 162.59 (q, $^1J_{\text{C-B}} = 49.7$ Hz, BAr^{F}_4 *ipso*-C), 156.04 (d, $^2J_{\text{C-Rh}} = 3.1$ Hz, Dipp *ipso*-C), 145.21 (s, Dipp *ortho*-C), 142.26 (s, pyridine *para*-C), 137.77 (s, ArC), 135.14 (bs, BAr^{F}_4 *ortho*-C), 129.75 (qq, $^2J_{\text{C-F}} = 31.6$ Hz, $^2J_{\text{C-B}} = 2.9$ Hz, BAr^{F}_4 *meta*-C), 128.79 (s, ArC), 125.85 (s, pyridine *meta*-C), 117.70–117.58 (m, BAr^{F}_4 *para*-C), 28.71 (s, Dipp CH(CH₃)₂), 22.78 (s, Dipp CH(CH₃)₂), 22.72 (s, Dipp CH(CH₃)₂), 16.44 (d, $^3J_{\text{C-Rh}} = 1.8$ Hz, imine NCCH₃). The signals for some aromatic carbons could not be located or were not assigned due to overlap with the 1,2-DFB solvent peaks.

ATR-FTIR: 2026 cm⁻¹ (s, $\nu(\text{C}\equiv\text{O})$)

4.5.8 Synthesis of $[\text{Rh}(\text{DippPDI})(\text{CN}^t\text{Bu})][\text{B}(\text{Ar}^{\text{F}})_4]$ (19)

$\text{Rh}(\text{DippPDI})\text{Cl}$ (50 mg, 0.08 mmol) and $\text{Na}(\text{BAr}^{\text{F}}_4)$ (72 mg, 0.08 mmol) were dissolved in 1,2-DFB (3 mL). A solution of $^t\text{BuNC}$ (7 mg, 0.08 mmol) in DFB (0.5 mL) was added dropwise. The reaction mixture was stirred for 3 days, then filtered. The filtrate was concentrated, then layered with pentane (30 mL) for one week. After filtration, $[\text{Rh}(\text{DippPDI})(\text{CN}^t\text{Bu})][\text{BAr}^{\text{F}}_4]$ was obtained as dark green crystals. Yield: 101 mg, 0.07 mmol, 82%. Anal. Calcd. (%) for $\text{C}_{70}\text{H}_{64}\text{N}_4\text{BF}_{24}\text{Rh}$: C, 54.92; H, 4.21; N, 3.66. Found: C, 54.17; H, 3.60; N, 2.79.

^1H NMR (600 MHz, 1,2-DFB/ C_6D_6): δ (ppm) 8.18–8.12 (m, 8H, BAr^{F}_4 *ortho*-CH) 7.73 (t, $^3J_{\text{H-H}} = 8.1$, 1H, pyridine *para*-CH), 7.50 (bs, 4H, BAr^{F}_4 *para*-CH), 7.46 (d, $^3J_{\text{H-H}} = 8.1$, 2H, pyridine *meta*-CH), 3.06 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 4H, Dipp CH(CH₃)₂), 1.79 (s, 6H, imine NCCH₃), 1.17 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 12H,

Dipp CH(CH₃)₂), 1.07 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 12H, Dipp CH(CH₃)₂), 0.70 (s, 9H, CNC(CH₃)₃). The signals for some aromatic protons could not be located due to overlap with the 1,2-DFB solvent peaks.

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 1,2-DFB/C₆D₆): δ (ppm) 178.60 (d, $^1J_{\text{C-Rh}} = 43.8$ Hz, CN^tBu), 172.01 (d, $^2J_{\text{C-Rh}} = 1.6$ Hz, imine NCCH₃), 162.59 (q, $^1J_{\text{C-B}} = 49.8$ Hz, BAr^F₄ *ipso*-C), 156.01 (d, $^2J_{\text{C-Rh}} = 3.2$ Hz, Dipp *ipso*-C), 146.13 (s, Dipp *ortho*-C), 138.58 (s, ArC), 137.42 (s, ArC), 135.14 (bs, BAr^F₄ *ortho*-C), 130.29–129.35 (m, BAr^F₄ *meta*-C), 127.65 (s, ArC), 125.85 (s, ArC), 117.71–117.58 (m, BAr^F₄ *para* C), 56.95 (s, CNC(CH₃)₃), 29.27 (s, CNC(CH₃)₃), 28.47 (s, Dipp CH(CH₃)₂), 23.00 (s, Dipp CH(CH₃)₂), 22.77 (s, Dipp CH(CH₃)₂), 16.05 (s, imine NCCH₃). The signals for some aromatic carbons could not be located or were not assigned due to overlap with the 1,2-DFB solvent peaks.

4.6 References

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Hetero-multimetallic Cyaphide Complexes

Abstract. Hetero-multimetallic complexes of the cyaphide ion are synthesized by the reaction of a gold(I) cyaphide complex with electron-rich metal centers. These reactions are driven by the low-lying $\text{C}\equiv\text{P}$ π^* orbitals and result in side-on bridging cyaphide complexes, though reactivity at the $\text{Au}-\text{C}$ bond can also occur for especially nucleophilic metals. These complexes are fully characterized, and the unusual chemical bonding in these species is discussed with the aid of theoretical calculations.

5.1 Bridging cyanide, acetylide, and cyaphide complexes

Multimetallic cyanide complexes almost invariably contain the cyanide ion in an end-on $\eta^1:\eta^1$ (or $\sigma + \sigma$) coordination mode, involving both the carbon-centered and nitrogen-centered lone pairs. Acetylide ions only have one lone pair available for metal coordination, thus the acetylide ion typically adopts an asymmetric $\eta^1:\eta^2$ (or $\sigma + \pi$) coordination mode in μ -acetylide bimetallic complexes. This involves bonding to one metal center *via* the carbon-centered lone pair and the second metal *via* the $\text{C}\equiv\text{C}$ π bond in a manner described by the Dewar-Chatt-Duncanson model (Figure 5.1).

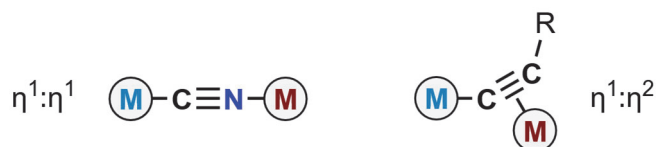


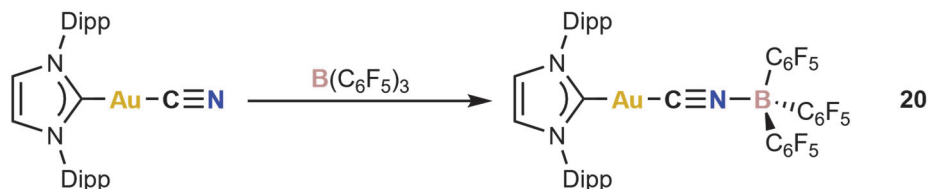
Figure 5.1. Dominant coordination modes for bridging cyanide and acetylide complexes.

The cyaphide ion has both carbon- and phosphorus-centered lone pairs as well as a reactive π bond, in principle enabling both $\eta^1:\eta^1$ and $\eta^1:\eta^2$ coordination modes. Prior to this work, the original platinum(II)/platinum(0) complex containing a $\eta^1:\eta^2$ -cyaphido ligand reported by Angelici in 1992 and its trimetallic derivatives remained the only example of multimetallic bridging cyaphide complexes (see Section 1.4.2).^[1,2]

5.2 Hetero-multimetallic $\eta^1:\eta^2$ bridging cyaphide complexes

5.2.1 Reactions of Au(IDipp)(CX) with metal electrophiles

The cyanide complex Au(IDipp)(CN) is known in the literature,^[3] and reacts with the electrophile B(C₆F₅)₃ to form a $\eta^1:\eta^1$ bridging cyanide complex {Au(IDipp)}(μ -CN){B(C₆F₅)₃} (**20**; Scheme 5.1).



Scheme 5.1. Synthesis of the gold(I) bridging cyanide complex **20**.

20 has a NHC carbenoid ¹³C NMR chemical shift of 183.1 ppm, and a ¹¹B{¹H} spectrum containing a broad singlet at –13.46 ppm, typical for B(C₆F₅)₃ adducts. X-ray diffraction confirms the linear end-on geometry, with Au1–C1–N1 and C1–N1–B1 angles of 174.1(2)° and 175.7(3)°, respectively (Figure 5.2).

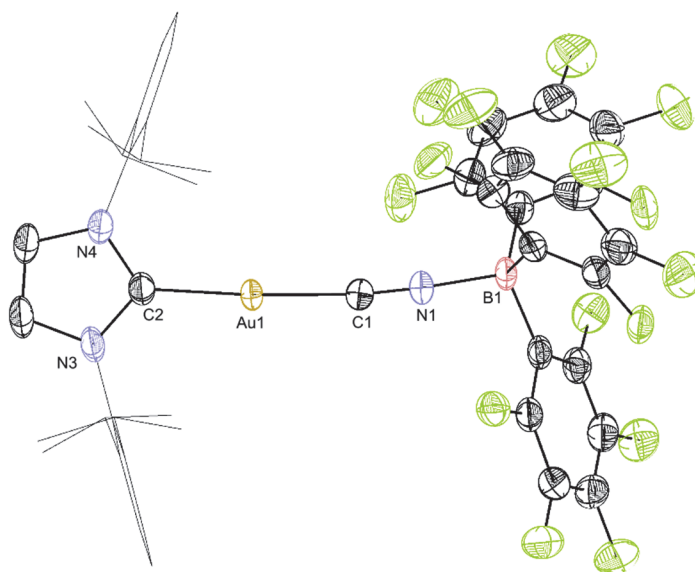
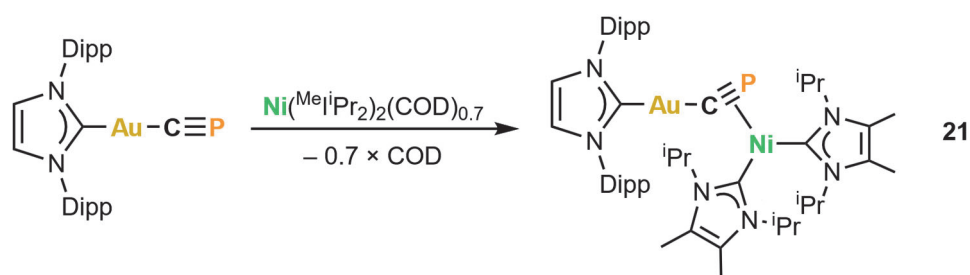


Figure 5.2. Solid-state structure of **20**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms and co-crystallized toluene are omitted for clarity. Dipp groups are depicted as wireframes.

In contrast, the cyaphide ion in the isostructural gold(I) complex Au(IDipp)(CP) (**7**) does not react with electrophiles in a controlled manner. Intractable mixtures of products result when **7** is reacted with Ru(dppe)₂(H)(OTf), Mo(dppe)₂(N₂)₂, and W(dppe)₂(N₂)₂, despite their ability to form stable η^1 -phosphaalkyne complexes.^[4–6] Reactions with other electrophiles (e.g. B(C₆F₅)₃ and W(CO)₅(THF)) also resulted in intractable product mixtures.

5.2.2 Synthesis of $\{\text{Au}(\text{IDipp})\}(\mu\text{-CP})\{\text{Ni}(\text{MeTiPr}_2)_2\}$

The umpolung reaction of **7** with metal nucleophiles was attempted, with the aim of targeting the electrophilic character of the cyaphide ion afforded by its low-lying π^* orbitals. As nickel(0) complexes of alkynes and phosphalkynes are well known,^[7,8] the reaction of **7** with the nickel(0) NHC complex $\text{Ni}(\text{MeTiPr}_2)_2(\text{COD})_{0.7}$ (as a mixture of $\text{Ni}(\text{MeTiPr}_2)_2(\text{COD})$ and $\{\text{Ni}(\text{MeTiPr}_2)_2\}_2(\mu\text{-COD})$; $\text{MeTiPr}_2 = 1,3$ -diisopropyl-4,5-dimethylimidazol-2-ylidene; COD = 1,5-cyclooctadiene) was attempted. When **7** is added to a solution of $\text{Ni}(\text{MeTiPr}_2)_2(\text{COD})_{0.7}$, free COD is rapidly displaced to give the hetero-bimetallic gold(I)/nickel(0) cyaphide complex $\{\text{Au}(\text{IDipp})\}(\mu\text{-CP})\{\text{Ni}(\text{MeTiPr}_2)_2\}$ (**21**; Scheme 5.2).



Scheme 5.2. Synthesis of the hetero-bimetallic gold(I)/nickel(0) cyaphide complex **21**.

21 has a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum with a singlet at 246.0 ppm and a doublet in its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 280.32 ppm ($^1J_{\text{C-P}} = 105.1$ Hz) corresponding to the cyaphide phosphorus and carbon atoms, respectively. The IDipp $^{13}\text{C}_{\text{NHC}}$ chemical shift is 198.46 ppm. In its Raman spectrum, the $\text{C}\equiv\text{P}$ vibrational stretching frequency appears at 1125 cm^{-1} , which is substantially lower than that observed for **7**. The solid-state structure of **21** was determined by single crystal X-ray diffraction (Figure 5.3).

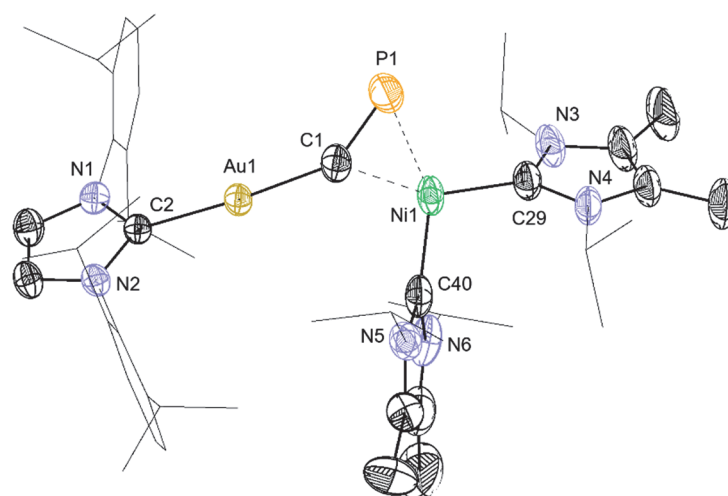
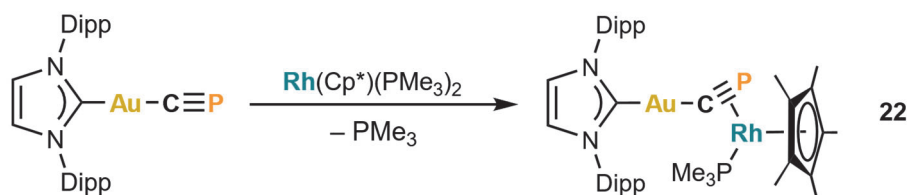


Figure 5.3. Solid-state structure of **21**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms and co-crystallized benzene are omitted for clarity. Dipp and $i\text{Pr}$ groups are depicted as wireframes.

21 has a bridging cyaphido ligand in a $\eta^1:\eta^2$ coordination mode. The cyaphide ion is bonded to the gold center $\eta^1, \kappa C$, with a Au1–C1 bond length of 1.992(4) Å, and a bent Au1–C1–P1 bond angle of 146.3(2)°. The IDipp ligand on the gold center has a Au1–C2 bond length of 2.024(4) Å. The nickel is bonded η^2 to the cyaphido ligand, closer to the carbon atom than the phosphorus atom, with a Ni1–C1 bond length of 1.919(4) Å and Ni1–P1 bond length of 2.201(1) Å. The cyaphide C1–P1 bond length is 1.642(4) Å, significantly elongated compared to its value in **7**, in line with the observed reduction in the $C\equiv P$ vibrational frequency. It lies in between the sum of carbon and phosphorus double bond (1.69 Å) and triple bond (1.54 Å) covalent radii.

5.2.3 Synthesis of $\{Au(IDipp)\}(\mu\text{-CP})\{Rh(Cp^*)(PMe_3)\}$

It has been previously demonstrated that the rhodium(I) piano stool complex $Rh(Cp^*)(PMe_3)_2$ behaves as a metal-centered Lewis base.^[9] Given the success of synthesizing **21** by an umpolung approach, the reaction of **7** with $Rh(Cp^*)(PMe_3)_2$ was also attempted. **7** reacts slowly with $Rh(Cp^*)(PMe_3)_2$ at room temperature *via* displacement of a trimethylphosphine ligand (observed by $^{31}P\{^1H\}$ spectroscopy). When the reaction is heated to 80 °C to favor PMe_3 liberation, the hetero-bimetallic gold(I)/rhodium(I) cyaphide complex, $\{Au(IDipp)\}(\mu\text{-CP})\{Rh(Cp^*)(PMe_3)\}$ (**22**), is prepared in good yield (~90%; Scheme 5.3).



Scheme 5.3. Synthesis of the hetero-bimetallic gold(I)/rhodium(I) cyaphide complex **22**.

The $^{31}P\{^1H\}$ NMR spectrum of **22** exhibits a doublet of doublets at 94.7 ppm ($^1J_{P-Rh} = 33.8$ Hz, $^2J_{P-P} = 4.7$ Hz) corresponding to the cyaphido ligand, and a doublet of doublets at –5.0 ppm ($^1J_{P-Rh} = 209.0$ Hz, $^2J_{P-P} = 4.7$ Hz) corresponding to the trimethylphosphine ligand. Its $^{13}C\{^1H\}$ NMR spectrum shows a doublet ($^3J_{C-P} = 4.0$ Hz) corresponding to the IDipp carbenoid carbon at 195.55 ppm. The cyaphide $C\equiv P$ stretching mode appears in its Raman spectrum at 1175 cm^{-1} , slightly higher than in **21**.

Single crystal X-ray crystallography of **22** reveals a hetero-bimetallic structure with a $\eta^1:\eta^2$ bridging cyaphido ligand (Figure 5.4).

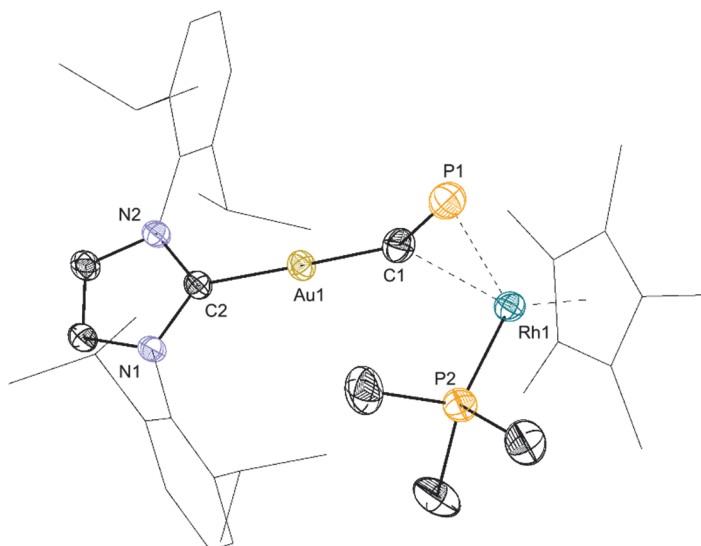
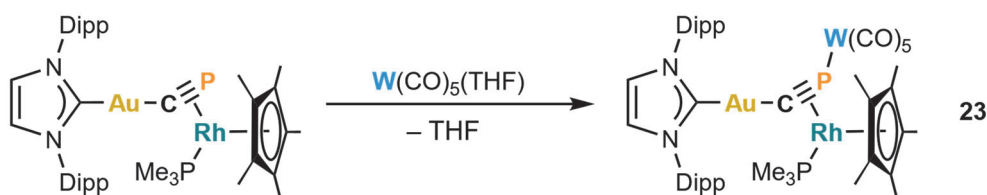


Figure 5.4. Solid-state structure of **22**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms and co-crystallized hexane are omitted for clarity. Dipp and Cp* groups are depicted as wireframes.

The cyaphide ion is bonded to the gold center with a Au1–C1 bond length of 1.975(4) Å, and the IDipp ligand is bonded to the gold center with a Au1–C2 bond length of 2.026(4) Å, both similar to their values in **21**. The Au1–C1–P1 bond angle is slightly less bent with an angle of 151.4(2)°. The side-on coordinated cyaphido ligand is bonded to rhodium with a Rh1–C1 bond length of 2.119(4) Å and a Rh1–P1 bond length of 2.371(1) Å. The cyaphide C1–P1 bond length is 1.631(4) Å, similar to its length in **21** and in good agreement with its measured Raman stretching frequency.

5.2.4 Synthesis of {Au(IDipp)}(μ₃-CP){Rh(Cp*)(PMe₃)}{W(CO)₅}

Examination of the molecular structures of **21** and **22** shows that despite η² coordination of the cyaphido ligand to a second metal, the cyaphide phosphorus atom remains sterically accessible for further coordination chemistry (see Section 1.4.2). This was probed by reacting **22** with a metal electrophile, W(CO)₅(THF). When **22** is added to a freshly prepared solution of W(CO)₅(THF), the THF molecule is displaced, resulting in the hetero-trimetallic gold(I)/rhodium(I)/tungsten(0) cyaphide complex {Au(IDipp)}(μ₃-CP){Rh(Cp*)(PMe₃)}{W(CO)₅} (**23**; Scheme 5.4).



Scheme 5.4. Synthesis of the hetero-trimetallic gold(I)/rhodium(I)/tungsten(0) cyaphide complex **23**.

23 has a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum containing a doublet of doublets with ^{183}W satellites at 48.5 ppm ($^1J_{\text{P-W}} = 174.7$ Hz, $^1J_{\text{P-Rh}} = 61.9$ Hz, $^2J_{\text{P-P}} = 13.4$ Hz) for the cyaphide phosphorus atom, and a doublet of doublets at -3.9 ppm ($^1J_{\text{P-Rh}} = 193.6$ Hz, $^2J_{\text{P-P}} = 13.4$ Hz) for the trimethylphosphine. Its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum exhibits a doublet with ^{183}W satellites at 202.52 ppm ($^1J_{\text{C-W}} = 126.0$ Hz, $^2J_{\text{C-P}} = 25.3$ Hz) for the axial carbonyl ligand, and a doublet at 198.01 ppm ($^2J_{\text{C-P}} = 6.9$ Hz) for the equatorial carbonyl ligands. The IDipp carbenoid carbon appears as a doublet at 193.94 ppm ($^3J_{\text{C-P}} = 6.4$ Hz). The cyaphide $\text{C}\equiv\text{P}$ stretching frequency was measured to be 1186 cm^{-1} by Raman spectroscopy, slightly higher than in the bimetallic precursor **22**. Due to the pseudo- C_{4v} symmetry at the tungsten center, four carbonyl stretching modes were observed by IR spectroscopy between 1881 and 2059 cm^{-1} ; three were detected by Raman spectroscopy between 1883 and 2062 cm^{-1} .

The structure of **23** was determined by single crystal X-ray crystallography, revealing a cyaphido ligand bridging the three metal centers in a $\eta^1:\eta^2:\eta^1$ coordination mode involving both the carbon and phosphorus lone pairs, as well as the $\text{C}\equiv\text{P}$ π manifold (Figure 5.5).

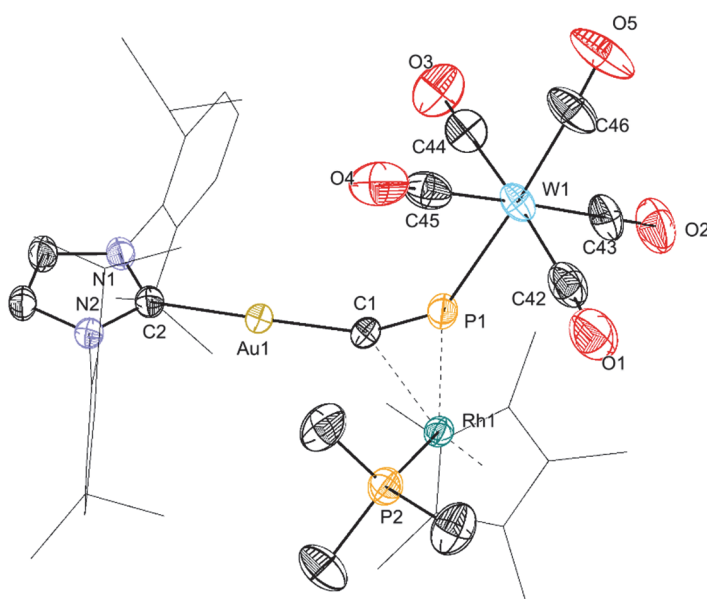


Figure 5.5. Solid-state structure of **23**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms and co-crystallized hexane are omitted for clarity. Dipp and Cp^* groups are depicted as wireframes.

In **23**, the Au1-C1 bond length is $1.991(4)\text{ \AA}$, the Au1-C2 bond length is $2.025(4)\text{ \AA}$, and the Au1-C1-P1 angle is $155.4(3)^\circ$. The rhodium center is displaced slightly closer to the phosphorus atom of the cyaphido ligand relative to **21**, with Rh1-C1 and Rh1-P1 bond lengths of $2.159(4)$ and $2.297(2)\text{ \AA}$, respectively. The W1-P1 bond length is $2.499(1)\text{ \AA}$ and the C1-P1-W1 angle is $144.6(2)^\circ$. The cyaphide C1-P1 bond length is $1.605(4)\text{ \AA}$, shorter than its length in the bimetallic precursor **22**. Along with the

slightly higher $\nu(\text{C}\equiv\text{P})$ stretching frequency, this suggests that the C–P bond order increases upon coordination to tungsten. This can be explained by a shift in polarization across the $\text{C}\equiv\text{P}$ bond toward the phosphorus atom, supported by the changes in Rh1–C1 and Rh1–P1 bond lengths, as well as the higher ^{31}P – ^{103}Rh coupling constant in **23** compared to **22** (61.9 vs. 33.8 Hz).

5.2.5 Bonding in the bent κP -cyaphido coordination mode

The nature of κP -cyaphido coordination at the tungsten center in **23** can be inferred from its spectroscopic data. Tungsten pentacarbonyl complexes of many ligands, including common phosphines, have been reported in the literature (Table 5.1). These are typically studied by vibrational spectroscopy as an alternative to the Tolman Electronic Parameter.^[10–12]

Table 5.1. Carbonyl vibrational stretching frequencies ($\nu(\text{C}\equiv\text{O})$), $^{13}\text{C}_{\text{CO}}$ NMR chemical shifts and ^{31}P – ^{183}W coupling constants ($^1J_{\text{P-W}}$) for $\text{W}(\text{CO})_5\text{L}$ complexes including **23**.

L =	$\nu(\text{C}\equiv\text{O}) / \text{cm}^{-1}$			$^{13}\text{C}_{\text{CO}} / \text{ppm}$		$^1J_{\text{P-W}} / \text{Hz}$	Ref.
	$A_1^{(1)}$	B_1	E	eq.	ax.		
PF_3	2103	–	1983	–	–	485	13
PCl_3	2094	1994	1980	193.9	197.0	426	14
PBr_3	2092	1991	1981	195.5	196.8	398	14
$\text{P}(\text{OPh})_3$	2083	–	1958	–	–	415	13
$\text{P}(\text{OMe})_3$	2081	1980	1952	–	–	398	15
PH_3	2080	1981	1952	–	–	–	16
$\text{P}(\text{OEt})_3$	2078	1976	1945	–	–	391	13
$\text{P}(\text{OBu})_3$	2077	1977	1944	–	–	390	13
PPh_3	2075	1980	1942	–	–	280	13
PPh_2Me	2073	1979	1939	–	–	245	15
PPh_2Et	2073	1979	1938	–	–	240	15
PPh_2^iPr	2074	1979	1937	–	–	240	15
PPh_2^nBu	2073	1978	1938	–	–	250	15
PPh_2^tBu	2072	1979	1937	–	–	240	15
PPh^nBu_2	2071	1975	1937	–	–	235	15

PMe ₃	2071	–	1937	197.3	199.1	227	14
P ⁿ Bu ₃	2070	1976	1934	–	–	227	13
22	2059	1972	1928	198.0	202.5	175	–
PCO [–]	2052	1960	1906	202.2	204.6	52	17

The carbonyl stretching frequencies in **23** are low when compared to tertiary phosphines, suggesting appreciable electron donation from **22** to the tungsten center upon forming **23**. This is also reflected in the somewhat high carbonyl ¹³C_{CO} chemical shifts, though these are less comprehensively studied in the literature. The ³¹P–¹⁸³W coupling constant reflects phosphine ligand donor strengths, but is also highly sensitive to the degree of s character in the phosphorus centered donor orbital. For example, the tungsten pentacarbonyl complex of the 2-phosphaethynolate ion, which binds side-on *via* a phosphorus p-orbital, has a very low ³¹P–¹⁸³W coupling constant (¹J_{P–W} = 52 Hz). The ³¹P–¹⁸³W coupling constant in **23** is relatively low (¹J_{P–W} = 175 Hz), indicating significant p character for the cyaphide phosphorus lone pair; this is consistent with the bent geometry of the complex.

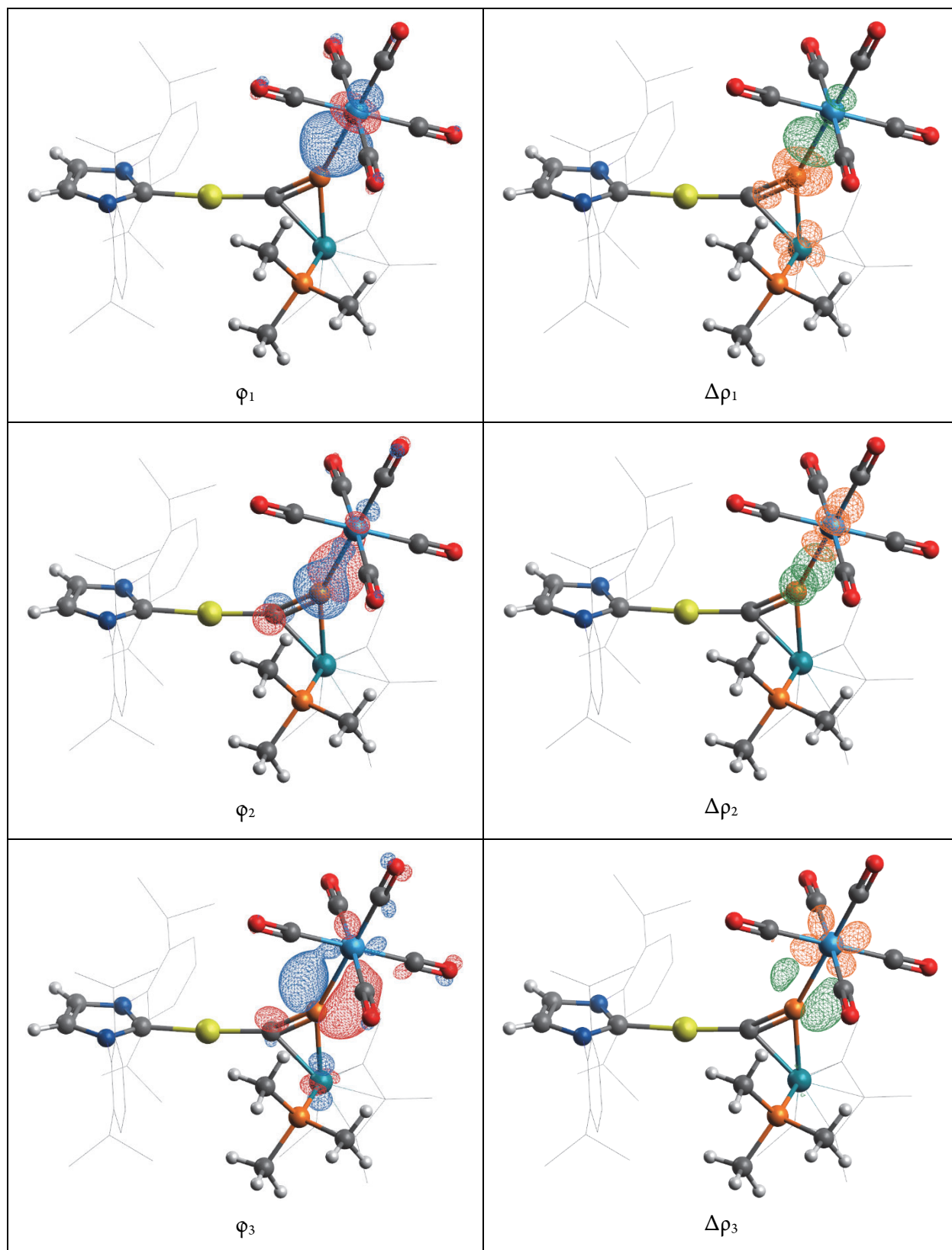
Table 5.2. Summary of EDA-NOCV analysis of the P–W bond in W(CO)₅L complexes including **23**, ETS-NOCV energies are listed from orbital contributions due to σ donation ($\Delta E_{\text{orb}}^{\sigma}$) and π backdonation ($\Delta E_{\text{orb}}^{\pi}$), in kcal mol^{–1}.

L =	ΔE_{tot}	ΔE_{steric}	ΔE_{disp}	ΔE_{oi}	$\Delta E_{\text{orb}}^{\sigma}$	$\Delta E_{\text{orb}}^{\pi}$
22	–37.73	83.13	–74.33	–46.53	–30.54	–11.50
PF ₃	–44.16	22.52	–4.64	–62.03	–29.67	–30.27
PH ₃	–39.74	8.98	–4.44	–44.28	–28.46	–14.03
PMe ₃	–50.50	6.19	–8.85	–47.85	–32.54	–12.29
PPh ₃	–44.19	22.82	–20.51	–46.49	–29.70	–12.37

$$\Delta E_{\text{tot}} = \Delta E_{\text{steric}} + \Delta E_{\text{disp}} + \Delta E_{\text{oi}} = \Delta E_{\text{steric}} + \Delta E_{\text{disp}} + \Sigma \Delta E_{\text{orb}}^{\pi}$$

EDA-NOCV analysis shows that for **23**, σ donation is the most dominant contribution to the P–W bond ($\Delta E_{\text{orb}}^{\sigma} = -30.54$ kcal mol^{–1}; Table 5.2). W–P π backdonation is attenuated. This is due to the effect of strong π backdonation from the rhodium center to the cyaphide moiety in the side-on η² coordination mode. The strong rhodium–cyaphide π backdonation also contributes to greater P–W σ donation; this can be seen in the difference density plot for the first NOCV, Δρ₁, which reveals a net transfer of electron density from rhodium to tungsten (Table 5.3).

Table 5.3. Contours of NOCVs φ_1 , φ_2 , and φ_3 , ($v > 0$), as well as their contributions to the deformation density, $\Delta\rho_1$, $\Delta\rho_2$, and $\Delta\rho_3$, (green: $\Delta\rho > 0$, orange: $\Delta\rho < 0$), for the P–W interaction in **23**. φ_1 corresponds to σ donation, whereas φ_2 and φ_3 correspond to π backdonation.



5.2.6 Bonding in the side-on η^2 -cyaphido coordination mode

The IDipp $^{13}\text{C}_{\text{NHC}}$ chemical shift was discussed in the previous chapter as a quantitative indicator of X–Au σ donation (see Section 4.3.2). $^{13}\text{C}\{^1\text{H}\}$ NMR characterization of **21**, **22**, and **23** show $^{13}\text{C}_{\text{NHC}}$ values of 198.46, 195.55, and 193.94 ppm, respectively, all higher than the value for the monometallic complex **7** ($^{13}\text{C}_{\text{NHC}} = 193.02$ ppm). This can be ascribed to two factors, either an increase in p-orbital character of the cyaphide carbon-centered lone pair, or an increase in electron density at the cyaphido ligand as a whole. The latter is supported by the increased C–P bond lengths in **21–23**, as well as by their reduced $\text{C}\equiv\text{P}$ vibrational stretching frequencies; both suggest population of a $\text{C}\equiv\text{P}$ π^* antibonding orbital by side-on metal π backdonation.

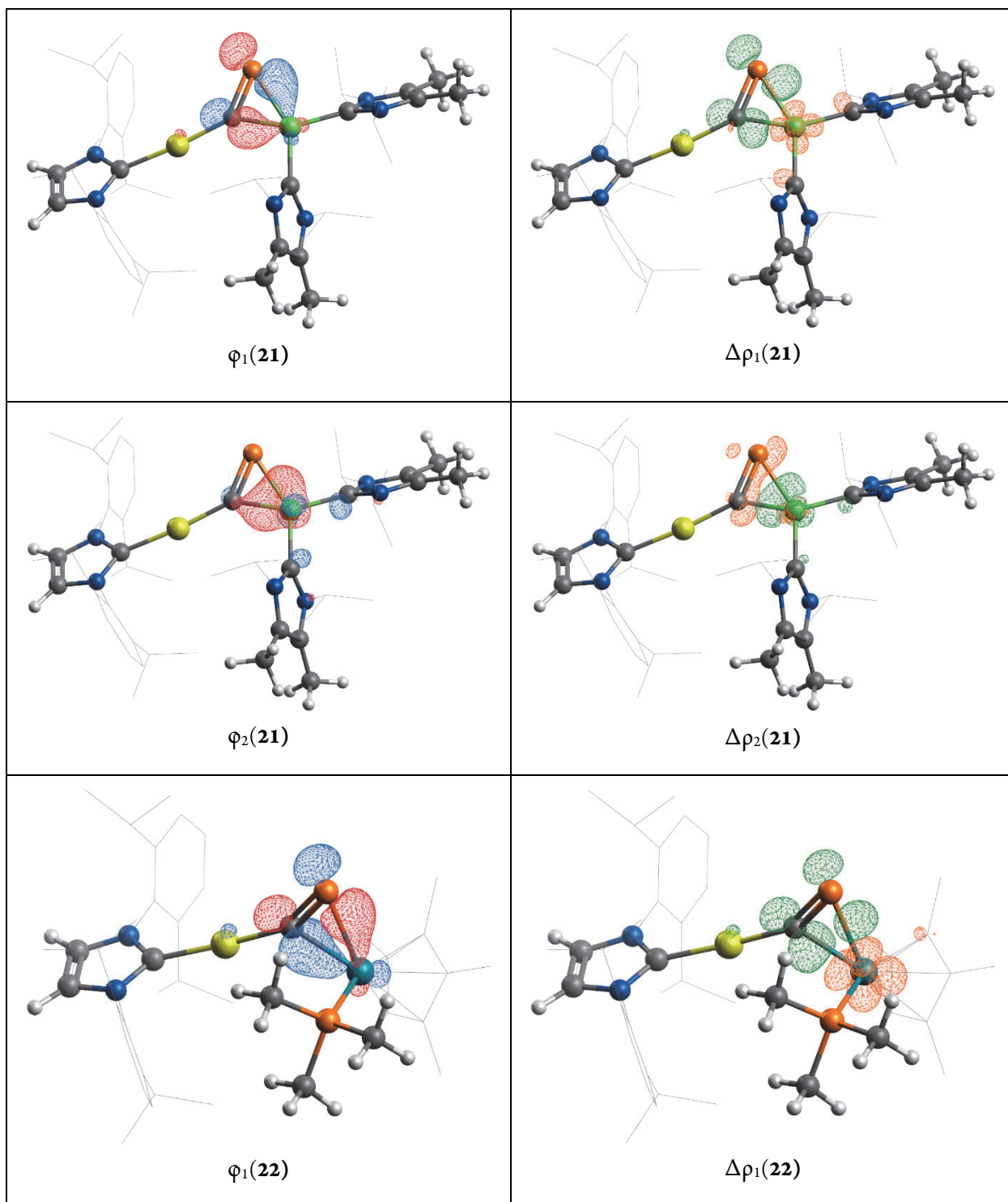
EDA-NOCV analysis was also used to identify σ and π donor/acceptor interactions for the $\text{M}-(\eta^2\text{-CP})$ bonds in **21–23** (Tables 5.4 and 5.5). In all three complexes, π backdonation to the in-plane $\text{C}\equiv\text{P}$ π^* antibonding orbital is the largest contribution to the total orbital interaction energy (**21**: $\Delta E_{\text{orb}}^{\pi} = -102.17$ kcal mol $^{-1}$; **22**: $\Delta E_{\text{orb}}^{\pi} = -59.20$ kcal mol $^{-1}$; **23**: $\Delta E_{\text{orb}}^{\pi} = -78.93$ kcal mol $^{-1}$). σ donation from the in-plane $\text{C}\equiv\text{P}$ π bonding orbital is the next largest contribution (**21**: $\Delta E_{\text{orb}}^{\sigma} = -11.95$ kcal mol $^{-1}$; **22**: $\Delta E_{\text{orb}}^{\sigma} = -25.70$ kcal mol $^{-1}$; **23**: $\Delta E_{\text{orb}}^{\sigma} = -24.72$ kcal mol $^{-1}$). For all three complexes, additional NOCVs for π donation from out-of-plane $\text{C}\equiv\text{P}$ π orbitals, as well as for δ backdonation to out-of-plane $\text{C}\equiv\text{P}$ π^* orbitals can also be identified, though these have low eigenvalues and are energetically insignificant. This reveals that the cyaphide ion behaves primarily as a π acceptor in the η^2 coordination mode, and is consistent with the experimental observation that **7** exhibits predominantly electrophilic reactivity at the cyaphido ligand.

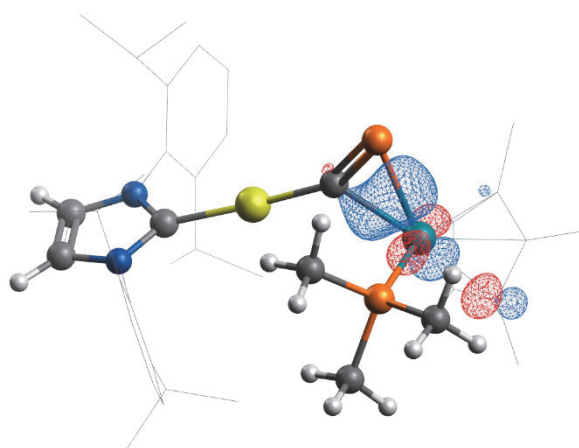
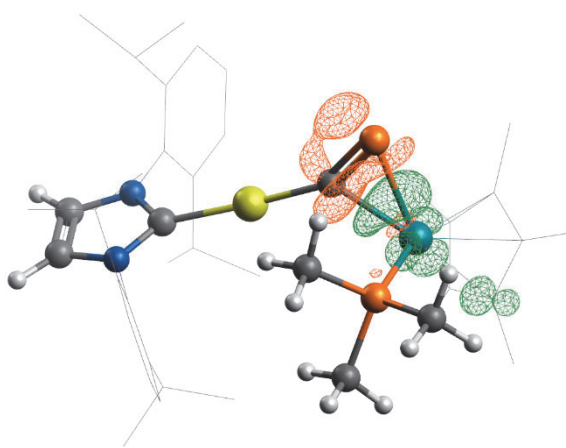
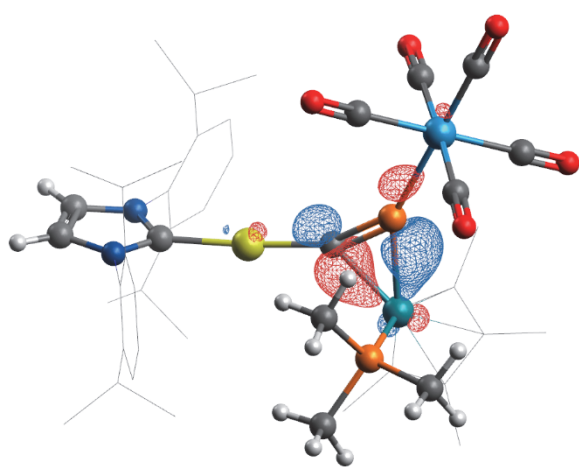
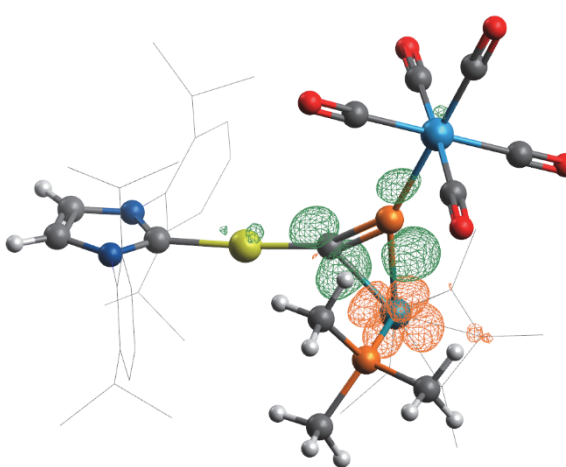
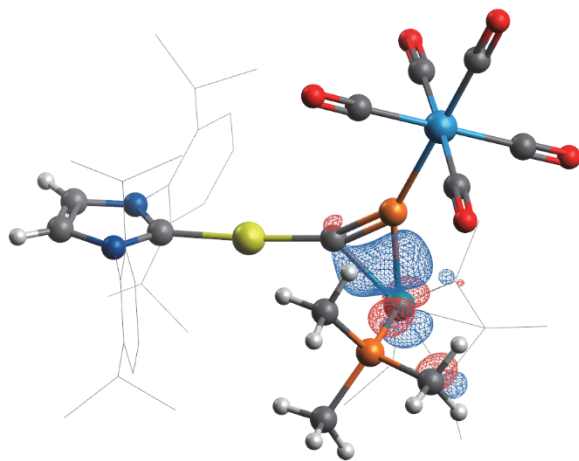
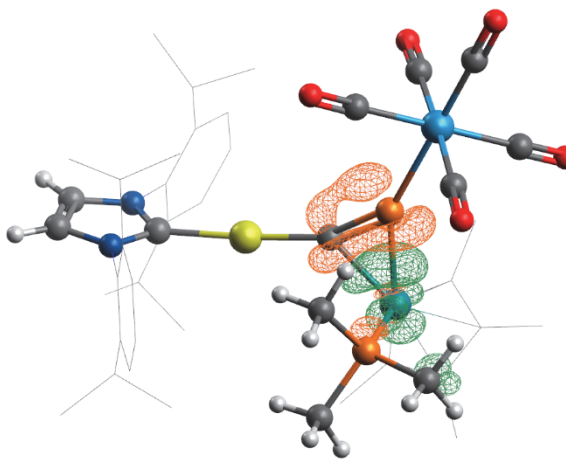
Table 5.4. Summary of EDA-NOCV analysis of the $\text{M}-(\eta^2\text{-CP})$ bonding interactions in **21–23**, including ETS-NOCV energies from orbital contributions due to σ donation ($\Delta E_{\text{orb}}^{\sigma}$) and π backdonation ($\Delta E_{\text{orb}}^{\pi}$), in kcal mol $^{-1}$.

	ΔE_{tot}	ΔE_{steric}	ΔE_{disp}	ΔE_{oi}	$\Delta E_{\text{orb}}^{\sigma}$	$\Delta E_{\text{orb}}^{\pi}$
21	–84.99	123.12	–75.38	–132.74	–11.95	–102.17
22	–62.72	98.51	–57.92	–103.32	–25.70	–59.20
23	–71.82	121.34	–69.52	–123.65	–24.72	–78.93

$$\Delta E_{\text{tot}} = \Delta E_{\text{steric}} + \Delta E_{\text{disp}} + \Delta E_{\text{oi}} = \Delta E_{\text{steric}} + \Delta E_{\text{disp}} + \Sigma \Delta E_{\text{orb}}^n$$

Table 5.5. Contours of NOCVs φ_1 and φ_2 , ($v > 0$), as well as their contributions to the deformation density, $\Delta\rho_1$ and $\Delta\rho_2$, (green: $\Delta\rho > 0$, orange: $\Delta\rho < 0$), for the $M-(\eta^2\text{-CP})$ bonding interactions in **21–23**. φ_1 corresponds to π backdonation, whereas φ_2 corresponds to σ donation.



 $\varphi_2(22)$  $\Delta\rho_2(22)$  $\varphi_1(23)$  $\Delta\rho_1(23)$  $\varphi_2(23)$  $\Delta\rho_2(23)$

In the multimetallic complexes **21–23**, the C–P bond length, Au–C–P bond angle, and C≡P Raman stretching frequencies all follow a similar trend. These data all correlate with the computed π backdonation contributions, reinforcing the idea that η^2 -cyaphido coordination is electrophilic in nature, and driven principally by its C≡P π^* LUMOs (Figure 5.6).

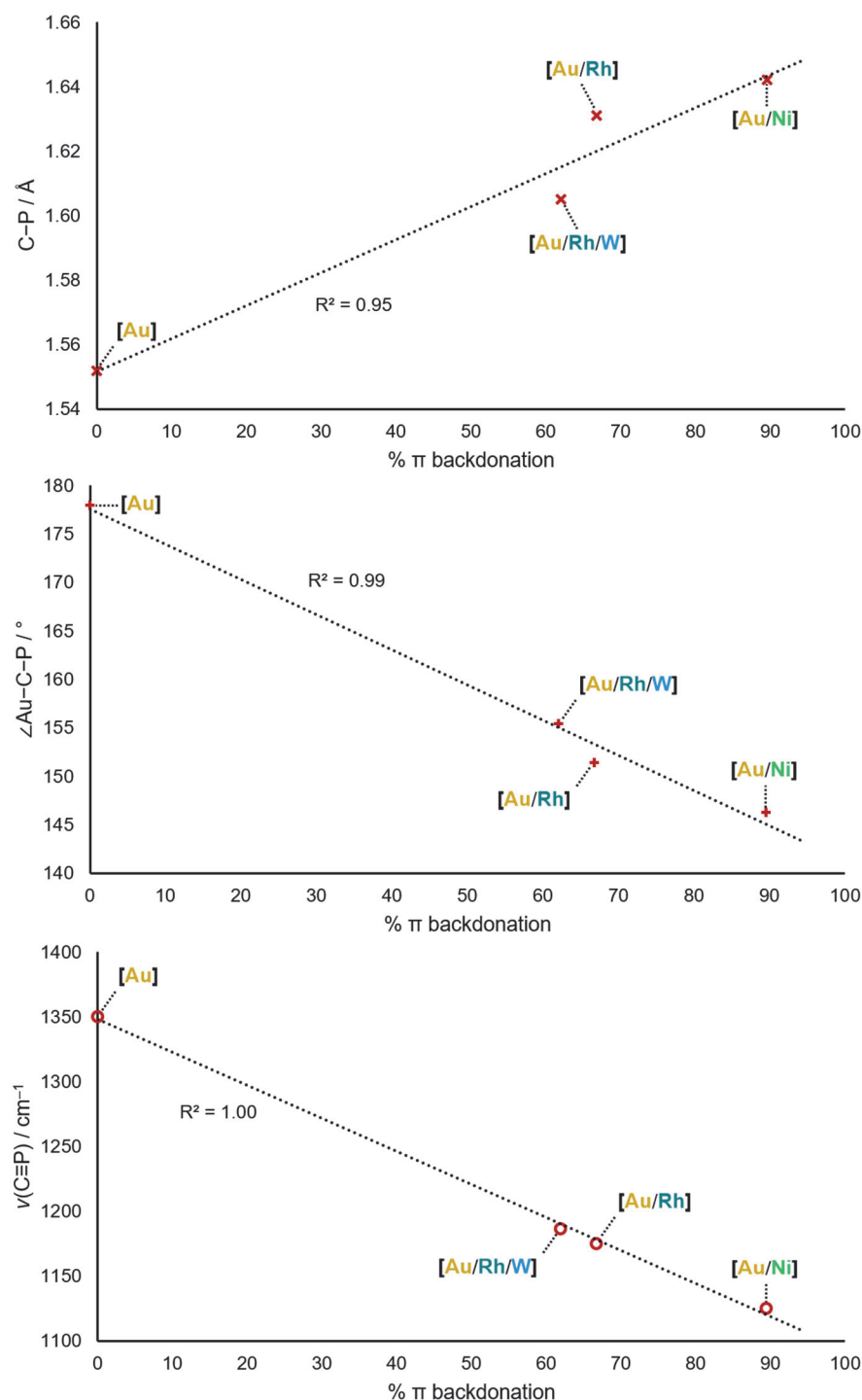


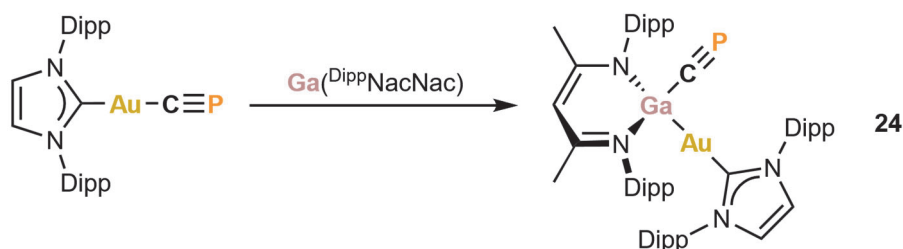
Figure 5.6. Calculated $M-(\eta^2\text{-CP})$ π backdonation contributions ($\Delta E_{\text{orb}}^{\pi}$, %) plotted against experimental C–P bond lengths (top), Au–C–P bond angles (middle), and C≡P Raman stretching frequencies (bottom) for **7**, **21**, **22**, and **23**.

5.3 Hetero-multimetallic complexes by covalent cyaphide transfer

5.3.1 Synthesis of $\text{Au}(\text{IDipp})\{\text{Ga}(\text{DippNacNac})(\text{CP})\}$

The LUMO driven reactivity of **7** to form multimetallic bridging cyaphide complexes with electron-rich metals mirrors the coordination chemistry of organic phosphaaalkynes (see Section 1.4.1). It has been shown recently that platinum(0) η^2 -arylphosphaaalkynes complexes can undergo C–C bond cleavage to afford cyaphide complexes by formal oxidative addition reactions (see Section 1.4.7).

An analogous Au–C bond cleavage reaction occurs when **7** is reacted with the gallium(I) nucleophile $\text{Ga}(\text{DippNacNac})$. **7** reacts cleanly with $\text{Ga}(\text{DippNacNac})$ at room temperature to give one product, $\text{Au}(\text{IDipp})\{\text{Ga}(\text{DippNacNac})(\text{CP})\}$ (**24**), the result of gallium(I) insertion into the Au–CP bond and the first example of a gallium cyaphide complex (Scheme 5.5). This reaction is also analogous to the previously reported gallium(I) insertion into the Au–Cl bond of $\text{Au}(\text{PPh}_3)\text{Cl}$.^[18]



Scheme 5.5. Synthesis of the gallium cyaphide complex **24**.

The cyaphide phosphorus atom of **24** appears in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 109.8 ppm, and the cyaphide carbon atom appears in its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum as a doublet at 251.61 ppm ($^2J_{\text{C-P}} = 20.9$ Hz). The C≡P vibrational stretching mode was observed by Raman spectroscopy at 1329 cm^{-1} . These data are comparable to those for the structurally related tin(II) cyaphide complex **5** (Section 3.2.3, $^{31}\text{P}\{^1\text{H}\}$: 122.4 ppm; $\nu(\text{C}\equiv\text{P})$: 1321 cm^{-1}).

Single crystal X-ray diffraction of **24** shows a solid-state structure with a distorted tetrahedral gallium center bonded to a linear gold center and to the cyaphide moiety *via* its carbon atom (Figure 5.7). The Au1–Ga1 bond length is $2.4074(2)\text{ \AA}$, and the Ga1–Au1–C2 angle is $172.01(5)^\circ$, showing a near-linear coordination geometry at gold. The cyaphido ligand is coordinated $\eta^1, \kappa\text{C}$ to the gallium center, with a Ga1–C1–P1 angle of $175.5(1)^\circ$ and Ga1–C1 bond length of $2.029(2)\text{ \AA}$. The cyaphide C1–P1 bond length is $1.550(2)\text{ \AA}$, similar to other terminal cyaphide complexes.

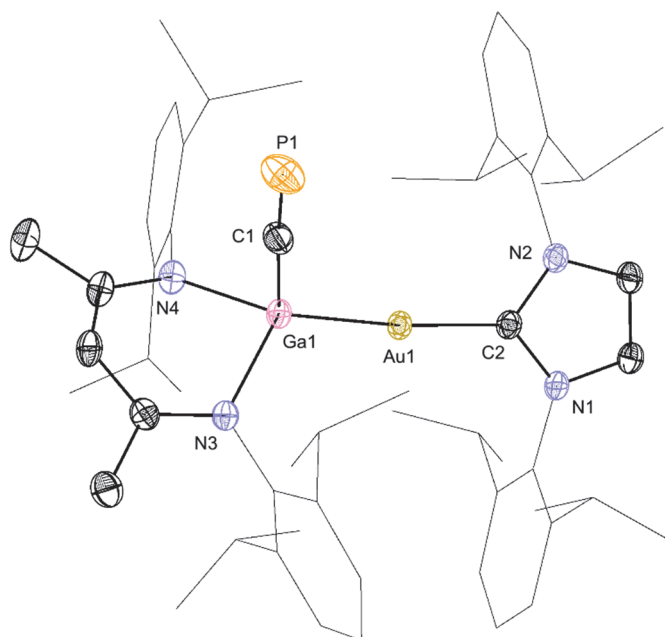
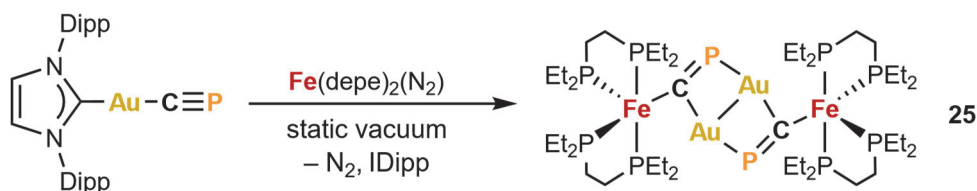


Figure 5.7. Solid-state structure of **24**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms and disordered ⁱPr components are omitted for clarity. Dipp groups are depicted as wireframes.

5.3.2 Synthesis of {Fe(depe)₂}₂(μ-C₂P₂Au₂)

In forming **24**, the insertion of a gallium(I) metal center into the Au–CP bond of **7** demonstrates a different mode of reactivity beyond η² coordination to electron-rich metals. A third outcome results when **7** reacts at an iron(0) center.

The reaction of **7** with Fe(depe)₂(N₂) (depe = 1,2-bis(diethylphosphino)ethane) under a static vacuum results in gas evolution and the formation of a dark orange-red solution with a complex ¹H NMR spectrum, including the presence of free IDipp ligand. On standing, the tetrametallic iron(0)/gold(I) complex {Fe(depe)₂}₂(μ-C₂P₂Au₂) (**25**) crystallizes as red blocks (Scheme 5.6).



Scheme 5.6. Synthesis of the tetrametallic iron(0)/gold(I) complex **25**.

The solid-state structure of **25** reveals a structure with two symmetry-related distorted trigonal bipyramidal iron centers, coplanar with a bridging six-membered ring containing two carbon atoms, two phosphorus atoms, and two gold atoms in a Dewar-benzene like arrangement (Figure 5.8).

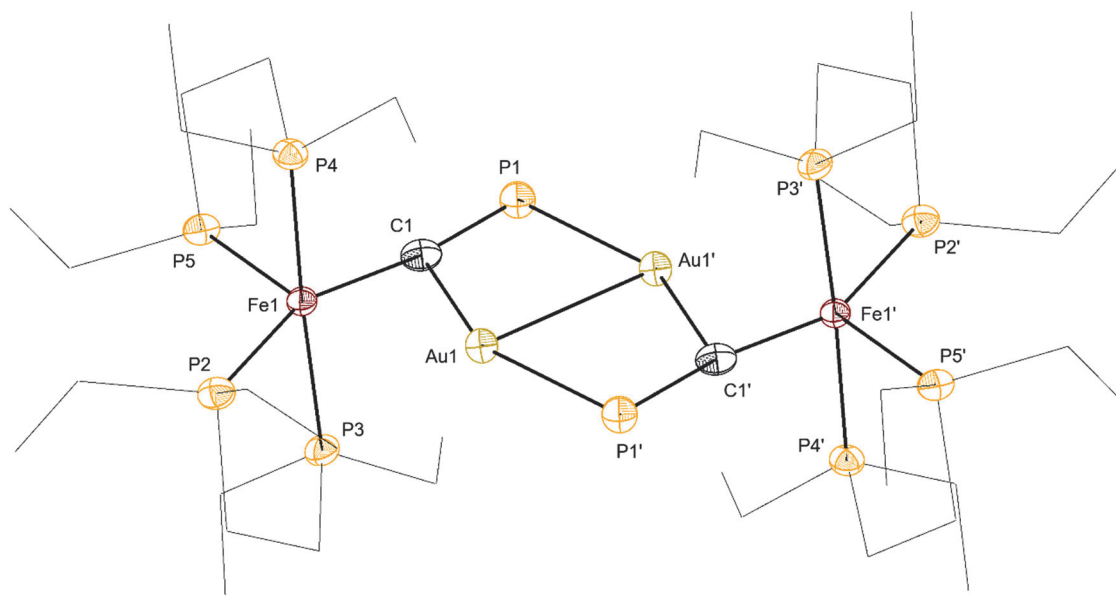


Figure 5.8. Solid-state structure of **25**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Ethyl and ethylene groups are depicted as wireframes.

The Fe1-C1-P1 angles are non-linear at $168.4(2)^\circ$ and the Fe1-C1 bond lengths are $1.801(3)$ Å, in between the sums of covalent radii for Fe-C single-bonds (1.91 Å) and double bonds (1.76 Å).^[19] The C1-P1 bond lengths are $1.676(3)$ Å, higher than those in the η^2 -cyaphido multimetallic complexes **21–23** ($1.605(4)$ – $1.642(4)$ Å), and in good agreement with the sum of covalent radii for C=P double bonds (1.69 Å).^[19] The Au1-C1 distances are $2.165(3)$ Å, significantly longer than the Au-CP bond length in **7** ($1.972(6)$ Å), and the Au1-P1 distances are $2.3671(8)$ Å. The Fe1-Au1 distances are $2.6402(5)$ Å, and the Au1-Au1 distance is $2.7933(2)$ Å, indicative of an aurophilic interaction. The structure of the $C_2P_2Au_2$ ring in **25** is quite unusual; the only other structurally authenticated Au_2X_4 species to adopt a Dewar-benzene structure is the $[Au_2Te_4]^{2-}$ anion.^[20]

The $^1H\{^{31}P\}$ NMR spectrum of **25** is complex due to the low symmetry of the iron centers, though its $^{31}P\{^1H\}$ NMR spectrum contains a multiplet at 148.7 ppm corresponding to the cyaphide phosphorus atom, and multiplets at 71.5 – 66.7 ppm corresponding to the depe ligands. The symmetric C=P vibrational stretching mode of **25** appears in its Raman spectrum at 1047 cm^{-1} , lower than the η^2 -C $\equiv$ P stretching frequencies in **21–23** (1125 – 1186 cm^{-1}), in line with its longer C-P bond length. The symmetric Au-Au stretching mode can also be observed at 117 cm^{-1} , which agrees well with the solid-state Au-Au bond length when correlated with other Au_2 -containing complexes in the literature.^[21]

25 was also investigated electrochemically by cyclic voltammetry (Figure 5.9). Its voltammogram shows a reversible one electron oxidation at -1.14 V vs. $Fe^{0/+}$, followed closely by a feature that at low scan rates

appears as a quasi-reversible one electron oxidation at -0.86 V vs. $\text{Fc}^{0/+}$ but at higher scan rates is indistinct from other irreversible oxidative features at higher potentials. Scanning cathodically, no reductive features are observed. Attempts to target the one- or two-electron oxidized cations of **25** were unsuccessful, possibly due to their solution instability or propensity for over-oxidation or disproportionation.

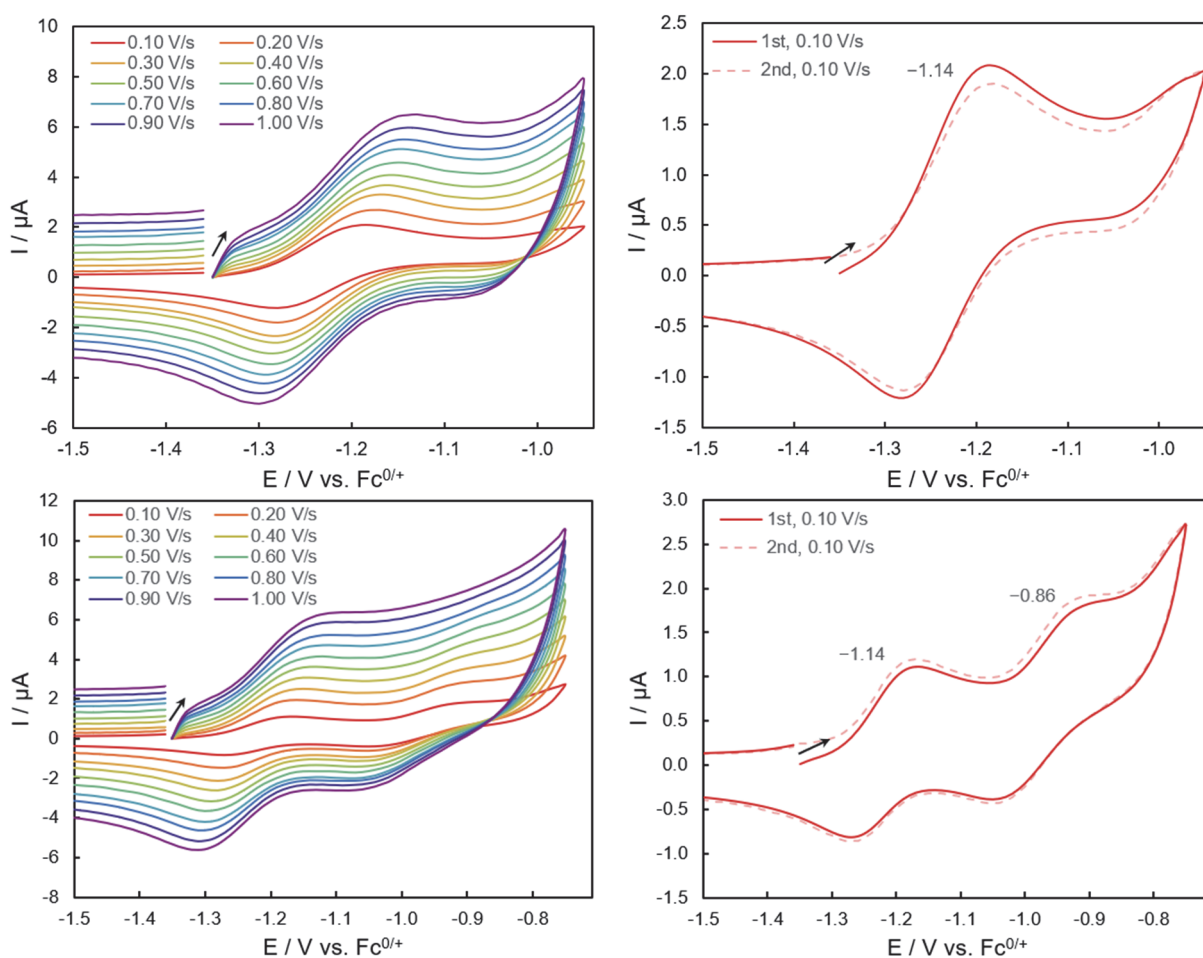
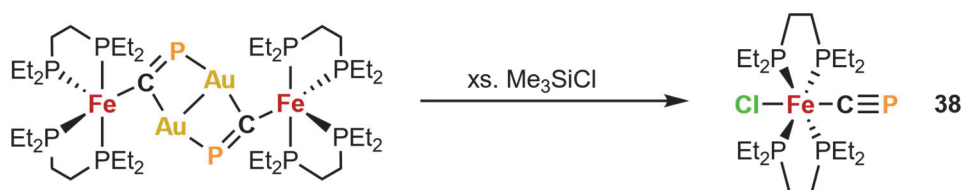


Figure 5.9. Cyclic voltammograms (THF, 0.2 M $[\text{NBu}_4][\text{PF}_6]$) of **25** (0.1 mM), scanned anodically from -2.35 to -0.95 V (top) or -2.35 to -0.75 V (bottom) at varying scan rates (0.10 to 1.00 V/s) (left), and twice at 1.00 V/s (right). All potentials were referenced to $\text{Fc}^{0/+}$.

However, treating **25** with excess Me_3SiCl results in oxidation to afford the iron(II) chloride/cyaphide complex $\text{Fe}(\text{depe})_2(\text{Cl})(\text{CP})$ (**38**, see Section 8.2.2), and metallic gold (Scheme 5.7). The identity of the reduced silane byproduct could not be determined, though it is likely to be oligo- or poly- silanes.

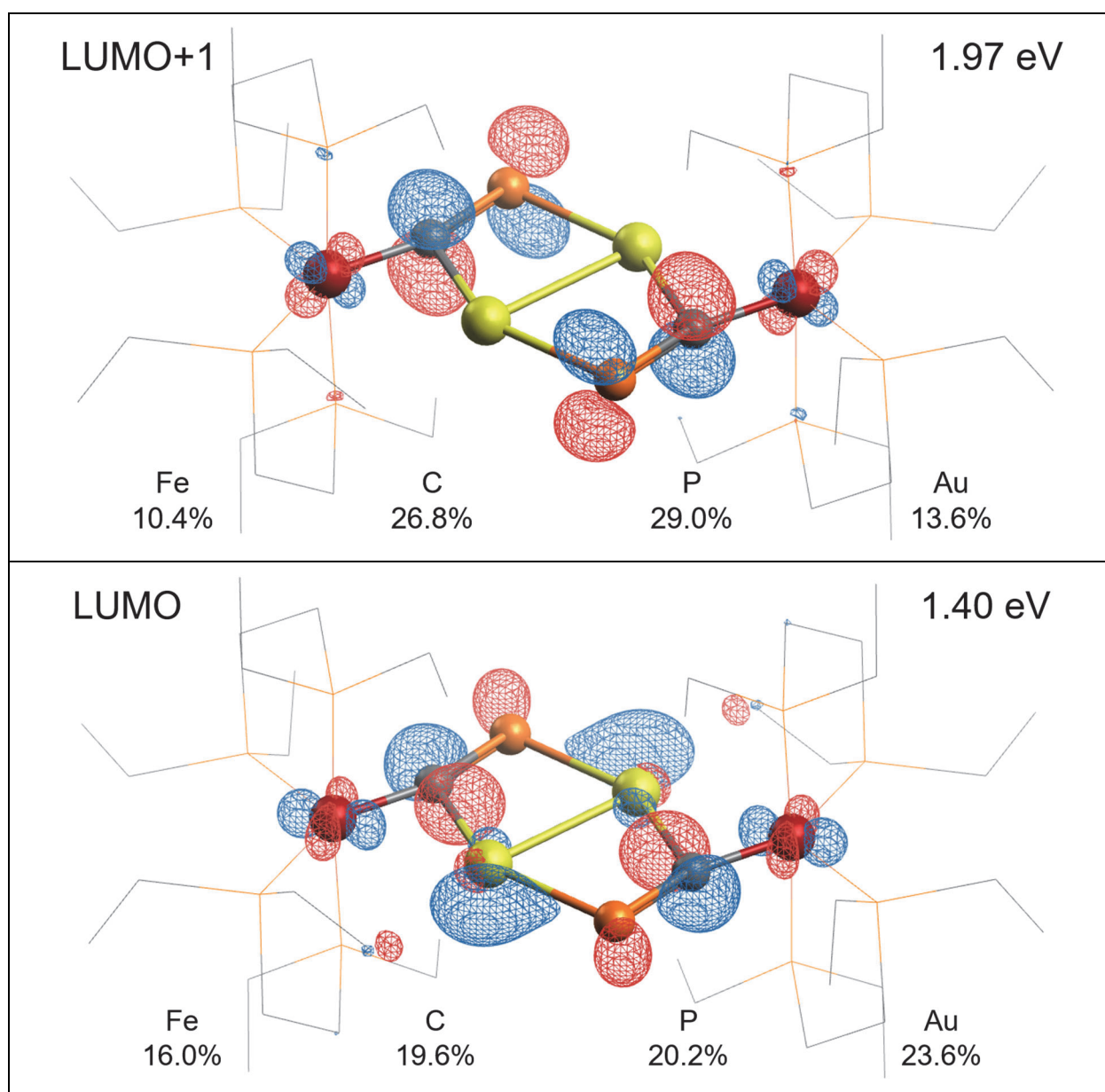


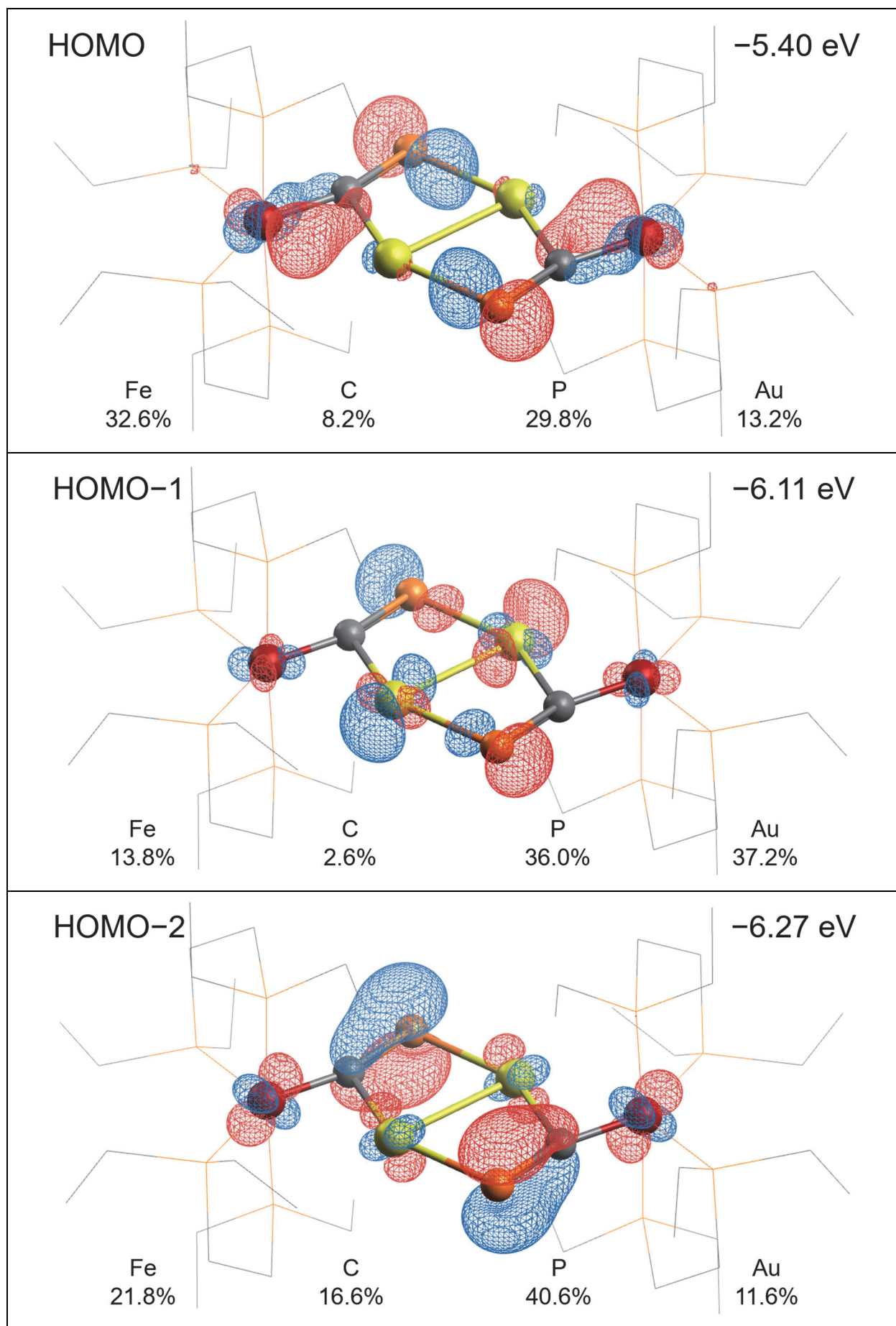
Scheme 5.7. Oxidation of **25** to the iron(II) cyaphide complex **38** (see Section 8.2.2) by Me_3SiCl .

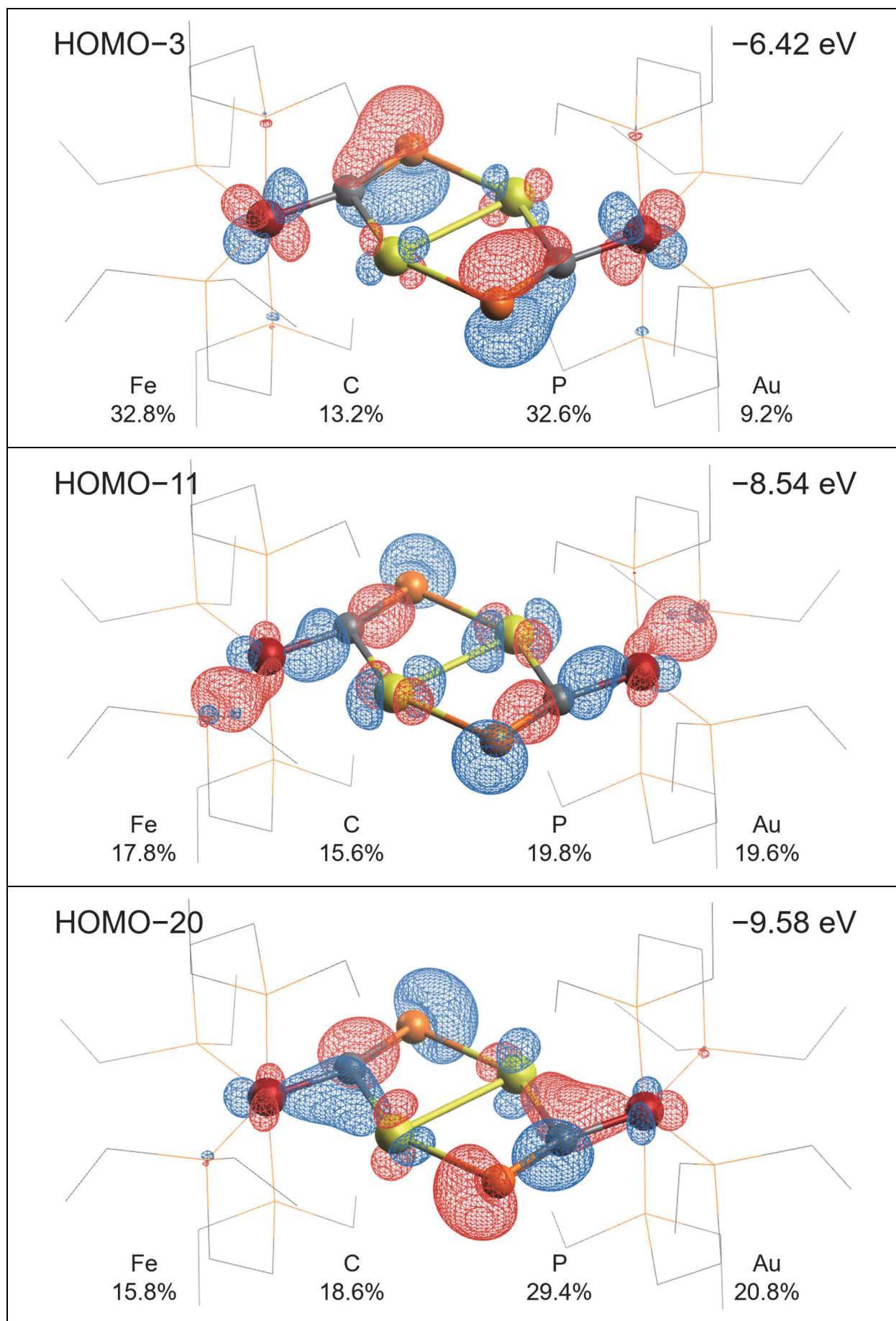
5.3.3 Bonding in $\{\text{Fe}(\text{depe})_2\}_2(\mu\text{-C}_2\text{P}_2\text{Au}_2)$

DFT calculations were used to provide insight into the electronic structure and bonding in **25** (Table 5.6). The HOMO and HOMO–1 show significant population of localized phosphorus 3p orbitals, suggesting a partial reduction in bond order due to strong Fe–CP backdonation and side-on gold coordination, in line with the short Fe–C bond length, long C–P bond length, and lower C=P vibrational frequency. The cyaphide σ orbitals are relatively low in energy, corresponding to the HOMO–11 and HOMO–20, the latter of which shows contributions from both gold and iron, reminiscent of the $3c\text{-}2e^-$ σ bonding orbitals in bridging carbonyls.

Table 5.6. Kohn-Sham molecular orbitals of **25**.







QTAIM was used to further analyze the bonding in **25** (Figure 5.10). The C=P bonds have an ellipticity of 0.28, suggesting double-bond character. The C–Au bonds are also significantly non-cylindrical, with an ellipticity of 0.18. This indicates some π contribution to the C–Au bond and that the cyaphide carbon to some extent has carbene character in a manner analogous to recently reported metallo-phosphinocarbenes.^[22,23]

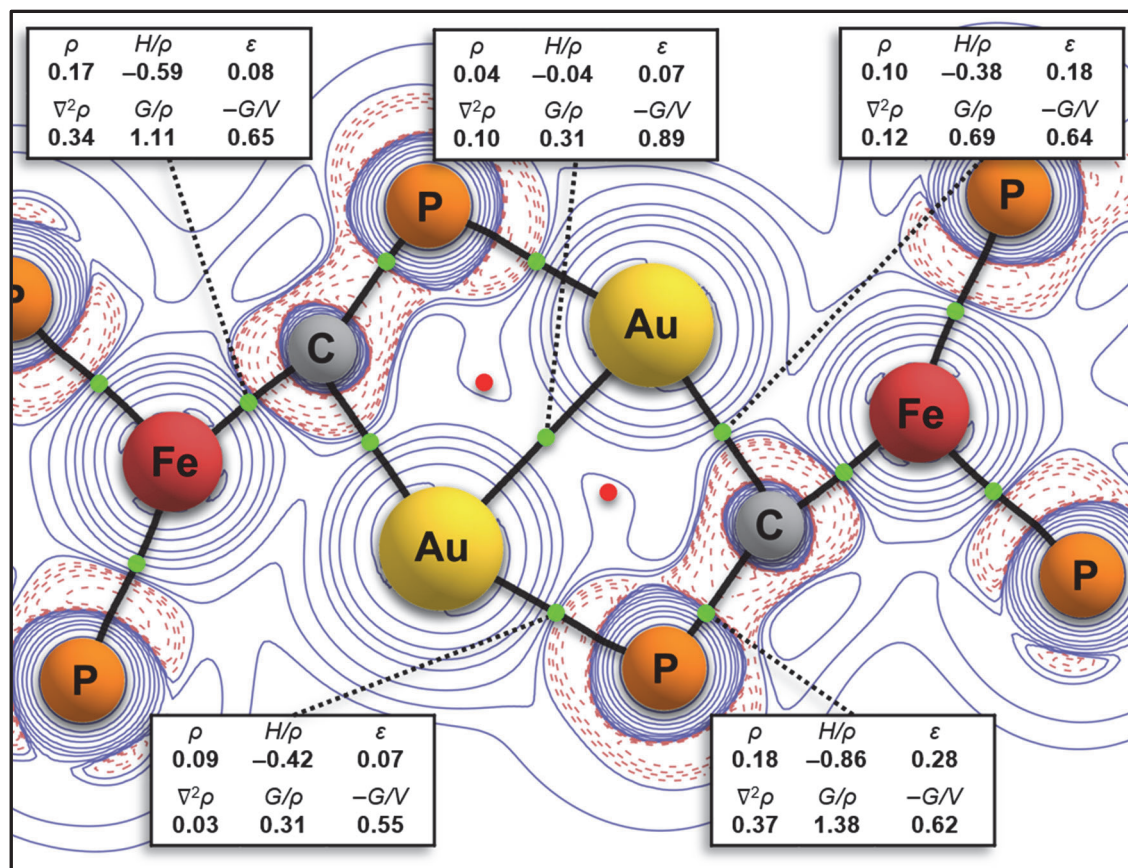


Figure 5.10. 2D QTAIM topological analysis of **25**. Parameters at bond critical points are specified in a.u.

Whereas **24** shows unambiguous transfer of the cyaphide group from gold to gallium, **25** represents an intermediary example of “incomplete” cyaphide transfer. This may be driven by the formation of an exceptionally strong Fe–C bond. However, the formation of an unsupported Au–Fe bond (similar to the Au–Ga bond in **24**) is likely to be unfavorable relative to Au incorporation into the $C_2P_2Au_2$ unit, where it is capable of forming bonding interactions to carbon, phosphorus, and another gold atom.

5.4 Conclusions

The gold(I) cyaphide complex **7** was investigated as a precursor to hetero-multimetallic complexes.

In contrast to the cyanide ion, which bridges metal centers in a linear $\eta^1:\eta^1$ fashion, the cyaphide ion adopts a $\eta^1:\eta^2$ bridging coordination mode in hetero-bimetallic complexes with nickel(0) (**21**) and rhodium(I) (**22**). This coordination mode is driven by very strong π backdonation into a $C\equiv P$ π^* orbital. Once the π manifold is engaged, reactivity at the cyaphide phosphorus lone pair is effectively unlocked, enabling access to the hetero-trimetallic gold(I)/rhodium(I)/tungsten(0) complex **23**.

Metal centers with even greater nucleophilicity can react at the Au–C bond, resulting in the transfer of the cyaphide ion from gold(I) to the nucleophilic metal center. Insertion of a gallium(I) center between the Au–C bond gives a terminal gallium cyaphide complex, **24**. “Incomplete” cyaphide transfer occurs at an iron(0) complex, giving an unusual tetrametallic complex with a planar $C_2P_2Au_2$ moiety.

Overall, the covalent gold(I) cyaphide complex **7** behaves as a metallo-phosphaalkyne, exhibiting electrophilic reactivity toward electron-rich metal centers. The low-lying π^* orbitals of the cyaphide ion play a critical role in these transformations. This is a general theme for the reactivity of cyaphide-containing molecules and is explored in the subsequent chapters.

Some of the work in this chapter has been published in *Angewandte Chemie*:

E. S. Yang, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2022**, 61, e202206783.

5.5 Experimental section

5.5.1 Synthesis of $\{\text{Au}(\text{IDipp})\}(\mu\text{-CN})\{\text{B}(\text{C}_6\text{F}_5)_3\}$ (20)

$\text{Au}(\text{IDipp})(\text{CN})$ (18 mg, 0.03 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (15 mg, 0.03 mmol) were dissolved in dichloromethane (1 mL), and the reaction mixture stirred for 15 min. The solvent was removed under vacuum, and the resulting residue was washed with hexane then crystallized from toluene by slow evaporation, affording $\{\text{Au}(\text{IDipp})\}(\mu_2\text{-CN})\{\text{B}(\text{C}_6\text{F}_5)_3\}$ as colorless crystals. Yield: 27 mg, 0.02 mmol, 82%. Anal. Calcd. (%) for $\text{C}_{46}\text{H}_{36}\text{AuBF}_{15}\text{N}_3$: C, 49.17; H, 3.23; N, 3.74. Found: 50.14; H, 3.17; N, 3.26.

^1H NMR (600 MHz, C_6D_6): δ (ppm) 7.10 (t, $^3J_{\text{H-H}} = 7.8$ Hz, 2H, Dipp *para*-CH), 6.92 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 4H, Dipp *meta*-CH), 6.11 (s, 2H, IDipp CH), 2.25 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 4H, Dipp CH(CH₃)₂), 1.21 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 12H, Dipp CH(CH₃)₂), 0.94 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 12H, Dipp CH(CH₃)₂).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): δ (ppm) 183.06 (IDipp CAu), 152.68 ($\mu_2\text{-CN}$), 148.64 (bd, $^1J_{\text{C-F}} = 242.2$ Hz, C_6F_5 *ortho*-C), 145.40 (Dipp *ortho*-C), 140.26 (bd, $^1J_{\text{C-F}} = 249.7$ Hz, C_6F_5 *para*-C), 137.50 (bd, $^1J_{\text{C-F}} = 248.9$ Hz, C_6F_5 *meta*-C), 133.01 (Dipp *ipso*-C), 131.73 (Dipp *para*-C), 124.69 (Dipp *meta*-C), 123.74 (IDipp CH), 117.93 (b, C_6F_5 *ipso*-C), 29.01 (Dipp CH(CH₃)₂), 24.56 (Dipp CH(CH₃)₂), 23.77 (Dipp CH(CH₃)₂).

$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6): δ (ppm) -12.70 (bs, $\text{B}(\text{C}_6\text{F}_5)_3$).

$^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, C_6D_6): δ (ppm) -133.94 (dd, $^3J_{\text{F-F}} = 23.7$ Hz, $^4J_{\text{F-F}} = 8.7$ Hz, C_6F_5 *ortho*-F), -158.37 (t, $^3J_{\text{F-F}} = 20.8$ Hz, C_6F_5 *para*-F), -164.84 (m, C_6F_5 *meta*-F).

5.5.2 Synthesis of $\{\text{Au}(\text{IDipp})\}(\mu\text{-CP})\{\text{Ni}(\text{MeTiPr}_2)_2\}$ (21)

$\text{Au}(\text{IDipp})(\text{CP})$ (50 mg, 0.08 mmol) and a 7:3 mixture of $\text{Ni}(\text{MeTiPr}_2)_2(\text{COD})$ and $\{\text{Ni}(\text{MeTiPr}_2)_2\text{Ni}\}_2(\mu_2\text{-COD})$ (41 mg, 0.08 mmol [$\text{Ni}(\text{MeTiPr}_2)_2$]) were dissolved in benzene (5 mL), immediately resulting in a brown-black solution. The reaction mixture was stirred for 1 h then filtered to remove any particulates. All volatiles were then removed under vacuum by lyophilization, affording $\{\text{Au}(\text{IDipp})\}(\mu\text{-CP})\{\text{Ni}(\text{MeTiPr}_2)_2\}$ as a brown powder. Yield: 70 mg, 0.07 mmol, 84%. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a concentrated benzene/hexane solution. Anal. Calcd. (%) for $\text{C}_{50}\text{H}_{76}\text{AuN}_6\text{NiP}$: C, 57.31; H, 7.31; N, 8.02. Found: 57.84; H, 6.79; N, 6.91.

^1H NMR (400 MHz, C_6D_6): δ (ppm) 7.13 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 2H, Dipp *para*-CH), 7.05 (d, $^3J_{\text{H-H}} = 7.4$ Hz, 4H, Dipp *meta*-CH), 6.33 (s, 2H, IDipp CH), 5.87 (sept, $^3J_{\text{H-H}} = 7.0$ Hz, 2H, $^{\text{MeTiPr}_2}$ CH(CH $_3$) $_2$), 5.82 (sept, $^3J_{\text{H-H}} = 7.0$ Hz, 2H, $^{\text{MeTiPr}_2}$ CH(CH $_3$) $_2$), 2.79 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 4H, Dipp CH(CH $_3$) $_2$), 1.99 (s, 6H, $^{\text{MeTiPr}_2}$ C(CH $_3$)), 1.85 (s, 6H, $^{\text{MeTiPr}_2}$ C(CH $_3$)), 1.51 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp CH(CH $_3$) $_2$), 1.22 (d, $^3J_{\text{H-H}} = 7.0$ Hz, 16H, Dipp CH(CH $_3$) $_2$), 1.14 (d, $^3J_{\text{H-H}} = 7.0$ Hz, 12H, $^{\text{MeTiPr}_2}$ CH(CH $_3$) $_2$), 1.12 (d, $^3J_{\text{H-H}} = 7.0$ Hz, 12H, $^{\text{MeTiPr}_2}$ CH(CH $_3$) $_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): δ (ppm) 280.32 (d, $^1J_{\text{C-P}} = 105.1$ Hz, μ_2 -CP), 207.84 (d, $^2J_{\text{C-P}} = 23.7$ Hz, $^{\text{MeTiPr}_2}$ CNi), 198.46 (IDipp CAu), 145.50 (Dipp *ortho*-C), 135.51 (Dipp *ipso*-C), 129.70 (Dipp *para*-C), 123.64 (Dipp *meta*-C), 123.33 ($^{\text{MeTiPr}_2}$ CCH $_3$), 121.99 ($^{\text{MeTiPr}_2}$ CCH $_3$), 121.88 (IDipp CH), 51.31 ($^{\text{MeTiPr}_2}$ CH(CH $_3$) $_2$), 50.93 ($^{\text{MeTiPr}_2}$ CH(CH $_3$) $_2$), 28.60 (Dipp CH(CH $_3$) $_2$), 24.28 (Dipp CH(CH $_3$) $_2$), 23.81 ($^{\text{MeTiPr}_2}$ CH(CH $_3$) $_2$), 22.26 (Dipp CH(CH $_3$) $_2$), 21.57 ($^{\text{MeTiPr}_2}$ CH(CH $_3$) $_2$), 10.26 ($^{\text{MeTiPr}_2}$ CCH $_3$), 10.22 ($^{\text{MeTiPr}_2}$ CCH $_3$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): δ (ppm) 246.0 (s, μ -CP).

Raman: 1125 cm^{-1} (mw, $\nu(\text{C}\equiv\text{P})$).

UV-vis: λ_{max} (nm) 317.

5.5.3 Synthesis of $\{\text{Au}(\text{IDipp})\}(\mu\text{-CP})\{\text{Rh}(\text{Cp}^*)(\text{PMe}_3)\}$ (22)

Au(IDipp)(CP) (100 mg, 0.16 mmol) and Rh(Cp *)(PMe $_3$) $_2$ (62 mg, 0.16 mmol) were dissolved in toluene (10 mL). The reaction mixture was heated at 60 °C overnight, resulting in an orange-red solution. All volatiles were removed under vacuum and the residue lyophilized from benzene (10 mL) to give $\{\text{Au}(\text{IDipp})\}(\mu\text{-CP})\{\text{Rh}(\text{Cp}^*)(\text{PMe}_3)\}$ as an orange-red powder suitable for further synthesis. Yield: 135 mg, 0.14 mmol, 90%. Anal. Calcd. (%) for $\text{C}_{41}\text{H}_{60}\text{AuN}_2\text{P}_2\text{Rh}\cdot\text{C}_6\text{H}_6$: C, 55.30; H, 6.52; N, 2.74. Found: 54.65; H, 5.90; N, 2.71. Compositionally pure crystals suitable for X-ray diffraction can be obtained by slow evaporation of a concentrated benzene/hexane solution.

^1H NMR (600 MHz, C_6D_6): δ (ppm) 7.20 (dd, $^3J_{\text{H-H}} = 7.8$ Hz, 2H, Dipp *para*-CH), 7.08 (dd, $^3J_{\text{H-H}} = 7.8$ Hz, 2H, Dipp *meta*-CH), 7.08 (dd, $^3J_{\text{H-H}} = 7.8$ Hz, 2H, Dipp *meta*-CH), 6.35 (s, 2H, IDipp CH), 2.70 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 2H, Dipp CH(CH $_3$) $_2$), 2.66 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 2H, Dipp CH(CH $_3$) $_2$), 1.89 (d, $^3J_{\text{H-Rh}} = 2.1$ Hz, 15H, Cp * C $_5$ (CH $_3$) $_5$), 1.55 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, Dipp CH(CH $_3$) $_2$), 1.53 (d, $^3J_{\text{H-H}} = 6.8$

Hz, 6H, Dipp CH(CH₃)₂), 1.11 (d, $J = 6.8$ Hz, 12H, Dipp CH(CH₃)₂), 0.89 (dd, $^2J_{\text{H-P}} = 8.6$ Hz, $^3J_{\text{H-Rh}} = 0.9$ Hz, 9H, PMe₃ P(CH₃)₃).

¹³C{¹H} NMR (151 MHz, C₆D₆): δ (ppm) 195.55 (d, $^3J_{\text{C-P}} = 4.0$ Hz, IDipp CAu), 145.91 (Dipp *ortho*-C), 145.86 (Dipp *ortho*-C), 135.26 (Dipp *ipso*-C), 130.47 (Dipp *para*-C), 124.22 (Dipp *meta*-C), 124.15 (Dipp *meta*-C), 122.63 (IDipp CH), 96.12 (dd, $^1J_{\text{C-Rh}} = 3.8$ Hz, $^2J_{\text{C-P}} = 3.8$ Hz, Cp* C₅(CH₃)₅), 29.08 (Dipp CH(CH₃)₂), 24.79 (s, (Dipp CH(CH₃)₂)), 24.70 (s, (Dipp CH(CH₃)₂)), 24.16 (Dipp CH(CH₃)₂), 19.50 (d, $^1J_{\text{C-P}} = 27.6$ Hz, P(CH₃)₃), 10.92 (Cp* C₅(CH₃)₅).

³¹P{¹H} NMR (162 MHz, C₆D₆): δ (ppm) 94.66 (dd, $^1J_{\text{P-Rh}} = 33.8$ Hz, $^2J_{\text{P-P}} = 4.7$ Hz, μ -CP), -5.02 (dd, $^1J_{\text{P-Rh}} = 209.0$ Hz, $^2J_{\text{P-P}} = 4.7$ Hz, PMe₃).

Raman: 1175 cm⁻¹ (m, $\nu(\text{C}\equiv\text{P})$).

UV-vis: λ_{max} (nm) 372, 411.

5.5.4 Synthesis of {Au(IDipp)}(μ₃-CP){Rh(Cp*)(PMe₃)}{W(CO)₅} (23)

W(CO)₅(THF) (approx. 21 mg, 0.05 mmol) was generated *in situ* by degassing a THF (0.5 mL) solution of W(CO)₆ (19 mg, 0.05 mmol) in a quartz flask, then irradiating with a 125 W mercury lamp for 4 h under a static vacuum. The resulting bright yellow solution was degassed to remove liberated CO, then cooled to -35 °C. The solution was then added dropwise to a solution of **22** (51 mg, 0.05 mmol) in THF (0.5 mL) at -35 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. All volatiles were then removed under vacuum, and the resulting orange-red residue extracted with hexane (10 mL). The mixture was filtered to remove any particulates, then concentrated by slow evaporation. Storage at -35 °C for 3 days afforded red crystals of {Au(IDipp)}(μ₃-CP){Rh(Cp*)(PMe₃)}{W(CO)₅}. The supernatant was decanted, concentrated further by slow evaporation, then stored at -35 °C for 3 days to afford a second crop. Yield: 48 mg, 0.04 mmol, 70%.

¹H NMR (600 MHz, C₆D₆): δ (ppm) 7.21 (t, $^3J_{\text{H-H}} = 7.8$ Hz, 2H, Dipp *para*-CH), 7.08 (dd, $^3J_{\text{H-H}} = 7.8$ Hz, $^4J_{\text{H-H}} = 1.4$ Hz, 2H, Dipp *meta*-CH), 7.06 (dd, $^3J_{\text{H-H}} = 7.8$ Hz, $^4J_{\text{H-H}} = 1.4$ Hz, 2H, Dipp *meta*-CH), 6.30 (s, 2H, IDipp CH), 2.63 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 2H, Dipp CH(CH₃)₂), 2.59 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 2H, Dipp CH(CH₃)₂), 1.72 (d, $^3J_{\text{H-Rh}} = 2.4$ Hz, 15H, Cp* C₅(CH₃)₅), 1.49 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, Dipp CH(CH₃)₂),

1.47 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, Dipp CH(CH₃)₂), 1.10 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, Dipp CH(CH₃)₂), 1.09 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, Dipp CH(CH₃)₂), 0.84 (dd, $^2J_{\text{H-P}} = 8.9$ Hz, $^3J_{\text{H-Rh}} = 0.9$ Hz, 9H, PMe₃ P(CH₃)₃).

¹³C{¹H} NMR (151 MHz, C₆D₆): δ(ppm) 202.52 (d, $^1J_{\text{C-W}} = 126.0$ Hz, $^2J_{\text{C-P}} = 25.3$ Hz, W(CO)₅ *ax.* CO), 198.01 (d, $^2J_{\text{C-P}} = 6.9$ Hz, W(CO)₅ *eq.* CO), 193.94 (d, $^3J_{\text{C-P}} = 6.4$ Hz, IDipp CAu), 145.82 (Dipp *ortho*-C), 145.82 (Dipp *ortho*-C), 134.91 (Dipp *ipso*-C), 130.59 (Dipp *para*-C), 124.28 (Dipp *meta*-C), 124.19 (Dipp *meta*-C), 122.67 (IDipp CH), 97.43 (dd, $^2J_{\text{C-P}} = 4.0$ Hz, $^1J_{\text{C-Rh}} = 4.0$ Hz, Cp* C₅(CH₃)₅), 29.08 (Dipp CH(CH₃)₂), 29.05 (Dipp CH(CH₃)₂), 24.78 (Dipp CH(CH₃)₂), 24.76 (Dipp CH(CH₃)₂), 24.11 (Dipp CH(CH₃)₂), 24.05 (Dipp CH(CH₃)₂), 18.76 (d, $^1J_{\text{C-P}} = 29.1$ Hz, PMe₃ P(CH₃)₃), 10.43 (Cp* C₅(CH₃)₅).

³¹P{¹H} NMR (162 MHz, C₆D₆): δ(ppm) 48.54 (dd, $^1J_{\text{P-W}} = 174.7$ Hz, $^1J_{\text{P-Rh}} = 61.9$ Hz, $^2J_{\text{P-P}} = 13.4$ Hz, μ₃-CP), -3.86 (dd, $^1J_{\text{P-Rh}} = 193.6$ Hz, $^2J_{\text{P-P}} = 13.4$ Hz, PMe₃).

ATR-FTIR: 2059 cm⁻¹ (m, ν(C≡O) A₁⁽¹⁾), 1972 cm⁻¹ (w, ν(C≡O) B₁), 1928 cm⁻¹ (s, ν(C≡O) E), 1881 cm⁻¹ (m, ν(C≡O) A₁⁽²⁾).

Raman: 2062 cm⁻¹ (m, ν(C≡O) A₁⁽¹⁾), 1977 cm⁻¹ (m, ν(C≡O) B₁), 1883 cm⁻¹ (m, ν(C≡O) A₁⁽²⁾), 1186 cm⁻¹ (s, ν(C≡P)).

UV-vis: λ_{max}(nm) 379, 414.

5.5.5 Synthesis of Au(IDipp){Ga(^{Dipp}NacNac)(CP)} (24)

Au(IDipp)(CP) (18 mg, 0.03 mmol) and Ga(^{Dipp}NacNac) (14 mg, 0.03 mmol) were dissolved in toluene (1 mL) and stirred overnight. The reaction mixture was filtered to remove any particulates, then concentrated and stored at -35 °C for 3 days, yielding colorless needles of Au(IDipp){Ga(^{Dipp}NacNac)(CP)}. The supernatant was decanted, and the crystals were then washed with cold hexane (2 × 0.5 mL) and dried under vacuum. Yield: 25 mg, 0.02 mmol, 78%. Anal. Calcd. (%) for C₅₇H₇₇N₄AuGaP: C, 61.35; H, 6.96; N, 5.02. Found: C, 62.09; H, 7.44; N, 4.64.

¹H NMR (600 MHz, C₆D₆): δ(ppm) 7.28 (t, $^3J_{\text{H-H}} = 7.7$ Hz, 2H, IDipp Dipp *para*-CH), 7.21 (dd, $^3J_{\text{H-H}} = 7.6$ Hz, $^4J_{\text{H-H}} = 1.6$ Hz, 2H, NacNac Dipp *meta*-CH), 7.18 (t, $^3J_{\text{H-H}} = 7.5$ Hz, 2H, NacNac Dipp *para*-CH), 7.04 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 4H, IDipp Dipp *meta*-CH), 7.00 (dd, $^3J_{\text{H-H}} = 7.5$ Hz, $^4J_{\text{H-H}} = 1.6$ Hz, 2H, NacNac Dipp *meta*-CH), 6.13 (s, 2H, IDipp CH), 4.93 (s, 1H, NacNac CH), 4.26 (sept, $^3J_{\text{H-H}} = 6.7$ Hz,

2H, NacNac Dipp **CH**(CH₃)₂), 3.34 (sept, ³J_{H-H} = 6.8 Hz, 2H, NacNac Dipp **CH**(CH₃)₂), 2.39 (sept, ³J_{H-H} = 6.9 Hz, 4H, IDipp Dipp **CH**(CH₃)₂), 1.58 (s, 6H, NacNac **CH**₃), 1.42 (d, ³J_{H-H} = 6.7 Hz, 6H, NacNac Dipp **CH**(CH₃)₂), 1.25 (d, ³J_{H-H} = 6.7 Hz, 6H, NacNac Dipp **CH**(CH₃)₂), 1.15 (d, ³J_{H-H} = 6.9 Hz, 6H, NacNac Dipp **CH**(CH₃)₂), 1.09 (d, ³J_{H-H} = 6.9 Hz, 12H, IDipp Dipp **CH**(CH₃)₂), 1.04 (d, ³J_{H-H} = 6.9 Hz, 12H, IDipp Dipp **CH**(CH₃)₂), 0.98 (d, ³J_{H-H} = 6.9 Hz, 6H, NacNac Dipp **CH**(CH₃)₂).

¹³C{¹H} NMR (151 MHz, C₆D₆): δ(ppm) 251.61 (d, ²J_{C-P} = 20.9 Hz, **CP**), 214.68 (s, IDipp **CAu**), 166.56 (s, NacNac **CNDipp**), 145.95 (s, NacNac Dipp *ortho*-**C**), 145.61 (s, IDipp Dipp *ortho*-**C**), 144.91 (s, NacNac Dipp *ortho*-**C**), 142.90 (s, NacNac Dipp *ipso*-**C**), 134.95 (s, IDipp Dipp *ipso*-**C**), 130.33 (s, IDipp Dipp *para*-**C**), 125.56 (s, NacNac Dipp *para*-**C**), 124.18 (s, NacNac Dipp *meta*-**C**), 124.09 (s, IDipp Dipp *meta*-**C**), 123.23 (s, NacNac Dipp *meta*-**C**), 122.51 (s, IDipp **CH**), 97.31 (s, NacNac **CH**), 30.50 (s, IDipp Dipp **CH**(CH₃)₂), 28.88 (s, IDipp Dipp **CH**(CH₃)₂), 28.87 (s, NacNac Dipp **CH**(CH₃)₂), 27.83 (s, NacNac Dipp **CH**(CH₃)₂), 25.42 (s, NacNac Dipp **CH**(CH₃)₂), 25.14 (s, IDipp Dipp **CH**(CH₃)₂), 24.77 (s, IDipp Dipp **CH**(CH₃)₂), 24.21 (s, IDipp Dipp **CH**(CH₃)₂), 23.93 (s, NacNac Dipp **CH**(CH₃)₂), 23.61 (s, NacNac **CH**₃).

³¹P{¹H} NMR (162 MHz, C₆D₆): δ(ppm) 109.8 (s, **CP**).

Raman: 1329 cm⁻¹ (s, ν(C≡P)).

5.5.6 Synthesis of {Fe(depe)₂}₂(μ-C₂P₂Au₂) (25)

Au(IDipp)(CP) (190 mg, 0.30 mmol) and Fe(depe)₂(N₂) (150 mg, 0.30 mmol) were dissolved in benzene (10 mL), then filtered to remove any remaining particulates. The dark orange-red solution was then freeze-pump-thaw degassed, during which vigorous gas evolution was observed on each thaw cycle. The degassed solution was left to stand under a static vacuum for 10 days, during which {Fe(depe)₂}₂(μ-C₂P₂Au₂) crystallizes as red blocks. The supernatant was decanted, then the solvent removed under vacuum. The resulting residue was washed with hexane (2 × 3 mL), then recrystallized from a toluene/acetonitrile layer to obtain a second crop of product as red needles. The crystalline product was washed with acetonitrile (2 × 5 mL) then dried under vacuum. Yield: 129 mg, 0.09 mmol, 61%. Anal. Calcd. (%) for C₄₂H₉₆Au₂Fe₂P₁₀·C₇H₈: C, 39.03; H, 6.89; N, 0.00. Found: C, 38.09; H, 6.85; N, 0.00.

¹H{³¹P} NMR (500 MHz, C₆D₆): δ(ppm) 3.13–3.00 (m, 2H, PCH₂CH₃), 3.02–2.91 (m, 2H, PCH₂CH₃), 2.88–2.75 (m, 2H, PCH₂CH₃), 2.48–2.37 (m, 2H, PCH₂CH₃), 2.39–2.29 (m, 2H,

PCH_2CH_3), 2.30–2.21 (m, 1H, $\text{C}_2\text{H}_4(\text{PEt}_2)_2$), 2.24–2.14 (m, 2H, PCH_2CH_3), 2.05–1.98 (m, 2H, $\text{C}_2\text{H}_4(\text{PEt}_2)_2$), 1.98–1.89 (m, 2H, PCH_2CH_3), 1.87–1.75 (m, 2H, $\text{C}_2\text{H}_4(\text{PEt}_2)_2$), 1.77–1.71 (m, 2H, PCH_2CH_3), 1.72–1.60 (m, 1H, $\text{C}_2\text{H}_4(\text{PEt}_2)_2$), 1.62–1.46 (m, 6H, PCH_2CH_3), 1.46–1.41 (m, 1H, $\text{C}_2\text{H}_4(\text{PEt}_2)_2$), 1.42–1.31 (m, 3H, PCH_2CH_3), 1.29–1.25 (m, 3H, PCH_2CH_3), 1.20–1.12 (m, 1H, $\text{C}_2\text{H}_4(\text{PEt}_2)_2$), 1.11–1.06 (m, 2H, $\text{C}_2\text{H}_4(\text{PEt}_2)_2$), 1.08–0.95 (m, 6H, PCH_2CH_3), 0.88–0.81 (m, 3H, PCH_2CH_3), 0.83–0.73 (m, 3H, PCH_2CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): δ (ppm) 31.62–30.86 (m, PCH_2CH_3), 30.28–29.63 (m, PCH_2CH_3), 28.92–27.98 (m, PCH_2CH_3), 27.51–26.56 (m, PCH_2CH_3), 25.02–24.16 (m, $\text{C}_2\text{H}_4(\text{PEt}_2)_2$), 23.87–23.48 (m, PCH_2CH_3), 23.43–22.83 (m, $\text{C}_2\text{H}_4(\text{PEt}_2)_2$), 22.23–21.46 (m, PCH_2CH_3), 20.98–19.83 (m, PCH_2CH_3), 15.89–15.21 (m, $\text{C}_2\text{H}_4(\text{PEt}_2)_2$), 15.21–14.53 (m, $\text{C}_2\text{H}_4(\text{PEt}_2)_2$), 11.85–10.98 (m, PCH_2CH_3), 10.31 (s, PCH_2CH_3), 9.99 (s, PCH_2CH_3), 9.72 (s, PCH_2CH_3), 9.57 (s, PCH_2CH_3), 9.10 (s, PCH_2CH_3), 8.94 (s, PCH_2CH_3), 8.68 (s, PCH_2CH_3), 8.58 (s, PCH_2CH_3).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C_6D_6): δ (ppm) 149.3–148.2 (m, CP), 73.1–71.0 (m, $\text{C}_2\text{H}_4(\text{PEt}_2)_2$), 71.0–70.0 (m, $\text{C}_2\text{H}_4(\text{PEt}_2)_2$), 67.3–65.9 (m, $\text{C}_2\text{H}_4(\text{PEt}_2)_2$).

Raman: 1047 cm^{-1} (m, $\nu(\text{C}\equiv\text{P})$), 117 cm^{-1} (m, $\nu(\text{Au}-\text{Au})$).

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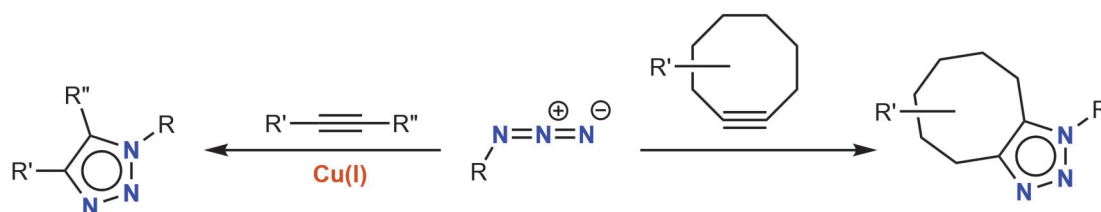
The Cyaphide-Azide “Click” Reaction

Abstract. Metal cyaphide complexes undergo 1,3-dipolar cycloaddition reactions with organic azides to afford metallo-triazaphospholes. These reactions proceed straightforwardly and regioselectively in high yields under mild conditions, reminiscent of the archetypal “click” reaction between alkynes and azides. The resulting metallo-triazaphospholes remain reactive and can be carbon-functionalized to give otherwise difficult to access protio- and iodo- species.

6.1 Azides in 1,3-dipolar cycloaddition reactions

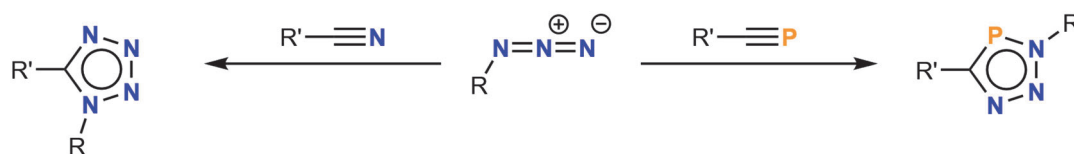
Organic azides are 1,3 dipoles and are thus capable of participating in 1,3-dipolar cycloaddition reactions with unsaturated molecules. The most widely used of these reactions are between azides and alkynes to produce 1,2,3-triazoles.^[1–5]

While these reactions can occur in the absence of catalysts (the classic Huisgen cycloaddition), the use of copper(I) catalysis (copper-catalyzed alkyne-azide cycloaddition, or CuAAC)^[6,7] or strained alkynes (strain-promoted alkyne-azide cycloaddition, or SPAAC)^[8] greatly accelerate reaction rates (Scheme 6.1). These variants are thought of as archetypal “click” reactions due to their mild reaction conditions, good selectivities, and high yields, and are used in a variety of applications, including the construction of interlocked molecules and biological labeling.^[9,10]



Scheme 6.1. Copper-catalyzed and strain promoted alkyne-azide 1,3-dipolar cycloaddition reactions.

1,3-dipolar cycloadditions between azides and other functionalities besides alkynes, including nitriles and phosphalkynes, are also known. These reactions result in 1,2,3,4-tetrazoles and 1,2,3,4-triazaphospholes, respectively (Scheme 6.2).^[11,12]



Scheme 6.2. 1,3-Dipolar cycloaddition reactivity of organic azides toward nitriles and phosphalkynes.

The regioselectivity of 1,3-dipolar cycloadditions are summarized by Houk’s rule, and depends on the frontier orbitals of the 1,3-dipole and dipolarophile.^[13] For phosphalkynes the outcome is almost invariably the 3*H*-1,2,3,4-triazaphosphole regioisomer (Figure 6.1), driven by the $C\equiv P$ bond polarity (see Section 1.3.2), though other isomers can sometimes result due to subsequent rearrangements.^[11]

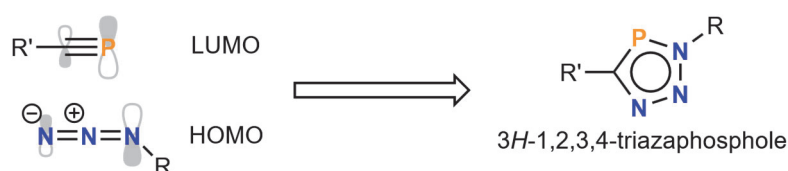
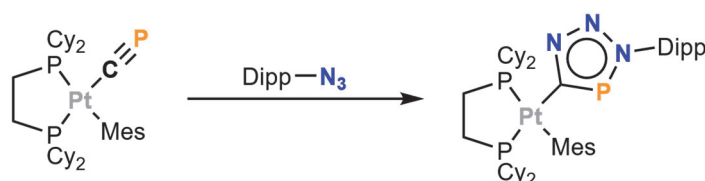


Figure 6.1. Regioselectivity of phosphalkyne-azide 1,3-dipolar cycloaddition reactions.

Triazaphospholes are of interest for use as ligand scaffolds or in luminescent materials.^[14,15] However, the low number of kinetically stable phosphalkynes severely limits the range of accessible triazaphospholes. For triazaphospholes made by this route, C-functionalization is limited to simple alkyl, aryl, or silyl substituents.^[12]

There is one example of a 1,3-dipolar cycloaddition reaction between an organic azide and a cyaphide complex, reported by Müller, Jones, and co-workers in 2021 (see Section 1.4.7).^[16] The platinum(II) cyaphide complex $Pt(dcyph)(Mes)(CP)$ reacts with 2,6-diisopropylphenyl azide to give a platinum(II) triazaphosphole complex (Scheme 6.3), though no further reactivity for this complex was investigated.

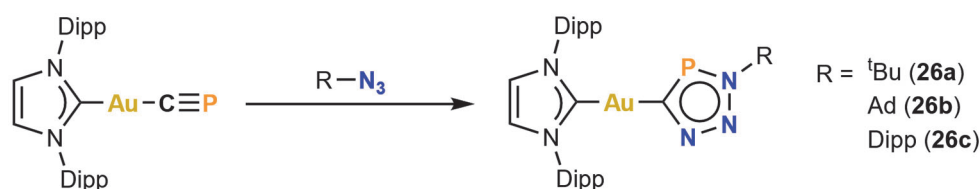


Scheme 6.3. Reaction of a platinum(II) cyaphide complex with 2,6-diisopropylphenylazide.

6.2 Cyaphide-azide 1,3-dipolar cycloaddition reactions

6.2.1 Synthesis of Au(IDipp)(CPN₃R) (R = ^tBu, Ad, Dipp)

The metallo-phosphaalkyne reactivity of the gold(I) cyaphide complex **7** was discussed previously in Chapter 5, and this analogy extends further to its reactivity with organic azides. **7** reacts with *tert*-butyl azide, 1-adamantyl azide, and 2,6-diisopropylphenyl azide to give the gold(I) triazaphosphole complexes Au(IDipp)(CPN₃R) [R = ^tBu (**26a**), Ad (**26b**), Dipp (**26c**); Scheme 6.4]. These reactions proceed regiospecifically at room temperature, with essentially quantitative conversion after several hours (by ³¹P{¹H} NMR spectroscopy), and the resulting gold(I) triazaphospholes can be isolated in very good yields (86–90%).



Scheme 6.4. Synthesis of the gold(I) triazaphosphole complexes **26a–c**.

26a–c have similar spectroscopic signatures. The triazaphosphole phosphorus atoms have ³¹P{¹H} chemical shifts of 191.2 ppm (**26a**), 189.3 ppm (**26b**), and 209.3 ppm (**26c**), in a similar region to organic triazaphospholes. The triazaphosphole carbon atoms appear as doublets in their ¹³C{¹H} spectra at 205.19 ppm (**26a**: ¹J_{C–P} = 82.0 Hz), 204.52 ppm (**26b**: ¹J_{C–P} = 81.9 Hz), and 208.03 ppm (**26c**: ¹J_{C–P} = 83.3 Hz). Their IDipp ¹³C_{NHC} chemical shifts are 196.51 ppm (**26a**), 196.54 ppm (**26b**), and 195.75 ppm (**26c**), slightly higher than in the cyaphide complex **7** and indicative of strong σ donating ability for the triazaphospholide anion.

The solid-state structures of **26a–c** were determined using X-ray crystallography (Figure 6.2). All three structures contain linear gold centers with C1–Au1–C2 angles of 179.5(3)°, 177.81(8), and 177.25(16)°, respectively. The Au1–C1 bond lengths are essentially identical at 2.022(8), 2.024(2), and 2.015(4) Å. The gold–NHC Au1–C2 bond lengths are also identical at 2.029(8), 2.027(2), and 2.019(4), and are in line with the ¹³C_{NHC} chemical shifts. The triazaphospholide rings in **26a–c** all correspond to the 3*H*-1,2,3,4 regioisomer, the same as organic triazaphospholes obtained from azides and phosphaalkynes, and exhibit similar bond metrics. The C1–P1 bond lengths are 1.685(8), 1.715(2), and 1.719(4) Å, and the C1–P1–N3 bond angles are 88.4(4)°, 88.42(9)°, 87.7(2)°.

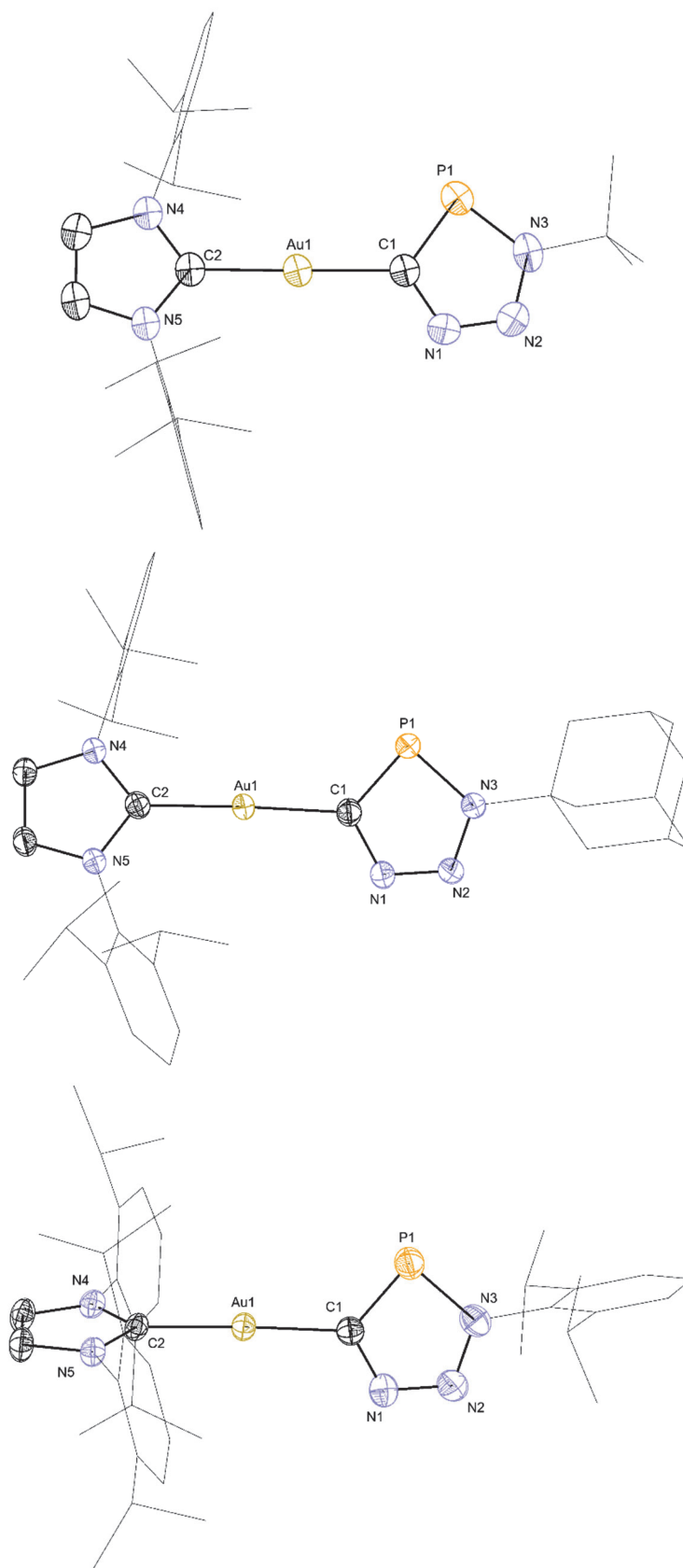
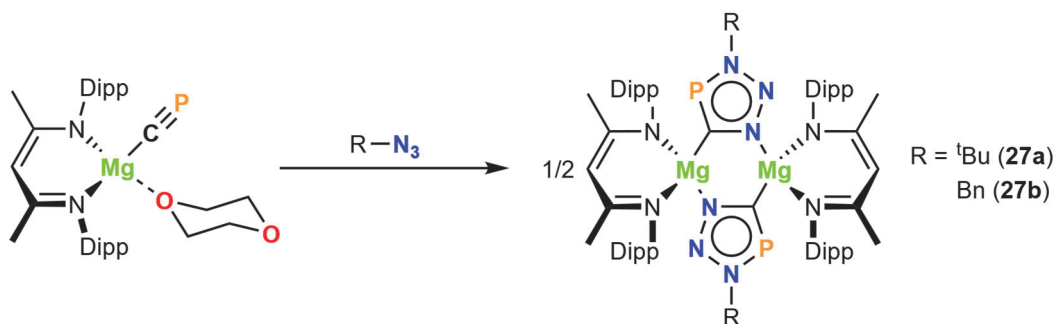


Figure 6.2. Solid-state structures of **26a** (top), **26b** (middle), and **26c** (bottom). Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms, disorder components, and co-crystallized solvent molecules are omitted for clarity. Dipp, ^tBu, and Ad groups are depicted as wireframes.

6.2.2 Synthesis of $\{\text{Mg}^{(\text{Dipp})\text{NacNac}}(\mu\text{-CPN}_3\text{R})\}_2$ ($\text{R} = \text{'Bu, Bn}$)

To probe the limitations of the cyaphide-azide 1,3-dipolar cycloaddition reaction, an ionic magnesium(II) cyaphide complex was reacted with organic azides.

In situ generated solutions containing the magnesium(II) cyaphide complex **1_{diox}** react with *tert*-butyl azide and benzyl azide to afford dimeric magnesium(II) triazaphosphole complexes $\{\text{Mg}^{(\text{Dipp})\text{NacNac}}(\mu\text{-CPN}_3\text{R})\}_2$ [$\text{R} = \text{'Bu}$ (**27a**), Bn (**27b**); Scheme 6.5].



Scheme 6.5. Synthesis of the magnesium(II) triazaphosphole complexes **27a** and **27b**.

When 2,6-diisopropylphenyl azide was used, the reaction instead results in an intractable mixture of products, possibly indicating that inverse electron demand cycloaddition pathways have been enabled. This suggests that highly electron-rich cyaphide complexes (e.g. **1_{diox}**) may not be electronically compatible with electron-poor aryl azides in 1,3-dipolar cycloaddition reactions.

Upon formation, **27a** and **27b** crystallize rapidly on standing, allowing for structural determination by single crystal X-ray diffraction (Figure 6.3). **27a** and **27b** adopt dimeric structures in which crystallographically equivalent magnesium centers are bridged by two equivalent triazaphosphole rings by their carbon atoms and adjacent nitrogen atoms. The Mg1–C1 bond lengths in **27a** and **27b** are 2.162(2) and 2.164(3) Å, respectively. The Mg1–N1 bond lengths are 2.105(2) and 2.109(2) Å, respectively. As with **26a–c**, the triazaphospholide rings in **27a–b** adopt the 3*H*-1,2,3,4 regioisomer. Their bond metrics are similar, with C1–P1 bond lengths of 1.714(2) and 1.725(3) Å and C1–P1–N3 bond angles of 89.44(7)° and 88.89(12)°, respectively.

27a–b are structurally related to other $\text{Mg}^{(\text{Dipp})\text{NacNac}}$ complexes of *N*-heterocycles, which also adopt similar dimeric forms.^[17]

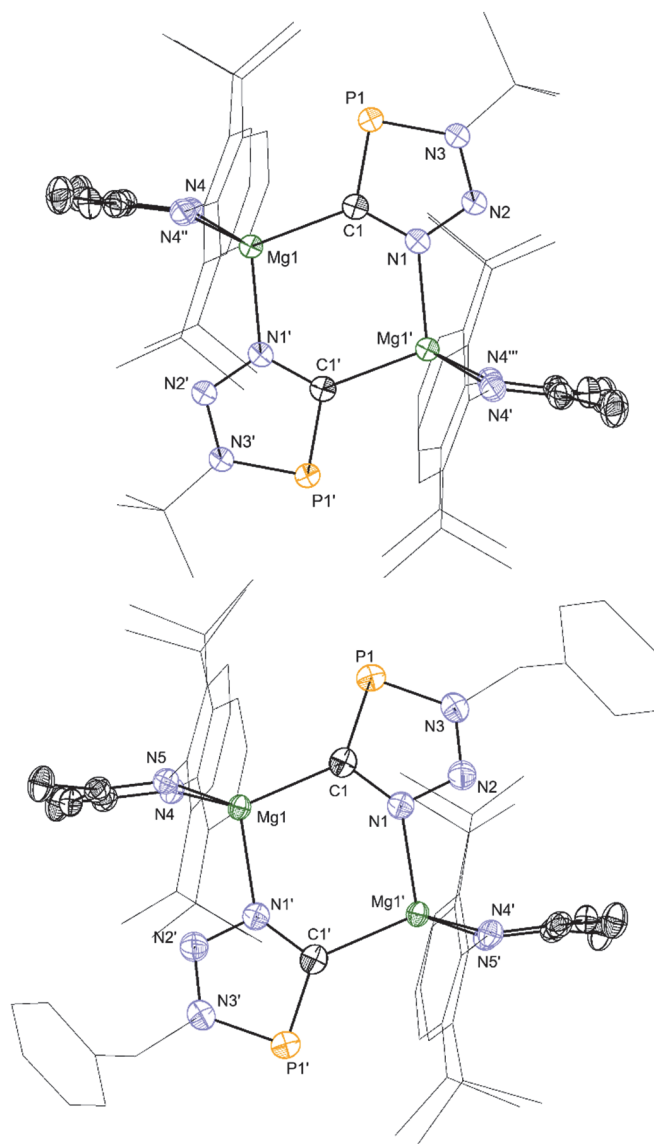
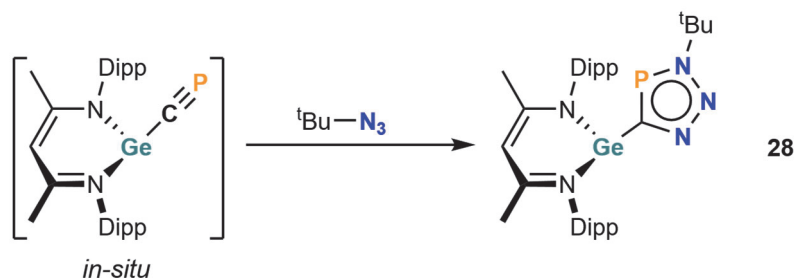


Figure 6.3. Solid-state structures of **27a** (top) and **27b** (bottom). Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Dipp, ^tBu, and Bn groups are depicted as wireframes.

27b is insoluble even in highly polar organic solvents (e.g. dimethylsulfoxide (DMSO) or 1,2-DFB), precluding characterization by NMR spectroscopy. **27a** has a single resonance in its $^{31}\text{P}\{^1\text{H}\}$ spectrum at 224.3 ppm corresponding to the triazaphosphole phosphorus atom, and a doublet resonance in its $^{13}\text{C}\{^1\text{H}\}$ spectrum at 207.15 ppm ($^1J_{\text{C-P}} = 93.3$ Hz) corresponding to the triazaphosphole carbon atom. Its ^1H NMR spectrum includes a significantly upfield-shifted isopropyl resonance (-0.64 ppm) due to close proximity to aryl diatropic ring currents, which shows that the dimeric structure is retained in solution. This is further supported by ^1H DOSY (diffusion-ordered spectroscopy) measurements, which give an estimated molecular weight of 1073 g mol^{-1} (actual: 1168 g mol^{-1}).^[18] The dimeric structure of **27a** appears to persist in donor solvents (e.g. THF, MeCN, pyridine), or in the presence of strong Lewis acids (e.g. $\text{B}(\text{C}_6\text{F}_5)_3$) or Lewis bases (e.g. DMAP).

6.2.3 Synthesis of $\text{Ge}(\text{DippNacNac})(\text{CPN}_3\text{tBu})$

As discussed in Section 3.1.3, the germanium(II) cyaphide complex **4** cannot be isolated due to its kinetic instability. However, treating an *in situ* generated toluene solution of **4** with *tert*-butyl azide results in rapid conversion to the germanium(II) triazaphosphole complex $\text{Ge}(\text{DippNacNac})(\text{CPN}_3\text{tBu})$ (**28**; Scheme 6.6). In stark contrast to **4**, the triazaphosphole complex **28** is air and moisture tolerant, and can be handled in ambient atmosphere for short periods of time.



Scheme 6.6. Synthesis of the germanium(II) triazaphosphole complex **28**.

28 has a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum containing a resonance at 196.9 ppm corresponding to the triazaphosphole phosphorus atom, and a $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum containing a doublet at 199.39 ppm ($^1J_{\text{C-P}} = 105.1$ Hz) for the triazaphosphole carbon atom. The structure of **28** was determined by single crystal X-ray crystallography (Figure 6.4).

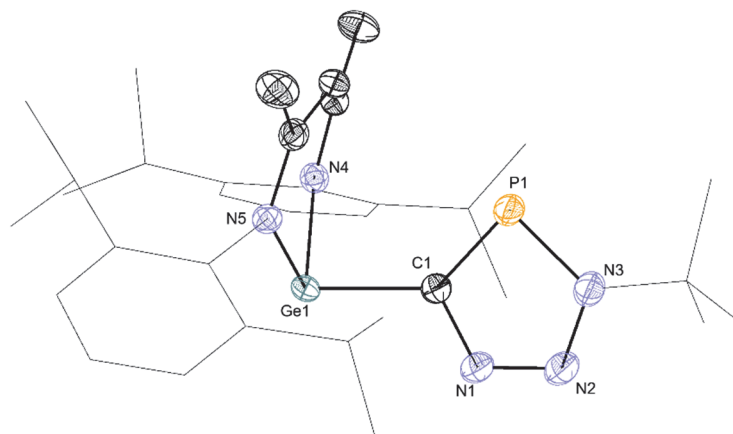


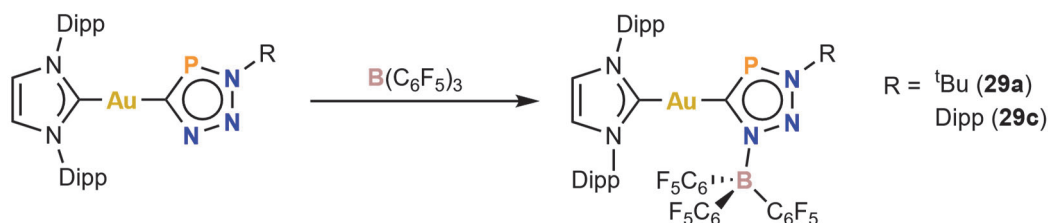
Figure 6.4. Solid-state structure of **28**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Dipp and *t*Bu groups are depicted as wireframes.

28 contains a three-coordinate germanium center, with a Ge1–C1 bond length of 2.038(2) Å. The triazaphospholide unit is metrically similar to those in **26a–c** and **27a–b**, with a C1–P1 bond length of 1.717(2) Å and C1–P1–N3 bond angle of 88.00(6)°.

6.3 Reactivity of metallo-triazaphospholes

6.3.1 Synthesis of $\{\text{Au}(\text{IDipp})\}(\mu\text{-CPN}_3\text{R})\{\text{B}(\text{C}_6\text{F}_5)_3\}$ ($\text{R} = \text{'Bu}, \text{Dipp}\}$)

The dimeric magnesium(II) complexes **27a–b** contain trisubstituted triazaphospholes, suggesting that the disubstituted triazaphospholes in the gold(I) complexes **26a–d** may be reactive toward adduct formation with Lewis acids. As expected, **26a** and **26c** react with $\text{B}(\text{C}_6\text{F}_5)_3$ to afford the trisubstituted triazaphosphole complexes $\{\text{Au}(\text{IDipp})\}(\mu\text{-CPN}_3\text{R})\{\text{B}(\text{C}_6\text{F}_5)_3\}$ [$\text{R} = \text{'Bu}$ (**29a**), Dipp (**29c**); Scheme 6.7].



Scheme 6.7. Synthesis of the gold(I) triazaphosphole $\text{B}(\text{C}_6\text{F}_5)_3$ adducts **29a** and **29c**.

Adduct formation results in the downfield shifting of the triazaphosphole $^{31}\text{P}\{^1\text{H}\}$ resonances compared to their disubstituted precursors (**29a**: 203.5 ppm; **29c**: 220.4 ppm). The triazaphosphole $^{13}\text{C}\{^1\text{H}\}$ resonances are also somewhat downfield shifted, with slightly reduced $^1J_{\text{C-P}}$ coupling constants [**29a**: 207.25 ppm ($^1J_{\text{C-P}} = 77.0$ Hz); **29c**: 210.38 ppm ($^1J_{\text{C-P}} = 80.3$ Hz)]. The $^{13}\text{C}_{\text{NHC}}$ chemical shifts of **29a** (190.92 ppm) and **29c** (190.40 ppm) are appreciably lower than in the disubstituted precursors, showing that $\text{B}(\text{C}_6\text{F}_5)_3$ adduct formation results in reduced σ donor ability for the triazaphosphole. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of **29a** and **29c** contain signals at -5.52 and -5.02 ppm, respectively (typical for $\text{B}(\text{C}_6\text{F}_5)_3$ Lewis adducts). Their $^{19}\text{F}\{^1\text{H}\}$ NMR spectra are complex, showing the C_6F_5 groups are spectroscopically inequivalent due to restricted rotation about the B–N bond.

The solid-state structures of **29a** and **29c** were determined by single crystal X-ray crystallography (Figure 6.5). In both cases, adduct formation has occurred *via* coordination of the triazaphosphole N1 nitrogen atom, with B1–N1 bond lengths of 1.606(6) and 1.604(5) Å, respectively. The C1–Au1–C2 angles for both **29a** and **29c** are bent slightly at $170.35(19)^\circ$ and $165.09(14)^\circ$, respectively, in order to accommodate the steric bulk of the $\text{B}(\text{C}_6\text{F}_5)_3$ groups. Otherwise, neither the Au–C bond lengths nor any of the bond metrics for the triazaphosphole rings are significantly altered upon adduct formation.

29a and **29c** are isolobal to abnormal or mesoionic carbenes, and can be conceptualized as gold(I) anionic carbene complexes. They are similar to other phosphorus-containing carbene analogs previously reported by Müller and co-workers, also derived from triazaphospholes.^[19,20]

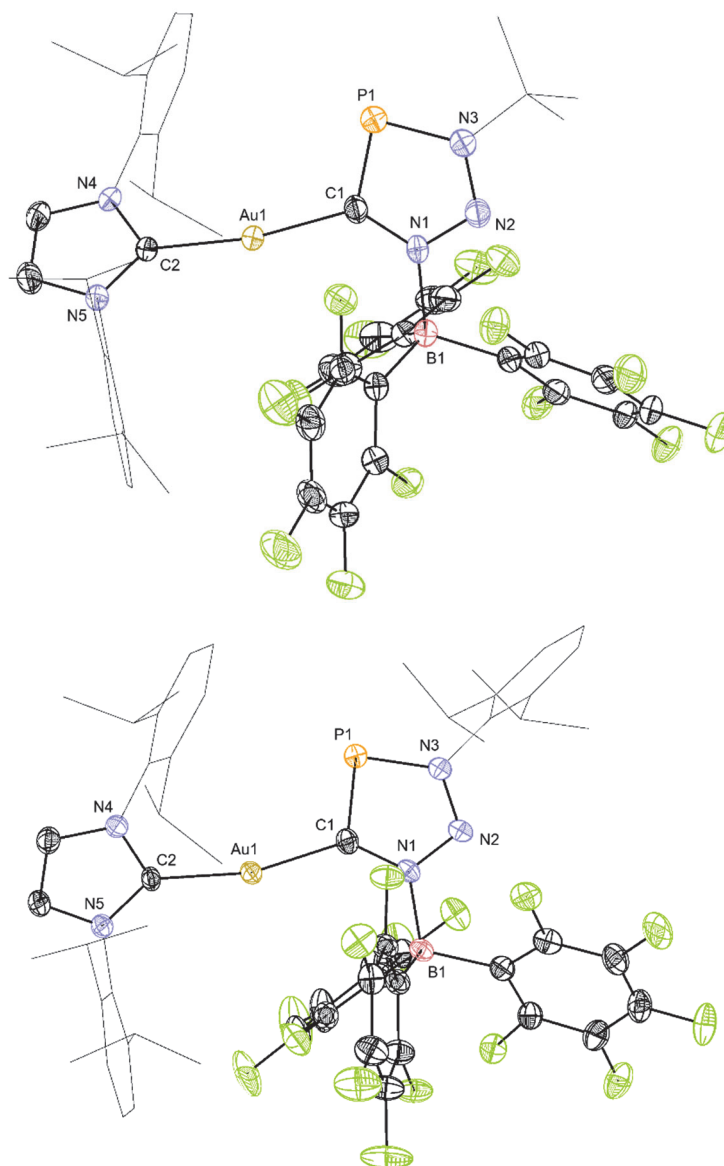
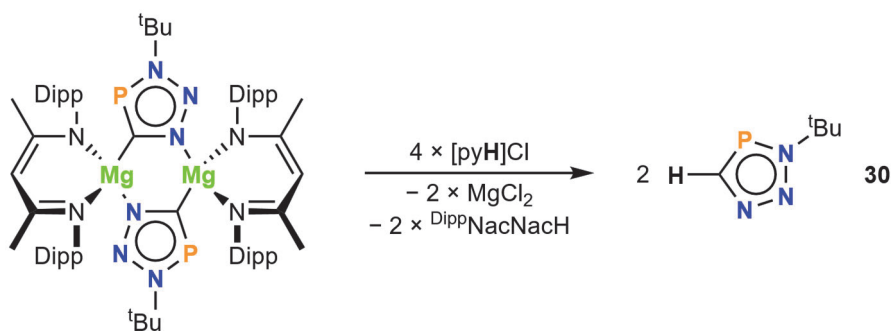


Figure 6.5. Solid-state structures of **29a** (top) and **29c** (bottom). Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Dipp and ^tBu groups are depicted as wireframes.

6.3.2 Synthesis of HCPN₃^tBu

The dimeric magnesium(II) triazaphosphole complexes **27a–b** contain polar Mg–C bonds that should allow for organometallic reactivity to afford C-functionalized triazaphospholes.

The reaction of **27a** with four equivalents of pyridinium chloride results in the protonation of both ^{Dipp}NacNac ligands as well as both triazaphospholide ions. The resulting parent *tert*-butyl triazaphosphole, HCPN₃^tBu (**30**), is a volatile liquid which can be separated from the reaction mixture *via* vacuum distillation (Scheme 6.8).



Scheme 6.8. Synthesis of parent *tert*-butyl triazaphosphole, **30**.

30 has a doublet in its ^1H NMR spectrum at 8.89 ppm ($^2J_{\text{H-P}} = 54.7$ Hz) corresponding to the CH proton, and a doublet in its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 164.10 ppm ($^1J_{\text{C-P}} = 51.7$ Hz) corresponding to the triazaphosphole carbon atom. Its ^{31}P NMR spectrum exhibits a pseudo-quartet at 174.9 ppm that collapses to a pseudo-triplet upon proton decoupling (Figure 6.6). A possible reason for the unexpected appearance of this resonance is discussed further in Section 6.3.3.

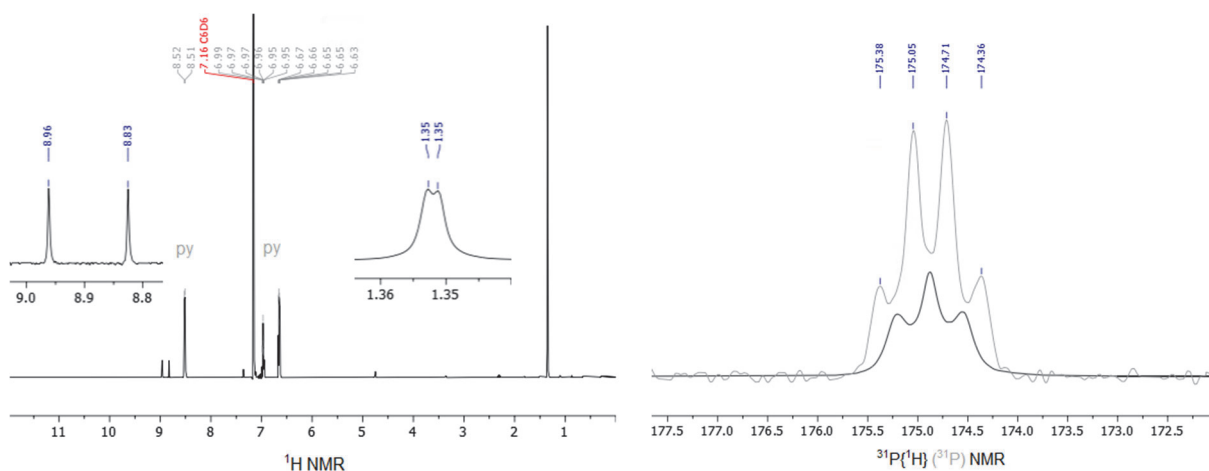


Figure 6.6. ^1H NMR spectrum of **30** (left). ^{31}P and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **30** (right).

Only two other examples of carbon-protonated triazaphospholes have been reported, both synthesized by 1,3-dipolar cycloaddition reactions between azides and HCP gas.^[21,22]

6.3.3 Synthesis of ICPN_3R ($\text{R} = \text{'Bu, Ad, Dipp}$)

The gold–triazaphosphole Au–C bonds in **26a–c** can also be cleaved to afford C-functionalized triazaphospholes by halogenation. Complexes **26a–c** react with iodine to afford Au(IDipp)I and the iodotriazaphospholes ICPN_3R [$\text{R} = \text{'Bu}$ (**31a**), Ad (**31b**), Dipp (**31c**)] (Scheme 6.9), which are the first examples of halogenated triazaphospholes.



Scheme 6.9. Synthesis of the iodotriazaphospholes **31a–c**.

The solid-state structures of **31a** and **31b** were determined by single crystal X-ray crystallography (Figure 6.7). The C1–I1 bond lengths are 2.083(6) and 2.080(3) Å, and the triazaphosphole rings exhibit similar bond metrics to the gold(I) triazaphosphole precursors **26a** and **26c**. Close-contacts can be found between neighboring molecules in the solid-state structure of **31a** corresponding to π - π and I... π non-covalent interactions.

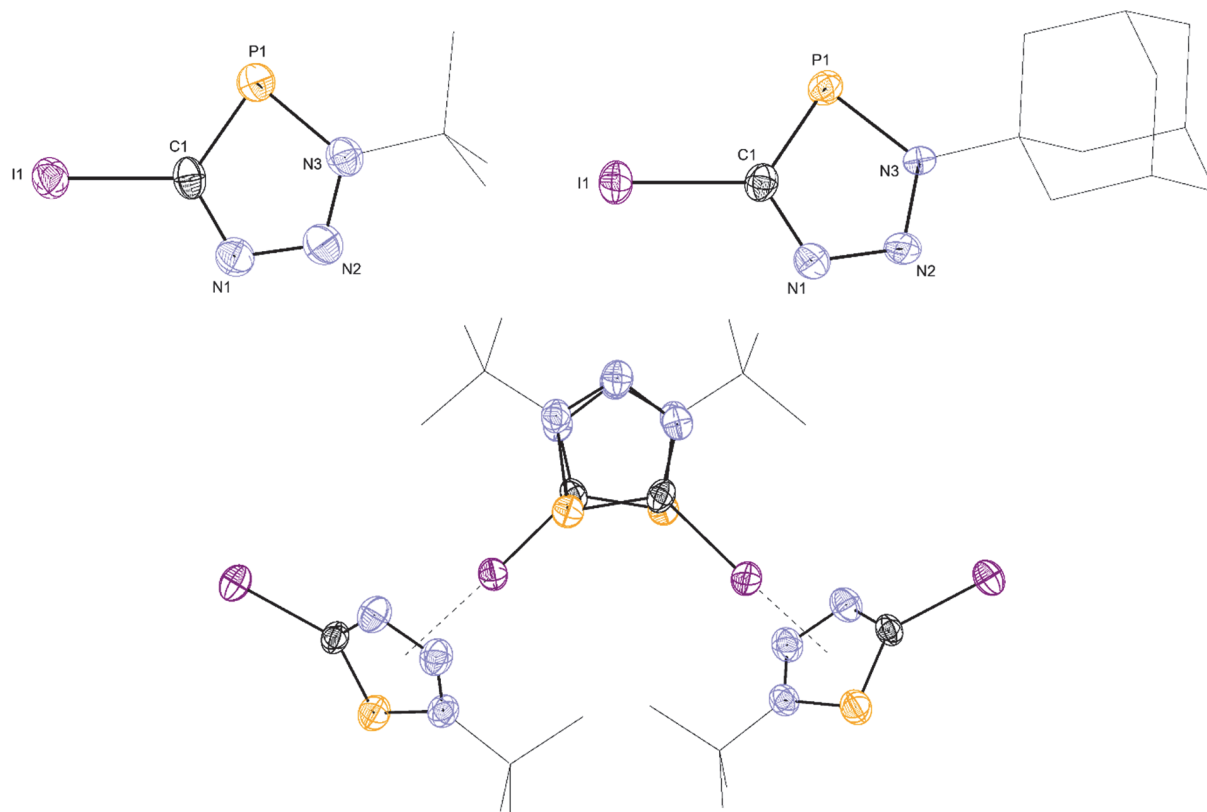


Figure 6.7. Solid-state structures of **31a** (top left) and **31b** (top right). Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. ^tBu and Ad groups are depicted as wireframes. Close-contacts and solid-state packing for a tetrameric aggregation unit of **31a** (bottom).

31a–c have $^{13}\text{C}\{^1\text{H}\}$ NMR spectra containing doublets corresponding to the triazaphosphole carbon atoms at 120.80 ppm ($^1J_{\text{C-P}} = 80.6$ Hz), 120.50 ppm ($^1J_{\text{C-P}} = 80.8$ Hz), and 123.36 ppm ($^1J_{\text{C-P}} = 83.5$ Hz), respectively. The triazaphosphole phosphorus atoms appear in their $^{31}\text{P}\{^1\text{H}\}$ spectra at 179.9, 180.1, and

194.7 ppm, respectively. For **31a** and **31b**, these $^{31}\text{P}\{^1\text{H}\}$ resonances appear as pseudo-triplet multiplets, whereas for **31c**, the $^{31}\text{P}\{^1\text{H}\}$ resonance appears as a simple singlet. This suggests that the multiplets for **30**, **31a**, and **31b** arise from solution aggregation, which is precluded for **31c** due to the steric bulk of the Dipp group. This is further corroborated by the appearance of the $^{31}\text{P}\{^1\text{H}\}$ resonance of **31b** in solvents with differing π stacking abilities. The resonance appears as a sharp pseudo-triplet in hexane, but broadens in benzene and 1,2-DFB (Figure 6.8).

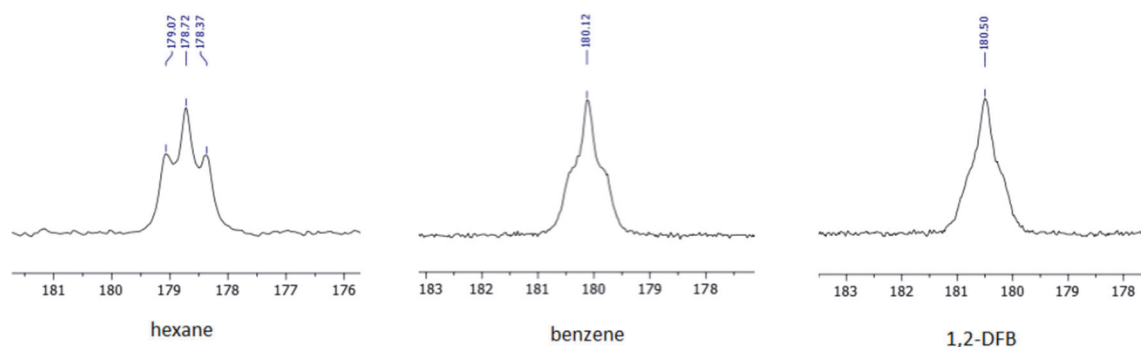


Figure 6.8. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **31b** in hexane (left), benzene (middle), and 1,2-difluorobenzene (right).

The aggregation of **31a** into dimeric and tetrameric aggregation units as observed in the solid-state were investigated by DFT calculations (Figure 6.9), which show that (in the gas phase) aggregation is highly thermodynamically favorable, with a π - π stacking energy of -11.1 kcal mol $^{-1}$.

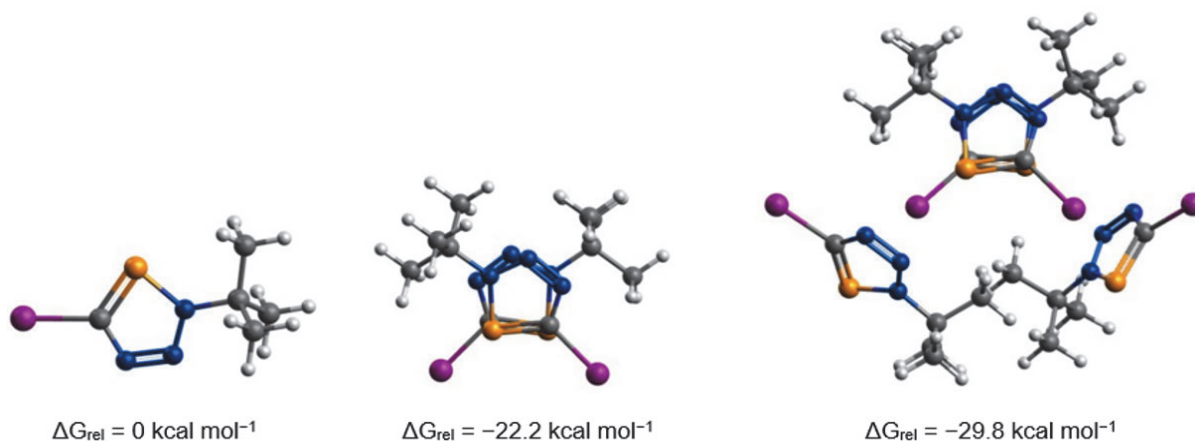


Figure 6.9. Relative energies of **31a** aggregates in the gas phase.

However, a convection compensated ^1H DOSY experiment (using $\text{Si}(\text{SiMe}_3)_4$ as an internal standard) results in a diffusion coefficient of $1.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ which is in good agreement with a monomeric unit of **31a**, though this could be due to rapid chemical exchange between aggregate units faster than the DOSY NMR timescale.^[23]

6.4 Conclusions

Metal cyaphide complexes undergo 1,3-dipolar cycloaddition reactions with organic azides to afford metallo-triazaphospholes. These reactions show traits that are hallmarks of classic “click” chemistry: they occur rapidly and selectively under mild conditions with regiospecificity, and the products are surprisingly air- and moisture-tolerant.

The cyaphide-azide “click” reaction can be performed using cyaphide complexes of s, p, and d-block metals. This reaction can be used to prepare the gold(I) triazaphospholes **26a–c** from a covalent cyaphide complex, the magnesium(II) triazaphospholes **27a–b** from an ionic cyaphide complex, and the germanium(II) triazaphosphole **28** from a kinetically unstable cyaphide complex.

Metallo-triazaphospholes can undergo a variety of subsequent reactions, including Lewis-acid coordination to afford **29a** and **29c**, protonation to the parent *tert*-butyl triazaphosphole **30**, and halogenation to the iodotriazaphospholes **31a–c**.

The propensity for the highly reactive cyaphide C≡P bond to undergo cycloaddition reactions has consequences for the stability of metal cyaphide complexes; these are discussed in the next chapter.

Some of the work in this chapter has been published in *Chemistry – A European Journal*:

E. S. Yang, A. Mapp, A. Taylor, P. D. Beer, J. M. Goicoechea, *Chem. Eur. J.* **2023**, e202301648.

A. Mapp contributed experimentally to the work in Sections 6.2.1, 6.3.1, and 6.3.3.

6.5 Experimental section

6.5.1 Synthesis of Au(IDipp)(CPN₃^tBu) (26a)

Neat *tert*-butyl azide (8 mg, 0.08 mmol) was added to a solution of Au(IDipp)(CP) (50 mg, 0.08 mmol) in toluene (1 mL) and stirred at room temperature for 2 h. The solution was concentrated by slow evaporation, yielding colorless crystals suitable for single crystal X-ray crystallography. The mixture was then stored at –35 °C for 3 days to yield colorless crystals which were isolated by filtration. Yield: 50 mg, 0.07 mmol, 86%. Anal. Calcd. (%) for C₃₂H₄₅AuN₃P: C, 52.82; H, 6.23; N, 9.62. Found: C, 52.49; H, 6.31; N, 9.00.

¹H NMR (600 MHz, C₆D₆): δ(ppm) 7.18 (t, ³J_{H-H} = 7.8 Hz, 2H, Dipp *para*-CH), 7.06 (d, ³J_{H-H} = 7.8 Hz, 4H, Dipp *meta*-CH), 6.35 (s, 2H, IDipp CH), 2.69 (sept, ³J_{H-H} = 6.9 Hz, 4H, Dipp CH(CH₃)₂), 1.53 (d, ³J_{H-H} = 6.9 Hz, 12H, Dipp CH(CH₃)₂), 1.42 (s, 9H, ^tBu C(CH₃)₃), 1.10 (d, ³J_{H-H} = 6.9 Hz, 12H, Dipp CH(CH₃)₂).

¹³C{¹H} NMR (151 MHz, C₆D₆): δ(ppm) 205.19 (d, ¹J_{C-P} = 82.0 Hz, CPN₃^tBu), 196.51 (d, ³J_{C-P} = 11.1 Hz, IDipp CAu), 145.90 (Dipp *ortho*-C), 134.80 (Dipp *ipso*-C), 130.68 (Dipp *para*-C), 124.26 (Dipp *meta*-C), 122.73 (IDipp CH), 59.69 (d, ²J_{C-P} = 5.1 Hz, ^tBu C(CH₃)₃), 32.03 (d, ³J_{C-P} = 5.0 Hz, ^tBu C(CH₃)₃), 29.14 (Dipp CH(CH₃)₂), 24.93 (Dipp CH(CH₃)₂), 23.98 (Dipp CH(CH₃)₂).

³¹P{¹H} NMR (162 MHz, C₆D₆): δ(ppm) 191.2 (s, CPN₃^tBu).

6.5.2 Synthesis of Au(IDipp)(CPN₃Ad) (26b)

1-adamantyl azide (20 mg, 0.11 mmol) was added to a solution of Au(IDipp)(CP) (71 mg, 0.11 mmol) in toluene (1 mL) and stirred at room temperature overnight. The solution was concentrated under vacuum, then stored at –35 °C for 3 days to yield colorless crystals which were isolated by filtration. Yield: 82 mg, 0.10 mmol, 90%. Anal. Calcd. (%) for C₃₈H₅₁AuN₃P: C, 56.64; H, 6.38; N, 8.69. Found: C, 57.05; H, 6.17; N, 8.43.

¹H NMR (600 MHz, C₆D₆): δ(ppm) 7.20 (t, ³J_{H-H} = 7.8 Hz, 2H, Dipp *para*-CH), 7.07 (d, ³J_{H-H} = 7.8 Hz, 4H, Dipp *meta*-CH), 6.39 (s, 2H, IDipp CH), 2.70 (sept, ³J_{H-H} = 6.9 Hz, 4H, Dipp CH(CH₃)₂), 2.17 (d, ³J_{H-H} = 2.8 Hz, 6H, Ad C{CH₂CHCH₂}₃), 1.85–1.77 (m, 3H, Ad C{CH₂CHCH₂}₃), 1.54 (d, ³J_{H-H} =

6.9 Hz, 12H, Dipp CH(CH₃)₂), 1.45–1.37 (m, 6H, Ad C{CH₂CHCH₂}₃), 1.11 (d, ³J_{H-H} = 6.9 Hz, 12H, Dipp CH(CH₃)₂).

¹³C{¹H} NMR (151 MHz, C₆D₆): δ(ppm) 204.52 (d, ¹J_{C-P} = 81.9 Hz), 196.54 (d, ³J_{C-P} = 11.0 Hz), 145.89 (Dipp *ortho*-C), 134.82 (Dipp *ipso*-C), 130.70 (Dipp *para*-C), 124.27 (Dipp *meta*-C), 122.78 (IDipp CH), 60.19 (d, ²J_{C-P} = 4.4 Hz, Ad C{CH₂CHCH₂}₃), 45.76 (d, ³J_{C-P} = 5.1 Hz, Ad C{CH₂CHCH₂}₃), 36.54 (Ad C{CH₂CHCH₂}₃), 30.28 (Ad C{CH₂CHCH₂}₃), 29.15 (Dipp CH(CH₃)₂), 24.94 (Dipp CH(CH₃)₂), 24.01 (Dipp CH(CH₃)₂).

³¹P{¹H} NMR (162 MHz, C₆D₆): δ(ppm) 189.3 ppm (s, CPN₃Ad).

6.5.3 Synthesis of Au(IDipp)(CPN₃Dipp) (1c)

Neat 2,6-diisopropylphenyl azide (17 mg, 0.08 mmol) was added to a solution of Au(IDipp)(CP) (50 mg, 0.08 mmol) in toluene (1 mL) and stirred at room temperature overnight. Crystals suitable for X-ray crystallography were obtained by concentrating the toluene solution followed by layering with hexane (5 mL). The supernatant solution was removed, and the crystals washed with pentane (2 × 2 mL), then dried under vacuum. Yield: 54 mg, 0.06 mmol, 81%. Anal. Calcd. (%) for C₄₀H₅₄N₅AuP·0.5(C₇H₈): C, 61.03; H, 6.76; N, 7.57. Found: C, 60.90; H, 6.49; N, 7.24.

¹H NMR (600 MHz, C₆D₆): δ(ppm) 7.12–7.09 (m, 2H, Dipp Ar-H), 7.02–7.00 (m, 7H, Dipp Ar-H), 6.32 (s, 2H, IDipp CH), 2.68 (sept, ³J_{H-H} = 6.9 Hz, 4H, Dipp CH(CH₃)₂), 2.15 (sept, ³J_{H-H} = 6.8 Hz, 2H, Dipp CH(CH₃)₂), 1.54 (d, ³J_{H-H} = 6.9 Hz, 12H, Dipp CH(CH₃)₂), 1.08 (d, ³J_{H-H} = 6.9 Hz, 12H, Dipp CH(CH₃)₂), 0.83 (d, ³J_{H-H} = 6.8 Hz, 6H, Dipp CH(CH₃)₂), 0.82 (d, ³J_{H-H} = 6.8 Hz, 6H, Dipp CH(CH₃)₂).

¹³C{¹H} NMR (151 MHz, C₆D₆): δ(ppm) 208.03 (d, ¹J_{C-P} = 83.3 Hz, CP), 195.75 (d, ³J_{C-P} = 10.9 Hz, CAu), 146.56 (Dipp Ar-C), 145.73 (Dipp Ar-C), 138.13 (d, ²J_{C-P} = 6.3 Hz, Dipp *ipso*-C), 134.66 (Dipp Ar-C), 130.77 (Dipp Ar-C), 128.95 (Dipp Ar-C), 124.30 (Dipp Ar-C), 123.45 (Dipp Ar-C), 122.80 (IDipp CH), 29.14 (Dipp CH(CH₃)₂), 28.27 (Dipp CH(CH₃)₂), 24.99 (Dipp CH(CH₃)₂), 24.39 (Dipp CH(CH₃)₂), 24.18 (Dipp CH(CH₃)₂), 23.96 (Dipp CH(CH₃)₂).

³¹P{¹H} NMR (162 MHz, C₆D₆): δ(ppm) 209.3 (s, CPN₃Dipp).

6.5.4 Synthesis of $\{\text{Mg}(\text{DippNacNac})(\mu\text{-CPN}_3\text{tBu})\}_2$ (27a)

$\text{Mg}(\text{DippNacNac})(\text{CP})(\text{diox})$ (approx. 130 mg, 0.23 mmol) was generated *in situ* in toluene (1 mL). Neat *tert*-butyl azide (23 mg, 0.23 mmol) was added, and the solution swirled to ensure complete mixing. The reaction solution was allowed to stand overnight, resulting in the formation of colorless crystals suitable for single crystal X-ray diffraction. The supernatant was decanted, and the crystals were washed with hexane (3 x 1 mL), then dried under vacuum. Yield: 120 mg, 0.10 mmol, 91%. Anal. Calcd. (%) for $\text{C}_{68}\text{H}_{100}\text{Mg}_2\text{N}_{10}\text{P}_2 \cdot (\text{C}_6\text{H}_{14})$: C, 70.86; H, 9.16; N, 11.17. Found: C, 70.68; H, 8.56; N, 10.84.

^1H NMR (400 MHz, C_6D_6): δ (ppm) 7.12–6.95 (m, 8H, Dipp *meta*-CH), 6.94–6.87 (m, 4H, Dipp *para*-CH), 4.97 (s, 2H, NacNac CH), 3.88 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 4H, Dipp CH(CH₃)(CH₃)), 2.57 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 4H, Dipp CH(CH₃)(CH₃)), 1.67 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp CH(CH₃)(CH₃)), 1.66 (s, 12H, NacNac CH₃), 1.54 (s, 18H, tBu C(CH₃)₃), 1.30 ($^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp CH(CH₃)(CH₃)), 0.99 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp CH(CH₃)(CH₃)), –0.64 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, Dipp CH(CH₃)(CH₃)).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6): δ (ppm) 207.15 (d, $^1J_{\text{C-P}} = 93.3$ Hz, CPN₃tBu), 168.23 (NacNac CNDipp), 146.62 (Dipp *ipso*-C), 143.17 (Dipp *ortho*-C), 141.73 (Dipp *ortho*-C), 124.66 (Dipp *meta*-C), 124.21 (Dipp *para*-C), 122.92 (Dipp *meta*-C), 95.03 (NacNac CH), 61.08 (d, $^2J_{\text{C-P}} = 2.9$ Hz, tBu C(CH₃)₃), 31.77 (d, $^3J_{\text{C-P}} = 4.6$ Hz, tBu C(CH₃)₃), 30.04 (Dipp CH(CH₃)(CH₃)), 27.60 (Dipp CH(CH₃)(CH₃)), 25.09 (Dipp CH(CH₃)(CH₃)), 24.66 (Dipp CH(CH₃)(CH₃)), 24.44 (Dipp CH(CH₃)(CH₃)), 24.23 (NacNac CH₃), 24.05 (Dipp CH(CH₃)(CH₃)).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): δ (ppm) 224.3 (s, CPN₃tBu).

6.5.5 Synthesis of $\{\text{Mg}(\text{DippNacNac})(\mu\text{-CPN}_3\text{Bn})\}_2$ (27b)

$\text{Mg}(\text{DippNacNac})(\text{CP})(\text{diox})$ (approx. 65 mg, 0.11 mmol) was generated *in situ* in toluene (1 mL). Neat benzyl azide (14 mg, 0.11 mmol) was added, and the solution swirled to ensure complete mixing. The reaction solution was allowed to stand for 3 h, resulting in the formation of colorless crystals. The supernatant was decanted, and the crystals were washed with hexane (3 x 1 mL), then dried under vacuum. Yield: 30 mg, 0.05 mmol, 43%. Anal. Calcd. (%) for $\text{C}_{80}\text{H}_{112}\text{Mg}_2\text{N}_{10}\text{P}_2 \cdot \text{C}_6\text{H}_{14}$: C, 72.66; H, 8.38; N, 10.59. Found: C, 72.26; H, 7.89; N, 9.94. The low solubility of $\{\text{Mg}(\text{DippNacNac})(\text{CPN}_3\text{Bn})\}_2$ in polar organic solvents e.g. THF, DMSO, and dichloromethane (DCM), precluded characterization by NMR spectroscopy.

6.5.6 Synthesis of $\text{Ge}(\text{DippNacNac})(\text{CPN}_3\text{tBu})$ (28)

$\text{Mg}(\text{DippNacNac})(\text{CP})(\text{diox})$ (approx. 42 mg, 0.07 mmol) was generated *in situ* in toluene (1 mL). $\text{Ge}(\text{DippNacNac})\text{Cl}$ (38 mg, 0.07 mmol) was added, and the reaction mixture stirred for 3 h. The reaction mixture was filtered, then *tert*-butyl azide (7 mg, 0.07 mmol) was added to the filtrate. The reaction solution was stirred overnight, then the solvent removed under vacuum. The residue was washed with hexane (3 x 1 mL), then recrystallized from toluene at $-35\text{ }^\circ\text{C}$ over 3 days. Yield: 32 mg, 0.06 mmol, 70%. Anal. Calcd. (%) for $\text{C}_{30}\text{H}_{41}\text{GeN}_2\text{P}$: C, 64.57; H, 7.97; N, 11.07. Found: C, 65.11; H, 8.28; N, 10.68.

^1H NMR (500 MHz, C_6D_6): δ (ppm) 7.16–7.09 (m, 4H, Dipp *meta*-CH), 6.98 (dd, $^3J_{\text{H-H}} = 6.3, 2.9$ Hz, 2H, Dipp *para*-CH), 5.22 (s, 1H, NacNac CH), 3.66 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 2H, Dipp CH(CH₃)₂), 2.92 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 2H, Dipp CH(CH₃)₂), 1.63 (s, 9H, *t*Bu C(CH₃)₃), 1.60 (s, 6H, NacNac CH₃), 1.38 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, Dipp CH(CH₃)(CH₃)), 1.18 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, Dipp CH(CH₃)(CH₃)), 0.98 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, Dipp CH(CH₃)(CH₃)), 0.62 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, Dipp CH(CH₃)(CH₃)).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6): δ (ppm) 199.39 (d, $^1J_{\text{C-P}} = 105.1$ Hz, CPN₃*t*Bu), 166.67 (NacNac CNDipp), 146.34 (Dipp *ipso*-C), 143.64 (Dipp *ortho*-C), 141.58 (Dipp *ortho*-C), 127.47 (Dipp *meta*-C), 124.90 (Dipp *para*-C), 124.41 (Dipp *meta*-C), 100.13 (d, $^5J_{\text{C-P}} = 6.7$ Hz, NacNac CH), 60.54 (d, $^2J_{\text{C-P}} = 4.5$ Hz, *t*Bu C(CH₃)₃), 32.39 (d, $^2J_{\text{C-P}} = 5.7$ Hz, *t*Bu C(CH₃)₃), 29.41 (Dipp CH(CH₃)₂), 28.70 (d, $^6J_{\text{C-P}} = 3.9$ Hz, Dipp CH(CH₃)₂), 26.01 (Dipp CH(CH₃)(CH₃)), 24.92 (Dipp CH(CH₃)(CH₃)), 24.73 (Dipp CH(CH₃)(CH₃)), 23.65 (Dipp CH(CH₃)(CH₃)), 23.64 (NacNac CH₃).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): δ (ppm) 196.9 (s, CPN₃*t*Bu).

6.5.7 Synthesis of $\{\text{Au}(\text{IDipp})\}(\mu\text{-CPN}_3\text{tBu})\{\text{B}(\text{C}_6\text{F}_5)_3\}$ (29a)

$\text{Au}(\text{IDipp})(\text{CPN}_3\text{tBu})$ (20 mg, 0.03 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (14 mg, 0.03 mmol) were dissolved in toluene (0.5 mL). The reaction mixture was stirred for 1 h, then concentrated by slow evaporation. Storage at $-35\text{ }^\circ\text{C}$ over 7 days yielded colorless crystals which were isolated by filtration, washed with pentane (3 x 0.5 mL), then dried under vacuum. Yield: 19 mg, 0.02 mmol, 56%. Anal. Calcd. (%) for $\text{C}_{50}\text{H}_{45}\text{AuBF}_{15}\text{N}_5\text{P} \cdot 2(\text{C}_7\text{H}_8)$: C, 54.02; H, 4.25; N, 4.92. Found: C, 53.95; H, 3.82; N, 5.25.

^1H NMR (600 MHz, C_6D_6): δ (ppm) 7.34 (t, $^3J_{\text{H-H}} = 7.8$ Hz, 2H, Dipp *para*-CH), 7.06 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 4H, Dipp *meta*-CH), 6.28 (s, 2H, IDipp CH), 2.55 (b, 4H, Dipp CH(CH₃)₂), 1.35 (b, 12H, Dipp CH(CH₃)₂), 1.00 (s, 9H, *t*Bu C(CH₃)₃), 0.95 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 12H, Dipp CH(CH₃)₂).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): δ (ppm) 207.25 (d, $^1J_{\text{C-P}} = 77.0$ Hz, CPN_3^tBu), 190.92 (d, $^3J_{\text{C-P}} = 3.5$ Hz, IDipp CAu), 149.88 (b, B(C_6F_5)), 148.30 (b, B(C_6F_5)), 145.66 (Dipp *ortho*-CH), 140.69 (b, B(C_6F_5)), 139.11 (b, B(C_6F_5)), 137.90 (b, B(C_6F_5)), 136.33 (b, B(C_6F_5)), 134.54 (Dipp *ipso*-CH), 130.92 (Dipp *para*-CH), 124.31 (Dipp *meta*-CH), 123.92 (IDipp CH), 63.73 (^tBu C(CH_3)₃), 30.33 (d, $^3J_{\text{C-P}} = 5.1$ Hz, ^tBu C(CH_3)₃), 29.01 (Dipp CH(CH_3)₂), 24.82 (Dipp CH(CH_3)₂), 23.68 (Dipp CH(CH_3)₂).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): δ (ppm) 203.5 ppm (s, CPN_3^tBu).

$^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, C_6D_6): δ (ppm) -124.46–-135.30 (m, B(C_6F_5)₃ *ortho*-CF), -156.82–-161.17 (m, B(C_6F_5)₃ *para*-CF), -161.18–-168.19 (m, B(C_6F_5)₃ *meta*-CF).

$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6): δ (ppm) -5.52 ppm (b, B(C_6F_5)₃).

6.5.8 Synthesis of $\{\text{Au}(\text{IDipp})\}(\mu\text{-CPN}_3\text{Dipp})\{\text{B}(\text{C}_6\text{F}_5)_3\}$ (29c)

$\text{Au}(\text{IDipp})(\text{CPN}_3^t\text{Bu})$ (20 mg, 0.03 mmol) and B(C_6F_5)₃ (14 mg, 0.03 mmol) were dissolved in toluene (0.5 mL) and stirred for 1 h. The solvent was removed *in vacuo* and the residue extracted into DCM (1 mL) and filtered. Storage at -35 °C over 7 days yielded colorless crystals which were washed with pentane (3 x 0.5 mL), then dried under vacuum. Yield: 13 mg, 0.0097 mmol, 41%. Anal. Calcd. (%) for $\text{C}_{58}\text{H}_{54}\text{AuBF}_{15}\text{N}_3\text{P}$: C, 51.80; H, 4.05; N, 5.21. Found: C, 50.88; H, 3.91; N, 5.90.

^1H NMR (600 MHz, C_6D_6): δ (ppm) 7.27 (t, $^3J_{\text{H-H}} = 7.8$ Hz, 2H, Dipp Ar-H), 7.04 (m, $^3J_{\text{H-H}} = 7.8$ Hz, 5H, Dipp Ar-H), 6.92 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 2H, Dipp Ar-H), 6.27 (s, 2H, IDipp CH), 2.51 (b, 4H, Dipp CH(CH_3)₂), 2.27 (b, 2H, Dipp CH(CH_3)₂), 1.30 (b, 12H, Dipp CH(CH_3)₂), 1.10 (b, 6H, Dipp CH(CH_3)₂), 0.95 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 12H, Dipp CH(CH_3)₂), 0.91 (b, 6H, Dipp CH(CH_3)₂).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): δ (ppm) 210.38 (d, $^1J_{\text{C-P}} = 80.3$ Hz, CPN_3Dipp), 190.40 (d, $^3J_{\text{C-P}} = 2.2$ Hz, IDipp CAu), 149.64 (b, B(C_6F_5)), 148.04 (b, B(C_6F_5)), 145.88 (Dipp Ar-C), 145.58 (Dipp Ar-C), 140.75 (b, B(C_6F_5)), 139.11 (b, B(C_6F_5)), 138.03 (b, B(C_6F_5)), 136.40 (b, B(C_6F_5)), 134.94 (d, $^3J_{\text{C-P}} = 3.8$ Hz, $\text{N}_3\text{Dipp ipso-C}$) 134.43 (Dipp Ar-C), 131.02 (Dipp Ar-C), 124.30 (Dipp Ar-C), 124.21 (Dipp Ar-C), 123.85 (IDipp CH), 29.00 (Dipp CH(CH_3)₂), 28.43 (Dipp CH(CH_3)₂), 24.69 (Dipp CH(CH_3)₂), 24.55 (Dipp CH(CH_3)₂), 23.79 (Dipp CH(CH_3)₂), 23.69 (Dipp CH(CH_3)₂). The signal for one of the Dipp aromatic carbons could not be located due to overlap with solvent peaks.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): $\delta(\text{ppm})$ 220.4 ppm (s, CPN_3Dipp).

$^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, C_6D_6): $\delta(\text{ppm})$ –124.41––167.21 (m, $\text{B}(\text{C}_6\text{F}_5)_3\text{CF}$).

$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6): $\delta(\text{ppm})$ –5.02 ppm (b, $\text{B}(\text{C}_6\text{F}_5)_3$).

6.5.9 Synthesis of HCPN_3^tBu (30)

$\{\text{Mg}(\text{DippNaCNac})_2(\text{CPN}_3^t\text{Bu})\}_2$ (48 mg, 0.04 mmol) and pyridinium chloride (19 mg, 0.16 mmol) were suspended in C_6D_6 (0.5 mL). The reaction mixture was sonicated for 1 h, after which the volatiles were distilled by vacuum transfer to an NMR tube.

^1H NMR (600 MHz, C_6D_6): $\delta(\text{ppm})$ 8.89 (d, $^2J_{\text{H-P}} = 54.6$ Hz, 1H, HCPN_3^tBu), 1.35 (d, $^4J_{\text{H-P}} = 0.6$ Hz, 9H, $^t\text{Bu C}(\text{CH}_3)_3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): $\delta(\text{ppm})$ 164.10 (d, $^1J_{\text{C-P}} = 51.7$ Hz, CPN_3^tBu), 61.43 (d, $^2J_{\text{C-P}} = 7.2$ Hz, $^t\text{Bu C}(\text{CH}_3)_3$), 61.43 (d, $^3J_{\text{C-P}} = 6.4$ Hz, $^t\text{Bu C}(\text{CH}_3)_3$).

^{31}P NMR (162 MHz, C_6D_6): $\delta(\text{ppm})$ 174.9 (m, $^2J_{\text{P-H}} = 55.0$ Hz, HCPN_3^tBu).

6.5.10 Synthesis of ICPN_3^tBu (31a)

A solution of iodine in hexane (4 mL, 0.016 M, 0.06 mmol) was added dropwise to a stirred solution of $\text{Au}(\text{IDipp})(\text{CPN}_3^t\text{Bu})$ (47 mg, 0.06 mmol) in toluene (5 mL). After stirring for 4 h, all volatiles were removed under vacuum. The residue was extracted with hexane (2 x 3 mL), which was then evaporated to dryness under vacuum to afford the product as an off-white powder. Crystals suitable for single crystal X-ray diffraction were obtained from hexane at –35 °C. Yield: 10 mg, 0.04 mmol, 58%. Anal. Calcd. (%) for $\text{C}_5\text{H}_9\text{N}_3\text{IP}$: C, 22.32; H, 3.37; N, 15.62. Found: C, 20.97; H, 2.67; N, 14.89.

^1H NMR (600 MHz, C_6D_6): $\delta(\text{ppm})$ 1.18 (d, $^4J_{\text{H-P}} = 0.9$ Hz, 9H, $^t\text{Bu C}(\text{CH}_3)_3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): $\delta(\text{ppm})$ 120.80 (d, $^1J_{\text{C-P}} = 80.6$ Hz, ICPN_3^tBu), 62.26 (d, $^2J_{\text{C-P}} = 6.0$ Hz, $^t\text{Bu C}(\text{CH}_3)_3$), 31.27 (d, $^3J_{\text{C-P}} = 6.4$ Hz, $^t\text{Bu C}(\text{CH}_3)_3$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): $\delta(\text{ppm})$ 179.9 (m, ICPN_3^tBu).

6.5.11 Synthesis of ICPN₃Ad (31b)

A solution of iodine in hexane (0.8 mL, 0.1 M, 0.08 mmol) was added to a solution of Au(IDipp)(CPN₃Ad) (64 mg, 0.08 mmol) in toluene (1 mL), which was then stirred overnight. All volatiles were removed under vacuum, and the resulting residue was extracted with hexane (2 x 3 mL). The hexane solution was evaporated to dryness, yielding the product as a colorless solid. Yield: 16 mg, 0.05 mmol, 58%. Anal. Calcd. (%) for C₁₁H₁₅N₃IP·0.5(C₆H₆): C, 43.53; H, 4.70; N, 10.88. Found: C, 42.96; H, 4.73; N, 10.77.

¹H NMR (400 MHz, C₆D₆): δ(ppm) 1.96–1.91 (m, 6H, Ad C{CH₂CHCH₂}₃), 1.81–1.75 (m, 3H, Ad C{CH₂CHCH₂}₃), 1.41–1.31 (m, 6H, Ad C{CH₂CHCH₂}₃).

¹³C{¹H} NMR (151 MHz, C₆D₆): δ(ppm) 120.50 (d, ¹J_{C-P} = 80.8 Hz, ICPN₃Ad), 62.90 (d, ²J_{C-P} = 5.3 Hz, Ad C{CH₂CHCH₂}₃), 45.16 (d, ³J_{C-P} = 6.5 Hz, Ad C{CH₂CHCH₂}₃), 35.93 (Ad C{CH₂CHCH₂}₃), 30.06 (d, ⁴J_{C-P} = 0.7 Hz, Ad C{CH₂CHCH₂}₃).

³¹P{¹H} NMR (162 MHz, C₆D₆): δ(ppm) 180.1 (m, ICPN₃Ad).

6.5.12 Synthesis of ICPN₃Dipp (31c)

A solution of iodine in hexane (0.8 mL, 0.1 M, 0.08 mmol) was added *via* syringe to a solution of Au(IDipp)(CPN₃Dipp) (67 mg, 0.08 mmol) in toluene (5 mL). The solution was stirred overnight at room temperature. All volatiles were removed under vacuum, and the resulting residue was extracted with hexane (2 x 3 mL). The hexane solution was evaporated to dryness, yielding the product as a dark red oil. Yield: 22 mg, mmol, 76%. Anal. Calcd. (%) for C₁₃H₁₇N₃IP: C, 41.84; H, 4.59; N, 11.26. Found: C, 46.36; H, 5.25; N, 10.56.

¹H NMR (400 MHz, C₆D₆): δ(ppm) 6.98 (d, 2H, ³J_{H-H} = 7.8 Hz, Dipp *meta*-CH), 2.10 (sept, ³J_{H-H} = 6.8 Hz, 2H, Dipp CH(CH₃)(CH₃)), 0.91 (d, ³J_{H-H} = 6.8 Hz, 6H, Dipp CH(CH₃)(CH₃)), 0.86 (d, ³J_{H-H} = 6.9 Hz, 6H, Dipp CH(CH₃)(CH₃)).

¹³C{¹H} NMR (151 MHz, C₆D₆): δ(ppm) 146.26 (d, ³J_{C-P} = 1.6 Hz, Dipp *ortho*-C), 134.78 (d, ²J_{C-P} = 6.3 Hz, Dipp *ipso*-C), 130.87 (Dipp Ar-C), 128.35 (Dipp Ar-C), 124.08 (Dipp Ar-C), 123.36 (d, ¹J_{C-P} = 83.5 Hz, CP), 28.69 (Dipp CH(CH₃)₂), 24.30 (Dipp CH(CH₃)₂), 24.07 (Dipp CH(CH₃)₂).

³¹P{¹H} NMR (162 MHz, C₆D₆): δ(ppm) 194.7 (ICPN₃Dipp).

6.6 References

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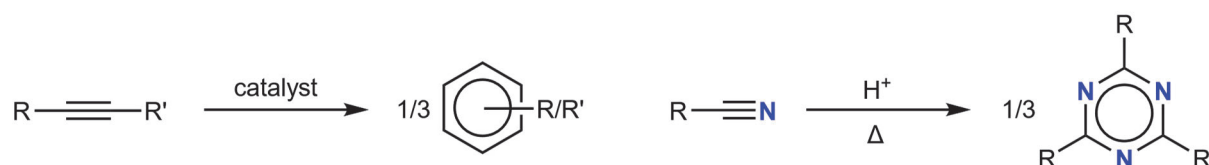
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Oligomerization of the Cyaphide Ion

Abstract. Metal cyaphide complexes are susceptible to oligomerization by formal cycloaddition reactions involving the reactive cyaphide $\text{C}\equiv\text{P}$ π bonds to give highly charged, conjugated organophosphorus anions. The synthesis, characterization, and bonding of the oligomers and their monomer precursors are discussed herein. The factors that favor oligomerization are elucidated, providing a framework for understanding the stabilization of metal cyaphide complexes.

7.1 Oligomerization of triply-bonded organic molecules

Organic molecules containing triple bonds are capable of undergoing oligomerization reactions, often driven by the formation of stable, aromatic products. This is exemplified by the cyclotrimerization of alkynes and nitriles (Scheme 7.1).

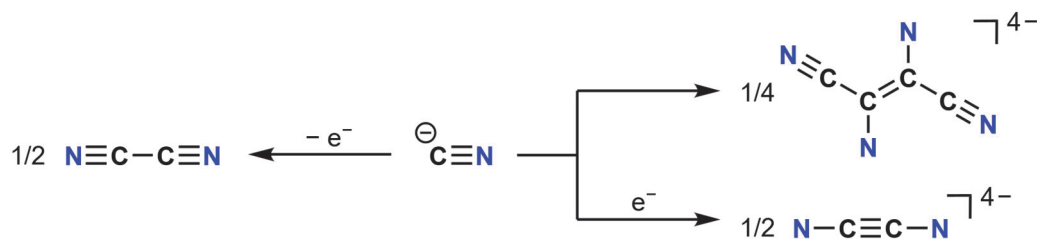


Scheme 7.1. Catalytic cyclotrimerization of alkynes and nitriles.

The trimerization of alkynes requires the use of metal catalysts (e.g. $\text{Co}(\text{Cp})(\text{CO})_2$), and is an atom-economical route to compounds containing substituted benzene rings.^[1] The trimerization of nitriles is usually conducted under forcing conditions, mediated by strong acids (e.g. TfOH), and is an important route to 1,3,5-triazoles in the synthesis of covalent organic frameworks (COFs).^[2]

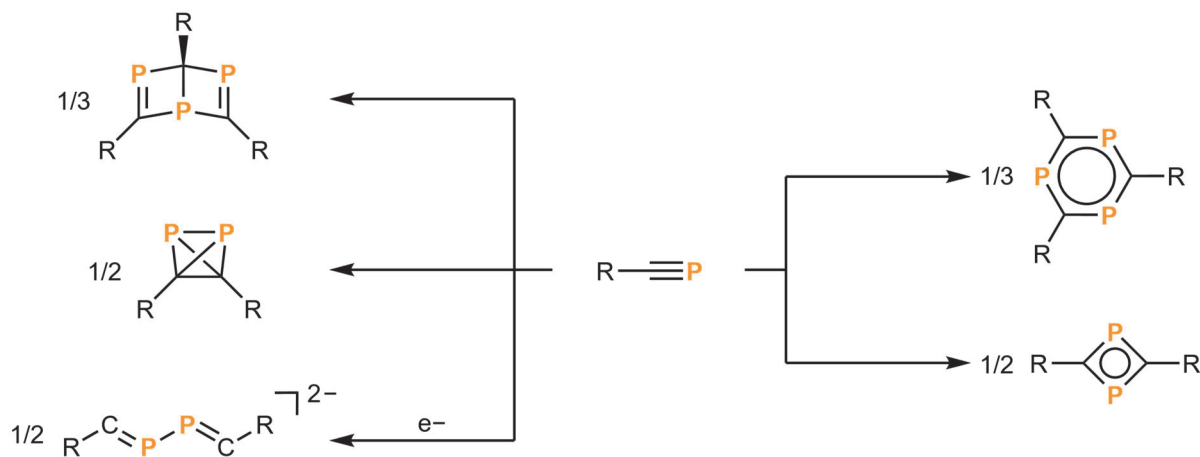
Unlike nitriles, the most common oligomerization mode for the cyanide ion is *via* oxidative C–C coupling to afford cyanogen (C_2N_2).^[3] Uncommonly, the cyanide ion can also undergo tetramerization to a $\text{C}_4\text{N}_4^{4-}$

moiety (mediated by vanadium(IV) or arsenic(III)),^[4,5] or reductive dimerization to $\text{C}_2\text{N}_2^{4-}$ (mediated by niobium(IV));^[6] Scheme 7.2).



Scheme 7.2. Oligomerization reactions of the cyanide ion.

Phosphaalkynes are the phosphorus-containing analogues of alkynes and nitriles, and can also oligomerize, though unlike alkynes and nitriles, there is no single preference for the outcomes of these reactions (Scheme 7.3).^[7]



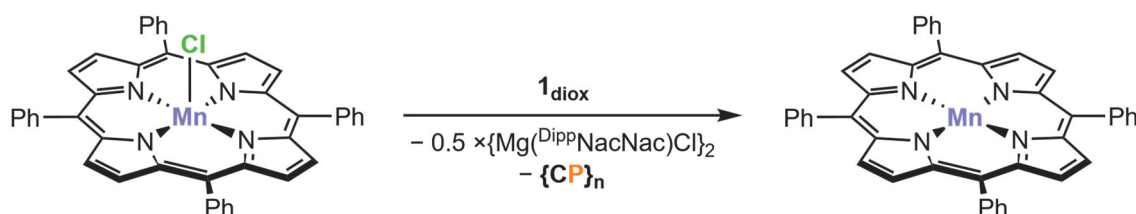
Scheme 7.3. Some oligomerization reactions of phosphaalkynes.

Phosphaalkynes can trimerize to give 1,3,5-triphosphabenzenes^[8,9] or dimerize to 1,3-diphosphacyclobutadienes,^[10] either catalytically or stoichiometrically in the coordination sphere of transition metals. These reactions are not limited to just producing π -conjugated molecules. For example, trityl phosphaalkyne can trimerize to afford a Dewar 1,3,5-triphosphabenzene,^[11,12] and *tert*-butyl phosphaalkyne can undergo a nickel(0) catalyzed dimerization to afford a diphosphatetrahedrane.^[13] Upon reduction by samarium(II), *tert*-butyl phosphaalkyne dimerizes to form 1,3-diphosphabutadiene-1,4-diide.^[14]

7.2 Oligomerization of the cyaphide ion

7.2.1 Oxidative cyaphide oligomerization

The cyaphide transfer chemistry discussed in Chapter 3 appears to be fairly general. Regardless of the identity of the metal halide, salt-metathesis almost always occurs as evidenced by the production of the $\{\text{Mg}(\text{DippNacNac})\text{X}\}_2$ byproduct. However, when the targeted cyaphide complex is insufficiently stabilized these reactions frequently result in decomposition to metallic precipitates. The identity of the phosphorus-containing decomposition products is unclear, as no distinct spectroscopic features can be observed by ^{31}P NMR, Raman, or IR spectroscopy, though it is possible that they result from oxidative cyaphide oligomerization or polymerization reactions.



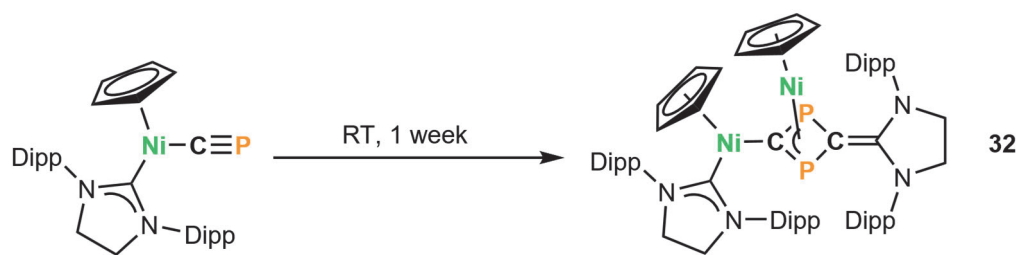
Scheme 7.4. Reduction of $\text{Mn}(\text{TPP})\text{Cl}$ to $\text{Mn}(\text{TPP})$ by $\mathbf{1}_{\text{diox}}$.

When $\mathbf{1}_{\text{diox}}$ is reacted with the manganese(III) porphyrin complex $\text{Mn}(\text{TPP})\text{Cl}$ (TPP = 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine), salt-metathesis occurs with the formation of $\{\text{Mg}(\text{DippNacNac})(\mu\text{-Cl})\}_2$ (identified by ^1H NMR spectroscopy), and the manganese(III) center is reduced to give the manganese(II) porphyrin complex $\text{Mn}(\text{TPP})$ (Scheme 7.4). This reaction is similar to the well-studied metal-mediated homocoupling of Grignard reagents.^[15] While the fate of the cyaphide ion could not be determined, oxidative homocoupling to oligomeric species is a distinct possibility.

7.2.2 Synthesis of $\{\text{Ni}(\text{SIDipp})(\text{Cp})\}\{\text{Ni}(\text{Cp})\}\{\mu\text{-(SIDipp)}\text{C}_2\text{P}_2\}$

In the coordination sphere of certain metal complexes, the cyaphide ion undergoes redox neutral oligomerization reactions to afford well-defined products, offering some insight into possible decomposition pathways for metal cyaphide complexes.

The synthesis of a nickel(II) cyaphide complex **8** was previously discussed in Section 3.2.2. In concentrated solutions, **8** slowly converts to an asymmetric dimer $\{\text{Ni}(\text{SIDipp})(\text{Cp})\}\{\text{Ni}(\text{Cp})\}\{\mu\text{-(SIDipp)}\text{C}_2\text{P}_2\}$ (**32**), which contains an SIDipp-stabilized $\text{C}_2\text{P}_2^{2-}$ anion (Scheme 7.5).



Scheme 7.5. Synthesis of the asymmetric bimetallic nickel(II) complex **32** from the dimerization of **8**.

32 exhibits two mutually-coupled doublets in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 130.3 and 119.9 ppm ($^2J_{\text{P-P}} = 65$ Hz), corresponding to the two phosphorus atoms of the $\text{C}_2\text{P}_2^{2-}$ ring, made inequivalent by the restricted rotation of the $\text{Ni}(\text{SIDipp})(\text{Cp})$ moiety. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show that the two SIDipp ligands are desymmetrized and that the two Cp ligands are inequivalent.

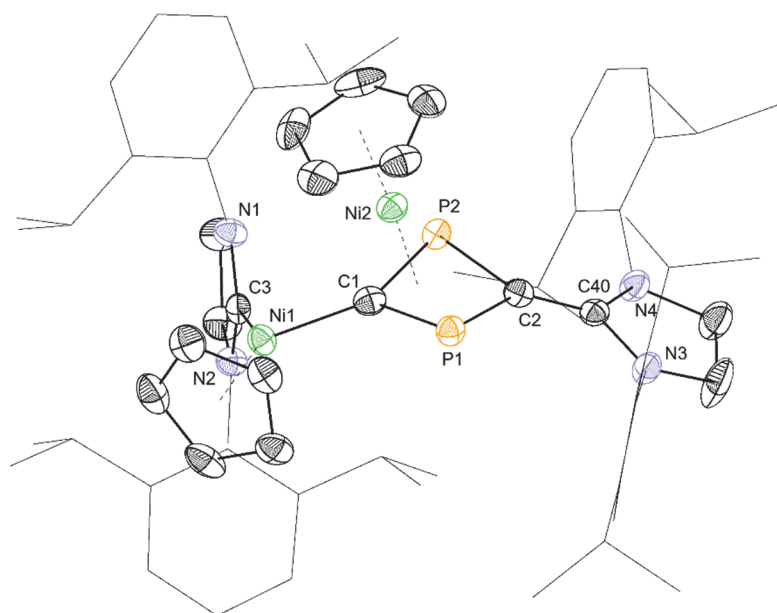


Figure 7.1. Solid-state structure of **32**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms and co-crystallized toluene are omitted for clarity. Dipp groups are depicted as wireframes.

The solid-state structure of **32** reveals that the C_2P_2 ring has inserted into a $\text{Ni}-\text{C}_{\text{NHC}}$ bond (Figure 7.1). The C_2P_2 ring has a $\text{C1}-\text{P1}$ bond length of 1.820(3) Å, a $\text{C1}-\text{P2}$ bond length of 1.794(3) Å, a $\text{C2}-\text{P1}$ bond length of 1.815(3) Å, and a $\text{C2}-\text{P2}$ bond length of 1.824(3) Å, all in between the sum of covalent radii for carbon–phosphorus single (1.96 Å) and double (1.69 Å) bonds. The ring is slightly puckered, with a 0.15 Å mean deviation from planarity, and has $\text{C1}-\text{P}-\text{C2}$ bond angles of 85.4(2)° and 85.9(2)°, and $\text{P1}-\text{C}-\text{P2}$ bond angles of 91.5(2)° and 90.6(2)°. The $\text{C2}-\text{C40}$ bond length is 1.352(4) Å, in good agreement with a $\text{C}=\text{C}$ double bond (1.34 Å). The C_2P_2 ring is bonded $\eta^1:\kappa\text{C}$ to the $\text{Ni}(\text{SIDipp})(\text{Cp})$ fragment, with a $\text{Ni1}-\text{C1}$ bond length of 1.892(3) Å. The $\text{Ni}(\text{Cp})$ fragment is instead

bonded $\eta^3:\kappa^1\text{C},\kappa^2\text{P}$ to the C_2P_2 ring, with a Ni2–C1 bond length of 1.992(2) Å and Ni2–P bond lengths of 2.253(1) and 2.266(1) Å. **32** is structurally similar to a proposed intermediate in the nickel-catalyzed dimerization of *tert*-butyl phosphaaalkyne to di-*tert*-butyldiphosphatetrahedrane.^[13]

7.2.3 Mechanism of the formation of $\{\text{Ni}(\text{SIDipp})(\text{Cp})\}\{\text{Ni}(\text{Cp})\}\{\mu\text{-(SIDipp)}\text{C}_2\text{P}_2\}$

The formation of **32** was investigated computationally using DFT (Figure 7.2). The computed mechanism first proceeds *via* a rate-limiting rearrangement step, in which migratory insertion of the cyaphide ion into the nickel–SIDipp bond results in an η^2 -phosphaallenide intermediate. This proceeds through a relatively high energy transition state (+30.3 kcal mol⁻¹) consistent with the long reaction times needed. Analogous migratory insertions have previously been reported for isocyanides at palladium(II) centers.^[16] The transient η^2 -phosphaallenide intermediate immediately reacts with another molecule of **8** in a [2+2] cycloaddition reaction, forming the $\text{C}_2\text{P}_2^{2-}$ ring. A low-barrier change in hapticity (+1.6 kcal mol⁻¹) from η^2 - η^3 finally results in the asymmetric dimer **32**. Plausible pathways could not be found for the formation of alternative $\eta^1:\eta^1$ or $\eta^2:\eta^2$ dimerization products. Furthermore, these symmetric dimers are both energetically metastable with respect to **32**.

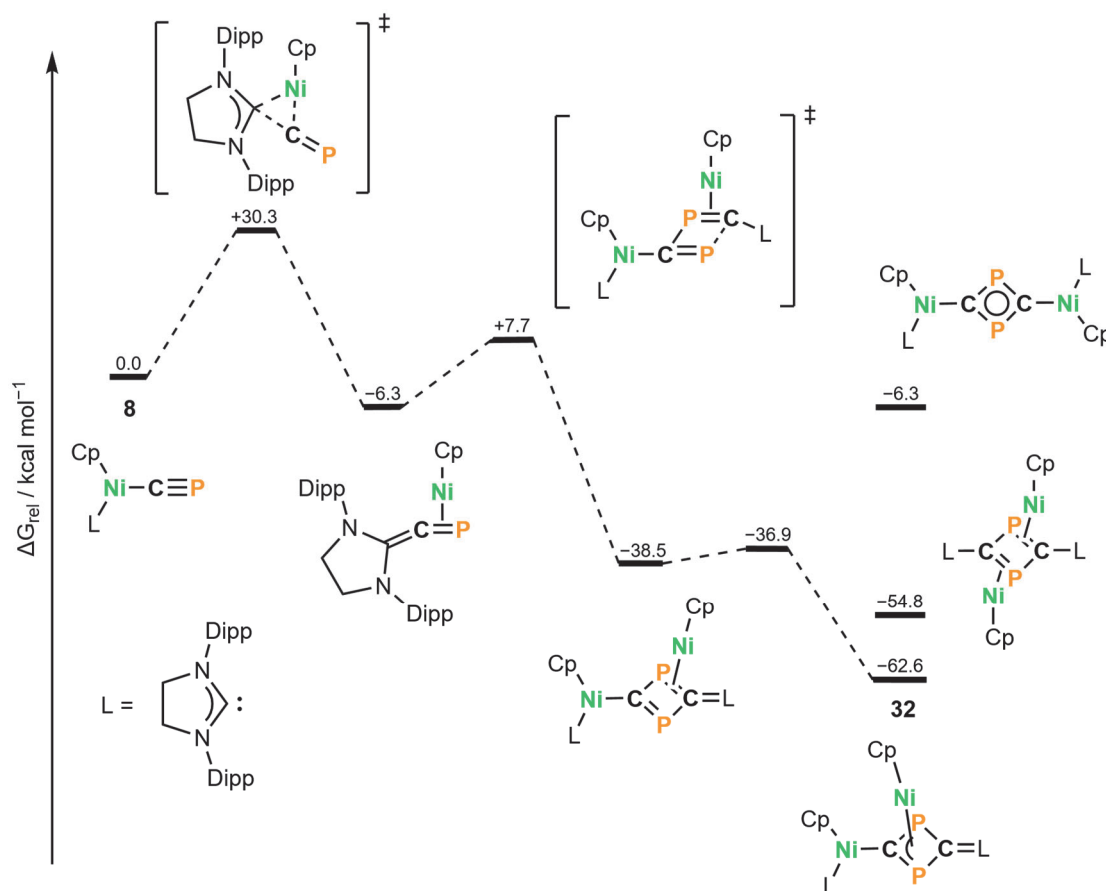
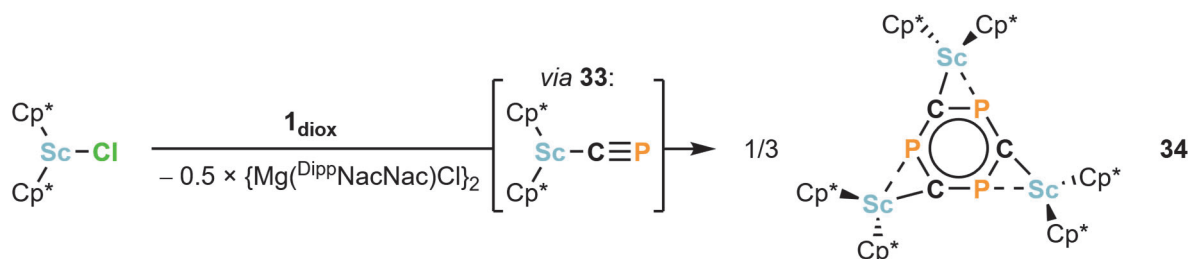


Figure 7.2. Computed mechanism for the formation of **32**.

7.2.4 Synthesis of $\{\text{Sc}(\text{Cp}^*)_2\}_3(\mu_3\text{-C}_3\text{P}_3)$

Oligomerization also occurs when the synthesis of the scandium(III) cyaphide complex $\text{Sc}(\text{Cp}^*)_2(\text{CP})$ (**33**) is attempted. The reaction of **1_{diox}** with one equivalent of $\text{Sc}(\text{Cp}^*)_2\text{Cl}$ results in the precipitation of an orange-red solid. When the reaction is conducted under slow-diffusion conditions, the product crystallizes as orange-red needles, allowing it to be identified as the trimetallic scandium(III) complex $\{\text{Sc}(\text{Cp}^*)_2\}_3(\mu_3\text{-C}_3\text{P}_3)$ (**34**; Scheme 7.6).



Scheme 7.6. Synthesis of the trimetallic scandium(III) complex **34** from the trimerization of **33**.

34 is insoluble in many polar organic solvents (e.g. DCM, MeCN, and 1,2-DFB) though is soluble in DMSO, in which it decomposes over the course of several hours. Nevertheless, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **34** reveals a broad resonance at 245.5 ppm ($\nu_{1/2} = 99$ Hz), and its ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show a single Cp^* environment.

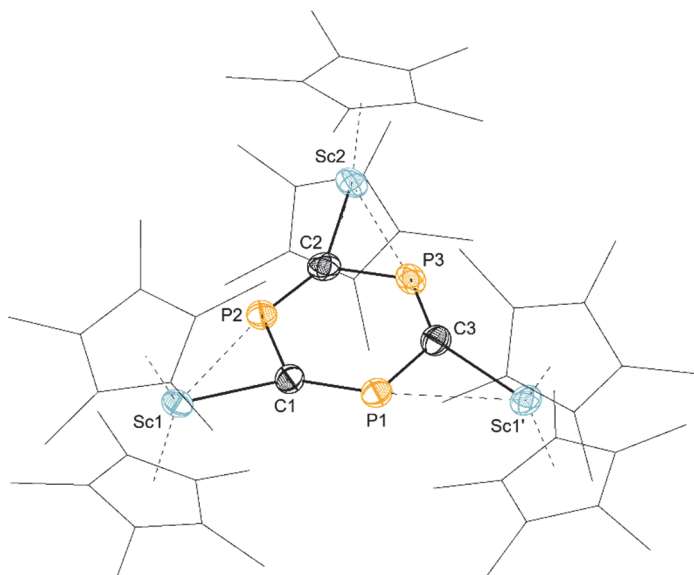


Figure 7.3. Solid-state structure of **34**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms and disorder components are omitted for clarity. Cp^* groups are depicted as wireframes.

The solid-state structure of **34** reveals a trimeric structure in which three $\text{Sc}(\text{Cp}^*)_2$ fragments are coordinated to a bridging $\text{C}_3\text{P}_3^{3-}$ unit, the trianion of 1,3,5-triphospha benzene (Figure 7.3). In the crystal

structure, the C_3P_3 ring is disordered over two chemically equivalent positions, precluding discussion of the crystallographically determined bond metrics. The DFT optimized minimum geometry is in good agreement with the modeled disorder components, and an eigenvector-following transition state optimization shows they are related by a low energy ($+1.0 \text{ kcal mol}^{-1}$) ring-rotation barrier (in the gas phase). This may also give rise to dynamic behavior in solution that accounts for the broad appearance of the $^{31}\text{P}\{^1\text{H}\}$ NMR signal.

The $C_3P_3^{3-}$ ion is planar in both the solid-state structure and in the calculated geometry, and Nucleus Independent Chemical Shift (NICS) calculations suggest that it is 6π Hückel aromatic (NICS(0) = -5.41 ppm; NICS(1) = -7.86 ppm; NICS_{zz}(0) = -12.49 ppm; NICS_{zz}(1) = -20.58 ppm). **34** has a C_3P_3 ring that is distinctly geometrically different to neutral 1,3,5-triphosphabenzene. Compared to ${}^t\text{Bu}_3\text{C}_3\text{P}_3$,^[9] **34** has lower P-C-P bond angles (**34**: XRD $124.1(4)^\circ$, calcd. 124.8° ; ${}^t\text{Bu}_3\text{C}_3\text{P}_3$: XRD $130.3(3)^\circ$, calcd. 130.4°), and higher C-P-C bond angles (**34**: XRD $116.4(3)^\circ$, calcd. 115.2° ; ${}^t\text{Bu}_3\text{C}_3\text{P}_3$: XRD $109.7(3)^\circ$, calcd. 109.6°). These bond angles are closer to the calculated values for the free $C_3P_3^{3-}$ anion (P-C-P: 122.1° ; C-P-C: 117.9°).

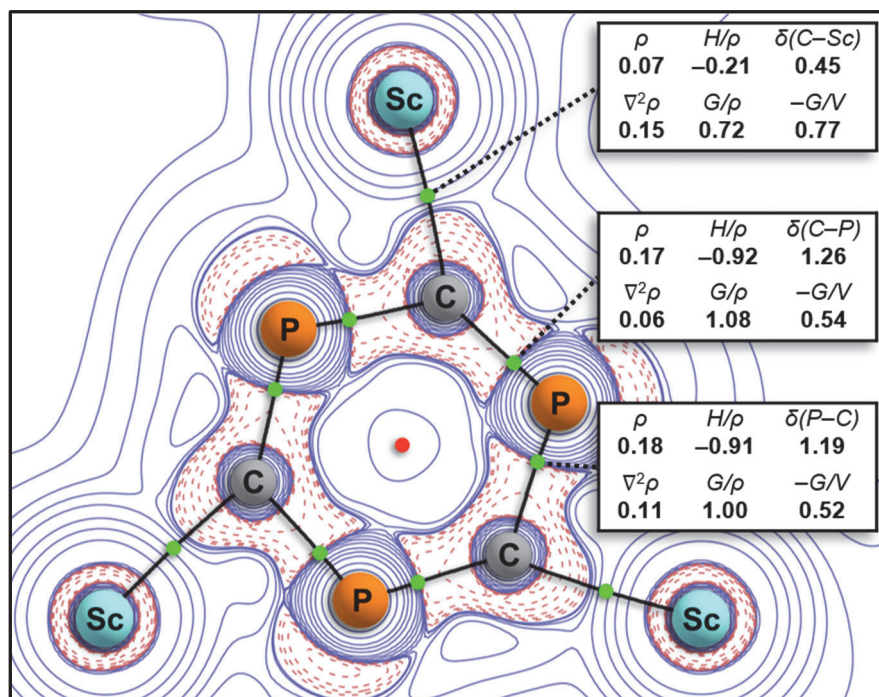


Figure 7.4. 2D QTAIM topological analysis of **34**. Parameters at bond critical points are specified in a.u.

To further investigate the nature of the bonding in **34**, QTAIM topological analysis was performed on the DFT calculated electron density (Figure 7.4). The Sc-C bond critical points suggest that they are highly polar dative bonds, with relatively low covalency as indicated by their low delocalization indices ($\delta(\text{Sc-C})$

= 0.45), electron densities ($\rho = 0.07$ a.u.) and energy densities ($H/\rho = -0.21$ a.u.). While the solid-state and computed geometries show side-on η^2 coordination of the $C_3P_3^{3-}$ ring to each scandium(III) center, no Sc–P bond paths were found. This suggests that the η^2 bonding mode arises due to electrostatic interactions between the phosphorus lone pairs and the scandium(III) ions. This indicates relatively weak Sc–P interactions, which is in line with the postulated dynamic ring-rotation behavior that gives rise to the crystallographic disorder and the broadened $^{31}P\{^1H\}$ NMR signal.

7.2.5 Mechanism of the formation of $\{Sc(Cp^*)_2\}_3(\mu_3-C_3P_3)$

A mechanism for the trimerization of **33** was computed using DFT (Figure 7.5). Initially, donor-acceptor association of coordinatively unsaturated monomer units of **33** occurs. This preorganizes a relatively low barrier (+21.7 kcal mol⁻¹) [2+2+2] cycloaddition to afford **34**. Donor-acceptor preorganization is likely critical for selective trimer formation; when the coordinatively saturated complex $Sc(Cp^*)_2(THF)Cl$ is used as a precursor the reaction results in an intractable mixture of products.

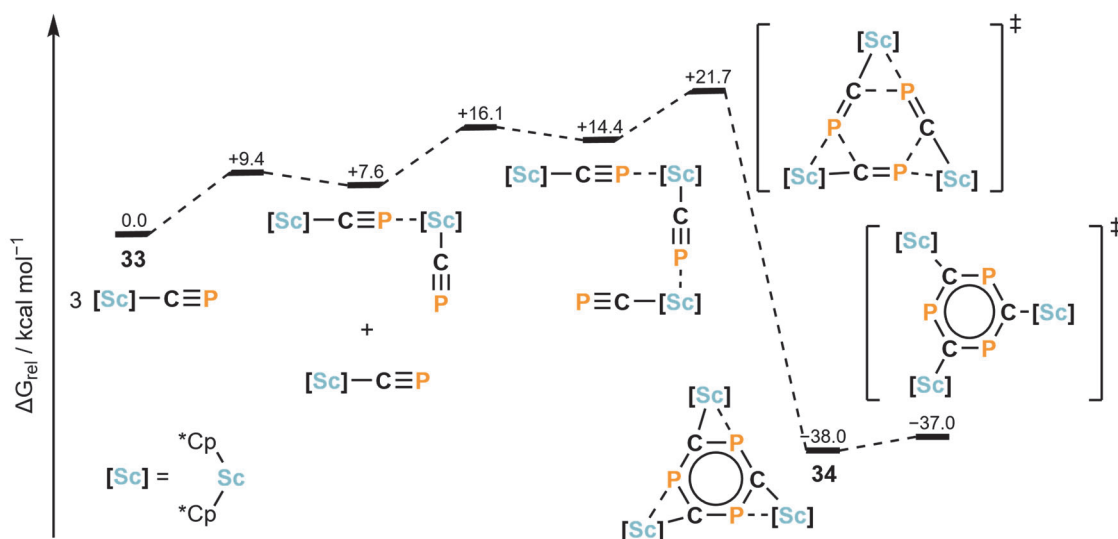


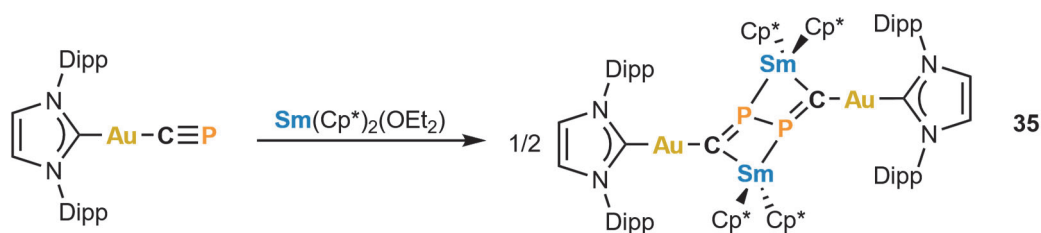
Figure 7.5. Computed mechanism for the formation of **34**.

7.2.6 Synthesis of $\{Au(IDipp)\}_2\{Sm(Cp^*)_2\}_2(\mu_4-C_2P_2)$

The gold(I) cyaphide complex **7** does not spontaneously oligomerize. However, many species that are isolobal to the cyaphide ion (including phosphalkynes,^[14] cyanides,^[6] alkynes,^[17] and carbon monoxide^[18]) can be coupled by metal-mediated reduction reactions.

Addition of a solution of $Sm(Cp^*)_2(OEt_2)$ to a solution of **7** results in the immediate precipitation of a brown solid that is insoluble even in highly polar organic solvents (e.g. 1,2-DFB, MeCN, and DMSO),

precluding characterization by NMR spectroscopy. However, when the reaction is conducted under slow-diffusion conditions, the product crystallizes as dark yellow-brown blocks. This allowed it to be identified crystallographically as the tetrametallic complex $\{\text{Au}(\text{IDipp})\}_2\{\text{Sm}(\text{Cp}^*)_2\}_2(\mu_4\text{-C}_2\text{P}_2)$ (**35**) containing a reduced cyaphide dimer, $\text{C}_2\text{P}_2^{4-}$, the tetraanion of 1,3-diphospha-butadiene (Scheme 7.7). **35** is closely related to a reductively coupled dimer of *tert*-butyl phosphaaalkyne,^[14] and is also structurally similar to carbene-stabilized C_2P_2 species.^[19]



Scheme 7.7. Synthesis of the tetrametallic gold(I)/samarium(III) complex **35**.

The solid-state structure of **35** shows a C_2P_2 unit in which two cyaphide moieties are joined by a P–P single bond (Figure 7.6), contrasting the behavior of the cyanide ion which reductively couples *via* the formation of a C–C bond. The C1–P1–P1' bond angle is $110.4(2)^\circ$, the P1–P1' bond length is $2.306(3)$ Å, and the C1–P1 bond lengths are $1.623(6)$ Å. The bridging C_2P_2 fragment is bonded κC to two gold centers, and $\kappa\text{C}:\kappa\text{P}$ to two samarium centers. The Au1–C1–P1 bond angles are $118.2(3)^\circ$, suggesting the carbon atoms are sp^2 hybridized. The Au1–C1 bond lengths are $2.031(5)$ Å, the Sm1–C1 bond lengths are $2.461(6)$ Å, and the Sm1–P1 bond lengths are $2.894(2)$ Å.

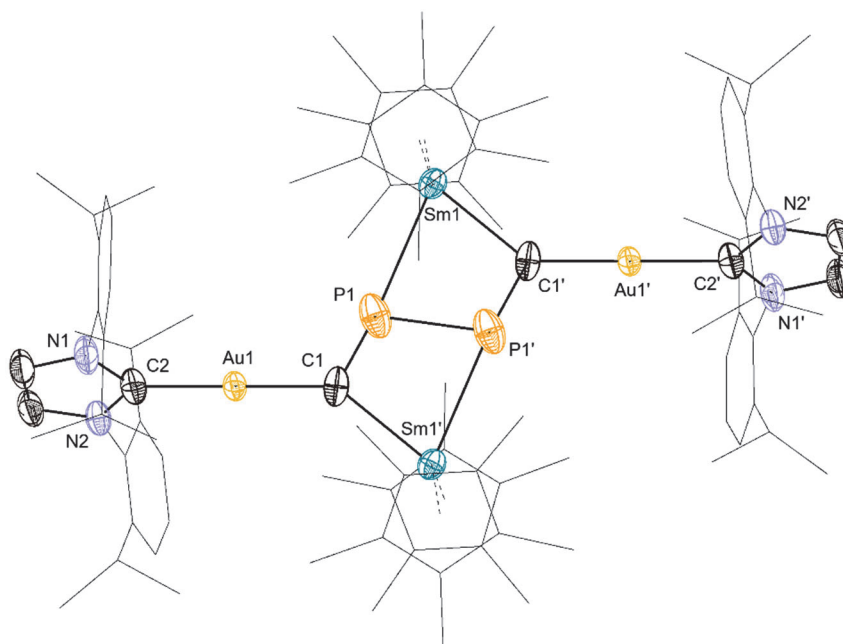


Figure 7.6. Solid-state structures of **35**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms and disorder components are omitted for clarity. Dipp and Cp^* groups are depicted as wireframes.

7.3 Stability of metal cyaphide complexes

The scandium (III) complex **33** and gold(I) complex **7** both contain cyaphido ligands that are very poorly sterically protected. Yet, while the former trimerizes spontaneously upon formation, the latter is very reticent to oligomerize, only doing so upon chemical reduction. This can be explained by their contrasting M–C bond characters. Scandium is an early 3d metal, and in the +3 oxidation state is a hard, charge-dense ion that forms predominantly ionic bonds in organometallic complexes. In contrast, gold is a late 5d metal, and in the +1 oxidation state forms strong covalent σ bonds with carbon due to relativistic contraction of the 6s orbital.^[20] For **33** and **7**, this difference in M–C bond covalency is reflected in several computed metrics.

QTAIM topological analysis was performed on the DFT calculated electron densities of **33** and **7** (Figure 7.7). While the parameters at the C–P bond critical points are similar for both complexes, the parameters for the M–C bond critical points differ significantly. The Sc–CP bond in **33** has very low covalent character, as indicated by its low delocalization index ($\delta(\text{Sc}-\text{C}) = 0.46$), energy density ($H/\rho = -0.21$ a.u.), and electron density ($\rho = 0.08$ a.u.). The Au–CP bond in **7** has substantially increased covalency compared to **33**, with relevant parameters that are greater by approximately a factor of two ($\delta(\text{Au}-\text{C}) = 1.13$; $H/\rho = -0.54$ a.u.; $\rho = 0.15$ a.u.).

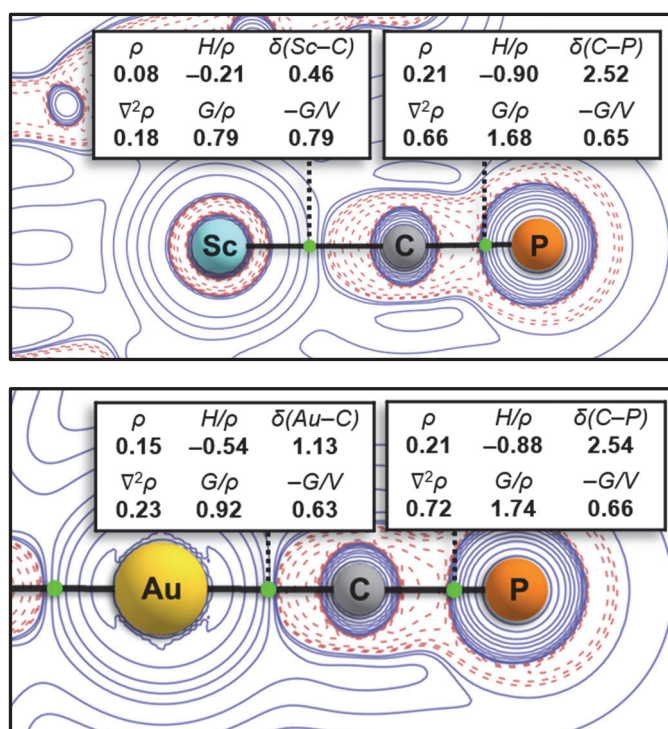


Figure 7.7. 2D QTAIM topological analysis of **33** (top) and **7** (bottom). Parameters at bond critical points are in a.u.

The differing Sc–CP and Au–CP bond covalencies in **33** and **7** can also be seen in their Wiberg bond indices (WBIs) and Natural Localized Molecular Orbital (NLMO) bond orders. **33** has a Sc–CP bond with a WBI of 0.44 and NLMO bond order of 0.31. **7** has an Au–CP bond with a WBI of 0.58 and NLMO bond order of 0.41. Moreover, NBO analysis identifies a charge-separated Lewis structure with a C→Sc dative bond for **33**, and a covalently bonded Lewis structure with for **7**.

These data suggest that electronic stabilization of the cyaphide ion by M–CP covalent bonding is extremely important for disfavoring the oligomerization of metal cyaphide complexes. This effect can be seen on the C≡P π – π^* orbital energy gap, which is smaller for **33** than for **7** (Figure 7.8).

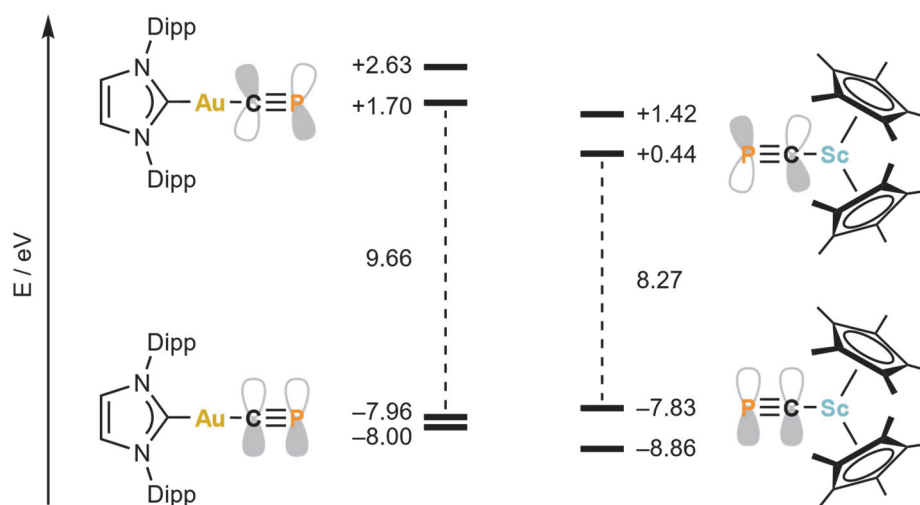


Figure 7.8. Energy level diagram comparing the C≡P π and π^* Kohn-Sham molecular orbitals in **33** and **7**.

The nickel(II) cyaphide complex **8** also has a covalent M–C bond, with a Ni–C delocalization index of 1.01 (Figure 7.9), a WBI of 0.55, and an NLMO bond order of 0.52. In this case, oligomerization occurs *via* a different pathway, initiated by the migratory insertion of the cyaphido ligand into the Ni–C bond of a *cis*-coordinated NHC ligand (see Section 7.2.4). This C–C bond formation step is similar to those reported for platinum(II) cyaphide complexes (see Section 1.7.4).^[21] These examples suggest that, at least for group 10 cyaphide complexes, *cis*-coordinated C-donor ligands are detrimental to stability.

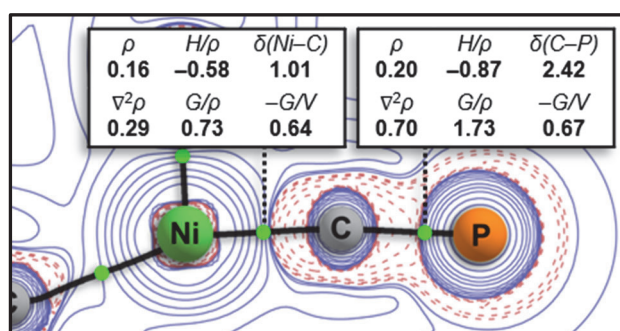


Figure 7.9. 2D QTAIM topological analysis of **8**. Parameters at bond critical points are in a.u.

7.4 Conclusions

The cyaphide ion is highly reactive in the coordination sphere of certain transition metal complexes, readily oligomerizing to form highly charged organophosphorus anions. The nickel(II) cyaphide complex **5** dimerizes *via* a mechanism involving migratory insertion into a Ni–C_{NHC} bond to give the asymmetric bimetallic complex **32**, containing a C₂P₂²⁻ fragment. The transient scandium(III) cyaphide complex **33** trimerizes upon formation to the trimetallic complex **34**, containing a C₃P₃³⁻ fragment. Oligomerization can be induced for the stable gold(I) cyaphide complex **7** using a samarium(II) reducing agent, resulting in the tetrametallic complex **35**, containing a C₂P₂⁴⁻ fragment.

Taking into consideration the results in this chapter and in those preceding it, the following principles for predicting the stability of metal cyaphide complexes can be proposed:

1. Metal–carbon bond covalency is crucial for electronic stabilization

Cyaphide complexes of late transition metals are more likely to be stable than those of early transition metals. M–C bond covalency is substantially improved for π basic metals.

2. Complexes of metals in relatively high oxidation states are unlikely to be stable

The cyaphide ion can act as a reductant toward transition metals, which is more likely to be favorable for high valent metals or those with high reduction potentials.

3. Nucleophilic carbon-donor ligands in *cis*- coordination sites can lead to unwanted reactivity

Due to the electrophilicity of the cyaphido ligand, C–C bond forming migratory insertion and reductive elimination reactions involving *cis*-coordinated nucleophiles are possible.

4. Steric protection can help compensate for poor electronic stabilization

The primary decomposition pathway for metal cyaphide complexes appears to be *via* oligomerization. Substantial steric bulk can prevent this from occurring.

These principles were used to inform the design of a particularly challenging synthetic target, namely a dicyaphide complex that can form stable μ - η^1 : η^1 -cyaphido multimetallic species. These are discussed in the next chapter.

Some of the work in this chapter has been published in *Angewandte Chemie*:

E. S. Yang, D. W. N. Wilson, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2023**, 62, e202218047.

7.5 Experimental section

7.5.1 Reaction of $\text{Mg}(\text{DippNacNac})(\text{CP})(\text{diox})$ with $\text{Mn}(\text{TPP})\text{Cl}$

A solution of $\text{Mg}(\text{DippNacNac})(\text{CP})(\text{diox})$ (approx. 32 mg, 0.06 mmol) in toluene (0.5 mL) was generated *in situ*, as in Section 2.4.1. This was added dropwise to a stirred solution of $\text{Mn}(\text{TPP})\text{Cl}$ (35 mg, 0.05 mmol) in toluene (0.5 mL) at room temperature, resulting in an immediate color change from dark green to dark purple. The mixture was stirred for 1 h, then filtered to remove a solid precipitate, identified as $\{\text{Mg}(\text{DippNacNac})(\mu\text{-Cl})\}_2$ by ^1H NMR spectroscopy.^[22] The filtrate was concentrated by slow evaporation, then stored at $-35\text{ }^\circ\text{C}$ for 1 day to afford dark purple crystals, which were identified as $\text{Mn}(\text{TPP})\cdot\text{C}_7\text{H}_8$ by single crystal X-ray crystallography.^[23] Yield: 24 mg, 0.04 mmol, 72%.

7.5.2 Synthesis of $\{\text{Ni}(\text{SIDipp})(\text{Cp})\}\{\text{Ni}(\text{Cp})\}\{\mu\text{-(SIDipp)}\text{C}_2\text{P}_2\}$ (32)

A solution of $\text{Ni}(\text{SIDipp})(\text{Cp})(\text{CP})$ (20 mg, 0.04 mmol) in toluene (0.5 mL) was concentrated by slow evaporation at room temperature over the course of 1 week, during which $\{\text{Ni}(\text{SIDipp})(\text{Cp})\}\{\text{Ni}(\text{Cp})\}\{\mu\text{-(SIDipp)}\text{C}_2\text{P}_2\}$ crystallizes as black crystals suitable for X-ray crystallography. The crystals were isolated by filtration and washed with cold hexane ($2 \times 0.5\text{ mL}$). Yield: 13 mg, 0.02 mmol, 64%. Anal. Calcd. (%) for $\text{C}_{66}\text{H}_{86}\text{N}_4\text{Ni}_2\text{P}_2\cdot\text{C}_7\text{H}_8$: C, 72.65; H, 7.85; N 4.64. Found: C 73.35; H, 8.33; N, 4.17. The low symmetry of the complex, the broad appearance of peaks, as well as some overlap with the residual solvent signal prevented the complete explicit assignment of ^1H and ^{13}C spectra.

^1H NMR (400 MHz, C_6D_6): δ (ppm) 7.62 (s, 1H, Dipp Ar-**H**), 7.30 (m, 4H, Dipp Ar-**H**), 7.08 (m, 6H, Dipp Ar-**H**), (s, 1H, Dipp Ar-**H**), 5.11 (s, 5H, Cp C_5H_5), 4.68 (s, 5H, Cp C_5H_5), 3.95 (b, 1H, SIDipp C_2H_4), 3.77 (b, 2H, Dipp $\text{CH}(\text{CH}_3)_2$), 3.66 (b, 1H, (b, 1H, SIDipp C_2H_4), 3.53 (m, 2H, SIDipp C_2H_4), 3.45 (m, 2H, Dipp $\text{CH}(\text{CH}_3)_2$), 3.37 (m, 1H, SIDipp C_2H_4), 3.15 (m, 1H, SIDipp C_2H_4), 3.05 (b, 1H, SIDipp C_2H_4), 2.83 (b, 1H, Dipp $\text{CH}(\text{CH}_3)_2$), 2.79 (b, 1H, Dipp $\text{CH}(\text{CH}_3)_2$), 2.51 (m, 2H, Dipp $\text{CH}(\text{CH}_3)_2$), 1.81 (b, 6H, Dipp $\text{CH}(\text{CH}_3)_2$), 1.68 (m, 3H, Dipp $\text{CH}(\text{CH}_3)_2$), 1.59 (m, 3H, Dipp $\text{CH}(\text{CH}_3)_2$), 1.55 (m, 3H, Dipp $\text{CH}(\text{CH}_3)_2$), 1.33 (b, 6H, Dipp $\text{CH}(\text{CH}_3)_2$), 1.24 (m, 3H, Dipp $\text{CH}(\text{CH}_3)_2$), 1.08 (m, 3H, Dipp $\text{CH}(\text{CH}_3)_2$), 1.03 (m, 3H, Dipp $\text{CH}(\text{CH}_3)_2$), 0.94 (m, 3H, Dipp $\text{CH}(\text{CH}_3)_2$), 0.84 (m, 3H, Dipp $\text{CH}(\text{CH}_3)_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): δ (ppm) 217.48 (s, SIDipp **CNi**), 149.96 (s, Dipp Ar-**C**), 148.85 (s, Dipp Ar-**C**), 147.61 (s, Dipp Ar-**C**), 146.71 (s, Dipp Ar-**C**), 140.78 (s, Dipp Ar-**C**), 140.12 (s, Dipp Ar-**C**), 139.40 (s, Dipp Ar-**C**), 138.08 (s, Dipp Ar-**C**), 136.91 (s, Dipp Ar-**C**), 125.81 (s, Dipp Ar-**C**), 125.45

(s, Dipp Ar-**C**), 124.99 (s, Dipp Ar-**C**), 123.81 (m, **C**₂**P**₂), 94.56 (s, Cp **C**₅**H**₅), 92.04 (s, Cp **C**₅**H**₅), 54.99 (s, SIDipp H₂**CND**Dipp), 52.84 (s, SIDipp H₂**CND**Dipp), 51.63 (s, SIDipp H₂**CND**Dipp), 29.51 (s, Dipp **CH**(**CH**₃)₂), 29.07 (s, Dipp **CH**(**CH**₃)₂), 28.61 (s, Dipp **CH**(**CH**₃)₂), 28.35 (s, Dipp **CH**(**CH**₃)₂), 27.95 (s, Dipp **CH**(**CH**₃)₂), 27.09 (s, Dipp **CH**(**CH**₃)₂), 26.90 (s, Dipp **CH**(**CH**₃)₂), 26.43 (s, Dipp **CH**(**CH**₃)₂), 25.95 (s, Dipp **CH**(**CH**₃)₂), 25.43 (s, Dipp **CH**(**CH**₃)₂).

³¹P{¹H} NMR (162 MHz, C₆D₆): δ(ppm) 130.3 (d, ²J_{P-P} = 65 Hz, **C**₂**P**₂), 119.9 (d, ²J_{P-P} = 65 Hz, **C**₂**P**₂).

7.5.3 Synthesis of {Sc(Cp*)₂}₃(μ₃-C₃P₃) (34)

Mg(^{Dipp}NacNac)(CP)(diox) (approx. 321 mg, 0.56 mmol) was generated *in situ* in toluene (3 mL). A solution of Sc(Cp*)₂Cl (150 mg, 0.43 mmol) in hexane (5 mL) was carefully layered on top of the solution of Mg(^{Dipp}NacNac)(CP)(diox) in a long, thin ampoule. The solutions were allowed to mix by diffusion at room temperature over 2 weeks, resulting in the formation of {Sc(Cp*)₂}₃(μ₃-C₃P₃) as red, rod-like crystals suitable for X-ray crystallography. The crystals were isolated by filtration, and washed with THF (3 × 5 mL) to remove residual {Mg(^{Dipp}NacNac)(μ-Cl)}₂. Yield: 140 mg, 0.13 mmol, 91%. Anal. Calcd. (%) for C₆₃H₉₀P₃Sc₃: C, 70.38; H, 8.44; N, 0.00. Found: C, 69.87; H, 8.09; N, 0.00. The product is insoluble in most organic solvents, though is soluble in DMSO, in which it decomposes over the course of several hours.

¹H NMR (500 MHz, d₆-DMSO): δ(ppm) 1.82 (s, 90H, (Cp* C₅(**CH**₃)₅)).

¹³C{¹H} NMR (126 MHz, d₆-DMSO): δ(ppm) 115.75 (Cp* C₅(**CH**₃)₅), 13.25 (Cp* C₅(**CH**₃)₅).

³¹P{¹H} NMR (202 MHz, d₆-DMSO): δ(ppm) 245.5 (b, ν_{1/2} = 99 Hz, **C**₃**P**₃).

7.5.4 Synthesis of {Au(IDipp)}₂{Sm(Cp*)₂}₂(μ₄-C₂P₂) (35)

In a long, thin ampoule, a solution of Sm(Cp*)₂(OEt₂) (40 mg, 0.08 mmol) in toluene (1 mL) was carefully layered on top of a solution of Au(IDipp)(CP) (50 mg, 0.08 mmol) in toluene (1 mL). The solutions were allowed to mix by diffusion at room temperature over 5 days, resulting in the formation of large brown crystals of {Au(IDipp)}₂{Sm(Cp*)₂}₂(μ₄-C₂P₂) suitable for X-ray crystallography. The supernatant solution was decanted, and the crystals washed with toluene (2 × 2 mL) and pentane (2 × 2 mL), then dried under vacuum. Yield: 74 mg, 0.07 mmol, 88%. Anal. Calcd. (%) for C₅₆H₇₂Au₂N₄P₂Sm₂: C, 54.94; H, 6.34; N, 2.67. Found: C, 54.68; H, 6.08; N, 2.26. The product was insoluble in all attempted common organic solvents, precluding characterization by NMR spectroscopy.

7.6 References

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Molecular Cyaphide Analogs of Prussian Blue

Abstract. The synthesis of highly stable iron(II) mono- and dicyaphide complexes is described. These are used as precursors to multimetallic iron complexes containing the cyaphide ion in end-on bridging coordination modes, structurally related to fragments of Prussian blue. The properties of these complexes are investigated using NMR and vibrational spectroscopy, X-ray crystallography, and cyclic voltammetry. Theoretical calculations provide insight into their electronic structures.

8.1 Conjugated multimetallic complexes

8.1.1 Cyanide complexes

As introduced in Section 1.2, Prussian blue and related analogs (PBAs) are archetypal examples of cyanide-containing inorganic materials. Multimetallic molecular bridging cyanide complexes are often studied as model systems of PBAs, allowing important features such as magnetic and electrochemical properties to be examined in detail.^[1,2]

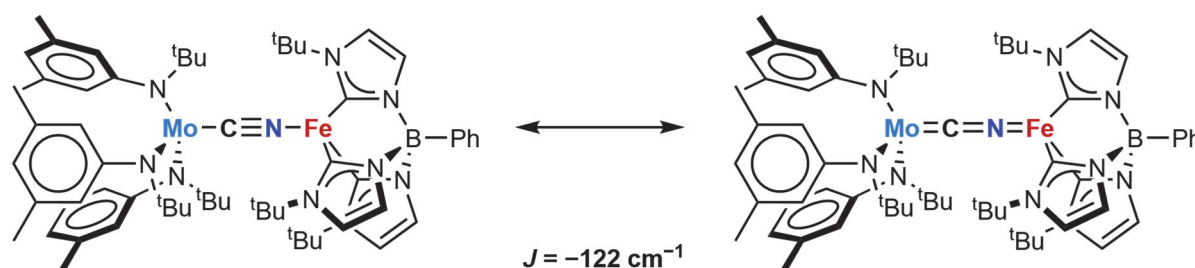


Figure 8.1. Strong antiferromagnetic coupling in a cyanide-bridged bimetallic iron(II)/molybdenum(III) complex.

For magnetic applications, the strength of antiferromagnetic coupling in PBAs is of critical importance. Through the study of a model molecular system, Harris, Smith, and co-workers demonstrated that metal-cyanide π backdonation is key to strong antiferromagnetic coupling (Figure 8.1);^[3] the π conjugation afforded by M–C π bonding is crucial to enabling efficient exchange coupling pathways.

8.1.2 Polyynes complexes

π conjugation is also key to the design of multimetallic complexes that are able to serve as electron-transport junctions.^[4] These “molecular wires” are envisioned to have applications in nanoscale devices, and rely on through-conjugation of organic π systems with metal d-orbitals to mediate electron transfer. Polyynes are frequently employed as bridging ligands for the design of molecular wires due to their two orthogonal π systems and low HOMO–LUMO gaps. Berke and co-workers have developed molecular wires based on octahedral iron(II) centers bridged by butadiyne-diide linkers (Figure 8.2).^[5–8]

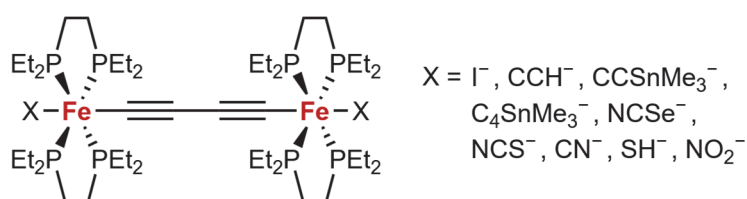


Figure 8.2. A series of butadiyne-diide-bridged bimetallic iron(II) molecular wires.

8.1.3 Cyaphide complexes

As discussed in Section 1.3.2, the cyaphide ion is an attractive potential bridging ligand for use in magnetic materials or molecular wires; its strong π accepting ability and low HOMO–LUMO gap would be greatly advantageous for use in these applications.

Crossley and co-workers have investigated several conjugated organometallic ruthenium(II) complexes containing terminal $\eta^1:\kappa\text{C}$ -cyaphido ligands (see Section 1.4.5).^[9] These include a bimetallic complex, though this eluded crystallographic characterization (Figure 8.3).^[10]

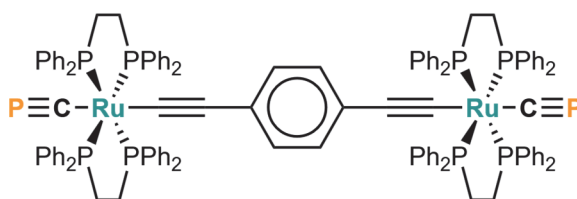


Figure 8.3. A bimetallic 1,4-bisethynylbenzene-diide-bridged ruthenium(II) complex with two $\eta^1:\kappa\text{C}$ -cyaphido ligands.

In these complexes, experimental analysis by UV-vis spectroscopy and cyclic voltammetry as well as theoretical analysis using DFT show significant participation of the $\text{C}\equiv\text{P}$ π and π^* orbitals in the conjugated π -systems. However, multimetallic cyaphide-bridged complexes remain elusive; neither complexes containing end-on bridging cyaphido ligands nor complexes containing multiple cyaphido ligands on a single metal center (i.e. dicyaphide complexes) are known.

8.2 Dicyaphide complexes

8.2.1 Synthesis of $M(18\text{-crown-6})(CP)_2$ ($M = \text{Zn, Cd}$)

As proposed in the previous chapter, metal cyaphide complexes likely decompose *via* pathways involving cyaphide oligomerization reactions. The synthesis of metal complexes bearing multiple cyaphido ligands therefore represents a significant challenge, as such complexes would be prone to intramolecular cyaphide oligomerization. Initially, two strategies were used to circumvent this problem. Metals in low oxidation states with negative reduction potentials were used to disfavor redox disproportionation, and equatorial supporting ligands were used to enforce *trans*-dicyaphide geometries.

The group 12 halides ZnCl_2 and CdCl_2 form *trans*-dichloride complexes with 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) crown ether macrocycles. The reaction of two equivalents of *in situ* generated $\mathbf{1}_{\text{diox}}$ with $\text{Zn}(18\text{-crown-6})\text{Cl}_2$ results in the formation of a single product by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, with the appearance of a resonance at 139.7 ppm. Similarly, for $\text{Cd}(18\text{-crown-6})\text{Cl}_2$ the reaction also results in the formation of one product, which appears as a singlet at 119.5 ppm with distinct ^{111}Cd and ^{113}Cd satellites ($^2J_{31\text{P}-111\text{Cd}} = 259\text{ Hz}$; $^2J_{31\text{P}-113\text{Cd}} = 272\text{ Hz}$) by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. These products were assigned as the zinc(II) and cadmium(II) dicyaphide complexes $\text{Zn}(18\text{-crown-6})(\text{CP})_2$ (**36**) and $\text{Cd}(18\text{-crown-6})(\text{CP})_2$ (**37**), respectively (Figure 8.4).

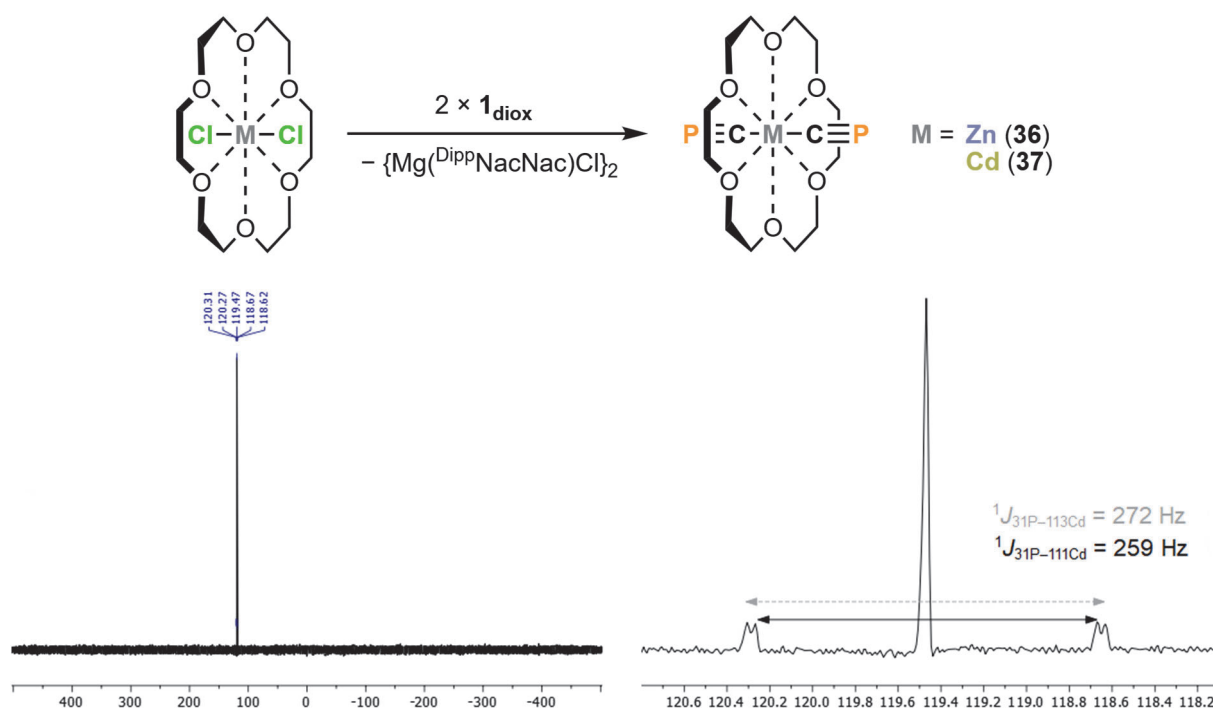


Figure 8.4. Synthesis of the zinc(II) and cadmium(II) dicyaphide complexes **36** and **37** (top). $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **37** (bottom).

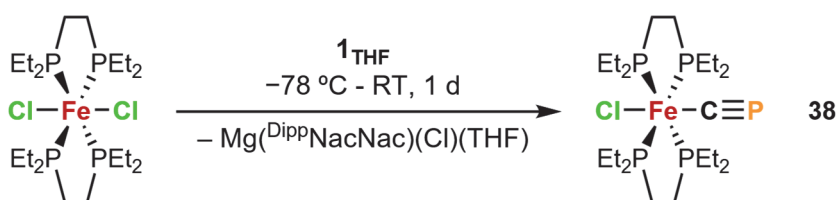
Further characterization of complexes **36** and **37** was precluded by their instability. Attempts at product isolation resulted in degradation in solution and in the solid state, as evidenced by the loss of $^{31}\text{P}\{^1\text{H}\}$ NMR signal as well as the production of insoluble precipitates and free 18-crown-6.

It was proposed in the previous chapter that in the absence of significant steric protection, metal cyaphide complexes can be stabilized by covalent M–C bonding (see Section 7.3). Zn–C and Cd–C bonds are borderline cases that can be considered as having partial ionic and covalent character. In the case of **36** and **37**, poor M–C covalency results in complexes that can be observed, but not isolated.

8.2.2 Synthesis of $\text{Fe}(\text{depe})_2(\text{Cl})(\text{CP})$ and $\text{Fe}(\text{depe})_2(\text{CP})_2$

The $\eta^1\text{:}\kappa\text{C}$ -cyaphido ligand is a strong σ donor and π acceptor (see Chapter 4), therefore M–CP covalency should be maximized for σ acidic and π basic metal centers. Octahedral iron(II) complexes of highly σ donating alkyl phosphines contain electron-rich metal centers, and are usually low-spin and inert to stereochemical isomerization. Therefore, an octahedral iron(II) *trans*-dichloride complex with equatorial alkyl phosphines was trialed as a precursor to a dicyaphide complex.

Dropwise addition of **1**_{THF} (generated from **3** in THF solution) to a THF solution containing one molar equivalent of $\text{Fe}(\text{depe})_2\text{Cl}_2$ at $-78\text{ }^\circ\text{C}$ results in the formation of the iron(II) cyaphide complex $\text{Fe}(\text{depe})_2(\text{Cl})(\text{CP})$ (**38**, Scheme 8.1).



Scheme 8.1. Synthesis of the iron(II) cyaphide complex **38**.

38 has a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum containing a pentet at 189.6 ppm ($^3J_{\text{P-P}} = 7\text{ Hz}$) corresponding to the cyaphide phosphorus atom, and a doublet at 66.1 ppm ($^3J_{\text{P-P}} = 7\text{ Hz}$) corresponding to the depe ligands. Its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum exhibits a weak, complex multiplet at 294.74 ppm corresponding to the cyaphide carbon atom. Raman spectroscopy shows a $\text{C}\equiv\text{P}$ vibrational stretching frequency of 1216 cm^{-1} , lower than in the octahedral ruthenium(II) complex $\text{Ru}(\text{dppe})_2(\text{Cl})(\text{CP})$ (1250 cm^{-1}),^[11] suggesting significant π backdonation.

Yellow-orange crystals suitable for single crystal X-ray diffraction were obtained in two polymorphs from toluene/hexane at $-35\text{ }^{\circ}\text{C}$, and reveal a structure containing an octahedral geometry at iron, with equatorial depe ligands and axially coordinated chlorido and cyaphido ligands (Figure 8.5). Unfortunately, crystallographic disorder of the chlorido and cyaphido ligands in both polymorphs precludes the reliable discussion of bond metrics.

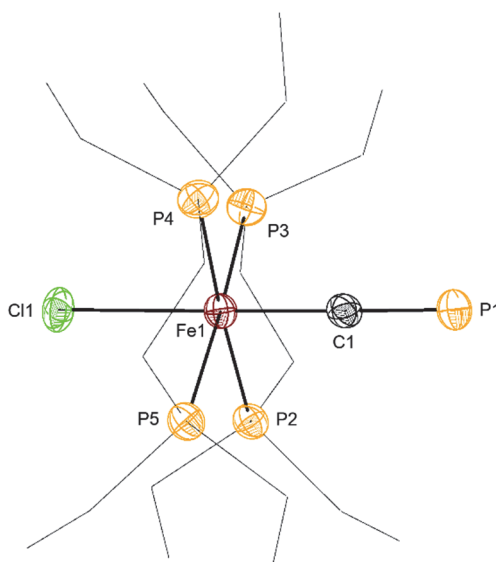
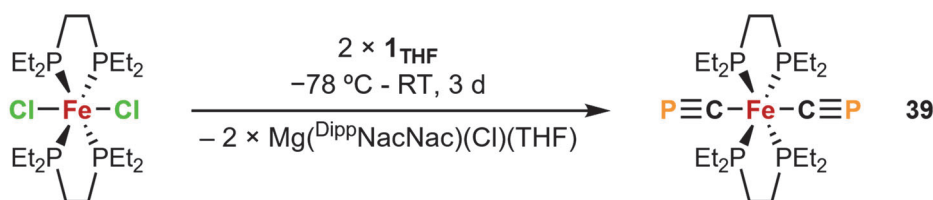


Figure 8.5. Solid-state structure of **38**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms and disorder components are omitted for clarity. Ethyl and ethylene groups are depicted as wireframes.

When two equivalents of **1**_{THF} are reacted with $\text{Fe}(\text{depe})_2\text{Cl}_2$, both chlorides are exchanged, resulting in the dicyaphide complex $\text{Fe}(\text{depe})_2(\text{CP})_2$ (**39**, Scheme 8.2). **39** has a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum containing a pentet at 180.1 ppm ($^3J_{\text{P-P}} = 9\text{ Hz}$) corresponding to the cyaphide phosphorus atoms, and a triplet at 66.0 ppm ($^3J_{\text{P-P}} = 9\text{ Hz}$) corresponding to the supporting depe ligands. Its Raman spectrum contains a very strong peak at 1256 cm^{-1} for the symmetric $\text{C}\equiv\text{P}$ stretching mode, higher than for **38** due to competitive π backdonation to the two *trans* cyaphido ligands.



Scheme 8.2. Synthesis of the iron(II) dicyaphide complex **39**.

Crystallization from toluene solution at $-35\text{ }^{\circ}\text{C}$ results in the formation of pale-yellow crystals, allowing the molecular structure of **39** to be determined by single crystal X-ray crystallography (Figure 8.6).

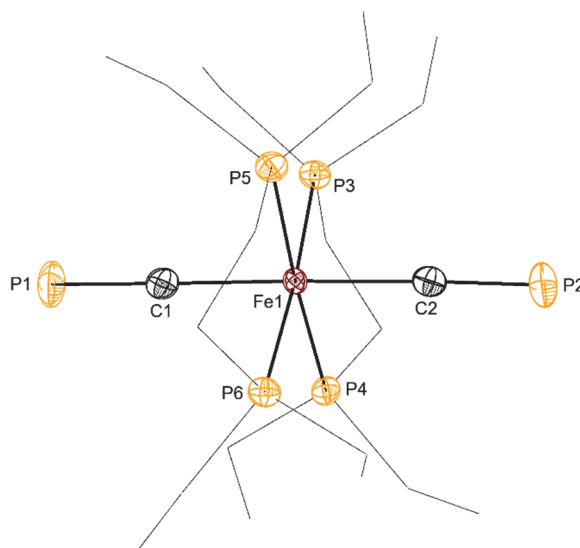


Figure 8.6. Solid-state structure of **39**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Ethyl and ethylene groups are depicted as wireframes.

The iron center adopts an octahedral geometry with equatorially coordinated depe ligands and Fe1–P bond lengths of 2.2403(7), 2.2310(6), 2.2412(7), and 2.2460(6) Å. The cyaphido ligands are axially coordinated with an essentially linear C1–Fe1–C2 bond angle of 178.60(9)° and Fe1–C bond lengths of 1.887(2) and 1.897(2) Å. The C1–P1 and C2–P2 bond lengths are 1.582(2) and 1.583(2) Å, respectively, slightly longer than those in related octahedral ruthenium(II) cyaphide complexes (e.g. 1.573(2) Å in Ru(dppe)₂(H)(CP)).^[12]

38 and **39** are remarkably stable compounds and are capable of being handled in air using wet solvents. The dicyaphide complex **39** has a half life of approx. 14 days in air when dissolved in wet benzene. The mono-cyaphide complex **38** is also air- and moisture-tolerant, albeit with a lower half life of approx. 3 days. In stark contrast, the dichloride precursor degrades over the course of several hours upon exposure to ambient atmosphere. Curiously, while both **38** and **39** are stable, their syntheses are only moderate-yielding and result in the production of a substantial quantity of pyrophoric dark brown byproducts; their identity and the reason for their formation is still unclear.

The stability of complexes **38** and **39** is likely due to a combination of factors. Firstly, strong Fe–C covalent bonds make the cyaphido ligands kinetically inert to displacement by water or dioxygen; this accounts for the high stability of the dicyaphide complex **39**. Secondly, partial M–C π bonding character due to metal-cyaphide π backdonation results in higher energy C $\equiv$ P π^* orbitals, attenuating their electrophilicity (*vide infra*).

Cyclic voltammetry was used to investigate the electrochemical behavior of **38** and **39** (Figure 8.7). Whereas the voltammogram of $\text{Fe}(\text{depe})_2\text{Cl}_2$ features a reversible oxidation at -0.62 V vs. $\text{Fc}^{0/+}$, the voltammograms of **38** and **39** reveal quasi-(ir)reversible oxidations (**38**: -0.56 V vs. $\text{Fc}^{0/+}$; **39**: -0.64 V vs. $\text{Fc}^{0/+}$), suggesting the cyaphido ligands are redox non-innocent. This is further supported by the appearance of reversible $n = 0.5$ e^- oxidations for **38** and **39** at higher potentials (**38**: 0.30 V vs. $\text{Fc}^{0/+}$; **39**: 0.19 V vs. $\text{Fc}^{0/+}$), attributed to the dimerization of **38** and **39** upon one electron oxidation.

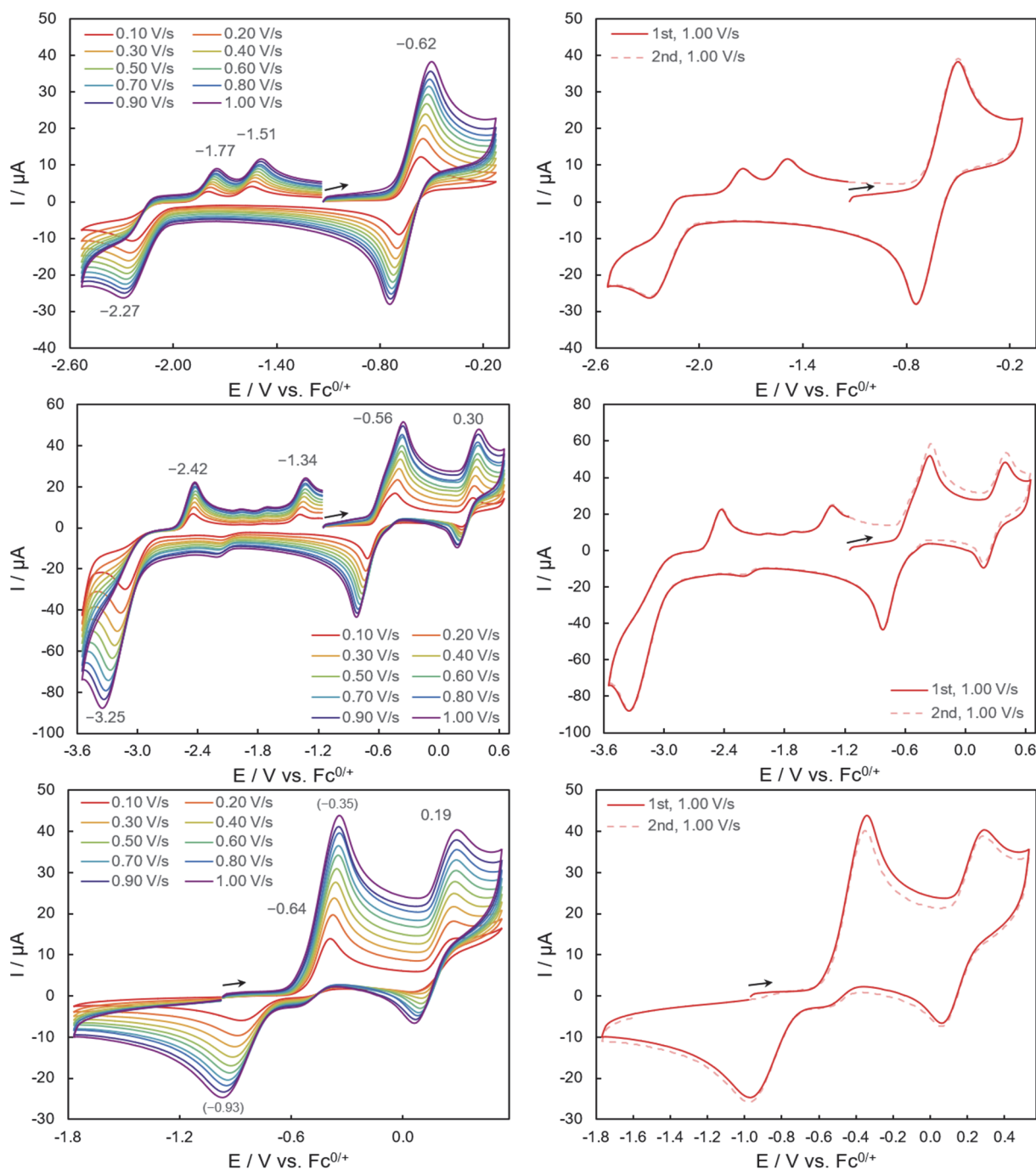


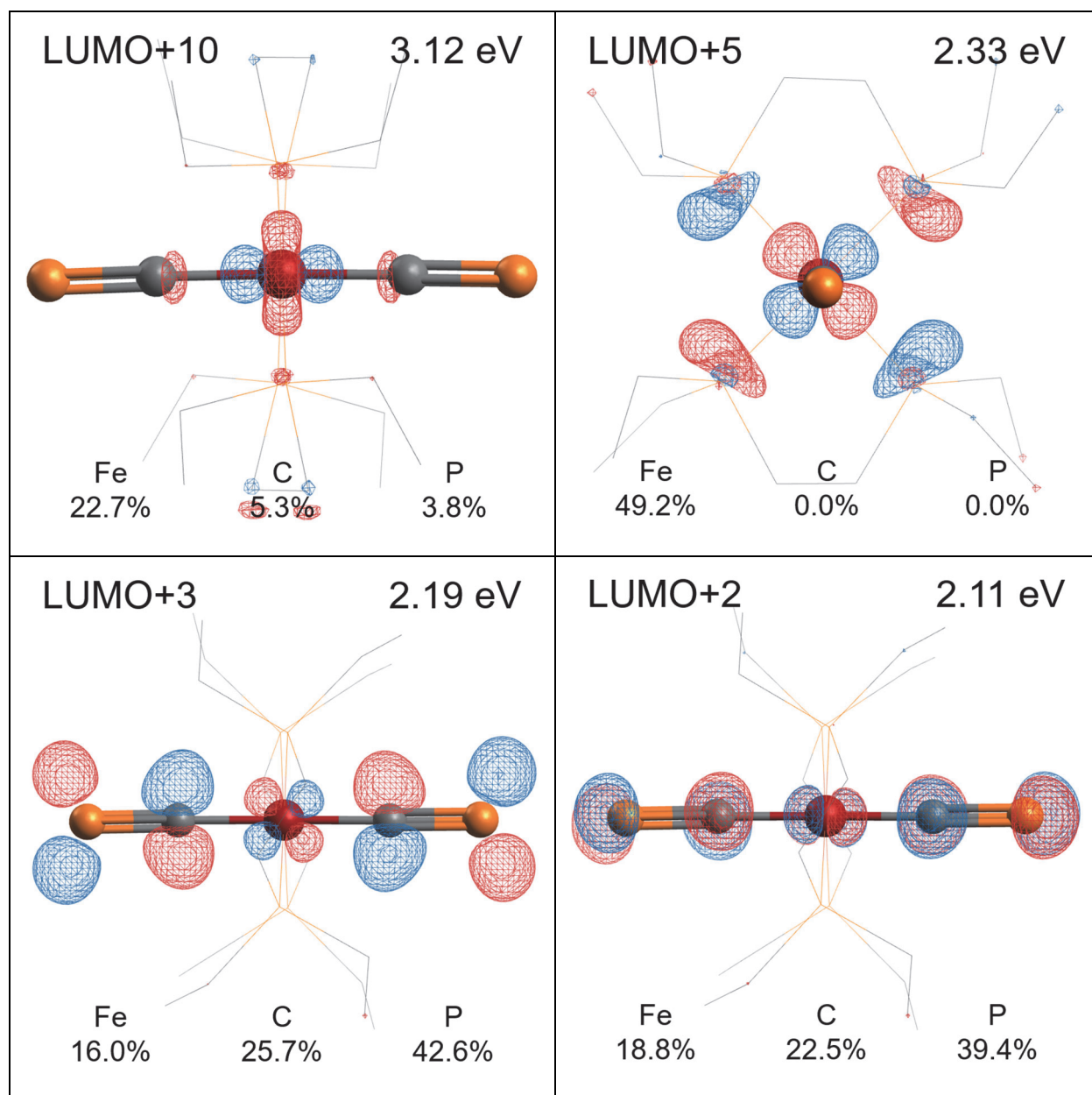
Figure 8.7. Cyclic voltammograms (1.0 mM in THF, 0.2 M $[\text{NBu}_4][\text{PF}_6]$) of $\text{Fe}(\text{depe})_2\text{Cl}_2$ (top), **38** (middle) and **39** (bottom) at varying scan rates (0.10 to 1.00 V/s) (left), and twice at 1.00 V/s (right). All potentials were referenced to $\text{Fc}^{0/+}$.

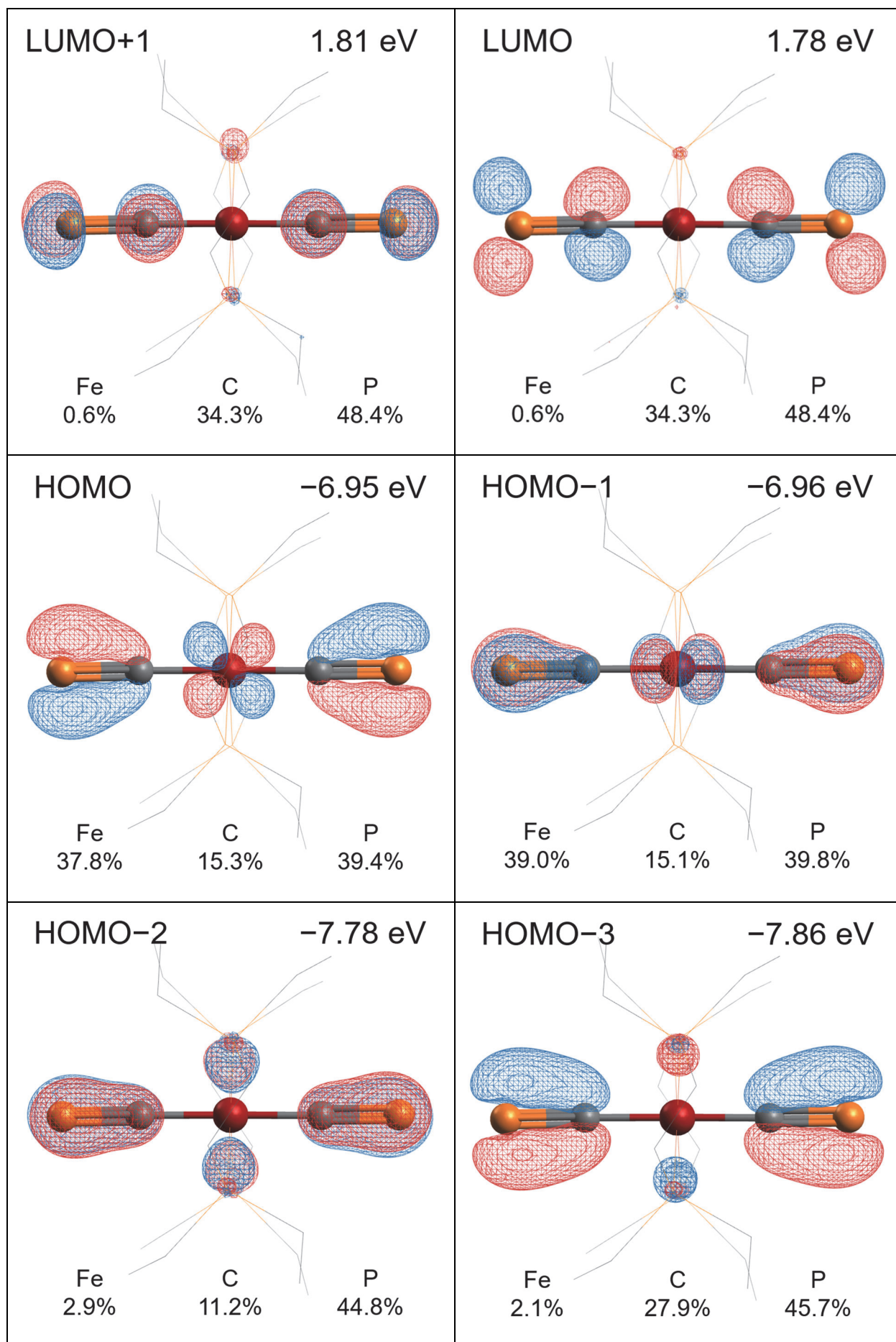
The chloride-containing complexes $\text{Fe}(\text{depe})_2\text{Cl}_2$ and **38** both show irreversible one electron reductions ($\text{Fe}(\text{depe})_2\text{Cl}_2$: -2.27 V vs. $\text{Fc}^{0/+}$; **38**: -3.25 V vs. $\text{Fc}^{0/+}$), with two half electron oxidations on the return waves. The reductions likely afford iron(I) species, which possibly go on to dimerize to bimetallic complexes capable of two distinct oxidations. No reductive events were observed for the dicyaphide complex **39** before solvent degradation.

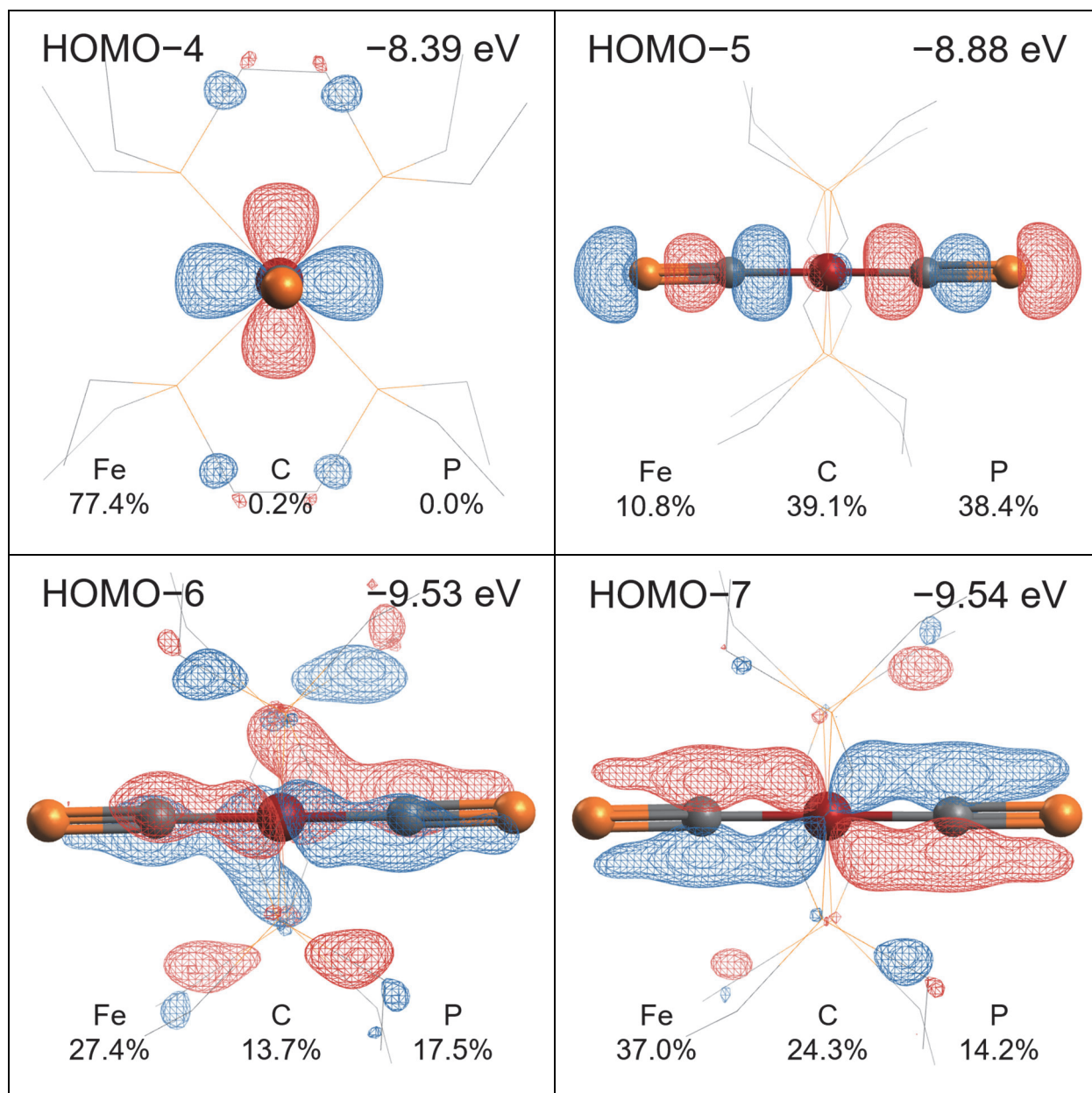
8.2.3 Electronic structure of $\text{Fe}(\text{depe})_2(\text{CP})_2$

The Kohn-Sham molecular orbitals of **39** were calculated using DFT (Table 8.1).

Table 8.1. Selected molecular orbital isosurface plots and per-MO Loewdin reduced orbital populations for **39**.







In **39**, the iron $3d_{xy}$, $3d_{x^2-y^2}$, and $3d_{z^2}$ orbitals are well-localized as the HOMO-4, LUMO+5, and LUMO+10, respectively, and their relative energies suggest that the axial cyaphido ligands are stronger-field than the equatorial phosphines. By contrast, the iron $3d_{xz/yz}$ orbitals are not well-localized and contribute to several MOs with Fe-CP π bonding/antibonding character. The essentially degenerate HOMO and HOMO-1 show significant contributions from both the iron $3d_{xz/yz}$ orbitals as well as the cyaphide $C\equiv P$ π orbitals, consistent with the redox non-innocence of the cyaphido ligands and their involvement in the one electron oxidation events observed by cyclic voltammetry. Ten of the frontier orbitals (the LUMO+3 to HOMO-3, as well as the HOMO-6 and HOMO-7) form two orthogonal delocalized π systems across the P-C-Fe-C-P chain (Figure 8.8).

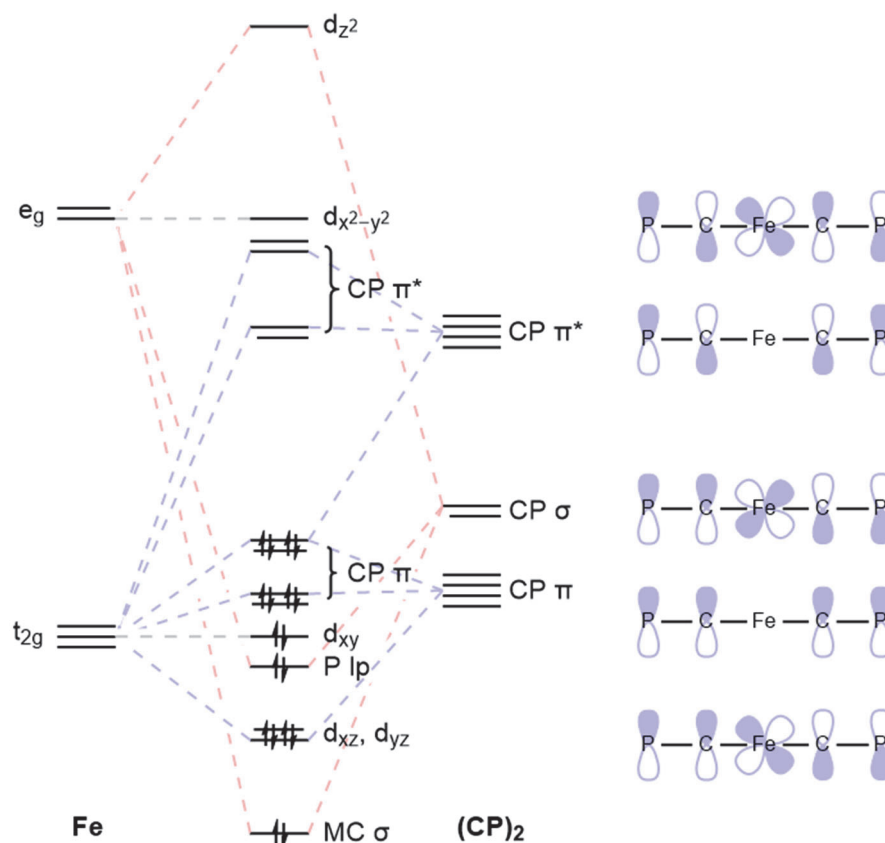


Figure 8.8. Qualitative MO diagram for **39**. MOs of π symmetry are shown in blue.

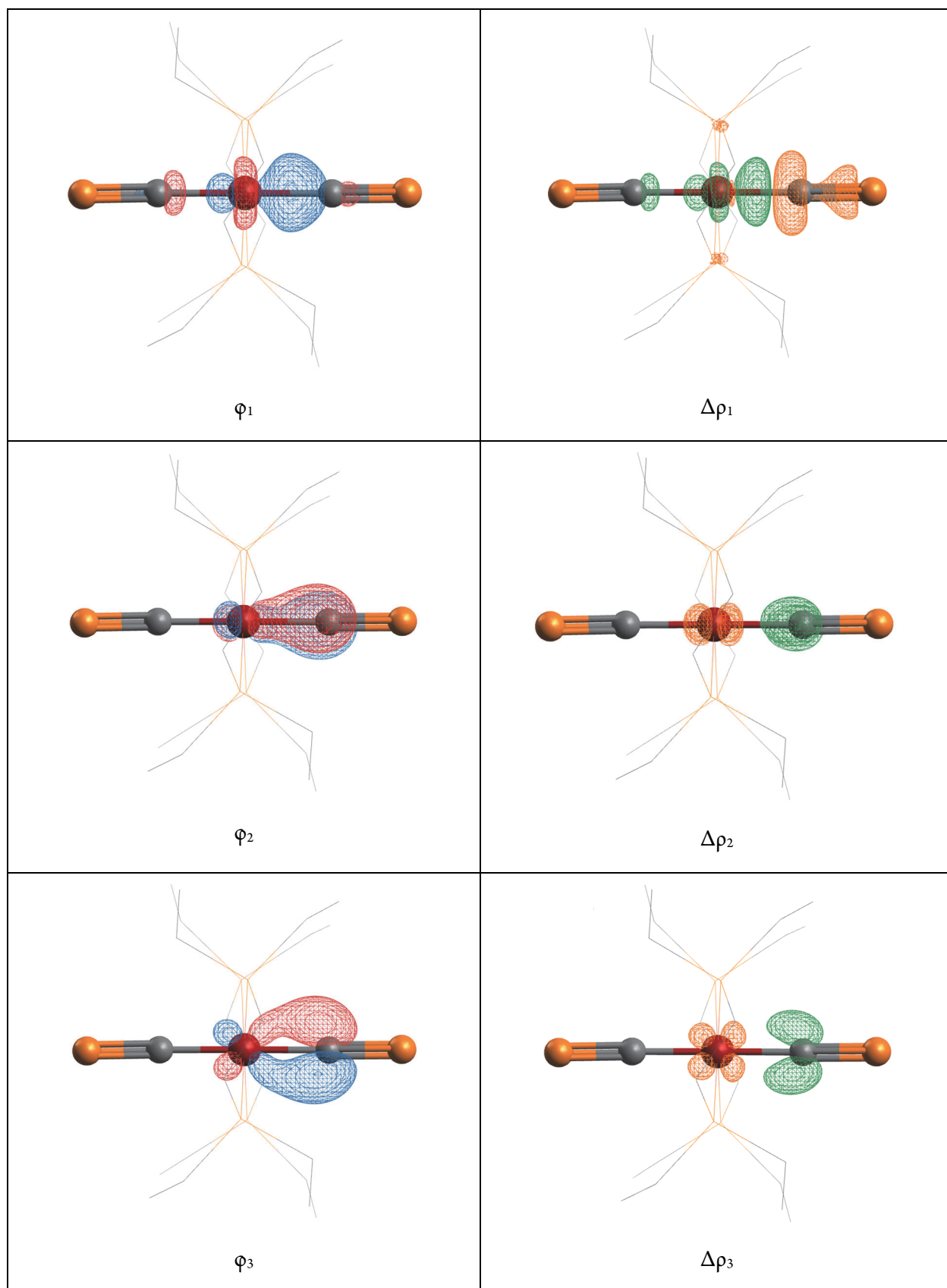
One of the Fe–CP bonding interactions in **39** was investigated using a fragment-based approach by EDA-NOCV analysis (Tables 8.2 and 8.3). Similar to the rhodium(I) cyaphide complex **9** (see Section 4.3.4), σ donation is the largest contribution to the Fe–CP bond ($\Delta E_{\text{orb}}^{\sigma} = -59.4 \text{ kcal mol}^{-1}$), though π backdonation is sizable ($\Delta E_{\text{orb}}^{\pi} = -24.6 \text{ kcal mol}^{-1}$). π backdonation also has the effect of reducing the polarization of the cyaphido ligand, which is reflected in the partial charges determined by Natural Population Analysis. For the magnesium(II) complex **1_{diox}**, the partial charges at the cyaphide carbon and phosphorus atoms are -1.22 and $+0.33$, respectively (see Section 2.2.6). For **39**, this difference is substantially reduced, and the partial charges are -0.75 and $+0.15$, respectively.

Table 8.2. Summary of EDA-NOCV analysis of one of the Fe–C bonds in **39**, including ETS-NOCV energies from orbital contributions due to σ donation ($\Delta E_{\text{orb}}^{\sigma}$) and π back-donation ($\Delta E_{\text{orb}}^{\pi}$), in kcal mol^{-1} .

	ΔE_{tot}	ΔE_{steric}	ΔE_{disp}	ΔE_{oi}	$\Delta E_{\text{orb}}^{\sigma}$	$\Delta E_{\text{orb}}^{\pi}$
39	-111.6	40.7	-39.3	-113.0	-59.4	-24.6

$$\Delta E_{\text{tot}} = \Delta E_{\text{steric}} + \Delta E_{\text{disp}} + \Delta E_{\text{oi}} = \Delta E_{\text{steric}} + \Delta E_{\text{disp}} + \Sigma \Delta E_{\text{orb}}^{\pi}$$

Table 8.3. Contours of NOCVs φ_1 , φ_2 , and φ_3 , ($v > 0$), as well as their contributions to the deformation density, $\Delta\rho_1$, $\Delta\rho_2$, and $\Delta\rho_3$, (green: $\Delta\rho > 0$, orange: $\Delta\rho < 0$), for one of the Fe–CP interactions in **39**. φ_1 corresponds to σ donation, whereas φ_2 and φ_3 correspond to π back-donation.

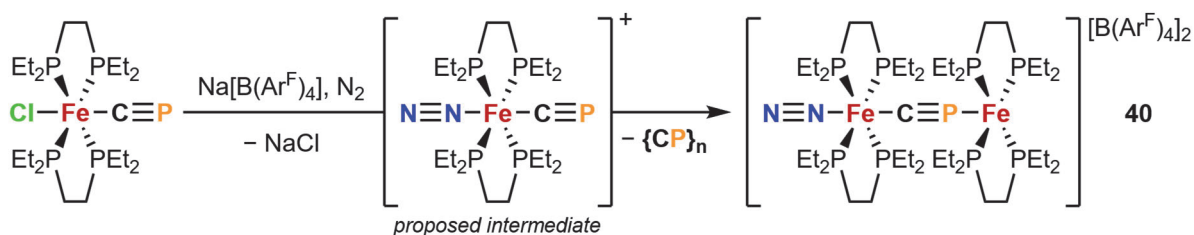


8.3 End-on cyaphide-bridged multimetallic complexes

8.3.1 Synthesis of $[\{\text{Fe}(\text{depe})_2\}_2(\text{N}_2)(\mu\text{-CP})][\text{B}(\text{Ar}^{\text{F}})_4]_2$

In Chapter 5, the gold(I) cyaphide complex **6** was used as a precursor in the attempted synthesis of linear bimetallic complexes containing end-on bridging cyaphido ligands (see Section 5.2.1). This invariably resulted in uncontrolled reactivity and decomposition, suggesting that κP coordination to a second metal destabilizes the cyaphide ion by further increasing its electrophilicity.

The remarkable stability of **38** and **39** suggests they may be suitable precursors to end-on cyaphide-bridged multimetallic complexes. Halide abstraction from **38** should afford an electrophilic iron(II) cation with a vacant site available for κP coordination by another cyaphide moiety. The addition of $\text{Na}[\text{B}(\text{Ar}^{\text{F}})_4]$ to **38** in 1,2-DFB results in a color change from yellow to deep red-brown. Slow diffusion of pentane into the reaction solution results in the formation of orange crystals, as well as an intractable mixture of unidentified oily byproducts. For the orange crystals, single crystal X-ray diffraction reveals a dicationic, bimetallic, mixed valent iron complex $[\{\text{Fe}(\text{depe})_2\}_2(\text{N}_2)(\mu\text{-CP})][\text{BAr}^{\text{F}}_4]_2$ (**40**), featuring a $\eta^1:\eta^1$ bridging cyaphido ligand (Scheme 8.3).



Scheme 8.3. Synthesis of the cyaphide-bridged bimetallic iron(II)/iron(I) complex **40**.

The solid-state structure of **40** shows two distinct iron centers with different geometries (Figure 8.9). One iron center has an octahedral geometry with two equatorially coordinated depe ligands exhibiting Fe1–P bond lengths of 2.2956(8), 2.2810(8), 2.2776(8), and 2.2665(7) Å, and one axially coordinated dinitrogen ligand with a Fe1–N1 bond length of 1.855(3) Å and N1–N2 bond length of 1.104(4) Å. The cyaphido ligand is coordinated *trans* to the dinitrogen ligand in an end-on κC fashion, with a N1–Fe1–C1 angle of 177.30(11)° and Fe1–C1–P1 angle of 178.18(16)°. The Fe1–C1 bond length is 1.924(3) Å, and C1–P1 bond length is 1.574(3) Å. The other iron center has a square pyramidal geometry, with a κP coordinated cyaphido ligand exhibiting a C1–P1–Fe2 bond angle of 174.33(10)° and P1–Fe2 bond length of 2.2199(7) Å. It is also coordinated by two depe ligands in the basal positions, with Fe2–P bond lengths between 2.2481(7) and 2.2534(8) Å.

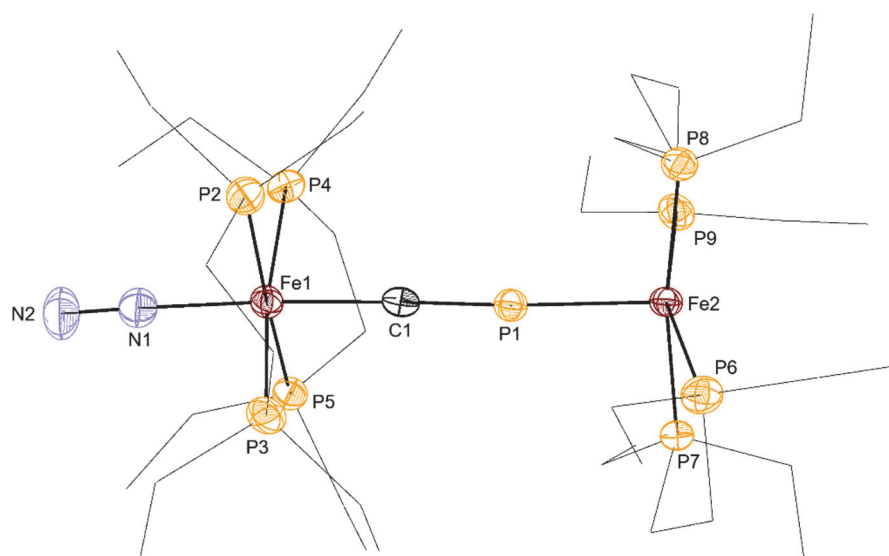
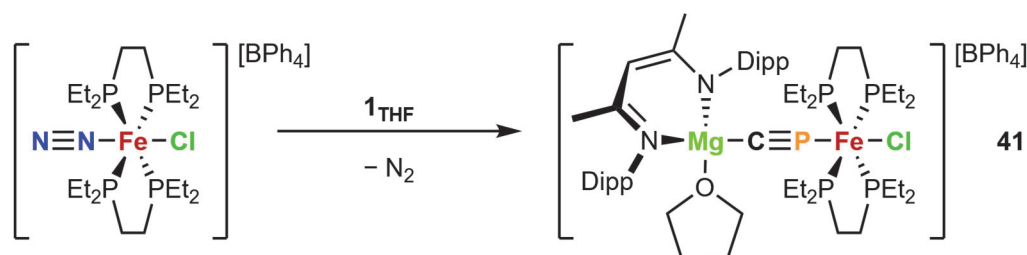


Figure 8.9. Solid-state structure of **40**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms and $[\text{B}(\text{Ar}^{\text{F}})_4]^-$ counterions are omitted for clarity. Ethyl and ethylene groups are depicted as wireframes.

Structural comparison of **40** with other known low-spin $\text{Fe}(\text{depe})_2$ complexes allows the octahedral iron center to be tentatively assigned as iron(II), and the square pyramidal center as iron(I).^[13–16] The concurrent one electron reduction of an iron center with the loss of one cyaphide fragment is reminiscent of the cyaphide-mediated reduction of $\text{Mn}(\text{TPP})\text{Cl}$ discussed in Section 7.2.1. It is possible that **40** forms *via* an unstable cationic iron(II) cyaphide intermediate. Redox disproportionation of this species would result in a cationic iron(I) center that can coordinate another iron(II) cyaphide fragment to form the stable bimetallic complex. Unfortunately, the concurrent formation of unidentified impurities (which may include disproportionation byproducts) prevented the bulk isolation of **40** in sufficient purity for meaningful further analysis.

8.3.2 Synthesis of $[\{\text{Mg}^{\text{Dipp}}\text{NacNac})(\text{THF})\}(\mu\text{-CP})\{\text{Fe}(\text{depe})_2\text{Cl}\}][\text{BPh}_4]$

Given that a cationic iron(II) cyaphide complex is a likely intermediate in the formation of **40**, the reaction of a cationic iron(II) chloride complex, $[\text{Fe}(\text{depe})_2(\text{Cl})(\text{N}_2)][\text{BPh}_4]$, with a cyaphide transfer reagent was attempted (Scheme 8.4).



Scheme 8.4. Synthesis of the bimetallic magnesium(II)/iron(II) bridging cyaphide complex **41**.

The dropwise addition of **1**_{THF} (generated *in situ* from **3** in d₈-THF) to a solution containing one equivalent of [Fe(depe)₂(Cl)(N₂)] [BPh₄] at −35 °C results in a color change to deep green. ³¹P{¹H} NMR spectroscopy of the reaction mixture at this stage shows a single product, with a pentet at 168.1 ppm (²J_{P-P} = 49 Hz) corresponding to the cyaphide phosphorus atom, and a doublet at 59.8 ppm (²J_{P-P} = 49 Hz) corresponding to the supporting depe ligands (Figure 8.10). ¹H NMR spectroscopy also shows the clean formation of one product containing one ^{Dipp}NacNac ligand and asymmetric depe ligands. Based on these data, this product is proposed to be a cyaphide-bridged bimetallic magnesium(II)/iron(II) complex [**1** Mg(^{Dipp}NacNac)(THF)}(μ-CP){Fe(depe)₂Cl}] [BPh₄] (**41**).

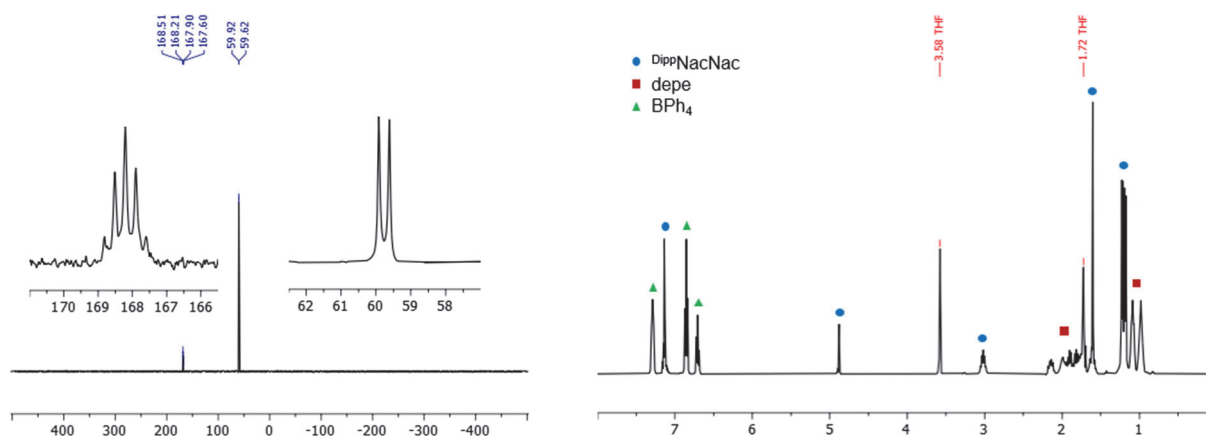


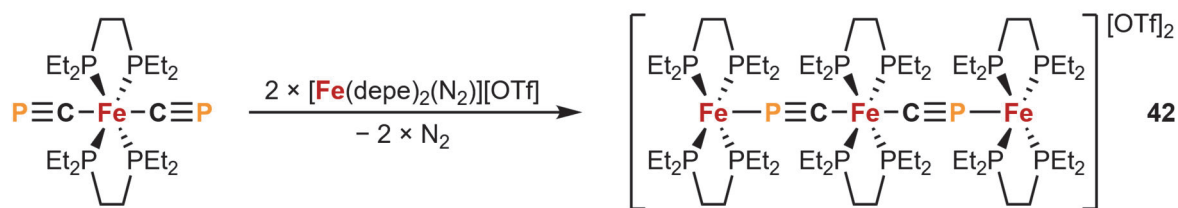
Figure 8.10. ³¹P{¹H} NMR spectrum of **41** (left). ¹H NMR spectrum of **41** (right)

While **41** can be generated and observed in solution, it degrades to an intractable mixture of products over the course of several hours, during which the color changes to red, and finally brown.

8.3.3 Synthesis of [{Fe(depe)₂}₃(μ-CP)₂][OTf]₂

The observation of a stable, linear Fe^{II}–CP–Fe^I moiety in **40** suggests that cyaphide-bridged multimetallic Fe^{II}/Fe^I complexes may be accessible *via* more rational syntheses.

The addition of the dicyaphide complex **39** to two equivalents of the cationic iron(I) dinitrogen complex [Fe(depe)₂(N₂)] [OTf] results in vigorous gas evolution and the formation of a yellow/purple dichroic solution. Slow diffusion of pentane into the reaction mixture results in the crystallization of the cyaphide-bridged trimetallic iron(I)/iron(II)/iron(I) complex [{Fe(depe)₂}₃(CP)₂][OTf]₂ (**42**) as dark purple crystals (Scheme 8.5). Notably, no reaction occurs between **39** and the comparable iron(II) complex [Fe(depe)₂(Cl)(N₂)] [BPh₄] (under a dinitrogen atmosphere), suggesting that binding is favored in the more electron-rich +1 oxidation state.



Scheme 8.5. Synthesis of the cyaphide-bridged trimetallic iron(I)/iron(II)/iron(I) complex **42**.

The solid-state structure of **42** was determined using single crystal X-ray crystallography (Figure 8.11). **42** contains one octahedral iron center and two square pyramidal iron centers bridged by two cyaphido ligands in a linear arrangement. The central iron atom is in an octahedral coordination environment, with two symmetry-related equatorial depe ligands with Fe1–P bond distances of 2.2489(5) and 2.2417(5) Å, and two symmetry-related axially coordinated κ C cyaphido ligands, with a C1–Fe1–C1' angle of 180.0° and Fe1–C1 bond lengths of 1.925(2) Å. The cyaphide C1–P1 bond lengths are 1.582(2) Å, unchanged from their lengths in **39**. The cyaphido ligands are each coordinated to an additional symmetry-related square pyramidal iron center in the apical position, with a C1–P1–Fe2 bond angle of 176.23(8)° and P1–Fe2 bond length of 2.2567(6) Å. Two depe ligands are also coordinated basally with Fe2–P bond lengths between 2.2319(6) and 2.2531(7) Å.

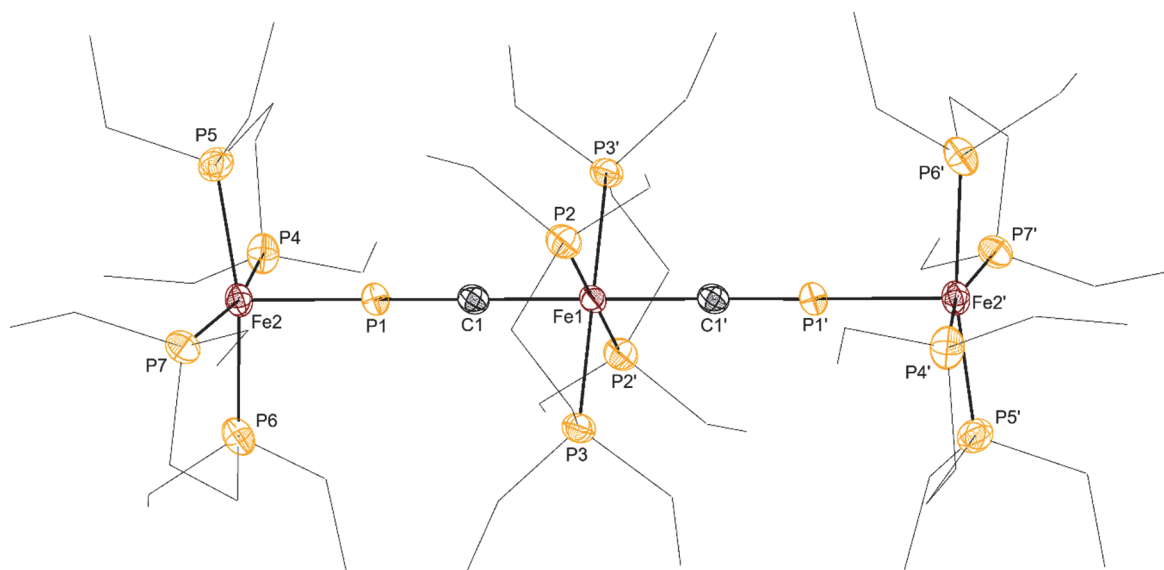


Figure 8.11. Solid-state structure of **42**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms and [OTf][−] counterions are omitted for clarity. Ethyl and ethylene groups are depicted as wireframes.

The symmetric C≡P vibrational stretching mode in **42** was observed at 1229 cm^{−1} by Raman spectroscopy, and is at a lower frequency than in **39** due to $\eta^1:\eta^1$ bridging coordination. The effective magnetic moment of **42** at room temperature was measured to be 2.6 μ_B using the Evans NMR method^[17] and is close to the ideal value for two uncorrelated $s = \frac{1}{2}$ spin centers (2.45 μ_B).

Cyclic voltammetry of **42** reveals several redox features (Figure 8.12). Anodically, there is a quasi-reversible $n = 2 e^-$ oxidation at -0.82 V vs. $\text{Fc}^{0/+}$ assigned as the oxidation of the two terminal iron(I) centers to iron(II), a quasi-irreversible $1 e^-$ oxidation at -0.46 V vs. $\text{Fc}^{0/+}$ assigned as the oxidation of the central iron(II) center to iron(III) (which leads to destabilization), and a further irreversible $2 e^-$ oxidation at 0.39 V vs. $\text{Fc}^{0/+}$. Cathodically, two overlapping quasi-reversible $1 e^-$ reductions appear as a $n = 2 e^-$ feature at -1.94 V vs. $\text{Fc}^{0/+}$, assigned as the reduction of the terminal iron(I) centers to iron(0).

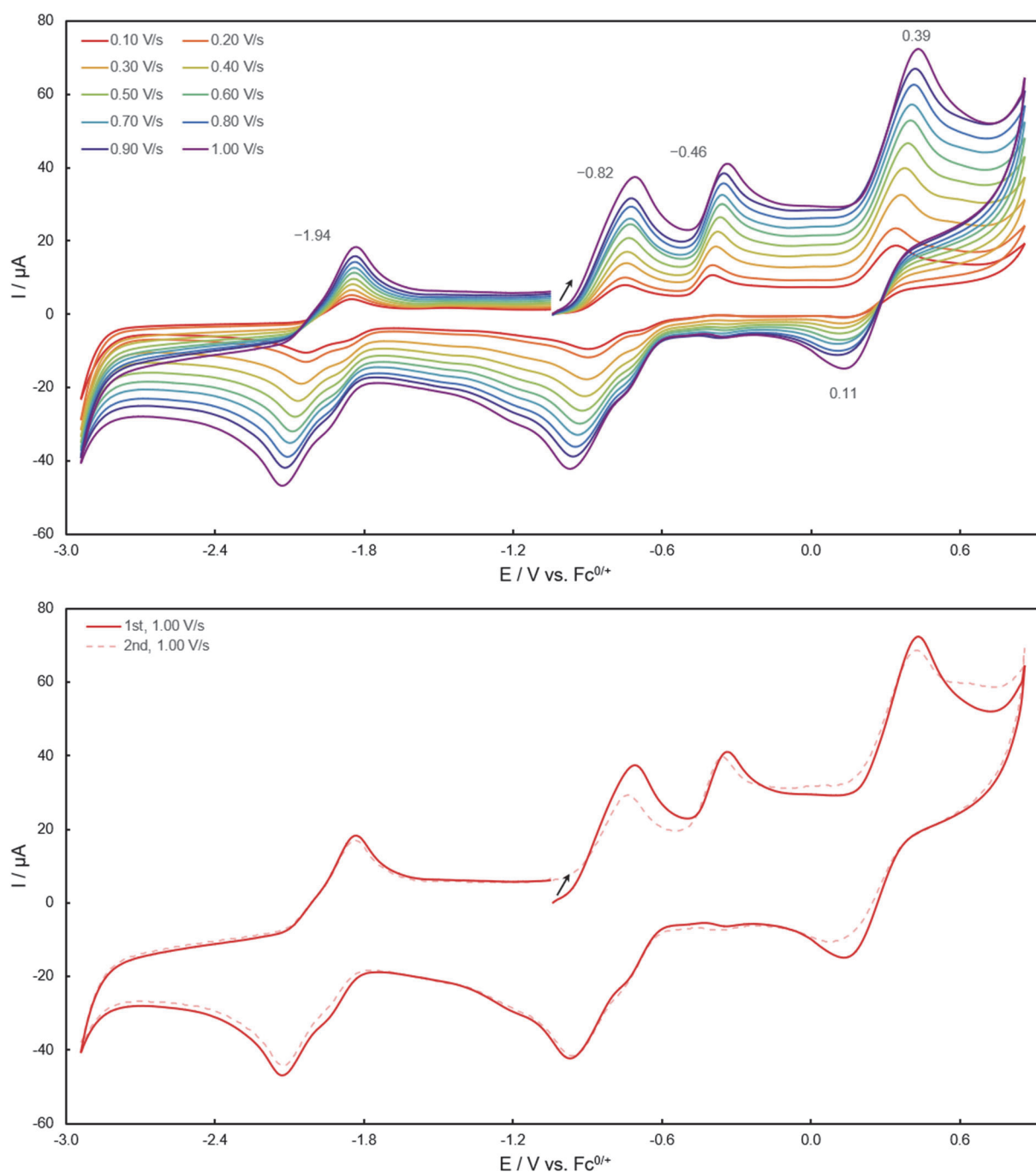
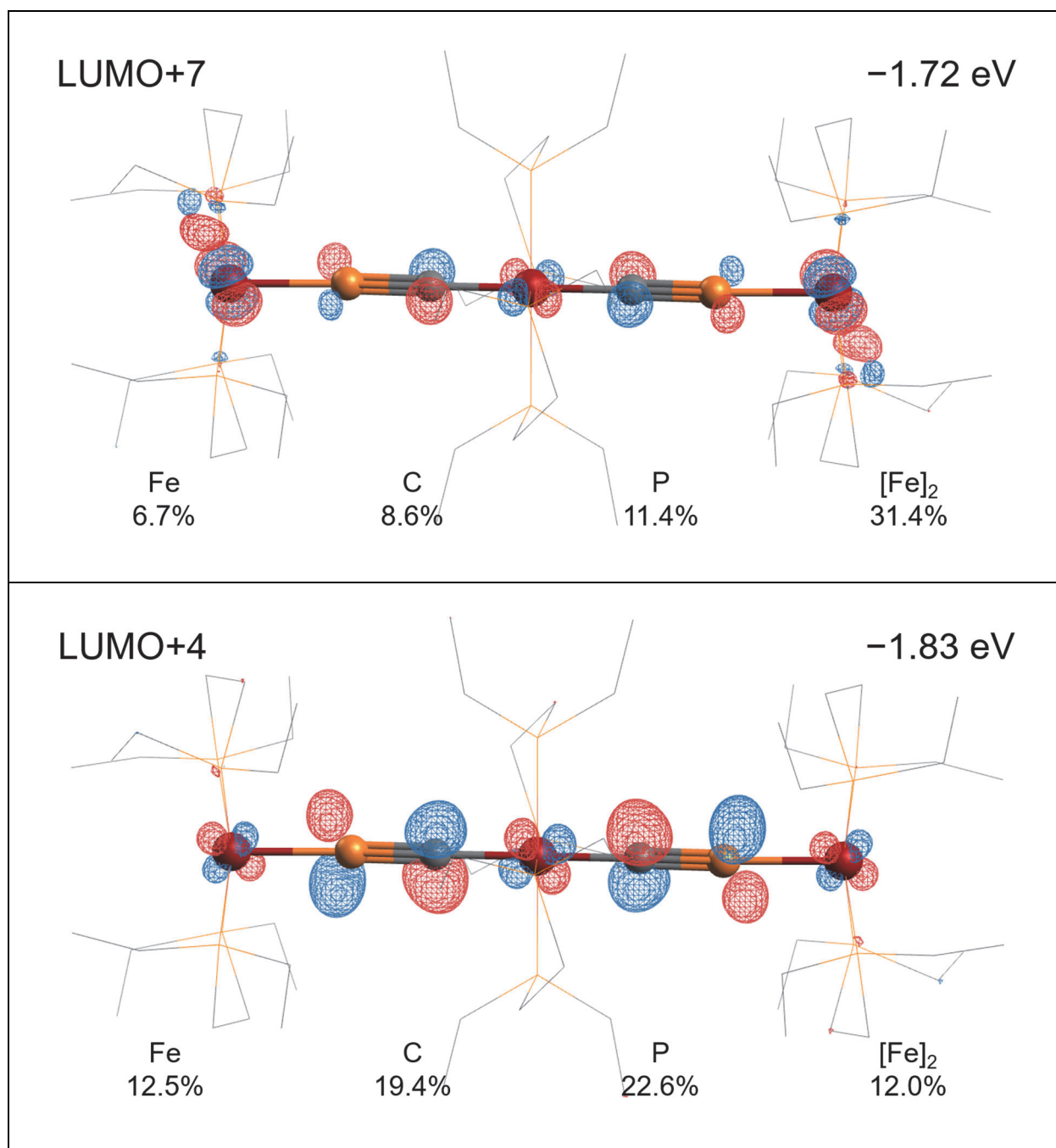


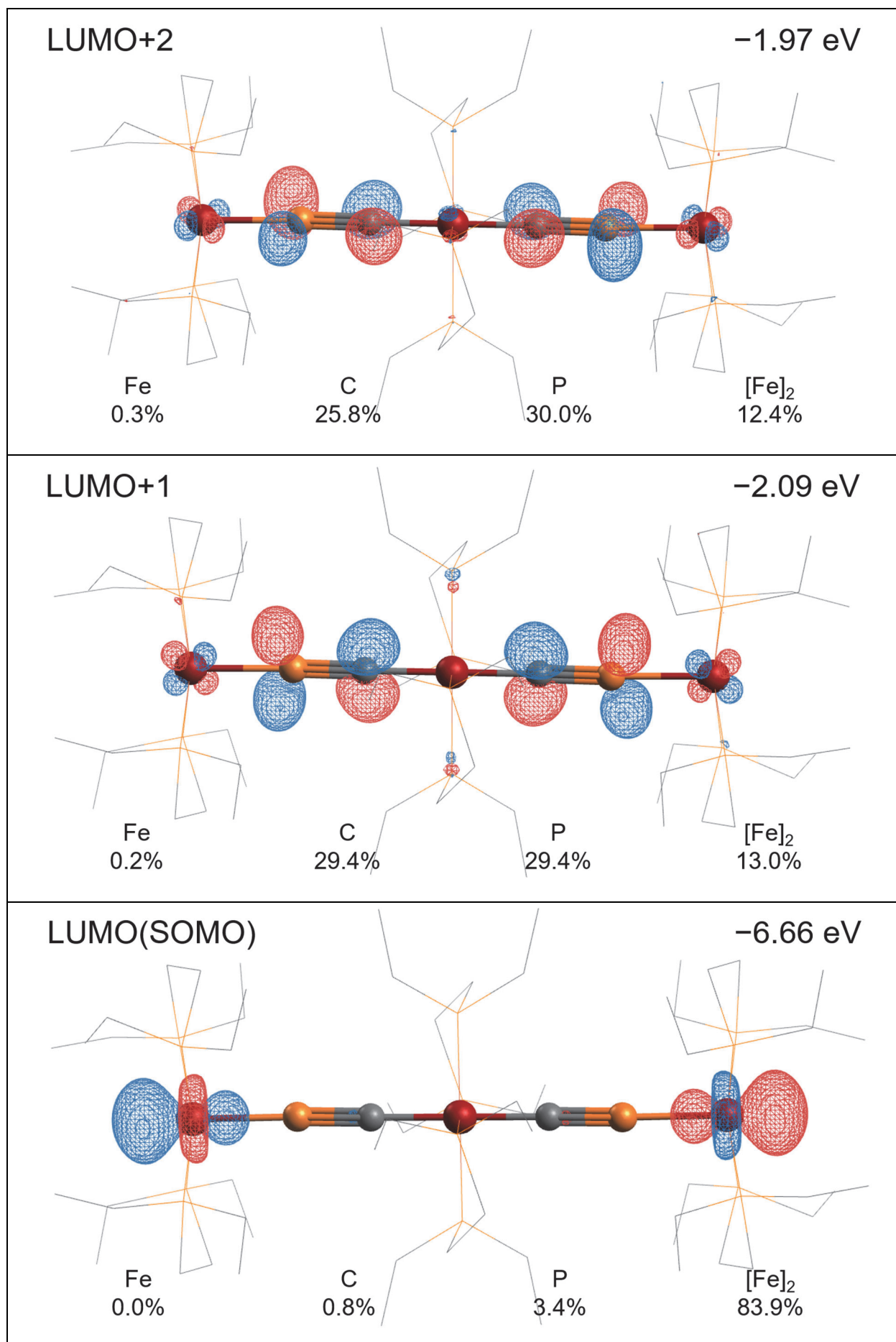
Figure 8.12. Cyclic voltammograms (1.0 mM in 1,2-DFB, 0.2 M $[\text{NBu}_4][\text{PF}_6]$) of **42** scanned anodically at varying scan rates (0.10 to 1.00 V/s) (top), and twice at 1.00 V/s (bottom). All potentials were referenced to $\text{Fc}^{0/+}$.

8.3.4 Electronic structure of $[\{\text{Fe}(\text{depe})_2\}_3(\mu\text{-CP})_2]^{2+}$

The electronic structure of the $[\{\text{Fe}(\text{depe})_2\}_3(\mu\text{-CP})_2]^{2+}$ cation in **42** was calculated using unrestricted DFT for the $S = 1$ triplet state. Two-electron molecular orbitals were constructed using the quasi-restricted orbital (QRO) approach (Table 8.4).

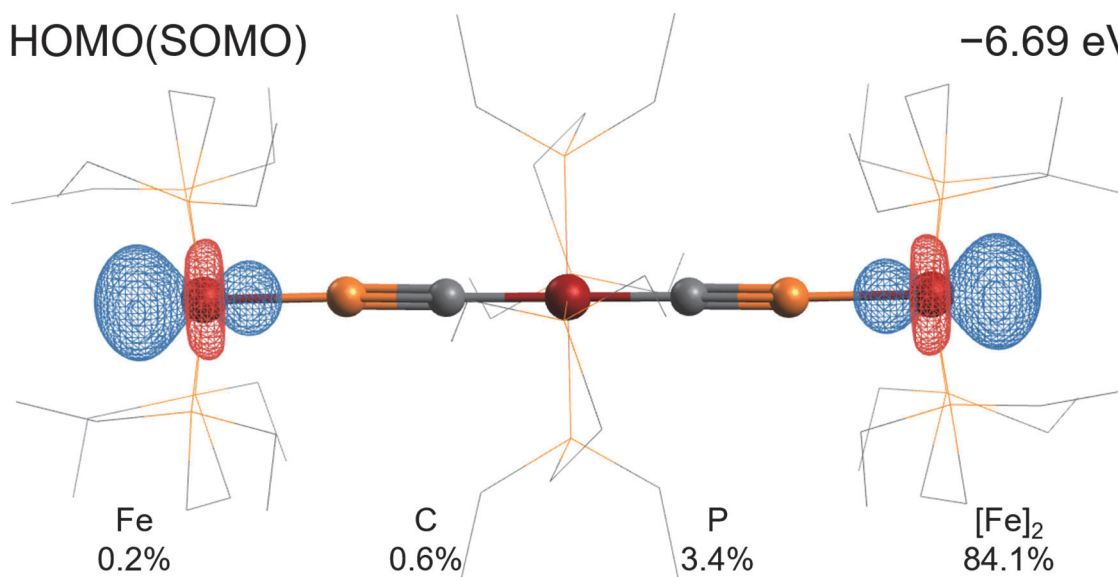
Table 8.4. Selected quasi-restricted orbital isosurface plots and per-QRO Loewdin reduced orbital populations for the cation in **42**, calculated for the $S = 1$ spin state.





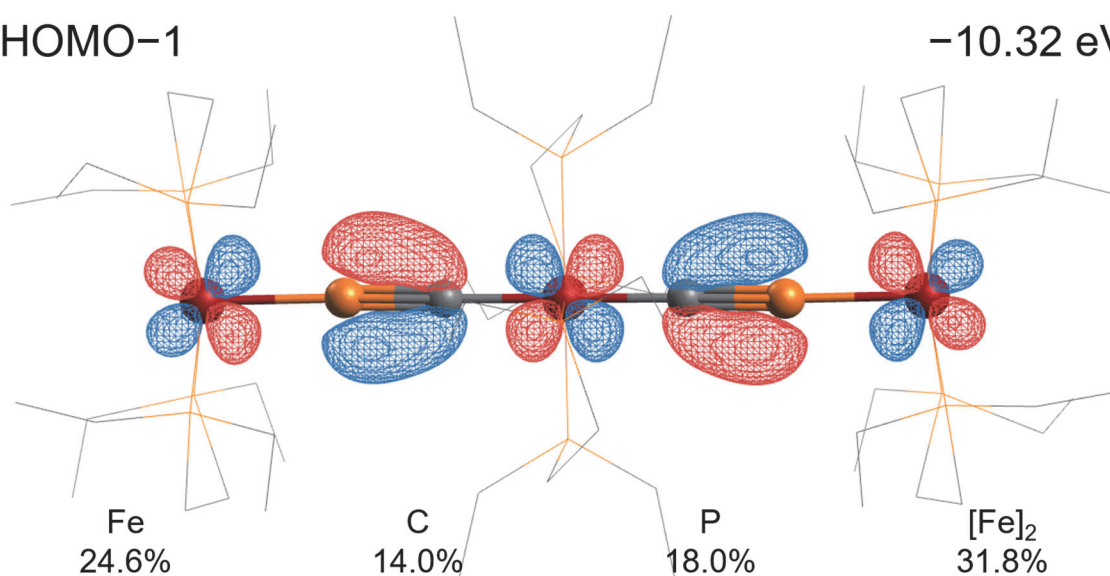
HOMO(SOMO)

-6.69 eV



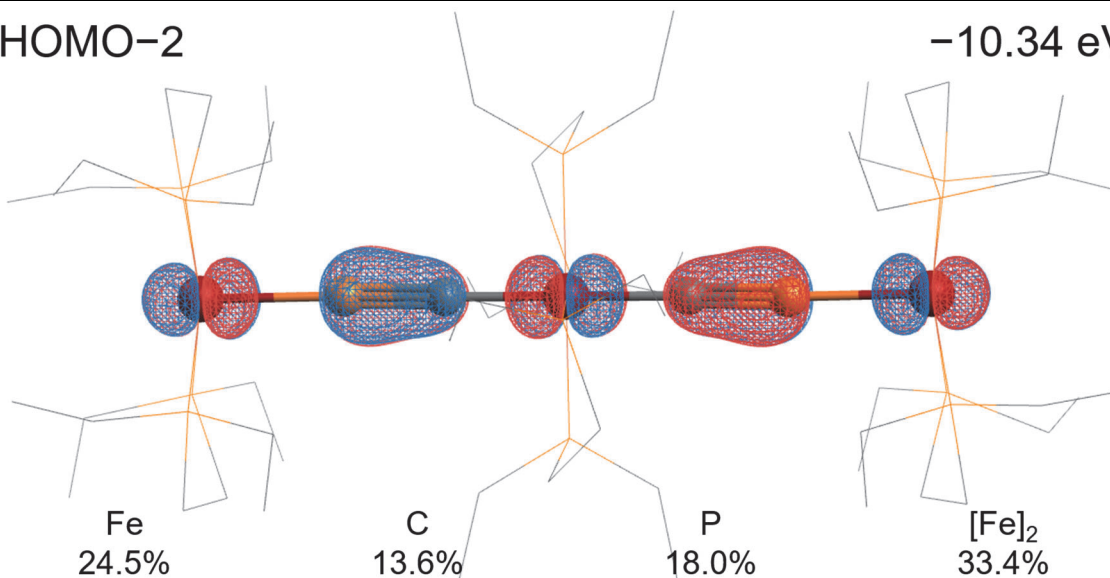
HOMO-1

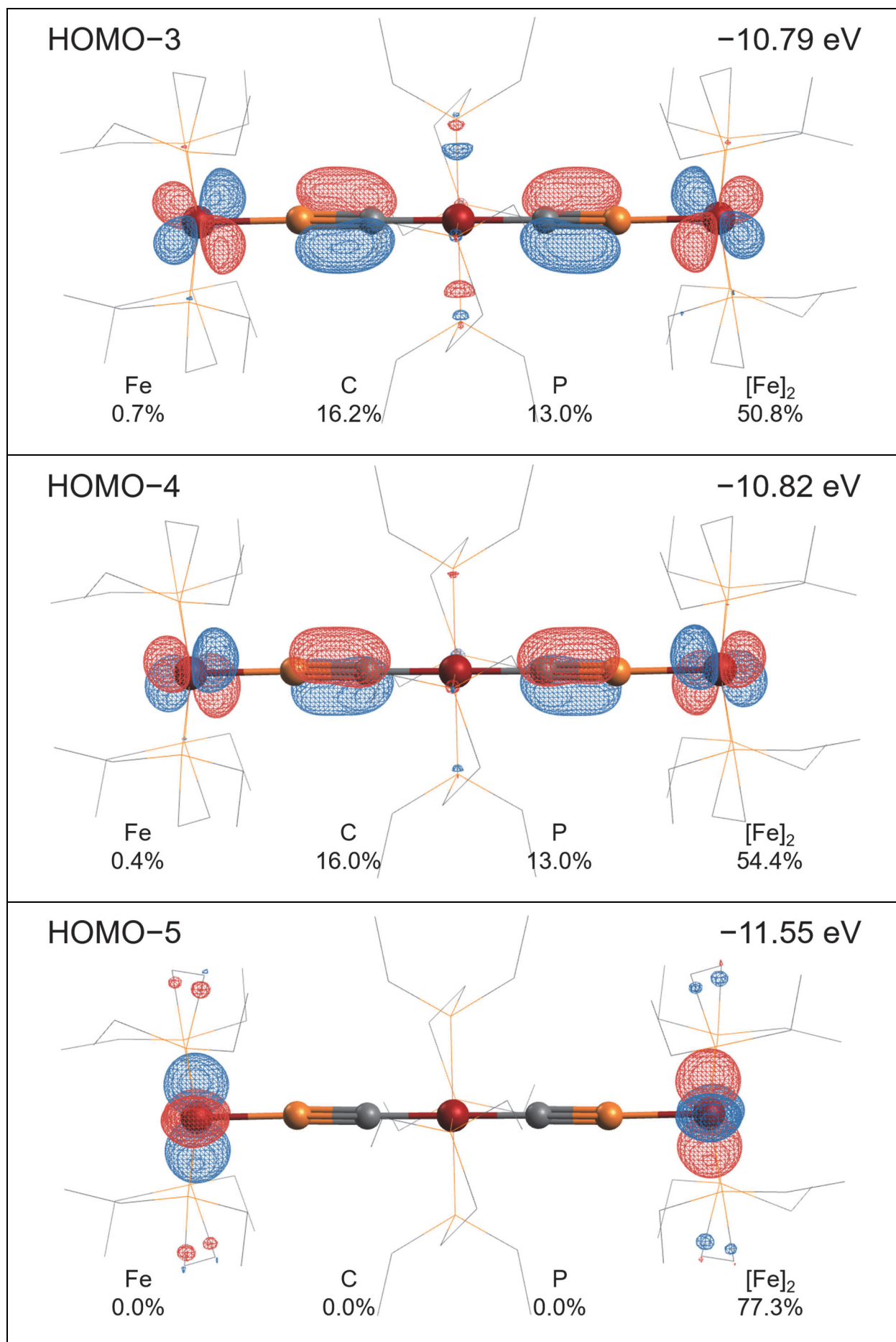
-10.32 eV



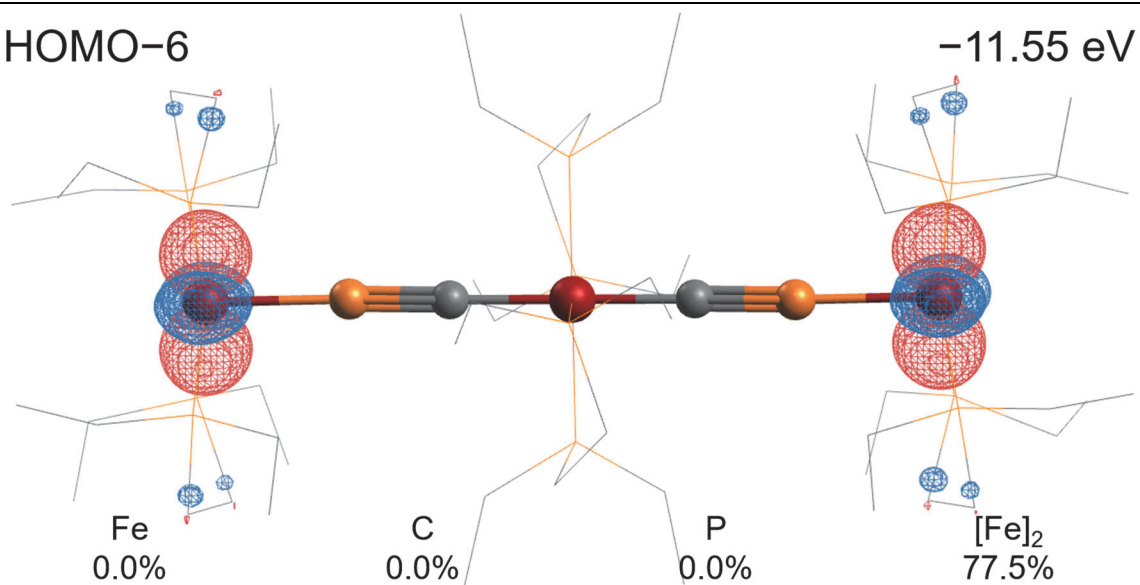
HOMO-2

-10.34 eV

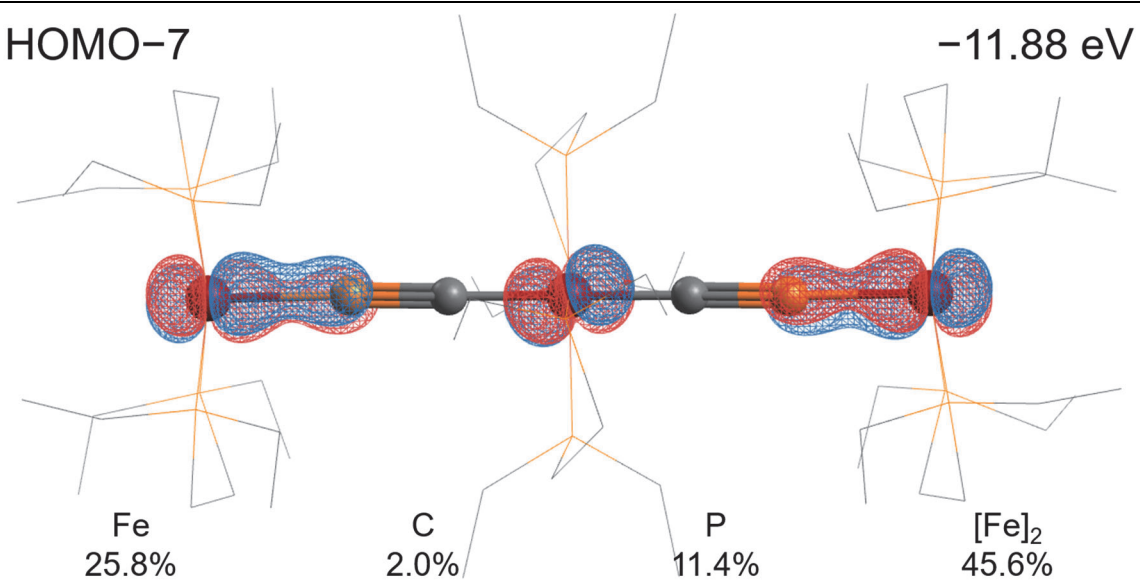




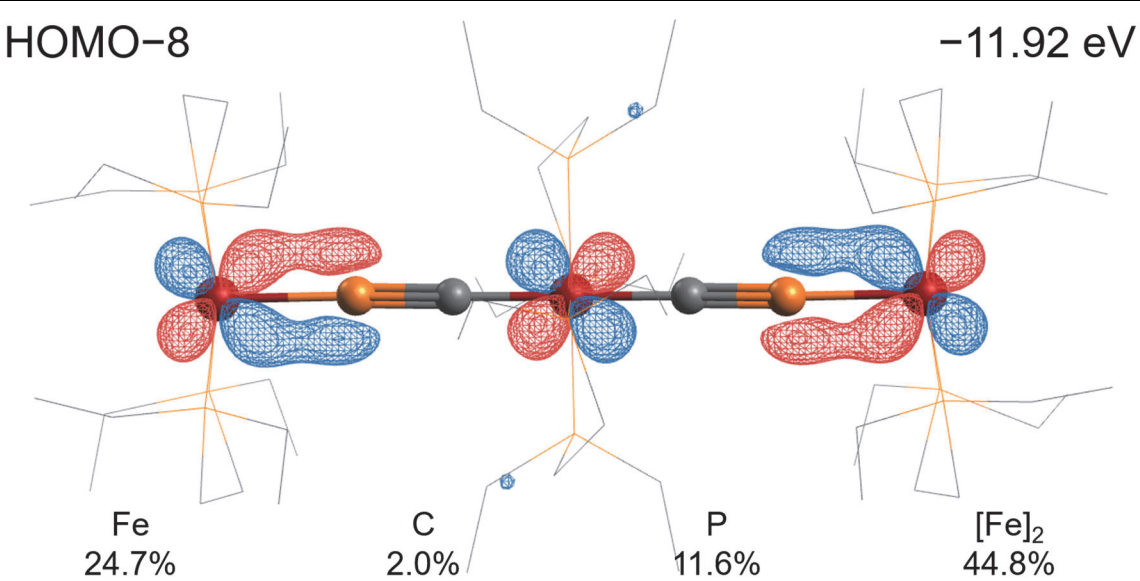
HOMO-6

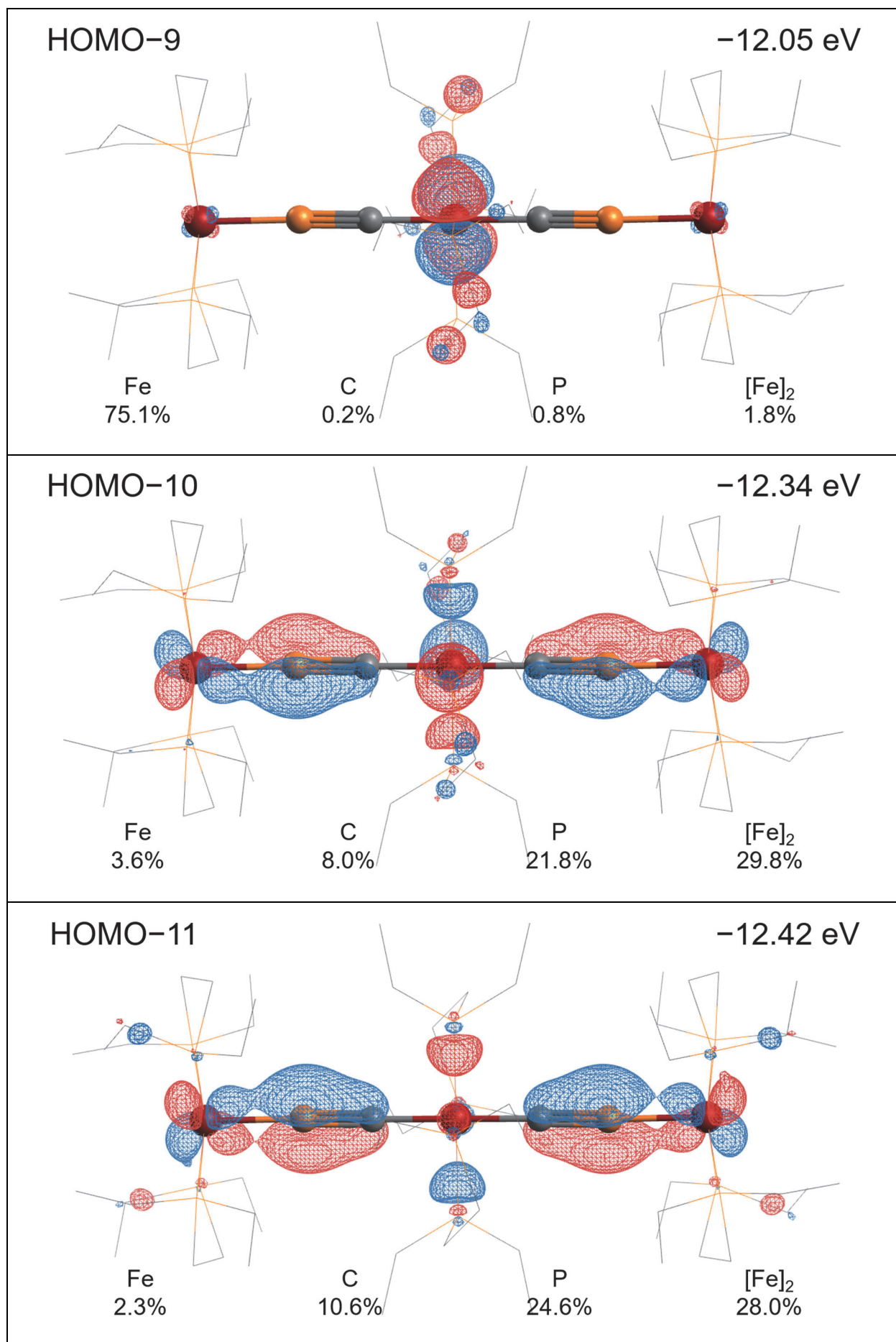


HOMO-7



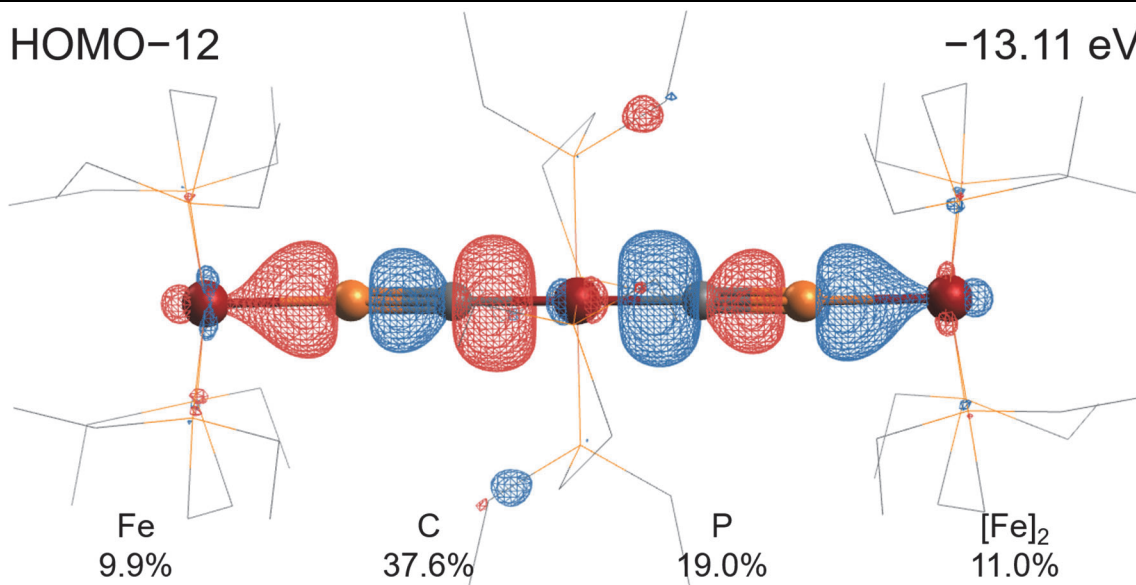
HOMO-8





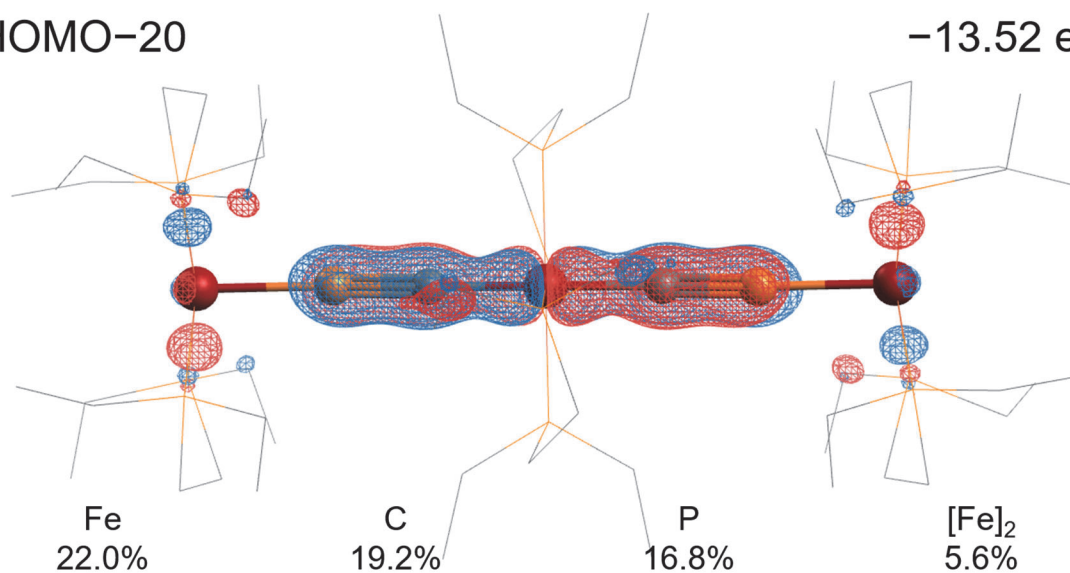
HOMO-12

-13.11 eV



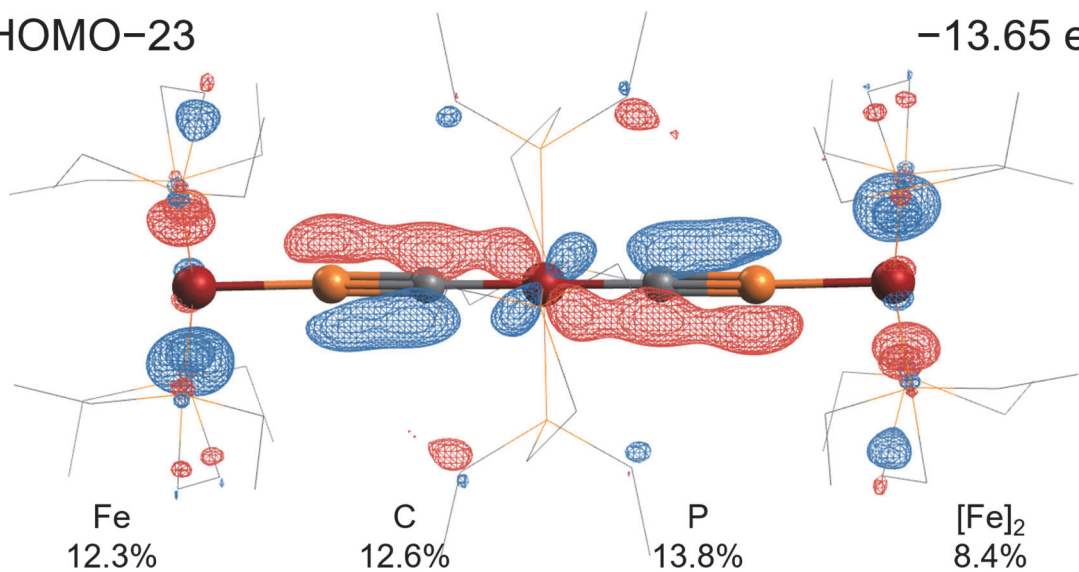
HOMO-20

-13.52 eV



HOMO-23

-13.65 eV



The two singly-occupied orbitals in **42** correspond to the essentially degenerate terminal iron $3d_{z^2}$ orbitals. The occupied $3d_{xy}$ orbitals correspond to the HOMO–5 and HOMO–6 for the two terminal iron atoms, and to the HOMO–9 for the central iron atom. Similar to the monometallic dicyaphide complex **39**, the $3d_{xz}$ and $3d_{yz}$ orbitals for all three iron centers are heavily involved in π bonding and antibonding interactions with the $C\equiv P$ π and π^* orbitals. In **42**, this results in two orthogonal delocalized π systems spanning the Fe–P–C–Fe–C–P–Fe seven atom chain (Figure 8.13).

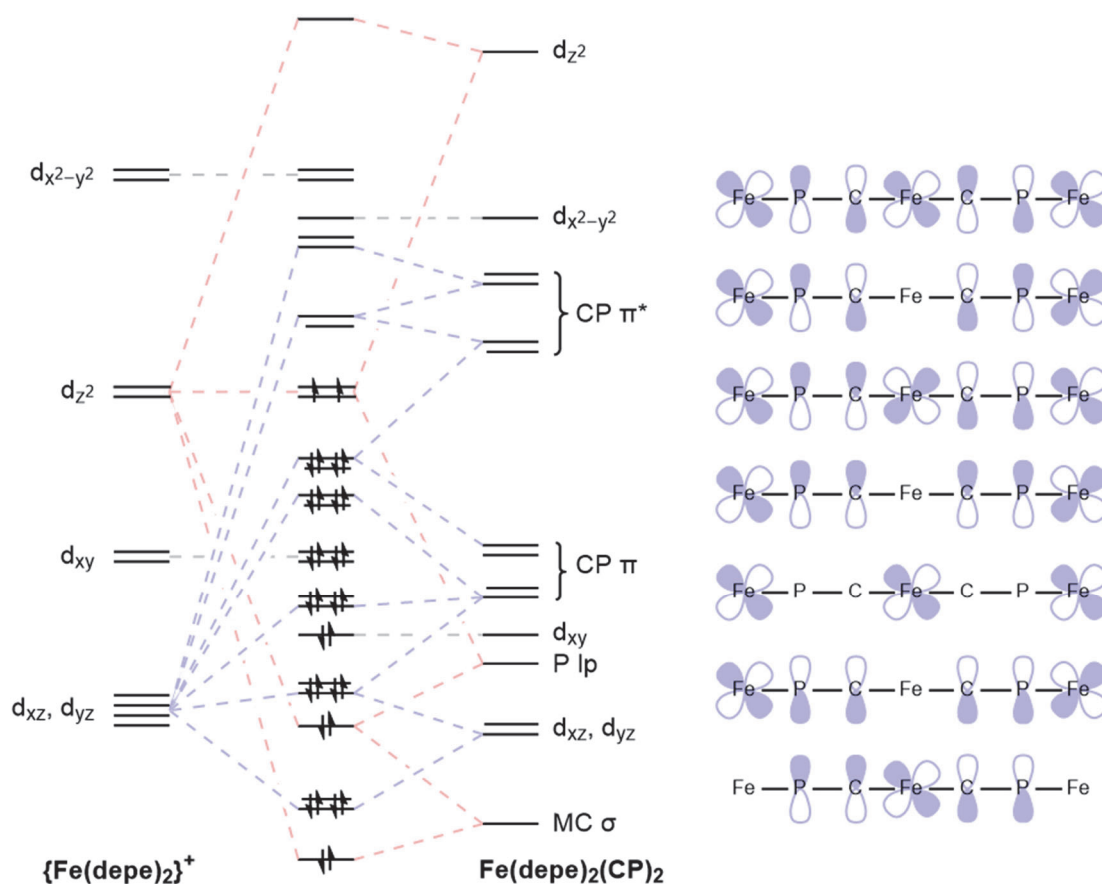


Figure 8.13. Qualitative MO diagram for the cation in **42**. MOs of π symmetry are shown in blue.

The end-on $\eta^1:\eta^1$ bridging coordination mode for the cyaphido ligands in **40** and **42** is unprecedented, and contrasts the preference for $\eta^1:\eta^2$ coordination previously found for the hetero-multimetallic cyaphide complexes **20–22** (see Chapter 5). This difference may be attributed to steric effects, where the octahedral coordination geometry at the iron(II) centers disfavors engagement of the CP π manifold when compared to the linear coordination geometry at the gold(I) centers. However a platinum(II) cyaphide complex with a similar steric profile, $Pt(PEt_3)_2(Cl)(CP)$, also prefers side-on $\eta^1:\eta^2$ bridging coordination (see Section 1.4.2), suggesting steric factors cannot be the only explanation and that end-on bridging is also favorable on electronic grounds.^[18,19] For **39**, this can be rationalized as the result of both decreased η^2 π accepting ability and increased $\eta^1:\kappa P$ σ donating ability (*vide supra*).

8.3.5 Synthesis of $([\{\text{Fe}(\text{depe})_2\}_3(\mu\text{-CP})_{3-x}(\text{Cl})_x][\text{B}(\text{Ar}^{\text{F}})_4]_2)_n$

40 and **42** demonstrate the ability for the cyaphide ion to act as an end-on bridging ligand between metal centers. While **40** and **42** are discrete molecular complexes, extended polymeric materials should in principle also be possible. Serendipitously, the attempted isolation of **40** under a purified argon atmosphere resulted in the crystallization of a small number of orange/green dichroic crystals that degrade slowly under a dinitrogen atmosphere, tentatively identified as the 1D polymer $([\{\text{Fe}(\text{depe})_2\}_3(\mu\text{-CP})_{3-x}(\text{Cl})_x][\text{B}(\text{Ar}^{\text{F}})_4]_2)_n$ (**43**; Figure 8.14).

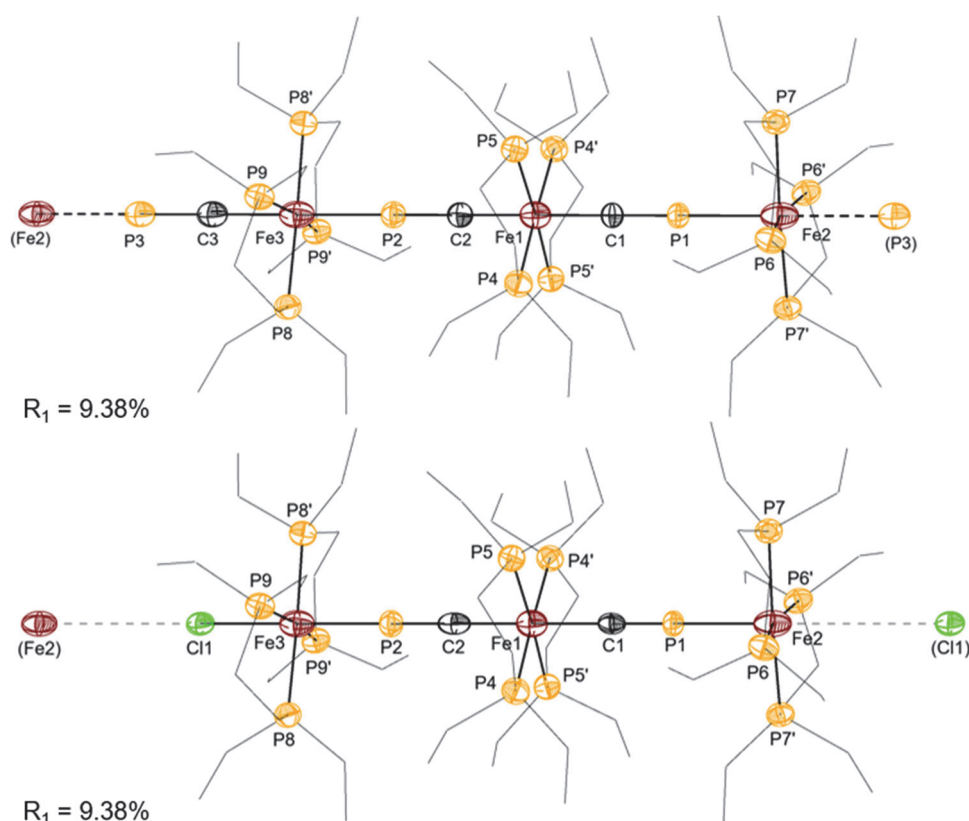


Figure 8.14. Solutions for the solid-state structure of **43** with three cyaphido ligands (top) and with one chlorido and two cyaphido ligands (bottom). Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms, $[\text{B}(\text{Ar}^{\text{F}})_4]^-$ counterions, and disorder components are omitted for clarity. Ethyl and ethylene groups are depicted as wireframes.

The structure of **43** contains an extended 1D polymeric arrangement of $\text{Fe}(\text{depe})_2$ units bridged by three heavily disordered bridging ligands. The asymmetric unit of **43** contains 1.5 $\text{Fe}(\text{depe})_2$ units and one $[\text{B}(\text{Ar}^{\text{F}})_4]^-$ counterion, suggesting there is one iron(I) center for every two iron(II) centers. Two of the bridging ligands can be modeled satisfactorily as disordered $\eta^1:\eta^1$ bridging cyaphido ligands. The identity of the third ligand is less clear; it can be modeled equally well as disordered cyaphide and chloride units. Regardless, this suggests that while κP coordination to iron(II) centers is possible, these bonds are very weak and are likely outcompeted by the coordination of dinitrogen.

8.4 Conclusions

The iron(II) mono- and dicyaphide complexes **38** and **39** are highly stable in comparison to other metal cyaphide complexes due to substantial stabilization by π backbonding. This stabilization allows access to stable multimetallic complexes that are structurally related to Prussian blue, and contain the cyaphido ligand in the elusive end-on bridging coordination mode.

Halide abstraction from complex **38** results in redox disproportionation and the formation of a cyaphide-bridged bimetallic iron(II)/iron(I) complex (**40**). Reaction of **39** with two equivalents of an iron(I) precursor affords a trimetallic iron(I)/iron(II)/iron(I) complex (**42**) containing two bridging cyaphido ligands. Cyclic voltammetry show quasi-reversible oxidation and reduction features, suggesting oxidized or reduced forms may also be stable. The electronic structures of **39** and **42** show that the cyaphide π and π^* orbitals participate in delocalized π systems with iron $3d_{xz}$ and $3d_{yz}$ orbitals.

Both **40** and **42** involve the coordination of the cyaphide phosphorus atom to relatively electron-rich iron(I) centers. Preliminary results (**43**) suggest that κP coordination to iron(II) centers is possible, and may enable the formation of cyaphide-bridged polymeric materials.

8.5 Experimental section

8.5.1 *In situ* generation of Zn(18-crown-6)(CP)₂ (36)

A solution of Mg(^{Dipp}NacNac)(CP)(dioxane) (approx. 126 mg, 0.22 mmol) in toluene (1 mL) was generated *in situ*, as in Section 2.4.1. Zn(18-crown-6)Cl₂ (44 mg, 0.11 mmol) was added as a solid, and the reaction mixture was stirred for 1 h. The reaction mixture was filtered, then the solvent was removed from the filtrate under vacuum. The resulting residue was extracted into hexane (5 mL), and the solvent removed under vacuum to yield an oily red-brown solid.

³¹P{¹H} NMR spectroscopy at this stage shows only one phosphorus-containing product, assigned as Zn(18-crown-6)(CP)₂, though ¹H NMR spectroscopy shows the presence of several impurities, including residual **2**. Attempted crystallization from pentane or hexane at room temperature or –35 °C results in the precipitation of a red oil containing an intractable mixture of products.

¹H NMR (400 MHz, C₆D₆): δ(ppm) 3.36 (br, 18-crown-6 CH₂).

³¹P{¹H} NMR (162 MHz, C₆D₆): δ(ppm) 139.7 (s, CP).

8.5.2 *In situ* generation of Cd(18-crown-6)(CP)₂ (37)

A solution of Mg(^{Dipp}NacNac)(CP)(dioxane) (approx. 126 mg, 0.22 mmol) in toluene (1 mL) was generated *in situ*, as in Section 2.4.1. Cd(18-crown-6)Cl₂ (49 mg, 0.11 mmol) was added as a solid, and the reaction mixture was stirred for 1 h. The reaction mixture was filtered, then the solvent was removed from the filtrate under vacuum. The resulting residue was washed with hexane (2 × 2 mL), then extracted with toluene (2 mL). The solvent was removed under vacuum to yield a beige solid.

³¹P{¹H} and ¹H NMR spectroscopy at this stage show the presence of one major product, assigned as Cd(18-crown-6)(CP)₂, though minor impurities are also present, including {Mg(^{Dipp}NacNac)(μ-Cl)}₂. Attempted crystallization from toluene, diethyl ether, or THF at room temperature or –35 °C, or from benzene, dioxane, or acetonitrile at room temperature results in the precipitation of an insoluble brown-black solid.

¹H NMR (400 MHz, C₆D₆): δ(ppm) 3.35 (br, 18-crown-6 CH₂).

³¹P{¹H} NMR (162 MHz, C₆D₆): δ(ppm) 119.5 (s, ²J_{31P–111Cd} = 259 Hz; ²J_{31P–113Cd} = 272 Hz, CP).

8.5.3 Synthesis of Fe(depe)₂(Cl)(CP) (38)

Under inert atmosphere, using dry solvents: {Mg(^{Dipp}NacNac)(CP)}₂ (250 mg, 0.26 mmol) was dissolved in THF (5 mL) and cooled to −78 °C, then added dropwise to a stirred solution of Fe(depe)₂Cl₂ (278 mg, 0.52 mmol) in THF (10 mL), also cooled to −78 °C. The dark brown solution was allowed to slowly warm to room temperature, then stirred at room temperature for 16 h. The solvent was removed under reduced pressure, and the resulting brown residue washed with a 0.1 M solution of THF in pentane (2 × 10 mL).

In air, using benchtop solvents: The reaction vessel was carefully opened to ambient atmosphere, then extracted with toluene (2 × 10 mL). The resulting brown solution was evaporated using a rotary evaporator, then dried under high vacuum. The resulting light brown residue was suspended in pentane (5 mL) with the aid of sonication, then left open to air for 2 h, allowing for the oxidation of an unidentified dark brown byproduct and for the pentane to evaporate. The resulting light yellow-brown solid was then extracted with toluene to afford an amber-yellow solution.

Under inert atmosphere: The solvent was removed under reduced pressure to yield Fe(depe)₂(Cl)(CP) as a yellow solid, which was dried under vacuum and stored under inert atmosphere. Crystals suitable for X-ray diffraction were obtained from toluene/hexane at −35 °C. Yield: 126 mg, 0.23 mmol, 45%. Anal. Calcd. (%) for C₂₁H₄₈ClFeP₅: C, 46.13; H, 8.85; N, 0.00. Found: C, 45.88; H, 8.29; N, 0.09.

¹H{³¹P} NMR (400 MHz, C₆D₆): δ(ppm) 3.03 (dq, 4H, ²J_{H-H} = 15.4 Hz, ³J_{H-H} = 7.8 Hz, PCH₂CH₃), 2.39 (dq, 4H, ²J_{H-H} = 15.4 Hz, ³J_{H-H} = 7.8 Hz, PCH₂CH₃), 1.94–1.82 (m, 4H, C₂H₄(PEt₂)₂), 1.74 (dq, 4H, ²J_{H-H} = 15.0 Hz, ³J_{H-H} = 7.5 Hz, PCH₂CH₃), 1.61 (dq, 4H, ²J_{H-H} = 15.0 Hz, ³J_{H-H} = 7.5 Hz, PCH₂CH₃), 1.25–1.16 (m, 4H, C₂H₄(PEt₂)₂), 1.13 (t, 12H, ³J_{H-H} = 7.7 Hz, PCH₂CH₃), 1.05 (t, 12H, ³J_{H-H} = 7.7 Hz, PCH₂CH₃).

¹³C{¹H} NMR (151 MHz, C₆D₆): δ(ppm) 295.24–294.09 (m, CP), 20.03 (p, C₂H₄(PEt₂)₂), 18.46 (p, PCH₂CH₃), 18.22 (p, PCH₂CH₃), 10.15 (PCH₂CH₃), 9.96 (PCH₂CH₃). Resonances corresponding to depe CH₂ carbons appear as pseudo-pentets due to second order virtual coupling.

³¹P{¹H} NMR (162 MHz, C₆D₆): δ(ppm) 189.6 (p, ³J_{P-P} = 7 Hz, CP), 66.1 (d, ³J_{P-P} = 7 Hz, C₂H₄(PEt₂)₂).

Raman: 1216 cm^{−1} (m, ν(C≡P)).

8.5.4 Synthesis of $\text{Fe}(\text{depe})_2(\text{CP})_2$ (39)

Under inert atmosphere, using dry solvents: $\{\text{Mg}(\text{DippNacNac})(\text{CP})\}_2$ (500 mg, 0.52 mmol) was dissolved in THF (5 mL) and cooled to -78°C , then added dropwise to a stirred solution of $\text{Fe}(\text{depe})_2\text{Cl}_2$ (265 mg, 0.50 mmol) in THF (10 mL), also cooled to -78°C . The dark brown solution was allowed to slowly warm to room temperature, then stirred at room temperature for 3 d. The solvent was removed under reduced pressure, and the resulting brown residue washed with a 0.1 M solution of THF in pentane (3×10 mL).

In air, using benchtop solvents: The reaction vessel was carefully opened to ambient atmosphere, then extracted with toluene (2×10 mL). The resulting brown solution was evaporated using a rotary evaporator, then dried under high vacuum. The resulting light brown residue was suspended in pentane (5 mL) with the aid of sonication, then left open to air for 2 h, allowing for the oxidation of an unidentified dark brown byproduct and for the pentane to evaporate. The resulting light yellow-brown solid was then extracted with toluene to afford a yellow solution.

Under inert atmosphere: The solvent was removed under reduced pressure to yield $\text{Fe}(\text{depe})_2(\text{CP})_2$ as a light-yellow solid, which was dried under vacuum and stored under inert atmosphere. Crystals suitable for X-ray diffraction were obtained from toluene at -35°C . Yield: 96 mg, 0.17 mmol, 35%. Anal. Calcd. (%) for $\text{C}_{22}\text{H}_{48}\text{FeP}_6$: C, 47.67; H, 8.73; N, 0.00. Found: C, 46.84; H, 8.35; N, 0.00.

$^1\text{H}\{^{31}\text{P}\}$ NMR (400 MHz, C_6D_6): $\delta(\text{ppm})$ 2.92 (dq, 8H, $^2J_{\text{H-H}} = 15.4$ Hz, $^3J_{\text{H-H}} = 7.7$ Hz, PCH_2CH_3), 1.72 (s, 8H, $\text{C}_2\text{H}_4(\text{PEt}_2)_2$), 1.67 (dq, 8H, $^2J_{\text{H-H}} = 15.0$ Hz, $^3J_{\text{H-H}} = 7.6$ Hz, PCH_2CH_3), 1.09 (t, 24H, $^3J_{\text{H-H}} = 7.6$ Hz, PCH_2CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): $\delta(\text{ppm})$ 299.26–298.33 (m, CP), 20.14 (p, $\text{C}_2\text{H}_4(\text{PEt}_2)_2$), 19.54 (p, PCH_2CH_3), 10.49 (PCH_2CH_3). Resonances corresponding to depe CH_2 carbons appear as pseudo-pentets due to second order virtual coupling.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): $\delta(\text{ppm})$ 180.1 (p, $^3J_{\text{P-P}} = 9$ Hz, CP), 66.0 (t, $^3J_{\text{P-P}} = 9$ Hz, $\text{C}_2\text{H}_4(\text{PEt}_2)_2$).

Raman: 1256 cm^{-1} (vs, $\nu(\text{C}\equiv\text{P})$).

8.5.5 Crystallization of $[\{\text{Fe}(\text{depe})_2\}_2(\text{N}_2)(\mu\text{-CP})][\text{B}(\text{Ar}^{\text{F}})_4]_2$ (40)

Under a dinitrogen atmosphere: $\text{Fe}(\text{depe})_2(\text{Cl})(\text{CP})$ (89 mg, 0.16 mmol) and $\text{Na}[\text{B}(\text{Ar}^{\text{F}})_4]$ (144 mg, 0.16 mmol) were dissolved in 1,2-DFB (2 mL) to afford a dark red solution. The solution was filtered to remove particulates, then layered with pentane (20 mL). After diffusion over 2 weeks, $[\{\text{Fe}(\text{depe})_2\}_2(\text{N}_2)(\mu\text{-CP})][\text{B}(\text{Ar}^{\text{F}})_4]_2$ crystallizes as large orange crystals suitable for single crystal X-ray diffraction.

Bulk samples are invariably contaminated by a brown oily residue that concomitantly precipitates from solution, preventing meaningful analysis on bulk material.

8.5.6 *In situ* generation of $[\{\text{Mg}(\text{DippNacNac})(\text{THF})\}(\mu\text{-CP})\{\text{Fe}(\text{depe})_2\text{Cl}\}][\text{BPh}_4]$ (41)

$\{\text{Mg}(\text{DippNacNac})(\text{CP})\}_2$ (8 mg, 0.01 mmol) was dissolved in $\text{d}_8\text{-THF}$ (0.2 mL) and cooled to -35°C , then added dropwise to a solution of $[\text{Fe}(\text{depe})_2(\text{Cl})(\text{N}_2)][\text{BPh}_4]$ (14 mg, 0.02 mmol) in $\text{d}_8\text{-THF}$ (0.2 mL), also cooled to -35°C .

The resulting green solution contains one product, tentatively assigned as $[\{\text{Mg}(\text{DippNacNac})(\text{THF})\}(\mu\text{-CP})\{\text{Fe}(\text{depe})_2\text{Cl}\}][\text{BPh}_4]$, which decomposes over several hours at room temperature or on attempted workup.

^1H NMR (400 MHz, C_6D_6): δ (ppm) 7.32–7.25 (m, 8H, BPh_4 *ortho*-CH), 7.20–7.06 (m, 6H, Dipp Ar-CH), 6.88–6.82 (m, 8H, BPh_4 *meta*-CH), 6.71 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 4H, BPh_4 *para*-CH), 4.88 (s, 1H, NacNac CH), 3.02 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 4H, Dipp CH(CH₃)₂), 2.22–2.08 (m, 4H, $\text{C}_2\text{H}_4(\text{PEt}_2)_2/\text{PCH}_2\text{CH}_3$), 2.08–1.95 (m, 4H, $\text{C}_2\text{H}_4(\text{PEt}_2)_2/\text{PCH}_2\text{CH}_3$), 1.95–1.86 (m, 4H, $\text{C}_2\text{H}_4(\text{PEt}_2)_2/\text{PCH}_2\text{CH}_3$), 1.86–1.78 (m, 4H, $\text{C}_2\text{H}_4(\text{PEt}_2)_2/\text{PCH}_2\text{CH}_3$), 1.60 (s, 6H, NacNac CH₃), 1.22 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 12H, Dipp CH(CH₃)₂), 1.18 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 12H, Dipp CH(CH₃)₂), 1.15–1.03 (m, PCH_2CH_3), 1.06–0.92 (m, 12H, PCH_2CH_3).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): δ (ppm) 168.1 (p, $^2J_{\text{P-P}} = 49$ Hz, CP), 59.8 (d, $^2J_{\text{P-P}} = 49$ Hz, $\text{C}_2\text{H}_4(\text{PEt}_2)_2$).

8.5.7 Synthesis of $[\{\text{Fe}(\text{depe})_2\}_3(\mu\text{-CP})_2][\text{OTf}]_2$ (42)

$\text{Fe}(\text{depe})_2(\text{CP})_2$ (31 mg, 0.06 mmol) was dissolved in toluene (0.5 mL), and added to a solution of $[\text{Fe}(\text{depe})_2(\text{N}_2)][\text{OTf}]$ (72 mg, 0.11 mmol) in 1,2-DFB (1.5 mL), resulting in gas evolution and the formation of a dark yellow/purple dichroic solution. The solution was filtered to remove particulates, then layered with toluene (20 mL). After slow diffusion over 1 week, $[\{\text{Fe}(\text{depe})_2\}_3(\mu\text{-CP})_2][\text{OTf}]_2$ crystallizes as dark purple crystals suitable for single crystal X-ray diffraction. Yield: 70 mg, 0.04 mmol, 70%. Anal. Calcd. (%) for $\text{C}_{64}\text{H}_{144}\text{F}_6\text{Fe}_3\text{O}_6\text{P}_{14}\text{S}_2 \cdot (\text{C}_6\text{H}_4\text{F}_2)$: C, 44.18; H, 7.84; N, 0.00. Found: C, 43.72; H, 8.04; N, 0.20.

Evans NMR (1,2-DFB, 298 K): $\mu_{\text{eff}} = 2.6 \mu_{\text{B}}$.

Raman: 1229 cm^{-1} (vs, $\nu(\text{C}\equiv\text{P})$).

8.5.8 Crystallization of $([\{\text{Fe}(\text{depe})_2\}_3(\mu\text{-CP})_{3-x}(\text{Cl})_x][\text{B}(\text{Ar}^{\text{F}})_4]_2)_n$ (43)

Under a dinitrogen atmosphere: $\text{Fe}(\text{depe})_2(\text{Cl})(\text{CP})$ (89 mg, 0.16 mmol) and $\text{Na}[\text{B}(\text{Ar}^{\text{F}})_4]$ (144 mg, 0.16 mmol) were dissolved in 1,2-DFB (2 mL) to afford a dark red solution. The solution was filtered to remove particulates, then layered with pentane (20 mL). After diffusion over 2 weeks, the supernatant was decanted from the mixture of $[\{\text{Fe}(\text{depe})_2\}_2(\text{N}_2)(\mu\text{-CP})][\text{B}(\text{Ar}^{\text{F}})_4]_2$ and other oily brown byproducts. The solid filtrants were dried under vacuum.

Under an argon atmosphere: The solids were extracted with diethyl ether ($3 \times 20 \text{ mL}$) to give a red-brown solution. On standing, a small quantity of dark crystals form, identified as $([\{\text{Fe}(\text{depe})_2\}_3(\mu\text{-CP})_{3-x}(\text{Cl})_x][\text{B}(\text{Ar}^{\text{F}})_4]_2)_n$. Under a dinitrogen atmosphere, these crystals degrade to a brown oil over the course of several hours.

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Conclusions and Future Work

9.1 Conclusions

This project has developed an improved understanding of the chemistry of the cyaphide ion, including its synthesis, properties, reactivity, and stability in mono- and multi-metallic complexes.

Magnesium(II) cyaphide complexes can be synthesized by the reductive deoxygenation of a siloxyphosphaalkyne. These can be used as organometallic cyaphide transfer reagents, enabling access to metal cyaphide complexes by simple salt-metathesis protocols.

In coordination to transition metal centers, the κ C-cyaphido ligand is not only a strong σ donor but also a strong π acceptor due to its low-lying $C\equiv P$ π^* orbitals. This also results in considerable electrophilic character, which can be leveraged to prepare hetero-multimetallic species including bi- and tri-metallic complexes with bridging cyaphido ligands in $\eta^1:\eta^2$ and $\eta^1:\eta^2:\eta^1$ coordination modes.

Metal cyaphide complexes can also serve as a synthon for other organophosphorus anions. Cycloaddition reactions between s, p, and d-block metal cyaphide complexes with organic azides result in metallo-triazaphospholes, which can be reacted further to afford C-functionalized species. The cyaphide ion can also undergo metal-mediated oligomerization reactions to afford $(CP)_2^{2-}$, $(CP)_3^{3-}$, and $(CP)_4^{4-}$ fragments, and is disfavored for complexes with significant metal–carbon bond covalency.

This was used to inform the design of stable iron(II) cyaphide complexes, including a dicyaphide complex. These were used as precursors to multimetallic iron complexes containing the cyaphide ion in end-on bridging coordination modes, structurally related to fragments of Prussian blue.

9.2 Future work

The iron cyaphide complexes **40** and **42** demonstrate the feasibility of using the cyaphide ion as a linear bridging ligand in Prussian blue-like multimetallic systems. In cyaphide analogs of Prussian-blue, the low-lying $C\equiv P$ π^* orbitals should allow for efficient magnetic coupling pathways. To probe this, cyaphide-

bridged complexes of metals with partially occupied π -symmetric d-orbitals (e.g. tetrahedral iron(II)), should be synthesized and studied.

Preliminary results (**43**) suggest that the formation of metal cyaphide coordination polymers should also be achievable, but that such systems are likely to have poor stability due to very weak CP–M bonding. The systematic coordination chemistry study in Chapter 4 was incredibly informative for the design of stable complexes containing the κ C-cyaphido ligand (**38** and **39**), and a similar study for the more elusive κ P-cyaphido coordination mode should also be highly informative for the design of stable complexes or coordination polymers containing the κ P-cyaphido ligand.

The $(\text{CP})_3^{3-}$ anion in **34** is intriguing in its own right as a potential precursor to functional triphosphabenzene, though the use of **34** in subsequent transformations was prevented due to its poor solubility. Ancillary ligand modification (for example using $\text{C}_5\text{H}_3(\text{SiMe}_3)_2^-$ instead of Cp^{*-}) should help circumvent this problem.

The cyaphide-azide “click” reaction is remarkably consistent and well-behaved, and should prove to be useful for the construction of more sophisticated triazaphosphole-containing systems. Further investigations into this are already under way.

The utility of cyaphide transfer in synthesizing metal cyaphide complexes has been demonstrated in this work, though its potential utility in preparing organic cyaphide-containing compounds has not been explored. The magnesium(II) cyaphide complexes **1L** and **3**, and the zinc(II) cyaphide complex **11** may be useful for the synthesis of otherwise difficult to access phosphalkynes.

Cyaphide transfer chemistry represents a general route to the synthesis of cyaphide-containing molecules, though in its current form has very poor atom economy. The cyaphide transfer reagents used in this work, **1L** and **3**, require the use of stoichiometric silylating reagents and magnesium(I) reductants, neither of which are incorporated into the final cyaphide-containing product. The synthesis of other cyaphide transfer reagents *via* more atom economical routes, for example by the direct reduction of the 2-phosphaethynolate ion, will be crucial for enabling the use of the cyaphide ion in practical applications.

Finally, while much progress has been made toward understanding the chemistry of the cyaphide ion, other heavy cyanide analogs, in particular the cyarside ion ($\text{C}\equiv\text{As}^-$), remain underexplored. As with the cyaphide ion, the synthesis of ionic cyarside complexes to use as cyarside transfer reagents would overcome a major hurdle to further developments in this area.

Experimental and Computational Details

10.1 General experimental methods

10.1.1 Synthetic methods

Unless specified otherwise, all reactions and product manipulations were carried out using standard Schlenk-line techniques under an inert atmosphere of argon or dinitrogen, or in a dinitrogen filled glovebox (MBraun UNIlab glovebox maintained at < 0.1 ppm H₂O and < 0.1 ppm O₂). All dry solvents were stored under inert atmospheres of argon or dinitrogen in gas-tight ampoules over activated 3 Å molecular sieves.

Pentane (Sigma Aldrich HPLC grade), hexane (Sigma Aldrich HPLC grade), benzene (anhydrous, Sigma Aldrich), toluene (Sigma Aldrich HPLC grade), diethyl ether (Sigma Aldrich HPLC grade), DCM (Sigma Aldrich HPLC grade), and acetonitrile (Sigma Aldrich HPLC grade) were purified using an MBraun SPS-800 solvent system. THF (Sigma Aldrich HPLC grade) was distilled over sodium/benzophenone. 1,2-DFB (Alfa Aesar, 98%) and pyridine (Sigma Aldrich HPLC grade) were distilled over CaH₂. Anhydrous methanol (Sigma Aldrich, 99.8%) was purchased and used as received.

C₆D₆ (Aldrich, 99.5%) was degassed and dried over CaH₂. d₈-toluene (Aldrich, 99.5%) and d₈-THF (Aldrich, 99.5%) were degassed and dried over Na/K alloy. CD₂Cl₂ (Aldrich, 99.5%) was degassed and dried over activated 3 Å molecular sieves. d₆-DMSO (Aldrich, 99.5%) was degassed and dried twice over activated 3 Å molecular sieves.

Magnesium chloride (Alfa Aesar, ultra dry, 99.9%), 4-dimethylaminopyridine (Sigma Aldrich, 99%), stearic acid (Sigma Aldrich, 97%), Me₃SiCl (Sigma Aldrich, 98%), ethynylmagnesium chloride (Sigma Aldrich, 0.5 M in THF), sodium acetylide (Sigma Aldrich 95%), *tert*-butyl isocyanide (Sigma Aldrich 98%), carbon monoxide (BOC), ethylene (BOC), potassium cyanide (TCI >98%), trimethylsilyl cyanide (Sigma Aldrich 98%), adamantyl azide (Sigma Aldrich, 97%), pyridinium chloride (Sigma Aldrich, 98%), iodine (Sigma Aldrich, 99.8%), and Mn(TPP)Cl (Sigma Aldrich, 95%) were purchased and used as

received. $^i\text{Pr}_3\text{SiOTf}$ (Alfa Aesar, 97%) was purified by vacuum distillation, and dried over activated 3 Å molecular sieves. Tetrabutylammonium cyanide (Sigma Aldrich, 95%) was recrystallized from anhydrous THF/hexane. $[\text{NBu}_4][\text{PF}_6]$ (Sigma Aldrich, 98%) was purified by two-fold recrystallization from methanol. Ferrocene (Sigma Aldrich, 98%) was purified by vacuum sublimation. Benzyl azide (Alfa Aesar, 94%) was distilled and dried over 3 Å molecular sieves. 18-crown-6 (Sigma Aldrich, 99%) was purified by recrystallization from acetonitrile.

$[\text{Na}(\text{diox})_x][\text{PCO}]$,^[1] $\{\text{Mg}(\text{DippNacNac})\}_2$,^[2] $\{\text{Mg}(\text{MesNacNac})\}_2$,^[2] $\text{Ge}(\text{DippNacNac})\text{Cl}$,^[3] $\text{Sn}(\text{DippNacNac})\text{Cl}$,^[3] $\text{Au}(\text{IDipp})\text{Cl}$,^[4] $\text{Co}(\text{DippPDI})\text{Cl}$,^[5] $\{\text{Zn}(\text{DippNacNac})(\mu\text{-Cl})\}_2$,^[6] $\text{Na}[\text{B}(\text{Ar}^F)_4]$,^[7] $\text{Co}(\text{DippPDI})\text{Me}$,^[8] $[\text{Co}(\text{DippPDI})(\text{N}_2)][\text{B}(\text{Me})(\text{C}_6\text{F}_5)_3]$,^[8] $\text{Rh}(\text{DippPDI})\text{Cl}$,^[9] $\text{Rh}(\text{DippPDI})\text{Me}$,^[10] $\text{Au}(\text{IDipp})(\text{CN})$,^[11] $\text{B}(\text{C}_6\text{F}_5)_3$,^[12] $\text{Rh}(\text{Cp}^*)(\text{PMe}_3)_2$,^[13] $\text{W}(\text{CO})_5(\text{THF})$,^[14] $\text{Ga}(\text{DippNacNac})$,^[15] $\text{Fe}(\text{depe})_2(\text{N}_2)$,^[16] $^t\text{BuN}_3$,^[17] DippN_3 ,^[18] $\text{Ni}(\text{SIDipp})(\text{Cp})\text{Cl}$,^[19] $\text{Sc}(\text{Cp}^*)_2\text{Cl}$,^[20] $\text{Sm}(\text{Cp}^*)_2(\text{OEt}_2)$,^[21] $\text{Zn}(\text{18-crown-6})\text{Cl}_2$,^[22] $\text{Cd}(\text{18-crown-6})\text{Cl}_2$,^[23] $\text{Fe}(\text{depe})_2\text{Cl}_2$,^[24] $[\text{Fe}(\text{depe})_2(\text{Cl})(\text{N}_2)][\text{BPh}_4]$,^[25] and $[\text{Fe}(\text{depe})_2(\text{N}_2)][\text{OTf}]$ ^[16] were synthesized according to previously reported synthetic procedures. The synthesis of $^i\text{Pr}_3\text{SiOCP}$ was adapted from the previously reported procedure.^[26] $\text{Ni}(\text{MeTiPr}_2)_2(\text{COD})$ and $\{(\text{MeTiPr}_2)_2\text{Ni}\}_2(\mu\text{-COD})$ were synthesized as a 7:3 mixture according to a previously reported procedure, and its stoichiometry determined by ^1H NMR spectroscopy.^[27]

Crystals of $\text{Rh}(\text{DippPDI})\text{Cl}$ suitable for single crystal X-ray diffraction were obtained from THF/pentane at -20°C . Crystals of $\text{Rh}(\text{DippPDI})\text{Me}$ suitable for single crystal X-ray diffraction were obtained from toluene/pentane at -35°C .

10.1.2 Characterization techniques

NMR spectra were acquired on a Bruker AVIII 400 MHz NMR spectrometer (^1H 400 MHz, ^{11}B 128 MHz, ^{19}F 377 MHz, ^{31}P 162 MHz), Bruker AVIII 500 MHz NMR spectrometer (^1H 500 MHz, ^{13}C 126 MHz, ^{31}P 202 MHz) or a Bruker Avance NEO 600 MHz NMR spectrometer with a broadband helium cryoprobe (^1H 600 MHz, ^{13}C 151 MHz). ^1H and ^{13}C NMR spectra were referenced to the most downfield solvent resonance (^1H NMR C_6D_6 : $\delta = 7.16$ ppm, CD_2Cl_2 : $\delta = 5.32$ ppm, $\text{d}_8\text{-THF}$: $\delta = 3.58$ ppm, $\text{d}_6\text{-DMSO}$: $\delta = 2.50$ ppm; ^{13}C NMR C_6D_6 : $\delta = 128.06$ ppm, $\text{d}_8\text{-THF}$: $\delta = 67.21$ ppm, $\text{d}_6\text{-DMSO}$: $\delta = 39.52$ ppm). ^1H and ^{13}C NMR spectra in 1,2-DFB were measured locked to a C_6D_6 capillary and referenced according to literature methods.^[28] ^{11}B NMR spectra were externally referenced to $\text{BF}_3\cdot\text{Et}_2\text{O}$ in C_6D_6 . ^{19}F NMR spectra were externally referenced to CFCl_3 . ^{31}P NMR spectra were externally referenced to an 85%

solution of H_3PO_4 in H_2O . Paramagnetic susceptibilities were determined by NMR using the Evans method.^[29,30]

Infrared spectra were acquired on a Thermo Scientific iS5 FTIR spectrometer using an iD3 ATR stage. Raman spectra were acquired on a Thermo Fisher Scientific DXR3 SmartRaman spectrometer using a 532 nm or 785 nm laser.

UV-vis absorption spectra were acquired for dilute toluene solutions on a Horiba Duetta spectrofluorometer at 298 K using an anaerobic quartz cuvette.

Cyclic voltammetry experiments were performed in a MBraun UNILab glovebox with a PalmSens Emstat3+ Blu potentiostat using a glassy carbon working electrode, a Pt wire counter electrode, and an Ag wire pseudo-reference electrode.

Elemental analyses were carried out by Elemental Microanalyses Ltd. (Devon, U.K.) or London Metropolitan University (London, U.K.). Samples (approx. 5 mg) were submitted in flame sealed glass tubes.

10.1.3 Single crystal X-ray diffraction data

Single crystal X-ray diffraction data were collected using an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector. Crystals were selected under Paratone-N oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N₂ cooling device. Data were collected at 150 K using mirror monochromated Cu K α ($\lambda = 1.54184 \text{ \AA}$) or Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation and processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).^[31] Structures were subsequently solved using direct methods and refined on F^2 using the SHELXL or SHELXT packages.^[32–34]

Table 10.1.1. Selected X-ray data collection and refinement parameters for **1_{diox}**, **2_{diox}**, **3**, **C₆H₆**, and **4**.

	1_{diox}	2_{diox}	3	4
Formula	C ₃₄ H ₄₉ MgN ₂ O ₂ P	C ₄₂ H ₇₀ MgN ₂ O ₃ Si	C ₇₂ H ₉₄ Mg ₂ N ₄ P ₂	C ₅₆ H ₇₉ Mg ₂ N ₄ OPSi
CCDC	2078056	2078057	–	–
Fw [g mol ⁻¹]	573.03	703.40	1126.07	931.91
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /n	I2/m	P2 ₁ /c
<i>a</i> (Å)	17.3179(5)	11.5488(1)	9.0909(1)	15.4507(1)
<i>b</i> (Å)	11.7439(5)	20.5766(2)	20.0448(2)	14.8983(2)
<i>c</i> (Å)	16.7377(6)	17.9650(1)	18.5178(2)	23.8298(3)
α (°)	90	90	90	90
β (°)	102.437(4)	92.549(1)	98.562(1)	90.423(1)
γ (°)	90	90	90	90
<i>V</i> (Å ³)	3324.2(2)	4264.89(6)	3336.80(6)	5485.21(11)
<i>Z</i>	4	4	2	4
Radiation, λ (Å)	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184
Temp (K)	150(2)	150(2)	150(2)	150(2)
ρ_{calc} (g cm ⁻³)	1.145	1.095	1.121	1.128
μ (mm ⁻¹)	1.147	0.906	1.091	1.178
Reflections collected	18539	48288	13404	66233
Independent reflections	6935	8888	3573	11447
Parameters	371	458	192	608
R(int)	0.0628	0.0305	0.0227	0.0332
R1/wR2, ^[a] I $\geq$ 2 σ I (%)	4.62/9.98	4.38/11.60	4.60/13.09	5.29/14.75
R1/wR2, ^[a] all data (%)	8.26/11.49	5.05/12.30	4.92/13.50	6.01/15.63
GOF	1.011	1.037	1.073	1.027

^[a] R1 = $[\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; wR2 = $\{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^{1/2}]\}^{1/2}$; w = $[\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where P = $[(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0439 and 0.27 for **1_{diox}**, 0.0617 and 1.60 for **2_{diox}**, 0.0758 and 2.91 for **3**, and 0.0898 and 3.58 for **4**.

Table 10.2. Selected X-ray data collection and refinement parameters for **6**, **7**, **9**, and **10**.

	6	7	9	10
Formula	C ₃₀ H ₄₁ N ₂ PSn	C ₂₈ H ₃₆ AuN ₂ P	C ₃₄ H ₄₃ CoN ₃ P	C ₃₄ H ₄₃ N ₃ PRh
CCDC	2078061	2078062	2086971	2242907
Fw [g mol ⁻¹]	579.31	628.52	583.61	627.59
Crystal system	triclinic	orthorhombic	orthorhombic	orthorhombic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	10.6402(6)	12.6983(1)	8.4877(3)	8.49660(10)
<i>b</i> (Å)	12.3336(7)	14.2088(1)	17.8622(6)	17.9973(2)
<i>c</i> (Å)	12.4077(7)	15.6353(1)	20.1786(5)	20.3635(2)
α (°)	88.304(5)	90	90	90
β (°)	69.334(5)	90	90	90
γ (°)	70.944(5)	90	90	90
<i>V</i> (Å ³)	1433.26(15)	2821.04(3)	3059.26(17)	3113.90(6)
<i>Z</i>	2	4	4	4
Radiation, λ (Å)	Mo K α , 0.71073	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184
Temp (K)	150(2)	150(2)	150(2)	150(2)
ρ_{calc} (g cm ⁻³)	1.342	1.480	1.267	1.339
μ (mm ⁻¹)	0.967	10.445	5.084	5.110
Reflections collected	21091	95325	23760	64682
Independent reflections	7335	5918	6325	6499
Parameters	317	297	362	362
R(int)	0.0529	0.0585	0.0544	0.0453
R1/wR2, ^[a] I $\geq$ 2 σ I (%)	4.10/7.35	2.97/7.47	4.21/10.47	2.14/5.62
R1/wR2, ^[a] all data (%)	5.73/8.10	3.16/7.69	5.03/11.05	2.25/5.69
GOF	1.043	1.121	1.018	1.068

^[a] $R1 = [\sum ||F_o| - |F_c||] / \sum |F_o|$; $wR2 = \{[\sum w(F_o)^2] - (F_c)^2\}^{1/2} / [\sum w(F_o)^2]^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2] / 3$ and the A and B values are 0.0208 and 0.93 for **6**, 0.0562 and 0.88 for **7**, 0.0616 and 0.65 for **9**, and 0.0360 and 0.80 for **10**.

Table 10.3. Selected X-ray data collection and refinement parameters for **12**, **13**, **14**, and **15**.

	12	13	14	15
Formula	C ₃₅ H ₄₄ CoN ₃	C ₃₉ H ₅₁ CoN ₃ NaO	C ₆₆ H ₅₅ BCoF ₂₄ N ₃ O	C ₇₀ H ₆₄ BCoF ₂₄ N ₄
CCDC	2242900	2242901	2242902	2242903
Fw [g mol ⁻¹]	565.66	659.74	1431.87	1486.99
Crystal system	orthorhombic	monoclinic	monoclinic	triclinic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /c	P2 ₁ /c	P-1
<i>a</i> (Å)	8.47050(10)	11.78850(10)	17.4943(5)	14.3644(2)
<i>b</i> (Å)	17.9094(3)	16.6101(2)	17.8665(6)	15.5532(2)
<i>c</i> (Å)	20.2338(3)	18.5455(2)	22.1081(6)	16.5724(2)
α (°)	90	90	90	91.0850(10)
β (°)	90	99.7630(10)	104.528(3)	102.7870(10)
γ (°)	90	90	90	99.3700(10)
<i>V</i> (Å ³)	3069.50(8)	3578.77(7)	6689.2(4)	3556.66(8)
<i>Z</i>	4	4	4	2
Radiation, λ (Å)	Mo K α , 0.71073	Cu K α , 1.54184	Mo K α , 0.71073	Cu K α , 1.54184
Temp (K)	150(2)	150(2)	150(2)	150(2)
ρ_{calc} (g cm ⁻³)	1.224	1.224	1.422	1.388
μ (mm ⁻¹)	0.586	4.125	0.367	2.835
Reflections collected	54167	78701	107320	89994
Independent reflections	8746	7475	15340	14746
Parameters	367	418	1007	954
R(int)	0.0472	0.0465	0.0566	0.0372
R1/wR2, ^[a] I $\geq$ 2 σ I (%)	3.64/7.21	3.01/8.06	6.14/15.31	4.58/12.42
R1/wR2, ^[a] all data (%)	4.84/7.69	3.40/8.31	9.24/16.60	4.85/12.66
GOF	1.068	1.037	1.061	1.077

^[a] $R1 = [\sum ||F_o| - |F_c||] / \sum |F_o|$; $wR2 = \{[\sum w(F_o - F_c)^2] / [\sum w(F_o)^2]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2] / 3$ and the A and B values are 0.264 and 1.06 for **12**, 0.456 and 1.06 for **13**, 0.0642 and 9.16 for **14**, and 0.0663 and 1.48 for **15**.

Table 10.4. Selected X-ray data collection and refinement parameters for **16**, **Rh_{Cr}**-1.33THF-0.66pent, **Rh_{Me}**-0.25tol-0.25hex, and **17**.

	16	Rh_{Cr} -1.33THF-0.66pent	Rh_{Me} -0.25tol-0.25hex	17
Formula	C ₇₅ H ₇₃ BCoF ₂₄ N ₅	C _{41.66} H _{61.66} ClN ₃ O _{1.33} Rh	C ₆₆ H ₅₅ BCoF ₂₄ N ₃ O	C ₃₅ H ₄₄ N ₃ Rh
CCDC	2242904	2242905	2242902	2242908
Fw [g mol ⁻¹]	1570.12	764.30	1431.87	609.64
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic
Space group	<i>P</i> -1	<i>C</i> 222 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	12.9433(2)	17.36740(10)	17.4943(5)	10.43020(10)
<i>b</i> (Å)	15.1992(3)	29.7047(2)	17.8665(6)	24.0268(2)
<i>c</i> (Å)	20.7647(3)	23.95240(10)	22.1081(6)	12.31850(10)
α (°)	76.385(2)	90	90	90
β (°)	79.845(2)	90	104.528(3)	93.2010(10)
γ (°)	87.162(2)	90	90	90
<i>V</i> (Å ³)	3907.87(12)	12356.88(12)	6689.2(4)	3082.25(5)
<i>Z</i>	2	12	4	4
Radiation, λ (Å)	Cu K α , 1.54184	Cu K α , 1.54184	Mo K α , 0.71073	Cu K α , 1.54184
Temp (K)	150(2)	150(2)	150(2)	150(2)
ρ_{calc} (g cm ⁻³)	1.334	1.232	1.422	1.314
μ (mm ⁻¹)	2.613	4.200	0.367	4.671
Reflections collected	44787	102303	107320	17807
Independent reflections	16152	12891	15340	6385
Parameters	1039	666	1007	361
R(int)	0.0355	0.0664	0.0566	0.0242
R1/wR2, ^[a] I $\geq$ 2 σ I (%)	5.22/13.83	3.80/9.81	6.14/15.31	2.92/7.41
R1/wR2, ^[a] all data (%)	6.09/14.70	4.15/10.20	9.24/16.60	3.02/7.48
GOF	1.044	1.036	1.061	1.102

^[a] R1 = $[\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; wR2 = $\{[\Sigma w(F_o)^2] - (F_c)^2\}^{1/2}/[\Sigma w(F_o)^2]^{1/2}$; where P = $[(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0818 and 0.98 for **16**, 0.0599 and 14.42 for **Rh_{Cr}**-1.33THF-0.66pent, 0.0987 and 0.86 for **Rh_{Me}**-0.25tol-0.25hex, and 0.0398 and 2.42 for **15**.

Table 10.5. Selected X-ray data collection and refinement parameters for **18**, **19**, **Rh_{C2H4}[B(Ar^F)₄]**, and **20**-tol.

	18	19	Rh_{C2H4}[B(Ar^F)₄]	20 -tol
Formula	C ₆₆ H ₅₅ BF ₂₄ N ₃ ORh	C ₇₀ H ₆₄ BF ₂₄ N ₄ Rh	C ₆₇ H ₅₉ BF ₂₄ N ₃ Rh	C ₅₃ H ₄₄ AuBF ₁₅ N ₃
CCDC	2242909	2242910	2242911	2171578
Fw [g mol ⁻¹]	1475.85	1530.97	1475.89	1215.69
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	P2 ₁ /c	P-1	P2 ₁ /c	P-1
<i>a</i> (Å)	17.5140(1)	14.4106(4)	17.5964(2)	12.9001(2)
<i>b</i> (Å)	17.7479(1)	15.5555(3)	17.6516(2)	14.2097(2)
<i>c</i> (Å)	22.3688(1)	16.6974(5)	22.6324(2)	16.5212(2)
α (°)	90	90.441(2)	90	67.537(1)
β (°)	104.161(1)	103.544(2)	104.7830(10)	83.160(1)
γ (°)	90	100.297(2)	90	64.777(1)
<i>V</i> (Å ³)	6741.75(7)	3575.45(17)	6797.04(13)	2528.37(7)
<i>Z</i>	4	2	4	2
Radiation, λ (Å)	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184
Temp (K)	150(2)	150(2)	150(2)	150(2)
ρ_{calc} (g cm ⁻³)	1.454	1.422	1.442	1.597
μ (mm ⁻¹)	3.031	2.871	2.994	6.306
Reflections collected	48569	39212	41283	63325
Independent reflections	13941	14755	13995	10499
Parameters	935	914	935	718
R(int)	0.0325	0.0382	0.0288	0.0292
R1/wR2, ^[a] I $\geq$ 2 σ I (%)	4.11/10.80	4.17/10.85	4.77/12.86	2.53/6.17
R1/wR2, ^[a] all data (%)	4.59/11.28	4.47/11.17	5.46/13.66	2.55/6.18
GOF	1.060	1.019	1.041	1.040

^[a] $R1 = [\sum ||F_o| - |F_c||] / \sum |F_o|$; $wR2 = \{[\sum w(F_o)^2] - (F_c)^2\}^{1/2} / [\sum w(F_o)^2]^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2] / 3$ and the A and B values are 0.0579 and 6.52 for **18**, 0.0629 and 3.07 for **19**, 0.0792 and 6.55 for **Rh_{C2H4}[B(Ar^F)₄]**, and 0.0278 and 3.53 for **20**-tol.

Table 10.6. Selected X-ray data collection and refinement parameters for **21**·2C₆H₆, **22**-hex, **23**·0.5hex, and **24**-tol.

	21 ·2C ₆ H ₆	22 -hex	23 ·0.5hex	24 -tol
Formula	C ₆₂ H ₈₈ AuN ₆ NiP	C ₄₇ H ₇₄ AuN ₂ P ₂ Rh	C ₄₉ H ₆₇ AuN ₂ O ₅ P ₂ RhW	C ₆₄ H ₈₅ AuGaN ₄ P
CCDC	2171579	2171580	2171581	–
Fw [g mol ⁻¹]	1204.03	1028.89	1309.71	1208.01
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	10.2343(1)	17.2262(1)	20.5170(3)	12.71270(10)
<i>b</i> (Å)	29.7930(2)	20.7164(2)	10.5200(2)	22.9597(2)
<i>c</i> (Å)	20.1214(1)	27.5711(2)	25.1336(4)	21.0072(2)
α (°)	90	90	90	90
β (°)	95.889(1)	90	97.197(2)	98.502(1)
γ (°)	90	90	90	90
<i>V</i> (Å ³)	6102.85(8)	9839.16(13)	5382.07(16)	6064.19(9)
<i>Z</i>	4	8	4	4
Radiation, λ (Å)	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184
Temp (K)	150(2)	150(2)	150(2)	150(2)
ρ_{calc} (g cm ⁻³)	1.310	1.389	1.616	1.323
μ (mm ⁻¹)	5.388	9.072	12.231	5.572
Reflections collected	147019	90393	56469	67534
Independent reflections	12731	10313	11127	12642
Parameters	648	494	566	728
R(int)	0.0477	0.0483	0.0845	0.0353
R1/wR2, ^[a] I $\geq$ 2 σ I (%)	3.33/8.54	3.70/9.02	6.93/17.51	2.11/5.05
R1/wR2, ^[a] all data (%)	3.86/8.91	4.04/9.38	9.06/19.90	2.43/5.23
GOF	1.056	1.030	1.050	1.059

^[a] $R1 = [\sum ||F_o| - |F_c||] / \sum |F_o|$; $wR2 = \{[\sum w[(F_o)^2 - (F_c)^2]^2] / [\sum w(F_o)^2]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2] / 3$ and the A and B values are 0.0433 and 9.73 for **21**·2C₆H₆, 0.0420 and 42.11 for **22**-hex, 0.0420 and 42.11 for **23**·0.5hex, and 0.0248 and 2.58 for **24**-tol.

Table 10.7. Selected X-ray data collection and refinement parameters for **25.2C₆H₆**, **26a.C₆H₆**, **26b.tol**, and **26c.C₆H₆**.

	25.2C₆H₆	26a.C₆H₆	26b.tol	26c.C₆H₆
Formula	C ₅₄ H ₁₀₈ Au ₂ Fe ₂ P ₁₀	C ₃₈ H ₅₁ AuN ₅ P	C ₄₅ H ₅₉ AuN ₅ P	C ₄₆ H ₅₉ AuN ₅ P
CCDC	–	2263738	2263730	2263731
Fw [g mol ⁻¹]	1572.73	805.77	897.90	909.91
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic
Space group	<i>P</i> -1	<i>Pnma</i>	<i>I</i> 2/ <i>a</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.8473(2)	16.2045(1)	20.7310(1)	12.5798(2)
<i>b</i> (Å)	13.0366(3)	10.6534(1)	16.1721(1)	16.7485(2)
<i>c</i> (Å)	13.6086(4)	23.8480(2)	26.0458(4)	22.2537(3)
α (°)	81.050(2)	90	90	90
β (°)	74.529(2)	90	102.725(1)	106.371(2)
γ (°)	76.115(5)	90	90	90
<i>V</i> (Å ³)	1626.66(7)	4116.95(6)	8517.74(15)	4498.60(12)
<i>Z</i>	1	4	8	4
Radiation, λ (Å)	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184
Temp (K)	150(2)	200(2)	150(2)	150(2)
ρ_{calc} (g cm ⁻³)	1.605	1.300	1.400	1.343
μ (mm ⁻¹)	14.356	7.296	7.113	6.742
Reflections collected	36191	48427	100264	88948
Independent reflections	6750	4547	8876	9366
Parameters	315	328	518	516
R(int)	0.0418	0.0510	0.0394	0.0755
R1/wR2, ^[a] I $\geq$ 2 σ I (%)	2.72/6.76	4.29/12.04	1.81/4.27	3.62/8.90
R1/wR2, ^[a] all data (%)	2.85/6.87	4.48/12.14	2.05/4.39	4.33/9.44
GOF	1.019	1.270	1.044	1.062

^[a] $R1 = [\sum ||F_o| - |F_c||] / \sum |F_o|$; $wR2 = \{[\sum w[(F_o)^2 - (F_c)^2]^2] / [\sum w(F_o)^2]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(\sum F_o)^2 + 2(\sum F_c)^2] / 3$ and the A and B values are 0.0380 and 3.93 for **25.2C₆H₆**, 0.0257 and 18.57 for **26a.C₆H₆**, 0.0193 and 9.81 for **26b.tol**, and 0.0399 and 9.14 for **26c.C₆H₆**.

Table 10.8. Selected X-ray data collection and refinement parameters for **27a**, **27b**·2tol, **28**, and **29a**.

	27a	27b ·2tol	28	29a
Formula	C ₆₈ H ₁₀₀ Mg ₂ N ₁₀ P ₂	C ₈₁ H ₁₀₄ Mg ₂ N ₁₀ P ₂	C ₃₄ H ₅₀ GeN ₃ P	C ₅₀ H ₄₅ AuBF ₁₅ N ₃ P
CCDC	2263733	2263734	2263735	2263736
Fw [g mol ⁻¹]	1168.13	1328.30	632.35	1239.65
Crystal system	monoclinic	triclinic	tetragonal	orthorhombic
Space group	C2/m	P-1	P4 ₂ /n	P2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	18.1532(2)	13.0652(5)	18.5981(1)	14.6085(2)
<i>b</i> (Å)	19.1427(2)	13.1025(6)	18.5981(1)	18.1164(2)
<i>c</i> (Å)	12.43930(10)	14.2674(7)	20.7899(1)	19.2324(3)
α (°)	90	114.624(4)	90	90
β (°)	122.232(1)	113.693(4)	90	90
γ (°)	90	95.063(4)	90	90
<i>V</i> (Å ³)	3656.53(7)	1934.86(17)	7191.00(8)	5089.92(12)
<i>Z</i>	2	1	8	4
Radiation, λ (Å)	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184
Temp (K)	150(2)	150(2)	150(2)	150(2)
ρ_{calc} (g cm ⁻³)	1.061	1.140	1.168	1.618
μ (mm ⁻¹)	1.033	1.037	1.783	6.576
Reflections collected	18582	18706	77157	28937
Independent reflections	3960	7813	7522	9631
Parameters	199	459	408	669
R(int)	0.0202	0.0167	0.0252	0.0262
R1/wR2, ^[a] I $\geq$ 2 σ I (%)	3.46/10.15	6.11/16.10	3.01/8.21	2.30/5.69
R1/wR2, ^[a] all data (%)	3.71/10.47	6.33/16.21	3.46/8.69	2.46/5.84
GOF	1.051	1.126	1.038	1.051

^[a] $R1 = [\sum ||F_o| - |F_c||] / \sum |F_o|$; $wR2 = \{[\sum w[(F_o)^2 - (F_c)^2]^2] / [\sum w(F_o)^2]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [((F_o)^2 + 2(F_c)^2)/3]$ and the A and B values are 0.0610 and 1.85 for **27a**, 0.0364 and 3.66 for **27b**·2tol, 0.0418 and 3.32 for **28**, and 0.025 and 4.24 for **29a**.

Table 10.9. Selected X-ray data collection and refinement parameters for **29c**-2CH₂Cl₂, **31a**, **31b**, and **32**-tol.

	29c -2CH ₂ Cl ₂	31a	31b	32 -tol
Formula	C ₆₀ H ₅₇ AuBCl ₄ F ₁₅ N ₃ P	C ₅ H ₉ IN ₃ P	C ₁₁ H ₁₅ IN ₃ P	C ₇₃ H ₉₄ N ₄ Ni ₂ P ₂
CCDC	2263737	2263739	2263740	2219151
Fw [g mol ⁻¹]	1513.65	269.02	347.13	1206.88
Crystal system	monoclinic	tetragonal	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 4 ₃ 2 ₁ 2	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	12.4556(2)	8.9844(1)	13.2814(4)	10.8597(2)
<i>b</i> (Å)	23.8012(3)	8.9844(1)	6.9637(2)	30.8769(5)
<i>c</i> (Å)	21.2193(2)	22.4971(6)	13.6715(3)	19.7884(4)
α (°)	90	90	90	90
β (°)	93.566(1)	90	96.888(2)	94.019(2)
γ (°)	90	90	90	90
<i>V</i> (Å ³)	6278.46(14)	1815.95(6)	1255.32(6)	6619.0(2)
<i>Z</i>	4	8	4	4
Radiation, λ (Å)	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184	Mo K α , 0.71073
Temp (K)	150(2)	100(2)	150(2)	150(2)
ρ_{calc} (g cm ⁻³)	1.601	1.968	1.837	1.211
μ (mm ⁻¹)	6.979	28.879	21.062	0.661
Reflections collected	76418	20189	8550	38385
Independent reflections	13093	1866	2600	8775
Parameters	784	95	145	746
R(int)	0.0579	0.1251	0.0317	0.0485
R1/wR2, ^[a] I $\geq$ 2 σ I (%)	3.54/8.19	5.23/14.80	2.35/5.27	4.87/11.72
R1/wR2, ^[a] all data (%)	4.74/8.85	5.81/15.33	3.39/5.82	7.54/12.85
GOF	1.076	1.067	1.061	1.075

^[a] $R1 = [\sum ||F_o| - |F_c||] / \sum |F_o|$; $wR2 = \{[\sum w[(F_o)^2 - (F_c)^2]^2] / [\sum w(F_o)^2]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2] / 3$ and the A and B values are 0.0351 and 11.40 for **29c**-2CH₂Cl₂, 0.0981 and 0.18 for **31a**, 0.0250 and 4.24 for **31b**, and 0.025 and 4.24 for **32**-tol.

Table 10.10. Selected X-ray data collection and refinement parameters for **34**, **35**, **38**, and **39**.

	34	35	38	39
Formula	C ₆₃ H ₉₀ P ₃ Sc ₃	C ₉₆ H ₁₃₂ Au ₂ N ₄ P ₂ Sm ₂	C ₂₁ H ₄₈ ClFeP ₅	C ₂₂ H ₄₈ FeP ₆
CCDC	2219152	2219150	–	–
Fw [g mol ⁻¹]	1075.13	2098.62	546.74	554.27
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	C2/c	P2 ₁ /n	P2 ₁ /n	P-1
<i>a</i> (Å)	20.7447(6)	13.3207(2)	10.3513(2)	10.2560(8)
<i>b</i> (Å)	14.3514(3)	22.0522(3)	12.8996(3)	11.3762(6)
<i>c</i> (Å)	20.3469(5)	16.0911(2)	10.4389(2)	13.4097(8)
α (°)	90	90	90	69.674(5)
β (°)	105.036(3)	96.152(1)	100.865(2)	76.369(6)
γ (°)	90	90	90	76.833(6)
<i>V</i> (Å ³)	5850.2(3)	4699.55(11)	1368.89(5)	1407.42(17)
<i>Z</i>	4	2	2	2
Radiation, λ (Å)	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184	Cu K α , 1.54184
Temp (K)	150(2)	150(2)	150(2)	150(2)
ρ_{calc} (g cm ⁻³)	1.221	1.483	1.326	1.308
μ (mm ⁻¹)	3.956	15.617	8.117	7.573
Reflections collected	25739	57858	8539	19204
Independent reflections	5157	9796	2822	5819
Parameters	355	515	164	262
R(int)	0.0451	0.0663	0.0331	0.0312
R1/wR2, ^[a] I $\geq$ 2 σ I (%)	5.32/14.98	3.85/9.01	6.15/17.06	3.57/9.25
R1/wR2, ^[a] all data (%)	6.30/15.93	5.33/9.94	6.83/17.80	4.50/9.85
GOF	1.053	1.066	1.060	1.052

^[a] $R1 = [\sum ||F_o| - |F_c||] / \sum |F_o|$; $wR2 = \{[\sum w[(F_o)^2 - (F_c)^2]^2] / [\sum w(F_o)^2]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [((F_o)^2 + 2(F_c)^2)/3]$ and the A and B values are 0.1146 and 1.77 for **34**, 0.0384 and 11.77 for **35**, 0.0956 and 1.23 for **38**, and 0.0432 and 1.02 for **39**.

Table 10.11. Selected X-ray data collection and refinement parameters for **40**·C₆H₄F₂, **42**·2C₆H₄F₂·tol, **43**_{cr}, and **43**_{ci}.

	40 ·C ₆ H ₄ F ₂	42 ·2C ₆ H ₄ F ₂ ·tol	43 _{cr}	43 _{ci}
Formula	C ₁₀₈ H ₁₂₂ B ₂ F ₄₉ Fe ₂ N ₂ P ₉	C ₇₇ H ₁₅₆ F ₈ Fe ₃ O ₆ P ₁₄ S ₂	C ₁₈₇ H ₁₆₈ B ₂ F ₄₈ Fe ₃ P ₁₅	C ₁₈₆ H ₁₆₈ B ₂ ClF ₄₈ Fe ₃ P ₁₄
CCDC	–	–	–	–
Fw [g mol ⁻¹]	2791.12	1995.26	3988.92	3981.39
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	P-1	P ₂ ₁ /n	P ₂ ₁ /c	P ₂ ₁ /c
<i>a</i> (Å)	17.1919(3)	17.91460(10)	14.61410(10)	14.67791(16)
<i>b</i> (Å)	19.9592(4)	14.23790(10)	18.1787(2)	18.2166(2)
<i>c</i> (Å)	20.5528(4)	20.23880(10)	29.3143(3)	29.4461(3)
α (°)	77.776(2)	90	90	90
β (°)	71.655(2)	107.00	99.4640(10)	99.5099(12)
γ (°)	67.805(2)	90	90	90
<i>V</i> (Å ³)	6163.3(2)	4936.62(5)	7681.79(13)	7765.15(16)
<i>Z</i>	2	2	2	2
Radiation, λ (Å)	Cu K α , 1.54184	Cu K α , 1.54184	Mo K α , 0.71073	Mo K α , 0.71073
Temp (K)	150(2)	150(2)	150(2)	150(2)
ρ_{calc} (g cm ⁻³)	1.508	1.342	1.725	1.722
μ (mm ⁻¹)	4.074	6.526	0.539	0.539
Reflections collected	164185	126872	60095	60095
Independent reflections	25631	10294	16039	16039
Parameters	1714	590	928	918
R(int)	0.0450	0.0417	0.0589	0.0589
R1/wR2, ^[a] I $\geq$ 2 σ I (%)	5.28/14.04	4.10/11.24	9.38/21.90	9.39/21.75
R1/wR2, ^[a] all data (%)	6.30/15.10	4.27/11.41	11.41/23.04	11.42/22.89
GOF	1.040	1.067	1.075	1.067

^[a] $R1 = [\sum ||F_o| - |F_c||] / \sum |F_o|$; $wR2 = \{[\sum w[(F_o)^2 - (F_c)^2]^2] / [\sum w(F_o)^2]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(\sum F_o)^2 + 2(F_c)^2] / 3$ and the A and B values are 0.0808 and 7.36 for **40**·C₆H₄F₂, 0.0623 and 4.75 for **42**·2C₆H₄F₂·tol, 0.0651 and 35.51 for **43**_{cr}, and 0.0632 and 36.79 for **43**_{ci}.

10.2 General computational methods

Density functional theory (DFT) calculations were performed using the ORCA 4.2.0 or 5.0.2 software packages.^[35–37] All methods were used as implemented. Analytical frequency calculations were carried out to verify all non-fragment geometries as either true minima ($N_{\text{imag}} = 0$) or saddle points ($N_{\text{imag}} = 1$). Natural Population Analysis were carried out using the NBO 7.0 program.^[38] Energy decomposition analysis was carried out using the ETS-NOCV approach^[39,40] as implemented in ORCA 5.0.2, with difference densities generated by Multiwfn 3.8.^[41] Quantum Theory of Atoms in Molecules (QTAIM) topology analysis was carried out using Multiwfn 3.8.^[41] Electrostatic potential surfaces were calculated using Multiwfn 3.8.^[41]

Sections 1.1.1, 1.3.2, and 4.3.1: Single point and geometry optimizations were performed using the ω B97X-D3 functional,^[42] the zero order regular approximation (ZORA) using HF model densities, and the relativistically contracted quadruple-zeta basis set with added polarization functions ZORA-def2-QZVPP.^[43,44]

Section 2.2.4: Geometry optimizations and single point calculations were performed using Becke's '88 gradient exchange functional,^[45] and Perdew's '86 correlation functional (BP86),^[46] with the resolution of identity (RI-J) approximation.^[47] Geometry optimizations were performed using the Karlsruhe split valence basis set (def2-SVP) with the general Weigend J auxiliary basis set (def2/J), and single point energies were obtained using the Karlsruhe triple zeta valence basis set (def2-TZVP).^[48,49] Single point energies were corrected using Grimme's D3 dispersion correction with Becke-Johnson damping (D3BJ),^[50] and gCP geometric counterpoise correction.^[51]

Sections 2.2.6, 5.3.3, 6.3.3, 8.2.2, and 8.3.4: Geometries were optimized using the B97-D3 functional and the def2-SVP basis set.^[48,52] Single point calculations were performed using the ω B97X-D3 functional^[42] and the Resolution of Identity approximation (RJCOSX),^[53,54] and corrected for relativistic effects using the zeroth order regular approximation (ZORA). The segmented all-electron relativistically contracted basis set SARC-ZORA-TZVPP was used for Au and I, and the relativistically contracted triple-zeta basis set ZORA-def2-TZVPP was used for all other atoms, along with the SARC/J auxiliary basis set.^[43,44]

Section 3.3: ³¹P NMR predictions were performed using optimized geometries obtained by the PBEh-3c composite method developed by Grimme and coworkers,^[55] which uses a composite Gaussian AO

basis set (def2-mSVP) for all atoms. The NMR shielding tensors were calculated using the Gauge Including Atomic Orbitals (GIAO) method,^[56–58] and were carried out with the one-parameter hybrid Perdew-Burke-Ernzerhof (PBE0) functional,^[59] using Jensen’s segmented contracted pcsSeg-3 basis set for phosphorus,^[60] and the composite def2-mSVP basis set for all other atoms. Relative chemical shifts were obtained using H₃PO₄ in water as a reference ($\delta = 0$ ppm), and scaled using an empirical linear scaling method that has been previously shown to improve the accuracy of chemical shift predictions.^[61–65] Solvent corrections for all structures were performed using the conductor-like continuum polarization model (CPCM), using spherical gaussian charges and a scaled van der Waals solute cavity surface.^[66,67]

Sections 4.3.2, 4.3.4, 7.2.3, 7.2.4, 7.2.5, and 7.3: Geometries were optimized using the B97-D3 functional and the def2-SVP basis set.^[48,52] Single point calculations were performed using the ω B97X-D3 functional^[42] and the Resolution of Identity approximation (RIJCOSX),^[53,54] and corrected for relativistic effects using the zeroth order regular approximation (ZORA). The segmented all-electron relativistically contracted basis set SARC-ZORA-TZVP was used for Au and Rh, and the relativistically contracted triple-zeta basis set ZORA-def2-TZVP was used for all other atoms, along with the SARC/J auxiliary basis set.^[43,44] Nucleus-Independent Chemical Shifts (NICS) were computed using the PBE0 functional and def2-TZVP basis set,^[48,59] and using the Gauge-Independent Atomic Orbitals (GIAO) method.

Sections 5.2.4 and 5.2.5: Geometries were optimized using the PBEh-3c method and the def2-mSVP basis set.^[55] Single point calculations were performed using the ω B97X-D3 functional^[42] and the Resolution of Identity approximation (RIJCOSX),^[53,54] and corrected for relativistic effects using the zeroth order regular approximation (ZORA). The segmented all-electron relativistically contracted basis set SARC-ZORA-TZVP was used for all heavy atoms (Rh, W, and Au), and the relativistically contracted triple-zeta basis set ZORA-def2-TZVP was used for all other atoms, along with the SARC/J auxiliary basis set.^[43,44]

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