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Synthesis and Characterisation of Dimolybdenum and Dirhenium Quintuple Bond Precursors

Andrew Faben

A thesis presented to the University of Huddersfield, School of Applied Sciences, as fulfilment for the Degree of MSc by Research (Chemistry).

Submitted

List of Abbreviations

Ad	Adamantyl
Ar’	C_6H_3-2,6-(C_6H_3-2,6-^{i}Pr$_2$)$_2$
CV	Cyclic voltammogram
DCM	Dichloromethane
DCB	1,2-Dichlorobenzene
DCyBA	Dicyclohexylbenzamidinate
DFT	Density functional theory
Dipf	N,N’-bis(2,6-diisopropylphenyl)formamidinate
DmAniF	Di(*m*-methoxyphenyl)formamidinate
DMSO	Dimethylsulfoxide
Dpf	Diphenylformamidinate
Dppa	N,N’-bis(diphenylphosphino)amine
Dppe	1,2-bis(diphenylphosphino)ethane
Dppm	1’1-bis(diphenylphosphino)methane
Et_2O	Diethyl ether
Fc	Ferrocene
HOMO	Highest occupied molecular orbital
ILCT	Intraligand charge transfer
IR	Infra-red
Ippa	Iminophosphonamide
MS	Mass spectrometry
NBO	Natural bond order
n-BuLi	*n*-butyllithium

NMR	Nuclear magnetic resonance
PCP	1,3-diphosphapropene
RT	Room temperature
TBA	Tetrabutylammonium
t-BuLi	*t*-butyllithium
TFA	Trifluoroacetate
THF	Tetrahydrofuran
Tmpf	N,N’-bis(2,4,6-trimethylphenyl)formamidinate
Tpg	1,2,3-triphenylguanidinate
TMS	Trimethylsilyl
UV	Ultraviolet

Abstract

The year 1964 saw the isolation of the first quadruply bonded complex which sparked the desire to prepare more of these compounds. It was in 1979 that theoretical scientists first proposed that a quintuple bond could exist with a D_{3h} geometry of the formula M_2L_6 the desire to isolate these compounds was set in motion, it was later actualised in 2005 when the first quintuple bonded dichromium complex was isolated. This discovery led to the generation of more quintuple bond complexes using the group VI elements; chromium and molybdenum and a host of bidentate N-donor ligands however, no such complexes exist that use the group VII elements (which could theoretically form a quintuple bond as well) or a different type of ligand, such as a P-donor.

A number of quadruply bonded dimolybdenum and dirhenium complexes have been synthesised as precursors for the production of new quintuple bonded dimolybdenum complexes and the first dirhenium quintuple bond. The employment of bulky ligands, such as bidentate phosphine, formamidinate and guanidinate ligands were used to stabilise the quadruply bonded precursors and improve the stability of the target quintuply bonded complexes. Reactions between $Mo_2(O_2CCH_3)_4$ [**1**] and bis(diphenylphosphino)amine (Hdppa) and $(NH_4)_4Mo_2Cl_8$ [**2**] with 1,2-bis(diphenylphosphino)ethane (dppe) in THF and ethanol respectively successfully yielded the bis-substituted products: $Mo_2(Hdppa)_2Cl_4$ [**3**] and $Mo_2(dppe)_2Cl_4$ [**4**] respectively. Meanwhile reacting $(TBA)_2Re_2Cl_8$ [**5**] with the respective formamidine or guanidine in DCB yielded $Re_2(dipf)_2Cl_4$ [**6**] (dipf = N,N'-bis(2,6-diisopropylphenyl)formamidinate), $Re_2(tmpf)_2Cl_4$ [**7**] (tmpf = N,N'-bis(2,4,6-trimethylphenyl)formamidinate) and $Re_2(tpg)_2Cl_4$ [**8**] (tpg = 1,2,3-triphenylguanidinate). Attempts were made to prepare the bis substituted dimolybdenum complex $Mo_2(tpg)_2Cl_4$, however it could not be fully characterised. The preparation of other dirhenium complexes utilising dicyclohexylbenzamidinate (DCyBA), diphenylformamidine (dpfH), an iminophosphonamide ligand and Hdppa as bridging ligands were attempted but yielded unsuccessful results.

UV-Vis spectra, IR spectra and cyclic voltammograms (CV) for complexes **[3]**, **[4]**, **[6]**, **[7]** and **[8]** are reported and discussed in this thesis and why they have the possibility to form a metal-metal quintuple bond. The UV-vis spectra of the molybdenum complexes, **[3]** and **[4]** show $\delta \rightarrow \delta^*$ transitions at 700 nm and 680 nm, respectively. The dirhenium complexes, **[6]**, **[7]** and **[8]**, exhibit $\delta \rightarrow \delta^*$ transitions at 621, 615 and 628 nm, respectively.

The CV of **[3]** displays a broad irreversible reduction at an $E_{1/2}$ value of -1.534, meanwhile, complexes **[4]** has two reversible one-electron reductions at $E_{1/2}$ = -1.829 V and -1.943 V. For the dirhenium complex **[6]**, two reversible one-electron reductions at $E_{1/2}$ = -1.348 V and -1.623 V are seen. Complex **[7]** displays one broad, irreversible reduction at $E_{1/2}$ = -1.898 V, meanwhile complex **[8]** had two one-electron reductions with one at $E_{1/2}$ = -1.374 V being irreversible and the second reduction being reversible at an $E_{1/2}$ value of -1.549 V.

Reductions using KC_8 and potassium hexafluorophosphate (as a halide abstractor) were attempted on complexes **[3]**, **[4]**, **[6]**, **[7]** and **[8]**, but were all unsuccessful resulting in unresolvable ^{1}H NMR spectra.

This thesis, while unsuccessful in isolating a quintuply bonded dimetal complex, has produced quadruply bonded dimolybdenum and dirhenium complexes that may still have the potential to be chemically reduced with cyclic voltammograms showing they can be electrochemically reduced.

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Dedications and Acknowledgements

I wish to thank Dr Nathan Patmore for granting me the opportunity to work in his research group and all the help and guidance he provided to me throughout the year.

I would also like to thank Ollie Glenister for his unending patience in teaching me all the necessary techniques associated with the research and sharing his knowledge both in and out of the lab.

1. Introduction

1.1 *The First Multiply Bonded Multinuclear Metal Complexes*

While not initially known to have a metal-metal quadruple bond, chromium (II) acetate, (Figure 1) was the first isolated compound of its kind by Eugène Peligot in 1844.[1,2] Its high metal-metal bond order was not recognised until after Cotton and co-workers studied the crystal structure of $[Re_2Cl_8]^{2-}$ in 1964 which was found to possess a Re-Re quadruple bond indicated by the short bond length between the two metals.[3]

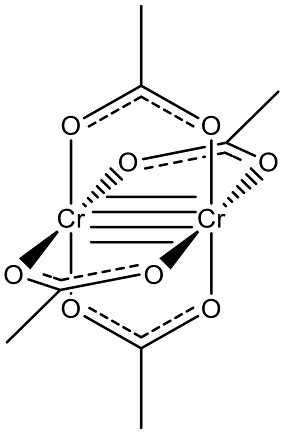

Figure 1: Structure of chromium (II) acetate.

While Peligot's complex was the first multiply bonded complex, it was the discovery of the crystal structure of $CsReCl_4$ in 1963 by two separate teams of scientists that sparked the interest in multiple metal-metal bonding.[4,5] The structure was found to be trinuclear with the three Re atoms forming a double bond to one another and therefore possessing a molecular formula of $Cs_3Re_3Cl_{12}$.

1.2 *Proving the Existence of a Quadruple Bond*

First isolated by Soviet chemists (but mislabelled as $[Re_2Cl_8]^{4-}$) and later resolved by Cotton, $[Re_2Cl_8]^{2-}$ was the key to recognition of a quadruple bond.[6,7] The indication of a metal-metal quadruple bond was due to the short Re-Re bond length of 2.24 Å that implied that the valence electrons of Re had some degree of interaction with one another.[8] Cotton first explained that the s, p_x, p_y and $d_{x^2-y^2}$ hybrid orbitals form four Re-Cl bonds, meanwhile a σ-bond is formed from hybrid the overlap of a pair of Re d_{z^2}-p_z hybrid orbitals and two π-bonds are formed from the d_{xz} and d_{yz} orbital pairs (Figure 2). The final unassigned metal orbitals are the d_{xy} orbitals, which both overlap (less favourably than the σ- and π-bonds) to form a δ-bond. The chlorides are in an eclipsed rather than a staggered conformation (Figure 3) due to the δ-bond formation.

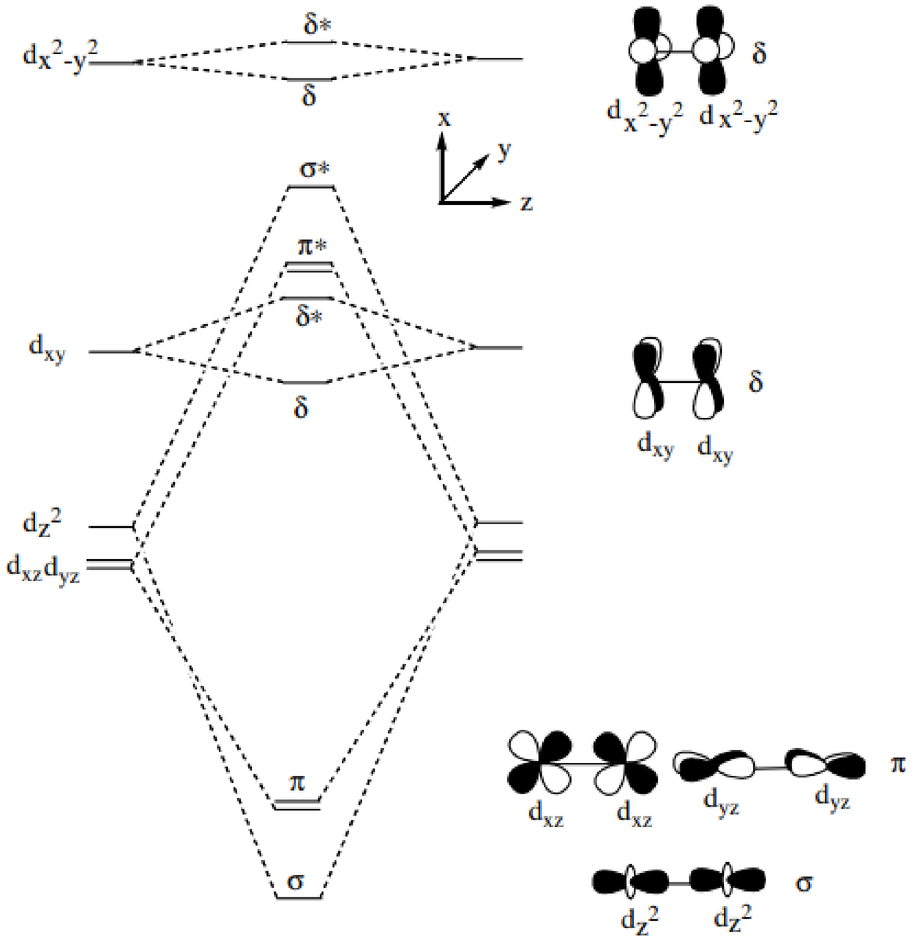

Figure 3: Energy level diagram of $[Re_2X_8]^{2-}$.[10]

The absorption spectrum of $[Re_2Cl_8]^{2-}$ showed an absorption at 14000 cm^{-1} (~715 nm) which was first ruled out as being the $\delta \rightarrow \delta^*$ transition as this transition is symmetry allowed and was weaker than what was expected of such a transition.[9] The transition was initially labelled as a $\delta \rightarrow \sigma_n$ MLCT but was later corrected as the low intensity of the $\delta \rightarrow \delta^*$ transition was found to be a result of the small overlap between the two *d* orbitals that form that *δ* bond.[3]

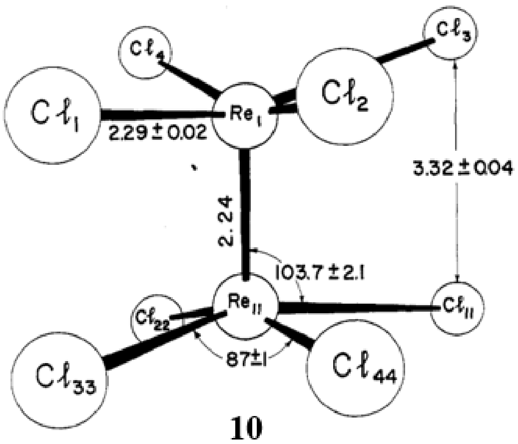

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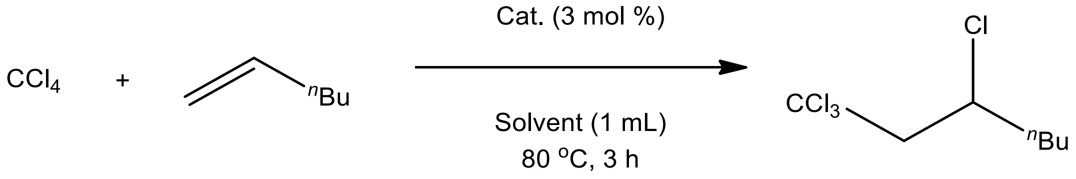
Figure 3: Energy level diagram of $[Re_2X_8]^{2-}$.[10]

1.3 *Uses of Quadruply Bonded Complexes*

Quadruply bonded paddlewheel dimolybdenum complexes have been utilised as catalysts in radical addition reactions of CCl_4 and trihaloalkanes to various alkenes to generate haloalkane products (Scheme 1).[11] The authors propose that the Mo_2 core transfers a single electron to the alkyl halide to generate the carbon radical, $\cdot CR_3$, while the halide anion formed may interact with the Mo_2 core (but may also behave as a separate anion). Addition of the carbon radical to the alkene forms Mo_2(II, III) and a new radical species whereby the alkyl chain has increased relative to the alkene used. A one-electron reduction of the dimolybdenum complex by the radical leads to regeneration of the Mo_2(II, II) catalyst.



Scheme 1: Radical addition of CCl_4 to an alkene using a group 6 dimetal complex.

The same researchers also found these paddlewheel complexes (Figure 4) could be used as catalysts in radical polymerisation reactions of methyl methacrylate (MMA) to generate PMMA.

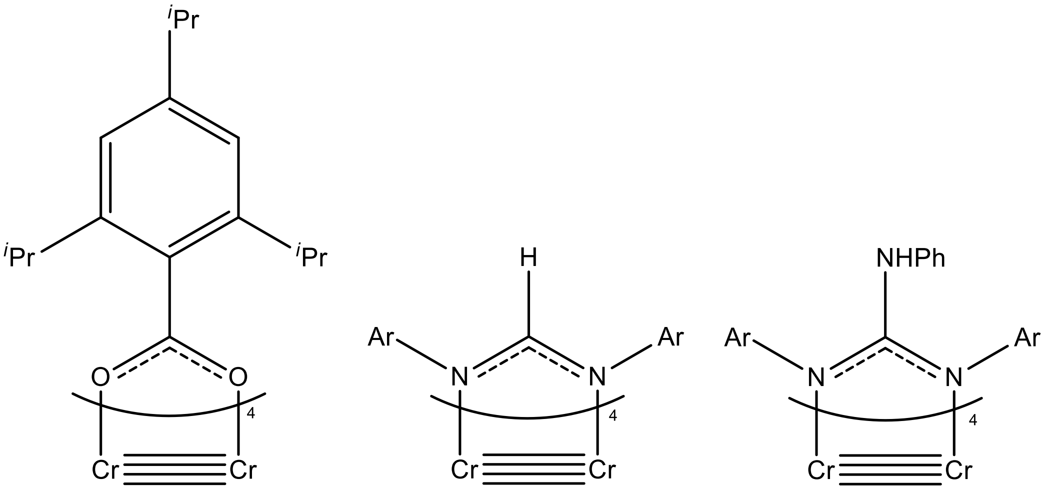


Figure 4: Group 6 catalysts.

Quadruply bonded complexes have also been used to examine electron transfer processes commonly using 'dimers of dimers' of dimolybdenum and ditungsten with a formation of $[M_2\text{-bridge-}M_2]^+$ (the bridge is an organic conjugated linker).[12] The study of these complexes can aid in the understanding of the mechanism, rate constant and activation barriers for electron transfer processes that occur in biological systems.[13,14]

Quadruply bonded tetracarboxylate complexes of dimolybdenum and ditungsten ($M_2(O_2CR)_4$) possess a long-lived singlet and triplet states suggesting that they could be suitable to compete with other well-known Ru^{2+} dyes that are currently used as photosensitisers (compounds that induce a chemical change within a different molecule in a photochemical process).[15,16]

1.4 *Higher Bond Orders*

Sextuple bonding has been achieved in the gaseous forms of Mo_2 and W_2 at low temperatures using laser vaporisation techniques.[17,18] The sextuple bond is formed from an overlap of the orbitals known to make a quadruple bond in addition to a further δ bond and a σ bond being added. Isolating these compounds for practical use may seem unrealistic, but these studies along with theoretical investigations on Nb_2 helped aid in the understanding of the bonding nature of these molecules, in addition to recognising the feasibility of experimental preparation of quintuply bonded complexes.[19]

In $[Re_2Cl_8]^{2-}$ the $d_{x^2-y^2}$ orbitals of the metal are used in ligand bonding; however, this orbital could theoretically be utilised to form a second δ-orbital if the δ and δ^* are reduced in energy such that the *δ*-bonding MO is at a lower energy than the *δ**-antibonding MO which would allow a bond order of five to be achieved. Hoffmann *et al.* were the first to suggest that a metal-metal quintuple bond could be made with a D_{3h} symmetry of the formula $M_2(LL)_3$ (where LL is a bidentate ligand, Figure 5).[20]

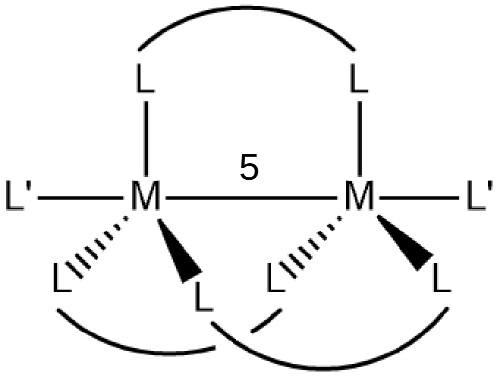


Figure 5: Hoffmann's theoretical structure of a quintuply bonded D_{3h} compound.

A second theoretical study published in 2001 by Weinhold and Landis predicted that group six metals (chromium, molybdenum and tungsten) with a *trans*-bent M_2H_2 geometry could form a metal-metal quintuple bond (using natural bond orbital (NBO) theory) which attempt to provide an accurate "natural Lewis structure" of transition metal complexes.[21]

Weinhold and Landis' theory was later actualised by Power *et al.* in 2005, after they isolated the first dichromium complex (Figure 6) possessing a metal-metal quintuple bond using a bulky monovalent terphenyl ligand with a Cr-Cr bond length of 1.8351(4) Å (noticeably shorter than the Re-Re quadruple bond in $[Re_2Cl_8]^{2-}$).[22]

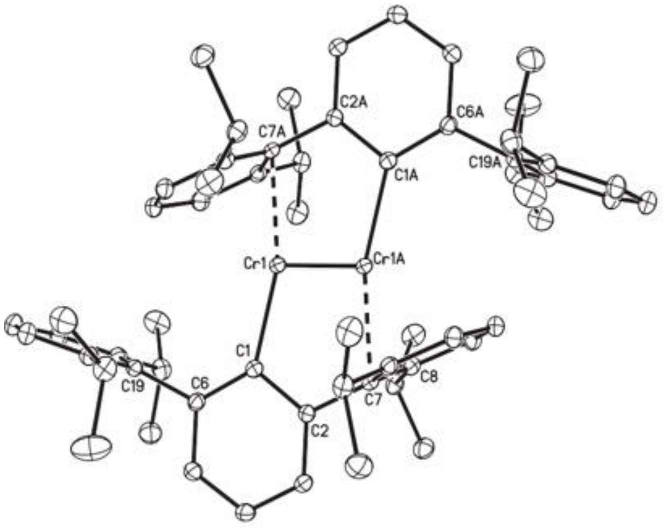


Figure 6: Crystal structure of Power's quintuply bonded dichromium complex with H atoms omitted.[22]

1.5 *Formation of a Quintuple Bond*

There are several criteria required in order to form a metal-metal quintuple bond. Each metal fragment would require a high spin configuration such that all five of their d-orbitals are singly occupied (and therefore have a d^5 electronic configuration) in order to allow maximum overlap and form a quintuple bond (Figure 7).[23,24] Additionally, suitable choice of ligand is essential in forming a high bond order bimetallic complex as the spin states of the metals are affected by the type of ligand bonded to them, thus σ-donor ligands should be avoided as they can induce low spin states by raising the σ^* orbitals of the metal. In order to maintain a sufficient overlap of the δ-orbitals, the coordinating ligand must be a weak π-donor ligand (such as an amine or phosphine). Use of π-acceptor ligands would reduce the overlap of the metal d-orbitals as a result of increased metal-ligand π-bonding. Furthermore, the metal centre should have a low coordination number to the ligands so that the d orbital overlap is maximised. Finally, in order to stabilise the quintuple bond, ligands that provide a steric bulk to the complex need to be employed. These prevent oligomerisation and polymerisation of the complex and help prevent unwanted reactions with the electron-rich dimetal core.

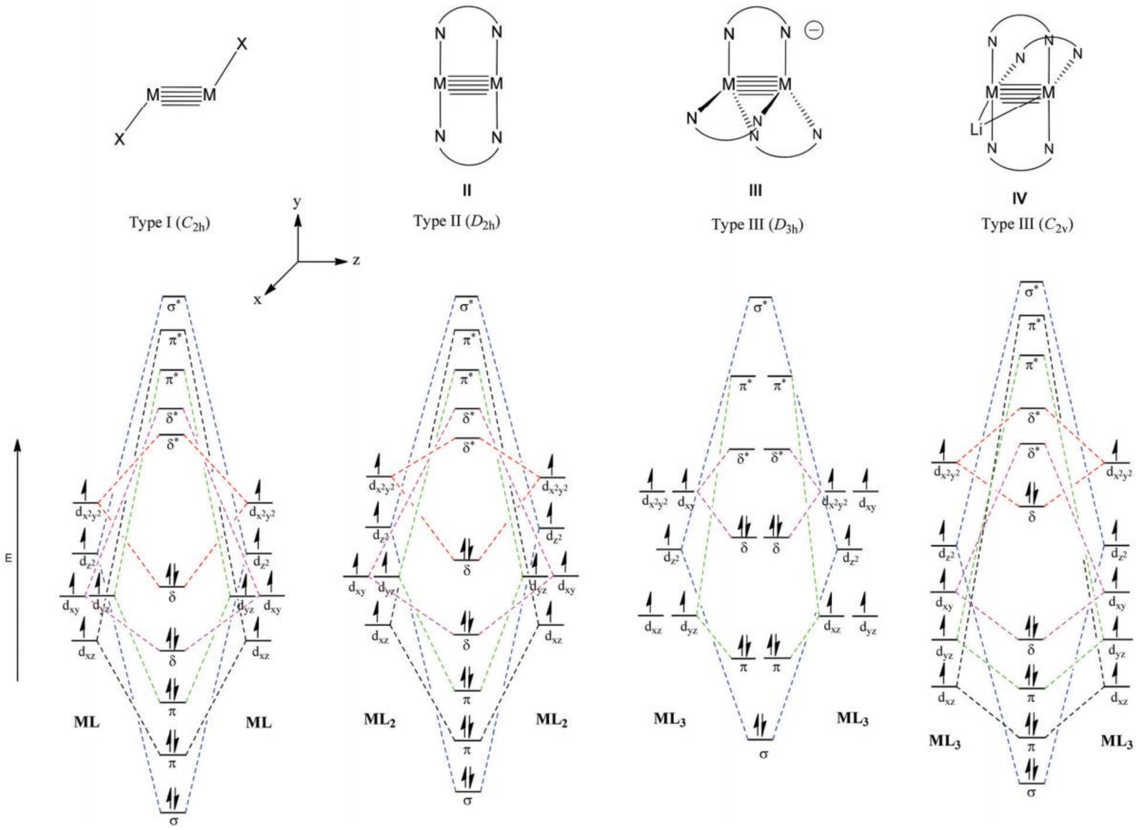


Figure 7: Geometries and respective MO diagrams of quintuply bonded complexes.[24]

1.6 *Progression from Power*

Following on from Power's landmark discovery of the first dichromium quintuple bond, a number of Cr-Cr and Mo-Mo quintuple bonds have since been isolated. The Theopold group unveiled the next dichromium quintuple bond with a Type II (D_{2h}) geometry (Figure 8) which was supported by two diazadiene ligands *trans* to one another with a bond length of 1.8028(9) Å.[25]

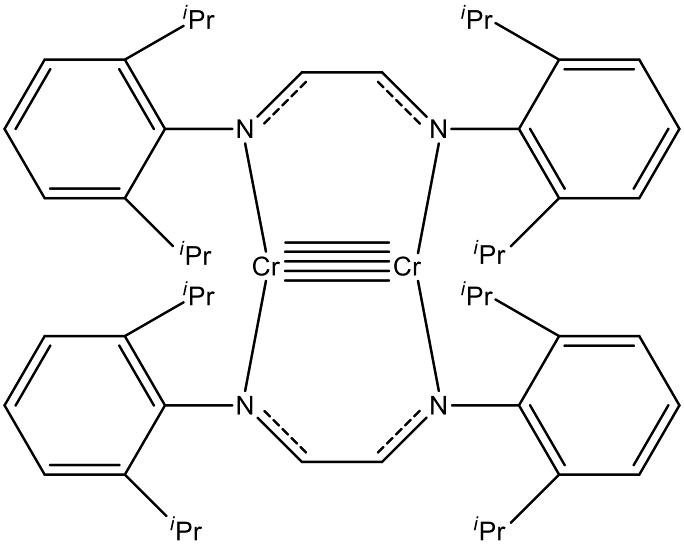


Figure 8: Theopold's diazadiene complex.

Tsai *et al.* then went on to make a series of dichromium and dimolybdenum complexes using various formamidinate ligands, with his first being an anionic lantern-type structure of Type III (D_{3h}) with the dichromium unit being surrounded by three ligands (Cr-Cr bond length of 1.7397(9) Å (Figure 9).[26] His group then went on to make a Type II (D_{2h}) dichromium complex using four different types of formamidinate complexes and then successfully isolated the first dimolybdenum quintuply bonded complexes in 2009 (Figure 10) using the *N,N'*-bis(2,6-diisopropylphenyl)formamidinate (dipf) ligand and a related substituent.[27,28] The bond lengths of these dimolybdenum complexes were notably longer than that of the dichromium formamidinate complexes by approximately 0.3 Å.

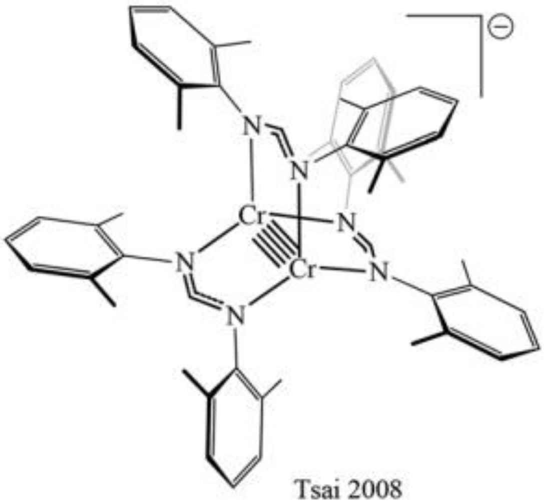


Figure 9: Tsai's lantern complex.[24,26]

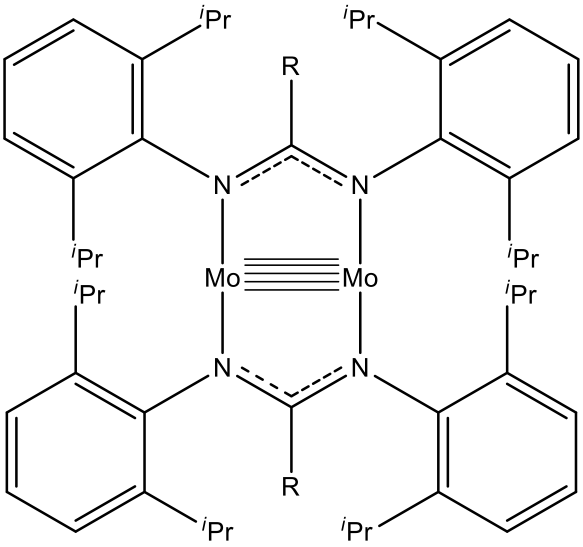


Figure 10: Tsai's dimolybdenum complexes (R = H, Ph).

The type IV (C_{2v}) geometry was discovered in 2012 by the Tsai group with the isolation of a tris-substituted formamidinate complex with a lithium atom bonding to both of the Mo atoms with the longest quintuple bond discovered of 2.0612(4) Å.[29]

An unusual example of the Type III quintuple bond is Lu's heterobimetallic Mn-Cr quintuply bonded complex which possesses a fairly short bond length of 1.8192(9) Å and the employment of a heptadentate ligand (Figure 11).[30]

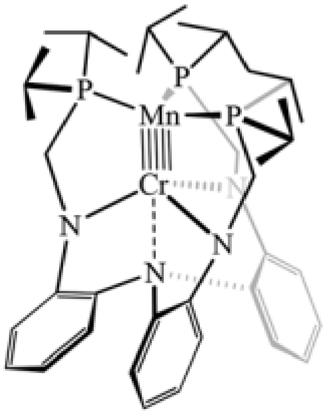


Figure 11: Lu group's Mn-Cr quintuply bonded complex.[24]

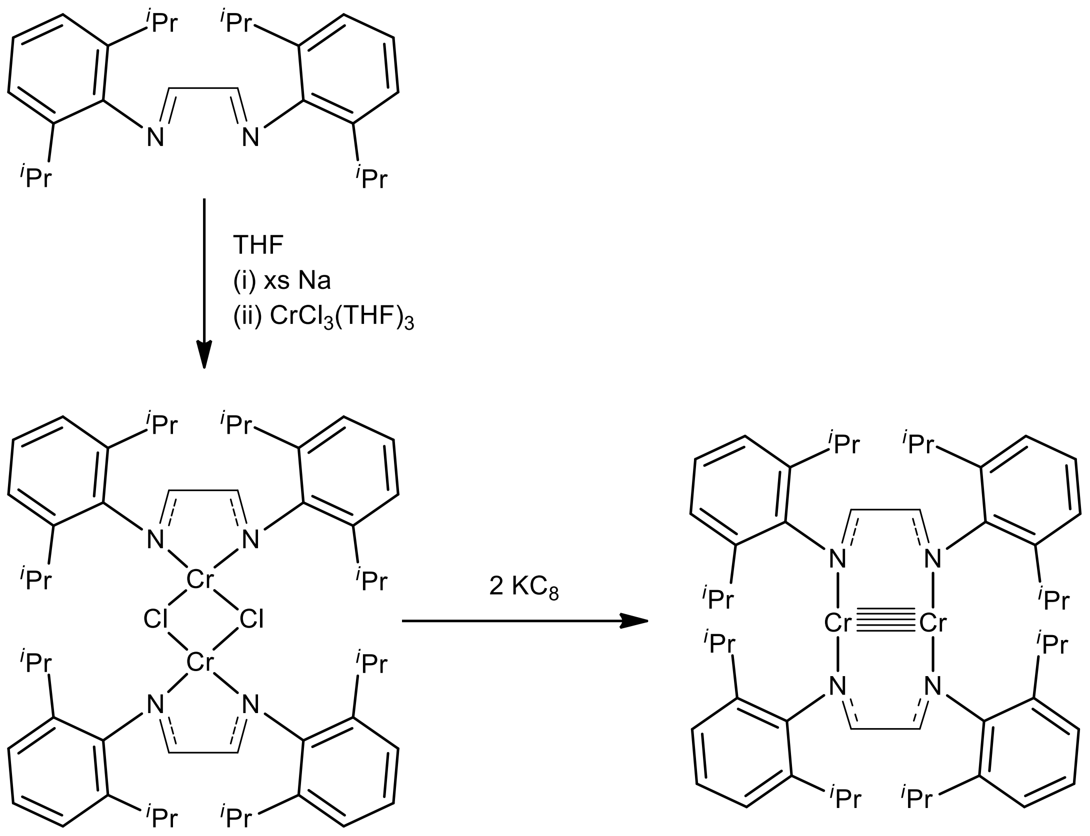
1.7 *General Synthetic Routes to Obtain a Quintuple Bond*

There are two known pathways to preparing a quintuply bonded complex. The first, and most abundant, is analogous to the Wurtz reductive coupling which was performed by Power *et al.* to prepare four quintuply bonded complexes in 2005 and 2007.[22,31,32] A metal halide, such as $CrCl_3(THF)_3$ or $[Mo_2Cl_8]^{4-}$, is reacted with an anionic ligand to form a mono- or binuclear chloride and subsequently reduced (most commonly with two equivalents of KC_8) to yield the quintuply bonded species (Scheme 2).[23]

$$\text{Metal chloride} \xrightarrow{\text{Anionic ligand}} \text{Mono- or binuclear chloride} \xrightarrow{\text{Reduction}} \text{Quintuple bond complex}$$

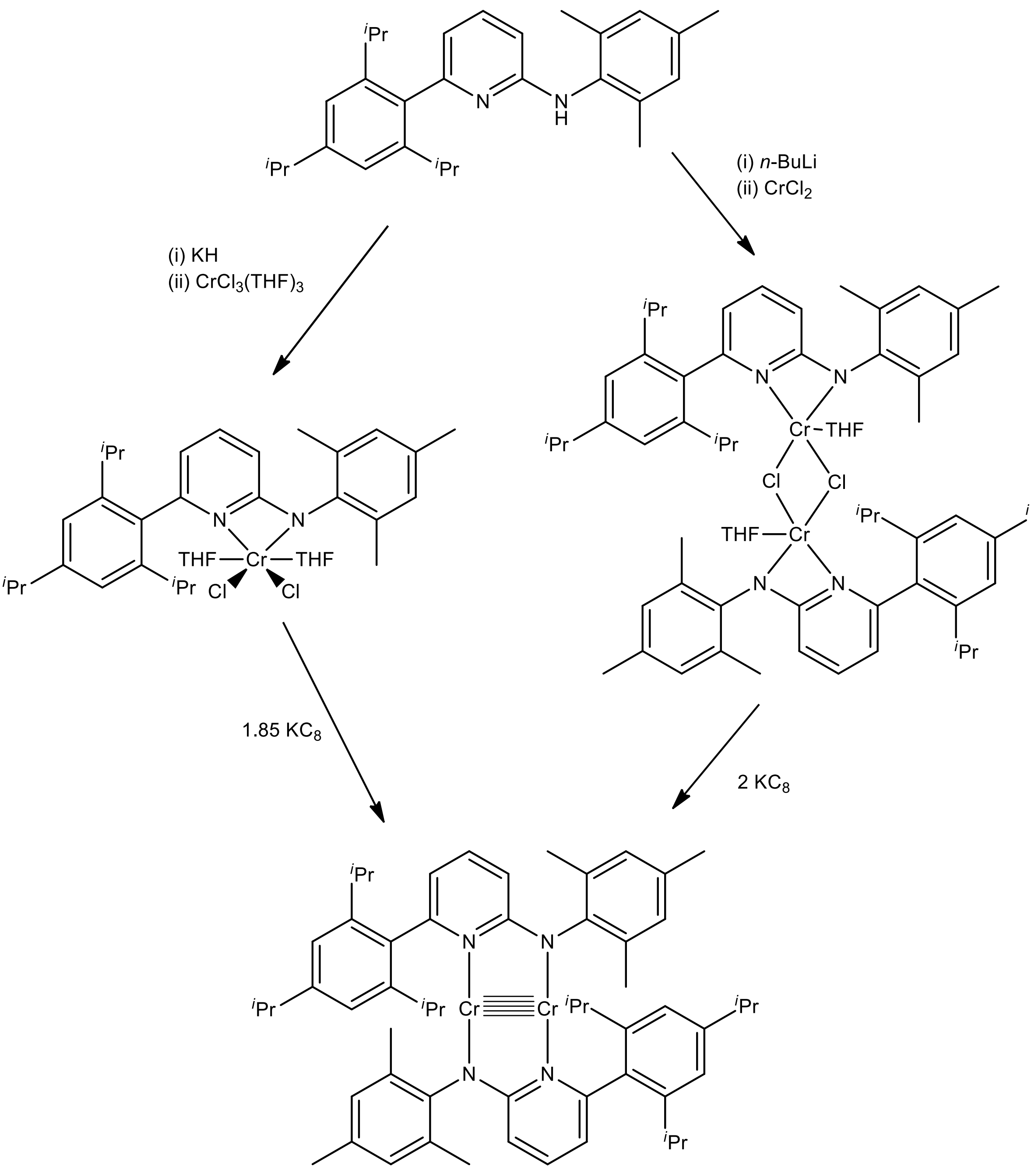
Scheme 2: Most common synthetic route to preparing a quintuple bond.

Theopold's dichromium diazadiene complex utilised the dichloro-bridged intermediate (Scheme 3) by way of stirring the anionic ligand (formed by stirring the ligand with excess sodium in THF for two days) with $CrCl_3(THF)_3$ for five hours and then by reducing it with KC_8 overnight.[19]



Scheme 3: Theopold's synthetic route.

Several of the dichromium complexes that have been made have the dichloro-bridged intermediate, such as Tsai's lantern complex (Figure 9) and Kempe's amidopyridine dichromium complex, which produced a mononuclear dichloro species when the ligand was reacted with KH and $CrCl_3(THF)_3$ or a dichloro-bridged when reacted with *n*-BuLi and $CrCl_2$ (Scheme 4).[33]

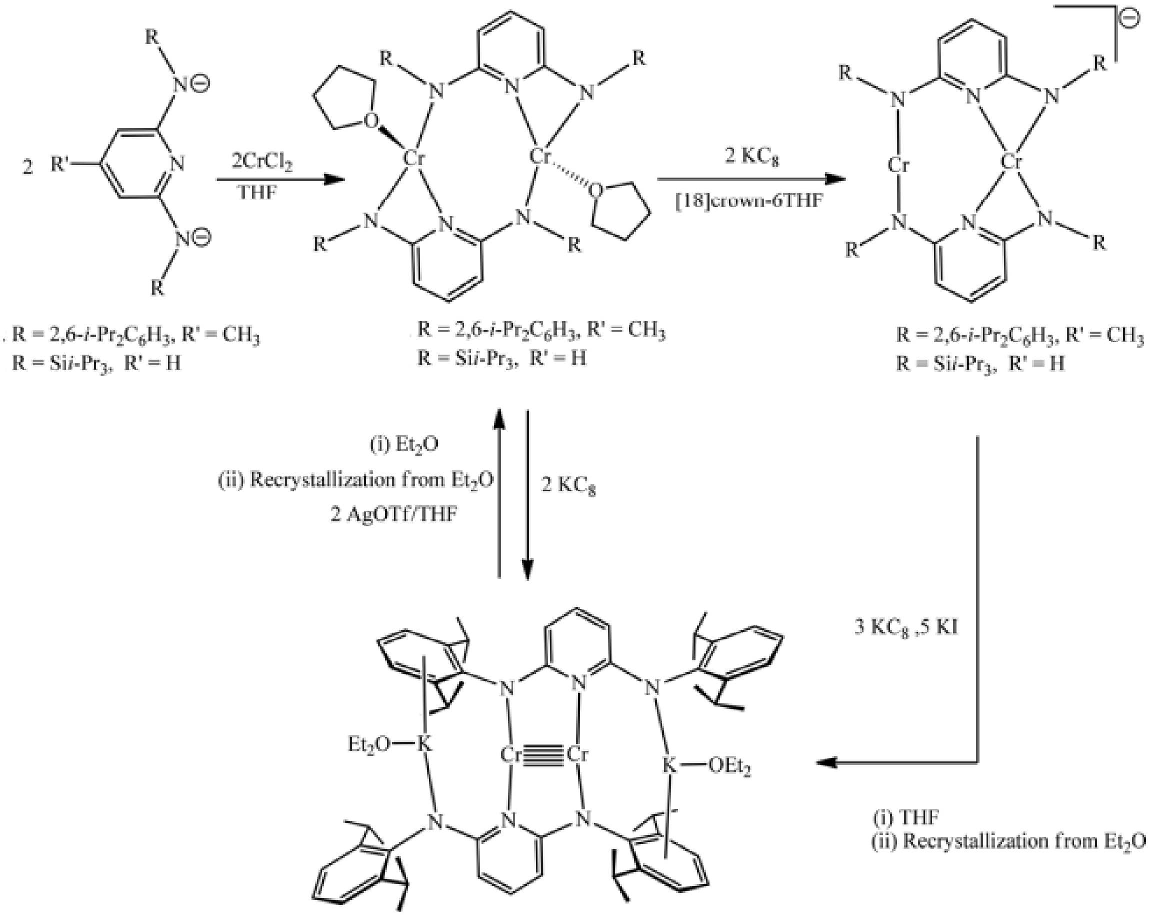


Scheme 4: Kempe's diverging synthetic routes to isolate a quintuply bonded complex.

Lu's group isolated the heterobimetallic complex containing an Mn-Cr quintuple bond (Figure 11) by way of deprotonating the heptadentate tris(phosphinoamido)amine ligand with *n*-BuLi and then reacting it with $CrCl_3$. The intermediate mono-chromium complex was then reacted with $MnCl_2$ and reduced with KC_8.[30]

The second method that has been used to prepare a quintuple bond avoids the chloro-bridging process by using derivatives of the bulky amidopyridine ligand (Scheme 5) and treating them with $CrCl_2$ in THF yielded a mixed-valent dichromium complex (with no Cr-Cr bond).[34]

Performing a one-electron reduction and treatment with [18]crown-6.THF produced a mixed-valent anionic complex with the Cr-Cr spacing being shorter. Further reduction and treatment with an excess of KI lead to the isolation of the quintuply bonded species that is stabilised by the potassium cations bonding to the ligands (and not the transition metal).

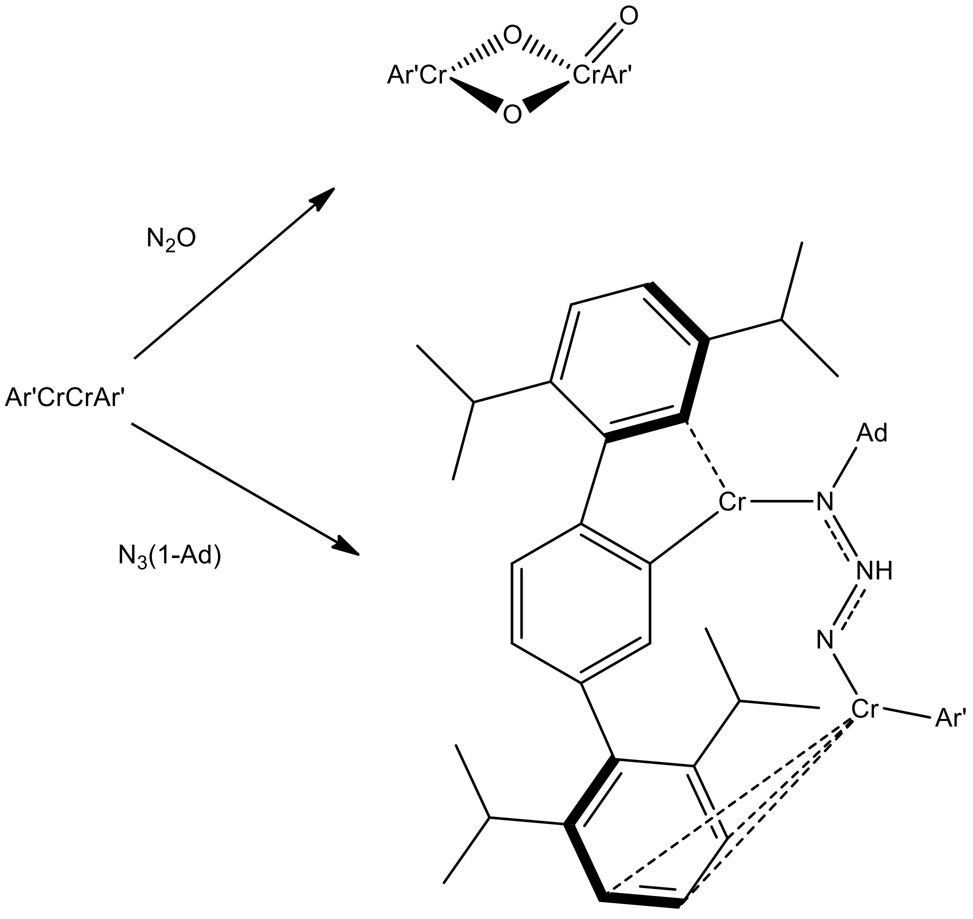


Scheme 5: Tsai's alternative method to the preparation of a quintuple bond.[24]

1.8 ***Reactivity of Quintuply Bonded Complexes***

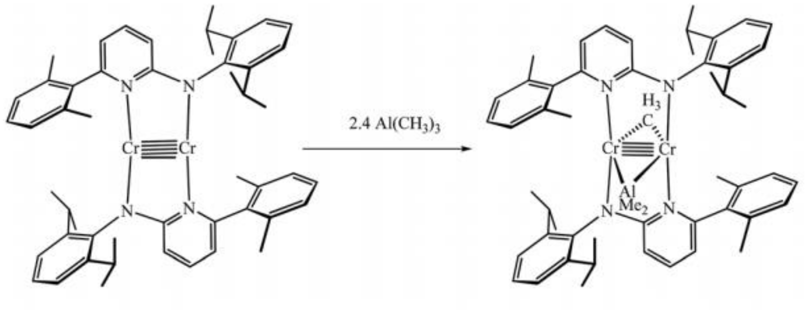
The quintuple bond unit is expected to be highly reactive and reducing towards small molecules due to the large steric bulk presented by the ligands preventing larger molecules from reacting with the complex.

The first study on the reactivity of the quintuple bond was on Power's Cr-Cr complex with N_2O and N_3(1-Ad) (Ad = adamantyl) which resulted in total cleavage of the quintuple bond (Scheme 6) to yield Ar'Cr(μ-O)$_2$Cr-(O)Ar' and Ar'Cr(μ_2:η^1,η^3-N_3(1-Ad))CrAr' (where Ar' is the bulky terphenyl ligand) respectively.[35] The reaction of Ar'CrCrAr' with N_2O resulted in a mixed valent state as one of the metal atoms is coordinated to an additional oxygen atom (along with the two oxo bridges) resulting in a Cr^{3+} and Cr^{5+} centre.



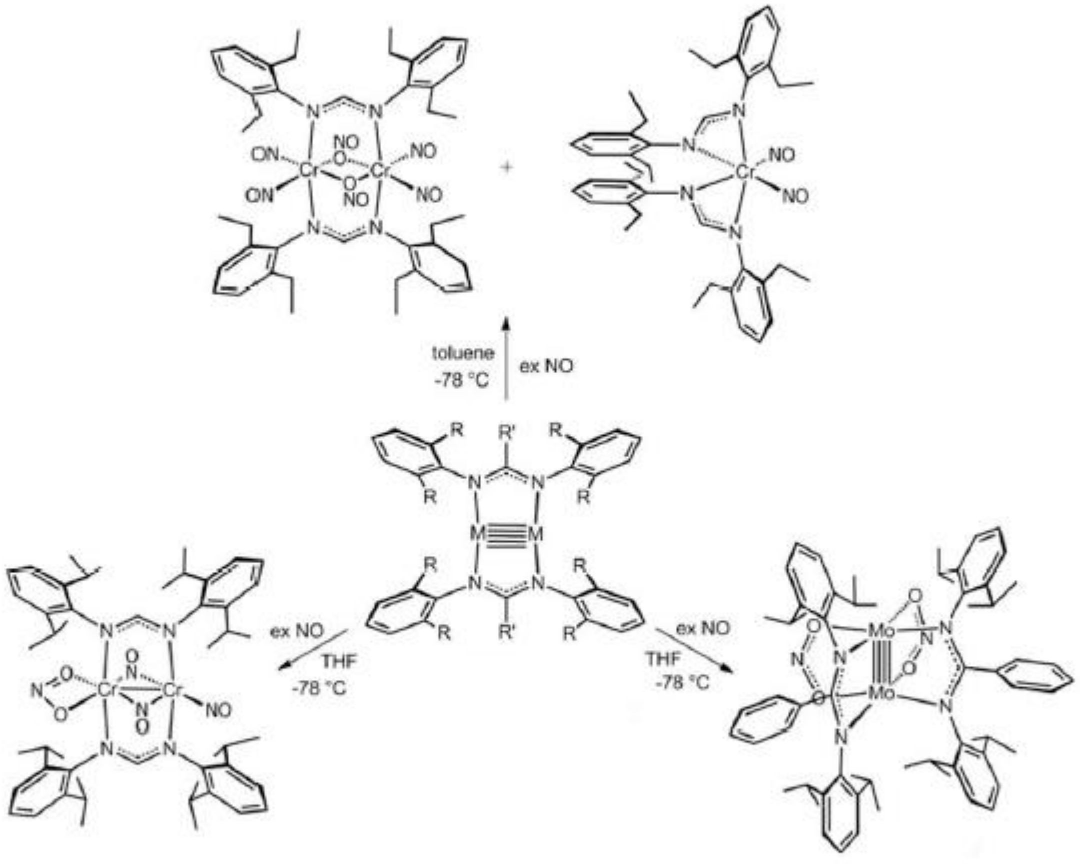
Scheme 6: Reactivity of Ar'CrCrAr' towards N_2O and N_3(1-Ad).

Kempe *et al.* showed applied the carboalumination reaction to their quintuply bonded complex (Scheme 7).[36] Carboalumination (and carbometallation) reactions are established reactions in chemistry which proceed via a *syn*-addition (same side or face) for alkenyl addition and *cis*-addition for alkyne reactions.[37] The reaction proceeded via insertion of the quintuple bond into one of the bonds between aluminium and carbon to yield the Cr-Cr quadruply bonded *trans*-[Cr_2(*μ*-Me)(*μ*-$AlMe_2$)(*$μ_2$*:*κ*^{1}:*κ*^{1}-Ar)$_2$] product, whereby the Cr-Cr unit is bridged by Al-Me_2 and CH_3 .



Scheme 7: Carboalumination reaction of Kempe's quintuply bonded complex.[24]

Tsai *et al*. explored the reactivity of dichromium and dimolybdenum quintuple bond amidinate complexes with nitric oxide.[38] The products of the reactions changed depending on solvent and temperature (Scheme 8). The chromium amidinate dimer produced (*κ*^{2}-NO_2)Cr(*μ*-NO)$_2$[*μ*-*κ*^{2}-(dipf)$_2$]CrNO (Scheme 8, bottom left) reacted in THF at -78 °C, meanwhile in toluene, at -78 °C, two species are isolated. The first is monomeric Cr(NO)$_2$[*κ*^{2}-(Ar')$_2$] and the second is the oxo-bridged Cr_2(*μ*-*κ*^{1}-ONO)$_2$(NO)$_4$[*μ*-*κ*^{2}-(Ar')$_2$] (Scheme 8, top left and top right respectively). At room temperature the monomeric chromium species is the only compound produced. The molybdenum amidinate dimer reacts with NO in THF at -78 °C to yield a quadruply bonded paddlewheel complex; *cis*-Mo_2[*μ*-*κ*^{1}:*κ*^{1}-NO_2]$_2$-[*μ*-*κ*^{2}-(dipf)$_2$] (Scheme 8, bottom right).



Scheme 8: Reactions of Cr and Mo quintuple bond dimers with NO in different solvents.[24]

In 2011 Kempe *et al*. demonstrated that their amidopyridine dichromium complex can be involved in [2+2] cycloaddition reactions with an equimolar amount of diphenylacetylene, phenylacetylene, trimethylsilylacetylene and *p*-tolylacetylene to yield the structure shown in Figure 12.[39] They also investigated the reaction of their complex with buta-1,3-diene and isoprene. The quintuple bond complex underwent a Diels-Alder-like reaction with the organic compound and bridged the dichromium bond resulting in a reduction of bond order in both the dienes (to two single C-C bonds) and a metal-metal quadruple bond (Scheme 9).[40]

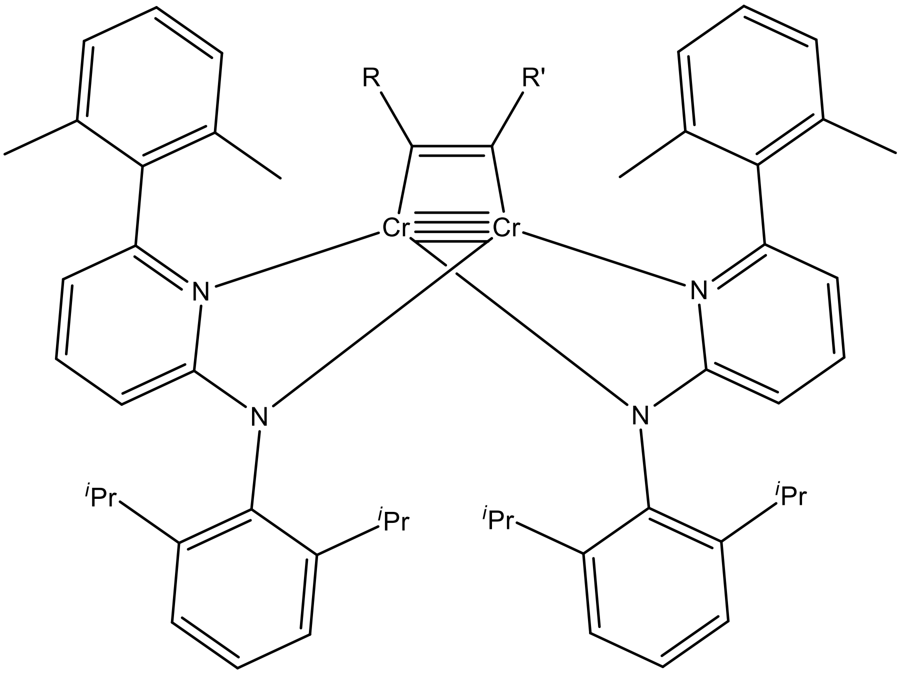
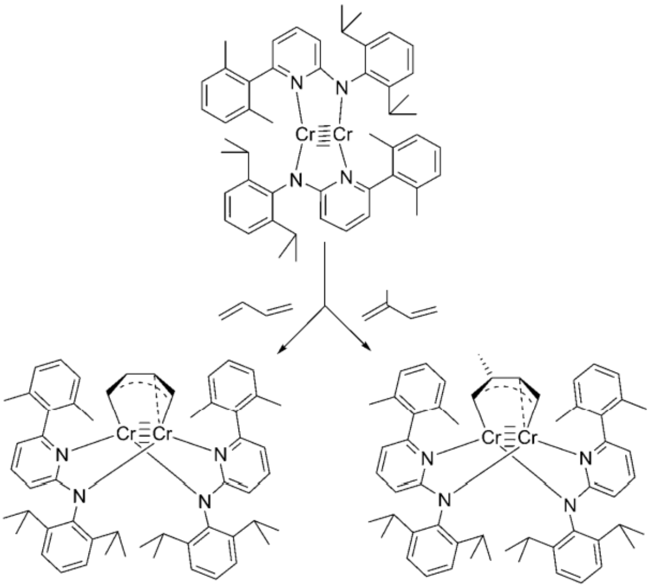
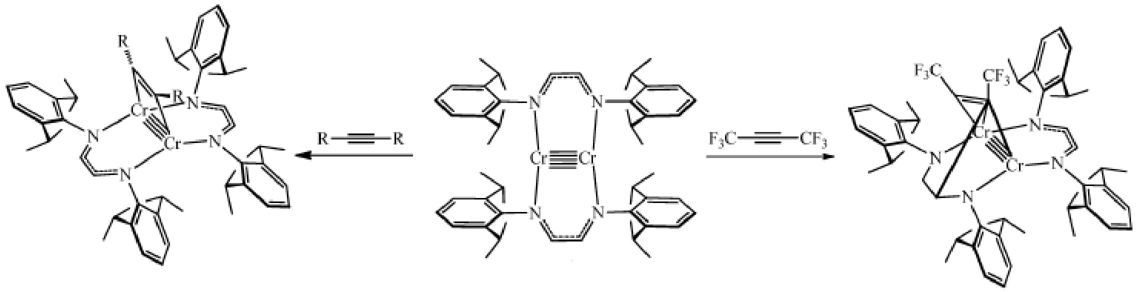


Figure 12: Product resulting from the [2+2] addition of an alkyne to Kempe's amidopyridine complex.[39]



Scheme 9: Reaction of Kempe's quintuply bonded complex with two dienes.[24]

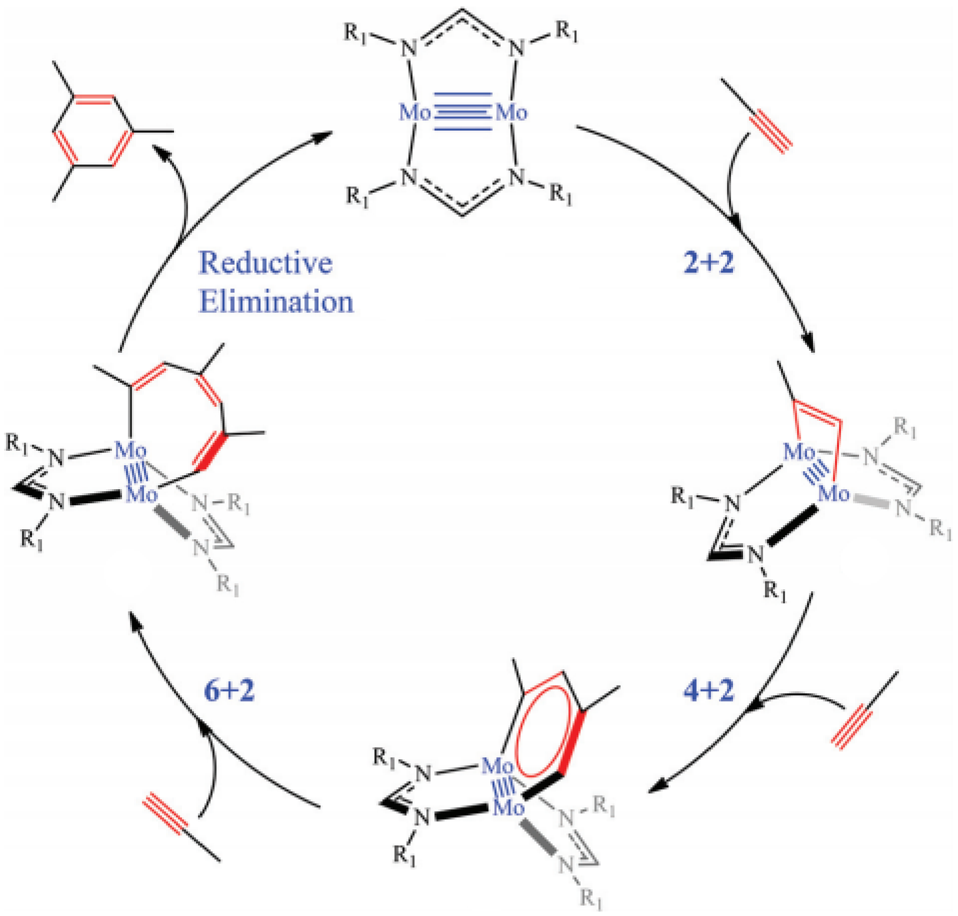
Theopold further investigated cycloaddition reactions with his dichromium diazadiene complex with four internal alkynes: 2-butyne, 3-hexyne, diphenylacetylene and the electron-deficient hexafluoro-2-butyne.[41] Addition occurred in a similar fashion to Kempe's work whereby the alkynes add across the Cr_2 unit with the exception of hexafluoro-2-butyne which also formed a bond to one of the ligands resulting in the formation of an iminoamide ligand (Scheme 10).



Scheme 10: Reactions of the diazadiene quintuple bond complex with internal alkynes.[24]

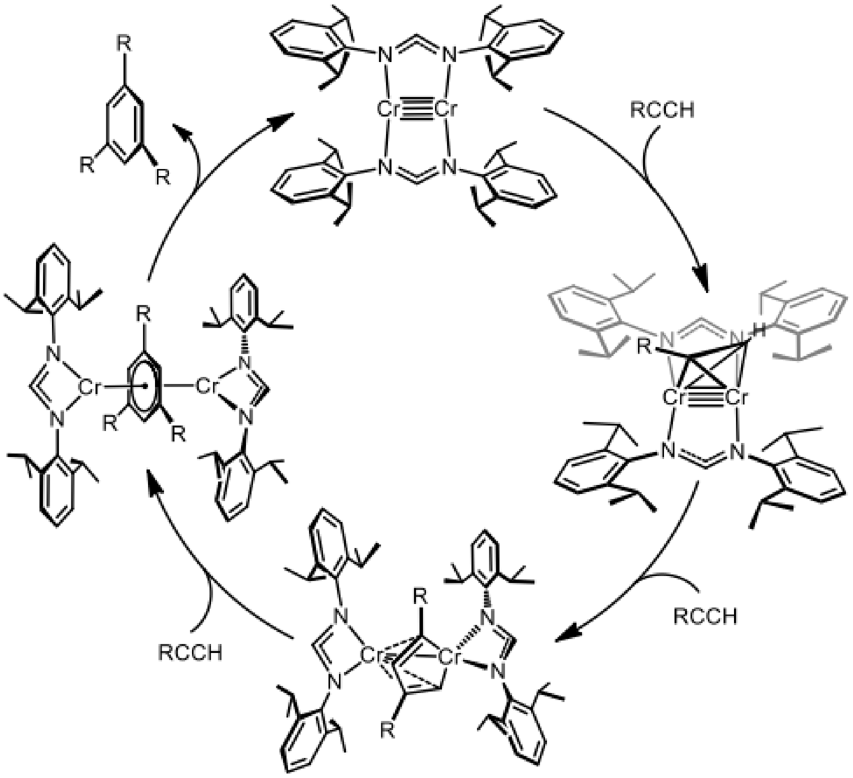
1.9 *Catalytic Activity of the Quintuple Bond*

The cycloaddition reactions performed by Kempe and Theopold led to theoretical studies being performed on the quintuply bonded dimolybdenum amidinate dimer as a catalyst in the formation of mesitylene.[42] Sakaki and Chen formulated a catalytic cycle (Scheme 11) using DFT involving a series of cycloadditions of methylacetylene onto the Mo_2 unit finishing with the reductive elimination of mesitylene. The first step involved a [2+2] cycloaddition of the alkyne with a dimolybdenum quintuply bonded complex to yield a four-membered metalacyclic compound which has been observed with Kempe's work (Figure 12).[39] A [2+4] addition then occurs with a second alkyne to afford a six-membered ring similar in structure to Theopold's addition of internal alkynes to the quintuple bond.[41] The [2+6] addition which had not previously been observed of a final alkyne yields an eight-membered ring intermediate which then undergoes reductive elimination to yield mesitylene and restore the quintuple bond.



Scheme 11: Catalytic cycle of a series of cycloadditions onto the Mo_2 quintuple bond complex.[24]

Tsai *et al.* successfully utilised the dichromium amidinate complex as a catalyst to form various 1,3,5-trisubstituted benzenes via a [2+2+2] cycloaddition with two equivalents of the terminal alkyne followed by an excess of the alkyne to produce the 1,3,5-trisubstituted benzene product.[43] The reaction proceeds in a different manner to the DFT study by Sakaki and Chen whereby the bond order of the Mo_2 complex is reduced by one, but complete cleavage of the Cr-Cr quintuple bond occurs during Tsai's cycloadditions and is restored upon reaction of the intermediate with an excess of the terminal alkyne (Scheme 12).



Scheme 12: Catalytic cycle of cycloaddition reactions of terminal alkynes with Tsai's dichromium quintuple bond complex.[43]

1.10 *The Future of Quintuple Bonding*

The field of quintuple bonding is still in its infancy stages with only a relatively small number of quintuply bonded compounds isolated. The electron-rich quintuple bond has shown interesting reactivity, and more remains to be explored.

1.10.1 *Molybdenum*

Three quintuply bonded dimolybdenum complexes have been isolated to date, all utilising the amidinate ligand to stabilise the Mo-Mo bond.[21-23] It may be worthwhile conducting experiments using the ligands previously used to isolate the dichromium quintuple bond such as Kempe's amidopyridine or guanidinate (Figure 13) complexes or Theopold's diazadiene dimer.[25,33,44,45] The lengths of the Mo-Mo quintuple bonds are longer than that of their dichromium analogues (by approximately 0.3 Å), and so use of the terphenyl ligand may prove to be less successful in isolating a dimolybdenum complex compared to other ligand scaffolds due to the longer Cr-Cr quintuple bond observed in Power's quintuply bonded complex.[23]

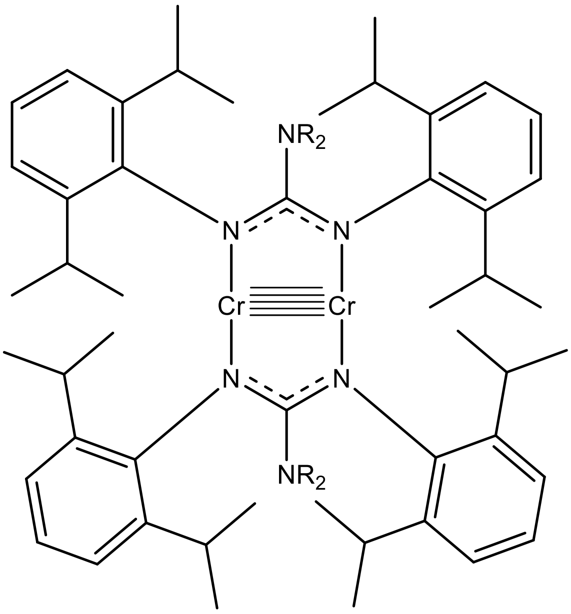
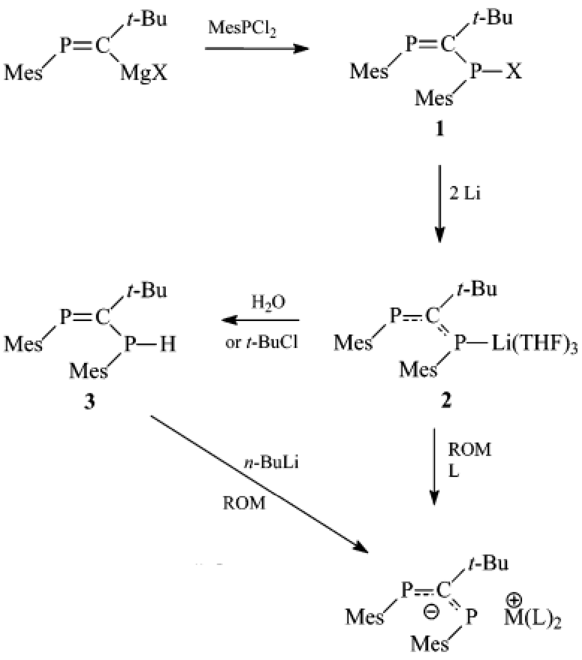


Figure 13: Kempe's dichromium guanidinate complex.

All but one of the ligand scaffolds utilises nitrogen donors to stabilise quintuple bonds and so investigation of different donor ligands may be worthwhile. Phosphorous-containing ligands are suitable for investigations, due to being in the same group as nitrogen and therefore having similar properties, but also due to a higher bonding capacity and being able to contribute a greater steric bulk towards enhancing the stability of the quintuple bond.

Ligands analogous to the formamidinates used by Tsai *et al*. that can be deprotonated such as 1,3-diphosphapropene (Scheme 13) which has been found to be capable of bridging in a dinickel complex (Figure 14) are also suitable targets for future work.[46]



Scheme 13: Reaction scheme for the preparation of 1,3-diphosphapropene (PCP) and its deprotonation.[46]

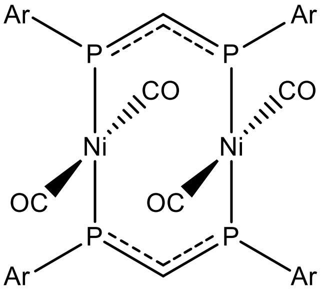


Figure 14: PCP as a bridging ligand.

No literature could be found that uses the PCP as a ligand in quadruple bonding, however there are compounds similar in its nature that have been found in Mo-Mo quadruple bond complexes. Quadruply bonded dimolybdenum complexes using the bidentate ligands, bis(diphenylphosphino)methane (dppm) and bis(diphenylphosphino)ethane (dppe) (the former of which can be deprotonated) have been successfully isolated.[47-49] Reduction of these compounds could potentially generate a quintuple bond and the methods used to prepare the complexes could be used with the PCP ligand.

1.10.2 *Heterobimetallic Complexes*

The isolation of the heterobimetallic Mn-Cr quintuple bonded complex by Lu *et al.* is the only known example of such a bond and is remarkable in the fact it uses two metals from two different groups (a group six and seven respectively).[30] A possible starting point for more quintuple bonds of this nature could be derived from chromium(II) molybdenum(II) tetraacetate, a quadruply bonded heterobimetallic complex (Figure 15).[50] While the Cr-Mo quadruple bond is stated to be rather labile and easily cleaved under mild conditions, using low temperatures (as used in the preparation of certain ditungsten compounds) may prove to yield more mixed-metal complexes.

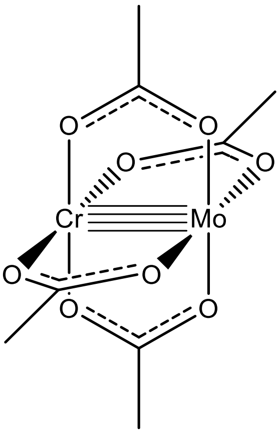


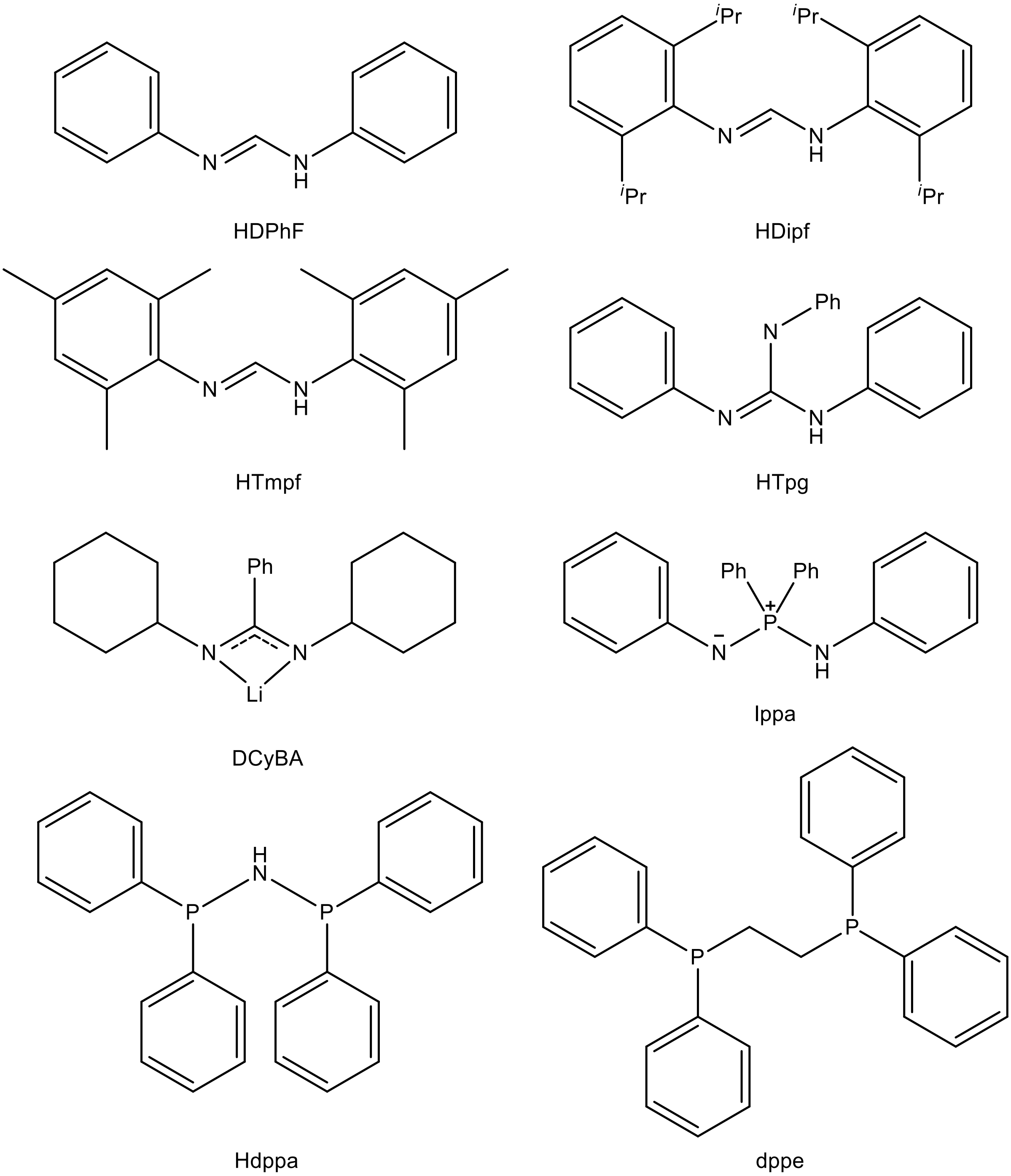
Figure 15: Quadruply bonded Cr(II)-Mo(II) tetraacetate.

1.10.3 *Rhenium*

Rhenium(III) complexes are isoelectronic to Mo(II) complexes and it is theorised that dirhenium compounds could potentially form quintuple bonds. DFT studies were performed using the complex $Cp_2Re_2(CO)$ and was predicted that the lowest energy form of the compound possessed a short rhenium-rhenium bond distance (that obeyed the 18-electron rule) and suggested that a quintuple bond could be achieved with dirhenium complexes.[51] With the use of a suitable ligand that does not interact with the $d_{x^2-y^2}$ atomic orbitals of rhenium, the five metal d-orbitals of each metal unit should overlap to form a quintuple bond.[52]

2. Aims

The aims of this project involved synthesising quadruply bonded dimolybdenum and dirhenium complexes that were believed to be potential precursors to new quintuply bonded dimetal species.



HDPhF

HDipf

HTmpf

HTpg

DCyBA

Ippa

Hdppa

dppe

Figure 16: The bulky bidentate proligands used in this research.

The first aim of this project is to prepare a variety of bidentate ligands that have a varying amount of steric bulk. For molybdenum a particular focus will be exerted on using bidentate bisphosphine ligands, such as dppa and dppe (Figure 15), due to the enhanced bonding capacity of phosphorous being able to provide a greater degree of steric bulk that N,N'-bidentate donors that have been employed previously in stabilising the quintuple bond.[23]

Following the successful synthesis of the P,P'-ligands, efforts will be made to react them with suitable precursors, $Mo_2(O_2CCH_3)_4$ and $[Mo_2Cl_8]^{4-}$, (complexes **[1]** and **[2]** respectively) in order to generate the potential quadruply bonded precursors.

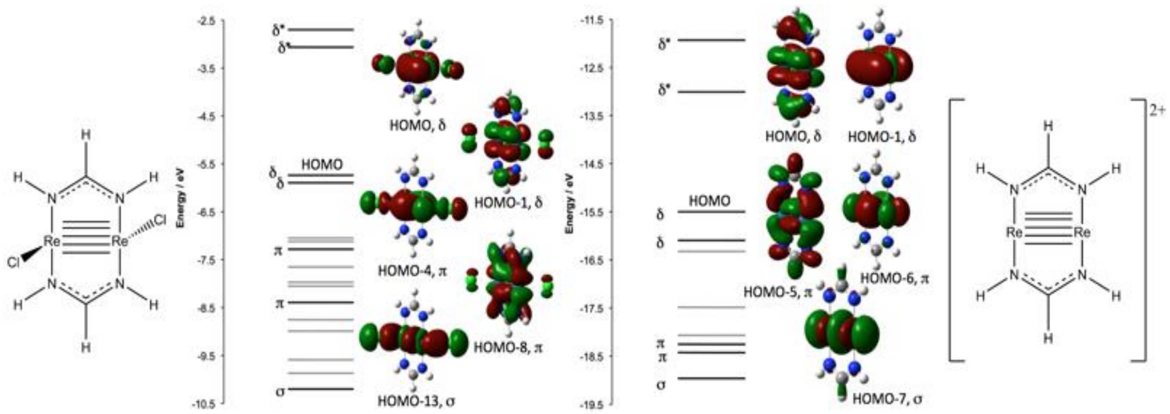


Figure 17: Energy profile diagram of theoretical quintuply bonded dirhenium complexes.

DFT studies by the Patmore group on Re-Re models (Figure 17) have proposed that synthesis of a Re(II)-Re(II) quintuply bonded complex is possible. These studies are supported by the works of a separate DFT study that identified the lowest energetic form of $Cp_2Re_2(CO)$ would possess a Re-Re quintuple bond.[51] Meanwhile, for the dirhenium species, efforts will be focused on preparing a variety of N,N'-bidentate ligands, such as the bulky formamidinates (DPhF, dipf and tmpf), guanidinates and benzamidinates (Figure 16). Synthesis of these ligands will then lead to preparation of the quadruply bonded dirhenium precursors of the formula $Re_2(NN)_2Cl_4$.

Characterisation of these complexes will then be undertaken to confirm their structure using ^1H NMR spectroscopy, IR spectroscopy and UV-Vis spectroscopy. Following on from this both dimolybdenum and dirhenium complexes will be tested for their feasibility in being reduced and therefore being able to form a metal-metal quintuple bond through the use of cyclic voltammetry.

After assessing the potential of the precursor to be reducible, attempts will then be made to chemically reduce the quadruply bonded complexes using a variety of suitable reducing agents such as KC_8 or sodium mercury amalgam. Should the quintuply bonded dimetal species be generated, the compound will be characterised by ^1H NMR spectroscopy, $^{31}P\ \{^1H\}$ NMR spectroscopy (for the relevant complexes), UV-vis spectroscopy, IR spectroscopy, EPR spectroscopy and X-Ray crystallography.

Should any quintuply bonded species be prepared it would be of considerable importance as it will expand the current understanding of bonding as a concept as well as producing new complexes with a new ligand architecture or showing that the group seven metals can also form quintuple bonds.

3. Quadruply Bonded Dimolybdenum Precursors

The most abundant methods of stabilising the quintuple bond is through nitrogen-donor ligands. This study has included phosphorous-based ligands that could be used to isolate a quintuple bond.[23,24] The ligands of main focus were N,N-bis(diphenylphosphino)amine (Hdppa) and 1,2-bis(diphenylphosphino)ethane (dppe). Other ligands, such as 1,2,3-triphenylguanidine (Htpg), N,N'-bis(2,4,6-trimethylphenyl)formamidine (Htmpf) and 1,1'-bis(diphenylphosphino)ferrocene (dppf) were also used to prepare dimolybdenum complexes, however they were not fully characterised. One of the benefits of using phosphine ligands is that they have two aryl groups per phosphorous atom, whereas N,N-donor ligands have only one aryl group per nitrogen atom. This results in increased steric bulk that can be used to protect the dimetal core.

3.1 *Proligands*

The synthesis of Hdppa was performed according to a modified literature procedure (Figure 16).[53] Two equivalents of chlorodiphenylphosphine were refluxed in toluene with one equivalent of hexamethyldisilazane for three hours. The toluene was removed under reduced pressure and the resulting yellow solid was washed with diethyl ether until it ran through clear and left a white solid with a 58 % yield obtained. The ^{1}H NMR spectrum of Hdppa showed that only the expected phenyl peaks and amine peaks at $\delta = 7.33\text{-}7.28$ and $\delta = 3.14$. The secondary amine proton was observed as a triplet due the phosphorus coupling. The $^{31}P\{^{1}H\}$ NMR spectrum displayed a single peak at $\delta = 42.98$ as expected.

The ligand, tmpf, was prepared according to a literature procedure (Figure 16).[54] Two equivalents of 2,4,6-trimethylaniline, one equivalent of triethyl orthoformate and a small amount of glacial acetic acid (5 mol %) was heated at 160 °C for three hours. The yellow liquid was recrystallised from toluene and isolated by filtration before washing with hexane and diethyl ether to yield colourless long crystals with a yield of 69 % obtained. The ^{1}H NMR was comparable to that recorded in the literature. The MS contained a single $[M+H]^{+}$ peak at 281.20 m/z as expected.

This ligand was chosen as it has been successfully employed by Tsai *et al*. in the synthesis of dichromium and dimolybdenum quintuply bonded complexes.[26-28]

The diphosphine, dppe, (Figure 16) was chosen due to the large steric bulk it provides. It was of interest due to its ability to behave as a bridging or chelating ligand depending on the method of preparation. It was less likely to yield a quintuple bond complex as it could not be reacted to generate an anionic ligand unlike its related compound 1,1-bis(diphenylphosphino)methane (dppm, Figure 26) which could be deprotonated using 1,3,4,5-tetramethylimidazol-2-ylidene with lithiation occurring on the methylene bridge (but was not used in this research due to time constraints).[55]

Guanidinate ligands were employed in quintuple bonding in dichromium complexes by Kempe *et al.* and were useful in making a shorter Cr-Cr quintuple bond compared to his amidopyridine complex.[56] Kempe states that the guanidinates can shorten the metal-metal bond due to the steric pressure that causes the flanking aryl regions of the ligand to be pushed down due to the N-group on top (Figure 21).

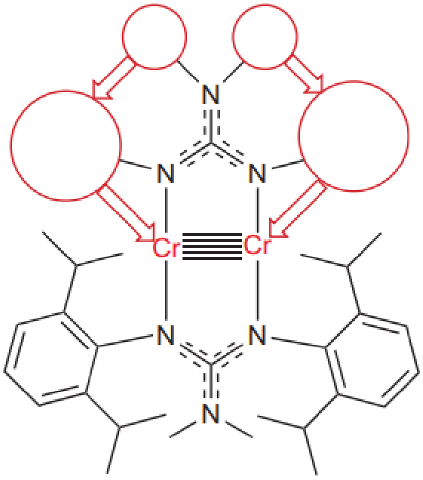


Figure 21: Guanidinate complex illustrating the pushing down of the ‘wings’ and its effect on the Cr-Cr bond length.[56]

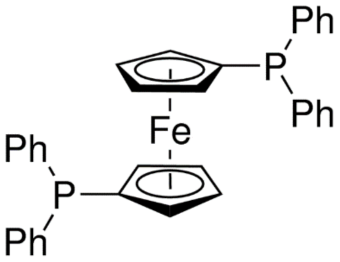


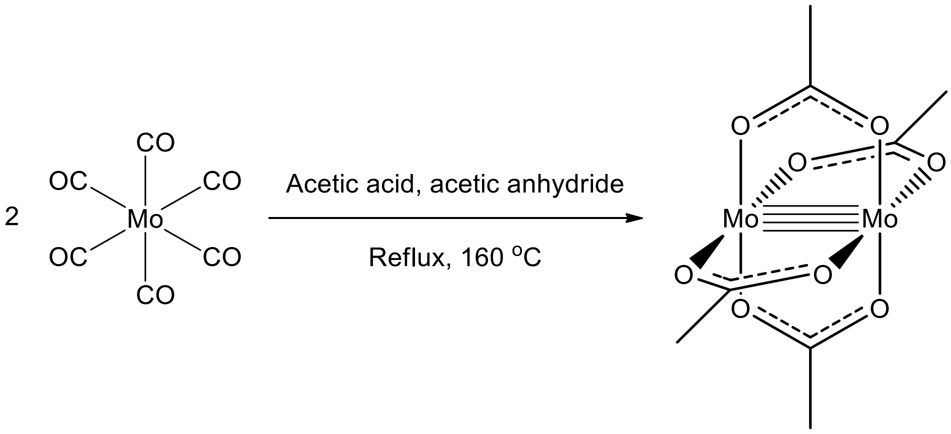
Figure 22: Structure of dppf.

Reactions of a dimolybdenum species with dppf (Figure 22) would likely produce a bridge too large to sufficiently stabilise a quintuple bond, but the monolithiation of ferrocene using *t*-BuLi may be applicable to dppf (with litihiation also occurring on one of the Cp rings) to generate an anionic ligand suitable for use in preparing a quintuply bonded precursor.[57] Furthermore, dppf acting as a bridge between dimolybdenum species has been reported only where no bonding occurs between the Mo_2 unit and so preparation of a quadruply bonded complex may be of interest.[58]

3.2 *Dimolybdenum Complexes*

3.2.1 *Synthesis of Dimolybdenum Precursors*

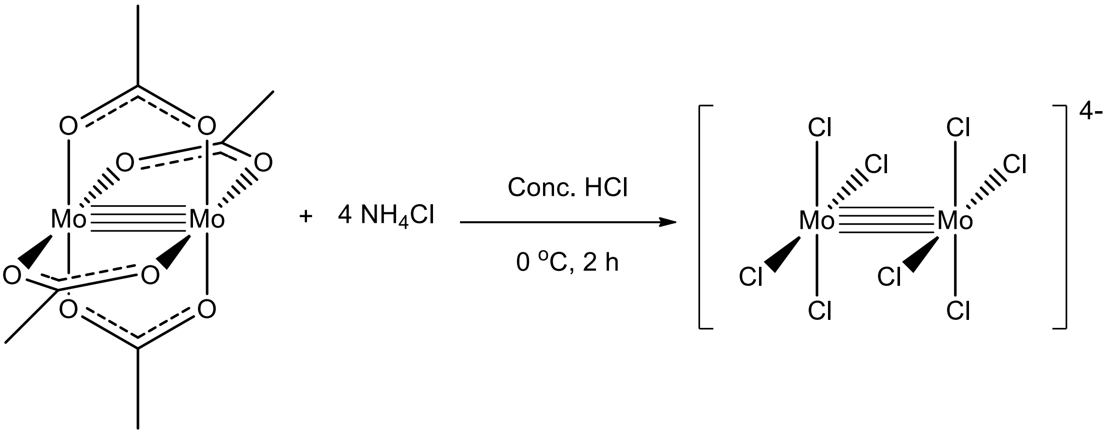
3.2.1.1 *Synthesis of* $Mo_2(O_2CCH_3)_4$ ***[1]***



Scheme 14: Preparation of the precursor $Mo_2(O_2CCH_3)_4$, **[1]**.

The complex $Mo_2(O_2CCH_3)_4$, **[1]**, was prepared according to a literature procedure (Scheme 14).[59,60] $Mo(CO)_6$ was refluxed in acetic acid and acetic anhydride for 24 hours, yielding the product as a bright yellow solid. The ^1H NMR spectrum in d_6-DMSO showed a single peak at δ = 2.61, as expected for this complex for the CH_3 region.

3.2.1.2 *Synthesis of* $(NH_4)_4Mo_2Cl_8$ ***[2]***

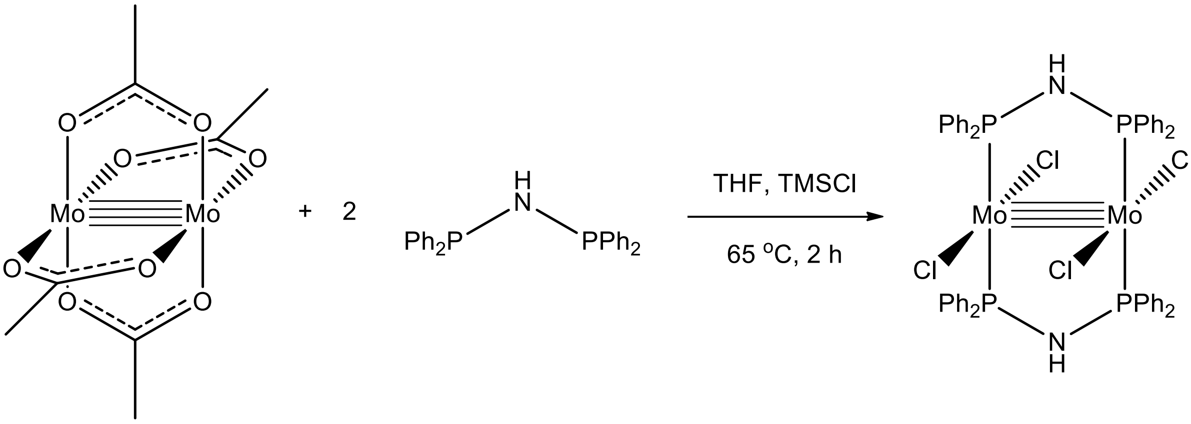


Scheme 15: Preparation of the precursor $(NH_4)_4Mo_2Cl_8$.

Complex $(NH_4)_4Mo_2Cl_8$, **[2]**, (Scheme 15), which is prepared from **[1]**, has been used in reactions to prepare the known dimolybdenum quintuply bonded complexes.[23,24] The synthesis of **[2]** is from the reaction of $Mo_2(O_2CCH_3)_4$ with ammonium chloride in concentrated HCl at 0 °C.[61] Stirring at this temperature for two hours yields a purple solid after filtering and washing with cold ethanol with a yield of 47 % obtained. Little data could be obtained from this complex due to its relative insolubility, lack of analysable protons for NMR study and lack of functional groups for IR spectroscopy. The UV-Vis spectrum of **[2]** in concentrated hydrochloric acid was obtained and a $\delta \rightarrow \delta^*$ transition was observed at 520 nm, in good agreement with the literature value.[3]

3.2.2 *Synthesis of Dimolybdenum Quadruply Bonded Complexes*

3.2.2.1 *Synthesis of $Mo_2(Hdppa)_2Cl_4$* ***[3]***

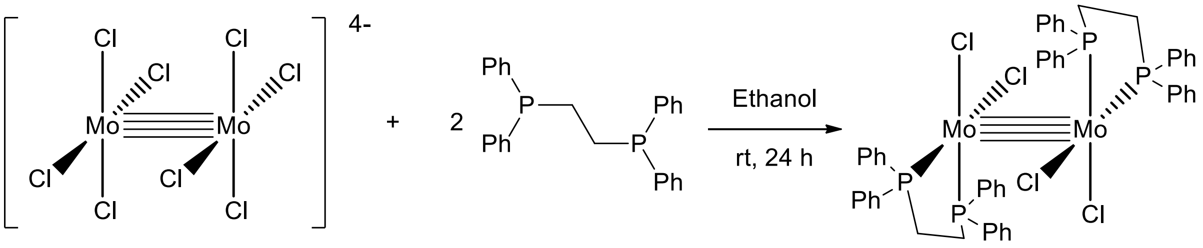


Scheme 16: Preparation of $Mo_2(Hdppa)_2Cl_4$, **[3]**.

$Mo_2(Hdppa)_2Cl_4$, **[3]**, was prepared according to a literature procedure (Scheme 16).[62] $Mo_2(O_2CCH_3)_4$ **[1]** was reacted with two equivalents of Hdppa and four equivalents of TMSCl and refluxed in THF for two hours. The green suspension in a purple solution was filtered and washed with THF. The green solid was identified as **[3]** by ^1H NMR and ^{31}P NMR, the IR and UV-vis spectra which also matched the literature. A purple solid was produced after evaporating the purple filtrate under reduced pressure and was found to be the stable intermediate, $Mo_2(Hdppa)_2(O_2CCH_3)_2Cl_2$, by NMR spectroscopy.

The ^1H NMR spectrum of **[3]** shows peaks indicative of mono-substituted phenyl rings at δ = 7.47 – 7.32. An amine peak at δ = 4.28 was also present as a broad singlet. The IR spectrum shows the NH stretch at 3045 cm^{-1}, the NH bending frequency could be tentatively assigned at 1483 cm^{-1}. The P-N bond was evidenced the broad region from 3200-2900 cm^{-1} and a medium intensity peak at 1095 cm^{-1}.[63]

3.2.2.2 *Synthesis of α-Mo$_2$(dppe)$_2$Cl$_4$* ***[4]***



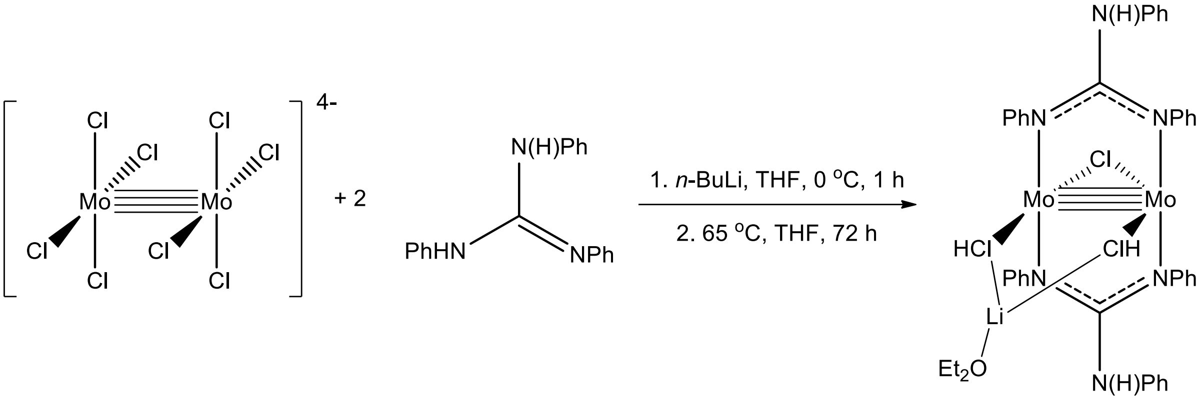
Scheme 17: Preparation of *α*-Mo$_2$(dppe)$_2$Cl$_4$.

Complex **[4]** was prepared according to a literature procedure (scheme 17).[64] **[2]** was reacted with two equivalents of dppe and stirred in ethanol for 24 hours. The blue-green suspension was filtered and dried and washed with cold ethanol. The solid was obtained in a yield of 48 % comparable to the literature yield of 46 %.[64] The ^{1}H NMR spectrum of **[4]** showed a multiplet in the region of δ = 7.37-7.25 that indicated mono-substituted phenyl rings and a triplet at δ = 2.03 from the ethyl protons between the two phosphorous atoms. The IR spectrum identifies a methylene peak of medium intensity at 1485 cm^{-1}. A strong peak at 1435 cm^{-1} is suggestive of a P-C bond being present as is expected for the compound.

An alternative method using Mo$_2$(O$_2$CCH$_3$)$_4$ was attempted in a method analogous to the preparation of **[3]**. Refluxing **[1]** with two equivalents of dppe and four equivalents of TMSCl in THF for 24 hours yielded a red-pink solid which was much later found to have been the much more desired (due to the bridging nature) *β*-form of Mo$_2$(dppe)$_2$Cl$_4$.[65] This complex did not undergo reduction attempts due to time-related constraints.

3.2.3 Attempted Syntheses

3.2.3.1 *$Mo_2(\mu\text{-}Cl)[(Cl_2Li(OEt_2)][\mu\text{-}\kappa^2\text{-}tpg]_2$*



Scheme 18: Proposed preparation of the potential complex $Mo_2(\mu\text{-}Cl)[(Cl_2Li(OEt_2)][\mu\text{-}\kappa^2\text{-}tpg]_2$.

The tpg ligand was believed to be a suitable ligand in stabilising the Mo-Mo quintuple bond due to guanidinate ligands being used in previous research by Kempe *et al.* in addition to these dichromium complexes possessing the shortest metal-metal bond of the known quintuply bonded complexes.[23,44,45] Furthermore, the dimolybdenum quintuple bonds appear to have longer metal-metal bonds compared to the dichromium complexes and so use of the tpg ligand may provide necessary in order to obtain a quintuple bond that is as short (or shorter) than Tsai's dimolybdenum compounds.[28,29]

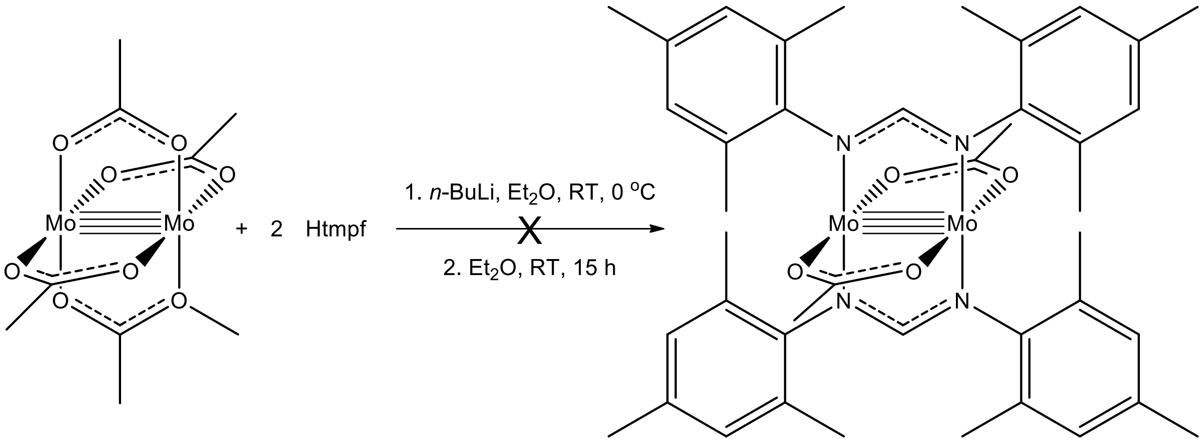
Two routes were proposed to synthesise the target complex $Mo_2(\mu\text{-}Cl)[(Cl_2Li(OEt_2))[\mu\text{-}\eta^2\text{-}tpg]_2$. The first and relatively simpler procedure (Scheme 18) involved following a method analogous to the preparation of the dimolybdenum formamidinate complexes.[28] The ligand was stirred in THF with *n*-BuLi for one hour and was then added into a solution of **[2]** which was then refluxed for three days. A red-brown solution formed that was evaporated and precipitated from diethyl ether to yield a red-brown solid.

The NMR spectrum showed resonances that agree with the proposed structure, such as having two different phenyl regions of peaks. The intensity of the diethyl ether peaks is lower than expected as some diethyl ether could have been lost in drying the complex.

The second method involved preparing the paddlewheel complex, $Mo_2(tpg)_4$, from an adapted literature preparation (using DCB as a solvent rather than diglyme).[66,67] Heating $Mo(CO)_6$ with two equivalents of Htpg in DCB at 160 °C for six hours yielded a black solid was obtained in good yield, but attempts to wash it with varying solvents did not yield the desired product.

The intention from preparing the paddlewheel complex was to attempt to directly reduce it using a strong reducing agent or to attempt to prepare a quadruply bonded intermediate of the formula $Mo_2(tpg)_2Cl_4$ using fluoroboric acid and then introduction of four equivalents of hydrochloric acid (after removing the fluoroboric acid) to encourage substitution of two guanidinate ligands. Unfortunately, due to time constraints repeating this reaction following the literature preparation could not be undertaken.

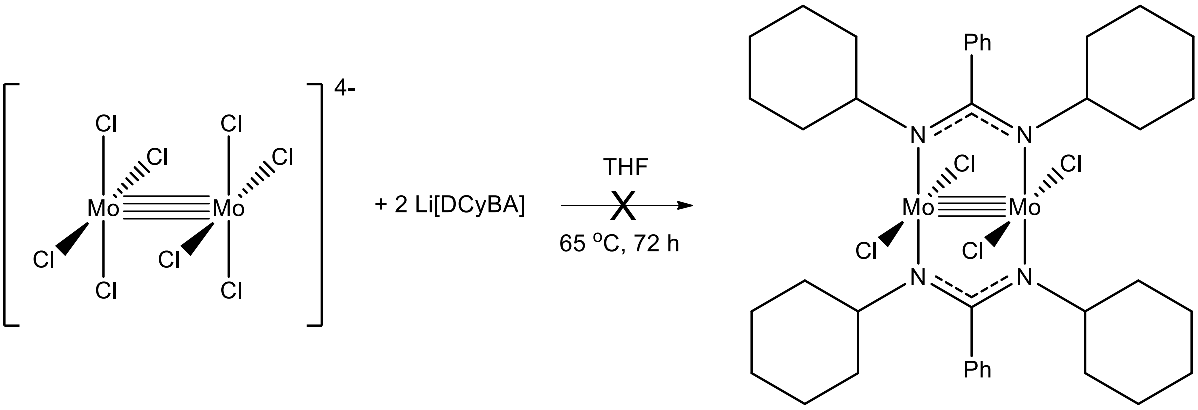
3.2.3.2 *$Mo_2(O_2CCH_3)_2(tmpf)_2$*



Scheme 19: Attempted preparation of $Mo_2(O_2CCH_3)_2(tmpf)_2$

Tsai *et al.* demonstrated the success of stabilising the Mo-Mo quintuple bond using the bulky dipf formamidinate ligand (Figure 10) and so an attempt to prepare another type of formamidinate dimolybdenum complex was undertaken using the slightly less bulky tmpf ligand (Scheme 19). $Mo_2(O_2CCH_3)_4$ was stirred with two equivalents of the deprotonated tmpf ligand (through stirring in n-BuLi in diethyl ether) for 15 hours at room temperature. It was found that no reaction occurred after removal of the solvent leaving a bright yellow solid assumed to be starting material. This method could be improved upon by using $[Mo_2Cl_8]^{4-}$ rather than $Mo_2(O_2CCH_3)_4$ and refluxing in THF for three days in a fashion analogous to Tsai's preparation of the precursor.[28]

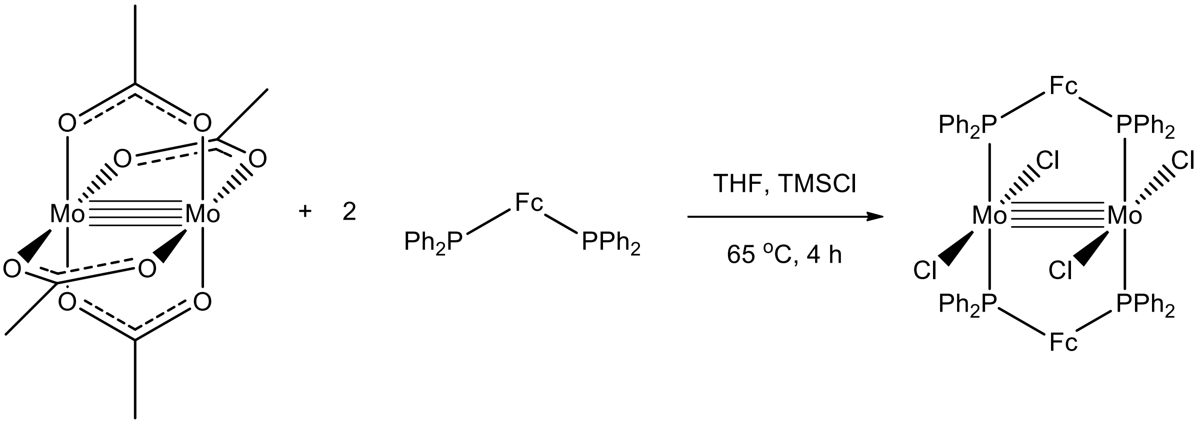
3.2.3.3 *$Mo_2(DcyBA)_2Cl_4$*



Scheme 20: Attempted preparation of $Mo_2(DCyBA)_2Cl_4$

The DcyBA ligand is a rather bulky ligand that was believed to be suitable in stabilising a quintuple bond. While the flanking cyclohexyl (cy) regions of the ligand are less bulky compared to other flanking groups such as that seen in the dipf or tmpf ligand, it was thought that the phenyl ring above the cyclohexyl rings could push the cy groups further down and protect the electron dense Mo_2 bond. Refluxing **[2]** with two equivalents of Li[DCyBA] in THF for three days yielded a 'sticky' dark-brown solid after removal of the solvent which was not isolated (Scheme 20). Reducing the reflux time may prove to yield a more fruitful result should the reactions be repeated.

3.2.3.4 *$Mo_2(dppf)_2Cl_4$*

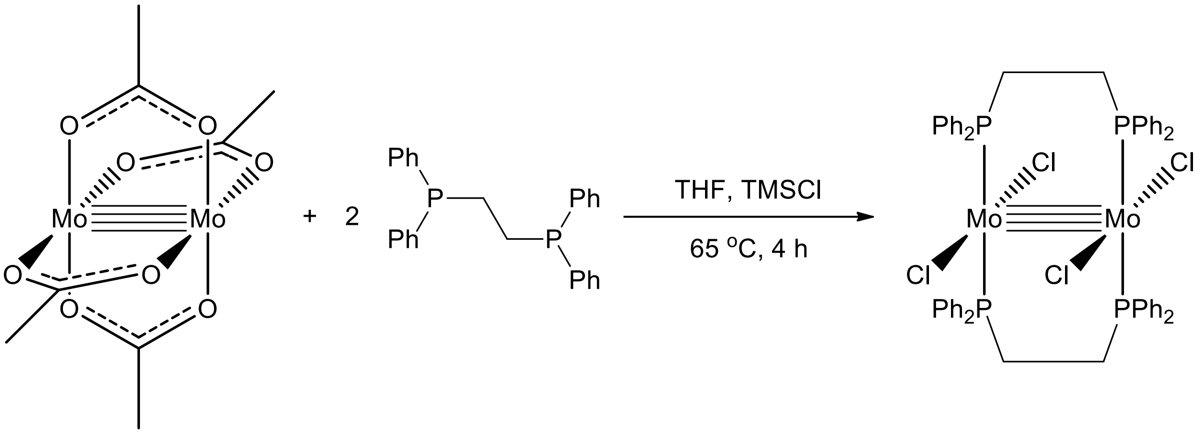


Scheme 21: Proposed preparation of the potential complex $Mo_2(dppf)_2Cl_4$.

No complexes were found to contain the dppf as a bridging ligand between a metal-metal quadruple bond and so preparation of this complex may prove to be useful in and of itself. The dppf ligand provides an immense amount of bulk and may be able to be deprotonated such that a suitable oxidation state is obtained for Mo so that it can be reduced. $Mo_2(O_2CCH_3)_4$ was refluxed in THF with two equivalents of dppf and an excess of TMSCl for four hours (Scheme 21). Filtering the suspension left a vibrant pink solid and bright orange solution.

An NMR spectrum of the pink solid was obtained for this product but could not be assigned as it appeared that a mixture of products had been prepared.

3.2.3.5 *β-Mo₂(dppe)₂Cl₄*



Scheme 22: Preparation of β-$Mo_2(dppe)_2Cl_4$.

After successful preparation of the α-form of $Mo_2(dppe)_2Cl_4$, its more suitable isomer was prepared wherein the ligand bridges across the Mo-Mo quadruple bond rather than chelating to one molybdenum atom each. Refluxing $Mo_2(O_2CCH_3)_4$ with two equivalents of dppe and an excess of TMSCl in THF for four hours yielded a red-brown suspension (scheme 22).[65] The suspension was filtered and washing with hexane to leave a red-brown solid. The ^{1}H NMR spectrum of the product was similar to that of the α-isomer complex.

3.2.4 *UV spectra*

UV-vis spectroscopy is of vital importance as it can reveal the relative energies of the orbitals of a compound via excitation of electrons from one orbital to another. In the context of quadruple and quintuple bonding, and with the aid of DFT studies of the individual complexes, it can be used to garner an understanding of the energy between the δ and δ* orbitals. The δ → δ* transitions are expected to display a weak absorption in the UV spectra as the overlap of the two d_{xy} orbitals of the metals that form the δ bond is small.[3]

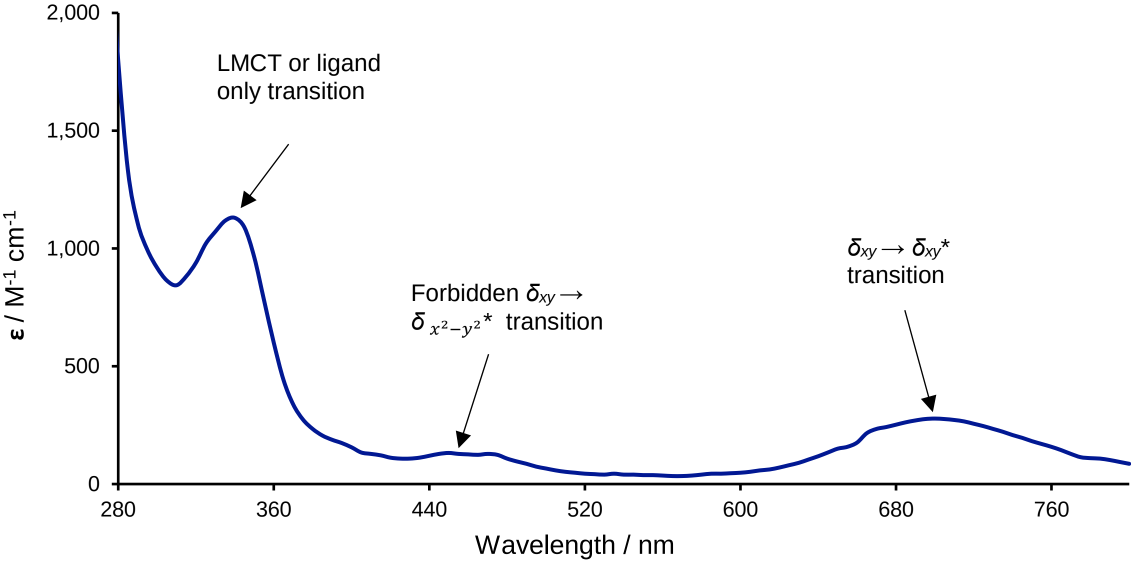


Figure 23: UV-vis spectrum of complex **[3]** recorded in DCM at room temperature.

The UV-vis spectrum of $Mo_2(Hdppa)_2Cl_4$ (complex **[3]**) is shown in Figure 23. The peak at 340 nm cannot be fully assigned without the aid of DFT, however it was tentatively assigned as either a non-bonding ligand orbital (Cl) → Mo_2-π* LMCT or a ligand-only transition. Literature reports assigned the low intensity peak at 455 nm to be a forbidden transition of $\delta_{xy} \rightarrow \delta_{x^2-y^2}{}^*$ and the peak at 705 nm to be the commonly observed $\delta_{xy} \rightarrow \delta_{xy}{}^*$ transition seen in quadruply bonded complexes.[62]

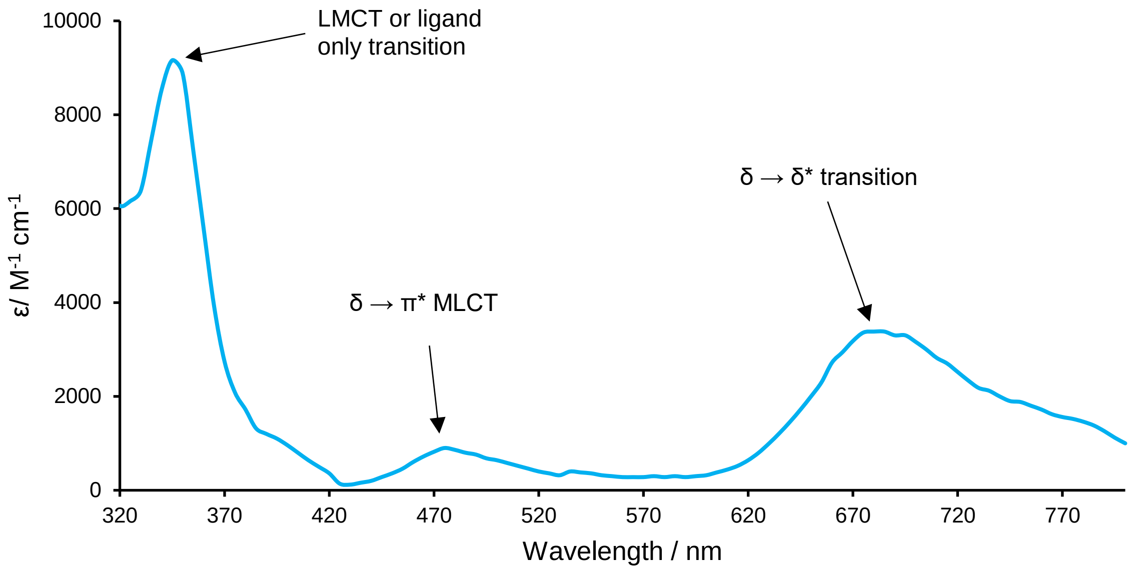


Figure 24: UV-Vis spectrum of complex **[4]** recorded in DMSO at room temperature.

The UV spectrum of **[4]** (Figure 24) appears to display similarities to **[3]**. The complex shows an intense peak at 345 nm which could be tentatively assigned as either a n → π* charge transfer or another LMCT as mentioned previously. The peak seen at 345 nm could also be a result of a ligand only transition. A weak absorption is seen at 475 nm that can be appointed as a δ → π* MLCT and a band of intermediary intensity (relative to the other two peaks) assigned as the δ → δ* transition is shown at 680 nm which is in good agreement with the literature value (δ → δ* = 676 nm).[64]

Complexes **[3]** and **[4]** can be compared to one of the common precursors to many quadruply bonded dimolybdenum complexes, $[Mo_2Cl_8]^{4-}$. Figure 25 shows the UV spectrum of $[Mo_2Cl_8]^{4-}$ and displays a broad absorption at approximately 520 nm which was assigned as a δ → δ* transition (which is in good agreement with the literature value).[68,69] This transition appears at a comparatively higher energy than that of complexes **[3]** and **[4]** which are seen at 705 nm and 680 nm respectively. The overall energy at which the transitions occurs may be related to the bulk of the ligands used with a larger ligand lowering the energy of the δ → δ* transition. Complex **[3]** has a δ → δ* transition that is lower in energy than complex **[4]** (despite having a similar level of steric hindrance) which may be a result of **[3]** having a shorter bridging gap than **[4]** resulting in an increased stability.

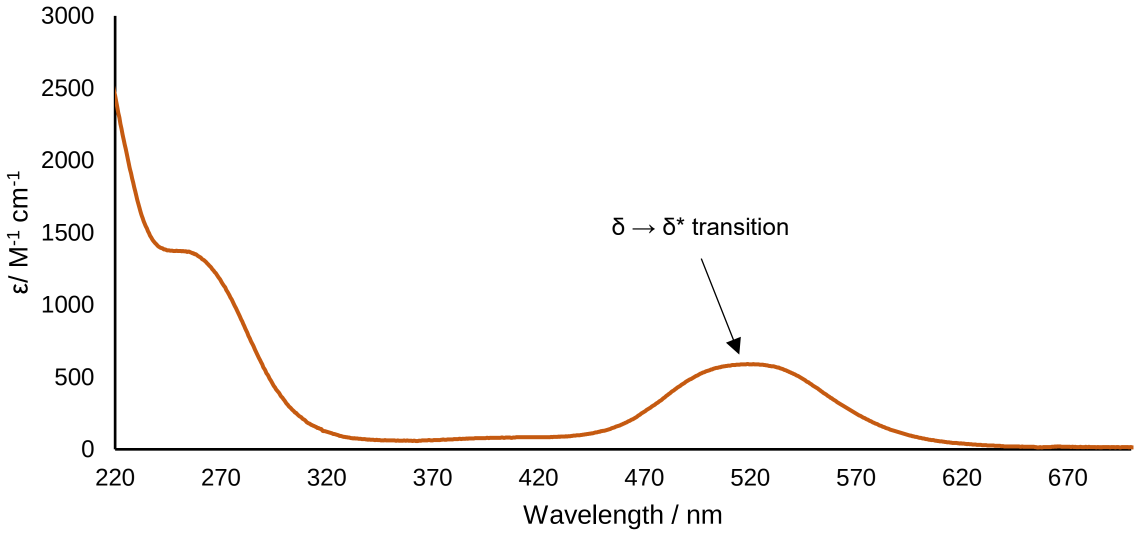


Figure 25: UV spectrum of **[2]** recorded in concentrated HCl recorded at room temperature.

3.2.5 *Cyclic Voltammetry*

Cyclic voltammetry is a technique used to give information about how easily a compound or substance can have an electron added to or removed from it electrochemically. This information can be applied to the complexes prepared as it can assess whether they are reducible and if they can could therefore have the potential to be chemically reduced to form a quintuple bond.

Figure 26 shows the cyclic voltammogram (CV) of complex **[3]**, $Mo_2(Hdppa)_2Cl_4$. A very broad quasi-reversible reduction is seen at $E_{1/2}$ = -1.534 V. The partial reversibility may be due to a change in the structure of the complex that is somewhat reversible, which could be a result of one or two of the chloride ligands bridging themselves across the quadruple bond. Due to the CV appearing more irreversible it could be proposed that some structural changes in the complex may be occurring that are irreversible such as a complete loss of chloride ligands.

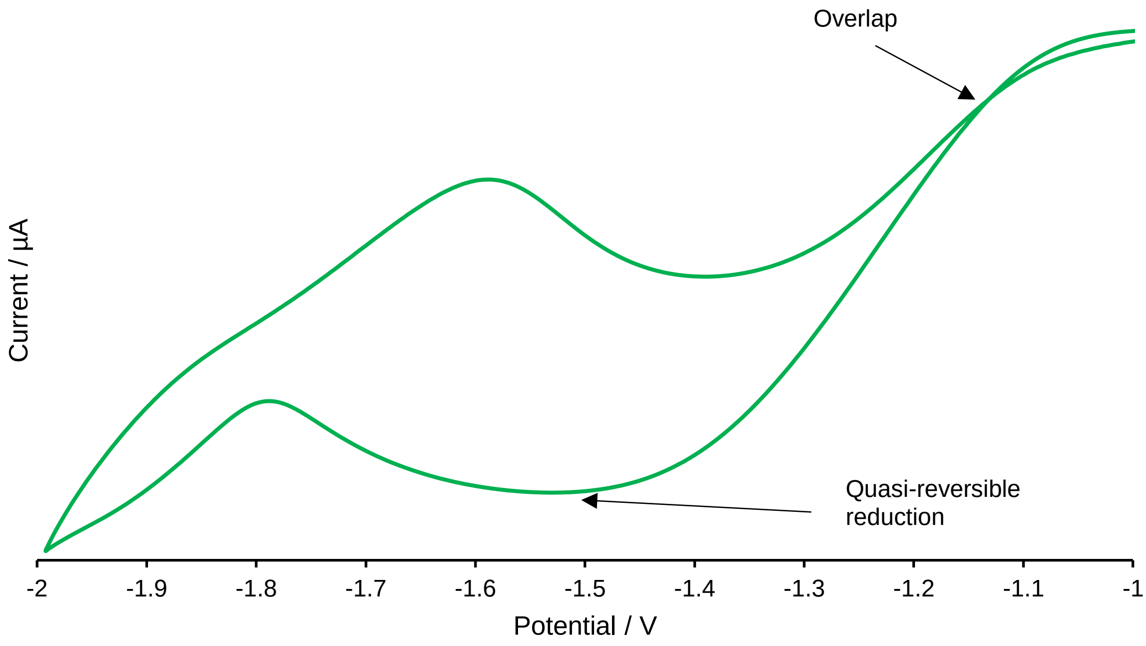


Figure 26: Cyclic voltammogram of complex **[3]**. CV in DCM with 0.1 M, TBAPF$_6$ recorded at a scan rate of 100 mV s^{-1} referenced against Fc/Fc$^+$.

Overlapping of the data points appears to occur at -1.132 V and -0.895 V (Figure 25, Table 1). This is the only complex of those studied in this research in which this occurs and may be due to a phenomenon called the nucleation crossover effect (NCE).[70] The NCE involves the creation of a new thermodynamically stable compound that deposits itself onto the electrode.[71,72]

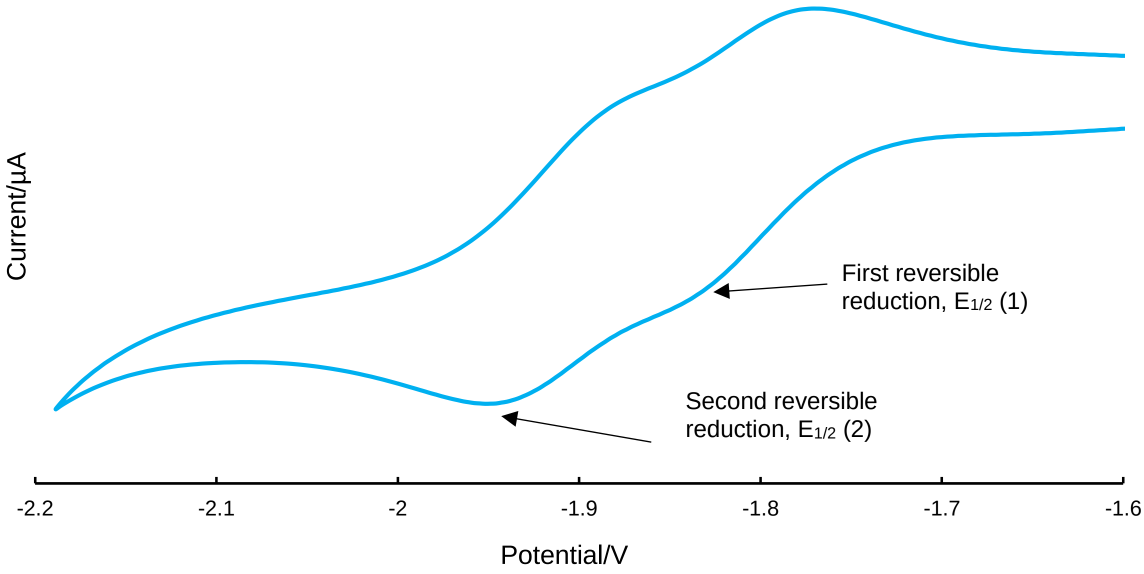


Figure 27: Cyclic voltammogram of complex **[4]**. CV in DMSO with 0.1 M TBAPF$_6$ solution recorded at a scan rate of 100 mV s^{-1} referenced against Fc/Fc$^+$.

Figure 27 shows the cyclic voltammogram of *α*-Mo$_2$(dppe)$_2$Cl$_4$ which can be shown to possess two reversible reductions at E$_{1/2}$ values of -1.829 V and -1.943 V (Table 1). The CV of a related complex, *β*-Mo$_2$(dppe)$_2$I$_4$ which showed a reversible one-electron oxidation at an E$_{1/2}$ of +0.62 V and an irreversible reduction at about -1.04 V.[74] The authors suggested that a metal-based redox process was occurring in which there was a removal of an electron from the δ-bonding orbital and an addition of an electron into the δ*-anti-bonding orbital that results in a decrease of bond order from 4 to 3.5. It could possibly be assumed that a similar process is occurring in the *α*- isomer of the complex and that unreacted ligand may be present resulting in two reductions (rather than one) being visible.

Table 1: Reduction potentials for complexes **[3]** and **[4]** in DCM and DMSO respectively with 0.1 M TBAPF$_6$ solution recorded at a scan rate of 100 mV s^{-1} referenced against Fc/Fc$^+$.

Complex	E$_{1/2}$ (1) / V	ΔE$_p$ (1) / V	E$_{1/2}$ (2) / V	ΔE$_p$ (2) / V
[3]	-1.534	0.054	N/A	N/A
[4]	-1.829	0.060	-1.943	0.063

3.2.6 *Summary*

Two previously reported complexes, $Mo_2(Hdppa)_2Cl_4$ and α-$Mo_2(dppe)_2Cl_4$, were prepared with the belief that they could form a new dimolybdenum quintuple bond due to their bulk. Attempts to prepare complexes that were of a similar nature to the dimolybdenum quintuply bonded complexes reported by Tsai *et al.* were performed however they were either unsuccessful with regards to $Mo_2(O_2CCH_3)_2(tmpf)_2$ and $Mo_2(DCyBA)_2Cl_4$ or were not fully characterised in the case of $Mo_2(\mu\text{-}Cl)[(Cl_2Li(OEt_2)][\mu\text{-}\eta^2\text{-}tpg]_2$.[26] The latter of these three complexes mentioned here may be of notable interest as it may be able to stabilise the quintuple bond better due to the central phenyl ring pushing down on the flanking phenyl groups resulting in a shorter metal-metal bond.[56]

4. Quadruply Bonded Dirhenium Precursors

In this study, we attempted to isolate the first example of Re-Re quintuple bond.[51] A variety of N-donor bidentate ligands were used to prepare novel quadruply bonded dirhenium complexes that were believed to be potential precursors to a quintuple bond compound. Formamidinate and guanidinate ligands were utilised due to their previous success in isolating a quintuple bond in dichromium and dimolybdenum complexes.[23,24]

Attempts to prepare the previously reported complexes $Re_2(dpf)_2Cl_4$ and $Re_2(DCyBA)_2Cl_4$ will also be reported.[75,76] Ventures were also taken out on preparing $Re_2(Hdppa)_2Cl_4$ and the exceptionally bulky $Re_2(ippa)_2Cl_4$ but were unsuccessful.[77]

4.1 *Proligands for Dirhenium Chemistry*

As mentioned previously, the formamidinate ligands were chosen due to their highly tuneable and bulky nature in addition to being used previously in quintuple bonding. The ligands, Hdipf, Htmpf and HdPhf (figure 16) were prepared according to an adapted literature procedure.[54] For the preparation of Hdipf and Htmpf, the respective aniline (2,6-diisopropylaniline or 2,4,6-trimethylphenylaniline) were heated at 160 °C for three hours along with a half equivalence of triethyl orthoformate and a small volume of acetic acid. The yellow solutions were then recrystallised from toluene and isolated by filtration. For the HdPhf ligand, the corresponding aniline was heated at 140 °C with triethyl orthoformate and acetic acid for four hours. The yellow solution was then triturated with cold pentane and filtered. All three proligands were isolated as colourless, crystalline solids.

The Htpg and dicyclohexylbenzamidinate ligands (Figure 16) are believed to behave similarly with regards to stabilising a quadruple and quintuple bond in a dirhenium complex. The central phenyl ring forces the flanking phenyl or cyclohexyl rings down to better protect the Re-Re centre and potentially reduce the Re-Re bond length.[56]

1,2,3-triphenyl guanidine was commercially available and believed to be able to facilitate a large enough bulk without employing mesityl or diisopropyl flanking regions. Li[DCyBA] was prepared by stirring phenyllithium in a diethyl ether / cyclohexane mixture with N,N'-dicyclohexylcarbodiimide for 12 hours. Evaporation of the solvent and addition of a 2:1 mixture of diethyl ether / toluene mixture yielded a beige suspension, which when filtered and washed with hexane, yielded a white solid.[78]

The Iminophosphonamide (ippa) ligand (Figure 16) provides a very large amount of steric bulk to a metal complex. It was chosen as it seems to be a good intermediate between the bisphosphine ligands (dppa, dppe and dppm) and the formamidinates and guanidinates. Ligands related to ippa have been shown to chelate in ruthenium and zirconium complexes, but no literature could be found on the potential bridging nature of ippa.[79,80]

The diaminophosphonium salt, [ippa]Br, which ippa is produced from is prepared by slowly adding a solution of bromine in DCM to a solution of chlorodiphenylphosphine in DCM at an ice-cold temperature. Stirring this mixture overnight and subsequent addition of aniline at 0 °C followed by stirring for a further 20 hours at room temperature yielded a white suspension, which was isolated by filtration.[81] The R group on the nitrogen is highly tuneable and so the degree of bulk provided can be decided from the choice of aniline.

Literature reports have shown that [ippa]Br can be mono or doubly deprotonated depending upon which base is used.[78] It was deemed necessary to only mono deprotonate the [ippa]Br ligand which was done by way of adding two equivalents of diethylamine to the salt and stirring in toluene for four hours.

4.2 *Dirhenium Complexes*

4.2.1 *Synthesis of Dirhenium Precursors*

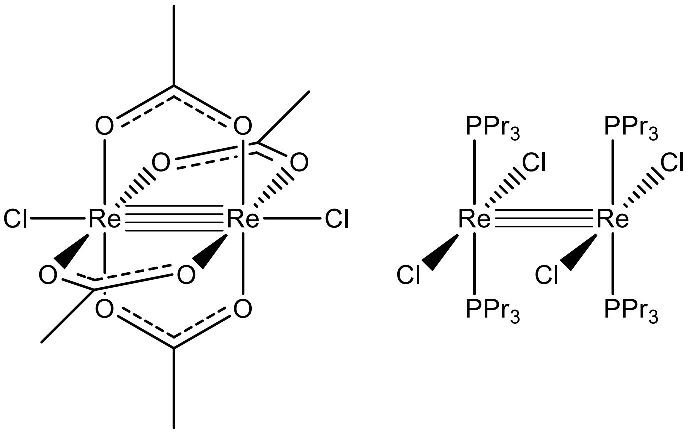


Figure 31: Dirhenium precursors $Re_2(O_2CCH_3)_4Cl_2$ (left) and $Re_2(PPr_3)_4Cl_4$ (right).

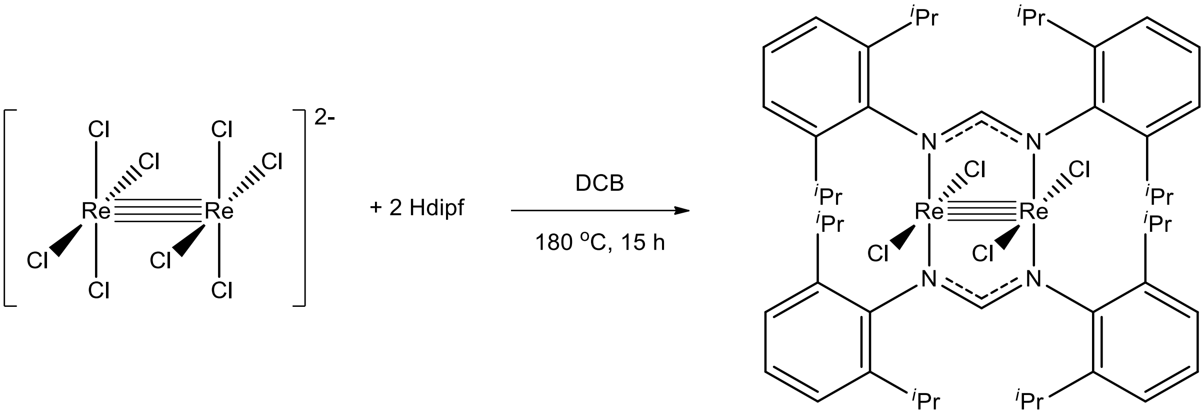
Three dirhenium complexes were used as starting materials to prepare the quadruply bonded dirhenium precursors. $[Re_2Cl_8]^{2-}$ was used to prepare most of the precursors as well as the intermediates.

Akin to how the reaction between $Mo_2(O_2CCH_3)_4$ and $[Mo_2Cl_8]^{4-}$ is reversible, so too is the preparation of $Re_2(O_2CCH_3)_4Cl_2$ (Figure 31) which is used in the preparation of some dirhenium precursors.[75,82] By refluxing $[Re_2Cl_8]^{2-}$ in glacial acetic acid with a small amount of acetic anhydride at 160 °C for one hour yielded a peach coloured solid which was separated by centrifugation due to the fineness of the solid being able to easily pass through the glass frit when attempting to filter the product.

This triply bonded complex, $Re_2(PPr_3)_4Cl_4$, (Figure 31) is useful in preparing the complex, $Re_2(Hdppa)_2Cl_4$ and is prepared by refluxing $[Re_2Cl_8]^{2-}$ with tri-*n*-propylphosphine in ethanol for ten days. Filtering the suspension left a blue-grey solid with the ^1H NMR spectrum showing the peaks expected of a *n*-propyl group.[77,83]

4.2.2 *Synthesis of Dirhenium Quadruply Bonded Complexes*

4.2.2.1 *Synthesis of $Re_2(dipf)_2Cl_4$* **[6]**



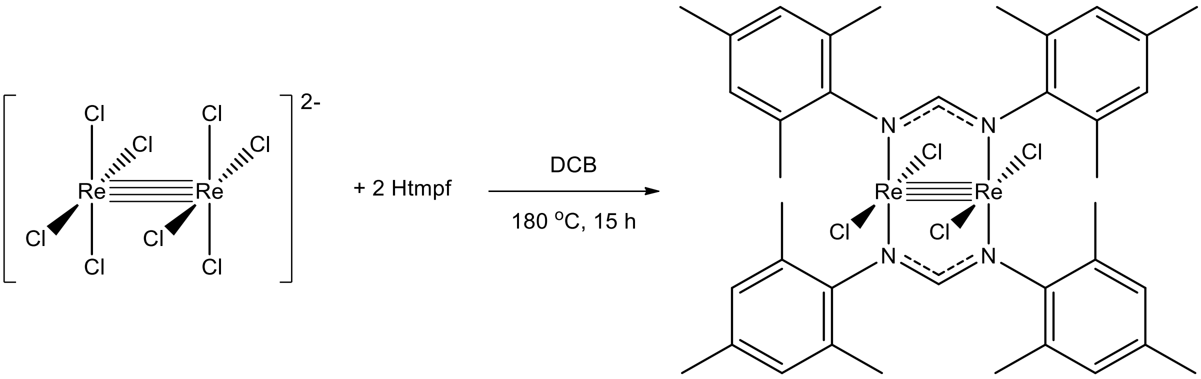
Scheme 23: Preparation of $Re_2(dipf)_2Cl_4$.

$Re_2(dipf)_2Cl_4$ **[6]** was synthesised by refluxing $[Re_2Cl_8]^{2-}$ with the Hdipf ligand in DCB at 180 °C for 15 hours (scheme 23). The green solution had the solvent removed by under reduced pressure and THF was added. The solution was filtered through Celite to remove trace amounts of unreacted $[Re_2Cl_8]^{2-}$, after which the solution was concentrated and layered with diethyl ether to yield a dark green, air stable solid.

A second route to synthesising this complex involved reacting $[Re_2Cl_8]^{2-}$ in the melt of the Hdipf ligand at 220 °C for 24 hours. While a green solid was obtained it was much harder to separate the excess ligand from the complex due to both of the substances possessing a similar solubility and a lower yield was obtained due to the tendency of the ligand to sublime.

The ^1H NMR spectrum of the complex confirms that **[6]** has indeed been synthesised due to the loss of the broad N-H peak that is visible in the ^1H NMR spectrum of the Hdipf ligand between δ = 9.66-8.35. The IR spectrum of the complex also shows the loss of the N-H stretching frequency that is visible in the ligand spectrum at 3018 cm^{-1}. Further confirmation is shown by the satisfactory elemental analysis obtained as the results were within +/- 0.4 % of the acceptable limit.

4.2.2.2 *Synthesis of $Re_2(tmpf)_2Cl_4$* ***[7]***



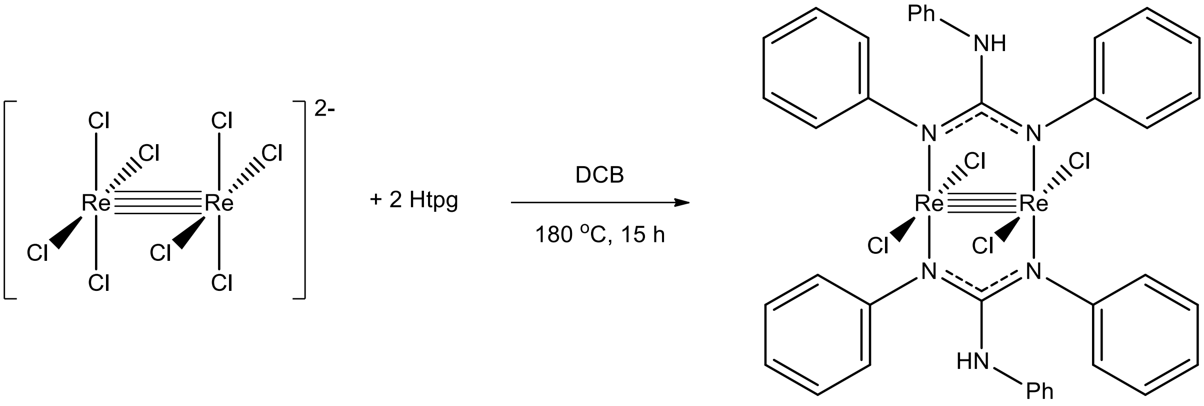
Scheme 24: Preparation of $Re_2(tmpf)_2Cl_4$.

$Re_2(tmpf)_2Cl_4$ **[7]** was prepared in a similar fashion to complex **[6]** whereby $[Re_2Cl_8]^{2-}$ was refluxed in DCB with two equivalents of the tmpf ligand for 15 hours (Scheme 24). Removal of the solvent by vacuum filtration followed by addition of THF and filtering through Celite left a green solution devoid of any residual starting materials. The solution was concentrated and layered with diethyl ether which caused crystals to form in a good yield (85 %) after three days at -26 °C.

Similarly, this complex could be prepared from a solid-state melt reaction using excess Htmpf and heating at 220 °C for 24 hours. This method was less favourable due to a tendency for the ligand to sublime and difficulty of separating the excess ligand from the complex due to them having near identical solubilities.

The ^1H NMR spectrum of $Re_2(tmpf)_2Cl_4$ aids in the confirmation that the complex was formed in a similar way to the ^1H NMR spectrum of **[6]** as the N-H peak is lost and the central methine proton is noticeably shifted from $\delta = 7.2$ to 7.74. Further confirmation is seen in the IR spectrum as the broad N-H stretching frequency at 3125 cm^{-1} that is seen in the ligand spectrum is absent in the spectrum of the complex.

4.2.2.3 *Synthesis of Re₂(tpg)₂Cl₄* ***[8]***



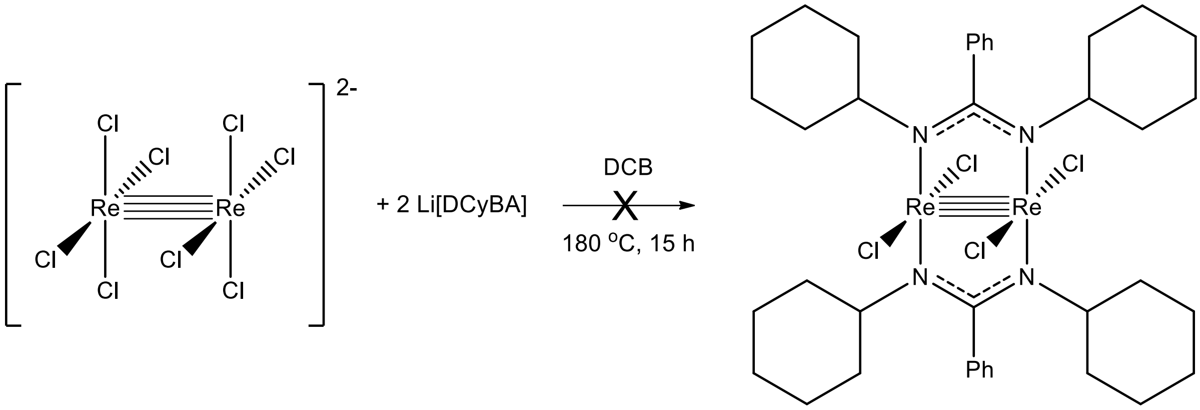
Scheme 25: Preparation of Re(tpg)$_2$Cl$_4$.

Tris-substituted and paddlewheel complexes using the tpg ligand that feature a dirhenium quadruple bond have previously been prepared, however there have been no published works on a trans-bis-substituted complex.[84,85] Refluxing [Re$_2$Cl$_8$]$^{2-}$with Htpg in DCB for 15 hours yielded a green solution (Scheme 25). Following a similar procedure to complexes **[6]** and **[7]** but layering with THF and cyclohexane rather than diethyl ether yielded a light green powder when filtered and was obtained in a moderate yield (51 %).

The structure of this complex cannot be entirely verified as a crystal structure was not obtained, however the method of preparation followed that of Walton's preparation of Re$_2$(DPhF)$_2$Cl$_4$ and due to the relative similarity between the formamidinate and guanidinate ligands it can be proposed that Re$_2$(tpg)$_2$Cl$_4$ was indeed prepared.[86]

4.2.3 Attempted Syntheses of Several Dirhenium Complexes

4.2.3.1 $Re_2(DCyBA)_2Cl_4$



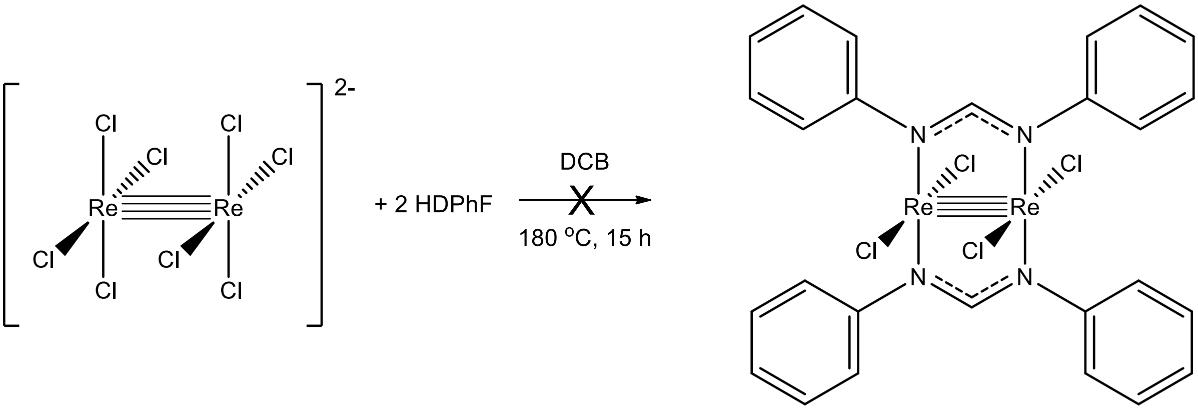
Scheme 26: Attempted preparation of $Re_2(DCyBA)_2Cl_4$.

While the complex $Re_2(DCyBA)_2Cl_4$ has been prepared in a previous report, attempts to make it in this project were unsuccessful.[74] Refluxing $[Re_2Cl_8]^{2-}$ in DCB with Li[DCyBA] for 15 hours yielded a green solution (Scheme 26). The DCB was evaporated via vacuum filtration and methanol was added, the solution was stirred and filtered, after which the methanol was evaporated and THF was then added and filtered again. The THF solution was concentrated and layered with hexane. Red crystals began to form overnight at -26 °C but decomposed to a black powder after an additional three days.

While the method in the literature differs from the one presented above as they use a different starting material, $Re_2(OAc)_4Cl_2$, and performed the reaction in the melt of the neutral ligand, the same product should still have been achieved as the colour of the crystals matched and the Schlenk tube used as a crystallisation vessel may not have been sealed sufficiently.

This complex showed promise in being capable of forming the first Re-Re quintuple bond due to the inherent bulk of the ligand used and the electrochemistry showed that it undergoes a quasireversible reduction at -1.08 V and an irreversible reduction at -2.19 V in THF. While the chemical structure of the reductive product(s) is unknown, the fact that it can undergo electrochemical reductions may indicate it can undergo a chemical reduction using a suitable reducing agent to form a quintuply bonded product. These irreversible reductions are desirable as it relates to a change in the structure which is expected in the reactions due to the expectation that the chloride ligands are to be ejected in order to stabilise the metal-metal bond.

4.2.3.2 *Re₂(DPhF)₂Cl₄*

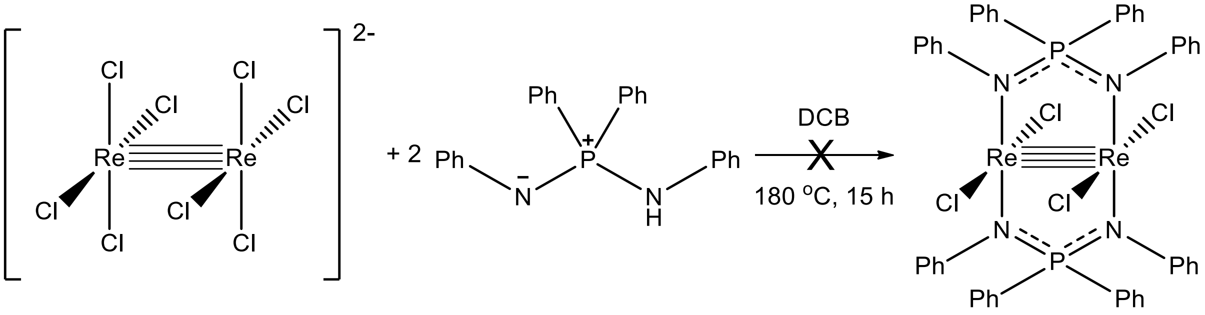


Scheme 27: Attempted preparation of $Re_2(DPhF)_2Cl_4$.

This complex has been prepared previously by Cotton *et al*. and later on by Walton *et al.* by two differing methods.[76,85] Cotton and co-workers prepared $Re_2(DPhF)_2Cl_4$ by way of treating $Re_2(DPhF)_3Cl_3$ in acetonitrile and DCM with 85 % fluoroboric acid and layering the red solution that formed with diethyl ether. Walton and his co-workers developed two methods to prepare the *trans* complex. The first involved heating $[Re_2Cl_8]^{2-}$ in a melt of the ligand at 150 °C for 15 hours and washing with DCM leaving red crystals. Their second method (and the method used in this project) involved refluxing $[Re_2Cl_8]^{2-}$ in DCB with two equivalents of the ligand for 24 hours. Cooling the mixture and adding diethyl ether caused the complex to precipitate.

The method used in the research diverged slightly (Scheme 27) from Walton's preparation where after refluxing the mixture, the DCB was instead evaporated and methanol was added and then filtered through Celite. The methanol in the green solution was evaporated and THF was added to the solid and layered with hexane. After 3 days at -26 °C it appeared that decomposition had occurred due to the colour change from green to black.

4.2.3.3 *Re₂(ippa)₂Cl₄*

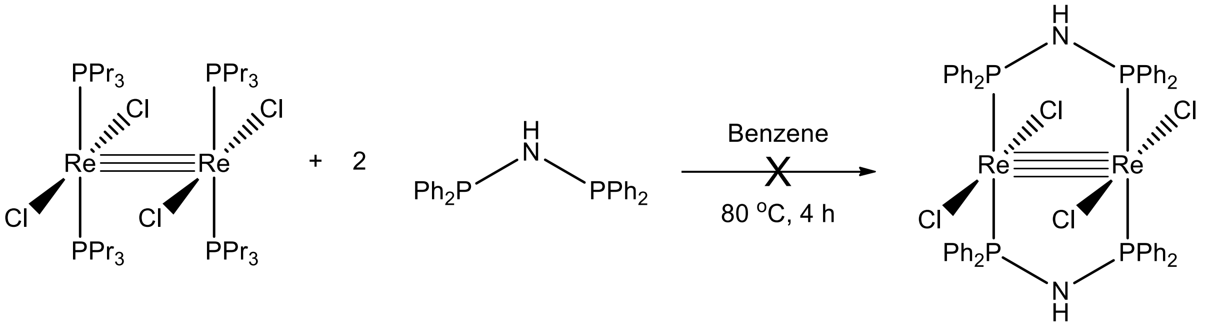


Scheme 28: Attempted preparation of $Re_2(ippa)_2Cl_4$.

Several attempts were made to prepare this complex wherein $[Re_2Cl_8]^{2-}$ was either refluxed (180 °C) or heated (60-90 °C) in DCB with two equivalents of the mono-deprotonated ippa ligand. All reactions initially formed a green solution upon the addition of DCB to the solid mix but soon decomposed to a black solution after application of heat.

These reactions may have been unsuccessful due to the presence of some diethylamine still remaining in the ligand or that the desired complex may have simply been too bulky to successfully bridge the Re-Re quadruple bond. Further drying of the ligand may be necessary but stirring in DCB for several days at room temperature may produce a positive result.

4.2.3.4 *Re₂(Hdppa)₂Cl₄*



Scheme 29: Attempted preparation of $Re_2(Hdppa)_2Cl_4$.

The synthesis of $Re_2(Hdppa)_2Cl_4{\cdot}2.5C_6H_6$ has been previously reported by Walton *et al.*[87] The method to prepare it was followed which yielded an unsuccessful result in this case. Refluxing $Re_2(P\text{-}n\text{-}Pr_3)_4Cl_4$ in benzene for four hours was expected to yield a blue-purple solid. Instead, a sticky black solid was obtained after removal of the solvent which may have been a result of the compound decomposing due to improper drying of benzene.

4.3 *UV-Vis Spectroscopy*

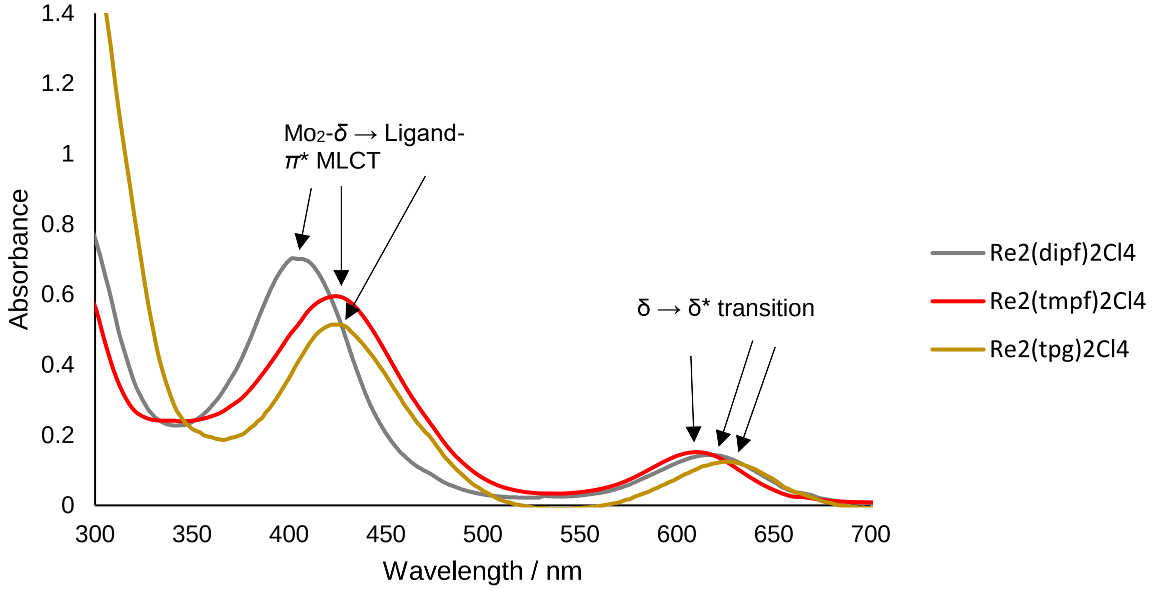


Figure 32: Collective normalised UV-Vis spectra of complexes **[6]**, **[7]** and **[8]** in DCM recorded at room temperature.

The UV-Vis spectra of complexes $Re_2(dipf)_2Cl_4$, $Re_2(tmpf)_2Cl_4$ and $Re_2(tpg)_2Cl_4$ (**[6]**, **[7]** and **[8]**) are shown in figure 32. Complex **[6]** (Figure 32, grey trace, Table 2) shows, with tentative assignment, either a non-bonding ligand orbital (n) to a *π** intraligand charge transfer (ILCT) or a ligand-only transition at approximately 300 nm. A second broader peak of a relatively similar intensity to the ILCT can be seen at 408 nm which was assigned as a Mo_2-*δ* → Ligand-*π** MLCT. The third weaker peak visible at 621 nm is assigned as the δ → δ* transition of the metal. Similar results are seen for complex **[7]** (Figure 32, red trace, Table 2) trace which displays a n → *π** ILCT or a ligand only transition at a slightly higher energy of 295 nm. The *δ* → *π** MLCT occurs at 425 nm and the small band assigned as a δ → δ* transition is visible at 615 nm. Complex **[8]** (Figure 32, yellow trace, Table 2) differs slightly from $Re_2(dipf)_2Cl_4$ and $Re_2(tmpf)_2Cl_4$ as an ILCT or ligand tranisiton is absent in the UV spectrum. However, the *δ* → *π** MLCT and δ → δ* transition bands are visible at wavelengths of 426 nm and 628 nm respectively. The δ → δ* transitions of the dirhenium quadruply bonded precursors (**[6]**, **[7]** and **[8]**) occur at a much lower energy than that of many dirhenium paddlewheel complexes, such as $Re_2Cl_2[(p\text{-}MeOC_6H_4)\text{-}NCHN(p\text{-}MeOC_6H_4)]_4$ which occurs at 418 nm.[88] This may be due to more chloride *π*-donor ligands being present on complexes **[6]** – **[8]** that raise the energy of the delta bond. The MLCTs and δ → δ* transitions of all three complexes are occur at a similar energy as they have similar stabilising ligands with the exception of the tpg complex where its bulk arises from the central phenyl ring pushing down the flanking two phenyl rings.

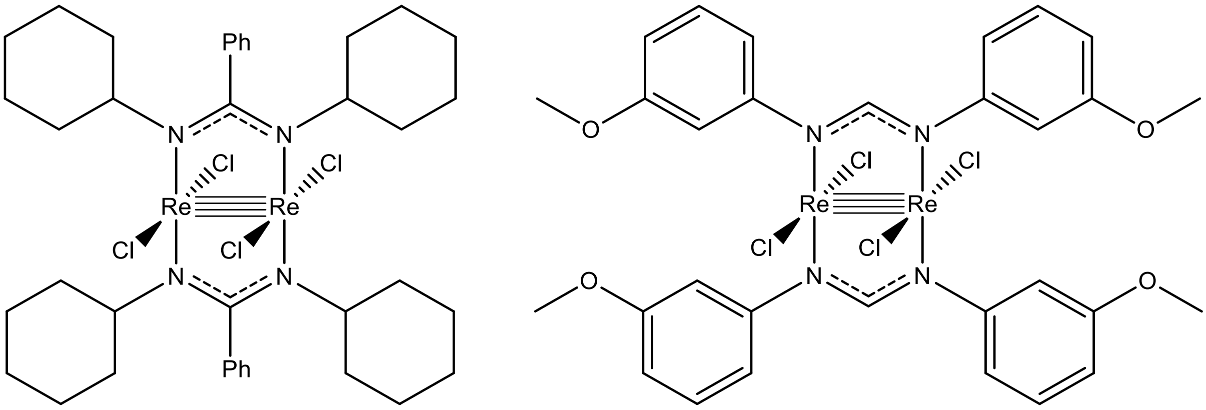


Figure 33: Re$_2$(DCyBA)$_2$Cl$_4$ (left) and Re$_2$(DmAniF)$_2$Cl$_4$ (right).

Re$_2$(DCyBA)$_2$Cl$_4$ and Re$_2$(DmAniF)$_2$Cl$_4$ (Figure 33) are similar in structure to the dirhenium precursors and have UV spectra that display $\delta \rightarrow \delta^*$ transitions at energies at an intermediate level between the paddlewheel complex, tetrakis-para-methoxyphenyldichloroformamidinate dirhenate, and the precursors which appear at wavelengths of 558 nm for Re$_2$(DCyBA)$_2$Cl$_4$ and 584 nm for Re$_2$(DmAniF)$_2$Cl$_4$.[74,75,85] It would have been expected for Re$_2$(DCyBA)$_2$Cl$_4$ and Re$_2$(tpg)$_2$Cl$_4$ to have similar UV spectra due to them being very similar in structure, however Re$_2$(tpg)$_2$Cl$_4$ has the lowest $\delta \rightarrow \delta^*$ transition energy of these six complexes. This effect is expected to result in the $\delta \rightarrow \delta^*$ transition being higher in energy as the Re-Re bond would be shorter, however this effect may be less pronounced as the tpg ligand may not be as bulky as the dipf or tmpf ligands. The stabilisation that these bidentate ligands provide to the Re-Re quadruple bond can be further confirmed by comparison to the starting compound which is far less bulky, $[Re_2Cl_8]^{2-}$ which has a $\delta \rightarrow \delta^*$ transition that is appears at approximately 510 nm.[90]

Table 2: UV-vis data for dirhenium complexes **[6]**, **[7]** and **[8]** in DCM.

Compound	$n \rightarrow \pi^*$ ILCT / ligand transition (nm)	$\delta \rightarrow \pi^*$ MLCT (nm)	$\delta \rightarrow \delta^*$ transition (nm)
Re$_2$(dipf)$_2$Cl$_4$	300	408	621
Re$_2$(tmpf)$_2$Cl$_4$	295	425	615
Re$_2$(tpg)$_2$Cl$_4$	N/A	426	628

4.4 *Cyclic Voltammetry*

Figure 34 displays the cyclic voltammogram of $Re_2(dipf)_2Cl_4$ **[6]** which displays two reductions at $E_{1/2}$ values of -1.348 V and -1.623 V(table 3). Given that these reductions are poorly resolved it is difficult to assign the reduction processes. However, it is likely that the first redox process (-1.35 V) corresponds to reduction of the Re_2^{6+} core, with ligand reductions occurring at lower potential (-1.62 V).

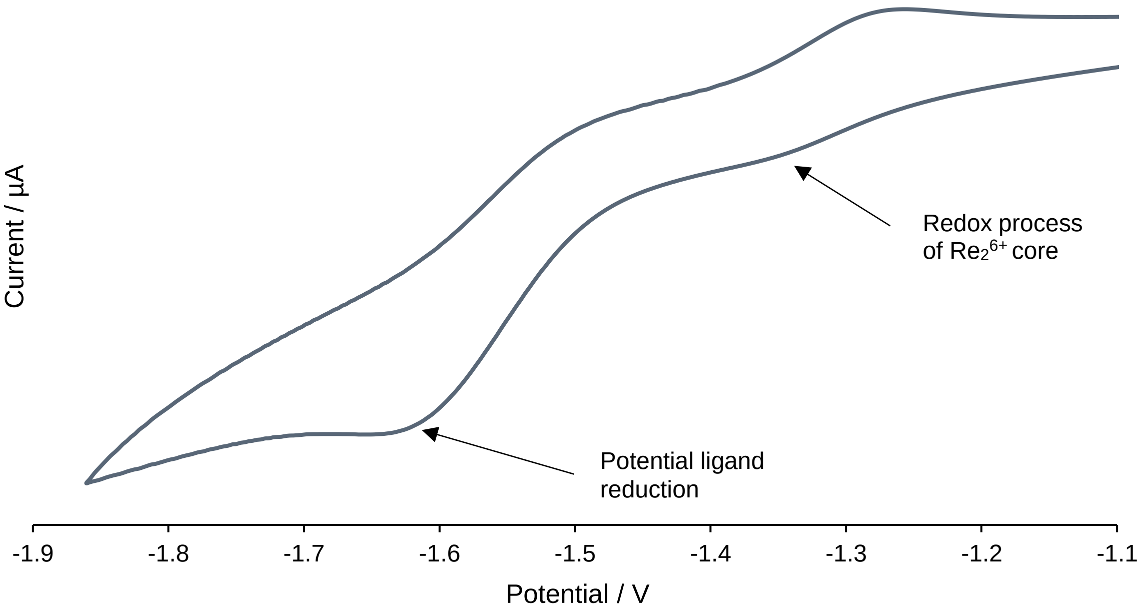


Figure 34: Cyclic voltammogram of complex **[6]**. CV in DCM with 0.1 M $TBAPF_6$ solution recorded at a scan rate of 100 mV s^{-1} referenced against Fc/Fc^+.

Shown in Figure 35 is the CV of $Re_2(tmpf)_2Cl_4$ **[7]** which has been tentatively assigned as showing a broad irreversible reduction at an $E_{1/2}$ value of -1.898 V (Table 3). This complex may not have been entirely dissolved in the solution and the peaks cannot be assigned with confidence. The irreversibility of this reduction may be due to a significant structural change within the molecule such as the loss of two of the chloride ligands that would occur when the complex is reduced, and a quintuple bond is formed.

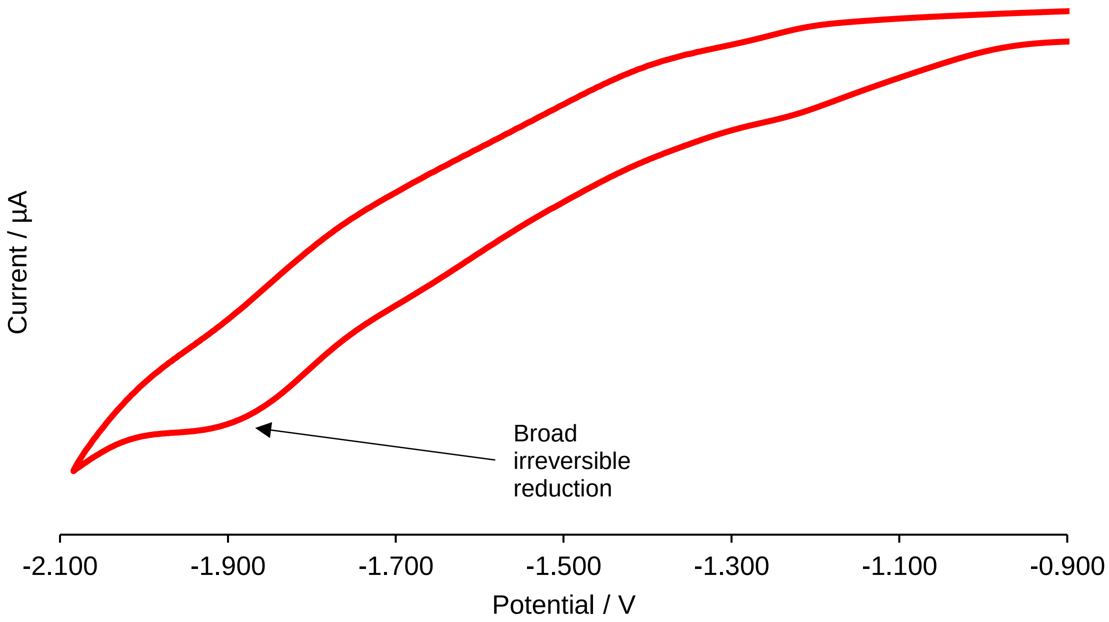


Figure 35: Cyclic voltammogram of complex **[7]**. CV in DCM with 0.1 M TBAPF$_6$ solution recorded at a scan rate of 100 mV s^{-1} referenced against Fc/Fc$^+$.

The CV of Re$_2$(tpg)$_2$Cl$_4$ **[8]** displays one reversible reduction at an E$_{1/2}$ value-1.549 V (Figure 36, Table 3). Due to the relative magnitudes of the reduction peaks, it is assumed that two one-electron reduction processes are occurring in the CV of **[8]**.

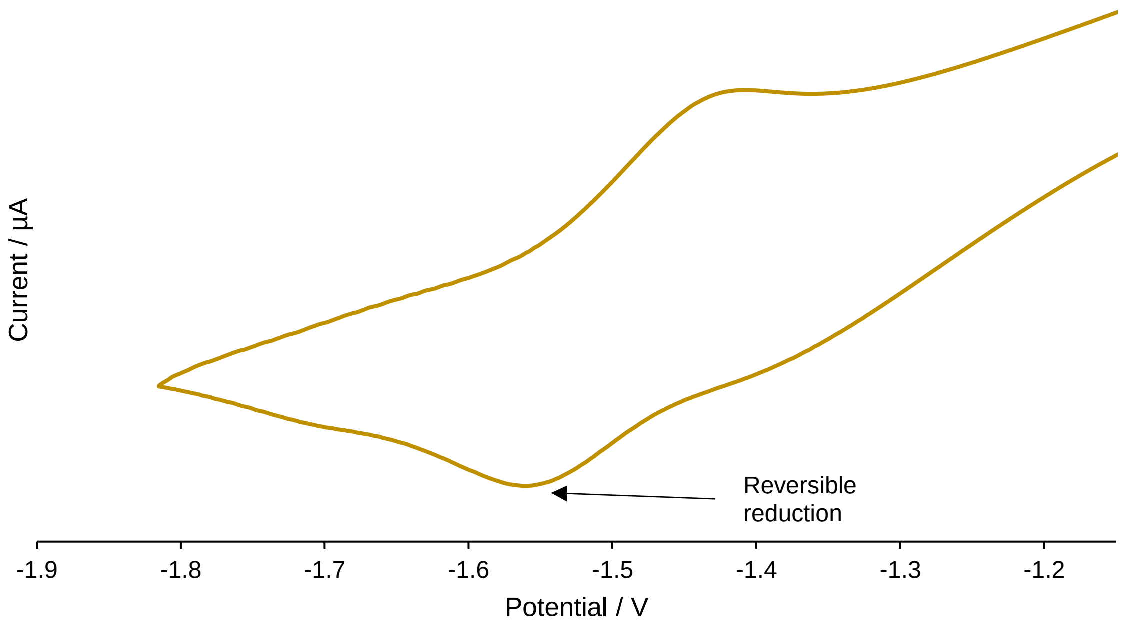


Figure 36: Cyclic voltammogram of complex **[8]**. CV in DCM with 0.1 M TBAPF$_6$ solution recorded at a scan rate of 100 mV s^{-1} referenced against Fc/Fc$^+$ (= 0.0 V).

Table 3: CV data of the dirhenium complexes in DCM with 0.1 M TBAPF$_6$ solution recorded at a scan rate of 100 mV s^{-1} referenced against Fc/Fc.

Complex	$E_{1/2}$ (1) / V	ΔE_p (1) / V	$E_{1/2}$ (2) / V	ΔE_p (2) / V	ΔE (1-2) / V	ΔE_p Reference / V
[6]	-1.348	0.084	-1.623	0.125	0.275	0.159
[7]	-1.898	0.060	N/A	N/A	N/A	0.179
[8]	-1.549	N/A	N/A	N/A	N/A	0.278

5. Reductions

Reductions of the known dichromium complexes involved using a dichloro-bridged dichromium complex with potassium graphite, meanwhile quadruply bonded dimolybdenum complexes have been used as precursors to form a quintuple bond upon reduction with potassium graphite.[23,24]

This research involved preparing quadruply bonded dimolybdenum and dirhenium complexes that were believed to be potential precursors to quintuple bonds. These complexes needed to be stabilised by a minimal amount of bulky anionic ligands. Furthermore, the metals need to be in an oxidation state of +1 or +2 for molybdenum and rhenium respectively so that they can form a quintuple bond.

The timeframe of this project permitted the preparation and attempted reductions of five quadruply bonded complexes using potassium graphite as a reducing agent. Other complexes were attempted to be prepared and while two were believed to have been successfully prepared, $Mo_2(\mu\text{-}Cl)[(Cl_2Li(OEt_2)][\mu\text{-}\eta^2\text{-tpg}]_2$ and $\beta\text{-}Mo_2(dppe)_2Cl_4$, they were not fully characterised and reductions were not attempted on these complexes.

Two methods were devised in reducing the complexes. The first followed in a fashion similar to the method used by Tsai *et al*. to prepare the quintuply bonded dimolybdenum complexes which involved stirring the complex in THF along with three or four equivalents of KC_8 for 24 hours. The second method was performed by reacting the complexes with three or four equivalents of KC_8 (a strong reducing agent) in addition to two equivalents of potassium hexafluorophosphate which was used in an attempt to abstract the chloride ligands from the complex and generate the desired quintuply bonded products after stirring for 24 hours.

All the attempts were unsuccessful as they all resulted in the formation of a yellow-brown solid. Crude NMR spectra were obtained from the reductions and all of which appeared to indicate decomposition of the compounds had occurred as they either resembled the NMR spectra of their respective ligands or had unassignable peaks. Examination of the ^{31}P NMR spectra obtained from the reductions of $\alpha\text{-}Mo_2(dppe)_2Cl_4$ and $Mo_2(Hdppa)_2Cl_4$ aided in confirmation that decomposition had occurred, because the peaks appeared at the same position in the attempted reduction NMR spectra as they did in the ligand spectra.

6. Conclusions

A variety of bulky bidentate ligands were successfully prepared in the belief that they could be used to stabilise quadruply bonded homobimetallic complexes that were thought to be potential precursors to quintuply bonded species.

For the dimolybdenum species, two bisphosphine ligands (Hdppa and dppe) were used as a primary focus. The dppe ligand was commercially available, while Hdppa was prepared from refluxing hexamethyldisilazane with chlorodiphenylphosphine. Hdppa could be deprotonated to form an anionic ligand (and therefore generate a dimolybdenum species that will possess a +1 oxidation state upon reduction). Other ligands were also used, such as 1,2,3-triphenylguanidine, dppf, tmpf and DCyBA. The ligands were characterised by ^{1}H NMR spectroscopy, ^{31}P NMR spectroscopy, IR spectroscopy and mass spectrometry and confirmed that pure products were prepared.

$Mo_2(Hdppa)_2Cl_4$ was successfully prepared by the reaction of $Mo_2(O_2CCH_3)_4$ with Hdppa and TMSCl. Assessment of the ^{1}H NMR and ^{31}P spectroscopy showed that the product had been prepared. The UV-Vis spectrum showed a MLCT at 475 nm and a $\delta \rightarrow \delta^*$ transition at 705 nm and the cyclic voltammogram displayed a broad quasi-irreversible reduction at $E_{1/2}$ = -1.534 V.

α-$Mo_2(dppe)_2Cl_4$ was synthesised through refluxing $[Mo_2Cl_8]^{4-}$ with dppe in ethanol and its isomer, β-$Mo_2(dppe)_2Cl_4$ was later prepared. The α-isomer has one ligand chelating to each molybdenum unit. The α-isomer was characterised by ^{1}H NMR spectroscopy, ^{31}P NMR spectroscopy, IR spectroscopy and UV-Vis spectroscopy which confirmed that the complex had been prepared successfully in addition to showing a MLCT at 475 nm and the $\delta \rightarrow \delta^*$ transition at 680 nm. The cyclic voltammogram of α-$Mo_2(dppe)_2Cl_4$ displayed two reversible reductions at $E_{1/2}$ values of -1.829 V and -1.943 V. The β-isomer of $Mo_2(dppe)_2Cl_4$ was later prepared by a method analogous to the preparation of $Mo_2(Hdppa)_2Cl_4$ mentioned above, however due to time constraints only the ^{1}H NMR and ^{31}P NMR spectra were obtained.

A method following the preparation of the dimolybdenum quintuple bond precursors stabilised by the formamidinate was utilised in preparing a similar complex using the bulky 1,2,3-triphenylguanidinate ligand. Unfortunately, the complex was not fully characterised, and the structure could not be verified as crystals were not obtained through any of the attempts to do so. The ^{1}H NMR spectrum and IR spectrum aided in suggesting that the complex had been successfully synthesised.

Reductions were attempted on $Mo_2(Hdppa)_2Cl_4$ and its deprotonated form as well as α-$Mo_2(dppe)_2Cl_4$ using KC_8 as a reducing agent and KPF_6 as a chloride abstractor. All attempts at reducing these complexes were unsuccessful as the ^1H NMR spectra and ^{31}P NMR spectra of the attempted reduced species indicated decomposition had occurred as the peaks corresponded with those of the ligand NMR spectra.

The dirhenium section of this research focused on preparing various novel quadruply bonded dirhenium complexes with bulky ligands that were believed to be potential precursors to a Re-Re quintuple bond. Efforts were focused on preparing complexes of the general formula $Re_2(NN)_2Cl_4$ where NN is a bulky formamidinate or guanidinate ligand. $Re_2(dipf)_2Cl_4$, $Re_2(tmpf)_2Cl_4$ and $Re_2(tpg)_2Cl_4$ were successfully prepared and characterised by ^1H NMR spectroscopy, IR spectroscopy, UV-Vis spectroscopy and cyclic voltammetry.

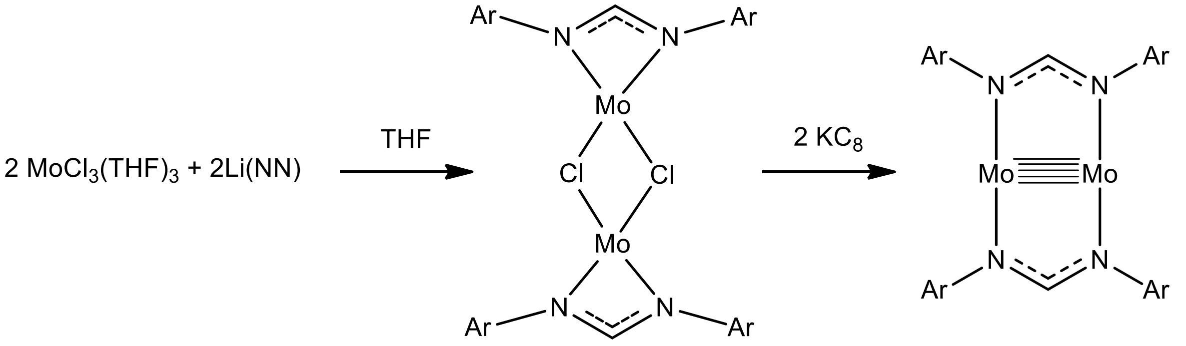
All three complexes were successfully prepared following the same method whereby $[Re_2Cl_8]^{2-}$ was refluxed in DCB with two equivalents of the relevant ligand for 15 hours. The UV-vis spectra of the three complexes all displayed a MLCT transition around 410 nm. The $\delta \rightarrow \delta^*$ transitions were observed at 621, 615 and 628 nm for $Re_2(dipf)_2Cl_4$, $Re_2(tmpf)_2Cl_4$ and $Re_2(tpg)_2Cl_4$ respectively. The CV of $Re_2(dipf)_2Cl_4$ displayed two reversible reductions at $E_{1/2}$ values of -1.348 V and -1.623 V, while $Re_2(tmpf)_2Cl_4$ showed a broad irreversible reduction at -1.898 V and $Re_2(tpg)_2Cl_4$ had one irreversible reduction and one reversible reduction at -1.374 V and -1.549 V respectively.

Reductions were attempted using an identical method to that of the dimolybdenum complexes where KC_8 was used as a reducing agent and KPF_6 was used to abstract the chlorides on the complex. Similar results were obtained for these reductions where a white-brown solid was obtained and the ^1H NMR spectra appeared to indicate decomposition of the complex had occurred. Although the initial attempts at reduction have proven unsuccessful, the successful isolation and characterisation of quadruply bonded dirhenium complexes with bulky amidinate ligands suggests that isolation of a group 7 quintuple bond could be achieved in future.

With an enhanced focus on the reduction stage, it may have been possible to have isolated a quintuple bond with the dipf and tpg bridging ligands being used to stabilise the metal bond due to the large amount of steric bulk they provide and that they can be electrochemically reduced according to the CVs of both complexes. The dimolybdenum complex using Hdppa as a ligand may also be of interest if the ligands can be successfully deprotonated first, as to do so would leave the target quintuple bond complex to be of the correct oxidation state. Use of the ippa ligand may be promising for the future as a completely new type of ligand architecture that still has the N-donor capacity that has seen the most success in the field of quintuple bonding.

6.1 *Future Work*

The preparation of dichromium quintuple bonds involved the use of $CrCl_3$ as a starting material, whereas the dimolybdenum complexes have utilised the $[Mo_2Cl_8]^{4-}$ anion to prepare the quintuple bond. It may therefore be a worthwhile avenue to devise reactions that use molybdenum (III) chloride (prepared from the reduction of molybdenum pentachloride by tin chloride) rather than $[Mo_2Cl_8]^{4-}$.[89] While rhenium may be in a different group to chromium and molybdenum it may also show successful results to use $ReCl_3$ as a starting material, particularly the employment of bulky ligands as the target binuclear dichloro-bridged intermediate species (Scheme 30) may aid in separating the sterically hindering ligands in addition to avoiding the chloride ligands that are present in the quadruply bonded precursors of the formula $Re_2(LL)_2Cl_4$.



Scheme 30: Theoretical reaction scheme using $MoCl_3$ and a dichloro-bridged intermediate species as a precursor to a quintuply bonded complex.

The ligands used to prepare the known quintuply bonded dichromium complexes could be prepared and used in reactions to potentially prepare related dimolybdenum and dirhenium complexes that have a metal-metal quintuple bond. The dipf ligand has been employed to prepare a dimolybdenum quintuple bond due to the highly tuneable nature of the formamidinate ligand allowing it to provide a large amount of bulk that can protect the dimetal unit.

Unlike chromium and molybdenum quintuply bonded complexes, a dirhenium complex of the same nature would possess a chloride ligand on each rhenium atom. These chlorides could potentially be substituted for a third bidentate ligand to increase the overall steric bulk of the complex and therefore better stabilising the metal-metal quintuple bond. Cotton *et al.* prepared the quadruply bonded complex $Re_2(DPhF)_3Cl_3$ (from which he prepared $Re_2(DPhF)_2Cl_4$), which could have the potential to form a quintuple bond as a reduction is stated at an $E_{1/2}$ value of -0.97 V.[76] $[Re_2(tpg)_3(O_2CCH_3)_4Cl]Cl$, a paddlewheel complex prepared by Mallick *et al*. could also be seen as a potential precursor that could form a dirhenium quintuply bonded complex that would be encapsulated by three bidentate ligands.[84] While cyclic voltammetry was not conducted on this complex, related compounds have been shown to be reducible (according to their CV data) and with the lability of the acetate group, it could be removed during reduction.

Only two separate methods were attempted in reducing the dimolybdenum and dirhenium quadruply bonded complexes. The first involved using KC_8 and stirring in THF for 24 hours at room temperature, the second was similar but also included KPF_6 in an attempt to help remove the chloride ligands. This method could be improved upon by varying the stoichiometry of KC_8 used in the reductions, furthermore, conducting the experiments at colder temperatures may help prevent decomposition of the resulting complexes.

KC_8 appears to be the most commonly used reducing agent to prepare complexes with a quintuple bond but using other reducing agents could yield successful results with the complexes used. One such example is the highly tuneable Jones' magnesium dimers which can have their reactivity altered by increasing or decreasing the steric bulk.[90] These dimers may be preferred over using KC_8 as a reducing agent as they have been shown to behave as a halide abstractor when used to reduce metal halides, which may be useful for the dimolybdenum and dirhenium complexes prepared during this research.[91]

7. Experimental

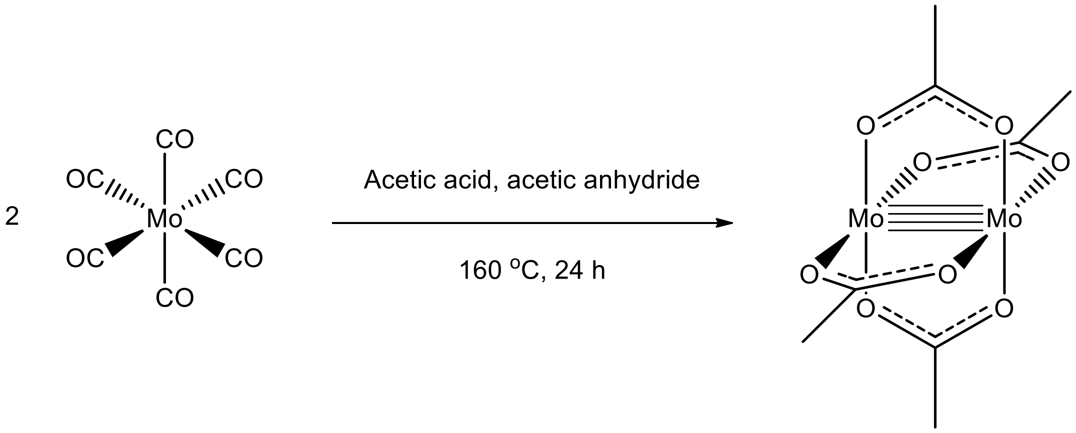
7.1 *Physical Methods*

All reactions were carried out under an atmosphere of nitrogen or argon using standard Schlenk line and glovebox techniques. The solvents used were purified and dried using calcium hydride prior to use with the exception of methanol and ethanol which were dried using magnesium and stored over type 3A molecular sieves. NMR spectra were recorded using a Bruker Avance (^{1}H 400.13 MHz) spectrometer in solutions of $CDCl_3$, d_2-DCM, d_6-DMSO and d_8-THF and referenced against their residual protio resonances. UV-vis spectra were recorded on a Shimadzu UV 3600+ using a quartz cuvette of a path length of 1 mm in concentrated hydrochloric acid, DCM, THF and DMSO. The IR spectra were obtained from a Thermo Scientific Nicolet 380 FT-IR spectrometer in the solid state. Mass spectra data was recorded and obtained from an Agilent 6530 Q-TOF MS. Elemental analysis was not performed on known complexes.

The Cyclic voltammograms were performed with a Palm Instruments EmStat 2 potentiostat using a platinum disc working electrode, a platinum wire counter electrode and a platinum wire reference electrode using 0.1 M $TBAPF_6$ electrolyte solutions in DCM or DMSO. Measurements were performed at scan rates between 100 – 500 mV s^{-1} at 100 mV s^{-1} intervals. The internal reference of Fc / Fc^+ couple was used and occurred at 0.00 V.

7.2 *Dimolybdenum Precursors*

7.2.1 *Preparation of $Mo_2(O_2CCH_3)_4$* [59,60]

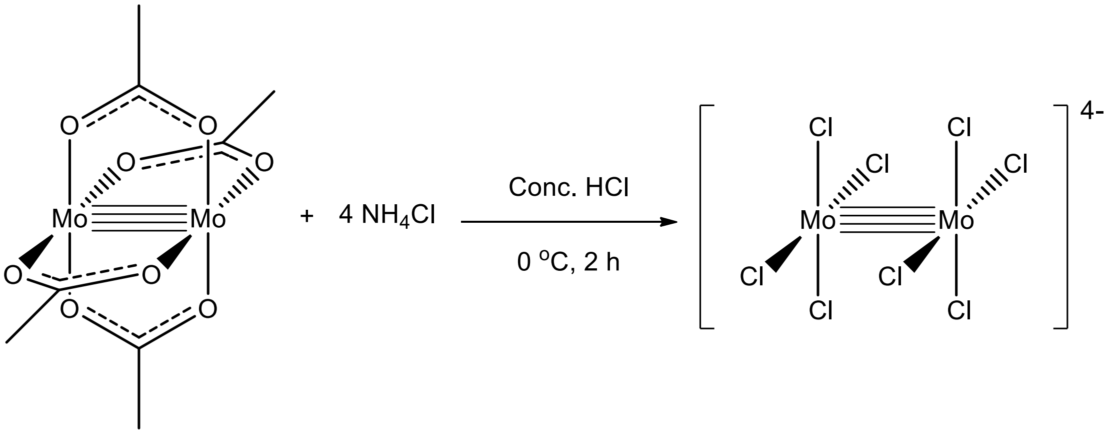


Scheme 23: Preparation of $Mo_2(O_2CCH_3)_4$.

$Mo(CO)_6$ (6.0 g, 23 mmol) was added to a Schlenk flask followed by a acetic acid (60 ml) and acetic anhydride (40 ml). The mixture was refluxed for 24 hours and filtered after cooling. The resulting dark yellow solid was washed with diethyl ether, hexane, ethanol, and a second portion of diethyl ether. The solid was isolated as a crystalline, bright yellow solid (2.1 g, 43%).

^1H NMR (400 MHz, d^6-DMSO) δ 2.61 (s, 12 H).

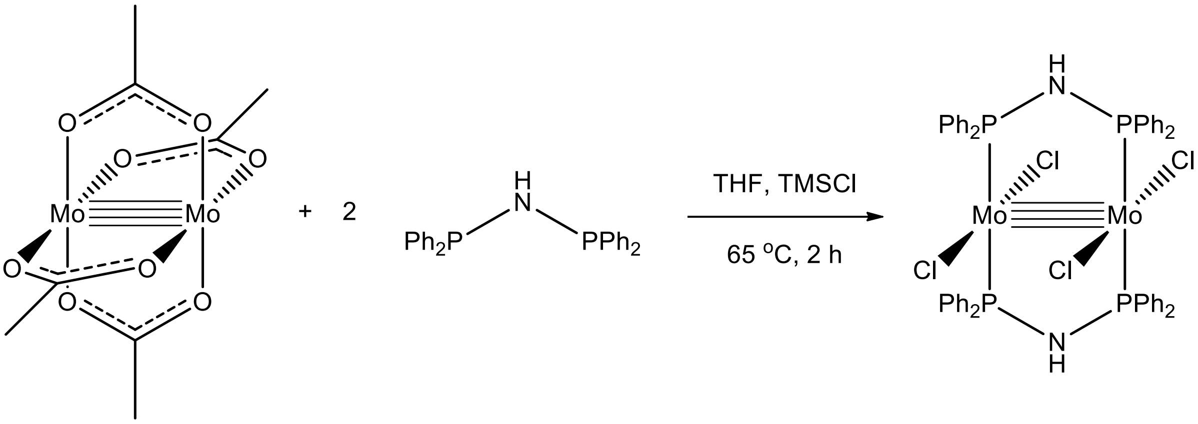
7.2.2 *Preparation of $(NH_4)_4Mo_2Cl_8$* [61]



Scheme 24: Preparation of $[Mo_2Cl_8]^{4-}$ from $Mo_2(O_2CCH_3)_4$.

A Schlenk tube containing $Mo_2(O_2CCH_3)_4$ (1.07 g, 2.5 mmol) and four equivalents of ammonium chloride (0.535 g, 10 mmol) as well as 30 mL of concentrated hydrochloric acid were stirred for 30 minutes until all the yellow solid had dissolved and a purple solid had precipitated. The mixture was then filtered and washed with cold ethanol to yield a purple solid (0.64 g, 47% yield). UV λ_{max} (HCl)/ nm 520 (ε = 11760 M cm^{-1}), 259 (ε = 26790 M cm^{-1}).

7.2.3 ***Preparation of $Mo_2(Hdppa)_2Cl_4$***[62]

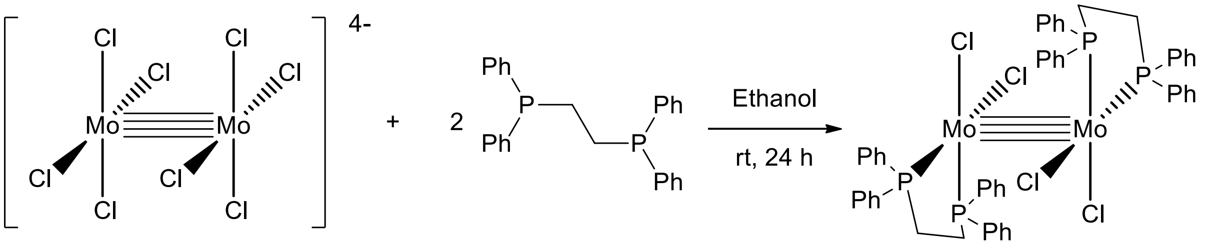


Scheme 25: Preparation of $Mo_2(Hdppa)_2Cl_4$ from $Mo_2(O_2CCH_3)_4$.

A Schlenk flask was charged with $Mo_2(O_2CCH_3)_4$ (0.5 g, 1.7 mmol), 2.2 equivalents of Hdppa (1.0 g, 2.6 mmol) and THF (30 mL). An excess of TMSCl (2.5 mL) was then added resulting in immediate colour changes of the solution from yellow to red to purple and then formation of a green suspension in a purple solution. The reaction mixture was refluxed for two hours, after which it was filtered and washed with THF and hexane leaving a bright green solid identified as $Mo_2(Hdppa)_2Cl_4$ (1.0 g, 78 %) and a purple solution which was found to be an intermediate $Mo_2(Hdppa)_2(O_2CCH_3)_2Cl_2$ after removal of the solvent.

^{1}H NMR (400 MHz, DCM) δ 7.47-7.32 (m, 40 H, J = 7.39 Hz), 4.28 (s, 2H). ^{31}P NMR (400 MHz, DCM) δ 73.39. IR ν (cm^{-1}) 3045 m, 1481 w, 1433 m, 1406 m, 1313 w, 1252 w, 1095 m, 911 m, 814 m, 739 m, 708 m, 690 vs, 523 s. UV λ_{max} (DCM) / nm 700 (ε = 2780 M cm^{-1}), 475 (ε = 1240 M cm^{-1}), 345 (ε = 1740 M cm^{-1}), 340 (ε = 11300 M cm^{-1}).

7.2.4 *Preparation of α-Mo_2(dppe)$_2Cl_4$* [64]

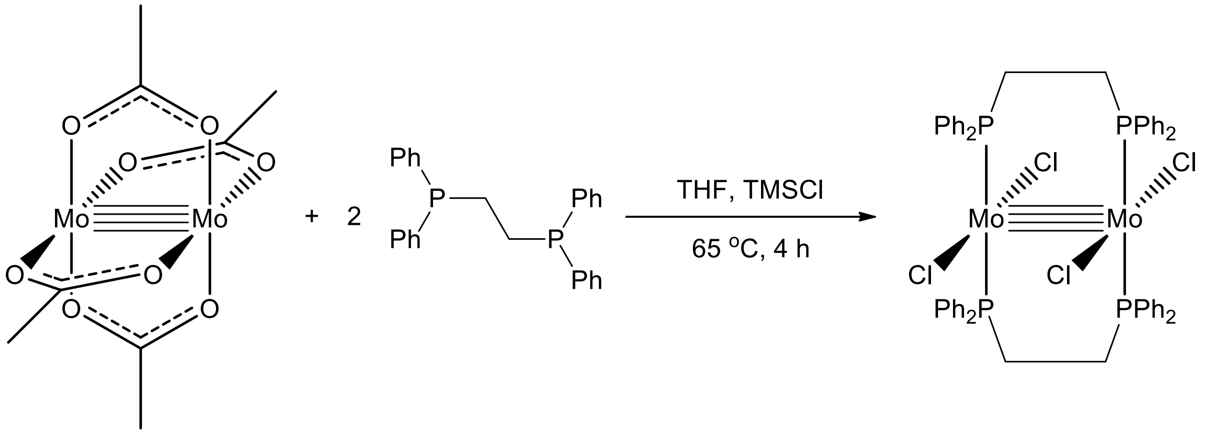


Scheme 26: Preparation of *α*-Mo_2(dppe)$_2Cl_4$ from $[Mo_2Cl_8]^{4-}$.

$(NH_4)_4Mo_2Cl_8$ (174 mg, 0.317 mmol) along with two equivalents of dppe (250 mg, 0.634 mmol) were added to a Schlenk flask. Ethanol (15 mL) was added to the flask and the reaction mixture was left to stir for 24 h. A green suspension formed which was filtered and washed with cold ethanol (10 mL) and hexane (15 mL). The solid was dried *in vacuo*. The final product was blue-green in colour and a yield of 182 mg (48 %) was obtained.

^{1}H NMR (400 MHz *d*^{6}-DMSO) δ 7.37-7.25 (m, 40H, J = 7.30 Hz), 2.03 (t, 8H, J = 2.03 Hz). ^{31}P NMR (400 MHz, *d*^{6}-DMSO) δ -14.29. IR ν (cm^{-1}) 1483 m, 1435 s, 1122 m, 1091 m, 737 s, 687 vs, 513 vs. UV λ_{max} (DMSO) / nm 675 (ε = 17860 M cm^{-1}), 480 (ε = 15360 M cm^{-1}), 390 (ε = 15700 M cm^{-1}), 345 (ε = 23660 M cm^{-1}).

7.2.5 *Preparation of β-Mo_2(dppe)$_2Cl_4$* [65]

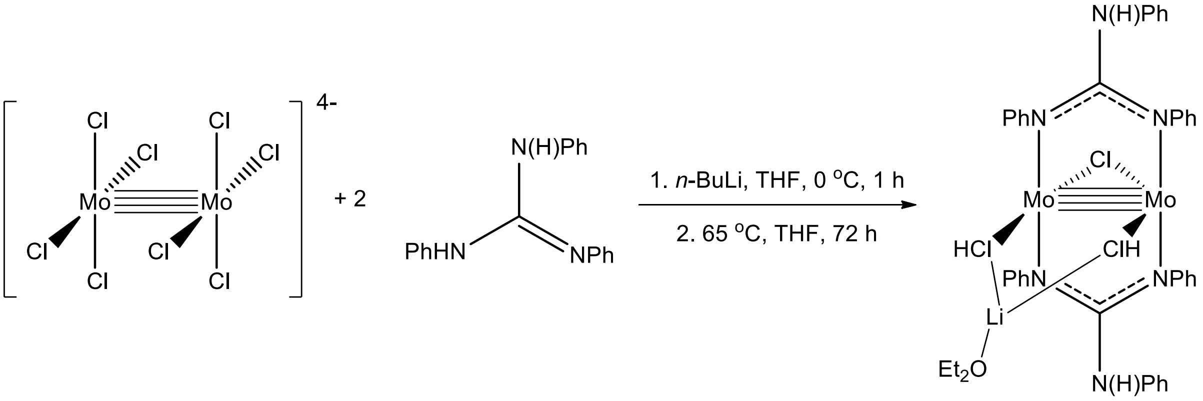


Scheme 27: Preparation of *β*-Mo_2(dppe)$_2Cl_4$ from $Mo_2(O_2CCH_3)_4$.

$Mo_2(O_2CCH_3)_4$ (250 mg, 0.584 mmol), two equivalents of dppe (470 mg, 1.17 mmol) and four molar equivalents of TMSCl (0.3 mL, 2.34 mmol) was added to a Schlenk tube and refluxed in THF at 65 °C for four hours. A green suspension formed initially, but it was soon replaced with a brown-red suspension. The suspension was cooled to room temperature, filtered and washed with hexane leaving a brown-red solid with a yield of 190 mg (28 %) obtained after drying overnight.

^{1}H NMR (400 MHz d^6-DMSO) δ 7.81-7.43 (m, 40H, J = 7.53 Hz), 2.41 (s, 8H, J = 2.41 Hz). ^{31}P NMR (400 MHz, d^6-DMSO) δ 30.20.

7.2.6 *Synthesis of $Mo_2(\mu\text{-}Cl)[Cl_2Li(OEt_2)][\mu\text{-}\eta^2\text{-}(tpg)]_2$*



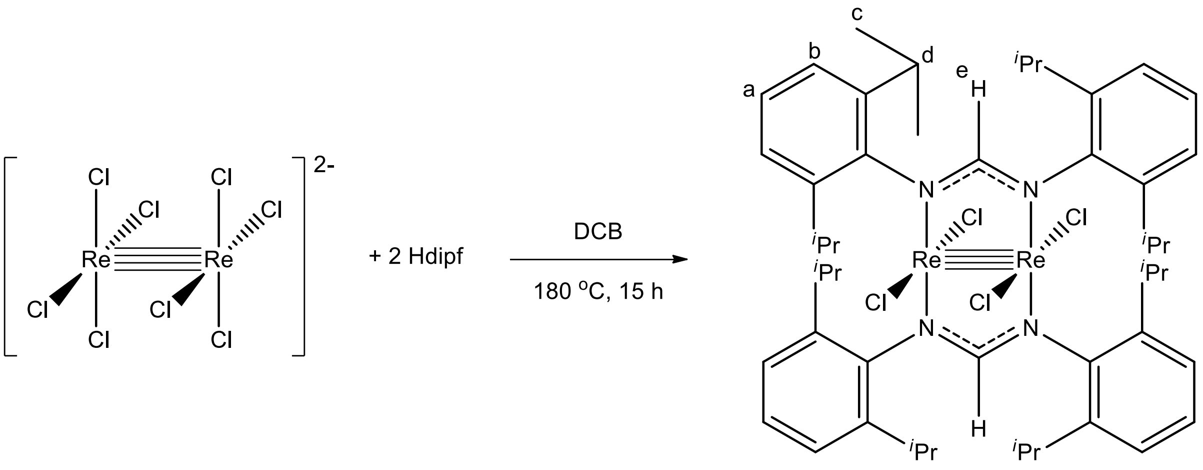
Scheme 28: Preparation of $Mo_2(\mu\text{-}Cl)[Cl_2Li(OEt_2)][\mu\text{-}\eta^2\text{-}(tpg)]_2$ from $[Mo_2Cl_8]^{4-}$.

To a stirred solution of Htpg (210 mg, 0.73 mmol) in THF (5 mL), n-BuLi (1 mL, 0.8 mmol) was added slowly at 0 °C and left to stir for one hour at room temperature. The yellow lithiated ligand solution was then added to a separate Schlenk tube containing $(NH_4)_4Mo_2Cl_8$ (100 mg, 0.36 mmol) in THF (5 mL). The mixture was refluxed at 65 °C for 72 hours forming a red-brown solution. The solvent was evaporated, and diethyl ether was added. The suspension was filtered and the solid was dissolved in THF and dried *in vacuo* to form a brown-red solid with a yield of 65 mg (38 %).

^{1}H NMR (300 MHz $CDCl_3$) δ 9.57 (br. s 2H), 7.23-7.08 (m, 30H, J = 7.15 Hz). IR v (cm^{-1}) 2962 m, 1581 m, 1487 m, 1074 s, 795 vs, 750 vs, 690 vs.

7.3 *Dirhenium Precursors*

7.3.1 *Synthesis of* $Re_2(dipf)_2Cl_4$

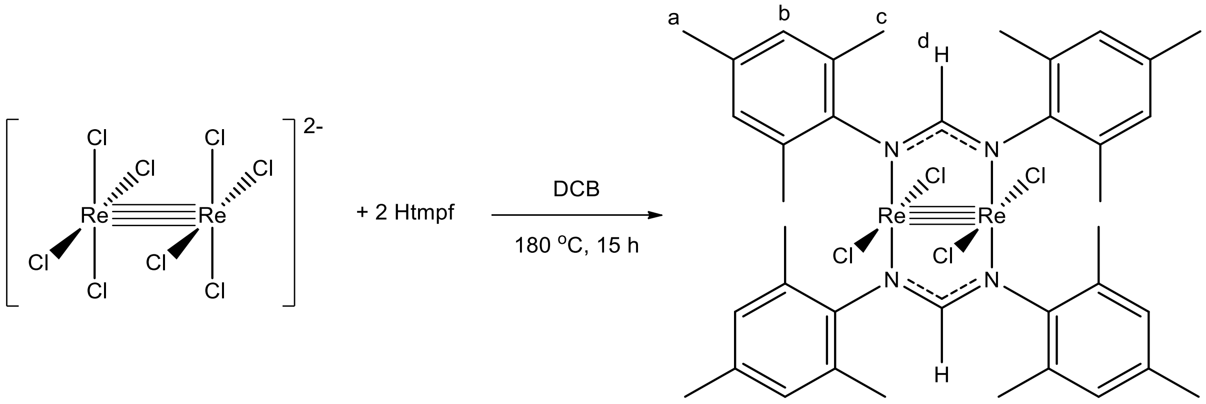


Scheme 29: Preparation of $Re_2(dipf)_2Cl_4$ from $[Re_2Cl_8]^{2-}$.

$(TBA)_2Re_2Cl_8$ (100 mg, 0.088 mmol) and Hdipf (64 mg, 0.18 mmol) were refluxed in a Schlenk tube in DCB (4 mL) for 15 hours. The solvent was evaporated *in vacuo* and THF (10 mL) was added forming a dark green solution which was filtered through Celite to remove any starting materials. The solution was concentrated to approximately 4 mL and was layered with diethyl ether (30 mL). The layered solution was left in a freezer for three days to yield a crop of dark green crystals (60 mg, 55 %).

^1H NMR (400 MHz $CDCl_3$) δ 7.41 (H_e, s, 2H), 7.14-7.09 ($H_{a,b}$, m, 12H, J = 7.12 Hz), 3.67 (H_d, m, 8H, J = 3.32 Hz), 1.12 (H_c, d, 48H, J = 1.17 Hz). IR v (cm^{-1}) 2958 m, 2358 vs, 1662 m, 1585 w, 1463 m, 1295 m, 1170 s, 800 vs, 752 vs. UV λ_{max} (DCM) / nm 618 (ε = 2880 M cm^{-1}), 408 (ε = 14000 M cm^{-1}), 300 (ε = 15360 M cm^{-1}). Anal. Calc for $C_{50}H_{70}Cl_4N_4Re_2$: C, 48.53; H, 5.72; N, 4.38; Found: C, 48.51; H, 5.79; N, 4.44.

7.3.2 *Synthesis of* $Re_2(tmpf)_2Cl_4$

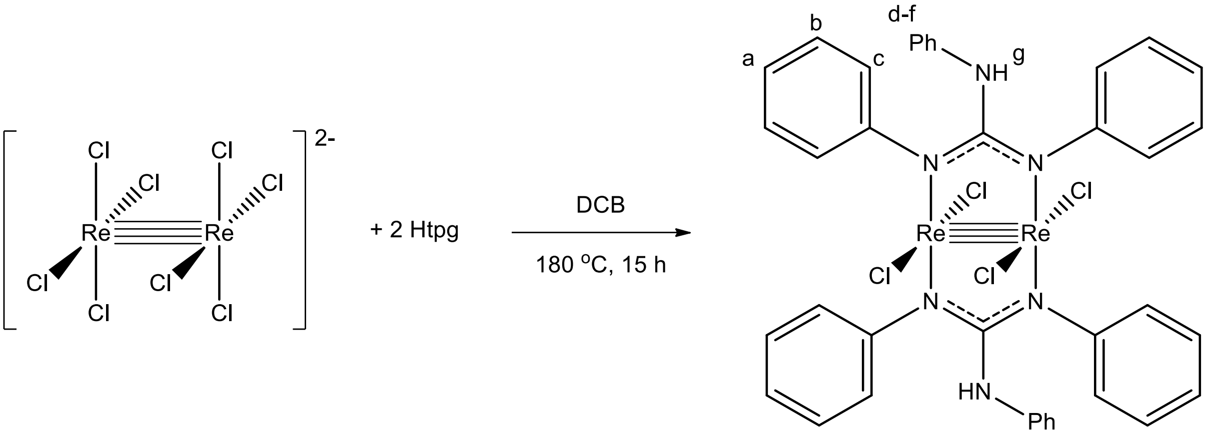


Scheme 30: Preparation of $Re_2(tmpf)_2Cl_4$ from $[Re_2Cl_8]^{2-}$.

$(TBA)_2Re_2Cl_8$ (100 mg, 0.088 mmol mmol) and two equivalents of Htmpf (49 mg, 0.18 mmol) was added to a Schlenk tube and refluxed in DCB (4 mL) for 15 hours. The solvent was evaporated *in vacuo* and THF (10 mL) was added. The green solution was filtered through Celite to remove starting materials and then concentrated to 5 mL and layered with diethyl ether (30 mL) and stored at -26 °C for three days which produced a crop of dark green crystals with a yield of 89 mg (85 %) obtained.

^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (H_d, s, 2H), 6.79 (H_b s, 8H), 2.26 (H_c, s, 24H), 2.18 (H_a s, 12H). IR ν (cm^{-1}) 2960 m, 1675 w, 1606 w, 1465 s, 1377 m, 1200 vs, 1014 vs, 796 vs. UV λ_{max} (DCM) / nm 610 (ε = 6060 M cm^{-1}), 425 (ε = 23800 M cm^{-1}), 295 (ε = 24400 M cm^{-1}). Anal. Calcd for $C_{38}H_{46}Cl_4N_4Re_2$: C, 42.34; H, 4.14; N, 5.39; Found: C, 42.39; H, 4.14; N, 5.46.

7.3.3 *Synthesis of $Re_2(tpg)_2Cl_4$*



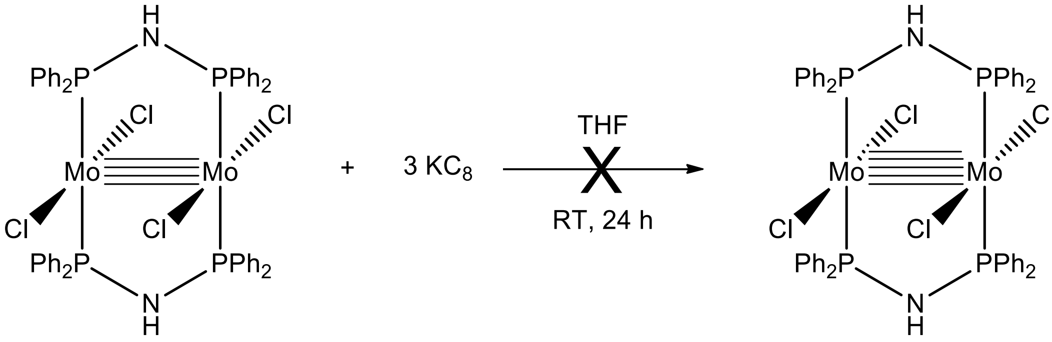
Scheme 31: Preparation of $Re_2(tpg)_2Cl_4$ from $[Re_2Cl_8]^{2-}$.

A Schlenk tube was charged with $(TBA)_2Re_2Cl_8$ (100 mg, 0.088 mmol) and Htpg (50 mg, 0.176 mmol) and refluxed in DCB (4 mL) for 15 hours. The solvent was evaporated and minimal THF (4 mL) was then added, the green solution was filtered through Celite and layered with cyclohexane. The layered solution deposited a crop of green crystals after three days at -26 °C and a yield of 49 mg (51 %) was obtained.

^1H NMR (400 MHz $CDCl_3$) δ 7.10 – 7.00 ($H_{a\text{-}c}$, m, 20H, J = 7.05 Hz), 6.85-6.72 ($H_{d\text{-}f}$, m, 10H, J = 6.79 Hz) 5.86 (s, 2H). IR ν (cm^{-1}) 3348 m, 2962 w, 1600 m, 1589 m, 1504 s, 1425 vs, 1360 s, 1256 m, 1016 m, 758 s, 690 vs. UV λ_{max} (DCM) / nm 626 (ε = 1240 M cm^{-1}), 426 (ε = 5140 M cm^{-1}), 288 (ε = 22800 M cm^{-1}). Anal. Calcd for $C_{38}H_{32}Cl_4N_6Re_2$: C, 45.02; H, 6.40; N, 4.46; Found: C, 45.12; H, 6.48; N, 4.55.

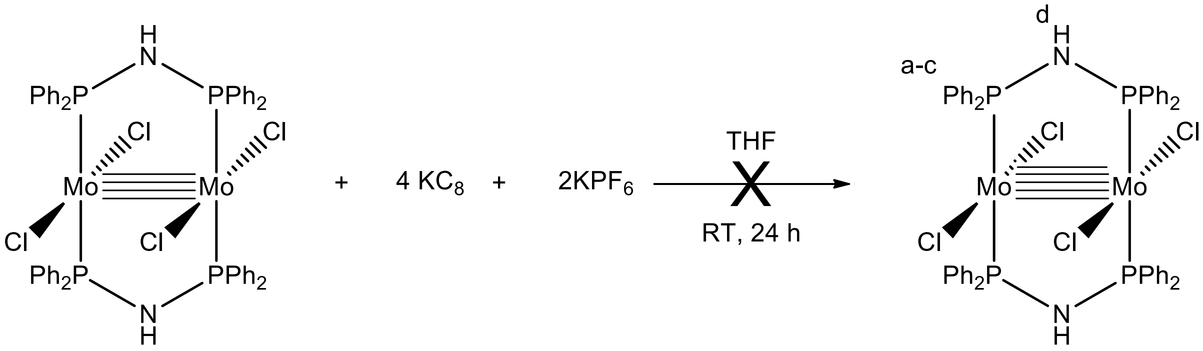
7.4 *Attempted Reductions*

7.4.1 *Mo₂(Hdppa)₂Cl₄*



Scheme 15: Attempted reduction of **[3]** with KC_8.

Method 1: $Mo_2(Hdppa)_2Cl_4$ (100 mg, 0.091 mmol) and KC_8 (36 mg, 0.27 mmol) were stirred in THF (10 mL) for 24 hours. The black suspension was filtered through Celite and washed with THF (4 x 10 mL). The pale-yellow solution was evaporated leaving a yellow-brown solid. The solid was assumed to be ligand and decomposition of the complex had occurred.

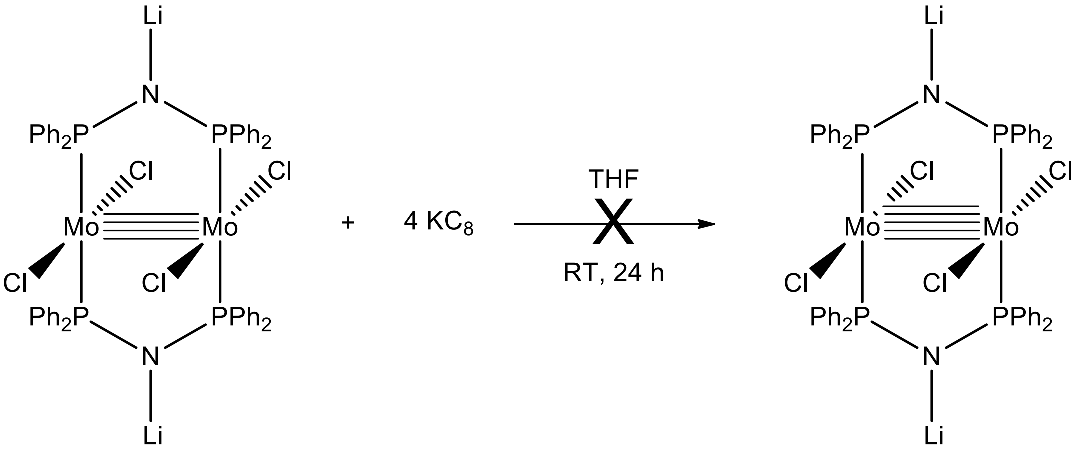


Scheme 16: Attempted reduction of **[3]** with KC_8 and KPF_6.

Method 2: $Mo_2(Hdppa)_2Cl_4$ (100 mg, 0.091 mmol), KC_8 (49 mg, 0.36 mmol) and KPF_6 (33 mg, 0.18 mmol) were stirred in THF (10 mL) for 24 hours. The black suspension was filtered through Celite and washed with THF to yield a dark brown solid (51 mg) and a ^{1}H NMR and ^{31}P {^{1}H} NMR spectra consistent with the ligand NMR spectra.

^{1}H NMR (400 MHz $CDCl_3$) δ 7.51-7.22 (H_{a-c}, m, 20H, J = 7.39 Hz), 3.74 (H_d, t, 1H, J = 3.74 Hz). ^{31}P NMR (400 MHz $CDCl_3$) 42.96.

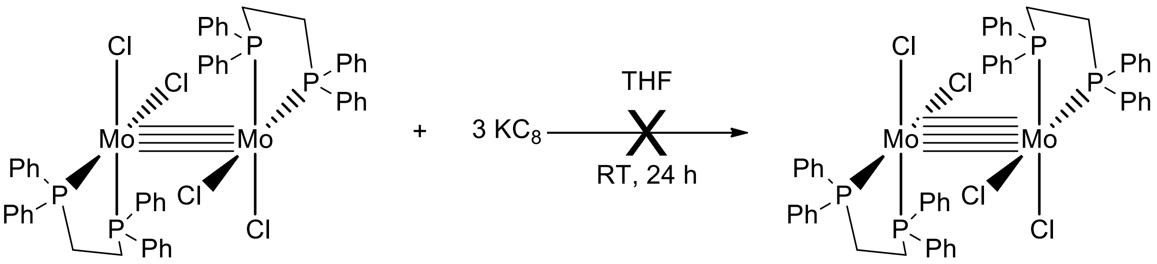
7.4.2 *$Mo_2[Li(dppa)]_2Cl_4$*



Scheme 17: Attempted reduction of $Mo_2[Li(dppa)]_2Cl_4$ using KC_8.

$Mo_2[Li(dppa)]_2Cl_4$ (100 mg, 0.090 mmol) and KC_8 (50 mg, 0.36 mmol) were added to a Schlenk tube and stirred in THF for 24 hours at room temperature. The resulting black suspension was filtered through Celite and washed with THF to form a pale-yellow solution. The solution was evaporated to yield a yellow-brown solid (40 mg).

7.4.3 *α-$Mo_2(dppe)_2Cl_4$*

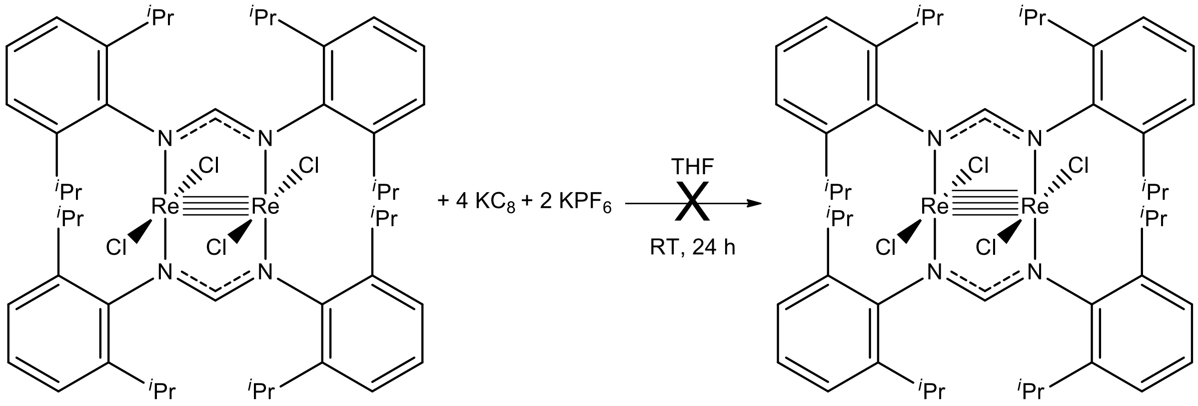


Scheme 18: Attempted reduction of *α*-$Mo_2(dppe)_2Cl_4$ using KC_8.

The dimolybdenum complex (60 mg, 0.051 mmol) and three equivalents of KC_8 (21 mg, 0.15 mmol) were stirred in THF overnight. The black suspension was filtered through Celite and washed with toluene and THF to form a pale-yellow solution, which left a pale-yellow solid (20 mg) after removing the solvent under reduced pressure.

^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 20H), 2.10 (s, 4H).

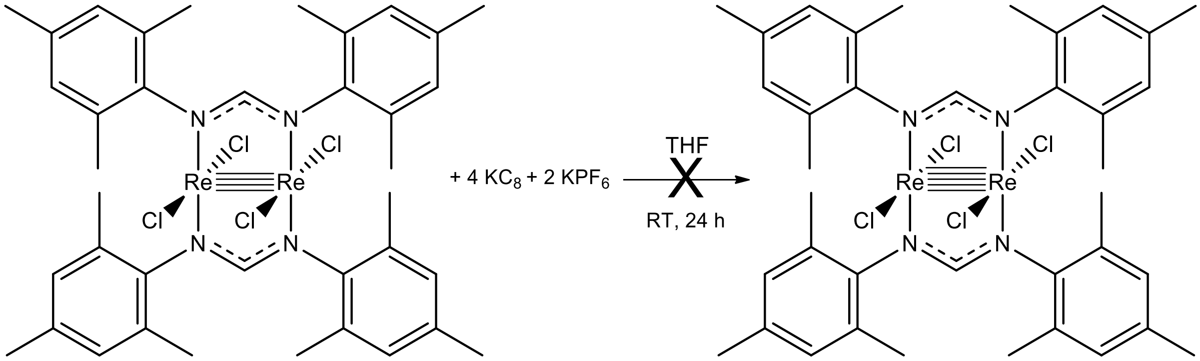
7.4.4 *$Re_2(dipf)_2Cl_4$*



Scheme 19: Attempted reduction of $Re_2(dipf)_2Cl_4$ using KC_8 and KPF_6.

$Re_2(dipf)_2Cl_4$ (19 mg, 0.015 mmol) was stirred in THF along with KC_8 (8 mg, 0.06 mmol) and KPF_6 (5 mg, 0.03 mmol) for 15 hours. The resulting black suspension was filtered through Celite and washed with toluene and THF. The pale-yellow solution was evaporated and left a white solid (15 mg). The NMR could not be resolved due to decomposition of the product.

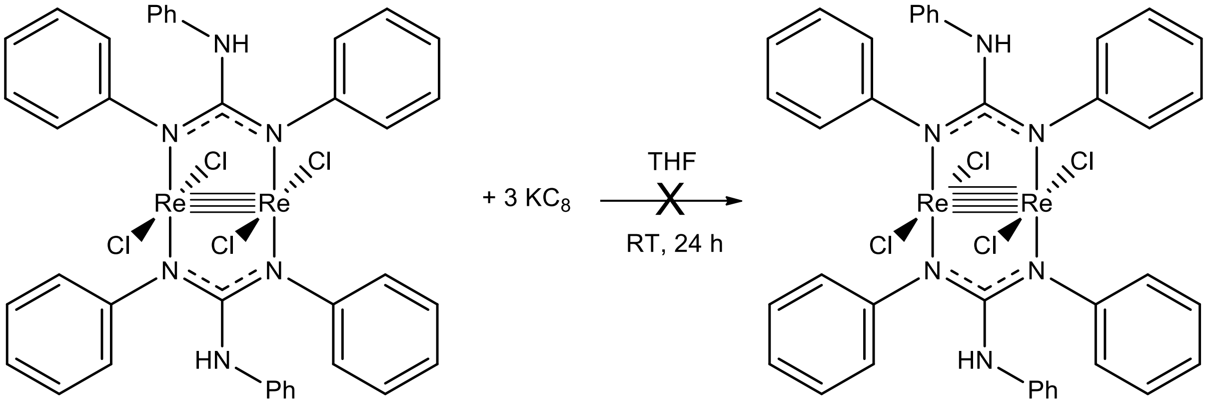
7.4.5 *$Re_2(tmpf)_2Cl_4$*



Scheme 20: Attempted reduction of $Re_2(tmpf)_2Cl_4$ using KC_8 and KPF_6.

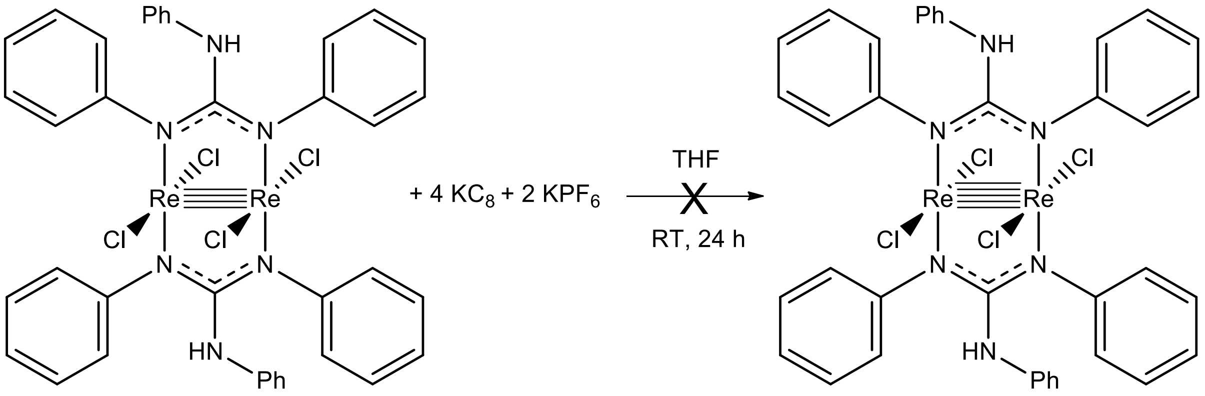
$Re_2(tmpf)_2Cl_4$ (25 mg, 0.023 mmol) was stirred with KC_8 (13 mg, 0.093 mmol) and KPF_6 (9 mg, 0.047 mmol) in THF for 15 hours after which it was filtered through Celite and washed with THF to yield a pale-yellow solution that formed a pale-yellow solid (21 mg) when the solvent was evaporated *in vacuo*. The NMR could not be identified due to poor resolution.

7.4.6 ***Re$_2$(tpg)$_2$Cl$_4$***



Scheme 21: Attempted reduction of Re$_2$(tpg)$_2$Cl$_4$ using KC$_8$.

Method 1: Re$_2$(tpg)$_2$Cl$_4$ (50 mg, 0.046 mmol) was stirred in THF with three equivalents of KC$_8$ (19 mg, 0.14 mmol) at room temperature for 15 hours. The suspension was filtered through Celite and washed with THF. The solvent was evaporated under reduced pressure to yield a brown solid (20 mg).

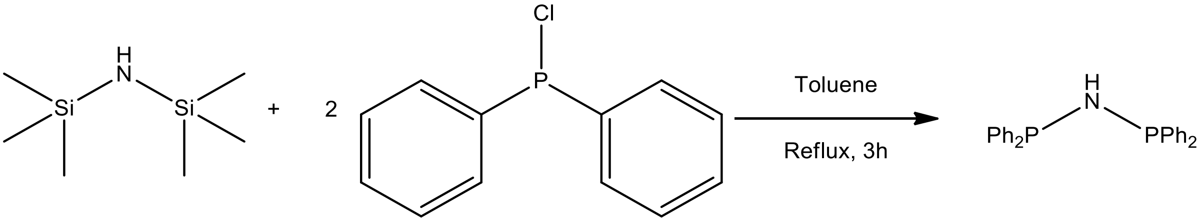


Scheme 22: Attempted reduction of Re$_2$(tpg)$_2$Cl$_4$ using KC$_8$ and KPF$_6$.

Method 2: Re$_2$(tpg)$_2$Cl$_4$ (28 mg, 0.026 mmol), KC$_8$ (14 mg, 1.03 mmol) and KPF$_6$ (10 mg, 0.052 mmol) was stirred in THF overnight, filtered through Celite and washed with THF until the solution ran through clear. The pale-yellow solution was evaporated to leave a pale-yellow solid (11 mg). The NMR of both solids could not be resolved due to their complexity, likely due to decomposition of the complex.

7.5 *Proligands*

7.5.1 *Preparation of Bis(diphenylphosphino)amine*[53]

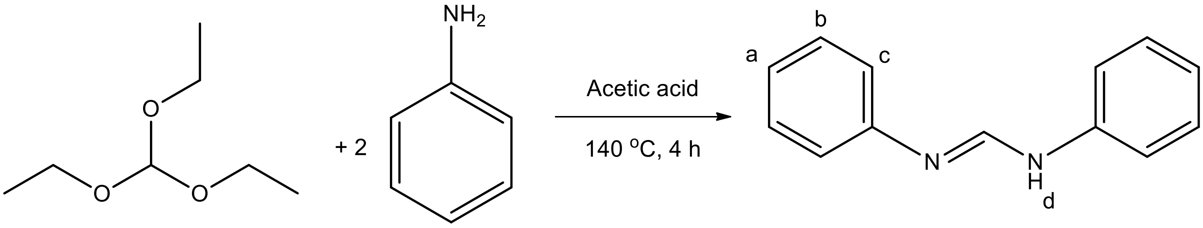


Scheme 32: Preparation of the ligand Hdppa.

Chlorodiphenylphosphine (6.6 mL, 36.8 mmol) was added slowly to a Schlenk flask containing hexamethyldisilazane (3.85 mL, 18.3 mmol). Toluene (30 mL) was added and the reaction was stirred vigorously under reflux for 3 h at 110 °C. The volatile materials were evaporated *in vacuo* and diethyl ether was added. The suspension was stirred vigorously, and the ether was decanted off. Subsequent additions and removals of ether was performed until it decanted out a clear liquid and the solid had changed from yellow to white. The solid was dried *in vacuo* and a yield of 4.08 g (58 %) was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 20H, J = 7.32 Hz), 3.14 (t, 1H, J = 3.14 Hz). ^{31}P NMR (400 MHz, $CDCl_3$) δ 42.98. IR ν (cm^{-1}) 3225 m, 3049 m, 1585 vw, 1095 s, 735 vs, 685 vs.

7.5.2 *Preparation of (E)-N,N'-diphenylformamidine*[54]

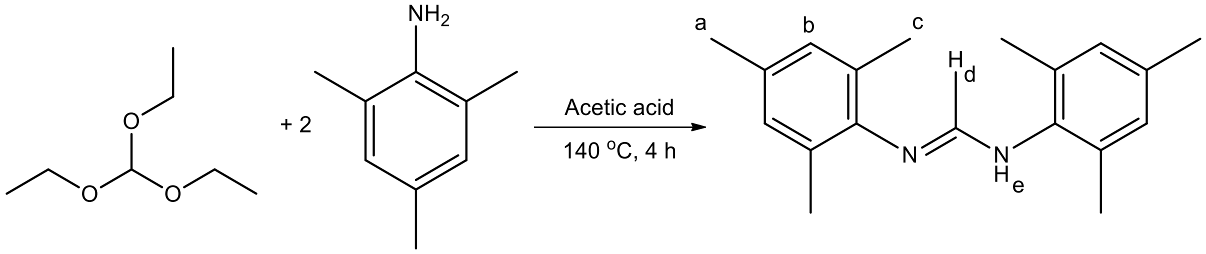


Scheme 33: Preparation of HDPhF.

Aniline (4.9 mL, 51 mmol), triethyl orthoformate (4.25 mL, 25.5 mmol) and glacial acetic acid (0.2 mL, 1.3 mmol) were added a 100 mL RBF and stirred at 140 °C for four hours. The yellow solution was triturated with cold pentane, filtered and washed with cold pentane to yield a pale-yellow solid (3.2 g, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (H_d, s, 1H), 7.40-7.33 (H_c, m, 4H, J = 7.37 Hz), 7.21-7.14 ($H_{a,b}$, m, 6H, J = 7.19 Hz).

7.5.3 *Preparation of (E)-N, N'-dimesitylformamidine* [54]

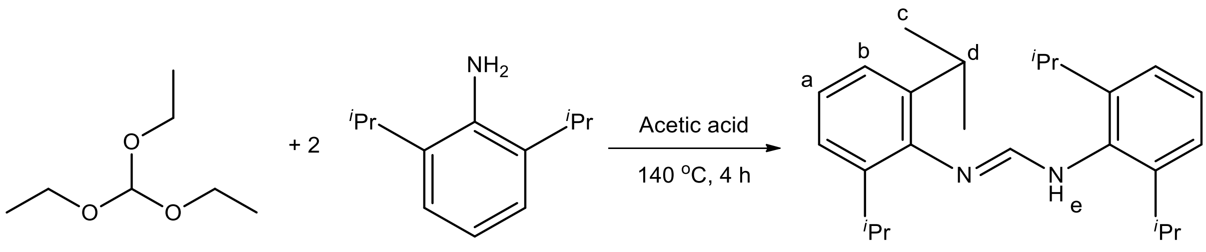


Scheme 34: Preparation of Htmpf.

A 100 mL RBF was charged with 2,4,6-trimethylaniline (14.5 mL, 100 mmol), triethyl orthoformate (8.3 mL, 50 mmol) and glacial acetic acid (0.1 mL, 2.5 mmol) and was heated for 3 hours at 160 °C. The mixture was then recrystallised from hot toluene and filtered with hexane and diethyl ether to yield a needle-like colourless solid with a yield of 9.7 g (69%) obtained.

^{1}H NMR (CDCl$_3$) δ 7.20 (H$_e$, s, 1H), 6.87 (H$_b$, s, 4H), 5.43 (H$_d$, br. s, 1H), 2.24 (H$_a$, s, 12H), 2.20 (H$_c$, s, 6H). IR 3125 w, 2910 m, 1635 vs, 1602 m, 1473 s, 1370 s, 1211 s, 850 s. HRMS (ESI) m/z calculated for $C_{19}H_{24}N_2+H^+$: 281.19; Found: m/z 281.20 $[M+H]^+$.

7.5.4 *Preparation of (E)-N, N'-bis(2,6-diisopropylphenyl)formamidine* [54]

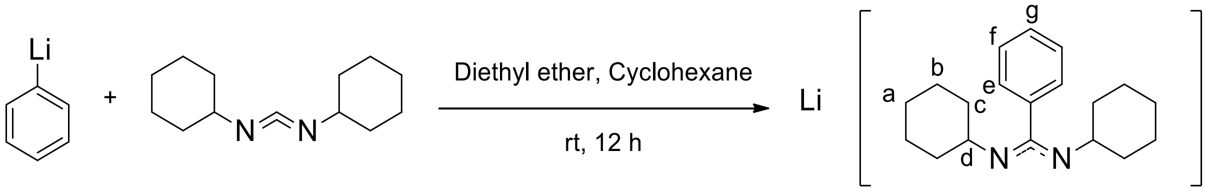


Scheme 35: Preparation of Hdipf.

An RBF containing 2,6-diisopropylaniline (18.8 mL, 100 mmol), triethyl orthoformate (8.4 mL, 50 mmol) and acetic acid (0.28 mL, 5 mmol) was refluxed at 160 °C for three hours. The yellow liquid was cooled to room temperature and recrystallised from hot toluene to yield colourless crystals which were filtered, washed with hexane and dried. A yield of 4.51 g (18 %) was obtained.

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.66-8.35 (H$_e$, br. s 1H), 7.13-7.09 (H$_{a,b}$, m, 6H, J = 7.18 Hz), 3.33 (H$_d$ m, 8H, J = 3.33 Hz), 1.13 (H$_c$ d, 24H, J = 1.13 Hz). IR 3018 vw, 2960 m, 1664 s, 1560 w, 1434 m, 1330 m, 1295 m, 1186 m, 756 s. HRMS (ESI) m/z calculated for $C_{25}H_{36}N_2+H^+$: 365.29; found m/z 365.30 $[M+H]^+$.

7.5.5 ***Preparation of (E)-N, N'-dicyclohexylbenzamidinate*** [78]

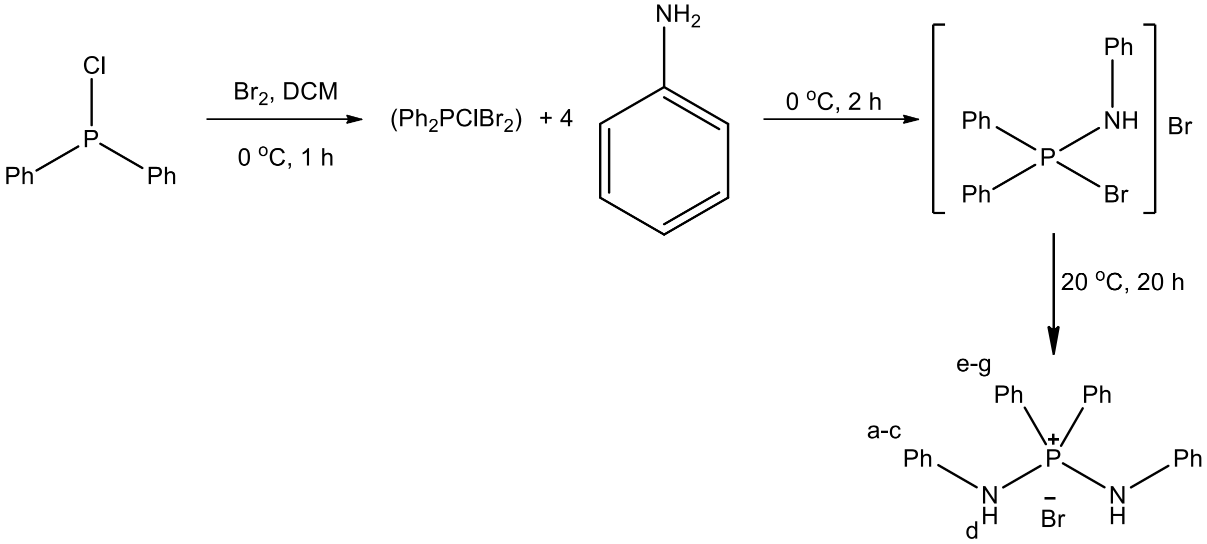


Scheme 36: Preparation of Li[DCyBA].

Phenyllithium (4.1 mL, 1.18 M, 24 mmol) in a 7:3 diethyl ether/cyclohexane mixture (10 mL) was added to a solution of N,N'-Dicyclohexylcarbodiimide (1 g, in diethyl ether (15 mL) and stirred for 12 hours. The solvent was removed and a 2:1 diethyl ether/toluene mixture was added which was cooled to -26 °C for 12 hours and a beige suspension formed after concentrating the solution to approximately 50 %. The suspension was filtered and washed with hexane to yield a white solid which was dried *in vacuo* (0.932 g, 69 %).

^1H NMR (400 MHz, d^6-DMSO) δ 7.28-7.11 ($H_{e\text{-}g}$, m, 5H, J = 7.20 Hz), 3.61 (H_d, m, 1H, J = 3.61 Hz), 2.73 (m, 1H), 1.98-0.80 (H_a-$_c$, m, 20H, J = 1.42 Hz). IR: 3030 w, 2916 m, 1470 vs, 1344 m, 1150 vw, 1056 m, 987 m, 888 w, 779 m, 700 vs, 657 w.

7.5.6 *Preparation of [ippa]Br* [81]

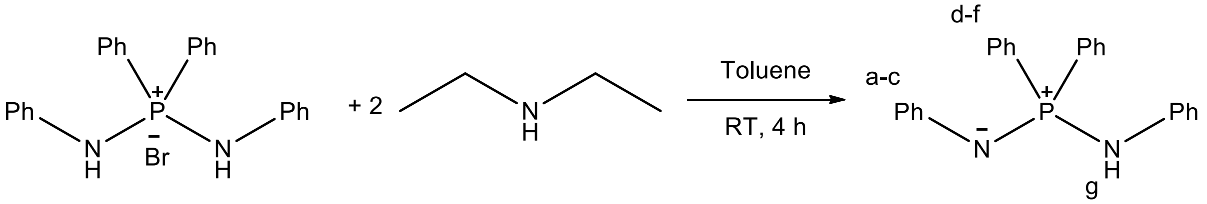


Scheme 37: Preparation of the precursor ligand [ippa]Br.

A solution of bromine (0.95 mL, 18.8 mmol) in DCM (12 mL) was added dropwise over 60 minutes to a separate solution of chlorodiphenylphosphine (3.38 mL, 18.8 mmol) in DCM (20 mL) at 0 °C. The reaction mixture was then stirred overnight, and then aniline (7 mL, 75.2 mmol) was added at 0 °C. Stirring of the mixture continued for 20 hours at room temperature and was subsequently filtered and washed with DCM to yield a white solid (14.7 g, 91 %).

^{1}H NMR (400 MHz, *d*^{6}-DMSO) δ 10.01 (H_d, s, 2H), 8.12-7.24 ($H_{a\text{-}c}$,$H_{e\text{-}g}$, m, 20H, J = 7.62 Hz),. ^{31}P NMR (400 MHz, *d*^{6}-DMSO) δ 24.12. IR 2850 m, 1490 vs, 1115 s, 1030 m, 740 vs, 680 vs.

7.5.7 *Preparation of ippa*[79]



Scheme 38: Preparation of the ligand ippa.

Diethylamine (3.04 mL, 29 mmol) was added to a solution of [HNPNH]Br in toluene (40 mL) and was stirred for four hours. The suspension was filtered and washed with toluene and dried *in vacuo* to yield a white solid (5.806 g, 97 %).

^{1}H NMR (400 MHz, d^6-DMSO) δ 7.99-6.97 ($H_{a\text{-}c}$,$H_{d\text{-}f}$, m, 20 H, J = 7.49 Hz), 6.54 (H_g, s, 1 H). ^{31}P {^{1}H} NMR (400 MHz, $CDCl_3$) -3.12. IR 2950 m, 2470 w, 1585 s, 1305 s, 1110 m, 1025 m, 755 s, 690 vs.

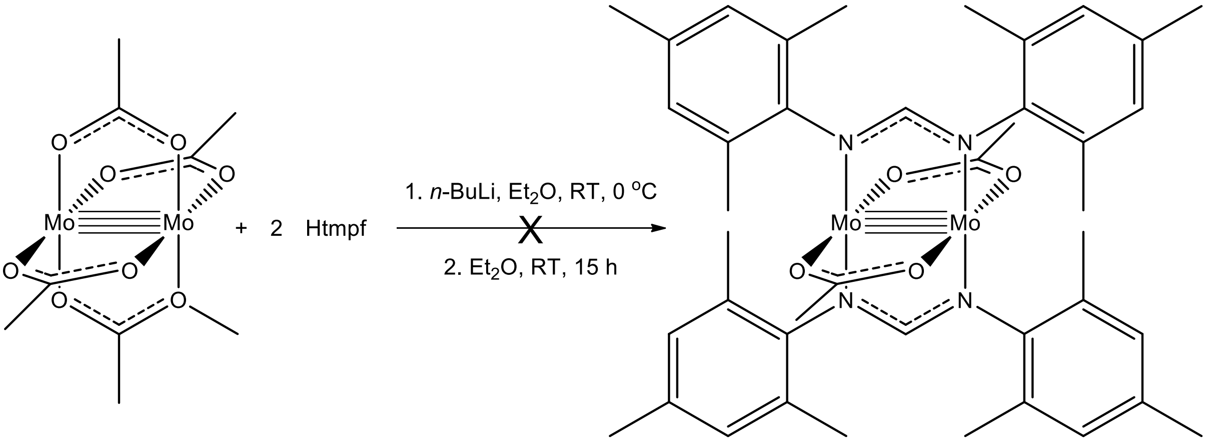
7.6 *Reducing Agents*

7.6.1 Preparation of p*otassium graphite* [92]

Potassium (115 mg, 2.94 mmol) was cut into small pieces and added to a Schlenk tube along with eight equivalents of graphite (280 mg, 24 mmol) and was heated with vigorous stirring at 275 °C for 40 minutes to yield a bronze coloured solid.

7.7 *Attempted Syntheses*

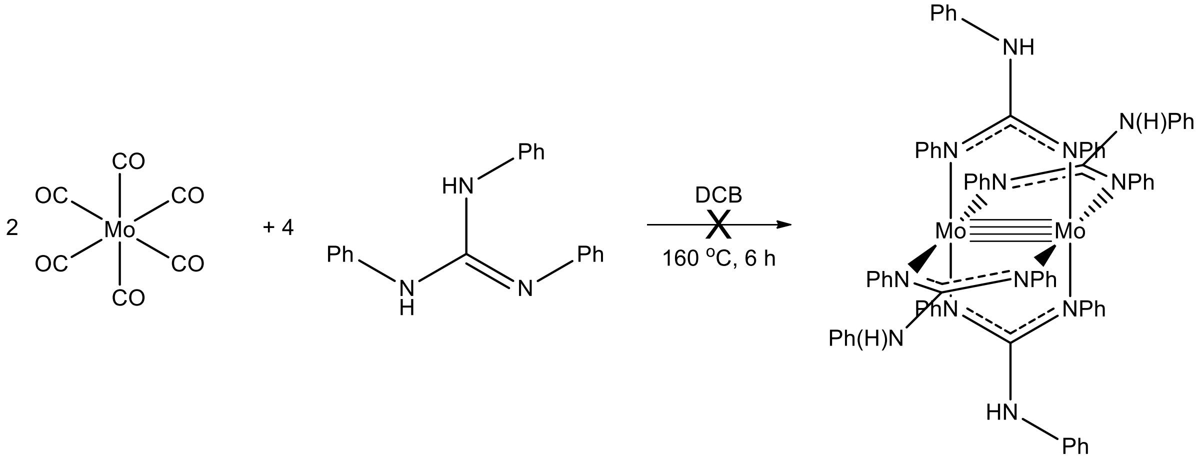
7.7.1 *$Mo_2(tmpf)_2(O_2CCH_3)_2$*



Scheme 39: Attempted preparation of $Mo_2(tmpf)_2(O_2CCH_3)_2$ from $Mo_2(O_2CCH_3)_4$.

A Schlenk tube was charged with $Mo_2(O_2CCH_3)_4$ (100 mg, 0.23 mmol) to which diethyl ether (8 mL) was added. Meanwhile, in a separate Schlenk tube, n-BuLi (0.6 mL, 0.81 M, 0.47 mmol) was added to a stirred solution of Htmpf (130 mg, 0. 0.47 mmol) in diethyl ether (5 mL) and stirred for one hour at 0 °C. The yellow/orange lithiated ligand solution was then transferred slowly to the Schlenk tube containing the metal complex at 0 °C and stirred for 15 hours at room temperature. The solvent was evaporated to leave a yellow solid assumed to be starting material.

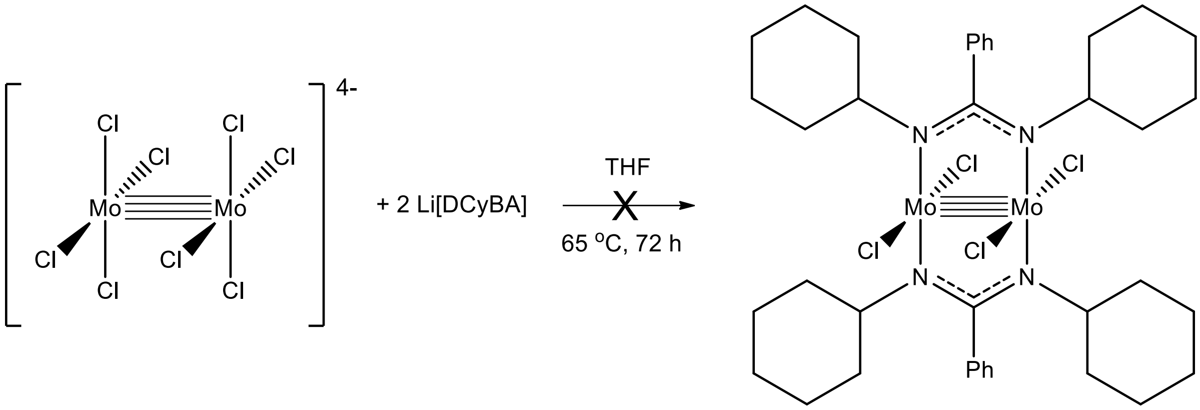
7.7.2 ***Mo₂(tpg)₄*** [66,67]



Scheme 40: Attempted preparation of $Mo_2(tpg)_4$ from $Mo(CO)_6$.

$Mo(CO)_6$ (0.5 g, 1.90 mmol) and Htpg (1 g, 3.79 mmol) was heated in DCB (20 mL) at 160 °C for six hours. The solvent was then removed under reduced pressure and diethyl ether was added. The black suspension was filtered and washed with diethyl ether and then dried *in vacuo* to leave a dark brown solid (1.07 g, 84 %).

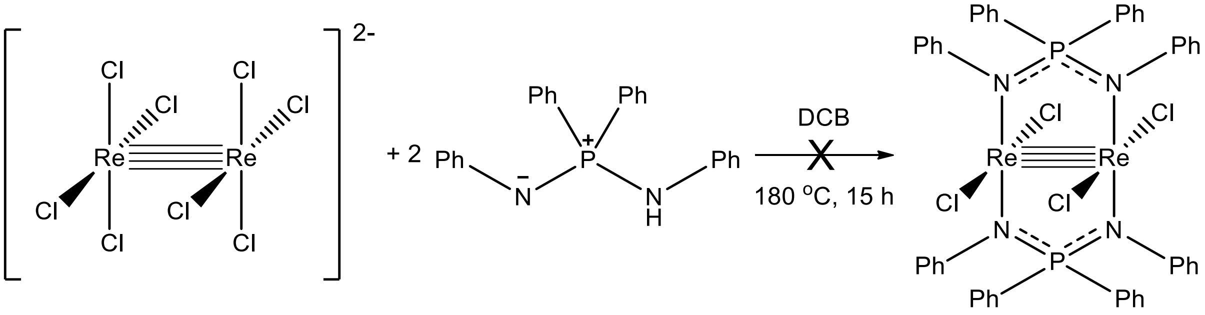
7.7.3 ***Mo₂(DCyBA)₂Cl₄***



Scheme 45: Attempted preparation of $Mo_2(DCyBA)_2Cl_4$ from $[Mo_2Cl_8]^{4-}$.

$(NH_4)_4Mo_2Cl_8$ (100 mg, 0.18 mmol) and Li[DCyBA] (110 mg, 0.40 mmol) were refluxed in THF (15 mL) for three days. The solvent was evaporated to leave a sticky dark-brown solid. A yield was not obtained.

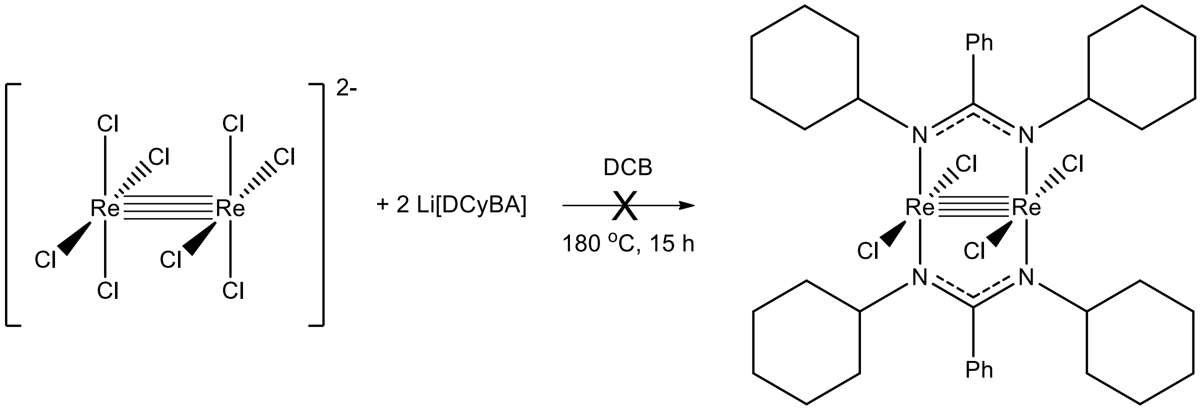
7.7.4 *$Re_2(ippa)_2Cl_4$*



Scheme 41: Attempted preparation of $Re_2(ippa)_2Cl_4$ from $[Re_2Cl_8]^{2-}$.

$(TBA)_2Re_2Cl_8$ (50 mg, 0.044 mmol) and NPNH (32 mg, 0.088 mmol) was refluxed in DCB for 15 hours. A green colour appeared initially but rapidly changed to brown indicating decomposition of the compound.

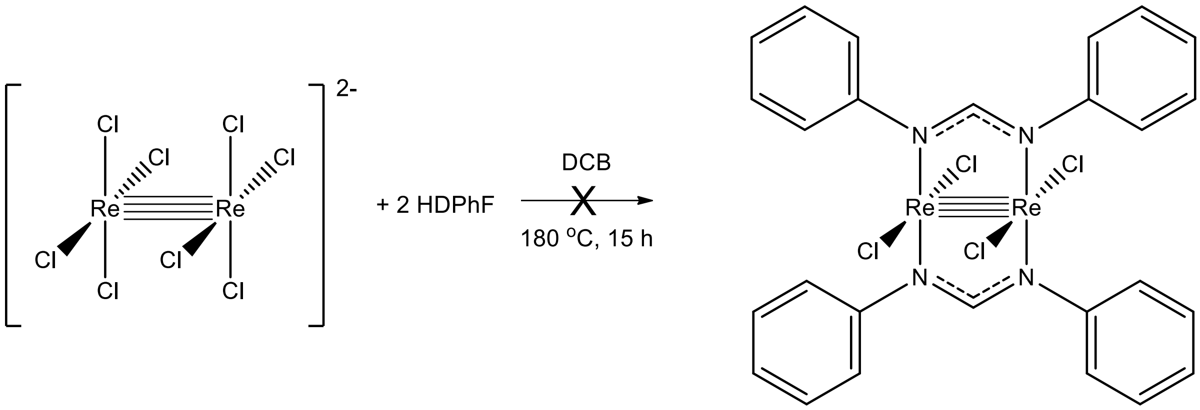
7.7.5 *$Re_2(DCyBA)_2Cl_4$*[75]



Scheme 42: Attempted preparation of $Re_2(DCyBA)_2Cl_4$ from $[Re_2Cl_8]^{2-}$.

$(TBA)_2Re_2Cl_8$ (50 mg, 0.044 mmol) was refluxed in DCB (4 mL) with two equivalents of Li[DCyBA] (24.3 mg, 0.088 mmol) for 15 hours. The solvent of the green solution was evaporated and methanol (20 mL) was added and stirred for 10 minutes. The solution was filtered, and the methanol was subsequently evaporated. THF was then added to the green solid and filtered again after which the THF was concentrated to approximately 4 mL and layered with hexane. Red crystals formed overnight at -26 °C but rapidly decomposed after an additional three days in those conditions to a black solid.

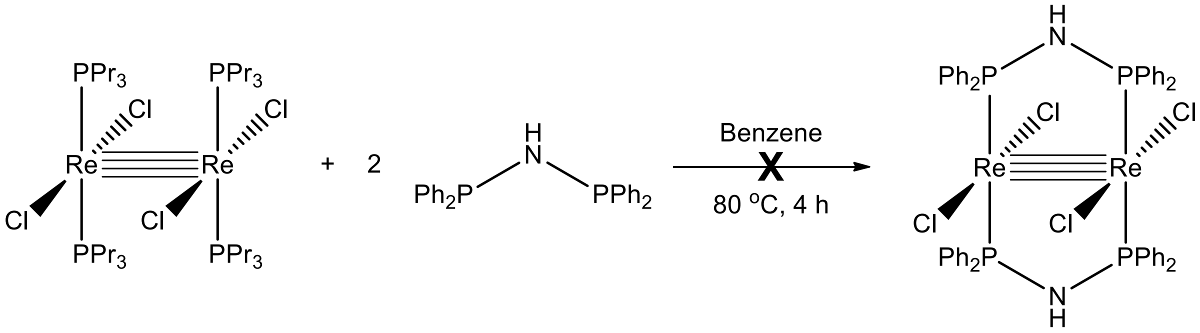
7.7.6 ***$Re_2(DPhF)_2Cl_4$***[76]



Scheme 43: Attempted preparation of $Re_2(DPhF)_2Cl_4$ from $[Re_2Cl_8]^{2-}$.

$(TBA)_2Re_2Cl_8$ (100 mg, 0.088 mmol) and two equivalents of DPhFH (30 mg, 1.76 mmol) were refluxed in DCB for 15 hours. Methanol was added to the solid after the DCB was evaporated and filtered through Celite. The green solution was evaporated and THF was added and layered with hexane. The solid appeared to decompose after three days as a colour change from green to black was observed.

7.7.7 ***$Re_2(Hdppa)_2Cl_4$***



Scheme 44: Attempted preparation of $Re_2(Hdppa)_2Cl_4$ from $Re_2(PPr_3)_4Cl_4$.

$Re_2(PPr_3)_4Cl_4$ (0.3 g, 0.260 mmol) was refluxed in benzene (15 mL) along with two equivalents of Hdppa (0.3 g, 0.778 mmol) without stirring for four hours. The solution was cooled and filtered and then washed with diethyl ether to leave a black solid which appeared to have decomposed. A yield of the solid was not obtained.

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