Coordination Chemistry Reviews, 134 (Part 1) (1994) 1–90

1. Molybdenum 1991[†]

Dorn M. Nixon

CONTENTS

[†] Reprints are not available.

0010-8545/94/$26.00
SSDI 0010-8545 (94) 04000–N

INTRODUCTION

The coordination chemistry of molybdenum, reported during 1991, has been reviewed. The complexes are grouped primarily by oxidation state of the molybdenum atom(s) (sections 1.1 to 1.7) and then further divided according to the ligand donor atom. Where a complex contains mixed donor atoms, priority is given to the donor atom nearest to the top left of the periodic table. Sections 1.8 and 1.9 contain reports of mixed valence molybdenum complexes and dimetallic compounds respectively. The final section, (1.10), deals with cluster species. In general, references to purely organometallic compounds have been omitted from this review although a range of phopshine complexes has been described; only discrete cluster compounds are included.

1.1 MOLYBDENUM(VI)

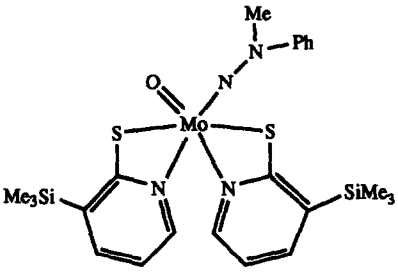
1.1.1 Complexes with nitrogen donor ligands

1.1.1.1 Monodentate ligands

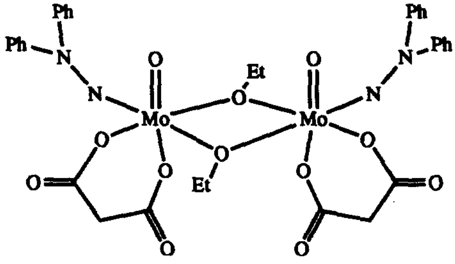
The monomeric nitrido complex $MoN(NPh_2)_3$ has been prepared by the reaction of $MoNCl_3$ and $LiNPh_2$ in thf [1]. Structural analysis showed the molybdenum atom to be in a tetrahedral environment with a Mo-N(nitride) bond of 1.634 Å and an average Mo-N(amido) distance of 1.992 Å. Two bis(amido)bis(imido) molybdenum complexes have been synthesised, also containing an N_4-tetrahedral geometry about a molybdenum(VI) centre [2]. The reaction of MoO_2Cl_2 with Ar′NCO (Ar′ = 2,6-diisopropylphenyl) in thf at 70 °C yields the dichloro product $(Ar'N)_2MoCl_2$.thf. The reactivity of this product was explored, resulting in derivatives of the form $(Ar'N)_2MoL_2$ (L = NEt_2, NHAr′, mesityl, neopentyl); of these $(Ar'N)_2Mo(NHAr')_2$ was structurally characterised (Mo-N(amido) = 1.987, 1.975 Å, Mo-N(imido) = 1.764, 1.753 Å, average N-Mo-N ≈ 109.5°). A similar strategy was used to synthesise $(Cp)Mo(N^tBu)_2Cl$ in high yield, *i.e. via* a dichlorobis(imido) complex as shown in equ. (1). The cyclopentadienyl complex was characterised by NMR spectroscopy, mass spectrometry, and elemental analysis [3].

$$\begin{tikzcd}
MoO_3 \arrow[r, "SOCl_2"] & MoOCl_4 \arrow[r, "(Me_3Si)_2O"] & MoO_2Cl_2 \arrow[r, "{}^tBuNCO"] & Mo(N^tBu)_2Cl_2 \arrow[d, "Li(Cp)"'] \\
 & & & (Cp)Mo(N^tBu)_2Cl
\end{tikzcd} \qquad \text{equ. (1)}$$

Several complexes containing hydrazido(2-) ligands have been reported. Considering the relevance of hydrazido complexes ($M{=}N{-}NH_2$) in the role of nitrogen complexation, and the related diazenido complexes ((M=N-NH) as an intermediate formed from the protonation of the initial N_2 complex, a study on related alkyl, NNR_2 and NNR molybdenum complexes has been reported [4]. The direct action of Me_2NNH_2 and PhNNH (with excess $[S_2CNEt_2]^-$ for the latter reagent) on $MoO_2(S_2CNEt_2)_2$ gave $MoO(NNMe_2)(S_2CNEt_2)_2$ and $Mo(NNPh)(S_2CNEt_2)_3$, respectively. Using 1,1-methylphenylhydrazine as the source of hydrazido(2-) ligand, MoO(NNMePh)(2-SC_5H_3N-3-$SiMe_3)_2$ was prepared from Mo_2O_3(2-SC_5H_3N-3-$SiMe_3)_4$ [5]. An alternative route involves the replacement of the two chloride ligands of $MoCl_2$(NNMePh)(2-SC_5H_3N-3-$SiMe_3)_2$ by an oxo ligand using atmospheric dioxygen. The complex MoO(NNMePh)(2-SC_5H_3N-3-$SiMe_3)_2$ (1) has been structurally characterised and the complex exhibits a *cis* oxo-hydrazido geometry with the hydrazido(2-) ligand in a linear η^1-coordination mode. The oxo-hydrazido complex $MoO(NNMePh)(acac)_2$ has also been characterised; this is a precusor to a novel dinuclear hydrazido(2-) complex that contains bridging alkoxy ligands [6]. On reacting $MoO_2(acac)_2$ with 1,1-diphenylhydrazine in methanol, either the above mononuclear complex or the dinuclear complex $\{MoO(NNMePh)(acac)(\mu\text{-}OMe)\}_2$ is formed, depending on the reaction temperature. The complex $MoO(NNMePh)(acac)_2$ can be directly converted into a series of the dinuclear complexes, with varying alkoxy ligands, by simply refluxing in the appropriate alcohol ROH (e.g. R = Me, Et, or ^nPr). Structural characterisation of the ethyl derivative (2) indicates extensive delocalisation through the Mo-N-N unit, with the following structural parameters: Mo-N = 1.784(1) Å, N-N = 1.298(2) Å, Mo-N-N = 169.5(1).

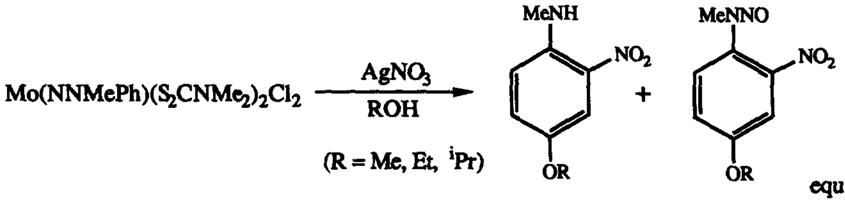


(1)



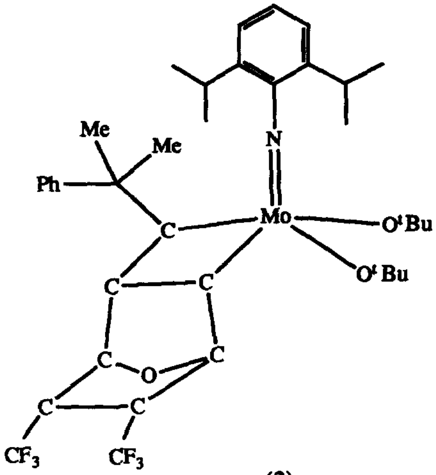
(2)

A potential use for hydrazido complexes was brought to light on studying the reactivity of $Mo(NNMePh)(S_2CNMe_2)_2Cl_2$ towards silver nitrate [7]. Adding 3.3 equivalents of $AgNO_3$ in alcoholic solvents results in cleavage of the hydrazido ligand from the metal and formation of alkoxyaniline derivatives as shown in equ. (2). A reaction pathway for this transformation is proposed, involving initial loss of one (or both) $(S_2CNMe_2)^-$ ligand(s) and coordination of a nitrate ligand to the molybdenum centre.

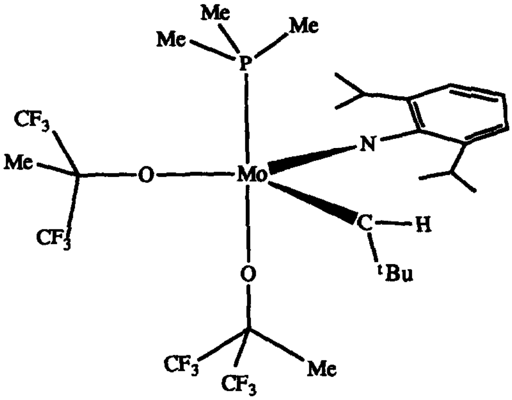


equ. (2)

The potential application as a polymerisation catalyst is the main theme explored on looking at the reactivity of the imido complex $Mo(NAr)(CHCMe_2R)(O^tBu)_2$ ($Ar = 2,6\text{-}C_6H_3\text{-}{}^iPr_2$; R = Me, C_6H_5) [8]. A range of 2,3-difunctionalised 7-oxanorbornenes and 7-oxanorbornadienes were reacted with this complex, with two outcomes. Whilst 7-oxanorbornadiene, 2,3-*endo*-*cis*-diacetoxy-7-oxanorbornene and 2,3-*endo*-*cis*-isopropylidenedioxy-7-oxanorbornene yield polymers with narrow molecular weight distributions, the reactions with 2,3-bis(trifluoromethyl)-7-oxanorbornadiene, 2,3-bis(dicarboxy)-7-oxanorbornadiene and 2,3-*trans*-dicyano-7-oxanorbornene lead to the stable metallacycloaddition products, namely $Mo(NAr)(CHCMe_2R)(O^tBu)_2$. The structure of the trifluoromethyl derivative shows the molybdenum to be in a square pyramidal environment, with the imido ligand in the apical position as illustrated in structure (3). Other five coordinate imido complexes have prepared by the addition of either PMe_3 or the amine $N(CH_2CH_2)_3CH$ to $Mo(CH^tBu)(NAr)(OR)_2$ ($Ar = 2,6\text{-}C_6H_3\text{-}{}^iPr_2$; $R = CMe(CF_3)_2$, $CMe_2(CF_3)$) [9]. Trimethylphosphine attacks a CNO face of the pseudo-tetrahedral complex to yield the structurally characterised, chiral, trigonal bipyramidal species (4), whilst $N(CH_2CH_2)_3CH$ adds to either a COO or NOO face to give achiral isomers, or to the CNO face to give chiral isomers analogous to that of the phosphine adduct. Variable temperature NMR spectroscopic studies have been carried out to determine the barriers of rotation for interconversion of the various isomers.



(3)

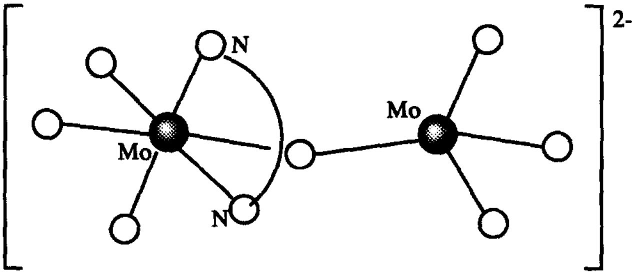


(4)

A brief account [10] has appeared concerning the non-linear optical and excited state properties of conjugated one-dimensional $[NM(OR)_3]_n$ polymers [M = Mo, W; R = CMe_3, CMe_2Et, $CMe_2(CF_3)$].

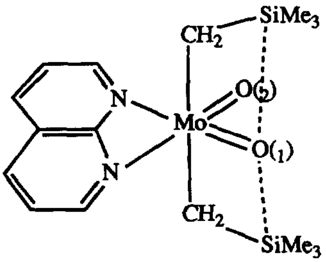
1.1.1.2 Didentate ligands

The dinuclear molybdenum(VI) oxo complex $[enH_2][O_3Mo(\mu\text{-}O)Mo(en)O_3]$ has been synthesised and structurally characterised [11]. The two molybdenum atoms within this complex have different coordination geometries: tetrahedral $[MoO_4]$ and octahedral $[MoO_4N_2]$ as shown in structure **(5)**. The diamine also plays two roles, coordinating as a didentate ligand and protonated as the cationic counterion.



(5)

Using $Mo(bpy)O_2X_2$ (X = Cl, Br) complexes as starting material, there have been two reports on the synthesis of bipyridyl-alkyl molybdenum complexes, with Grignard reagents being the source of the alkyl ligand. The reaction of 2 equivalents of trimethylsilyl magnesium bromide with the bromo-molybdenum complex yielded (2,2'-bipyridyl)dioxobis(trisilyl)molybdenum(VI) [12]. An unusual feature about this product was revealed upon structural analysis. The molybdenum atom is in a distorted octahedral environment, due, in part, to an intramolecular interaction between the silicon atoms and one of the oxo ligands as illustrated in **(6)**. The O-Si distance for this interaction (3.32(1) Å) is considerably less than the sum of the O and Si van der Waals radii (3.6 Å), and cannot be explained purely on the grounds of crystal packing. 2-Methylbenzylmagnesium bromide has been utilised in an analogous reaction, giving $Mo(bpy)O_2(CH_2C_6H_4Me)_2$ [13]. Whilst this complex is stable in the solid form, in solution it decomposes yielding the oxygenated organic compounds 2-methylbenzaldehyde and 2-methylbenzylalcohol as the main products. Their formation is rationalised in terms of a pseudo "keto-enol" tautomeric equilibrium between one oxo and methylbenzyl ligand.



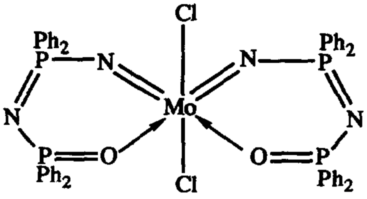
Si-O(1) = 3.32(1) Å

Si-O(2) = 3.95(1) Å

(6)

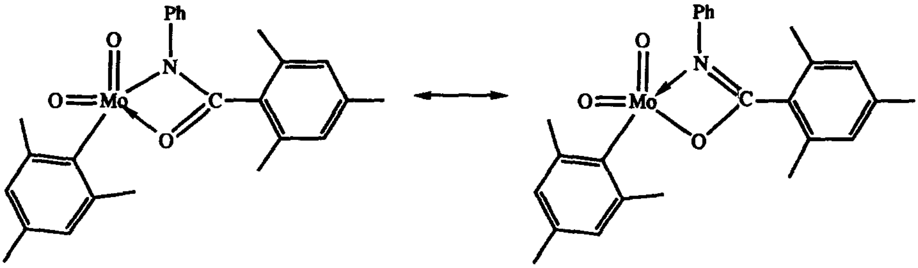
1.1.1.3 Didentate ligands with nitrogen and oxygen donors

The reaction of $MoCl_4$ with $[H_2NPPh_2NPPh_2NH_2]Cl$ results in the formation of two molybdenum(VI) complexes [14]. The first of these, $Mo(\mu\text{-}NPPh_2NPPh_2N)Cl_3$, was previously known whilst the second product, $Mo(\mu\text{-}NPPh_2NPPh_2O)Cl_2$ (7) is reported to be the first example of a bicyclic phosphorane iminato complex. The 1:1 adduct of this new compound with MeCN crystallises and shows a *cis* arrangement of the two Mo-N bonds. This is rationalised in terms of efficiency of π-bonding; the short Mo-N bond lengths (average 1.778 Å) typify double bond character and are close to values obtained for other molybdenum(VI) imido complexes.



(7)

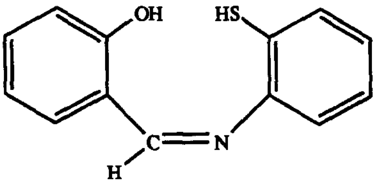
The reactivity of the isocyanate PhNCO with dioxo and diimido molybdenum complexes has been explored [15]. In the case of the dioxo complex $Mo(O)_2(mes)_2$ (mes = 2,4,6-$C_6H_2Me_3$) the expected outcome of forming $Mo(NPh)_2(mes)_2$, with the concurrent release of CO_2, was not observed. Instead, the isocyanate inserts into the molybdenum-mesityl bond to give a four membered MoNCO-ring as shown in structure (8). This product was identified by ^{13}C NMR spectroscopy but decomposed to an amide complex on chromatographic work-up.



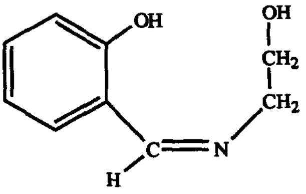
(8)

1.1.1.4 Tridentate ligands with nitrogen and oxygen/sulfur donors

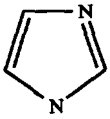
The tridentate Schiff's base ligands salicylidene-2-aminothiophenol (**9**) and *N*-(hydroxyethyl)salicylideneimine (**10**) form chelating *O,N,S*- and *O,N,O*-molybdenum oxo complexes, respectively [16,17]. In each case, addition of imidazole (**11**), or an imidazole derivative L, to these complexes results in the formation of a 6-coordinate, diamagnetic $MoO_2(O\text{-}N\text{-}X)L$ complexes (X = O, S) which are non-electrolytes. Infrared spectroscopy indicates the presence of a *cis* $\{MoO_2\}^{2+}$ core and ^1H NMR spectroscopy is used to establish the mode of coordination of the ligands to the molybdenum centre. In the case of the thiophenol-complex, the lability of the imidazole ligand is also explored with the use of conductiometric measurements [17].



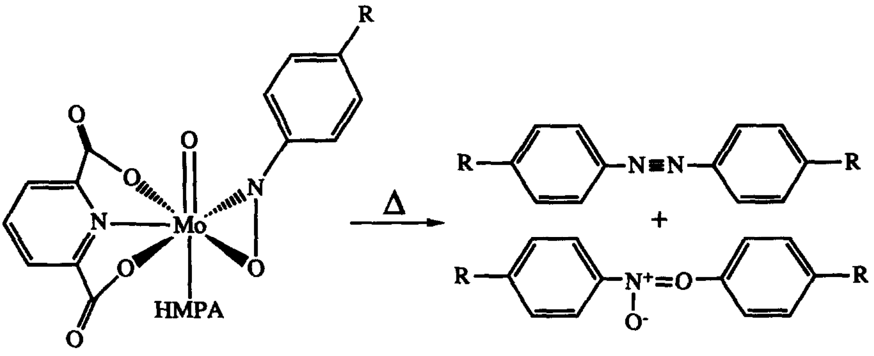
(9)



(10)



(11)



R = H, OCH_3, CH_3, F, Cl, Br, $COCH_3$, NO_2

HMPA = hexamethylphosphoramide

(12)

Activation of aromatic amides has been achieved using the complex oxoperoxo(pyridine-2,6-dicarboxylato)(hexamethylphosphoramide)molybdenum(VI) [18]. A proposed reaction scheme involves initial attack by the nitrogen of the amine at the electrophilic peroxy oxygen atom of the molybdenum complex. Subsequent rearrangement and loss of water gives a complex containing a hydroxyamido ligand (**12**); this product has been isolated in yields greater than 80%. On heating, this new compound decomposes to give azoxy (< 2%) and azo benzenes (10%).

1.1.1.5 Tetradentate ligands with nitrogen and oxygen/sulfur donors

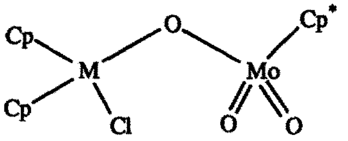
There have been two reports containing information about molybdenum peroxo-complexes containing tetradentate Schiff's bases[19, 20]. Factors that influence the mode of coordination of the (O_2) ligand have been examined. These include the effect of changing the σ-donor nature of *ONN'O'*-donor ligands, *viz.* changing from $[(C_6H_4)\{NC(H)(C_4H_4O)\}_2]^{2-}$ to $[\{NC(H)(C_4H_4O)\}_2]^{2-}$ [19], and the influence on varying the transition metal for complexes of the formula $MO(O_2)(C_{30}H_{24}N_4S_4)$ (including M = Mo), where the ligand $[C_{30}H_{24}N_4S_4]^{2-}$ provides an *SNN'S'*-donor set [20].

1.1.2 Complexes with oxygen donor ligands

Oxygen-transfer from peroxometallates is shown to be a new and general route for the synthesis of oxopolymetallates [21]. Amid the higher nuclearity polymolybdates obtained, a rational synthesis for the dinuclear anion $[Mo_2O_7]^{2-}$ is presented. Treatment of MoO_3 with hydrogen peroxide gives the peroxomolybdate $[Mo_2O_2(\mu\text{-}O)(O_2)_4(H_2O)_2]^{2-}$, then use of PPh_3 as an oxygen abstracting agent yields the dinuclear oxo complex as shown in equ. (3). Structural analysis reveals that the two MoO_3 fragments are bridged by a single oxygen atom, (∠Mo-O-Mo = 180.0(9)°), and the terminal oxygen atoms of each fragment are staggered with respect each other.

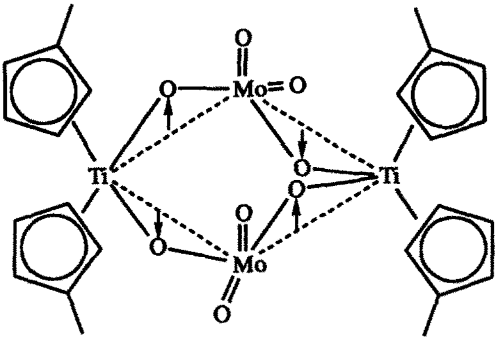
$$[Mo_2O_2(\mu\text{-}O)(O_2)_4(H_2O)_2]^{2-} + 4PPh_3 \rightarrow [Mo_2O_7]^{2-} + 4OPPh_3 + 2H_2O \qquad \text{equ. (3)}$$

Structural analysis has been carried out on a similarly bridged dimer, namely $(Cp^*MoO_2)_2O$ [22]. The intramolecular packing forces of four crystallographically independent molecules have been examined, with reference to the various intermolecular bond parameters. The ranges of values are ∠Mo-O-Mo =172.7 to 180.0°, Mo=O = 1.667(8) to 1.721(5) Å, and Mo-(μ-O) = 1.855(6) to 1.894(4) Å. The same molybdenum fragment, $Cp^*MoO_2(\mu\text{-}O)$, is present in a series of hetero-dimetallic μ-oxo compounds [23]. Complexes of the formula $M(Cp)_2Cl(\mu\text{-}O)MoCp^*O_2$ (**13**) (M = Ti, Zr, V) have been synthesised as part of a study on the reactivity of the oxyanion $[Cp^*MoO_3]^-$ with $[(Cp)_2MCl]^+$ fragments (from the corresponding neutral dihalide). A similar type of approach has been used to prepare another Ti-Mo oxo compound. Reaction of $[MoO_4]^{2-}$ with a related titanium source, $(\eta^5\text{-}MeC_5H_4)_2TiCl_2$, gives the complex $\{(\eta^5\text{-}MeC_5H_4)_2Ti(\mu_2\text{-}MoO_4)\}_2$ (**14**) which contains an eight-membered titanium-molybdenum-oxo ring [24]. Structural analysis shows that the four metal atoms are coplanar, with the oxygen atoms displaced up and down alternately around the ring.



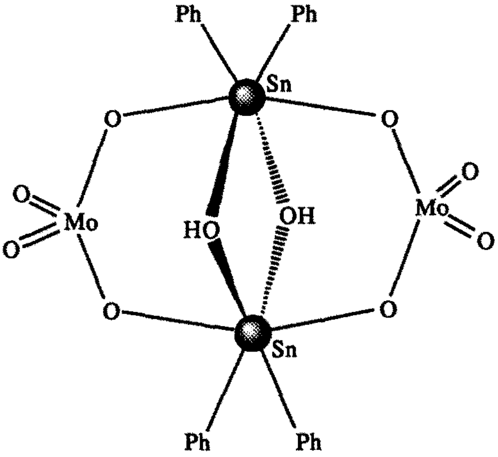
M = Ti, Zr, V

(13)



(14)

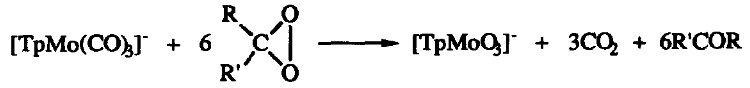
An eight-membered ring is also present in the diorganotin molybdate $(^{n}Bu_4N)_2[(Ph_2Sn)_2(\mu\text{-}OH)_2(\mu\text{-}MoO_4)_2].4CH_2Cl_2$ **(15)** [25]. This is prepared from the reaction of $(^{n}Bu_4N)_2[Mo_2O_7]$ with Ph_2SnCl_2 and $(^{n}Bu_4N)OH$ in acetonitrile, and the product has been structurally characterised. Two *cis* diphenyltin units are linked both via (O-Mo-O) bridges (creating the eight-membered ring) and via two hydroxy bridges (giving rise to a four-membered Sn-O-Sn-O ring). ^{17}O and ^{119}Sn NMR spectral data indicate that the solid state structure is retained in solution.



(15)

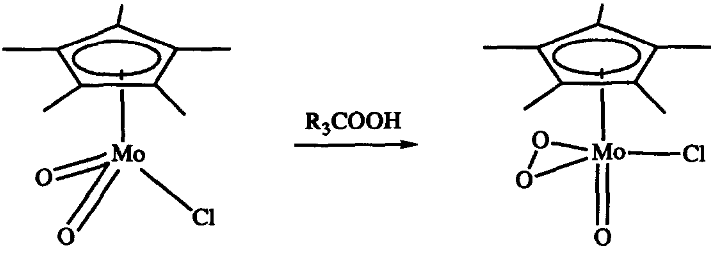
Starting with the molybdenum(0) complex $[TpMo(CO)_3]^-$ [Tp = hydrotris(1-pyrazoyl)borate], oxidative decarbonylation with dioxirane gives $[TpMoO_3]^-$ quantitatively as is shown in equ. (4) [26]. Although this monomer is formed very readily, two molybdenum(V) intermediates have been isolated from the reaction mixture, namely the known dimer $\{TpMoO_2\}_2$

and a new tetramer $\{TpMoO_2\}_4$. Both the tetramer and the monomer have been structurally characterised. Irradiation of $Cp^*Mo(CO)_3Cl$ in the presence of O_2 also results in oxidative decarbonylation, forming Cp^*MoO_2Cl (16) [27]. This new complex acts as a catalyst in the conversion of alkylhydroperoxides and alkenes to the corresponding epoxides and alcohols. In the absence of alkene, Cp^*MoO_2Cl reacts directly with alkylhydroperoxides to give the peroxo complex $Cp^*MoO(O_2)Cl$ (17), though this molybdenum complex is shown to be inert to further reaction with alkenes, *i.e.* it is *not* an intermediate in the catalytic reaction.

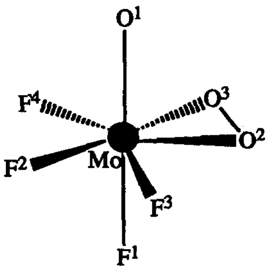


$$[TpMo(CO)_3]^- + 6\,RR'CO_2 \longrightarrow [TpMoO_3]^- + 3CO_2 + 6R'COR$$ equ. (4)

The structure of the peroxo complex $K_2[MoO(O_2)F_4].H_2O$ (18) has been redetermined [28]. Together with molybdenum-doped $K_2[Nb(O_2)F_5].H_2O$, the results of single crystal EPR spectroscopic investigations have been analysed and extended Hückel calculations on the system have been carried out.



(16) **(17)**



(18)

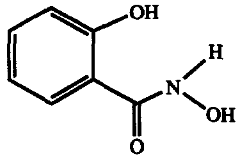
Bond lengths (Å)

Mo-F^1	2.037(10)
Mo-F^2	1.976(8)
Mo-F^3	1.974(9)
Mo-F^4	1.972(10)
Mo-O^1	1.709(11)
Mo-O^2	1.948(11)
Mo-O^3	1.951(11)
O^2-O^3	1.419(15)

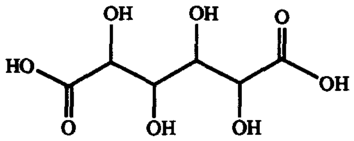
There have been two reports on the chemistry of $MoO_2(mes)_2$. The anion $[MoO_3(mes)]^-$ is the product from the reaction of $MoO_2(mes)_2$ with ethylidenetriethylphosphorane in thf at 0°C [29].

A reaction scheme is proposed that involves coordination of the ethylidene to one molecule of $MoO_2(mes)_2$ with subsequent oxygen transfer from this adduct to another molecule of $MoO_2(mes)_2$ via an oxo bridged dimeric intermediate. The structure of the resultant anion has been determined as the $[Ph_4P]^+$ salt. Dimesityl ketone (5% yield) and 1,1'-bis(mesitoyl)-1,1',4,4'-tetrahydro-4,4'-bipyridine (25% yield) can be prepared from this same starting material, $MoO_2(mes)_2$, on reacting with CO (3 atm) in pyridine at room temperature [30]. The high oxidation state of the molybdenum inhibits the coordination of the CO ligand to the metal centre, and a mechanism is proposed in which CO insertion into the molybdenum-mesityl bond is the initial step. The analogous reactions are repeated with $Mo(N^tBu)_2(mes)_2$, producing the diketone in a much higher yield (60%).

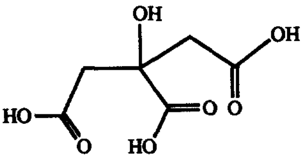
Several complexes between molybdenum and organic acids have been isolated, and these contain various ratios of molybdenum : acid [31-34]. The results with salicylhydroxamic acid (**19**), citric acid (**20**), D-glucaric acid (**21**) and compound (**22**) are summarised in Table 1.



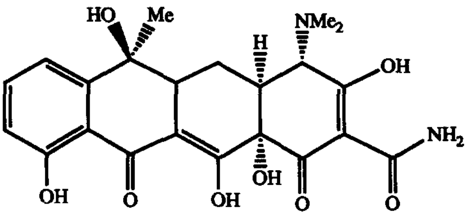
(19)



(21)



(20) 'H_4cit'



(22)

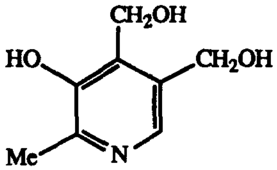
Table 1 *Molybdenum complexes with acids (19)-(22).*

Acid	Mo:ligand ratio	Comments	ref
(19)	1:1, 1:2		[31]
(20)	1:1	$[MoO_3(cit)(OH)_2]^{4-}$	[32]
	2:2	$[(MoO_2)_2O(cit)_2]^{6-}$, $[(MoO_2)_2O(Hcit)_2]^{4-}$	
(21)	2:1†	pH 1-2, high concentration	[33]
	1:1, 2:2	pH 1-2, low concentration	
	2:1†	pH 4.5-6	
	2:1†	pH 6-8.5	
(22)	1:1, 1:2		[34]

† Complexes are distinct from one another.

A dimeric oxo complex $Na_5[Mo_2O_6L].14H_2O$ is obtained from the reaction of $Na_2[MoO_4]$ with H_5L (H_5L = 1-hydroxyethylidenediphosphonic acid) [35]. Structural analysis shows that each molybdenum atom is in a distorted octahedral array of six oxygen atoms. One molybdenum atom is coordinated by one bridging and three terminal oxygen atoms plus an oxygen atom from each phosphonate group; the other is coordinated by one bridging and two terminal oxygen atoms, two phosphonate oxygen atoms and a deprotonated alkyl oxygen atom.

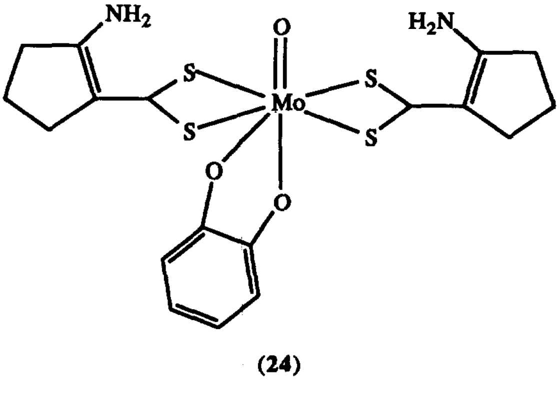
Potentially of biological significance, vitamin B_6 (HPN) (23) forms a 2:1 complex with molybdenum(VI) [36]. The complex $MoO_2(PN)_2.3H_2O$, formed from the reaction between $Na_2[MoO_4]$ and HPN.HCl in aqueous solution, has been structurally characterised. The $[PN]^-$ ligand is didentate, coordinating through the 4-hydroxymethyl and phenolic oxygen atoms.



"HPN"

(23)

The reactivity of coordinated oxygen ligands in *cis*-$MoO_2(acda)_2$ has been investigated where Hacda = 2-aminocyclopent-1-ene-1-carbodithioic acid [37]. Using catechols as reagents, oxygen abstraction results in complexes of the general formula $MoO(L)(acda)_2$ (24), where H_2L is a catechol. These complexes have been isolated and spectroscopically characterised. On a similar theme, oxygen abstraction reactions of dioxo-molybdenum(VI) complexes with PPh_3 have been investigated [38]. The subsequent dimerisation between the starting complex $MoO_2(S_2CNR_2)_2$ (R = Me, Et, ^iPr, ^iBu, Ph, or $PhCH_2$) and the reduced product $MoO(S_2CNR_2)_2$ to the oxo-bridged molybdenum(V) complex $Mo_2O_3(S_2CNR_2)_4$ is very sensitive to the electron donating ability of the substituents on the dithiocarbamate ligand. This study focuses on the effect on the dimerisation equilibrium constant of varying the substituent R.

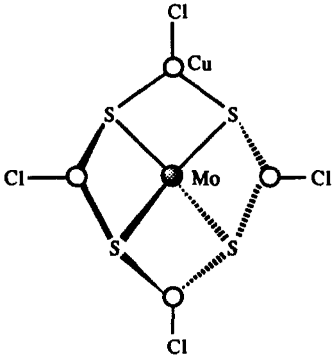


(24)

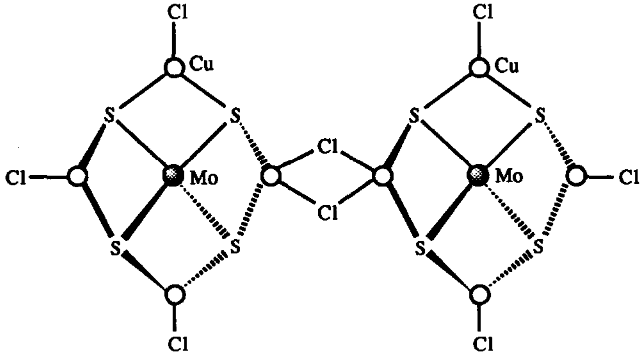
1.1.3 Complexes with sulfur donor ligands

The reaction between $MoO(S_2CNR_2)_2$ (R = Me, Et, Pr, Bu) and propylene sulfide (C_3H_6S) is a new efficient route to the 7-coordinate, blue complexes $MoO(S_2)(S_2CNR_2)_2$ [39]. Although this class of complex has been synthesised previously, this one pot reaction results in a much higher yield. At temperatures greater than 160°C partial decomposition occurs, and the dimeric complex $Mo_2O_2(\mu\text{-}S)_2(S_2CNR_2)_2$ is obtained.

Addition of copper(I) chloride to salts of $[MoS_4]^{2-}$ in CH_2Cl_2 or MeCN results in the formation of new dimetallic complexes that display various geometries whilst retaining the same Mo:S:Cu composition of 1:4:4 [40]. Crystal structures of the anion $[MoS_4Cu_4Cl_4]^{2-}$ with three different sets of counterions have been solved. The presence of the cation $[Bu_4N]^+$ results in a structure with discrete anions (**25**) separated by the $[Bu_4N]^+$ cations. With the mixed cationic combination $\{[Ph_4P][Pr_4N]\}^{2+}$, there is a dimeric aggregation (**26**) in the solid state, whilst with $[Pr_4N]^+$ as the counterion, a polymerised linear anionic chain is present in the lattice. The variation in the solid state structures is discussed in terms of the cation sizes.



(**25**)



(**26**)

1.1.4 Complexes with halide donor ligands

Hydrogen chloride complexes of a series of fluoride compounds, including MoF_6, in a solid argon matrix at 12K have been studied by IR spectroscopy [41]. Two distinct 1:1 complexes are obtained for molybdenum, with HCl bonding through either the H or the Cl atom, *i.e.* MoF_6-HCl and MoF_6-ClH.

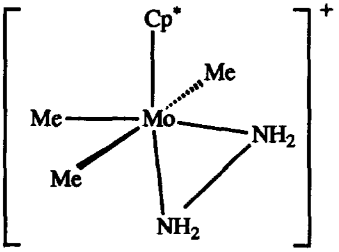
Chlorinated solvents provide the source of halide in the preparation of complexes of the formula $[(Cp)(Cl)(PMe_3)_2MoCR]Cl$ [42]. Photolysis of the molybdenum(IV) carbene complex $(Cp)L_2MoCR$ [L = CO, $P(OMe)_3$] in the presence of PMe_3 in chlorinated solvents results in oxidation, as well as ligand substitution. The chlorine plays a dual role, as both a ligand and a counterion.

1.2 MOLYBDENUM(V)

1.2.1 Complexes with nitrogen donor ligands

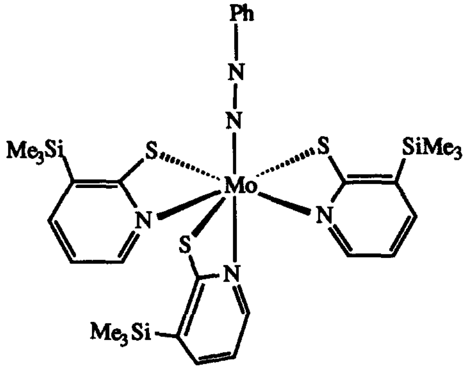
1.2.1.1 Mononuclear complexes

Conversion of an amino ligand to an amido, imido and then nitrido ligand has been achieved starting from the molybdenum(V) complex $[Cp^*Mo(Me)_3(NH_3)_x][OTf]$ (x = 1,2; HOTf = triflic acid). Deprotonation yields the unstable amido complex $Cp^*Mo(Me)_3(NH_2)$ (for both x = 1 and 2), which is oxidised by $[CpFe]^+$ to give the molybdenum(VI) imido complex $Cp^*Mo(Me)_3NH$. A further deprotonation, using $LiN(SiMe_3)_2$, produces the bridged nitrido complex $Cp^*MoMe_3(NLi)$. The initial preparation of $[Cp^*Mo(Me)_3(NH_3)_x]^+$ involves the reaction of $Cp^*Mo(Me)_3OTf$ with ammonia; if this starting material is reacted directly with LiN_2H_3, the final nitrido complex is obtained directly. Work on this system also covers hydrazine as a ligand [44], with potential relevance to the reduction of dinitrogen to ammonia. The cationic complex $[Cp^*Mo(Me)_3(N_2H_4)]^+$ has been synthesised. The hydrazine ligand adopts an η^2-bonding mode as shown in structure (27). Reduction of this complex by sodium amalgam results in cleavage of the N-N bond of the hydrazine ligand, and formation of NH_3 and the imido complex $Cp^*Mo(Me)_3NH$.

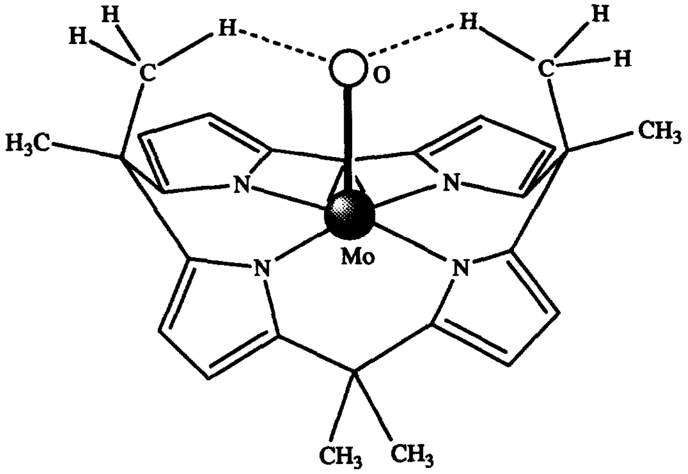


(27)

Continuing the work on sterically hindered thiolate ligands, mentioned earlier [5], a 7-coordinate molybdenum(V) diazenido complex has been synthesised and structurally characterised [45]. Mo(NNC$_6$H$_5$)(2-SC$_5$H$_3$N-3-SiMe$_3$)$_3$ has a pentagonal bipyramidal geometry, with the phenyldiazenido ligand occupying an axial position (**28**). The uncommon, near linearity of this ligand (∠Mo-N-N = 171.7(3)°) together with the bond lengths (Mo-N = 1814(3), N-N = 1216(5) Å) indicate considerable delocalisation.



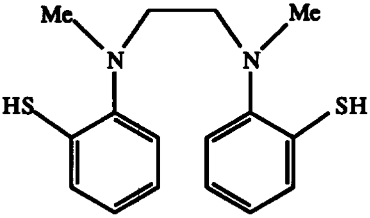
(28)



H---O distances 2.111 Å and 2.102 Å

(29)

The ligand *meso*-octamethyl-porphyrin (H$_4$L) has been used to bind the oxomolybdenum(V) ion [46]. X-ray analysis of [Li(thf)$_4$][Mo(O)L] reveals hydrogen-bonding between the oxo group and two of the *meso*- methyl groups in the anion (29). The compound *N,N'*-dimethyl-*N,N'*-bis(2-mercaptophenyl)-1,2-diaminoethane (H_2L') (30) also acts as a tetradentate ligand. Complexes of the formula $[MoOXL']^-$ and [MoO(XH)L'] (X = O, S) have been synthesised to act as models for molybdenum(V) sites in xanthine oxidase [47]. Using EPR spectroscopy as a tool, information as to the coordination of the molybdenum(V) centres in the various enzyme sites has been obtained.



(30)

1.2.1.2 *Dinuclear complexes*

A series of reports has appeared on dimeric (MeC_5H_4)Mo(imido) complexes containing oxo or sulfido ligands [48-51]; the main topics covered are:

(i) oxidation of $[(MeC_5H_4)Mo(CO)_3]_2$ by nitrobenzene to give the oxoimido complexes $(MeC_5H_4)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}NPh)$, $[(MeC_5H_4)MoO(\mu\text{-}NPh)]_2$ and $(MeC_5H_4)_2Mo_2O(NPh)(\mu\text{-}O)(\mu\text{-}Ph)$ [48];

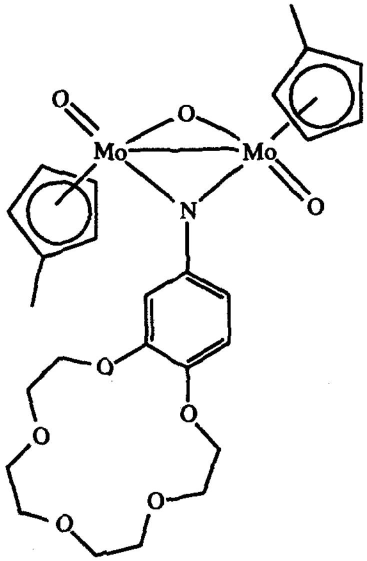
(ii) the reactivity of $(MeC_5H_4)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}NPh)$, including the reaction with H_2S to give $(MeC_5H_4)_2Mo_2(S)(\mu\text{-}O)(\mu\text{-}NPh)$ with subsequent studies on the reactivity of this product [49];

(iii) electrochemistry of complexes of the formula $(MeC_5H_4)_2Mo_2X(NPh)(\mu\text{-}NPh)_2$ (X = NPh, S, O) and the oxo-dimer $\{(MeC_5H_4)MoO(\mu\text{-}O)\}_2$, the results being interpreted in terms of the π-donor abilities of the ligands NPh^{2-}, S^{2-} and O^{2-} [50];

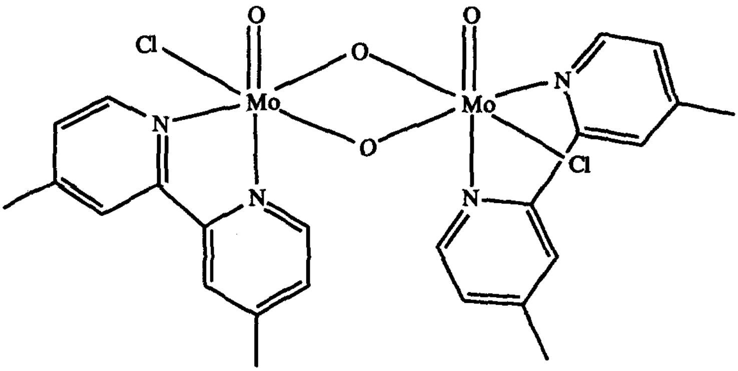
(iv) synthesis and electrochemistry of the crown ether imido complexes $(MeC_5H_4)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}N(\text{benzo-15-crown-5}))$ (31) and $\{(MeC_5H_4)MoO[\mu\text{-}N(\text{benzo-15-crown-5})]\}_2$, and their reactivity with phenylisocyanate [51].

In the above examples, the source of imido ligands is either a nitrobenzene-derived reagent or phenylisocyanate. On studying the photochemical reactions of $Cp_2Mo_2(CO)_6$ with azobenzene, $Cp_2Mo_2(\mu\text{-}NPh)_2(\mu\text{-}\eta^1\text{-}N_2H_2)$ is obtained as the major product; the subsequent oxidation of this product gives the oxo-imido complex $Cp_2Mo_2O_2(\mu\text{-}NPh)_2$ in almost 50% yield (based on the carbonyl starting dimer) [52].

Flash photolysis of the complexes $[Mo_2O_4(H_2O)_{6-x}(NCS)_x]^{(2-x)+}$ (x = 1, 2) in aqueous acid has been studied as a continuation of studies on the parent complex cation $[Mo_2O_4(H_2O)_6]^{2+}$ [53]. Three μ-oxo-bis(oxo-molybdenum(V)) species are identified as intermediates, namely $[Mo_2O_3(H_2O)_8]^{4+}$, $[Mo_2O_3(NCS)(H_2O)_7]^{3+}$ and $[Mo_2O_3(NCS)_2(H_2O)_6]^{2+}$, which decay following first order kinetics to molybdenum(VI) products and dihydrogen. Another class of molybdemum(V) oxo-dimer containing benzimidazole ligands has been studied [54]. $[Mo_2O_4(Cl)(L)(L^1)(H_2O)_2].nH_2O$ and $[Mo_2O_4(Cl_2)(L^2)_2].2H_2O$ (L = benzimidazole; L^1 = EtOH,H_2O; n = 0-2; L^2 = 2-acetylbenzimidazole, 2-benzylbenzimidazole or 2-(*o*-aminophenyl)benzimidazole) have been isolated and characterised spectroscopically. The data indicate the presence of a $\{Mo_2O_4\}^{2+}$ core. Also reported in this work were several mononuclear, octahedral molybdenum(V) complexes containing the derivatised ligands 2-(hydroxymethyl)benzimidazole and 2-(α-hydroxyethyl)benzimidazole.



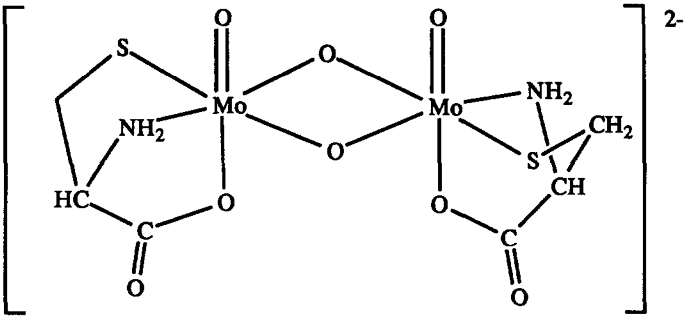
(31)



(32)

An oxo-dimer containing the didentate nitrogen donor ligand 4,4'-dimethyl-2,2'-dipyridyl (dmbpy) can be synthesised by one of two routes. The complex $Mo_2O_2(\mu\text{-}O)_2(Cl)_2(dmbpy)_2$, (32), can be obtained from the reaction of $Mo_2Cl_4(MeCN)_4$ with O_2 and dmbpy, or alternatively by the direct oxidation of $Mo_2Cl_4(dmbpy)_2$ with oxygen [55]. Structural analysis indicates that the terminal oxygen atoms are in a *syn*-configuration, and the Mo-Mo distance of 2.562(2)Å is typical of a molybdenum(V)-molybdenum(V) single bond.

Circular dichroism spectrophotometry has been used to study the effects of various cationic surfactants on the complex dianion $[Mo_2(\mu\text{-}O)_2(O)_2(R\text{-cysteinato})_2]^{2-}$ (33) in aqueous micellar solutions [56]. Depending upon the concentration of the surfactant, *e.g.* $[CH_3(CH_2)_{15}N(CH_3)_3]Br$, the didentate $[R\text{-cysteinato}]^{2-}$ ligand either partially dissociates a $-CO_2^-$ arm or is totally liberated.



(33)

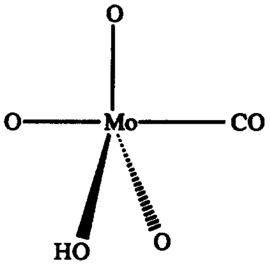
1.2.2 *Complexes with phosphorus donor ligands*

The reaction of $MoCl_4(PPh_3)_2$ with $2,4,6\text{-}{}^iPr_3C_6H_2SH$ in CH_2Cl_2, followed by the introduction of excess O_2, results in a dinuclear molybdenum(V) oxo complex containing both thiolate and phosphine ligands [57]. The structure of the product, $Mo_2O_4(2,4,6\text{-}{}^iPr_3C_6H_2S)_2(PPh_3)_2$, shows the common $\{Mo_2O_4\}^{2+}$ core with a typical Mo-Mo distance of 2.595(4) Å. Each molybdenum atom is in an irregular, square-based pyramidal geometry, with the terminal oxygen donor ligand in the apical site.

1.2.3 *Complexes with oxygen donor ligands*

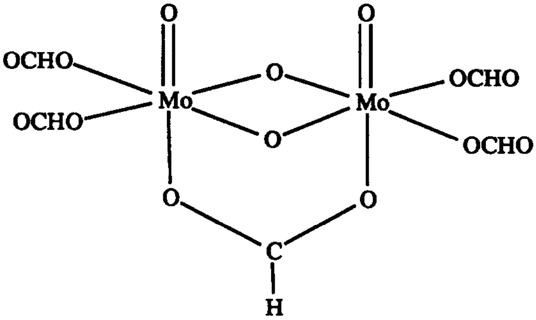
1.2.3.1 *Simple oxygen donor ligands*

An EPR spectroscopic study on the coordination sphere of molybdenum(V) centres in UV-irradiated silica-supported MoO_3 catalysts has been carried out to determine the number of coordination vacancies at the transition metal centre, with relevance to the absorption/catalytic properties [58]. Absorption of ^{13}CO and H_2 results in a $Mo(O)_3(OH)^{13}CO$ environment (34), as indicated by the hyperfine structure (attributed to the ^{13}CO ligand) in the EPR spectrum.



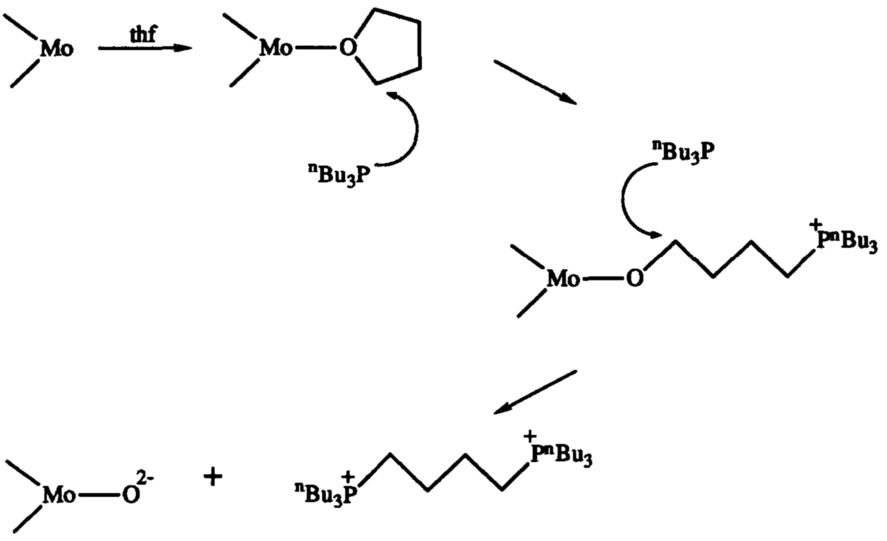
(34)

The complex anions $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$ and $[Mo_2O_4(OCHO)_4(\mu\text{-}O_2CH)]^{3-}$ (35) have been structurally characterised. They both contain two molybdenum centres octahedrally coordinated by six oxygen atoms [59, 60]. The latter complex contains a strong non-complexing acid, and is quantitatively hydrated to $[Mo_2O_4(H_2O)_6]^{2+}$; this provides a viable alternative route to this hydrated complex [60].



(35)

A range of carboxylate complexes $Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)(RCO_2)_2$ (R = n-pentyl, n-hexyl, n-heptyl, iso-octyl, cyclohexyl and phenyl) have been synthesised to investigate the effect of presence of a sulfur bridging atom compared to the related dioxo bridged complexes [61]. The bis(sulfido) bridged molybdenum complex $[Mo_2O_2Br_4(\mu\text{-}S)_2]^{2-}$ has been synthesised and structurally characterised [62]. Whilst there are no exceptional features about this anion, an intriguing transformation involving thf and $^nBu_3P$ to the cation $[^nBu_3P(CH_2)_4P^nBu_3]^{2+}$ takes place during the synthesis of the anion $[Mo_2O_2Br_4(\mu\text{-}S)_2]^{2-}$. The molybdenum(V) dimer is prepared from $Mo_3S_7Br_4$, $^nBu_3P$ and thf, and although no intermediates were isolated, a viable route to the products is shown in Scheme1.



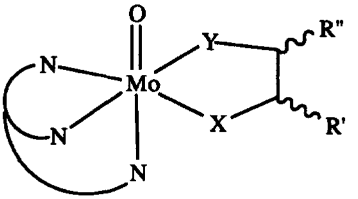
Scheme 1

Finally, a range of chalcogen complexes of the general formula $Cp_2Mo_2O_2(\mu\text{-}X)(\mu\text{-}Y)$ ($X,Y = O, S, Se$) have been prepared by a variety of routes [63]. The selenium complexes, *cis*- and *trans*-$Cp_2Mo_2(O)_2(\mu\text{-}Se)_2$ and *trans*-$Cp_2Mo_2O_2(\mu\text{-}Se)(\mu\text{-}O)$ have been structurally characterised. Recrystallisation of the latter complex in hexane-CH_2Cl_2 gave the complex *cis*-$Cp_2Mo_2O_2(\mu\text{-}Se)_{0.8}(\mu\text{-}Cl)_{1.2}$. There are several other oxo-molybdenum complexes containing more exotic sulfur ligands, and these are discussed in section 1.2.4.

1.2.3.2 Didentate ligands with oxygen and sulfur donors

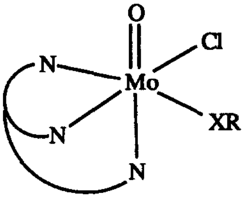
Spectroscopic and electrochemical studies have been carried out on a series of monomeric oxymolybdenum(V) complexes containing 5-membered chelate rings with oxygen and/or sulfur donor atoms (36) [64]. The mono alkoxo and alkanethiolato complexes, LMoO(Cl)(XR) (37) have also been included in the study, and the effect of the number of methylene units on the reduction potentials of the complexes has been discussed.

Reduction of $[Mo_2O_2(O_2CC(S)Ph_2)_2]^{2-}$ provided a route to the first structurally characterised molybdenum(V) complex containing both coordinated thiolate and carboxylate groups [65], *i.e.* the first example of a $Mo^VO(S_2O_2)$ donor set (38). The bulky phenyl groups of the $Ph_2C(S)CO_2^-$ ligands prevent the square pyramidal mononuclear complex from dimerising to the usual μ-oxo dimolybdenum(V) complexes. An alternative route to $[MoO(O_2CC(S)Ph_2)_2]^-$ involves the reaction of the same molybdenum(VI) starting complex with aliphatic thiols under acidic conditions [66]. In this report, the electrochemical properties of the molybdenum(V) complex are investigated.



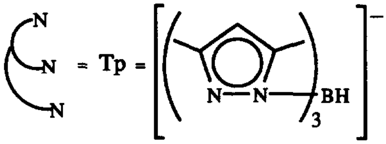
X	Y	R'	R"
O	S	H	H
O	S	Me	H
O	S	Me	Me
O	O	Me	Me
S	S	Me	Me

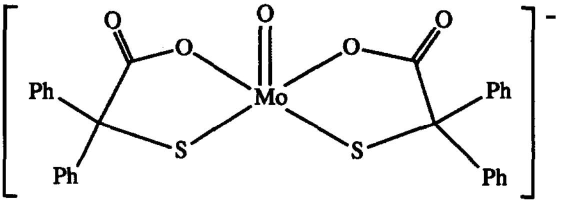
(36)



X	R
O	Me
O	Et
O	n-Pr
S	Et
S	n-Pr
S	i-Pr

(37)



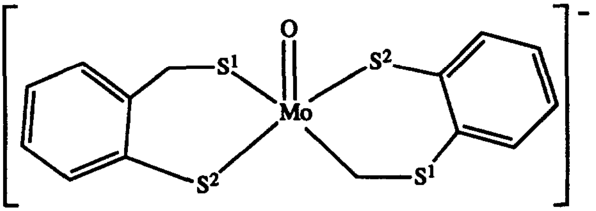


(38)

A dimeric complex $Mo_2L_5(H_2O)_2$ ($H_2L = HSCH_2COOH$) is obtained by the direct action of H_2L on $MoO_3.H_2O$ under an argon atmosphere [67]. Using a range of techniques (EPR, IR, NMR and electronic spectroscopies, magnetic susceptibility measurements, cyclic voltammetry and XPS measurements) both molybdenum atoms are found to be octahedrally coordinated through the *O*- and *S*-donor atoms of ligand L and the water molecules; the two molybdenum centres are in slightly different environments due to the presence of three asymmetrically bridging ligands.

1.2.4 Complexes with sulfur donor ligands

The complex $[NEt_4][MoO(\alpha,2\text{-toluenedithiolate})_2]$ (39) contains a distorted tetragonal-pyramidal $MoOS_4$ core [68]. The two classes of Mo-S bond, *i.e.* molybdenum-arenethiolate and molybdenum-alkanethiolate, are distinctly different in length, and this is rationalised in terms of π-bonding between the sulfur atoms and the molybdenum centre.

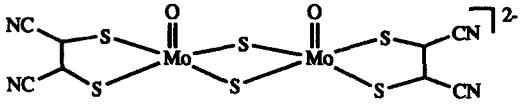


Mo-S^1(av) = 2.37(1) Å

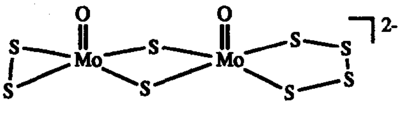
Mo-S^2(av) = 2.42(1) Å

(39)

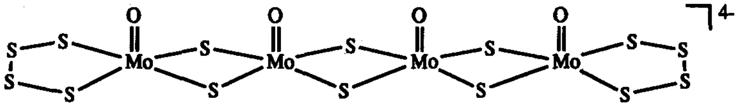
An increasing number of complexes with a $[\{MoO(\mu\text{-}S)\}_2]^{2+}$ core are now known, and a range of didentate sulfur ligands [55, 69-71]. The molybdenum atom resides in an *S₄O*-square-based pyramidal environment with the oxo ligand in an apical site. The crystal structures of the complexes $[Mo_2O_2(\mu\text{-}S)_2(1,2\text{-dicyanoethylene-}2,2\text{-dithiolate})_2]^{2-}$ **(40)** and $[Mo_2O_2(\mu\text{-}S)_2(S_2)(S_4)]^{2-}$ **(41)** [69] have been determined. The structure of the extended tetranuclear molybdenum complex anion $[\{(S_4)MoO(\mu_2\text{-}S)_2MoO(S)\}_2]^{4-}$ **(42)** has also been solved [70]. Infrared and Raman spectroscopies are also very useful in determining the presence of μ-S, S_2 and S_4 ligands for this class of compound. The effect of isotope substitution by ^{34}S on various infrared and Raman absorptions has been investigated for the complex $[\{MoO(\mu\text{-}S)_2(S_2)\}_2]^{2-}$ as well as the bromo complex $[\{Mo(\mu S_2)Br_4\}_2]^{2-}$ **(43)** [71].



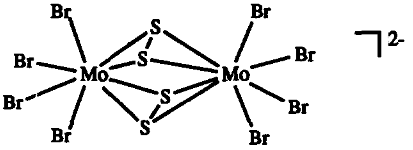
(40)



(41)

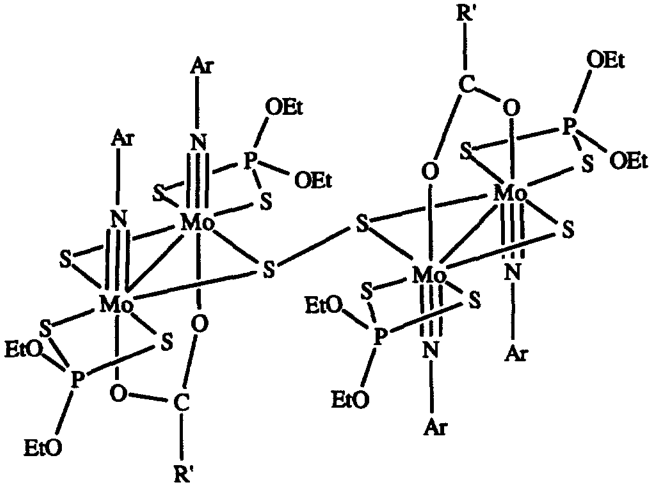


(42)



(43)

The complexes $Mo_2(NC_6H_4CH_3)_2[S_2P(OC_2H_5)_2]_2(S)(O_2CCH_3)(SSR)$ and $\{Mo_2(NC_6H_4CH_3)_2\text{-}[S_2P(OC_2H_5)_2]_2S_2(O_2CCH_3)\}_2$ **(44)** have been used to generate dimolybdenum thiyl radicals [72] by photolysis using UV or visible radiation. Complexes containing $Mo_2(\mu\text{-}S\cdot)$ radicals are formed in each case, and these have been trapped and observed by EPR spectroscopy. The radical species abstract hydrogen atoms from thf, and can also be used to polymerise styrene and effect the *cis-trans* isomerisation of 2-butene.



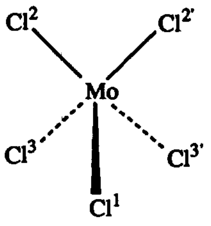
(44)

1.2.5 Complexes with halide donor ligands

Refinement of electron diffraction data for gaseous $MoCl_5$ (45) gives rise to two descriptions for the structure of this molecule. One is based on a distorted square-based pyramid and the other on a distorted trigonal prism with one apex removed [73]. The structural parameters for the two refinements are given in Table 2.

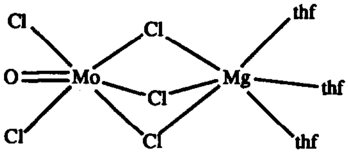
Table 2 *Geometrical parameters for the two refinements of $MoCl_5$*

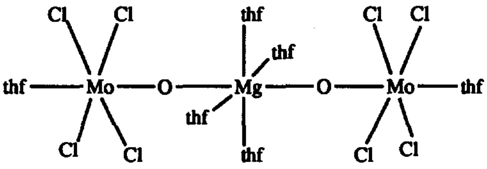
	I	II
Bond angles /deg		
Cl^{3}-Mo-Cl^{1}	87.8(4)	87.9(3)
Cl^{3}-Mo-$Cl^{3'}$	90.4(1)	87.9(3)
Cl^{2}-Mo-$Cl^{2'}$	90.4(1)	84.2(8)
Cl^{2}-Mo-Cl^{3}	85.6(4)	90.7(1)
Cl^{1}-Mo-Cl^{2}	113.1(5)	111.6(5)
Cl^{2}-Mo-$Cl^{3'}$	158.4(9)	160.5(7)
Bond lengths /Å		
Mo-Cl^{3}	2.269(1)	2.234(2)
Mo-Cl^{1}	2.207(5)	2.234(2)
Mo-Cl^{2}	2.269(1)	2.291(3)



(45)

Two molybdenum-magnesium complexes are obtained on reacting $MgCl_2(thf)_2$ with the complex $MoCl_3O(thf)_2$. If the reagents are in a 1:1 ratio, then the trichloro-bridged complex $MoOCl_2(\mu\text{-}Cl)_3Mg(thf)_3$ (46) is produced, whereas if the molybdenum starting material is in 2-fold excess, a linear Mo-O-Mg-O-Mo complex, $\{(thf)Cl_4MoO\}_2Mg(thf)_4$ (47), is produced. Both complexes have been structurally characterised.





(46)

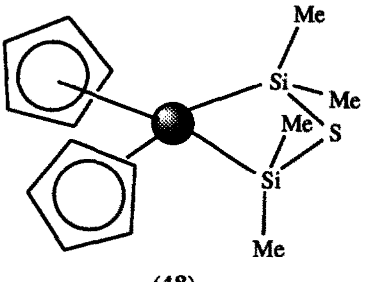
(47)

1.3 MOLYBDENUM(IV)

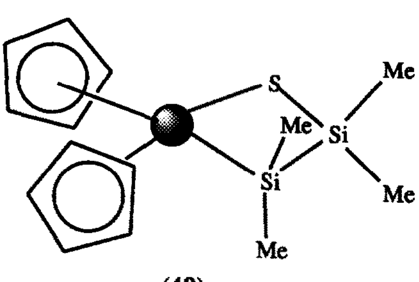
1.3.1 Complexes with group 14 donor ligands

The reaction of the η^2-disilene complex $Cp_2Mo(\eta^2\text{-}Me_2SiSiMe_2)$ with a variety of inorganic and organic substrates has led to new compounds as a result of either Mo-Si or Si-Si bond cleavage [75]. For example, with S_8 in benzene at 25°C, the only product is the molybdenum(IV) complex $Cp_2Mo[(SiMe_2)_2S]$ (48), the sulfur atom having inserted into the Si-Si bond. With Ph_3PS as the source of sulfur, (48) is still produced (25% yield), but the main product (75% yield) is the isomeric compound where the sulfur atom has inserted into the Mo-Si bond (49). Both isomers have been structurally characterised.

Oxidation of the stannane complex $Mo(SnPh_3)(CO)_3L$ (L = Cp, Cp* or η^5-C_9H_7 - indenyl) to give the carbene complex $Mo(SnPh_3)(CO)_2\{=C(OEt)R\}L$ can be achieved by reaction with LiR (R = Me, Ph) followed by $[OEt_3][BF_4]$ [76]. The reactivity of both stannane and carbene complexes (for L = Cp, Cp*) with iodine is examined, the former undergoing oxidative addition of iodine and substitution of the stannane ligand to give $MoI_3(CO)_2L$.



(48)

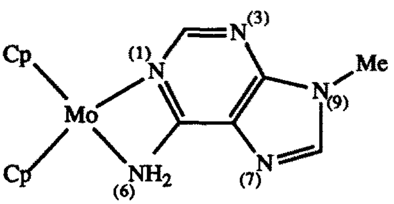


(49)

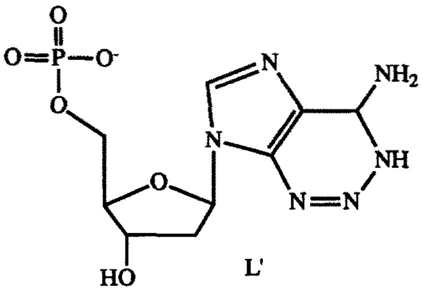
1.3.2 Complexes with nitrogen donor ligands

The reactivity of the imide complexes $Mo(NAr)(CH_2CHSiMe_3)(OR)_2$ (Ar = 2,6-diisopropylphenyl; R = $CMe(CF_3)_2$ or ^tBu) has been studied [77]. One of the more intriguing results is the outcome of the reaction with excess ethene. For R = $CMe(CF_3)_2$ the vinyltrimethylsilane is displaced by a dimerised C_4H_8 ligand; for R = ^tBu the complex $Mo(CH_2CH_2CH_2)(NAr)(O^tBu)_2$ is produced, although this decomposes to the imido bridged dimer $\{Mo(O^tBu)_2(\mu\text{-}NAr)\}_2$.

The coordination of molybdenocene fragments to DNA is modelled in the complexes $[Cp_2MoL]^+$ where HL = 9-methyladenine or 1-methylcytosine [78]. The structure of the methyladenyl complex shows *N,N'*-chelation with the molybdenum atom in a tetrahedral environment as illustrated in structure (**50**). Two isomers exist in solution; one has the solid state structure and the other is chelated through the atoms N(6) and N(7). Amid the other complexes reported is a dimeric complex $[Cp_2MoL']_2$ where L' contains a phosphate group as a model for the phosphodiester backbone of DNA (**51**). The various sites available for coordination to the molybdenum centres are discussed.

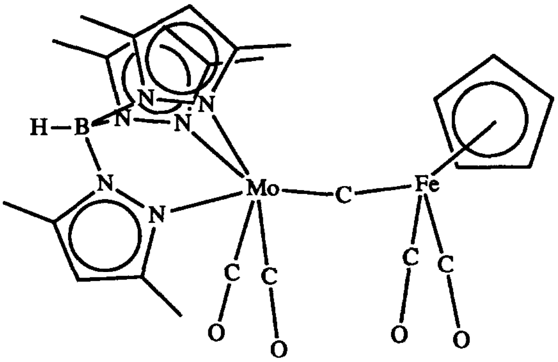


(50)

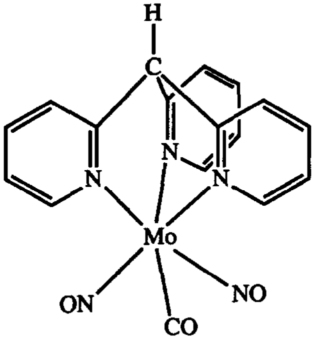


(51)

The bulky nature of the tridentate nitrogen donor ligand tris(3,5-dimethylpyrazolyl)borate (Tp) has been utilised to prevent nucleophilic attack at the molybdenum centre of the carbene complex $Tp(CO)_2MoCCl$ [79]. Reaction with aryloxide anions results in a clean conversion to aryloxylcarbyne complexes. Structural analysis of the related complex $Tp(CO)_2MoCFe(CO)_2Cp$ (**52**) indicates that the $CFe(Cp)(CO)_2$ fragment can be treated as a carbene ligand: a typical Mo-C bond length of 1.819(6) Å and an Mo-C-Fe angle of 172.2(5)° are observed [80]. A similar nitrogen donor set is generated by the ligand $HC(py)_3$ as observed in the complex $[HC(py)_3Mo(NO)_2(CO)][SbF_6]_2$ (**53**) [81]. Due to the high effective charge on the metal centre, the CO ligand is readily lost to generate the Lewis acid $[HC(py)_3Mo(NO)_2][SbF_6]_2$; the adduct formation of this unsaturated compound with a wide range of aldehydes, ketones and esters is investigated.

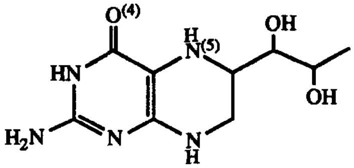


(**52**)

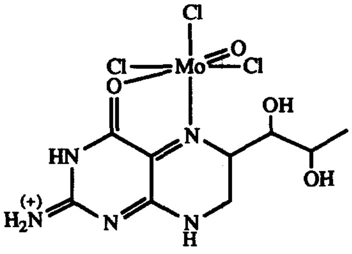


(**53**)

Addition of MoO_2Cl_2 to the pterin 6β-5,6,7,8-tetrahydro-L-biopterin (**54**) in methanol results in almost quantitative reduction of the molybdenum atom to the octahedral molybdenum(IV) complex containing the cationic ligand 1,5-*quinoid*-7,8-dihydro-6*H*-L-biopterin (**55**) [82]. Structural analysis shows that the molybdenum atom is coordinated by N(5) and O(4) of the pterin ligand, with an unusually short Mo-N distance of 2.02Å; the chloride ligands are in a meridonial arrangement.



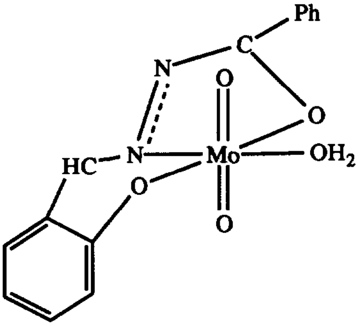
(**54**)



(**55**)

Eight coordinate MoN_4X_4 (X = O, S, Se) complexes have been prepared using the didentate *N,X*-donor ligand 5-^{t}butyl-2-hydroxypyrimidinato $[bhpm]^-$ and its mercapto and hyroseleno derivatives, $[bmpm]^-$ and $[bspm]^-$, respectively [83]. Whilst $Mo(bhpm)_4$ was too air sensitive to be isolated, Mo(bmpm)$_4$ and Mo(bspm)$_4$ have been fully characterised. The effect on stability of changing the donor atom from oxygen through to selenium is discussed. Two substituted pyridine-2-thiol ligands have proved to be very versatile on reaction with chloro and bromo molybdenum complexes [84]. A whole range of products has been structurally characterised with the pyridine-2-thiol ligands adopting an *N,S*-chelating mode of bonding, as well as acting as the terminal or bridging ligand (in dimeric complexes) bonding through the thiolato sulfur atom (see section 1.3.5).

A meridial *N,O,O'*-donor set is provided by the tridentate ligand [2(α-oxidobenzylidenehydrazonomethyl)phenolate]$^-$ [85]. The structural parameters of the complex $MoO_2(C_{14}H_{10}N_2O_2)(H_2O)$ (**56**) indicate considerable delocalisation within the tridentate ligand. The N-N bond length is 1.403(4) Å. This value is intermediate between a single and double bond. A typical Mo-N bond length of 2.261(3) Å is observed.



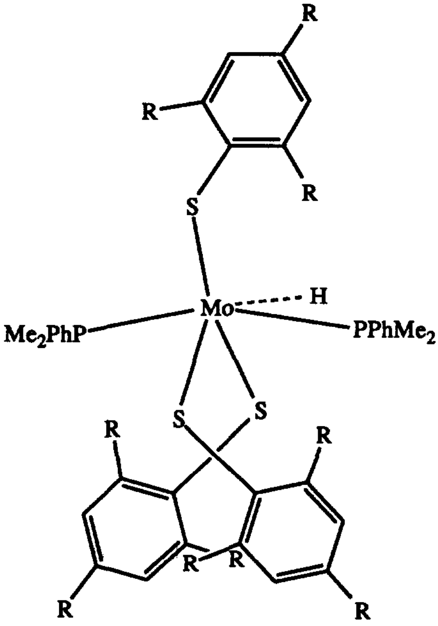
(56)

1.3.3 Complexes with phosphorus donor ligands

Two reports have broached the subject of the so called "bond stretch isomers" of the complex *cis-mer* $MoOCl_2(PR_3)_3$ ($PR_3 = PEt_2Ph, PMe_2Ph$) [86, 87]. Whilst only one Mo=O stretch is observed in the infrared spectrum, two distinctly different Mo-O bond lengths were found on structural characterisation (1.698(8) and 1.866(7) Å). A reinvestigation of the structure [86] revealed that the different bond lengths appeared to be due to an $MoCl_3(PR_3)_3$ impurity present in the sample rather than due to different isomers.

Phosphine ligands have been used to stabilise the unsaturated chloro complex $CpMoCl_3$ [88]. The eighteen electron adducts $CpMoCl_3(R_2PCH_2CH_2PR_2)$ (R = Me or Ph) and $CpMoCl_3(P(OCH_2)_3CEt)_2$ have been obtained by simple addition of the free phosphine ligand, although use of PMe_3 results in decomposition. The hydrido phosphine complexes $[MoH(SC_6H_2R_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ (**57**) (R = Me or ^{i}Pr) have been prepared and structurally characterised [89]. The geometry about the molybdenum centre is based upon a distorted trigonal bipyramid with the three thiolate ligands in the equatorial plane and the phosphine ligands essentially *trans*. The hydride ligand was not located directly; its presence was established by ^{1}H

NMR and IR spectroscopies. Reactions with the neutral ligands L (L = $R'C_5H_4N$, $P(OR'')_3$, MeCN; R' = H, 2-,3-,4-Me; R" = Me, Et) result in phosphine substitution giving a series of complexes $MoH(SC_6H_2R_3\text{-}2,4,6)_3(PMe_2Ph)L$; in contrast reaction with CO results in the displacement of the hydride and one thiolate ligand [90]. The structure of $[Mo(SC_6H_2{}^iPr_3\text{-}2,4,6)_2(PMe_2Ph)_2(CO)_2$ (**58**) reveals a trigonal prismatic coordination sphere about the molybdenum atom.



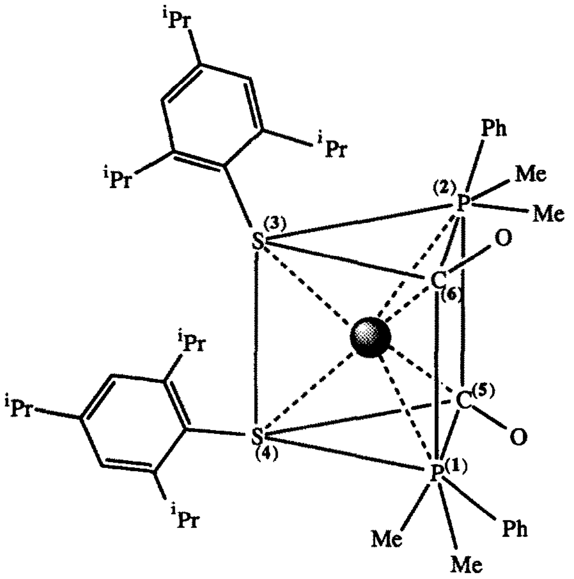
(**57**) R = Me, ^{i}Pr

1.3.4 *Complexes with oxygen donor ligands*

It has already been seen with molybdenum(VI) complexes that CO ligands can act as a source of oxo ligand (see section 1.1.2); cleavage of the C-O bond in a molybdenum carbonate complex also yields an oxo ligand, with liberation of CO_2 [91]. In this case there is no formal change in oxidation state of the metal centre; the source of energy for the transformation (equ. (5)) is from an argon ion laser.

$$Cp_2Mo\text{-}CO_3 \xrightarrow{h\upsilon} Cp_2Mo{=}O + CO_2 \qquad \text{equ. (5)}$$

The structures of the complex $MoCl_4(dme)$ (dme = 1,2-dimethoxyethane) and its adduct with 15-crown-5 have both been solved [92]. Each complex contains a distorted octahedral $MoCl_4O_2$ centre. The UV-VIS and magnetic properties of $MoCl_4(dme)(15\text{-crown-}5)$ are discussed.

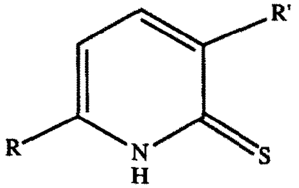


Mo-P(1)	2.459(2) Å
Mo-P(2)	2.463(2) Å
Mo-S(3)	2.464(1) Å
Mo-S(4)	2.395(1) Å
Mo-C(5)	1.954(5) Å
Mo-C(6)	1.981(5) Å

(58)

1.3.5 Complexes with sulfur donor ligands

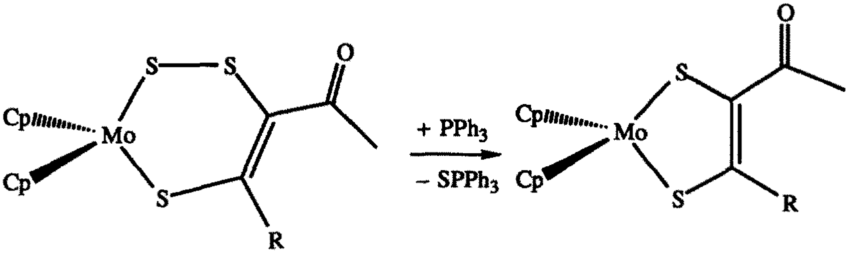
The pyridine-2-thiol ligands 3-(trimethylsilyl)pyridine-2-thiol and 3,6-bis-(^{t}butyldimethyl)pyridine-2-thiol have already been mentioned as versatile, didentate nitrogen/sulfur ligands (section 1.3.2.2). They can also act as neutral, monodentate sulfur ligands (L and L', respectively in structure (**59**)) [84]. A variety of mononuclear and dinuclear molybdenum(IV) and molybdenum(III) complexes have been synthesised and structurally characterised, including $MoX_4L'_2$ (X = Br, Cl), $MoCl_3L'_3$, $MoBr_3L_3$ and $Mo_2Cl_6L_3$.



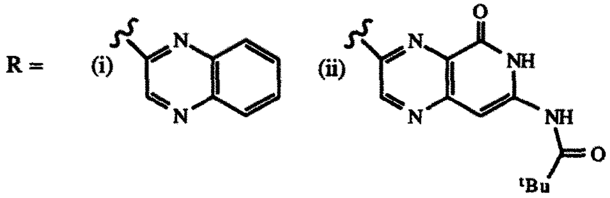
(59)

L : R = H, R' = $SiMe_3$
L' : R = R' = Si $^tBuMe_2$

On using $Cp_2Mo(\eta^2\text{-}S_4)$ as a starting material, addition of the alkyne MeC(O)CCR results in formation of the perthiolate-thiolate complex $Cp_2Mo(MeC(O)C(S_2){=}C(S)R)$ (**60**); the alkyne inserts into the S_4^{2-} ligand with loss of one sulfur atom [93]. Further reaction with PPh_3 results in sulfur abstraction, giving the corresponding dithiolate complex $Cp_2Mo(MeC(O)C(S){=}C(S)R$ (**61**). Both classes of complex have been structurally characterised and can be considered as model compounds for molybdopterin-containing enzymes. The same strategy was applied using the related alkyne PhCCR (R as before, but only the phthalazine substituent (i) as defined in structure (**60**)) and $[Mo(S)(S_4)_2]^{2-}$ [94]. In this case an octahedral tris(dithiolate) complex (**62**) is obtained. The redox chemistry of this product is explored both electrochemically and using I_2 as an oxidant. Taking this technique a stage further, MeC(O)CCC(O)Me has been reacted with a range of molybdenum sulfido complexes: $[Mo(S_4)_2]^{2-}$, $[MoS(S_4)_2]^{2-}$, $[Mo_2O_2S_7]^{2-}$, $[Mo_2O_2S_9]^{2-}$, $[Mo_2S_{10}]^{2-}$ and $[Mo_2S_{12}]^{2-}$. This generated a variety of complexes containing the ligand 1,2-dicarbomethoxy-1,2-ethylenedithiolate [95]. A proposed mechanism involves electrophilic attack of the alkyne on either Mo=S or Mo-S_2 with subsequent insertion to give unstable vinyl sulfides or vinyl disulfides, which decompose to the final thiolate ligand.



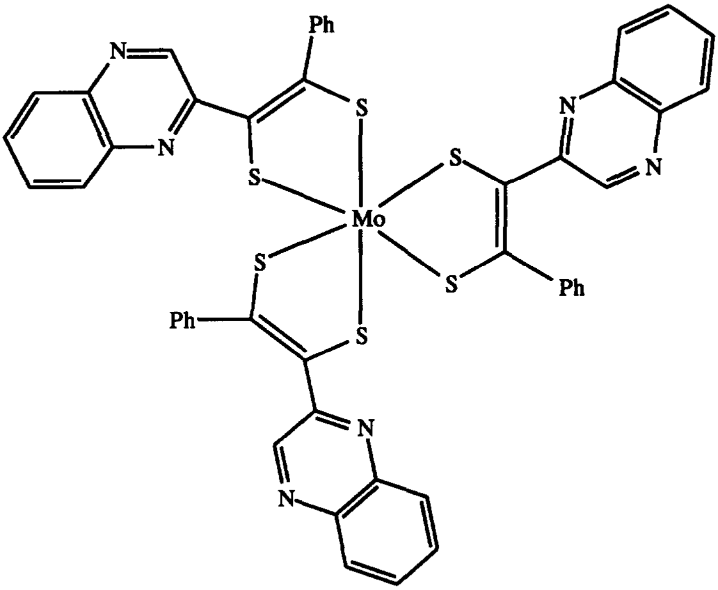
(**60**) (**61**)



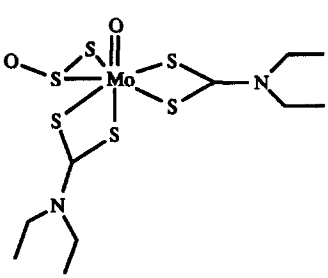
An alternative approach has been used to synthesise tris(dithiolate) molybdenum(IV) complexes analogous to (**62**), in which 1,3,4,6-tetrathiapentalene-2,5-dione is used as the source of dithiolate ligand [96]. Reaction of $[MoS_4]^{2-}$ with this reagent results in a formal two electron reduction of the molybdenum(VI) centre, and the dianionic complex $[Mo(S_2C_2S_2CO)_3]^{2-}$ is isolated. The oxidation of this dianion back to a molybdenum(VI) complex can be achieved electrochemically, and the reactivity of this neutral complex is compared with $[Mo(S_2C_2S_2CO)_3]^{2-}$. Electrochemistry is also the topic of a report on a tris(quinoxaline-2,3-dithiolate) molybdenum(IV) complex [97]. There are two distinct redox active sites; one ligand based and the other on the molybdenum centre.

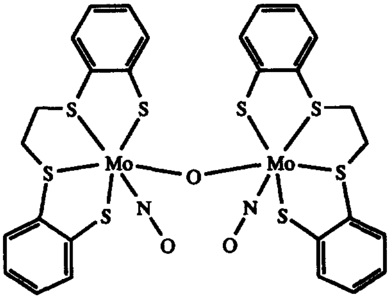
Another class of didentate sulfur ligands is based upon the carbodithioate group. The anion $[Cp^*Mo(S_4)(S_2CO)]^-$, which contains a chelating dithiocarbonate ligand, has been isolated and structurally characterised [98]. Obtained from the reaction of a polysulfide solution with $Cp^*Mo(CO)_3(CH_3)$, the metal centre has undergone oxidation with elimination of the carbonyl and alkyl ligands. Two different carbodithioate ligands are present in the complexes

$Mo(S_2CNR_2)_n(acda)_{4-n}$ (R = Et, Pr; n = 2, 3; Hacda = 2-aminocyclopent-1-ene-1-carbodithioate) [99]. The differing properties of these complexes are rationalised in terms of the σ–donor and π-acceptor properties of the sulfur ligands. The complex $Mo(O)(S_2CNEt_2)_2(S_2O)$ **(63)** has been structurally characterised [100]. The S_2O ligand is bound to the molybdenum centre in a side on manner through both S atoms, and forms part of the equatorial plane of a distorted pentagonal bipyramidal geometry.



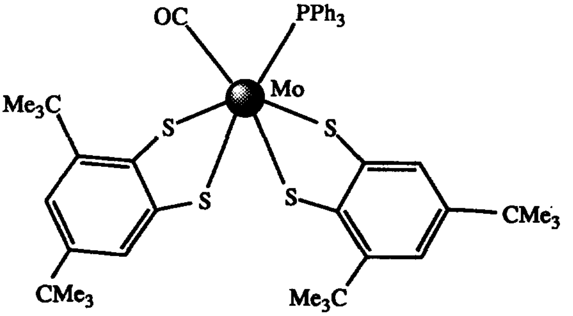
(62)





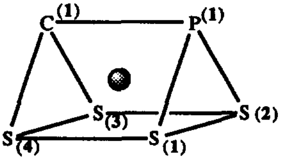
(63) **(64)**

The dianionic ligand 2,3,8,9-dibenzo-1,4,7,10-tetrathiodecane(2-), ('S_4'), coordinates to molybdenum *via* two thiolato and two thioether sulfur atoms in the complex {Mo(NO)('S_4')}$_2$(μ-O) **(64)** [101]. The μ-oxo ligand in this dimeric complex acts as both a σ- and π-donor ligand, the short Mo-O bond distances (1.866(6) and 1.891(6) Å, respectively) being indicative of double bond character. The related ligand ('$^{bu}S_4$'), having tertiary butyl groups on the 3 and 5 positions of the two benzyl rings, forms the molybdenum(II) carbonyl complex $Mo(CO)_3$('$^{bu}S_4$'), which undergoes intriguing redox chemistry [102]. Fragmentation of the tetradentate ligand giving two didentate dithiolate ligands occurs with the loss of ethylene; a CO ligand is also lost to form the molybdenum(IV) complex Mo('$^{bu}S_2$')$_2$$(CO)_2$. The structure of the related phosphine substituted complex Mo('$^{bu}S_2$')$_2$(CO)(PPh_3) **(65)** shows that the molybdenum atom is in a S_4CP pseudo-trigonal prismatic environment. The same transformation for the parent ('S_4') ligand has been achieved for the complex Mo(NO)(Cl)('S_4'), giving either [Mo('S_2')$_2$(O)]$^{2-}$ or [Mo('S_2')$_2$(NO)]$^{3-}$ depending on the reaction conditions [103].



(65)

Core:

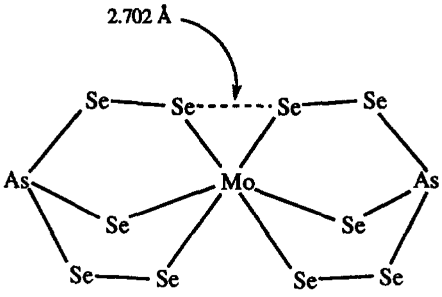


Mo-C(1)	2.042(6) Å
Mo-P(1)	2.517(2) Å
Mo-S(1)	2.349(2) Å
Mo-S(2)	2.358(2) Å
Mo-S(3)	2.364(2) Å
Mo-S(4)	2.350(2) Å

The reactivity of the crown thioether complex *trans*-$Mo(N_2)_2$(syn-Me_8[16]aneS_4) towards sources of S^{2-} ligands has been explored [104]. Replacement of both N_2 ligands by terminal sulfido ligands is possible using either S_8 or two equivalents of ^{t}BuSH, the latter reagent undergoing C-S bond cleavage. The structure of the product *trans*-$Mo(S)_2$(syn-Me_8[16]aneS_4) shows the molybdenum atom to be slightly displaced (0.031(5) Å) from the plane of the crown ether ring.

1.3.6 Complexes with selenium donor ligands

A complex of molybdenum containing the metal atom in a coordination sphere of six selenium atoms is synthesised in the reaction of $(^nBu_4N)_2[MoSe_4]$ with excess As_4Se_4 [105]. On solving the structure of the product $(^nBu_4N)_2[MoAs_2Se_{10}]$ **(66)** by means of X-ray diffraction, ambiguity arose as to the formal oxidation state of the molybdenum atom. Whilst each $AsSe_5$ ligand can be considered as trianionic, formally indicating a molybdenum(IV) centre, one Se···Se contact is shorter than would be expected from a simple van der Waals interaction. However, this distance of 2.702 Å is also longer than that expected for a single Se-Se bond (approximately 2.35 Å); if the interaction does constitute a 2-centre 2-electron bond, then the molybdenum atom would have a formal oxidation state of +2. Hence the actual formal oxidation state of molybdenum in this complex depends on how the Se···Se interaction is interpreted.

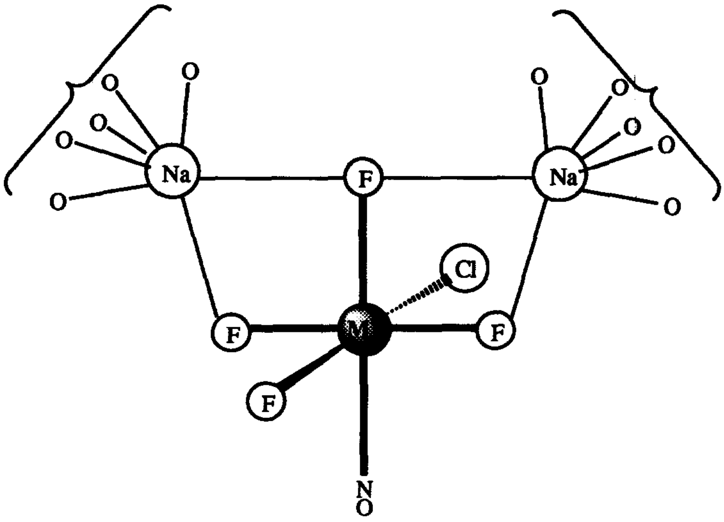


(66)

1.3.7 Complexes with halide and hydride ligands

Chloro and mixed chlorofluoro nitrosyl molybdenum complexes are obtained from the addition of NaF in MeCN to $MoCl_2(NO)_2$ at room temperature, in the presence of 15-crown-5 [106]. Structures of the two products isolated $[Na(15\text{-crown-}5)]_2(MeCN)[MoCl_4(NO)_2]$ and $[Na(15\text{-crown-}5)]_2[MoF_4Cl(NO)]$ are presented. The crystal structure of the latter compound reveals an interaction between the three ions of the molecular formula, each sodium centre being linked to the five oxygen atoms of the crown ether as well as the two fluoride ligands of the anionic molybdenum complex. This generates an unusual geometry about the fluoride atom *trans* to the nitrosyl ligand as shown in structure **(67)**.

Another class of didentate sulfur ligands is based upon the carbodithioate group. The anion $[Cp^*Mo(S_4)(S_2CO)]^-$, which contains a chelating dithiocarbonate ligand, has been isolated and structurally characterised [98]. Obtained from the reaction of a polysulfide solution with $Cp^*Mo(CO)_3(CH_3)$, the metal centre has undergone oxidation with elimination of the carbonyl and alkyl ligands. Two different carbodithioate ligands are present in the complexes $Mo(S_2CNR_2)_n(acda)_{4-n}$ (R = Et, Pr; n = 2, 3; Hacda = 2-aminocyclopent-1-ene-1-carbodithioate) [99]. The differing properties of these complexes are rationalised in terms of the σ–donor and π-acceptor properties of the sulfur ligands. The complex $Mo(O)(S_2CNEt_2)_2(S_2O)$ **(63)** has been structurally characterised [100]. The S_2O ligand is bound to the molybdenum centre in a side on manner through both S atoms, and forms part of the equatorial plane of a distorted pentagonal bipyramidal geometry.



(67)

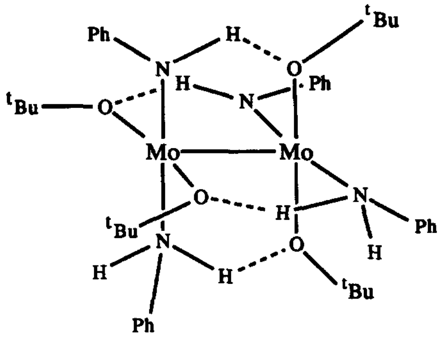
There have been two reports on the formation of Cp/Cp* molybdenum complexes which also contain halide ligands. The unstable compound $CpMoCl_3$ [88], generated either by oxidation of $CpMoCl_2$ with $PhI.Cl_2$, through reduction of $CpMoCl_4$ with $TiCl_3$ or by valence conproportionation of $CpMoCl_2$ and $CpMoCl_4$, has been mentioned previously (see section 1.3.3). Interaction between atomic molybdenum and C_5Me_5H results in the formation of the hydrido complex $Mo(Cp^*)_2H_2$; the reactivity of this product has been explored, and one area of investigation was the conversion to $Mo(Cp^*)_2I_2$ [107].

1.4 MOLYBDENUM(III)

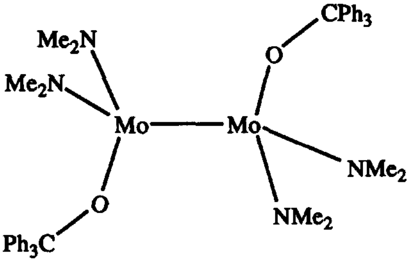
1.4.1 Complexes with nitrogen donor ligands

A range of mononuclear molybdenum(III) complexes containing imidazole ligands has been synthesised and spectroscopically characterised [108]. The effective magnetic moments of the complexes $[MoL_3X_3]$ ($X = Cl^-, Br^-, NCS^-$; L = imidazole, benzimidazole and their respective 2-methyl derivatives) are in accord with an octahedral molybdenum(III) centre. Infrared studies indicate that the imidazole ligands bond to the molybdenum atom *via* the tertiary nitrogen atom, and also that each thiocyanate ligand coordinates through its nitrogen atom.

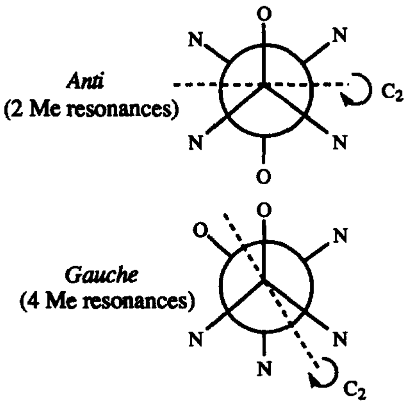
Examples of dimeric molybdenum alkoxide, amide and amine complexes have been reported, together with structural analyses [109,110]. Reaction of $Mo_2(O^tBu)_6$ with aniline results in the formation of $Mo_2(O^tBu)_4(HNPh)_2(H_2NPh)_2$ **(68)** in about 80% yield [109]. The structure shows the presence of hydrogen-bonding between the amide/amine ligands and the oxygen atom of the alkoxy ligand. The molybdenum atoms are in a square planar O_2N_2-environment with a Mo-Mo bond length of 2.2538(7) Å, typical for a Mo≡Mo triple bond. Using the bulkier alkoxy group $OCPh_3$ (and the silicon analogue $OSiPh_3$), amine complexes of the formula $Mo_2(OEPh_3)_2(NMe_2)_4$ (E = C, Si) have been prepared [110]. Structural analysis for E = C indicates an *anti* arrangement of the amine and alkoxy ligands (**69**), though in solution variable temperature ^1H NMR spectroscopy indicates the presence of both *anti* and *gauche* rotamers.



(68)



(69)

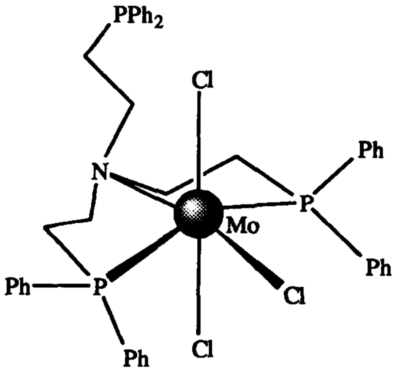

end on view:

The catalytic activity of $Cs_2[Mo_2Cl_5H(NO)_2]$ towards oxygenation of NO with insufficient oxygen has been described [111]. The report also includes a synthetic method to prepare this complex and solution IR data, indicating the presence of bridging nitrosyl, hydride and chloro ligands together with two absorptions at 310(w) and 295(m) due to stetching modes of the terminal chlorine atoms. Finally, a dimeric fluoro complex containing pyridine ligands has been structurally characterised [112]; this is discussed in section 1.4.5.

1.4.2 Complexes with phosphorus donor ligands

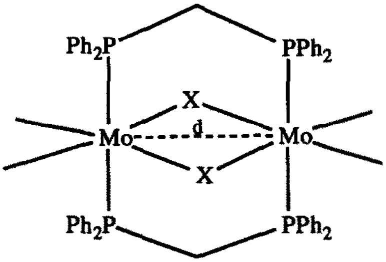
Various attempts have been made to synthesise the seventeen electron mononuclear molybdenum complex $CpMoX_2(dmpe)$ (X = Cl, Br, I) [113]. As a result of this work both the molybdenum(IV) complex $[CpMoCl_3(dmpe)]^-$ and the mixed molybdenum(II)/molybdenum(III) salt $[CpMo(dmpe)_2]^+[MoBr_4(dppe)]^-$ have been structurally characterised; the desired complex was formed, but it proved unstable with decomposition products as above.

The complex $MoX_3(thf)_3$ (X = Cl, Br, I) has been utilised as a convenient starting material for reaction with a variety of phosphines; the labile thf ligands readily undergo substitution [114-118]. Amongst the studies undertaken, mononuclear phosphines of the type PPh_xR_{3-x} (R = Me, Et; x = 0-3) and PR'_3 (R' = ^{n}Pr, ^{n}Bu) have been considered. Complexes of general formulae $Mo_2X_6L_4$ and $Mo_2X_6L_3$ (X = halide; L = phosphine) have been characterised, the former consisting of an edge-sharing bioctahedral geometry, and the latter a face-sharing geometry. Various mechanisms are proposed for the formation of the different products, with consideration given to the differing bulk of the phosphine ligands used [116]. Structures are reported for $Mo_2Cl_6(PMe_2Ph)_4$ [115], $Mo_2X_6(PMe_2Ph)_3$ (X = Br [114], Cl [115]) and $Mo_2Cl_6(PEt_3)_3$ [115]. Not surprisingly, $Mo_2X_6(dppe)_2$ also transpires to have an edge-shared bioctahedral configuration [117]. The mononuclear species $MoX_3(dppe)(thf)$ has been isolated, and this dimerises in non-coordinating solvents following the loss of the thf ligand. A more unexpected result is obtained when the thf ligands are displaced by the tripodal ligand $N(CH_2CH_2PPh_2)_3$ (for X = Cl) [118]. Structural analysis shows that whilst the amine is indeed acting as a tridentate ligand, coordination is through the amine nitrogen atom and the two phosphorus atoms. The third PPh_2 group is pendant as illustrated in structure (**70**). The coordination adopted (*N* and 2*P* as opposed to 3*P*) is discussed, along with the fact that a *mer*-arrangement of chloride ligands is observed.



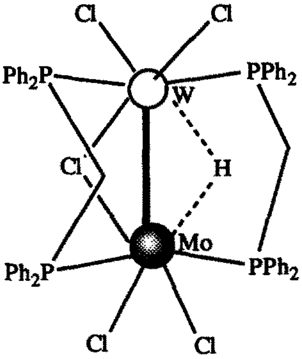
(70)

An alternative synthetic route is used to obtain the dppm analogues of $MoX_6(dppe)_2$. Oxidative addition of halogens Y_2 (Y = Cl, Br, I) to the quadruply-bonded $Mo_2X_4(dppm)_2$ gives the edge-sharing, bioctahedral molecules $Mo_4X_4Y_2(dppm)_2$ in high yield [119]. All combinations of X and Y (X and Y = Cl, Br, I) are now known and the complexes have been investigated both electrochemically and by IR and UV spectroscopies. Structures of $Mo_2Cl_4I_2(dppm)_2$, $Mo_2Br_6(dppm)_2$ and $Mo_2I_6(dppm)_2$ (71), with bridging chlorine, bromine and iodine atoms respectively, have been compared. The increasing Mo-Mo distances of 2.827(1), 2.879(2) and 3.061(1) Å in the series are primarily due to increasing size of the bridging atom. A related heterodimetallic complex $MoW(Cl_4)(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-}dppm)_2$ (72) has been characterised as the first multiply-bonded heteronuclear edge-sharing bioctahedral complex [120]. Whilst the bridging hydride was not located by the X-ray diffraction, its presence was supported by IR and NMR spectroscopic data.



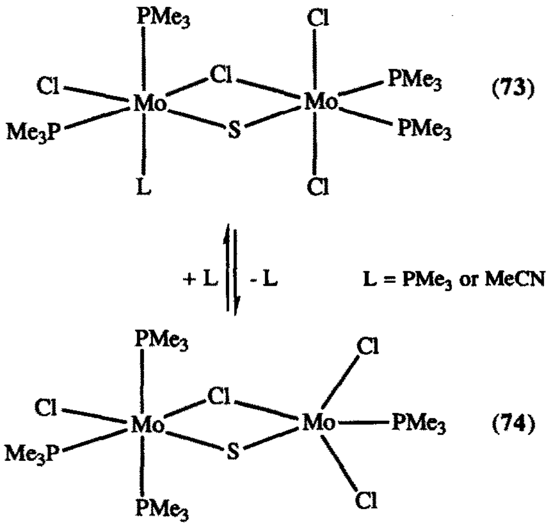
X = Cl d = 2.827(1) Å
Br 2.879(2) Å
I 3.061(1) Å

(71)



Mo-W = 2.4932(6) Å

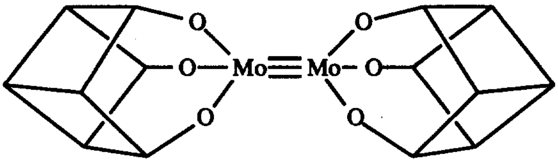
(72)



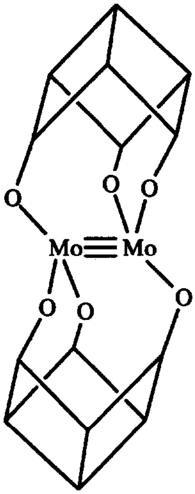
(73)

(74)

Labile or coordinatively unsaturated molybdenum(III) dimers are the final topic of this section. The compound $SPMe_3$ proves to be a useful reagent with $Mo(PMe_3)_4Cl_2$ [121]; sulfur abstraction results in the formation of a dimeric molybdenum(III) complex of the formula $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (**73**). Trimethylphosphine is readily lost from this complex to form a unique dimer with one molybdenum atom 5-coordinated and the other 6-coordinated as shown in structure (**74**). This loss of PMe_3 is reversible, as is the reaction of the unsaturated complex with MeCN which yields the related compound $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_4(MeCN)$. The structures of all three products have been solved crystallographically. One notable feature about this work is the use of $SPMe_3$ as a source of sulfur, with P-S bond cleavage and sulfur atom transfer to the molybdenum centre. Typically, as encountered earlier [93], phosphines are used to *abstract* sulfur from metal complexes, due to the favourable strength of the P-S bond (*ca.* 385 kJ mol^{-1}).



(**75**)



(**76**)

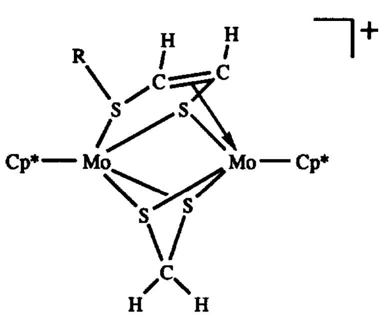
1.4.3 Complexes with oxygen donor ligands

Furthering the understanding of dimeric molybdenum alkoxides of general formula $Mo_2(OR)_6$, the bonding present in these complexes has been investigated using Fenske-Hall type molecular orbital calculations on the model hydroxy compound $Mo_2(OH)_6$ [122]. The short Mo-O bonds are found to be due to significant O(pπ)-Mo(dπ) bonding, with a lesser ionic contribution. The thermal decomposition of $Mo_2(OR)_6$ ($R = CMe_3$, $c\text{-}C_6H_{11}$) under helium has also been studied. These complexes have proved to be single source precursors for molybdenum carbides and oxides [123]. Returning to the actual synthesis of this type of complex, more novel examples with didentate and tridentate oxygen donor ligands have been prepared [124, 125]. Using the bulky diols 2,5-dimethylhexane-2,5-diol (H_2L^1) and 2,2'-methylene-bis(6-^{t}butyl-*p*-cresol) (H_3L^2), reaction with

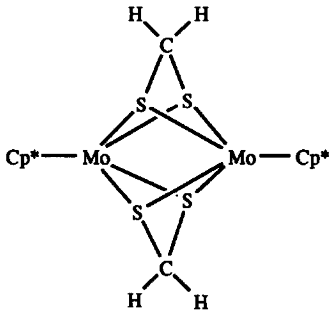
$Mo_2(NMe_2)_6$ yields $Mo_2(L^1)_3(HNMe_2)_2$, $Mo(L^1)_3$ and $Mo_2(NMe_2)_2(HL^2)$ [124]. In the two former complexes the diolate ligands span the Mo-Mo triple bond giving rise to eight membered rings; the latter complex, crystallographically characterised, contains seven membered rings. Reaction of $Mo_2(O^tBu)_6$ with the tripodal, cage-like ligand trisilanol $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ was hoped to create the complex $Mo_2\{(c\text{-}C_6H_{11})_7Si_7O_9(O)_3\}_2$, each 3-siloxy ligand chelating each molybdenum centre. This is shown schematically in structure (75) [125]. Whilst a complex of this formula was obtained, a far less symmetrical arrangement of the siloxy ligands was observed from the solid state structure determination as represented in (76).

1.4.4 *Complexes with sulfur donor ligands*

Transformations of the $Mo_2(\mu\text{-}S)_4$ core of the two molybdenum(IV) dimeric complexes $[Cp_2Mo_2(\mu\text{-}SR)(\mu\text{-}S_2CH_2)]^+$ and $Cp^*{}_2Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2CH_2)$ results in two new molybdenum(III) dimeric clusters [126, 127]. For the former complex, addition of various alkenes $H_2C{=}CHR'$ converts the (μ-S)(μ-SR) ligands into the chelating thiolate-thioether ligand RSC(H)=C(R')S. The product with R = ^{t}Bu, R' = H has been isolated and crystallised, and the structure indicates that the double bond of this new ligand interacts with one of the molybdenum atoms as indicated in structure (77). The bis(sulfido) complex has been reacted with chloroform in the presence of 1 to 2 atmospheres of H_2 at 50°C. Again, a chelating ligand is formed, this time from the two monodentate (μ-S) ligands; the resulting product is $Cp^*{}_2Mo_2(\mu\text{-}S_2CH_2)_2$ (78).



(77)



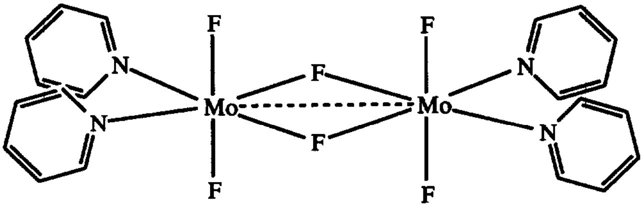
(78)

Examples of molybdenum(III) complexes with pyridine-2-thiol ligands, binding exclusively through the thiol sulfur atom, have already been mentioned in section 1.3.5.

1.4.5 *Complexes with halide ligands*

The bulk of the examples of molybdenum(III) complexes containing halides as ligands also contain phosphine ligands; these have been mentioned already in section 1.4.2 [113-121].

The hexafluoro complex $Mo_2F_4(\mu\text{-}F)_2(py)_4$ **(79)** provides the first example of an edge-sharing, bioctahedral complex containing bridging fluoride ligands [112]. Another unexpected feature revealed during structural analysis is that the four pyridine ligands are all in equatorial sites. This contrasts with the tungsten and tantalum chloro analogues, where two pyridine ligands on one metal centre are equatorial, and the two bonded to the other metal centre are in axial sites.



Mo-N	2.272(4)-2.94(3) Å
Mo-μF	1.913 Å (av)
Mo-F(axial)	1.841 Å (av)
Mo-Mo	2.533(1) Å

(79)

1.5 MOLYBDENUM(II)

1.5.1 Complexes with boron donor ligands

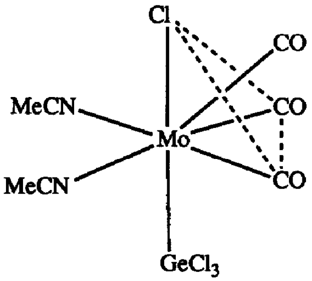
The nonaborane anions $[NMe_4][B_9H_{14}]$ and $[NMe_4][B_9H_{12}]$ have been reacted with the seven coordinate molybdenum(II) complexes $MoI_2(CO)_3L_2$ (L = PPh_3, PPh_2Me, $PPhMe_2$) [128]. The known metallaborane 6,6,6,6-$(CO)_2(PPh_3)_2$-6-MoB_9H_{13} was isolated in a low yield (12%), though this was an improvement over previous results using the cation $[N^nBu_4]^+$ (4% yield).

1.5.2 Complexes with group 14 donor ligands

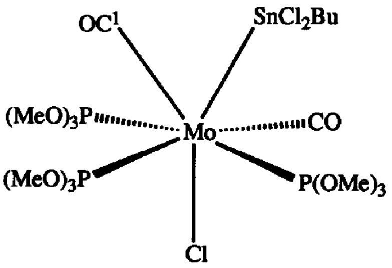
Although this review is not concerned with organometallic compounds, it is the benzyl ligand that is the interesting feature of the 'piano stool' complexes $Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$ and $Cp^*Mo(NO)(CH_2Ph)Cl$ [129]. Both solution and solid state data indicate that it adopts an η^2-bonding mode, acting as a three electron donor ligand.

The synthesis of $MoCl(GeCl_3)(CO)_3(NCMe)_2$ **(80)** and its reactions with EPh_3 (E = P, As, Sb) give rise to several new seven coordinate molybdenum complexes [130]. The proposed structure for **(80)** is a face-capped octahedron, and depending on the solvent used (CH_2Cl_2/MeCN) either $MoCl(GeCl_3)(CO)_3(NCMe)(EPh_3)$ or $MoCl(GeCl_3)(CO)_2(NCMe)_2(EPh_3)$ can be prepared. The reaction of this latter compound with but-2-yne, for E = P, results in formation of the novel complex $MoCl(GeCl_3)(CO)(NCMe)(PPh_3)(\eta^2\text{-}MeC_2Me)$ in a good yield [131]. The molybdenum centre is surrounded by six different ligands. Applying the same synthetic strategy, the related tin complex $Mo(CO)_3(NCMe)_2(SnCl_2Bu)Cl$ has been prepared [132]. Again, the displacement of CO and

NCMe ligands is examined, but in this report phosphite ligands $P(OR)_3$ (R = Me, Et) are used. The structure of $Mo(CO)_2\{P(OMe)_3\}_3(SnCl_2Bu)Cl$ (**81**) is best described as a cross between a distorted face-capping octahedral geometry, with Sn or C(1) in the capping position, and a distorted trigonal prismatic geometry, with the Cl ligand capping a square face.



(80)



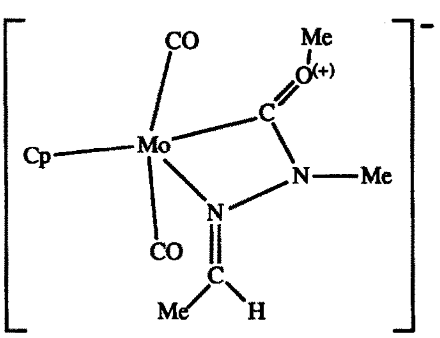
(81)

1.5.3 Complexes with nitrogen donor ligands

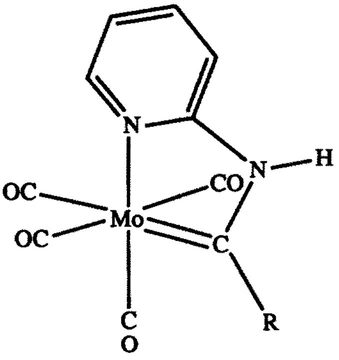
'Piano stool' molybdenum(II) complexes show interesting and unexpected coordination chemistry. Interconversions of terminal isocyanate ligands CNEt and CN^{t}Bu have been examined under the effect of thermolysis and of chemical reagents [133-135]. Alkyl migration from the metal centre of complexes of general formula $Cp^*Mo(CO)_2R(CNR')$ gives complexes containing RC=NR' ligands, which adopt an η^2 bonding mode [133,134]. Further reaction of this iminoacyl product, $Cp^*Mo(CO)_2(\eta^2\text{-}RC{=}NR')$, with more isocyanide results in insertion products containing a four membered MoC_2N ring [135]. A $MoCN_2$-ring is present in the anionic 'piano stool' complex $CpMo(CO)_2[C(OMe)NMeNCHMe]$ (**82**) [136]. This product is one of several nitrogen-containing complexes obtained from the reactions of $CpMe(CO)_3(\eta^1\text{-}CH_2COR)$. The reaction of aminopyridine with the molybdenum carbene complex $Mo(CO)_5[{=}CR(OEt)]$ (R = Me, Ph) results in the loss of ethanol and carbon monoxide, and formation of a chelating pyridine-carbene complex (**83**) [137]. Further reaction of this product with diphenyl acetylene provides a synthesis for some previously unknown pyrrolinones.

Deprotonation of the complex *trans*-$[Mo(NMe)Cl(dppe)_2]^+$ results in the imide ligand being converted to a reactive methylenamide ligand $(N{=}CH_2)^-$, which loses dihydrogen on oxidation to form the cyanide ligand in *trans*-$[Mo(CN)Cl(dppe)_2]$ [138]. ^{13}C NMR spectroscopic labelling studies indicate that an intramolecular Mo-NC to Mo-CN framework rearrangement occurs. The methylenamide ligand is also replaced readily by NCX (X = O, S, Se), the structure of the sulfur analogue showing that the NCX ligand coordinates via the nitrogen atom, as an isocyanate.

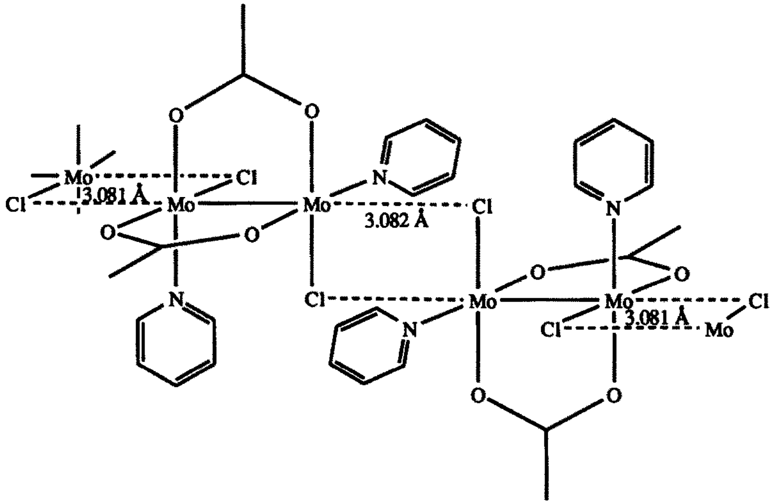
The reaction of $Mo_2(O_2CMe)_2Cl_2(dppe)$ with pyridine gives rise to the dimeric and mononuclear pyridine complexes $Mo_2Cl_2(O_2CMe)_2Py_2$ and $MoOCl_2(dppe)Py$. Both of these have been structurally characterised [139]. Molecules of the dimeric product (**84**) are linked via Cl···Mo bridges to form infinite chains.



(82)



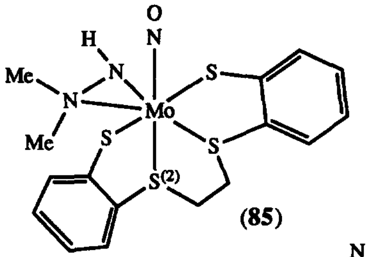
(83)



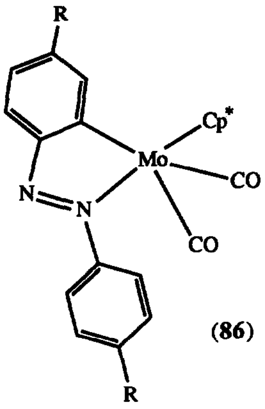
(84)

The tetracationic complex $[Mo_2(MeCN)_{10}]^{4+}$ has been synthesised as a potential starting material for other dimolybdenum complexes, since the Mo_2^{4+} core is surrounded by neutral, weakly coordinating ligands (Mo-N 2.129(6), 2.600(13) Å) [140]. This bright blue compound is unstable in air, readily turning brown, and is also hygroscopic; preliminary investigations show that it undergoes substitution with other ligands.

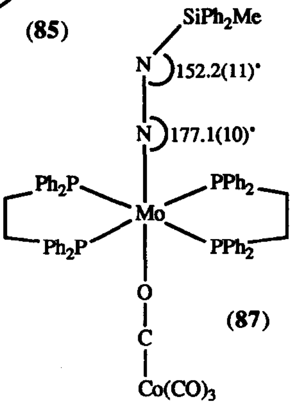
As seen with the higher oxidation states of molybdenum, there is great interest in hydrazido and related ligands coordinating to molybdenum centres. The hydrazines $NHNR_2$ (R = H, Me) bind in a 'side-on' fashion to the molybdenum(II) centre in the complexes $Mo(NHNR_2)(NO)('S_4')$ (**85**) [141]. Structural analysis of the dimethyl derivative shows the molybdenum atom to be in a distorted pentagonal bipyramidal environment, with one sulfur atom, S(2), and the nitrosyl ligand in the axial sites. The ^{95}Mo NMR chemical shift is compatible with the assignment of a formal oxidation state of +2 for the metal centre. Two other complexes with N_2 based ligands have been prepared using quite different routes. Photolysis or thermolysis of $Cp^*Mo(CO)_3Me$ in the presence of aromatic diazenes $RC_6H_4N{=}NC_6H_4R$ (R = H, *p*-Me) results in formation of the chelated complex $Cp^*Mo(R\text{-}C_6H_3N{=}NC_6H_4R)(CO)_2$ **(86)**, where one aromatic ring has undergone cyclometallation [142]. The silylhydrazenido complex *trans*-$[Mo(NNSiR_2R')(dppe)_2][(\mu\text{-}CO)Co(CO)_3]$ (R, R' = Ph, Me) **(87)** is prepared from the dinitrogen complex $Mo(N_2)_2(dppe)_2$ and $R_2R'SiCo(CO)_4$ [143]. One nitrogen atom undergoes silylation. Structural parameters for the diphenyl methyl product show delocalised bonding within the hydrazenido ligand with the N-N, N-Si bond lengths being 1.21(1) and 1.73(1) Å, respectively.



(85)



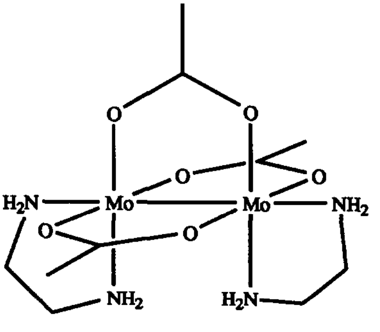
(86)



(87)

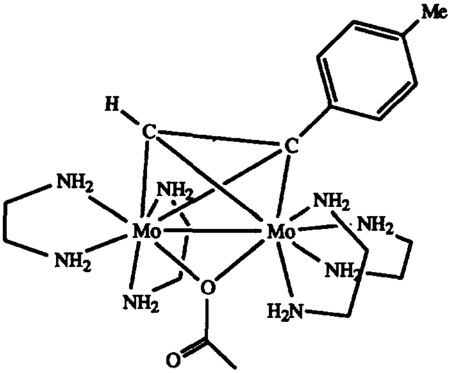
Examples of didentate amidinato ligands with a one carbon linker have been reported for both a mononuclear complex (creating a four membered MoNCN-ring) [144] and a dinuclear complex (with a five membered Mo_2NCN-ring) [145]. Both $CpMo(CO)_2[(NPh)_2CMe]$ and $Mo_2(O_2CPh)_2[(NSiMe_3)_2CPh]$ have been crystallographically characterised. The $(NR)_2CR'$ ligands bond symmetrically with average Mo-N bond lengths of 2.18 and 2.117 Å for the mononuclear and dinuclear complexes, respectively.

A range of didentate amine complexes has been synthesised from $Mo_2(O_2CMe)_4$ [146]. The solid state structures of the products, derived from amine addition or from substitution of one $[O_2CMe]^-$ ligand, are presented. The dimolybdenum complexes $Mo_2(O_2CMe)_4L$, with L = $Me(H)NCH_2CH_2N(H)Me$, $H_2NCH_2CH_2CH_2NH_2$, form infinite 1-D chain structures, the Mo_2-units being linked by the didentate amino ligands; $[Mo_2(O_2CMe)_3L'_2]^+[O_2CMe]^-$ (L' = $H_2NCH_2CH_2NMe_2$, $H_2NCH_2CH_2N(H)Me$) are present as discrete molecules in the solid state, with hydrogen-bonding between the equatorial diamine hydrogen atoms and oxygen atoms of the displaced acetate group as shown in **(88)**. In related work [147], $Mo(O_2CMe)_4$ is reacted with the parent ethylenediamine in the presence of alkynes $4\text{-}RC_6H_4CCH$ (R = H, Me, ^iPr), giving rise to the first example of alkyne addition to a Mo-Mo quadruple bond. The structure of the methyl product $[Mo_2(\mu\text{-}4\text{-}MeC_6H_4CCH)(\mu\text{-}O_2CMe)(en)_4][O_2CMe]_3.2(en)$ (**89**) is presented, as is a discussion about the isomerism in these systems. Work on the complex $Mo_2(O_2CCF_3)_4$ has shown that the trifluoromethylacetate ligands are displaced by the didentate ligand bipyridine [148]. Two isomers of the formula $Mo_2(O_2CCF_3)_4(bpy)_2$ are produced. As in (**88**) and (**89**), the acetate ligands adopt either monodentate or didentate bonding modes, forming the neutral complex $Mo_2(\eta^1\text{-}O_2CCF_3)_4(bpy)_2$ and the ion pair complex $[Mo_2(\mu\text{-}O_2CCF_3)_2(bpy)_2](O_2CCF_3)_2$. The bpy ligands chelate to a single molybdenum centre in each case. Another example of a bpy complex with a monodentate RCO_2^- ligand is obtained on exchanging Cl^- for $C_3F_7CO_2^-$ in the complex $[MoCl(CO)_2(\eta^3\text{-}CH_2C(CONRR')C{=}CH_2)L]^-$ (L = bpy, phen) [149], though the main theme of this article is the bonding and reactivity of the butadienyl ligand



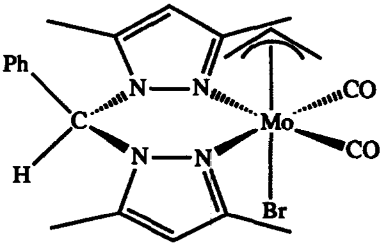
e.g. L = $H_2NCH_2CH_2NH_2$

(88)



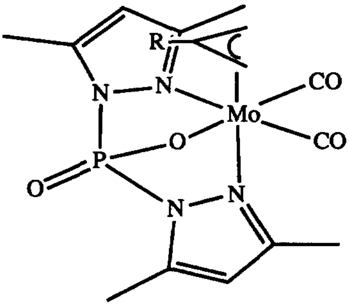
(89)

A range of didentate pyrazol-1-yl complexes have been prepared using the ligands RHCPz' (R = H, Ph; pz' = pyrazol-1-yl, 3,5-dimethylpyrazol-1-yl) [150]. The $Mo(RHCpz')(CO)_2(\pi\text{-allyl})Br$ complexes could be prepared either by allyl bromination of $Mo(RHCpz')(CO)_4$ or by the reaction of $Mo(MeCN)_2(CO)_2(\pi\text{-allyl})Br$ with HRCpz'. The structure of the dimethylpyrazol-1-yl derivative (R = Ph) is reported (**90**). The related $R^1C(H)C(R^2)CH_2$ (R^1, R^2 = H, Me, Ph) allyl bromo and chloro H_2Cpz' complexes have been prepared under mild conditions [151], and some of these *cis*-complexes are fluxional.

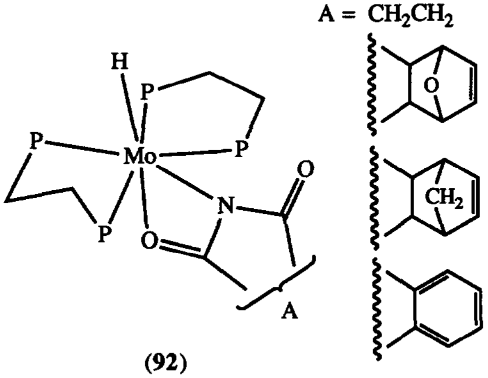


(90)

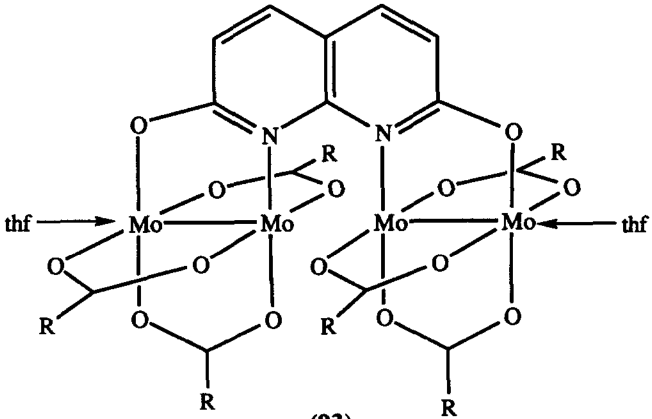
The ligand Tp has already been encountered as a tridentate nitrogen donor ligand for molybdenum(IV) and molybdenum(V) complexes (see 1.3.2.1, 1.2.3.2). A mixture of aminocarbyne, η^2-iminoacyl and η^2-acyl Tp molybdenum complexes are prepared by the addition of MeI to $Na[TpMo(CO)_2(^tBuNC)]$ [152]. The reactivity of these products and that of the starting material is explored further. A synthesis of the carbyne complex $Tp(CO)_2MoCH$ is also reported, together with a dimerisation reaction which produces $\{Tp(CO)_2Mo\}_2(\mu\text{-}CCH_2)$ [153]. The phosphine pyrazolyl tris-(3,5-dimethyl-1-pyrazolyl) phosphine oxide was reacted with $Mo(MeCN)_2(CO)_2(X)(\eta^3\text{-}CH_2CHRCH_2)$ (X = Cl, Br; R = H, Me, Ph), in the expectation that the former would act as a didentate nitrogen donor ligand [154]. This was not observed; instead, partial hydrolysis of the phosphine oxide gave the unexpected product $Mo(CO)_2(\eta^3\text{-}CH_2CHRCH_2)(PO_2(C_3N_2Me_2H)_2)$ (**91**), containing an *N,N′,O*-chelating ligand.



(91)



(92)



(93)

Other molybdenum(II) complexes containing multidentate *N,O*-donor ligands, obtained by design, include a series of seven coordinate complexes of cyclic amides [155]. NMR spectroscopic data show that the complexes have fluxional pentagonal bipyramidal structures in solution (**92**). *N,N′,O,O′*-donor sets have been used to link Mo_2-units together [156,157], using, for example, 1,8-

naphthyridinyl-2,7-dioxide. Depending upon reaction conditions, either a discrete molecule containing two Mo_2-units linked together or an extended polymer of ≈20 formula units can be obtained. The crystal structure of the former product (93) has been solved, and can be considered as a model for the tetranuclear subunit of the polymer.

Finally, the dinuclear molybdenum(II) complex of the tetradentate ligand dibenzotetraaza[14]annulene has been reacted with tetracyanoethylene [158]. The consequent interconversions of the oxidised mononuclear and quadruply bonded dinuclear products are examined chemically and electrochemically.

1.5.4 Complexes with phosphorus donor ligands

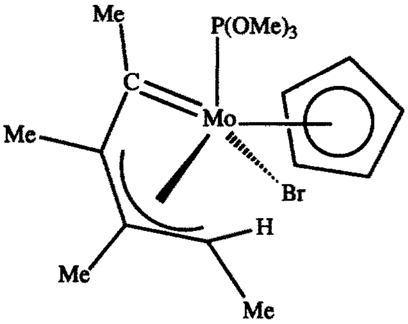
1.5.4.1 Monodentate ligands

A new route to derivatives of molybdenocene using mild conditions has been reported; the report includes a structural analysis of the derivative $Cp_2Mo(P^nBu_3)$ [159]. Reactions of such phosphine complexes with alkyl halides, halogens and diethyldisulfide have also been investigated. The structure of a triethylphosphine complex has been solved as part of a kinetic and spectroscopic study of transients produced by the flash photolysis of $Mo(CO)_3(PR_3)X_2$ (X = Br, Cl; R = aryl, alkyl or a mix of these) [160]. The unsaturated complex $Mo(CO)_2(PEt_3)_2Br_2$, characterised crystallographically, is one of the class of transients produced in the photolysis process.

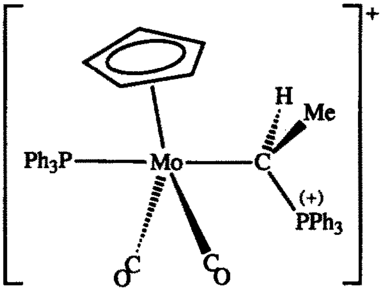
Earlier, it was seen how $MoI_2(CO)_3L_2$ (L = PPh_3, PPh_2Me, $PPhMe_2$) could be used as a reactant [128] (see section 1.5.1); the syntheses of the triphenylphosphine derivative and related complexes containing a range of didentate oxygen donor ligands have also been reported [161]. Variable temperature NMR spectroscopic studies have been carried out on the dimethylphenylphosphine derivative $MoI_2(CO)_3(PMe_2Ph)_2$ [162].

Although mainly organometallic in nature, the reactions of $P(OMe)_3$ with $[CpMo(=C(Me)CHMe)(\eta^2\text{-}MeC_2Me)Br][BF_4]$ [163] and PPh_3/Me_3O^+ with $[CpMo(MeCHO)(CO)_2]^-$ [164] produce interesting conversions of the organic ligands as well as forming phosphine/phosphite derivatives. In the first example, C-C coupling gives rise to the butadienyl complex $[CpMo(=C(Me)\text{-}\eta^3\text{-}\{C(Me)C(Me)CH(Me)\}\{P(OMe)_3\}Br]^+$ (94) while the second reaction yields, amongst other products, *trans*-$[Mo\{CHMe(PPh_3)\}(CO)_2(PPh_3)(Cp)]^+$ (95). Reacting a range of phosphines and phosphites with the bis(hexafluorobut-2-yne) complexes $[Mo(SR)(CF_3CCCF_3)_2Cp]$ (R = C_6F_5, ^iPr) results in several conformational changes of the alkyne ligands, including cyclisation to a cyclobutadiene based ligand [165].

Application of the NMR active molybdenum nuclei provides a convenient method to assist the characterisation of complexes. Solid state ^{31}P NMR spectroscopic studies of cyclic and acyclic phosphine complexes of the type $MoPPh_2(CH_2)_n$ (n = 3, 4) and $MoPPh_2R$ (R = Et, Pr, Bu, pentyl) have aimed at correlating the chemical shift and $^{95/97}Mo\text{-}^{31}P$ coupling constants with structural features of the compounds [166], whilst ^{95}Mo NMR spectroscopy has been used directly in the investigation of $[CpMo(CO)_2L_2]^+$ complexes. Here, L includes a range of phosphine and phosphite ligands, as well as other group 15 donor atoms (As, Sb, Bi) [167]. Decomposition of these complexes in polar solvents gives low yields of $[CpMo(CO)_3L]^+$, the 'piano stool' structure of which has been determined for L = PPh_3.

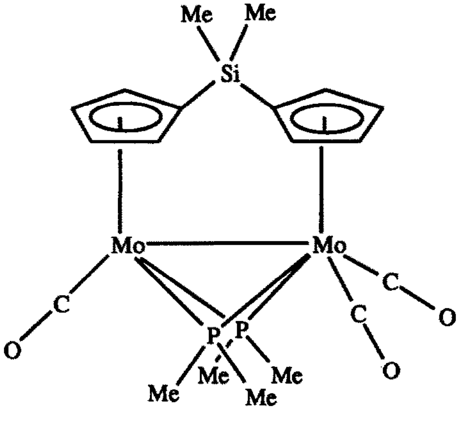


(94)



(95)

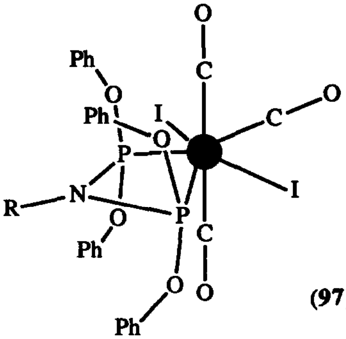
Suitable for duet piano playing is the linked complex $Me_2Si\{(\eta^5\text{-}C_5H_4)Mo\}_2(CO)_3(\mu\text{-}PMe_2)_2$ (96) which has been prepared along with the arsenic analogue [168]. An X-ray structural analysis has been carried out for the phosphine derivative. Two other dimetallic molybdenum complexes with phosphorus donor ligands are $Mo_2Cl_4(PMePh_2)_4$ and $Mo_2(OC_6F_5)_4(PMe_3)_4$ [169, 170]. Both complexes are square prismatic in structure, and in each case the isomerism of this type of system is discussed.



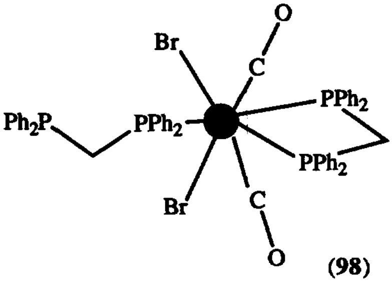
(96)

1.5.4.2 *Multidentate ligands*

Extending work seen already [161, 162], $MoI_2(CO)_3(NCMe)_2$ has been reacted with one equivalent of a monodentate ligand L (L = PPh_3, $AsPh_3$, $SbPh_3$) followed by half an equivalent of a didentate phosphine L'-L' (L'-L' = dppm, dppe, dppb, dppf) [171]. In this way, high yields of the seven coordinate dimetallic phosphine bridged complexes $Mo_2I_4(CO)_6L_2(\mu\text{-}L'\text{-}L')$ can be synthesised. Infrared and ^{1}H NMR spectroscopic data and elemental analyses are presented for the range of complexes obtained. Using the same molybenum starting material, direct reaction with diphosphazane ligands $RN(P(OPh)_2)_2$ (R = Me, Ph) gives the distorted pentagonal bipyramidal complexes $MoI_2(CO)_3\{(P(OPh)_2)_2NR\}$ [172], with the phosphazane ligand binding to two of the equatorial sites as shown in structure (97).

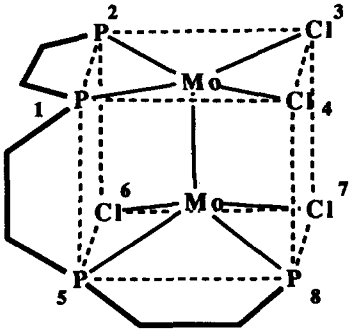


(97)



(98)

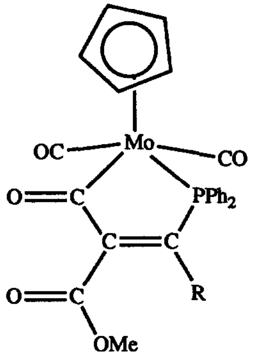
The ligands dppe and dppm have been used to displace the bis(3,5-dimethylpyrazol-1-yl)-methane ligand (H_2Cpz_2) from the complexes $Mo(H_2Cpz_2)(CO)_2Br_2$ and $Mo(H_2Cpz_2)(CO)_2(\eta^3$-allyl)Br [173]. The structure of the product $Mo(dppm)_2(CO)_2Br_2$ (98) shows the two different bonding modes for dppm within one molecule. The complex $CpMo(dppe)(CO)(C_2H_4)$ has been prepared from the dicarbonyl complex $CpMo(dppe)(CO)_2$, and the analogous work has been repeated for the dimethoxyphosphinoethane derivative. Subsequent reactions of the alkene products with carbanion nucleophiles have been carried out [174].



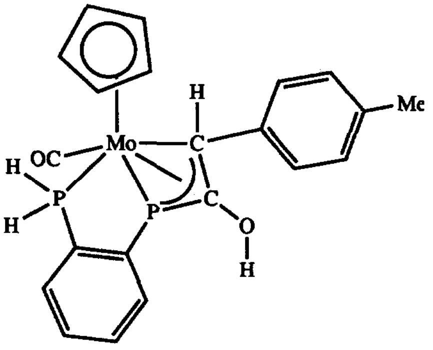
(99)

Following on from a look at the isomerism in square prismatic complexes MoX_4L_4 in which X = halide and L = neutral monodentate ligand [170], a related complex $MoCl_4\{Ph_2P(CH_2)_2P(Ph)(CH_2)_2P(Ph)(CH_2)_2PPh_2\}$ has been synthesised to see how restraining the 'L_4' donor set affects the ligand distributions [175]. Of thirteen possible isomers, for all monodentate ligands the most common geometry is that of the 1,3,6,8 ismer and this is attributed to on steric factors. For didentate L_2 ligands, the 1,2,7,8- and 1,3,5,7-geometries are most frequently observed. Using this tetradentate ligand, another geometric isomer is seen for the first time, *viz.* 1,2,5,8 as illustrated in structure (**99**).

Two examples of multidentate organophosphorus ligands have been synthesised. The molybdenum phosphido complex $CpMo(CO)_3PPh_2$ reacts with electron deficient alkynes $RCC(CO_2Me)$ (R = H, CO_2Me) to give cyclic complexes of the general formula $CpMo(CO)_2(Ph_2PCR{=}C(CO_2Me)CO)$ (**100**) [176]. The chelating ring is formed by linking of the phosphido group, the alkyne and one CO ligand. A carbonyl ligand is also transformed into part of the chelating ligand in the synthesis of $CpMo\{\sigma,\eta^3\text{-}C_6H_4(PH_2)(PC(OH)CH(C_6H_4Me\text{-}4))\text{-}1,2\}(CO)$ (**101**) from the carbyne complex $CpMoC(C_6H_4Me\text{-}4)(CO)_2$ and the didentate phosphine $C_6H_4(PH_2)_2\text{-}1,2$ [177]. The central phosphorus atom of the chelating core can be considered to be part of a phospha-allyl moiety.



(100) R = H, CO_2Me



(101)

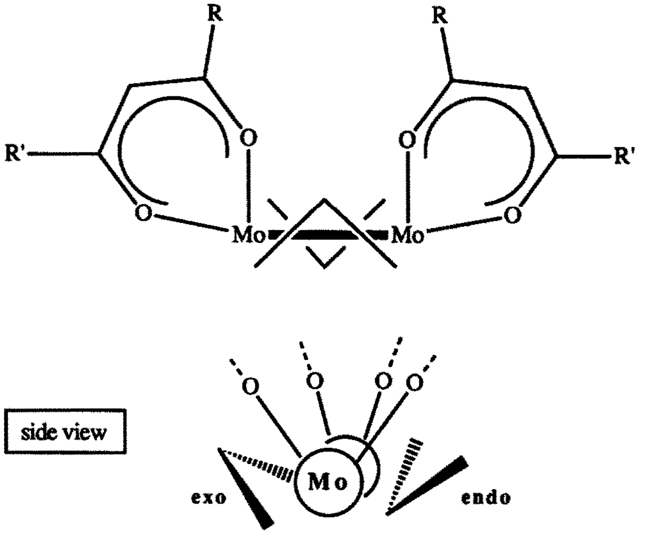
1.5.5 *Complexes with bismuth donor ligands*

Exchange reactions of $Mo_2Cp_2(CO)_6$ have been discussed, including reactions with Bi_2Ph_4 [178]. $MoCp(BiPh_2)(CO)_3$ can be formed on stirring the reactants together for three days, though no reaction takes place in the absence of daylight. In contrast, the same product can be prepared in the dark if $[MoCp(CO)_3]^-$ and $BiPh_2Cl$ are used as reactants.

1.5.6 *Complexes with oxygen donor ligands*

Various complexes with RCO_2^- ligands have been synthesised and investigated [179-181]. Lability studies have involved looking at scrambling reactions between $Mo_2(O_2CR)_4$ and $Mo_2(O_2CR')_4$ (R = ${}^tBu$; R' = $CH_2{}^tBu$, p-${}^tBuC_6H_4$) and related MeCN solvated systems [179]. Unsaturated aliphatic carboxylate bridging ligands are targetted for a study of molybdenum complexes as potential polymerisation catalysts. Complexes of the form $Mo_2(\mu\text{-}O_2CR)_4$ (R = $HC{=}CH_2$, $MeC{=}CH_2$, $H_2C\text{-}C(H){=}CH_2$) as well as the cationic species $[Mo_2(\mu\text{-}O_2CR)_2(MeCN)_4]^{2+}$ have been prepared [180, 181].

The β-diketones of general formula R(C=O)CH_2(C=O)R' (R, R' = Me, CF_3) selectively protonate terminally bonded η^3-allyl ligands of $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$ to produce complexes of formula $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^2\text{-R(C=O)CH(C=O)R')}$ (**102**) [182]. Multinuclear NMR spectroscopy has been used to elucidate the structures of the three products obtained, and a geometry with one exo bridging allyl and one endo bridging allyl is proposed.



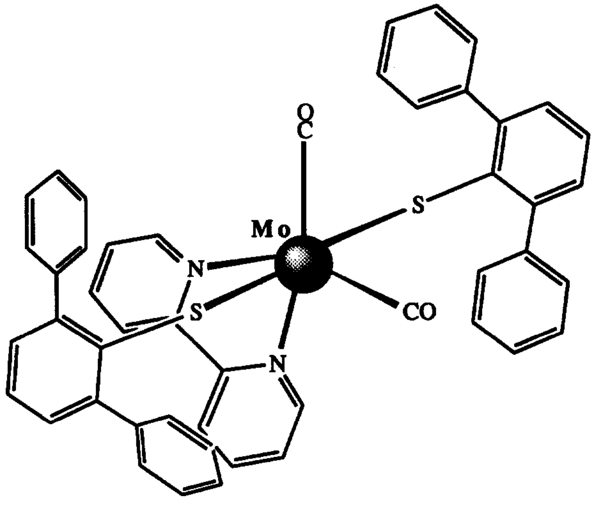
(102)

1.5.7 Complexes with sulfur donor ligands

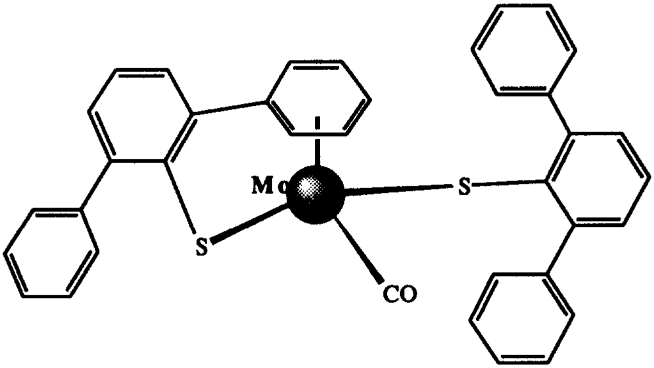
A range of thiolate complexes MoSR(Cp)(CO)(PhCCPh) (R = Me, Et, ^{n}Pr, ^{i}Pr, ^{t}Bu) has been prepared by the addition of TlSR to the chloro complex MoCl(Cp)(CO)(PhCCPh) [183]. Restricted rotation of the SR ligand, owing to S(pπ)-Mo(dπ) bonding, results in two isomeric forms of the product. Diphenylthiophenol (dptH) complexes of molybdenum show that as well as acting as a monodentate thiolate ligand, as in $Mo(dpt)_2(CO)_2(bpy)$ (**103**), dpt^- can adopt a novel 'didentate' bonding mode with one phenyl ring bound in η^6 fashion to the metal centre [184]. This is observed for $Mo(dpt)_2(CO)$ (**104**), the geometry of which can be described as a distorted 'three-legged piano stool'.

Three different synthetic routes can be used to prepare the sixteen electron complexes $Mo\{\eta^2\text{-}(S,S')\}(CO)_2(\eta^3\text{-allyl})$ [(*S,S'*) = *N,N*-diethyldithiocarbamato, pyrrolidine-1-carbodithioate] [185]. Addition of didentate phosphines results in the displacement of one CO ligand and the formation of eighteen electron complexes $Mo\{\eta^2\text{-}(S,S')\}(CO)(\eta^3\text{-allyl})\{\eta^2\text{-}(P,P')\}$ where (*P,P'*) = dppm or dppe. The versatile complex $MoI_2(CO)_3(NCMe)_2$ (see sections 1.5.4.1 and 1.5.4.2 above) has been employed yet again; this time as a basis from which to synthesise the species $\{Mo(\mu\text{-}I)(CO)_3[S_2CN(CH_2Ph)_2]\}_2$ and $MoI(CO)_3L(S_2CNR_2)$ (L = PPh_3, $AsPh_3$, $SbPh_3$; R = Me, Et, CH_2Ph) [186]. Some related complexes containing the didentate sulfur ligand $S_2C(Pcy_3)$

have also been characterised, *viz.* $[MoI(CO)_3L(S_2C(Pcy_3))]^+I^-$ (L as before plus $P(OPh)_3$) [187], as well as $[Mo(CO)_3(S_2C(Pcy_3))]^{2+}2[I]^-$ and $MoI_2(CO)_3(S_2C(Pcy_3))$.



(103)

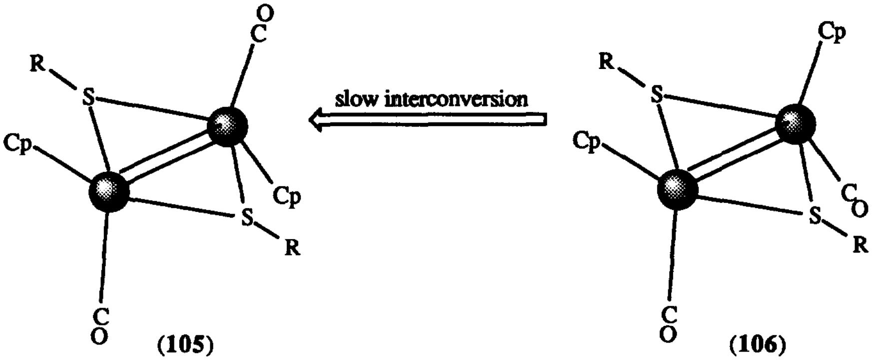


(104)

The oxidation and fragmentation of the molybdenum(II) carbonyl complex $Mo(CO)_3(^{'bu}S_4')$ [112] has already been discussed (see section 1.3.5) as a route to molybdenum(IV) dithiol complexes. The related phosphine derivative $Mo(CO)_2(PR_3)(^{'bu}S_4')$ (R = Me, Ph) has also been characterised [188]. Solution NMR spectroscopic studies indicate fluxionality in solution with the complex exhibiting a higher degree of symmetry than expected.

The half-sandwich cyclopentasulfido complex $Cp^*Mo(NO)S_5$ has been synthesised from $Cp^*Mo(NO)I_2$ and methanolic ammonium polysulfide [189]. Structural analysis of the tungsten analogue shows the S_5 ligand to be in a chair conformation. The related pentaselenido complex has also been characterised from the analogous reaction with HSe solutions.

Finally, electrochemical reduction of the molybdenum(III) dinuclear complexes $[Mo_2Cp_2(CO)_2(\mu\text{-}SMe)_3]^+$ and $[Mo_2Cp_2(CO)_2(X_2)(\mu\text{-}SMe)_2]$ (X = Cl, Br) gives the common molybdenum(II) product $Mo_2Cp_2(CO)_2(\mu\text{-}SMe)_2$ **(105)** [190]. The final thermodynamic product is the *trans* isomer, although in each case the *cis* isomer **(106)** is the kinetic product and is produced as an intermediate. The reactivity of both isomers towards isocyanide is reported.

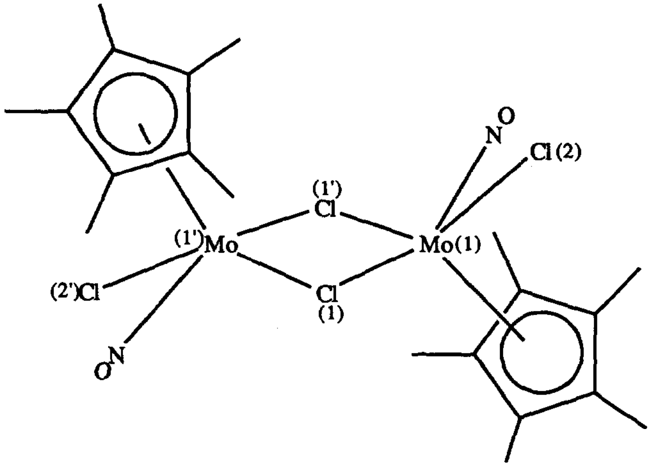


(105) **(106)**

1.5.8 *Complexes with halide ligands*

Many of the complexes with phosphine ligands are halophosphine complexes; these have been considered earlier in sections 1.5.4.1 and 1.5.4.2. The majority of the remaining complexes with halide ligands are better classed as organometallic: the reaction of molybdenum complexes with organohalo compounds can result in halide transfer to the metal centre [191, 192], whilst the addition of HX (X = Br, I) to $Mo(RNC)_6$ complexes gives rise to coupling of two RCN ligands to form a complexed alkyne ligand $[MoX(RNC)_4\{\eta^2\text{-}R(H)N\text{-}CC\text{-}N(H)R\}]$ [193]. Photolysis of organometallic polyurethanes containing $(\text{-}C_5H_4)_2Mo(CO)_6$ units along the polymer backbone produces results that are similar to those obtained for $CpMo(CO)_6$ [194]. After 11 hours of radiation in CCl_4/thf the Mo-Mo bond undergoes cleavage and the chloro product $\{Cl(CO)_3MoC_5H_4\text{-}CH_2CH_2OC(O)NH(CH_2)_3\}_2$ is isolated. Coupling and rearrangements of the CF_3CCCF_3 ligands obtained from the reaction of $MoCpX(CO)_3$ (X = Br, I) with this alkyne are the focus of another report [195]. The halide plays no role in the conversions. The iodo complex $(MeC_5H_4)Mo(CO)_3I$ is an unexpected product from the reaction of $(C_5H_4I)Mo(CO)_3Me$ with $(Me_3SnC_5H_4)(Cp)TiCl_2$ in the presence of a palladium(0) catalyst [196]. The linking of two Cp rings to form a fulvalene heterometallic complex and Me_3SnI, the predicted outcome, was not observed: methyl/iodine exchange was the only reaction seen.

An improved synthesis of dichloronitrosyl molybdenum complexes is achieved using PCl_5 as a chlorinating agent [197]. The reaction of $Cp'Mo(NO)(CO)_2$ (Cp' = Cp, Cp*) with an equimolar quantity of PCl_5 gives $\{Cp'Mo(NO)Cl_2\}_2$ in 80-95% yield. The structural characterisation of the Cp* derivative **(107)** shows two 'piano stool' monomers linked in a *trans* geometry by two bridging chloride ligands.

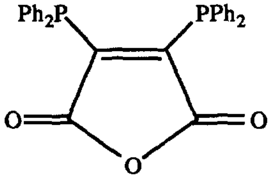


(107)

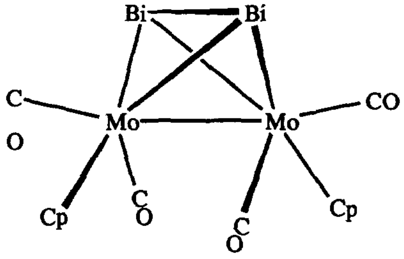
Mo(1)-Cl(1) 2.559(2) Å
Mo(1)-Cl(2) 2.406(2) Å
Mo(1)-Cl(1') 2.495(2) Å

1.6 MOLYBDENUM(I)

The dimer $\{(C_5Ph_5)Mo(CO)_3\}_2$ has been reacted with the chelating phosphine 2,3-bis-(diphenylphosphino)maleic anhydride, L_2 **(108)**, to try and obtain information on the equilibrium between $\{(C_5Ph_5)Mo(CO)_3\}_2$ and its 17 electron monomer [198]. Two products are obtained; the 17 electron complex $(C_5Ph_5)Mo(CO)_2(L_2\text{-}P)$ and the 19 electron complex $(C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$. The phosphine coordinates in 'dangling' and didentate modes, respectively. Structural characterisations of the didentate phosphine molybdenum(0) and molybdenum(I) complexes $[Mo(CCPh)(dppe)(\eta\text{-}C_7H_7)]^{n+}$ (n = 0, 1) are used to examine the effect of a one electron oxidation on the structural parameters [199]. The major alteration with oxidation is the increase in Mo-P bond lengths, from 2.467(1) and 2.477(1) Å in the neutral complex to 2.538(2) and 2.538(3) Å, respectively, in the cationic complex. All the results reported are consistent with a metal based redox process.



(108)



(109)

Either solid state thermolysis or solution photolysis of $Bi\{Mo(CO)_3(C_5H_4Me)\}_3$ produces the dimetallic complex $Mo_2(CO)_4(C_5H_4Me)_2(\mu\text{-}\eta^2\text{-}Bi_2)$ **(109)** in which the Bi_2-ligand acts as a four electron donor [200]. Extended Hückel calculations have been used to look at charge distribution in this new system and the results suggest that the best description of the molybdenum atoms is d^5 molybdenum(I).

EPR spectroscopic studies have been carried out on paramagnetic complexes formed from the photolysis of $Mo(CO)_6$ and $\{(MeC_5H_4)Mo(CO)_3\}_2$ with diketones [201, 202]. In the former case, 9,10-phenanthrene and 1,2-acenaphthene coordinate to $Mo(CO)_4$ fragments in a chelating fashion with the unpaired electron density residing mainly on the quinone ligands with a small amount of delocalisation to the metal centre.

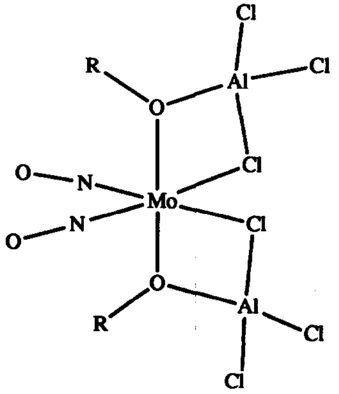
1.7 MOLYBDENUM(0)

1.7.1 Complexes with nitrogen donor ligands

With possible relevance to the biological reduction of N_2 to NH_3, the reactivity of the molybdenum(0) complex $Mo(N_2)_2(dpepp)(PPh_3)$ (dpepp = $O(CH_2CH_2PPh_2)_2$) with strong acids has been explored [203,204]. The initial stage of the reaction encompasses protonation at one of the N_2 ligands and intramolecular reorganisation to give a hydrazido(2-) molybdenum(IV) intermediate; this either disproportionates or reacts with reducing agents, *e.g.* $SnCl_2$, to give various yields of N_2 and NH_3. In an effort to elucidate the role of iron in nitrogenase, the reaction between $[FeH(H_2)(dmpe)_2]^+$ and $Mo(N_2)_2(dppe)_2$ has been carried out in the hope of obtaining an N_2 bridging Mo-Fe complex [205]. In practice, the reaction shown in equ. (6) is followed. The driving

$$2[FeH(H_2)(dmpe)_2]^+ + Mo(N_2)_2(dppe)_2 \longrightarrow 2[FeH(N_2)(dmpe)_2]^+ + MoH_4(dppe)_2 \qquad \text{equ. (6)}$$

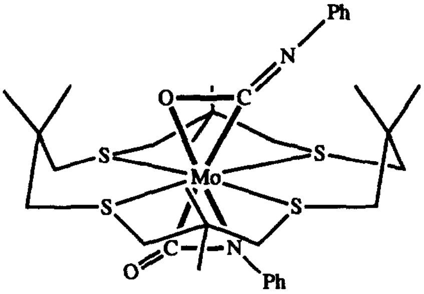
force for the reaction is thought to be the Mo-H bond energy, since IR spectroscopic data indicate that N_2 binds more strongly to a molybdenum centre than to iron. The related starting material *trans*-$Mo(N_2)_2(dppe)(dppx)$ (x = m, p) has been used to prepare complexes containing dmf as a ligand [206]. Under reflux in benzene under argon, these complexes react with dmf to give Mo(CO)(dmf)(dppe)(dppx), though an attempted recrystallisation under nitrogen of the dppm product gave crystals of *trans* -$Mo(CO)(N_2)$(dppe)(dppm) instead.



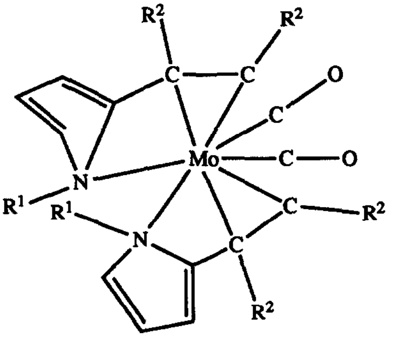
(110)

A range of dinitrosyl molybdenum complexes, in the presence of either Et_4NSn and $AlCl_3$, or $EtAlCl_2$, can act as catalysts for alkene metathesis [207-209]. For example, a 1:2 adduct (**110**) is formed between $Mo(NO)_2(OR)_2$ and $AlCl_3$; the aduct then interacts with the Et_4Sn [207]. This could be through an alkoxy ligand or directly with the molybdenum centre. Absorptions in the NO stretching region of the IR spectrum of the complex $(Et_3Sn{\cdot}AlCl_3)_2(\mu\text{-}OR)_2Mo(NO)_2(=CHMe)$ indicates the presence of a *cis* $Mo(NO)_2$ core and a d^6 configuration for the molybdenum centre [209].

A discrimination of the C=O and C=N bonds in PhNCO is observed in the macrocyclic complex *trans* -$Mo(\eta^2\text{-}PhNCO)_2$(*syn*-$Me_8[16]aneS_4$) (**111**) [210]. The η^2-*O,C* bonding mode of PhNCO is sterically less demanding than the η^2-*C,N* bonding mode, and hence occupies the more congested site. An eight coordinate complex of molybdenum has been structurally characterised [211]. Two dimethyl-7-acetyl-7-azabicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate ligands each bond *via* the nitrogen and two carbon atoms to a $Mo(CO)_2$ fragment (**112**). There are two independent molecules per unit cell, and Mo-N bond distances are 2.336(4), 2.339(5), 2.347(5) and 2.361(5) Å.



(**111**)

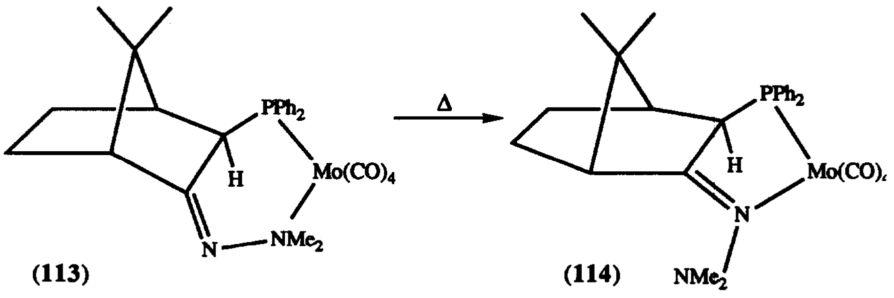


(**112**)

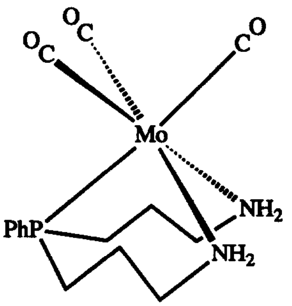
R^1 = COMe
R^2 = CO_2Me

3-Diphenylphosphinocamphordimethylhydrazone acts as a chelating *N,P*-donor ligand on complexation with metal (M) carbonyls, forming a six-membered MPCCNN-ring (**113**) [212]. On heating, isomerisation occurs with the formation of a five-membered ring containing an *exo* Me_2N-group (**114**). This latter complex has been structurally characterised for M = Mo. A tridentate

P,N,N'-donor set is provided by bis(3-aminopropyl)phenylphosphine (bap) [213]. This ligand adopts a facial mode of coordination to a $Mo(CO)_3$ fragment (**115**).



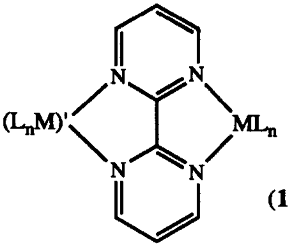
(113) **(114)**



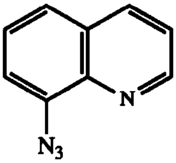
(115)

A series of complexes $Mo(N\text{-}N)(CO)_4$, where (N-N) is a didentate amine ligand, have been prepared from the direct reaction of $Mo(pip)(CO)_4$ (pip = piperidine) and (N-N) in CH_2Cl_2 at 40°C [214]. One product, $Mo\{(PhCH_2)(H)NCH_2CH_2NMe_2\}(CO)_4$ has been structurally characterised, and the greater donor ability of an α-N(H) nitrogen atom as compared to an α-N(R) nitrogen atom is discussed. Bipyridine is one of the ligands used to displace acetonitrile from $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_9)]^+$ [215]. To compensate for the loss of all three MeCN ligands on addition of a molar equivalent of the didentate bpy ligand, the *cyclo*-C_7H_9 moiety converts to an η^5-bonding mode. The product is $[Mo(CO)_2(bpy)(\eta^5\text{-}C_7H_9)]^+$ and this reacts reversibly with MeCN giving an η^5-η^3 interconversion to $[Mo(CO)_2(NCMe)(bpy)(\eta^3\text{-}C_7H_9)]^+$. Closely related to bpy is 2,2'-bipyrimidine (bpym) and this has been used to synthesise 'back to back' complexes [216–218]. A set of homo and heterodinuclear complexes of the general formula $(L_nM)'(\mu\text{-bpym})(ML_n)$ (**116**) has been characterised, including $L_nM{=}(L_nM)'{=}Mo(CO)_4$.

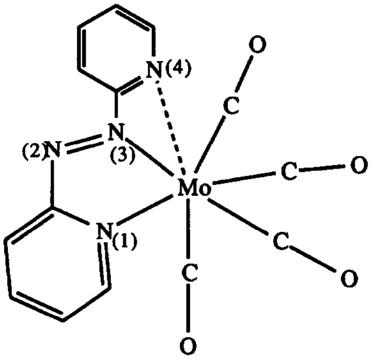
A more unusual didentate nitrogen ligand is provided by 8-azidoquinoline (**117**) [219]. On coordinating to a source of $Mo(CO)_3X$, where X = CO, PPh_3, or labile solvent molecule (S), N_2 is lost and a bent nitrene complex is obtained which is stabilised by the chelating nature of the ligand. For X = PPh_3 this product turns out to be an intermediate to a phosphinimine complex $Mo(CO)_3(S)(N(PPh_3)(C_9H_6N))$. On substitution of CO for S, structural characterisation of the complex was achieved. The Mo(CO)$_4$ unit is also observed coordinated by azo-2,2'-pyridine (apy) [220]. A mononuclear species is formed, with a 'dangling' pyridyl group (**118**), as well as dinuclear cobalt and copper species. Structural characterisation of Mo(CO)$_4$(apy) shows that the free pyridyl group has been rotated into a *cis* configuration (compared to *trans* in the free ligand) and this is explained in terms of the steric interaction between a pyridyl hydrogen atom and a carbonyl ligand, as well as a possible weak Mo···N interaction.



(116)



(117)

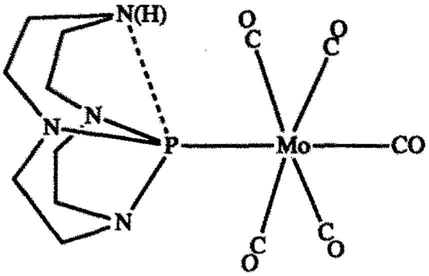


Mo-N(1) = 2.197(2) Å
Mo-N(3) = 2.190(2) Å
Mo-N(4) > 3 Å

(118)

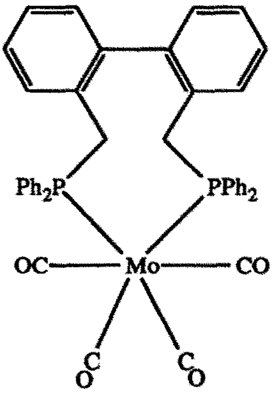
1.7.2 Complexes with phosphorus donor ligands

As part of a study on restricted rotations in metal-arene complexes, the complex dicarbonyl-{η^6-1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene}(biphenylphosphine) molybdenum(0) was synthesised [221]. The structure is reported and shows steric interactions between the phosphine ligand and the ethyl substituents of the complexed arene ligand. NMR spectroscopic data are also discussed. Binding energies are the target of kinetic studies on ligand substitution for the complexes M(CO)$_3$(Pcy$_3$)$_2$(L) [M = Cr, Mo, W; L = py, P(OMe)$_3$] [222]. An intermediate species Mo(CO)$_3$(Pcy$_3$)$_2$ is proposed, with stabilisation of the unsaturated metal centre by an agostic Mo···H···C interaction. The ligand cyclenophosphorane (L) coordinates to molybdenum *via* the phosphorus atom in LMo(CO)$_5$ (**119**) [223]. The structure of the complex shows that the axial NH group interacts with the coordinating phosphorus atom (P···N is 2.356(23)Å); the reactivity of this nitrogen atom towards electrophiles is examined.



(119)

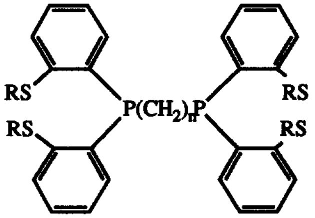
A considerable amount of work has been carried out on molybdenun(0) complexes containing didentate phosphorus ligands. The structures of *cis*-(dppm)(dppe)Mo$(CO)_2$ and *cis*-(dppe)$(Ph_2PCH{=}CHPPh_2)$Mo$(CO)_2$ have been solved [224]. The structural parameters of the two complexes are compared. Molecular orbital analyses are used to investigate the bonding and reactivity of *trans*-Mo$(CNMe)_2$(dppe)$_2$ and aminocarbyne derivatives [225]. Here, comparisons between the neutral and protonated, (*i.e.* {CN(H)Me} unit) complexes are made. Exchange reactions of *trans*-Mo$(CO_2)_2(PMe_3)_4$ with the chelating phosphines *P-P* (*P-P* = dmpm, dmpe, depe, dppe) and isocyanides CNR (R = ^{t}Bu, Cy) provide efficient routes to the new $(CO_2)_2$ adducts [226]. The various possible isomers for products of general formula *trans*-Mo$(CO_2)_2$(*P-P*)$(PMe_3)_2$, *trans*-Mo$(CO_2)_2$(*P-P*)$_2$ and *trans*-Mo$(CO_2)_2$(depe)(PMe_3)(CNR) are discussed together with a presentation of variable temperature NMR spectrosopic studies. Increasing the alkyl chain length, $Ph_2P(CH_2)_6PPh_2$ (dpph) has been reacted with Mo$(CO)_6$ [227]. Depending upon the reaction conditions two different outcomes are observed. On reflux in decahydronaphthalene, dehydrogenation of dpph to dpphn (dpphn = $(Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2)$ occurs, along with the formation of Mo$(CO)_3$(dpphn). Using toluene as the refluxing solvent, the dpph ligand remains intact and the dimer *trans*-Mo$_2(CO)_8(\mu$-dpph$)_2$ is formed. The same length of chain (C_6) is provided by 2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl (bdppmbp) [228]. Using Mo$(CO)_4$(nbd) as the source of molybdenum, Mo$(CO)_4$(bdppmbp) **(120)** was synthesised, with the diphosphine ligand adopting a *cis* coordination with a P-Mo-P' bite angle of 103.54(2)°.



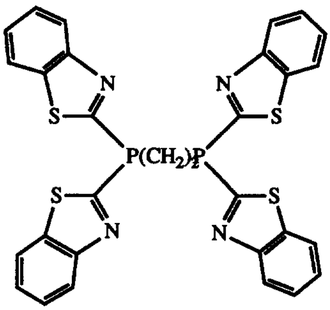
(120)

There have been two reports on the coordination chemistry of $CH_2=C(CH_2PPh_2)_2$ to $Mo(CO)_4$ and the related 1,3-bis(diphenylphosphino)-2-methylallyl complex obtained on deprotonation [229,230]. This latter complex, $[Mo(CO)_4(MeC(CHPPh_2)_2]^-$, reacts readily with electrophiles generating the tridentate phosphine ligand 1,2,3-tris(diphenylphosphino)-2-methylpropan-1-ene on reaction with Ph_2PX (X = halogen) [230].

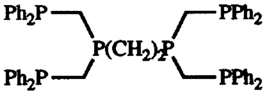
(121) L:



n = 1, R = Me: mtppm
n = 2, R = Me: mtppe
n = 2, R = ^iPr: itppe

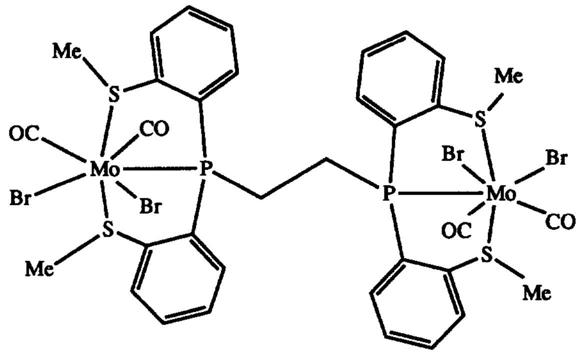


dbtpe



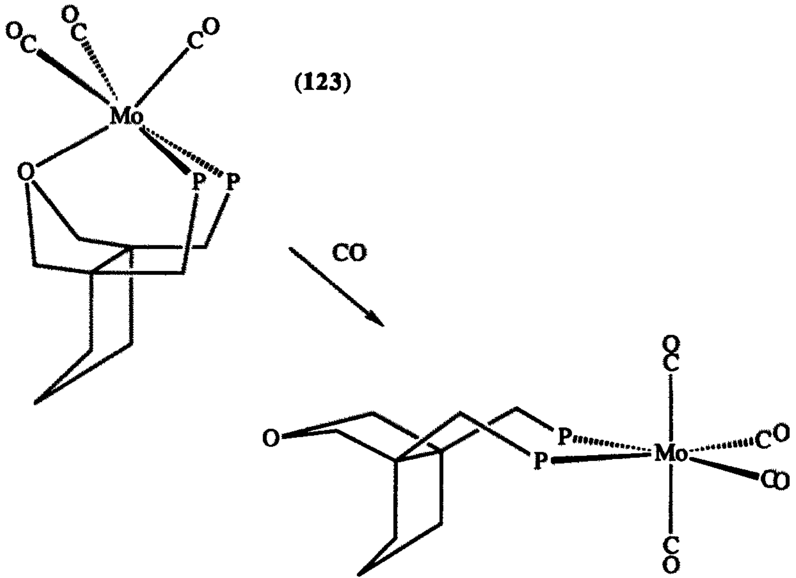
dppme

(122)



A novel didentate phosphine ligand (L_2) is provided by bis(di-*tert* -butylphosphino)sulfur diimide, $^tBu_2P(NSN)P^tBu_2$, as well as the asymmetric analogues $^tBu_2P(NSN)P(^tBu)(Ph)$ and $^tBu_2P(NSN)PPh_2$ [231]. Using $Mo(CO)_3(thf)$ as the molybdenum source leads to formation of a dinuclear linked complex $\{Mo(CO)_5\}_2(L_2)$ as well as the chelate complex $Mo(CO)_4(L_2)$. If $Mo(CO)_4(nbd)$ is used as an alternative starting material the latter chelate complex is obtained exclusively. Whilst acting as a didentate ligand is a standard bonding mode adopted by bis{bis(2-methylthiophenyl)phosphino}methane (mtppm) and related ligands (**121**), other more exotic bonding modes, in which coordination takes place *via* phosphorus and sulfur donor atoms are observed. Examples are $\{Mo_2(CO)_2Br_2\}_2$(mtppm) (**122**) and $\{Mo(CO)_3\}_2(\mu\text{-}L)$ (L = mtppm, mtppe and itppe, defined in (**121**)) [232]. The coordination chemistry of dppme is also explored.

A potential P_2O-donor set is provided by the ligand *cis*-1,5-bis{(diphosphenyl)methyl}-3-oxabicyclo[3.3.0]octane, L [233, 234]. The reaction of this ligand with (cycloheptatriene)$Mo(CO)_3$ does yield the *fac* complex (L-*P*,*P'*,*O*)$Mo(CO)_3$ (**123**), although the reaction of this complex with CO [233] or use of the alternative molybdenum source (piperidine)$Mo(CO)_4$ [234] results in the formation of (L-*P*,*P'*)$Mo(CO)_4$ (**124**) with the oxygen appendage dangling freely.

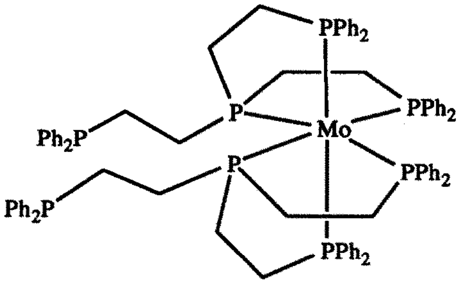


(123)

(124)

Increasing the number of phosphorus donor atoms, there is a study on the stability of *fac*/*mer* isomers of $[Mo(CO)_3(\eta^3\text{-}P_2P')]^{n+}$ [n = 0,1; P_2P' = bis(2-diphenylphosphinoethyl)-phenylphosphine] [235]. Although potentially a tetradentate, tris(2-diphenylphosphinoethyl)-phosphine also adopts a η^3-bonding mode [236]. The complex $Mo\{P(CH_2CH_2PPh_2)_3\}_2$ (**125**) has been structurally characterised and shows an unexpected 'MoP_6' coordination sphere about the molybdenum centre.

Whilst (cyclo-P_5)(Cp) complexes are already known, the first examples of carbonyl (η^5-P_5) complexes have been prepared from the reaction of P_5^- with $[M(CO)_3(RCN)_3]$ (R = Me, Et) or $M(CO)_6$ (M = Cr, Mo, W) [237]. The resulting product $[(\eta^5\text{-}P_5)Mo(CO)_3]^-$ is identified spectroscopically; the ^{31}P NMR spectrum shows a single peak at δ 141.6.

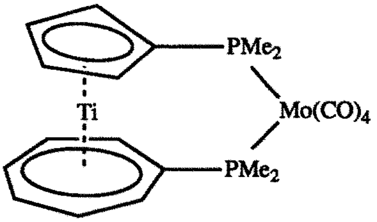


Mo-P = 2.393(3)-2.525(3) Å

$\angle$P-Mo-P = 77.8(1)-107.3(1)°

(125)

Another group of molybdenum phosphine complexes can be classified as dimetallic, but with no direct Mo-M bond (for dimetallic complexes containing Mo-M bonds see section 1.9). The classic example of this type of complex contains dppf as a ligand. There have been two reports concerning Mo(CO)$_5$(η^1-dppf). One report differentiates the two chemically distinct phosphorus environments by X-ray photoelectron spectroscopy [238] (a potential tool for diagnosing pendant and coordinating phosphines). The other piece of work studies thermal decarbonylation of the chelating complex Mo(CO)$_4$(dppf) using a variety of solvents [239]. Similar to dppf, didentate phosphinotitanocene and zirconocene ligands have been used to coordinate to molybdenum carbonyl fragments [240, 241]. Amongst the products characterised are {(η^5-C$_5$H$_4$PR$_2$)$_2$ MCl$_2$}Mo(CO)$_3$ (R = Ph, 4-C$_6$H$_4$Me; M = Ti, Zr) [240] and {(η^5-C$_5$Me$_4$PPh$_2$)TiCl$_2$}Mo(CO)$_4$ [241]. The former contains an Mo-M bridging chloride ligand, whilst in the latter, both chloride ligands are bonded solely to the titanium centre. An unusual bridging phosphine ligand is provided by {η^5-(dimethylphosphino)cyclopentadienyl)}{η^7-(dimethylphosphino)cycloheptadienyl}titanium [242]. This ligand reacts with Mo(CO)$_6$ in xylene under reflux to give the chelated heterodimetallic complex **(126)** in high yield.

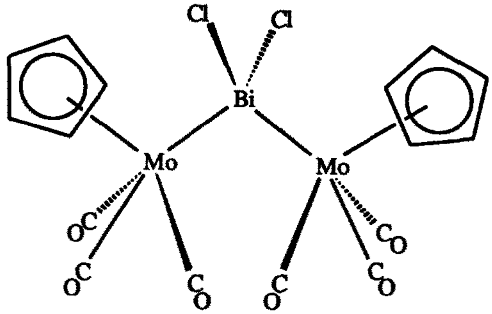


(126)

The molybdenum/rhodium complex (CO)$_3$Mo(μ-dppm)$_2$Rh(CO)Cl has been used as a starting material to form (CO)$_3$Mo(μ-dppm)$_2$(μ-SO$_2$)RhCl by passing SO$_2$ through a solution of the former complex [243]. Structural analysis shows that one of the molybdenum carbonyl ligands is semi-bridging between the two metal atoms. Finally, an unusual type of dimetallic complex is obtained from *cis* -Mo(CO)$_4${Ph$_2$P(CH$_2$CH$_2$O)$_n$CH$_2$CH$_2$PPh$_2$} (n = 3-5), a type of metallacrown ether [244]. Titration with LiBF$_4$ or NaBF$_4$ yields 1:1 adducts for both alkali metals when n = 5 and 1:1 and 2:1 adducts with Li^+ and Na^+, respectively, when n = 4. The reaction may be followed by ^{31}P NMR spectroscopy.

1.7.3 Complexes with bismuth donor ligands

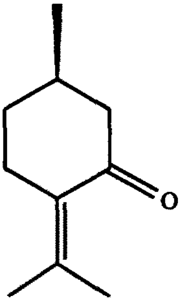
The salt $[\mathrm{PPN}][\mathrm{BiCl_2}\{\mathrm{Mo(CO)_3(Cp)}\}_2]$ **(127)** has been synthesised and structurally characterised [245]. The bismuth atom is tetrahedrally coordinated with direct bonds to each molybdenum centre (Mo-Bi bond lengths 2.944(1) and 3.032(2)Å). The complex can be considered as two $[\mathrm{Mo(CO)_3(Cp)}]^-$ fragments interacting with a $[\mathrm{BiCl_2}]^+$ fragment; these interactions are studied by theoretical calculation using various geometries for the complex.

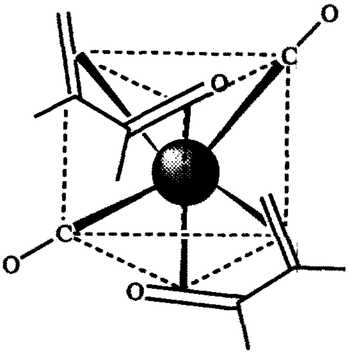


(127)

1.7.4 Complexes with oxygen donor ligands

The chiral enone *R*-(+)-pulegone **(128)** forms the η^4-1-oxa-1,3-diene complex $(\mathrm{pulegone})_2\mathrm{Mo(CO)_2}$ on reaction with $\mathrm{Mo(CO)_3(thf)_3}$ [246]. A comparison of solution spectroscopic data with those of the structurally characterised tungsten analogue indicates a coordination geometry about the molybdenum atom that is best described as a distorted trigonal prism **(129)**.



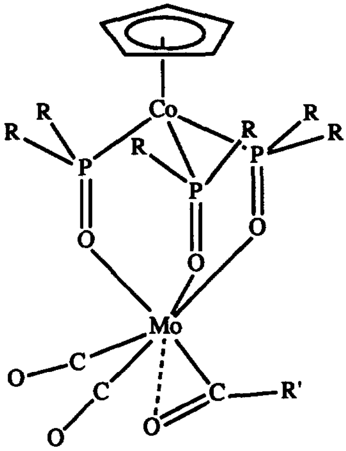


(128) **(129)**

The coordination chemistry of CO_2 to molybdenum in *trans*-$Mo_2(CO_2)_2(PMe_3)_4$ has been examined by vibrational spectroscopy [247]. Complete assignment of all vibrational modes of both the FTIR and Raman spectra are made, and the conclusion is that CO_2 is bound in a side-on manner. Exchange reactions of *trans*-$Mo_2(CO_2)_2(PMe_3)_4$ with a range of didentate phosphines and isocyanides [226] have been discussed in section 1.7.2.

The anionic tricarbonyl complexes $[Mo(X,Y)(CO)_3(PR_3)]^-$ have been synthesised by the *in situ* reaction of $Mo(CO)_3L_3$ ($L_3 = C_7H_8$, 3MeCN, 3py) with $(X,Y)^-$ and PR_3 ($(X,Y)^- =$ 2-picolinate (*O,O'*), 2-quinaldinate (*O,O'*), xanthates (*S,S'*), pyridine-2-thiolate (*S,N*); R = Ph, CH_2CH_2CN) [248]. Surprisingly, these products could not be isolated either by reaction of $Mo(CO)_4(PPh_3)_2/Mo(CO)_3(PPh_3)_3$ with (X,Y) donors, or by treatment of $[Mo(CO)_4(X,Y)]^-$ with phosphine.

An unusual O_3-donor set is provided by $[(Cp)Co\{P(O)R_2\}_3]^-$ (L_R) [249]. The molybdenum(0) anionic complexes $[L_RMo(CO)_3]^-$ (R = OMe, OEt, O^iPr) are reacted with various iodides R'I to give the oxidised σ-allyl complex. Partial or complete isomerisation follows, depending upon the steric restraints of R' and L_R) to a η^2-acyl compound (130).



(130)

1.7.5 *Complexes with sulfur donor atoms*

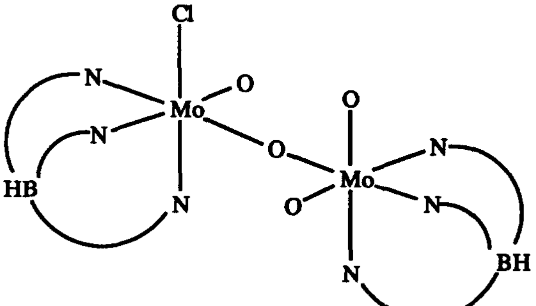
Synthetic routes to molybdenum(0) carbonyl complexes containing the xanthates $[S_2COEt]^-$ and $[S_2COC_6H_{11}]^-$ have been mentioned briefly in the preceding section, along with formation of a complex containing pyridine-2-thiolate, which acts as an *S,N*-donor ligand [248]. The tridentate crown thioether 1,4,7-trithiacyclononane, L, also forms a molybdenum(0) carbonyl complex, namely $Mo(CO)_3(L)$ [250]. The synthesis of this product along with the chromium and tungsten analogues is reported.

1.7.6 *Complexes with halide and hydride ligands*

The mechanism for the protonation of the molybdenum(0) ethene complex $Mo(C_2H_4)_2(dppe)_2$ with HX (X = Cl, Br) in thf at 25°C has been studied by stopped flow spectrophotometry [251, 252]. There appear to be two pathways operating: a slow, direct protonation on the metal centre or a rapid protonation of the C_2H_4 ligand followed by a relatively slow β-hydrogen migration from the new ethyl ligand to the molybdenum atom. Either route leads to the formally oxidised molybdenum(II) complex $[Mo(H)(C_2H_4)_2(dppe)_2]^+$. This product slowly loses ethene with subsequent binding of Cl^- to yield, ultimately, $MoCl_2(dppe)_2$ and ethane. If a more concentrated solution of HCl is used initially, the molybdenum(IV) complex cation $[MoH_2(C_2H_4)_2(dppe)_2]^{2+}$ is obtained prior to its decomposition to $MoH_2Cl_2(dppe)$.

1.8 MIXED VALENCE MOLYBDENUM COMPLEXES

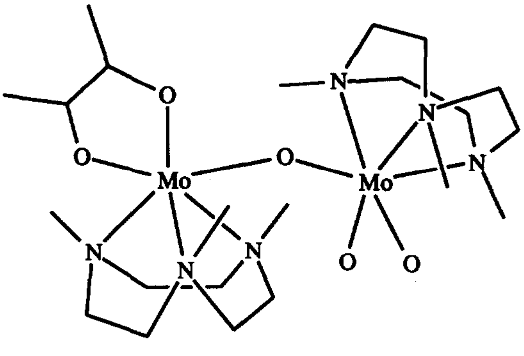
On oxidation of the bridged molybdenum(V) dimer $[Mo_2O_4(H_2O)_6]^{2+}$ to the corresponding molybdenum(VI) dimer, with a source of chromium(V), a pink intermediate chromium(IV) complex is obtained [253, 254]. No indication of any formation of dinuclear Mo-Cr products was found, so it is proposed that oxidation of the molybdenum(V) dimer proceeds in one electron steps through a reactive transient, namely the mixed valence complex $[Mo^{V}Mo^{VI}O_4(H_2O)_6]^{3+}$. The complex $TpMo^{V}OCl(\mu\text{-}O)Mo^{VI}O_2Tp$ (**131**) (Tp = tris(3,5-dimethylpyrazolyl)borate) provides the first example of a structurally characterised $Mo^{V}Mo^{VI}$ dinuclear complex [255]. It is obtained as an unexpected product on reaction of $TpMoO_2Cl$ with Grignard reagents in an attempt to synthesise $TpMoO_2R$. A possible reaction pathway is shown in equ. (7) and R_2 has been isolated from the reaction mixture as supportive evidence of the pathway. A similar $Mo^{III}Mo^{VI}$ complex has also been structurally characterised [256]. $[L'(acac)Mo^{III}(\mu\text{-}O)Mo^{VI}O_2L'](BPh_4)_2$ (**132**) (L' = 1,4,7-trimethyl-1,4,7-triazacyclononane) is synthesised from $Mo^{III}Br_3L'$ and excess Na(acac). As in the previous example, the two units are linked by a μ-oxo bridge: $Mo^{III}\text{-}\mu(O) = 2.034(4)$ Å, $Mo^{VI}\text{-}\mu(O) = 1.804(4)$ Å.



(131)

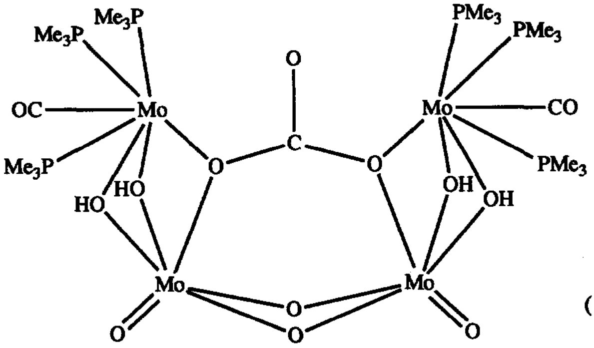
$$\text{(i)}\quad TpMo^{VI}O_2Cl + RMgX \longrightarrow TpMo^{V}O_2 + {}^{1}/_{2}R_2 + MgXCl$$

$$\text{(ii)}\quad TpMo^{V}O_2 + TpMo^{VI}O_2Cl \longrightarrow TpMo^{VI}O_2(\mu\text{-}O)Mo^{V}OClTp \qquad \text{equ. (7)}$$



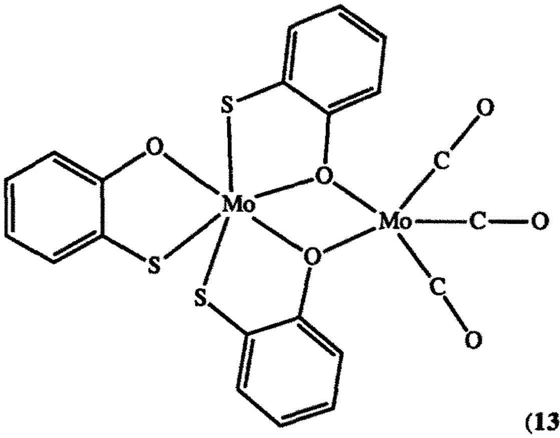
(132)

Trinuclear $M^{VI}Mo^{IV}M^{VI}$ complexes (M = Mo, W) have been prepared by reacting $(PPh_4)MS_4$ with $MoO_2(acac)_2$ in boiling acetonitrile [257]. For the homonuclear case, crystals of composition $Mo_3O_{1.9}S_{8.1}$ were obtained, which structural analysis showed to contain a $Mo^{VI}(\mu\text{-}S)_2Mo^{IV}(O)(\mu\text{-}S)_2Mo^{VI}$ core with an Mo-Mo-Mo angle of 151.3°. An unusual tetrametallic mixed valence $Mo^{II}Mo^{V}$ complex is obtained on reacting either $\{Mo(\mu_2\text{-}\eta^1,\eta^2\text{-}CO_3)(CO)(PMe_3)_3\}_2$ or $Mo(CO_3)(CO)(PMe_3)_4$ with water [258]. The structure of $Mo_4(\mu_4\text{-}CO_3)(CO)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OH)_4(PMe_3)_6$ **(133)** shows a novel type of bonding for a carbonate ligand. The two molybdenum(V) centres are six coordinate, whilst the two molybdenum(II) centres are seven coordinate.



(133)

Although, as far as the structural parameters indicate, both molybdenum centres of $[(Cp^*Mo)_2(\mu\text{-}I)_4]^+I_3^-$ are equivalent (all Mo-I = 2.78±0.01Å, all Mo-I-Mo = 58.4±0.2°), in terms of formal oxidation states this quadruply iodo-bridged complex contains a molybdenum(III) and a molybdenum(IV) centre [259]. The Mo-Mo distance of 2.718(3) Å implies that there is a direct metal-metal bond, and this is in accord with theoretical calculations which predict that the five metal d electrons reside in a strongly σ-bonding molecular orbital and three degenerate non-bonding orbitals of δ symmetry. Whilst the average oxidation state of the molybdenum atoms of the dianionic complex $Mo_2(CO)_3(S,O\text{-}C_6H_4\text{-}1,2)_3$ **(134)** is +2, X-ray photoelectron spectra and electrochemical results show, in fact, that the two molybdenum atoms are in different oxidation states [260]; the absence of a molybdenum(0) centre is established. Structural analysis reveals that the anion has a pseudo C_3 axis through the molybdenum atoms which possess distorted trigonal prismatic and octahedral coordination geometries.



(134)

Although not mixed valence, in the sense of a discrete molecular compound containing two molybdenum atoms in different oxidation states, the ionic complex $[Mo(S_2CNEt_2)_4]_2[MoCl_4].HNEt$ has been synthesised and structurally characterised [261]. The structure shows the molybdenum(II) centre of $[MoCl_4]^{2-}$ to be tetrahedrally coordinated by chloride ligands (Mo-Cl = 2.275-2.295 Å; Cl-Mo-Cl = 105.8-114°), and the molybdenum(III) centres of the $[Mo(S_2CNEt_2)_4]^+$ cations to be eight coordinate by sulfur atoms.

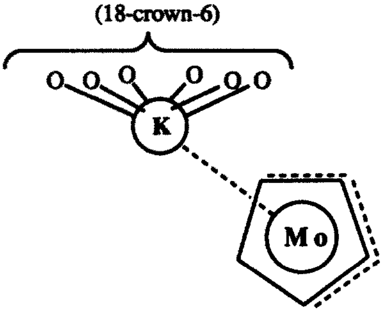
1.9 HETERODIMETALLIC MOLYBDENUM COMPLEXES

1.9.1 Group 1

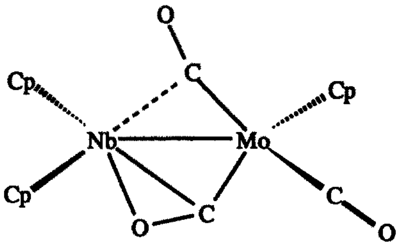
Amidst a report of complexes containing transition metal-hydrogen-alkali bonds, predominantly of tungsten complexes, the structure of $[K(18\text{-crown-}6)][Mo(Cp)_2H]$ (**135**) is presented [262]. This product is prepared in high yield from the reaction of $Mo(Cp)_2H_2$ and KH in the presence of 18-crown-6. The Mo···K distance of 3.614Å, together with the fact that the potassium ion is displaced by 0.87Å out of the plane of the oxygen atoms of the crown ether ligand and towards the molybdenum atom, is very suggestive of the existence of a covalent Mo-H-K bridge. This is also supported by a peak in the residual electron density map of the structural analysis, with $R = 0.041$ at a distance 1.71Å from molybdenum atom and 2.80Å from potassium centre.

1.9.2 Transition metals

Common starting materials for heteronuclear complexes of molybdenum are the dimers $Cp_2Mo_2(CO)_6$ and $Cp_2Mo_2(CO)_4$. For example, the complexes $Cp_2MMo(Cp)(CO)_3$ (M = Nb, Ta) can be prepared by heating the molybdenum dimers with Cp_2MH_3 and $Cp_2M(CO)H$, respectively [263]. Three different modes of bonding for the three CO ligands are seen in this dimetallic complex: terminal, semi-bridging and bridging (136). Using $Re_2(CO)_{10}$ and $HPPh_2$ as reagents with $Cp_2Mo_2(CO)_6$ in xylene under reflux gives $Re_4(CO)_4(\mu\text{-}H)(\mu\text{-}PPh_2)MoCp(CO)_2$ as one of the major products (27% yield) [264]. The structure of this hydrido complex is presented, along with the reactions of proton exchange for isolobal $\{M(PPh_3)\}^+$ fragments (M = Au, Ag, Cu).



(135)



(136)

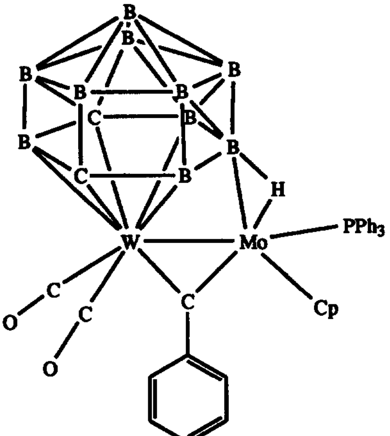
There have been two reports on dimetallic carbaborane complexes [265, 266]. The compounds $MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)(Cp)$ (137) and $MoCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^4\text{-}C_4Me_4)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)$ (138) have been structurally characterised. In the latter complex, the molybdenum atom is bound to the open face of the carboranyl ligand, and in the former the tungsten atom is in this site. Compounds related to these two products are also discussed and multinuclear NMR spectroscopic results are presented.

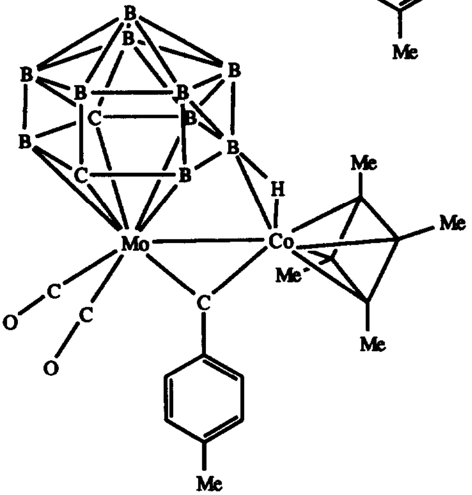
The alkyl complex $CpMoCH_2CCR$ (R = Me, Ph) reacts with either $Fe_2(CO)_9$ or $M_3(CO)_{12}$ (M = Fe, Ru) to give the heteronuclear μ-allenyl complexes $(CO)_3Fe(\mu\text{-}\eta^2,\eta^3\text{-}RC{=}C{=}CH_2)MoCp(CO)_2$ and $(CO)_6M_2(\mu_3\text{-}\eta^1,\eta^2,\eta^3\text{-}RC{=}C{=}CH_2)MoCp(CO)_2$, respectively [267]. Further reactivity of these products is explored, including CO substitution, protonation, I_2 oxidation and metal framework expansion. Moving across the periodic table to cobalt, $Cp_2Mo(\eta^2\text{-}CO_2)$ forms the hydride bridged complex $Cp_2Mo(\mu\text{-}H)(\mu\text{-}CO)Co(CO)_3$ on reaction with $HCo(CO)_4$ [268]. The structure and bonding of this product are described in detail [Mo-H =

1.64(3), Co-H = 1.88(3), Mo-Co = 2.8449(4) Å; Mo-H-Co = 108.(1)°]. Results of extended Hückel calculations indicate a 4-centred 4-electron Mo-H-Co-(CO) bond, and only a weak direct Mo-Co interaction.

(137)

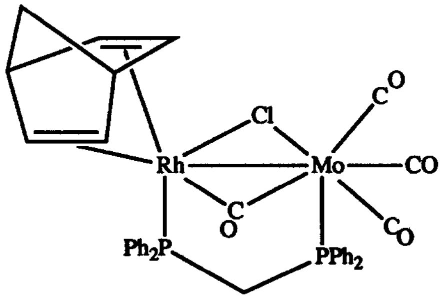
Mo-W = 2.702(1) Å



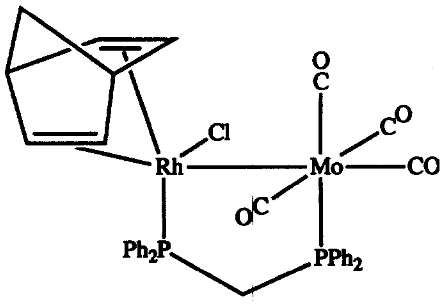


(138)

Mo-Cr = 2.540(1) Å



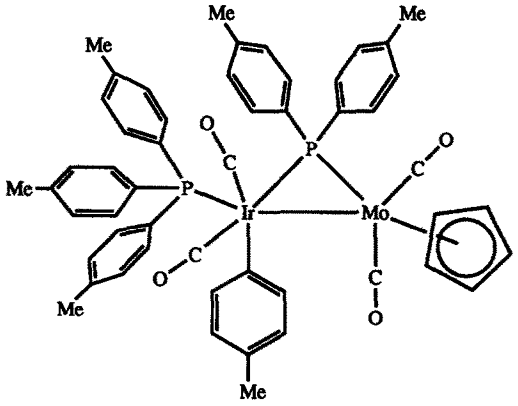
(139) - solid state



(140) - in solution

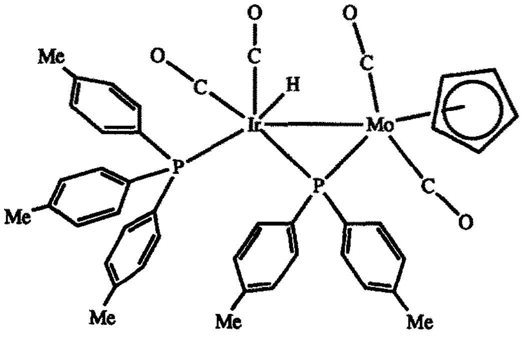
The complex $Mo(CO)_3(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)Rh(nbd)$ **(139)** is prepared by ring opening of $Mo(CO)_4(dppm)$ with $\{RhCl(nbd)\}_2$ [269]. The solid state structure of **(139)** reveals a Mo-Rh distance of 2.945Å, indicative of a M-M single bond; the metal atoms are asymmetrically bridged by dppm, CO and Cl ligands. There is no evidence of a bridging CO ligand in solution, so an alternative structure **(140)** is proposed with cleavage of the CO and Cl bridges.

Elimination of methane occurs between $HMoCp(CO)_3$ and *trans*-$MeIr(CO)\{P(p\text{-tolyl})_3\}_2$ giving rise to the formation of $Cp(CO)_2Mo\{\mu\text{-}P(p\text{-tolyl})_2\}Ir(p\text{-tolyl})\{P(p\text{-tolyl})_3\}(CO)_2$ **(141)** [270]. Whilst this product is unreactive towards CO, MeI and PhCCPh, it reacts readily with H_2 to eliminate toluene and form the corresponding mono-hydride complex **(142)** as well as a trihydride complex $Cp(CO)_2(H)Mo\{\mu\text{-}P(p\text{-tolyl})_2\}Ir(H)_2(CO)\{P(p\text{-tolyl})_3\}$. The structures of both **(141)** and **(142)** are presented, the former containing a *trans*-arrangement of carbonyl ligands on the iridium centre, and the latter a *cis*-arrangement.



(141)

Ir-Mo	2.976(2) Å
Ir-μP	2.376(2) Å
Mo-μP	2.412(3) Å
Mo-P-Ir	76.9(1)°

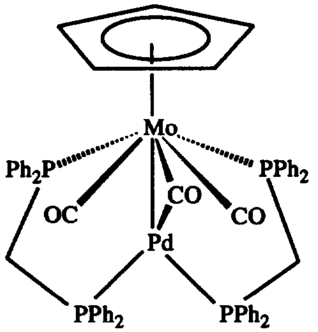


(142)

Ir-Mo	2.957(1) Å
Ir-μP	2.334(3) Å
Mo-μP	2.391(3) Å
Mo-P-Ir	77.5(1)°

The reactivity of the dimer $Cp(CO)NiMo(CO)_3(C_5H_4Me)$ towards dienes has been examined [271]. Depending upon the diene used, the Ni-Mo bond of the starting material is either broken or retained. In the latter category is $CpNi\{\mu\text{-}\eta^1,\eta^3\text{-}C(CMe_2)CH_2\}Mo(CO)_2(C_5H_4Me)$, which isomerises on silica gel to $CpNi\{\mu\text{-}\eta^1,\eta^3\text{-}C(Me)C(Me)CH_2\}(\mu\text{-}CO)Mo(CO)(C_5H_4Me)$. The synthesis and consequential reactivity of the dimeric Mo-Pd and Mo-Pt complexes

$[Pd(\mu\text{-}CO)(\mu\text{-}dppm)_2MoCp(CO)_2]^+$ **(143)** and $Pt(Cl)(PPh_3)(\mu\text{-}dppm)MoCp(CO)_2$ have also been described [272]. The former product is made by heterolytic metal-metal bond cleavage of the trinuclear cluster $PdMo_2Cp_2(CO)_5(\mu\text{-}dppm)$ with a molar equivalent of dppm; the $[PF_6]^-$ salt of **(143)** has been structurally characterised. This reveals a square pyramidal $CpMoP(1)P(3)(CO)_2$ fragment geometry, with the Cp ligand in an apical position.

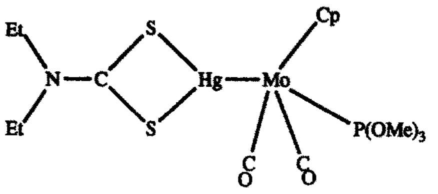


Mo-Pd = 2.799(1) Å

(143)

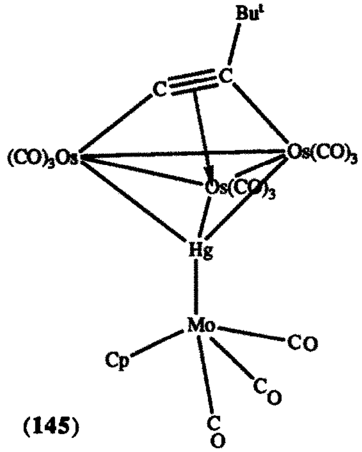
The remaining transition metal/molybdenum complexes are Hg-Mo based [273-276]. Both $MoCp(CO)_3(SnPh_3)$ and $Mo(CO)_3(\eta^2\text{-}N,N')(\eta^1\text{-}dppm)$ (N,N' = bpy, phen, 2,9-dimethylphen (dmp)) have been reacted with HgX_2. For the first complex [273], (X = Cl, $OCOCF_3$) different compounds are isolated, their formation depending upon the reaction conditions. For example, using acetone as the solvent, addition of five equivalents of $Hg(OCOCF_3)_2$ results in the formation of the asymmetric complex $MoCp(CO)_3(HgOCOCF_3)$ whereas with chloroform as the solvent $Mo\{(\eta^5\text{-}C_5(OCOCF_3)_5\}(CO)_3(HgOCOCF_3)$ is produced. Three types of complex are obtained from $Mo(CO)_3(\eta^2\text{-}N,N')(\eta^1\text{-}dppm)$ and HgX_2 (X = Cl, Br, I, CN, SCN) [274], namely: $[Mo(CO)_3(\eta^2\text{-}N,N)(X)_2]Hg$ (N,N' = bpy, phen; X = Cl, Br, CN, SCN or N,N' = dmp; X = CN), $[Mo(CO)_3(\eta^2\text{-}N,N')(\mu\text{-}dppm)HgI][HgI_3]$ (N,N' = bpy, phen) and $Mo(CO)_3(\eta^2\text{-}dmp)(HgX)(X)$ (X = Cl, Br, I, SCN). A rationalisation of the factors determining which class of complex is formed is presented as well as elemental analysis, conductivity measurements and IR spectra for all the products obtained.

A structural analysis of $(dtc)HgMoCp(CO)_2P(OMe)_3$ **(144)** has been carried out and the results compared with those for the tricarbonyl derivative [275]. The solid state structure of **(144)** contains discrete molecules with a shortest Hg-S intermolecular distance of 6.12 Å. This contrasts with $(dtc)MoCp(CO)_3$ where such an interaction is present; this difference is attributed to a knock-on effect of the bulkier phosphite ligand as well as an electronic contribution. Whilst officially a cluster compound, $(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)Os_3(CO)_9(\mu_3\text{-}Hg)MoCp(CO)_3$ **(145)** can be considered as a trimetallic $L_nHgMoCp(CO)_3$ complex [276]. Its preparation emphasises this, with the iodide ligand of L_nHgI being replaced by a source of $[MoCp(CO)_3]^-$.



(144)

Mo-Hg = 2.680(1) Å

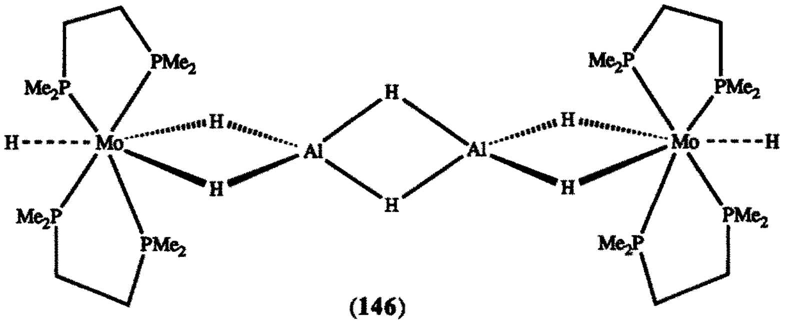


(145)

Mo-Hg = 2.718(3) Å

1.9.3 Group 13

Although not strictly dimetallic, $\{MoH(AlH_4)(dmpe)_2\}_2$ **(146)** can be better described as two linked $Mo(H_2)Al$ dimers rather than a cluster compound [277]. Each molybdenum atom is seven coordinate and, although the terminal molybdenum hydride ligands were not located directly in the structural determination, there is an apparently vacant site *trans* to the μ-hydrogen atoms.



(146)

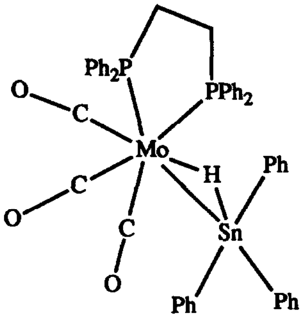
Photolysis of $\{CpMo(CO)_3\}_2$ and InR_3 (R = Et, ${}^tBu$, neopentyl) forms $CpMo(CO)_3InR_2$ efficiently [278]. The reaction is thought to follow a radical pathway which implies substantial Mo-In bond strength. As a consequence of this, direct photolysis of the molybdenum dimer and indium metal was carried out. This resulted in the reversible formation of $\{CpMo(CO)_3\}_3In$. Related work with $ZnEt_2$ is also presented.

1.9.4 Group 14

Carbaborane molybdenum, cobalt and tungsten complexes have been mentioned already in section 1.9.2. A similar type of complex, with a molybdenum atom capping the *nido* face of $[C_2B_9H_{11}]^{2-}$, is synthesised from equimolar quantities of $TlC_2B_9H_{11}$, $Mo(CO)_3(MeCN)_3$ and

Ph_3SnCl along with PPNCl in MeCN [279]. With a direct Mo-Sn bond, the product $[PPN][\eta^5\text{-}C_2B_9H_{11})Mo(CO)_3(SnPh_3)]$ can be considered formally to contain molybdenum(0) and tin(IV) centres. The same oxidation assignment is made for the molybdenum and tin atoms in the complex $Mn(CO)_5(Me)_2Sn(MoCp(CO)_3)$ [280]. The reactions of this and related complexes with iodine are used to compare the tin-transition metal bond reactivites.

Two synthetic routes have been used to prepare the stannyl complex $(CO)_3(dppe)Mo(H)SnPh_3$ (147), either the thermolysis of $Mo(CO)_3(dppe)(S)$ (S = thf, acetone) with $HSnPh_3$ or the photolysis of $Mo(CO)_4(dppe)$ with the same stannane [281]. Spectroscopic NMR coupling constants indicate that the stannane ligand adopts a η^2-coordination to the molybdenum centre, and this has been confirmed structurally for a related chromium complex.



(147)

1.10 SELECTED CLUSTERS

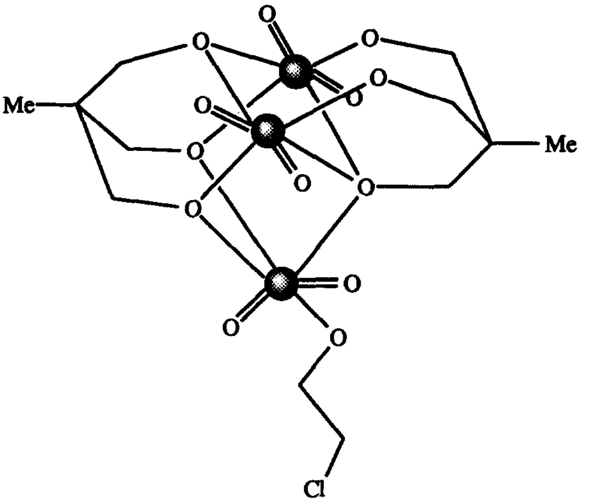
This section details molybdenum complexes containing three or more metal atoms. Two classes of molybdenum compounds that fall into this category are cubanes, based on Mo_4S_4 or Mo_4Se_4 cubes, and polyoxomolybdates of general formula Mo_xO_y. As both of these areas of molybdenum chemistry widely studied, reference is only made to discrete molecular compounds that exhibit novel and interesting features of coordination chemistry.

1.10.1 Polyoxomolybdates

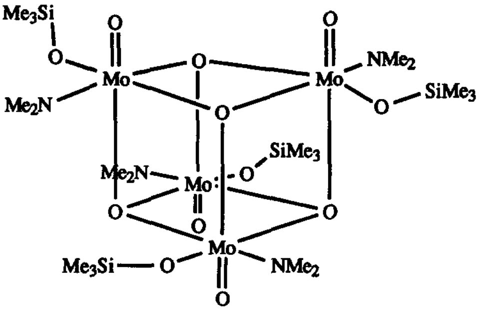
Reaction of $[^nBu_4N]_4[Mo_8O_{26}]$ with 2-hydroxymethyl-2-methyl-1,3-propan-diol (H_3hmmp) in MeCN yields $[^nBu_4N]_2[Mo_3O_7(hmmp)_2]$ which readily undergoes protonation or alkylation to give the related oxo cluster $[^nBu_4N][Mo_3O_6(OR)(hmmp)_2]$ (R = H, alkyl) [282]. If the initial reaction is carried out using chloroethanol as the solvent, an alkylated product with R = CH_2CH_2Cl is obtained directly. Structural analysis of this product (148) shows each molybdenum atom to be coordinated by six oxygen atoms in a distorted octahedral geometry.

There have been two structural characterisations of Mo_4-oxo clusters containing $[Mo^{VI}_4O_8]^{8+}$ cores. The first of these, $Mo_4O_4(\mu_3\text{-}O)_4(OSiMe_3)_4(NHMe_2)_4$ (149) was produced as a minor product in the condensation of MoO_3 with Me_3SiNMe_2 [283]. For the second compound, the $[Mo_4O_8]^{8+}$ core is the building framework of a larger heterometallic cluster

$\{Mo_4O_4Cr(C_{15}H_{20}N_4)\}_4$ **(150)** where –O-Cr-O– groups bridge four pairs of molybdenum atoms diagonally [284]. Another dimetallic cluster that has been isolated and structurally characterised is $\{NaMoO_2(OC_2H_4OMe)_3\}_2$ **(151)** [285]. This product, along with $\{NaMo_2O_4(OR)_5(ROH)\}_2$ (R = ^{i}Pr, Et) is prepared by means of a conductiometric titration of molybdenum and sodium alkoxide precursors so as to obtain a 1:1 composition of the two metals.

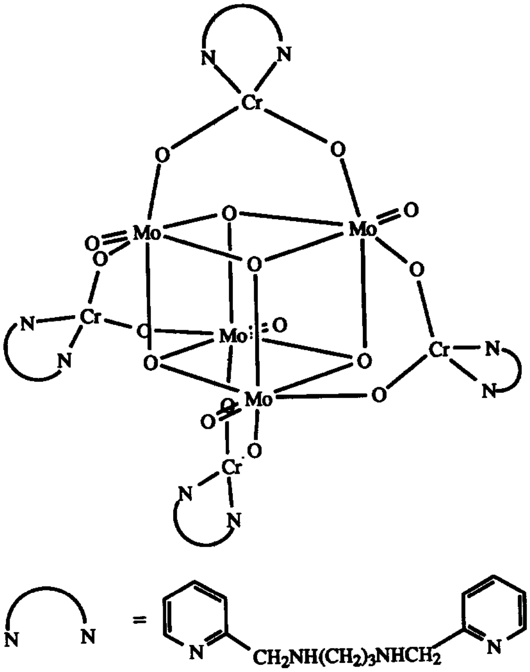


(148)

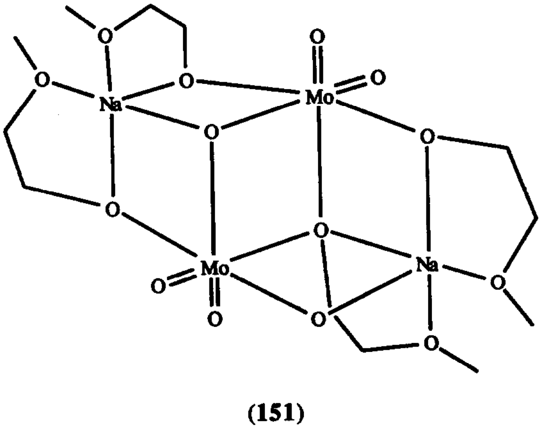


(149)

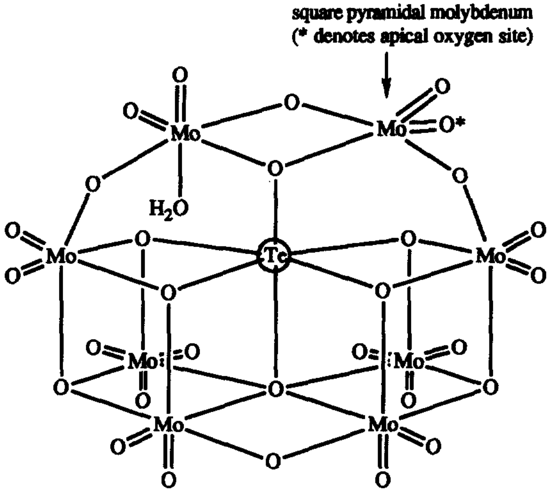
A novel five coordinate molybdenum atom is the distinguishing feature of the tellurium polymolybdate $(^{n}Bu_4N)_4[TeMo_8O_{29}(OH_2)]$, $(^{n}Bu_4N)_4$**(152)** [286]. Structural analysis shows one molybdenum atom to be in a distorted square pyramidal MoO_5-environment. The four basal oxygen atoms are coplanar to within 0.05Å, and the molybdenum atom is displaced by 0.45Å out of the plane.



(150)



(151)



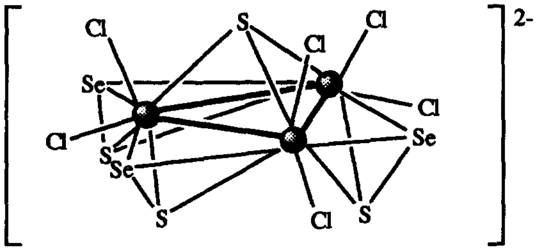
square pyramidal molybdenum
(* denotes apical oxygen site)

(152)

1.10.2 *Complete and incomplete cubane clusters*

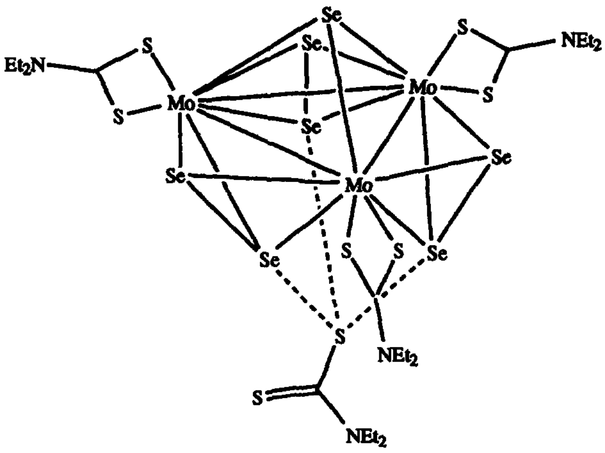
1.10.2.1 *Homometallic clusters*

Two new compounds containing $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cores have been prepared from $Mo_3S_7X_4$ ($X = Cl, Br$) by the reaction with PEt_3 [287]. The role of the phosphine is to desulfurise a $\mu\text{-}S_2{}^{2-}$ ligand to the corresponding S^{2-} ligand with formation of Et_3PS. The products, $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PEt_3)_3(H_2O)_2.OPEt$ and $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_4(PEt_3)_3(OPEt_2H)(H_2O).2thf$ have been structurally characterised and an explanation for the formation of HEt_2PO in the latter cluster is presented. The related triangular compound $[Mo_3S_7X_6]^{2-}$ ($X = Cl, Br, NCS$) is used in reactions with KSCN and KSeCN [288]. With the second reagent, stereoselective substitution of one sulfur atom of $\mu_2\text{-}S_2$ ligands occurs, and the structure of the product $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}SSe)_3Cl_6]^{2-}$ (**153**) has been determined showing that the selenium atoms essentially lie in the Mo_3 plane.

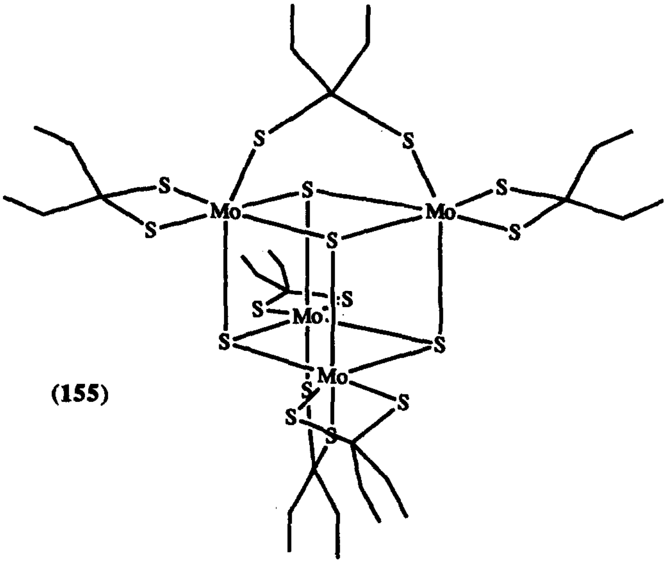


(153)

A whole range of incomplete cubane clusters based on $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3]^{4+}$ and containing didentate ligands has been synthesised and characterised by various techniques including mass spectrometry, where very distinct fragmentation pathways are observed [289-291]. Ligands that provide O/N/ S atoms for binding are used in the system, and typical examples are ligands derived from 8-hydroxyquinoline, *N,N*-diethylthiocarbamate (dtc)$^-$, 2-mercaptobenzoic acid (H_2mba) and catechol. As part of the study, structural analysis of [$Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)(dtc)$]I [290] and [$HNEt_3$][$Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(mba)_3$] [291] have been undertaken. Selenium based clusters containing dtc$^-$ ligands have also been synthesised [292] using a new route from polymeric forms of $Mo_3Se_7X_4$ (X = Cl, Br). Consideration of the structure of $Mo_3Se_7(dtc)_4$ implies that the complex is better treated as an ionic compound: [$Mo_3Se_7(dtc)_3$]$^+$dtc$^-$ (**154**) and, as shown earlier for sulfur, reaction of (**154**) with phosphine gives a Mo_3Se_4 compound, $Mo_3Se_4(dtc)_4(PPh_3)$.



(154)

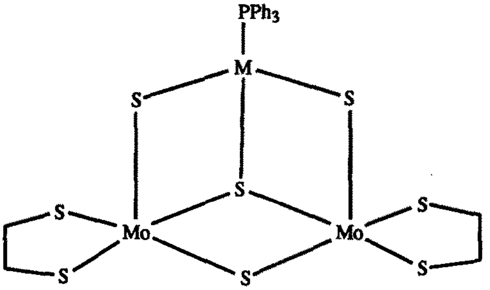


(155)

Analysis of structural features and qualitative MO calculations are the topics of work on complete cubane clusters with dtp ligands [$dtp^- = {}^-S_2P(OEt)_2$] [293]. Clusters with both Mo_4S_4 and Mo_4S_3O-cores are considered, and eight structures are presented, for example $Mo_4S_4(\mu\text{-dtp})(\eta^2\text{-dtp})_4$ **(155)**, along with synthetic routes to these new cubanes. The synthesis and properties of cationic Mo_4S_4- and Mo_4Se_4-based cubanes containing tetracyano-ligands and having *e.g.* $[Fe_4(NO)_4(\mu_3\text{-}S)_4]^-$ as the counterion have also been explored [294]. Along with several structural analyses, electrical conductivities and magnetic properties are described.

1.10.2.2 Heterometallic clusters

Incomplete cubanes based on Mo_2MS_4 (M = Cu, Ag) **(156)** have been synthesised. The copper product $(Et_4N)[(MoCuS_4)(edt)_2(PPh_3)]$ is prepared from the molybdenum dimer $(Et_4N)[MoS_4(edt)_2]$ and $Cu(PPh_3)_2(dtp)$ [295] and the structural parameters of the original dimer are compared with those of the product. In the analogous silver complex [296], a structural comparison with the homometallic $[Mo_3S_4]^{4+}$ cluster core is made.



	Cu	Ag
Mo-Mo	2.852(2)	2.881(4) Å
Mo-M	2.802(2)	3.010(4) Å
	2.760(2)	3.227(4) Å

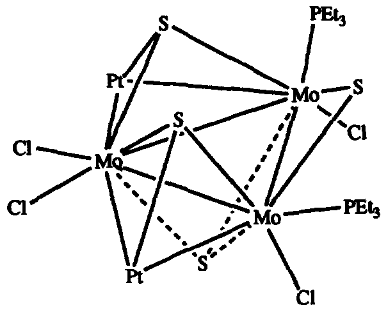
(156) M = Cu, Ag

Another type of mixed metal incomplete cubane cluster is obtained by the replacement of tungsten with molybdenum [297]. The cationic aqua-clusters $[Mo_2WS_4(H_2O)_9]^{4+}$ and $[MoW_2S_4(H_2O)_9]^{4+}$ complete the series of $[M_3S_4(H_2O)_9]^{4+}$ clusters ($M_3 = W_3$, W_2Mo, Mo_2W, Mo_3). All four clusters are isomorphous and in the heterometallic examples the molybdenum and tungsten atoms are statistically disordered.

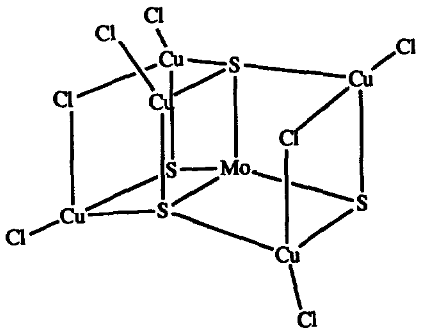
Starting with the incomplete molybdenum aqua cubane $[Mo_3S_4(H_2O)_9]^{4+}$, direct reaction with a variety of metals (M) yields clusters containing complete Mo_3MS_4-cubane cores [298,299]. Depending upon the metal, either a discrete cubane, singly or doubly bridged cubane clusters are obtained. A structurally characterised example of each type of product is available for M = Ni, Hg and Co as the clusters $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ **(157)**, $[\{(H_2O)_9Mo_3S_4\}_2Hg]^{8+}$ **(158)** and $[\{(H_2O)_9Mo_3S_4Co\}_2]^{8+}$ **(159)**, respectively. Starting with either the nickel product or the related molybdenum/iron cubane, reaction with copper(II) ions results in exchange of the heterometal and formation of a $[Mo_3CuS_4(aq)]^{4+}$ cubane [300].

The complex $Cp_2Mo_2Co_2(CO)_4S_3$ **(160)** can be converted into a $Mo_2Co_2S_4$ based cubane **(161)** using either thiophene or thiophenol as a source of sulfur [301]. The reverse reaction is also possible under an atmosphere of carbon monoxide, the sulfur now being lost as COS. The potential of this system as homogeneous hydrodensulfurisation catalysts is discussed. Complex **(160)** also reacts with phenyl phosphine to give a cubane like cluster that contains a (μ_3-PPh) group **(162)**; further reaction results in substitution of $PPhH_2$ for carbonyl on the cobalt atoms with cluster core rearrangement [302].

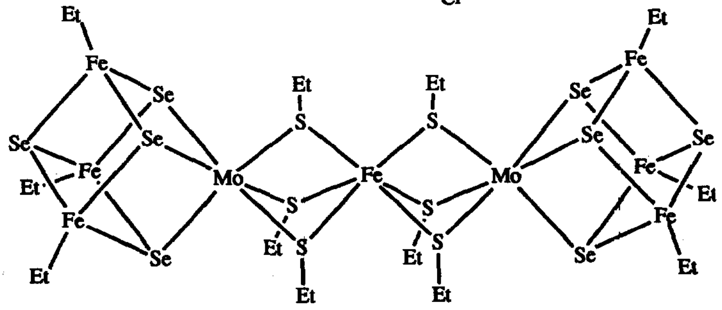
Addition of $Pt(cod)_2$ to $Mo_3X_4Cl_4(PEt_3)_3(MeOH)_2$ (X = S, Se) produces an unexpected result [303]. The incomplete cubane core remains as such, and two $Pt(PEt_3)_2$ fragments cap Mo_2S faces externally to give the mixed metal product $Mo_3Pt_2X_4Cl_4(PEt_3)_6$ **(163)**. The structure of the sulfur derivative shows that the Mo_3Pt_2 framework is essentially planar.



(163)



(164)



(165)

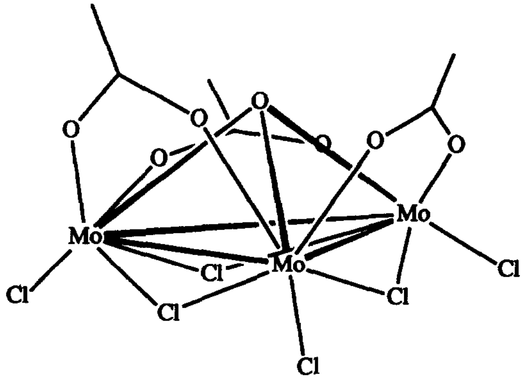
The synthesis and structure of the large Mo-Cu-S cluster compound $(^{n}Bu_4N)_4[Cu_{12}Mo_8S_{32}]$ has been presented [304]. The anion contains a condensed cubane-like $Cu_{12}Mo_8$ dimetallic cage. There are two classes of molybdenum atom in the cluster: those with terminal and μ_3-S atoms, and those with μ_2-S and μ_4-S atoms. In each case the molybdenum atoms are tetrahedrally coordinated and Mo-S bond lengths lie in the range 2.065(29)-2.301(17) Å.

There are examples of dimetallic cubane based clusters where molybdenum metal is a minority component. The copper/molybdenum double cubane $[MoS_4(CuCl)_5Cl_2]^{4-}$ (**164**) is one such example [305], as are two linked selenium cubanes that contain $MoFe_3Se_4$ cores [306]: $[Mo_2Fe_6Se_8(SEt)_9]^{3-}$ and $[Mo_2Fe_7Se_8(SEt)_{12}]^{3-}$ (**165**).

1.10.3 Other clusters

1.10.3.1 Homometallic clusters

Trinuclear molybdenum clusters containing chloro and acetate ligands have been prepared. The cluster $[Mo_3OCl_6(OAc)_3]^-$ is synthesised from $MoCl_3.3H_2O$ and either an acetic anhydride/acetic acid (HOAc) mixture or a one molar solution of acetic acid directly [307]. Each molybdenum atom is in a distorted octahedral environment with an average oxidation state of 3.33; the 8 molybdenum d electrons are delocalised over the Mo_3 cluster (average Mo-Mo = 2.570(2)Å). The related dianionic cluster and its phosphine derivatives $[Mo_3OCl_{3+n}(OAc)_3(PMe_3)_{3-n}]^{1-n}$ (n = 1, 2) (**166**) have also been prepared [308]. Structures are presented for both values of n as well as for the unsubstituted cluster with n = 3. A comparison of Mo-Mo bond lengths is shown in Table 3. The molybdenum atoms have a formal oxidation state of +3.



(**166**)

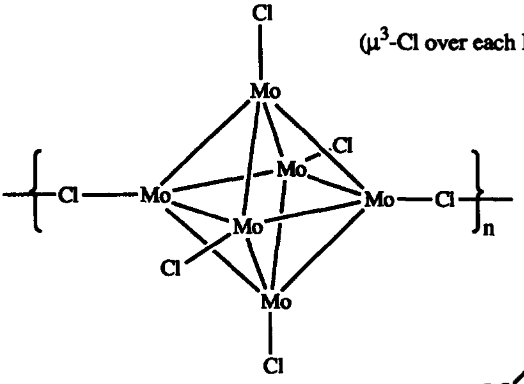
Structural analysis has also been carried out on the iodo clusters $Mo_3HI_7L_3$ (L = PEt_3, PPh_3) [309]. Whilst the hydride ligand is not located directly in the structure determination, ^1H NMR spectral data indicate that it adopts a μ_3-bonding mode with respect to the Mo_3 triangle. Comparisons are made between the structural features of the two clusters as well as with previously characterised species (L = thf, MeCN, PhCN).

Table 3 *Structural parameters for the clusters* $[Mo_3OCl_{3+n}(OAc)_3(PMe_3)_{3-n}]^{1-n}$

n	Mo-Mo bond length (Å)		
1†	2.5878(5)	2.6117(5)	2.5764(5)
	2.597(1)	2.608(1)	2.5673(9)
2	2.637(1)	2.573(1)	2.567(1)
3	2.617(1)	2.598(1)	2.598(1)

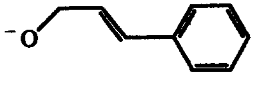
† Two structural analyses with and without thf in the unit cell.

Higher nuclearity halide molybdenum clusters have also been characterised. Intermolecular ligand exchange reactions between $[(Mo_6Cl_8)F_6]^{2-}$ and $[(Mo_6Cl_8)X_6]^{2-}$ (X = Cl, Br, I) have been carried out [310]. The mixed cluster ions $[(Mo_6Cl_8)F_nX_{6-n}]^{2-}$ (n from 1 to 6) have been characterised by their distinctive ^{19}F NMR chemical shifts. The structure of the chloro cluster $NaMoCl_{13}$, prepared from NaCl and $MoCl_2$ (1:6) at 850°C, consists of a 1-D chain of $Mo_6(\mu_3\text{-}Cl)_8Cl_4(\mu\text{-}Cl)_{2/2}$ moieties (**167**) [311]. The structure and physical properties of this cluster are discussed. Retaining the $[Mo_8Cl_6]^{4+}$ core, a cluster with (*E*)-cinnamylalcoholate ligands has been prepared [312]. Six of these *O*-donor ligands (**168**) bond terminally to the molybdenum atoms *i.e.* in place of the terminal and bridging chloride ligands in (**167**).



(μ^3-Cl over each Mo_3-face not shown)

(**167**)

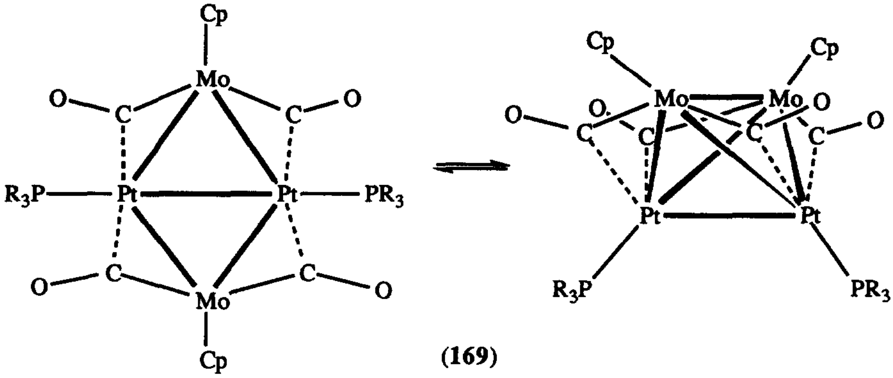


(**168**)

1.10.3.2 Heterometallic clusters

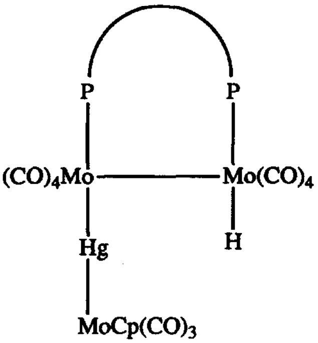
The complex $[Mo(CO)_4I_3]^-$ reacts with two or three equivalents of $[Fe_2S_2(CO)_6]^{2-}$ to produce either $[MoFe_4S_3(CO)_{14}]^{2-}$ or $[MoFe_6S_6(CO)_{16}]^{2-}$ [313]. Both clusters have been characterised structurally, though for the former this was done *via* the triethyl phosphine derivative. The molybdenum atom was shown to be in a S_3Fe_2-square pyramidal environment for the first product, and a distorted S_6-trigonal prismatic environment for the second. If $[Mo(CO)_5I]^-$ is used instead as the source of molybdenum, the reaction produces $[Mo_2Fe_2S_2(CO)_{12}]^{2-}$ which contains an octahedral $Mo_2Fe_2S_2$-core. Mechanistic schemes for the formation of all three products are presented.

The core isomerism from a planar to a tetrahedral geometry of Pt_2Mo_2 clusters is examined both experimentally and theoretically [314]. Clusters of the formula $Pt_2Mo_2(C_5H_4Me)_2(CO)_6(PR_3)$ **(169)** have been synthesised for a wide range of phosphines, and ^{31}P NMR spectral data show how the ratio of isomers depends on solvent and temperature as well as the steric and electronic effects of the phosphine ligands.



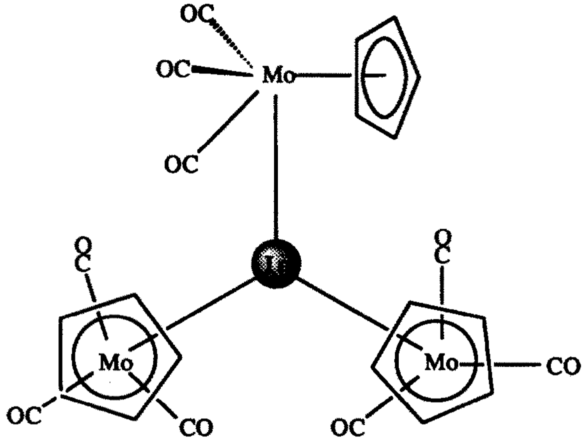
(169)

Tri- and tetra-nuclear compounds have been prepared which contain the metals mercury and molybdenum. Two results have been reported where the products can be better regarded as a chain of metal atoms as opposed to a condensed cluster [315, 316]. Interaction of $Cp(CO)_3MHgX$ (M = Cr, Mo, W; X = Cl, Br, I, N_3, SCN) with $M'(CO)_3(bpy)$ (M' = Mo, W) fragments results in the formation of dimetallic compounds $Cp(CO)_3M(\mu\text{-}Hg)M'(X)(CO)_3(bpy)$ which contain M-Hg-M'-X linkages [315]. The formation of these products can be rationalised by the $M'(CO)_3(bpy)$ fragment inserting into the Hg-X bond. The same Mo-Hg dimer (X = Cl) is used to form a Mo_3Hg compound by reaction with $[Mo_2(CO)_8(\mu\text{-}H)(\mu\text{-}L)]^-$ (L = dppm, dppe, dppp) [316]. Unlike the corresponding tungsten system, from which a spiked triangle cluster is obtained, due to ligand redistribution the tetrametallic chain type complex $(CO)_4(H)Mo(\mu\text{-}L)Mo(CO)_4\{HgMo(CO)_3Cp\}$ **(170)** is formed.



(170)

Trigonal planar complexes are formed between $[Mo(CO)_3Cp]^-$ fragments and the late group 13 elements indium and thallium [278, 317]. These heteroatoms are directly bonded to the molybdenum atoms by unsupported bonds. Both compounds $E\{M(CO)_3Cp\}_3$ (E = Ir, Th) **(171)** have been structurally characterised and comparisons are made between them [317]. Extended Hückel calculations investigate the nature of the Mo-In bonding. The related $InXL\{Mo(CO)_3Cp\}_2$ (X = Cl, I; L = X, thf, py) compounds have also been synthesised [318] and an exploration of their solution properties is reported.



(171)

REFERENCES

1. Z. Gebeyenu, F. Weller, B. Neumüller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 593 (1991) 99.
2. N. Bryson, M.-T. Youinou, J. A. Osborn, *Organometallics*, 10 (1991) 3389.
3. J. Sundermeyer, *Chem. Ber.*, 124 (1991) 1977.
4. J.R. Dilworth and J.R. Miller, *J. Chem . Ed.*, 68 (1991) 788.
5. E. Block, H. Kang and J. Zubieta, *Inorg. Chim. Acta,* 181 (1991) 227.
6. C. Bustos, C. Manzur, H. Gonzalez, R. Schrebler, D. Carrillo, C. Bois, Y. Jeannin and P. Gouzerh, *Inorg. Chim. Acta,* 185 (1991) 25.
7. M.M. Baum and E.H. Smith, *J. Chem. Soc., Chem. Commun.*, (1991) 431.
8. G.C. Bazan, J.H. Oskam, H.-N. Cho, L. Y. Park and R.R. Schrock, *J. Am. Chem. Soc.*, 113 (1991) 6899.
9. R.R. Schrock, W.E. Crowe, G.C. Bazan, M. DiMare, M.B. O'Regan and M.H. Schofield, *Organometallics,* 10 (1991) 1832.
10. T.P. Pollagi, T.C. Stoner, R.F. Dallinger, T.M. Gilbert and M.D. Hopkins, *J. Am. Chem. Soc.*, 113 (1991) 703.
11. P. Román, A. Luque, J.M. Gutiérrez-Zorrilla and S. Garcia-Granda, *Polyhedron,* 10 (1991) 2057.
12. F. Djafri, R. Lai, M. Pierrot and J. Regnier, *Acta Crystallogr., Sect. C,* 47 (1991) 1374.
13. H. Arzoumanian, H. Krentzien and H. Teruel, *J. Chem. Soc., Chem. Commun.*, (1991) 55.
14. M. Rietzel, H.W. Roesky, K.V. Katti, M. Noltemeyer, M.C.R. Symons and A. Abu-Raqabah, *J. Chem. Soc., Dalton Trans.*, (1991) 1285.
15. R. Lai, S. Mabille, A. Croux and S. Le Bot, *Polyhedron,* 10 (1991) 463.
16. R.N. Mohanty, V. Chakravorty and K.C. Dash, *Polyhedron,* 10 (1991) 33.
17. R.N. Mohanty, V. Chakravorty and K.C. Dash, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, 30 A(5) (1991) 457; *Chem. Abstr.*, 115 (1991) 63378t.

18. E.R. Møller and K.A. Jørgensen, *Acta Chem. Scand.*, 45 (1991) 546.
19. M.T.H. Tarrafder and A.R. Khan, *Polyhedron*, 10 (1991) 819.
20. M.T.H. Tarrafder and A.R. Khan, *Polyhedron*, 10 (1991) 973.
21. R.G. Bhattacharyya and S. Biswas, *Inorg. Chim. Acta*, 181 (1991) 213.
22. A.L. Rheingold and J.R. Harper, *J. Organomet. Chem.*, 403 (1991) 335.
23. M.S. Rau, C.M. Kretz, L.A. Mercando and G.L. Geoffroy, *J. Am. Chem. Soc.*, 113 (1991) 7421.
24. T. Carofiglio, C. Floriani, M. Rosi, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 30 (1991) 3245.
25. B. Krebs, B. Lettmann, H. Pohlmann and R. Fröhlich, *Z. Kristallogr.* 1996 (1991) 231.
26. S. Wolowiec and J.K. Kochi, *Inorg. Chem.*, 30 (1991) 1215.
27. M.K. Trost and R.G. Bergman, *Organometallics*, 10 (1991) 1172.
28. G. Ramakrishnan, P.S. Rao and S. Subramanian, *J. Chem. Soc., Dalton Trans.*, (1991) 3185.
29. H. Arzoumanian, R. Lai, S. LeBot, M. Pierrot and F. Ridouane, *Inorg. Chim. Acta*, 182 (1991) 173.
30. R. Lai, S. LeBot and F. Djafri, *J. Organomet. Chem.*, 410 (1991) 335.
31. Kh.T. Sharipov, G.A. Alimova and N.N. Tananaeva, *Koord. Khim.*, 17 (1991) 467; *Chem. Abstr.*, 114 (1991) 254837f.
32. A. Samotus, A. Kanas, M. Dudek, R. Grybos and E. Hodorowicz, *Transition Metal Chem.*, 16 (1991) 495, *Chem. Abstr.*, 115 (1991) 293628d.
33. M.L. Ramos, M.M. Caldeira and V.M.S. Gil, *Inorg. Chim. Acta*, 180 (1991) 219.
34. M. Jelikic-Stankov, D. Malesev, D. Veselinovic and Z. Radovic, *Polyhedron*, 10 (1991) 455.
35. I.A. Krol, Z.A. Starikova, V.S. Sergienko and E.O. Tolkacheva, *Zh. Neorg. Khim.*, 36 (1991) 406; *Chem. Abstr.*, 115 (1991) 20886q.
36. V. Kh. Sabirov, I.A. Litvinov and A.N. Yunuskhodzhaev, *Koord. Khim.*, 17 (1991) 44; *Chem. Abstr.*, 114 (1991) 177235d.
37. S.B. Kumar and M. Chaudhury, *J. Chem. Soc., Dalton Trans.*, (1991) 2169.
38. K. Unoura, Y. Kato, K. Abe, A. Iwase and H. Ogino, *Bull. Chem. Soc. Jpn.*, 64 (1991) 3372.
39. X.F. Yan and C.G. Young, *Aust. J. Chem.*, 44 (1991) 361.
40. F. Sécheresse, S. Bernés, F. Robert and Y. Jeannin, *J. Chem. Soc., Dalton Trans.*, (1991) 2875
41. R.D. Hunt, L. Andrews and L. Mac Toth, *Inorg. Chem.*, 30 (1991) 13829.
42. J.D. Carter, K.B. Kingsbury, A. Wilde, T.K. Schoch, C.J. Leep, E.K. Pham and L. McElwee-White, *J. Am. Chem. Soc.*, 113 (1991) 2947.
43. T.E. Glassman, M.G. Yale and T.R. Schrock, *Organometallics*, 10 (1991) 4046.
44. T.R. Schrock, T.E. Glassman and M.G.Vale, *J. Am. Chem. Soc.*, 113 (1991) 725.
45. E. Block, G. Ofori-Okai, H. Kang and J. Zubieta, *Inorg. Chim. Acta*, 190 (1991) 179.
46. D. Jacoby, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Chem. Soc., Chem. Commun.* (1991) 220.
47. G.L. Wilson, R.J. Greenwood, J.R. Pilbrow, J.T. Spence and A.G. Wedd, *J. Am. Chem. Soc.*, 113 (1991) 6803.
48. J. Fletcher, G. Hogarth and D.A. Tocher, *J. Organomet. Chem.*, 403 (1991) 345.
49. J. Fletcher, G. Hogarth and D.A. Tocher, *J. Organomet. Chem.*, 405 (1991) 207.
50. G. Hogarth, P.C. Konidaris and G.C. Saunders, *J. Organomet. Chem.*, 406 (1991) 153.
51. M.L.H. Green, G. Hogarth and G.C. Saunders, *J. Organomet. Chem.*, 421 (1991) 233.
52. E.A. Vasyvtinskaya, I.L. Eremenko, A.A. Pasynskii, S.E. Nefedov, A.I. Yanovskii and Yu.T. Struchkov, *Zh.. Neorg. Khim.*, 36 (1991) 1707; *Chem. Abstr.*, 115 (1991) 232431n.
53. D.O. Martire, M.C. Gonzalez, M.R. Feliz, L. Cafferata and A.L. Capparelli, *Int. J. Chem. Kinetics*, 23 (1991) 457.
54. S.R. Girish and V.B. Mahale, *Chem. Abstr.*, 115 (1991) 221780z.
55. J.I. Dulebohn, T.C. Stamatakos, D.L. Ward and D.G. Nocera, *Polyhedron*, 10 (1991) 2813.
56. Y. Sasaki and M. Miyashita, *Inorg. Chim. Acta*, 183 (1991) 15.
57. P.T. Blower, J.R. Dilworth, D. Mocherone and J. Zubieta, *Inorg. Chim. Acta.*, 179 (1991) 203.
58. B. Canosa, A.R. Gonzales-Elipe and M. Che, *J. Catal.*, 131 (1991) 300.
59. A.N. Startsev, S.A. Shkuropat, O.V. Klimov, M.A. Fedotov, P.E. Kolosov, V.K. Fedorov, S.P. Degtyarev and D.I. Kochubei, *Koord. Khim.*, 17 (1991) 229; *Chem. Abstr.*, 115 (1991) 20869m.
60. M. Broroson and A. Hazell, *Acta Chem. Scand.*, 45 (1991) 758.
61. A.L. Doadrio-Villarejo, M.T. Calabuig, C.V. Ragel and A. Doadrio-Lopez, *Transition Metal Chem.*, 16 (1991) 508; *Chem. Abstr.*, 115 (1991) 293629e.
62. F.A. Cotton, R.L. Luck and C.S. Miertschin, *Inorg. Chem.*, 30 (1991) 1155.

63. M. Gorzellik, H. Bock, Liu Gang, B. Nuber and M.L. Ziegler, *J. Organomet. Chem.*, 412 (1991) 95.
64. C-S.J. Chang and J.H. Enemark, *Inorg. Chem.*, 30 (1991) 683.
65. V. Sanz, T. Picher, P. Palanca, P. Gomez-Romero, E. Llopis, J.A. Ramirez, D. Beltran and A. Ceruilla, *Inorg. Chem.*, 30 (1991) 3113.
66. E. Llopis, A. Domenech, J.A. Ramirez, A. Ceruilla, P. Palanca, T. Picher and V. Sanz, *Inorg. Chim. Acta*, 189 (1991) 29.
67. M.S. Sastry and S.K. Kulshreshtha, *J. Inorg. Biochem.*, 41 (1991) 79; *Chem. Abstr.*, 114 (1991) 177220v.
68. N. Ueyama, N. Yoshinaga, A. Kajiwara, A. Nakamura and M. Kusunoki, *Bull. Chem. Soc. Jpn.*, 64 (1991) 2458.
69. R. Bhattacharyya, P.K. Chakraborty, P.N. Ghosh, A.K. Mukherjee, D. Podder and M. Mukherjee, *Inorg. Chem.*, 30 (1991) 3948.
70. D. Coucouvaris, A. Toupadakis, J.D. Lane, S.M. Koo, C.G. Kim and A. Hodjikyriacov, *J. Am. Chem. Soc.*, 113 (1991) 5271.
71. V.P. Fedin, B.A. Kolesov, Y.V. Mironov, O.A. Geras'ko and V.Y. Fedorov, *Polyhedron*, 10 (1991) 997.
72. A.C. Lizano, M.G. Munchof, E.K. Haub and M.E. Noble, *J. Am. Chem. Soc.*, 113 (1991) 9204.
73. J. Brunvoll, S. Gundersen, A.A. Ischenko, V.P. Spiridonov and T.G. Strand, *Acta Chem. Scand.*, 45 (1991) 111.
74. P. Sobota, J. Ejfler, T. Atuzinski and T. Lis, *Polyhedron*, 10 (1991) 2457.
75. D.H. Berry, J. Chey, H.S. Zipin and P.J. Carroll, *Polyhedron*, 10 (1991) 1189.
76. H. Adams, N.A. Bailey, G.W. Bentley, G. Hough, M.J. Winter and S. Woodward, *J. Chem. Soc., Dalton Trans.*, 11 (1991) 749.
77. J. Robbins, G.C. Bazan, J.S. Murdzek, M.B. O'Regan and R.R. Schrock, *Organometallics*, 10 (1991) 2902.
78. L.Y. Kuo, M.G. Kanatzidis, M. Sabat, A.L. Tipton and T.J. Marks, *J. Am. Chem. Soc.*, 113 (1991) 9027.
79. G.M. Jamison, P.S. White and J.L. Templeton, *Organometallics*, 10 (1991) 1954.
80. M. Etienne, P.S. White and J.L. Templeton, *J. Am. Chem. Soc.*, 113 (1991) 2324.
81. J.W. Faller and Y. Ma, *J. Am. Chem. Soc.*, 113 (1991) 1579.
82. B. Fischer, J. Strähle and M. Viscontini, *Helv. Chim. Acta*, 74 (1991) 1544.
83. C.J. Donahue, V.A. Martin, B.A.Schoenfelner and E.C. Kosinski, *Inorg. Chem.*, 30 (1991) 1588.
84. E. Block, M. Gernon, H. Kang, G. Ofori-Okai and J. Zubieta, *Inorg. Chem.*, 30 (1991) 1736.
85. H. Sur, R. Ghosh, S. Roychowdhuri and S. Seth, *Acta Crystallogr., Sect. C*, 47 (1991) 306.
86. K. Yoon, G. Parkin and A.L. Rheingold, *J. Am. Chem. Soc.*, 113 (1991) 1437.
87. P.J. Desrochers, K.W. Nebesny, M.J. LaBarre, S.K. Lincoln, T.M. Loehr and J.H. Enemark, *J. Am. Chem. Soc.*, 113 (1991) 9193.
88. R. Poli and M.A. Kelland, *J. Organomet. Chem.*, 419 (1991) 127.
89. T.E. Burrow, A. Hills, D.L. Hughes, J.D. Lane, R.H. Morris and R.L. Richards, *J. Chem. Soc., Dalton Trans.*, (1991) 1813.
90. T.E. Burrow, A.J. Lough, R.H. Morris, A. Hills, D.L. Hughes, J.D. Lane and R.L. Richards, *J. Chem. Soc., Dalton Trans.*, (1991) 2519.
91. M. Henary, W.C. Kaska and J.I. Zink, *Inorg. Chem.*, 30 (1991) 1674.
92. E. Hey-Hawkins and H.G. vonSchnering, *Z. Naturforsch. B., Chem. Sci.*, 46 (1991) 307; *Chem. Abstr.*, 115 (1991) 20944g.
93. R.S. Pilato, K.A. Eriksen, M.A. Greaney, E.I. Stiefel, S. Goswami, L. Kilpatrick, T.G. Spiro, E.C. Taylor and A.L. Rheingold, *J. Am. Chem. Soc.*, 113 (1991) 9372.
94. C.L. Soricelli, V.A. Szalai and S.J. Nieter-Burgmayer, *J. Am. Chem. Soc.*, 113 (1991) 9877.
95. D. Coucouvanis, A. Hadjikyriakov, A. Toupadakis, S-M Koo, O. Ileperuma, M. Draganjac and A. Salifoglov, *Inorg. Chem.*, 30 (1991) 754.
96. X. Yang, G.K.W. Freeman, T.B. Rauchfuss and S.R. Wilson, *Inorg. Chem.*, 30 (1991) 3034.
97. S. Boyde and C.D. Garner, *J. Chem. Soc., Dalton Trans.*, (1991) 713.
98. S.L. Gales, W.T. Pennington and J.W. Kolis, *J. Organomet. Chem.*, 419 (1991) C10.
99. S.B. Kumar and M. Chaudhury, *J. Chem. Soc., Dalton Trans.*, (1991) 1149.
100. D.S. Brown, C.F. Owens, B.G. Wilson, M.E. Welker and A.L. Rheingold, *Organometallics*, 10 (1991) 871.
101. D. Sellmann, B. Seubert, F. Knoch and M. Moll, *Z. Anorg. Allg. Chem.*, 600 (1991) 95.
102. D. Sellmann, F. Grasser, F. Knoch and M. Moll, *Angew. Chem., Int. Ed. Engl.*, 30 (1991) 1311.
103. S.K. Ibrahim and C.J. Pickett, *J. Chem. Soc., Chem. Commun.*, (1991) 246.

104. T. Yoshida, T. Adachi, K. Matsumura, K. Kawazu and K. Baba, *Chem. Lett.* (1991) 1067.
105. S.C. O'Neal, W.T. Pennington and J.W. Kolis, *J. Am. Chem. Soc.*, 113 (1991) 710.
106. E. Rentschler, W. Massa, S. Vogler, K. Dehnicke, D. Fenske, G. Baum, *Z. Anorg. Allg.Chem.*, 592 (1991) 59.
107. F. Geoffrey, N. Cloke, J.P. Day, J.C. Green, C.P. Morley and A.C. Swain, *J. Chem. Soc., Dalton Trans.*, (1991) 789.
108. K.M. Prasad, A.N. Tripathy and N.M. Thakur, *Polyhedron,* 10 (1991) 323.
109. M.H. Chisholm, I.P. Parkin, W.E. Streib and K.S. Folting, *Polyhedron,* 10 (1991) 2309.
110. M.H. Chisholm, I.P. Parkin, J.C. Huffman, E.H. Lubkovsky and K. Folting, *Polyhedron,* 10 (1991) 2839.
111. J.O. Dziegielewski, K. Filipek and B. Jezowska-Trzebiatowska, *Polyhedron,* 10 (1991) 429.
112. L. Kiriazis, R. Mattes and F. Obst, *Inorg. Chim. Acta,* 181 (1991) 157.
113. B.E. Owens and R. Poli, *Inorg. Chim. Acta,* 179 (1991) 229.
114. J.C. Gordon, H.D. Mui, R. Poli and K.J. Ahmed, *Polyhedron,* 10 (1991) 1667.
115. R. Poli and H.D. Mui, *Inorg. Chem.*, 30 (1991) 65.
116. R. Poli and J.C. Gordon, *Inorg. Chem.*, 30 (1991) 4550.
117. R. Poli and B.E. Owens, *Gaz. Chim. Ital.*, 121 (1991) 413; *Chem. Abstr.*, 115 (1991) 293609y.
118. M.J. Fernández-Trujillo, M.G. Basallote, P. Valerga, M.C. Puerta and D.L. Hughes, *J. Chem. Soc., Dalton Trans.*, (1991) 3149.
119. F.A. Cotton, L.M. Daniels, K.R. Dunbar, L.R. Falvello, C.J. O'Connor and A.C. Price, *Inorg. Chem.*, 30 (1991) 2509.
120. F.A. Cotton, C.A. James and R.L. Luck, *Inorg. Chem.*, 30 (1991) 4370.
121. K.A. Hall, S.C. Critchlow and J.M. Mayer, *Inorg. Chem.*, 30 (1991) 3593.
122. R.H. Cayton, M.H. Chisholm, E.R. Davidson, V.F. DiStasi, P. Du and J.C. Huffman, *Inorg. Chem.*, 30 (1991) 1020.
123. D.V. Baxter, M.H. Chisholm, V.F. DiStasi and J.A. Klang, *Chem. Materials,* 3 (1991) 221.
124. M.H. Chisholm, I.P. Parkin, K. Folting, E.B. Lubkovsky and W.E. Streib, *J. Chem. Soc., Chem. Commun.*, (1991) 1673.
125. T.A. Budzicnowski, S.T. Chacon, M.H. Chisholm, F.J. Fener and W. Streib, *J. Am. Chem. Soc.*, 113 (1991) 689.
126. J. Birnbaum, R.C. Haltiwanger, P. Bernatis, C. Teachout, K. Parker and M. Rakowski Dubois, *Organometallics,* 10 (1991) 1779.
127. M. Maciejewski Farmer, R.C. Haltiwanger, F. Kvietok and M. Rakowski Dubois, *Organometallics,* 10 (1991) 4066.
128. P.K. Baker, M.A. Beckett and L.M. Severs, *Polyhedron,* 10 (1991) 1663.
129. N.H. Dryden, P. Legzdiris, J. Trotter and V.C. Yee, *Organometallics,* 10 (1991) 2857.
130. P.K. Baker and D. ap Kendrick, *Inorg. Chim. Acta,* 188 (1991) 5.
131. P.K. Baker and D. ap Kendrick, *Polyhedron,* 10 (1991) 2519.
132. D. Miguel, J.A. Pérez-Martinez, V. Riera and S. Garcia-Granda, *Polyhedron,* 10 (1991) 1717.
133. E. Carmona, P.J. Daff, A. Monge, P. Palma, M.L. Poveda and C. Ruiz, *J. Chem. Soc., Chem. Commun.*, (1991) 1503.
134. A.C. Filippou, W. Grünleitner, E.O. Fischer, W. Imhof and G. Huttner, *J. Organomet. Chem.*, 413 (1991) 165.
135. A.C. Filippou, W. Grünleitner, C. Völkl and P. Kiprof, *J. Organomet. Chem.*, 413 (1991) 181.
136. G-M. Yang, G-H. Lee, S-M. Peng and R-S. Liu, *Organometallics,* 10 (1991) 1305.
137. B. Denise, P. Dubost, A. Parlier, M. Rudler, H. Rudler, J.C. Daran, J. Vaissermann, F. Delgado, A.R. Arevalo, R.A. Toscano and C. Alvarez, *J. Organomet. Chem.*, 419 (1991) 377.
138. A. Hills, D.L. Hughes, C.J. MacDonald, M.Y. Mohammed and C.J. Pickett, *J. Chem. Soc., Dalton Trans.*, (1991) 121.
139. J.-D. Chen, F.A. Cotton and S-J. Kong, *Inorg. Chim. Acta,* 190 (1991) 103.
140. F.A. Cotton and K.J. Wiesinger, *Inorg. Chem.*, 30 (1991) 871.
141. D. Sellmann, W. Kern, G. Pöhlmann, F. Knoch and M. Moll, *Inorg. Chim. Acta,* 185 (1991) 155.
142. H. Kisch and D. Garn, *J. Organomet. Chem.*, 409 (1991) 347.
143. A.C. Street, Y. Mizobe, F. Gotoh, I. Mega, H. Oshita and M. Hidai, *Chem. Lett.*, (1991) 383.
144. B. Gaylani, I. French, A.J. Pick and S.C. Wallwork, *Acta Crystallogr., Sect. C,* 47 (1991) 257.
145. A. Zinn, F. Weller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 594 (1991) 106.
146. B.W. Eichhorn, M.C. Kerby, K.J. Ahmed and J.C. Huffman, *Polyhedron,* 10 (1991) 2573.
147. M.C. Kerby, B.W. Eichorn, L. Doviken and K.P.C. Vollhardt, *Inorg. Chem.*, 30 (1991) 156.
148. J.H. Matonic, S-J. Chen, S.P. Perlepes, K.R. Dunbar and G. Christou, *J. Am. Chem. Soc.*, 113 (1991) 8169.

149. B.J. Brisdon, R.J. Deeth, A.G.W. Hodson, C.M. Kemp, M.F. Mahon and K.C. Molley, *Organometallics,* 10 (1991) 1107.
150. K-B. Shiu, C-J. Chang, S-L. Wang and F-L. Liao, *J. Organomet. Chem.*, 407 (1991) 225.
151. V.S. Joshi, A. Sarkar and P.R. Rajamoharan, *J. Organomet. Chem.*, 409 (1991) 341.
152. A.S. Gamble, P.S. White and J.L. Templeton, *Organometallics,* 10 (1991) 693.
153. G.M. Jamison, A.E. Bruce, P.S White and J.L. Templeton, *J. Am. Chem. Soc.*, 113 (1991) 5057.
154. V.S. Joshi, V.K. Kale, K.M. Sathe, A. Sarkar, S.S. Tavale and C.G. Suresh, *Organometallics,* 10 (1991) 2898.
155. S. Kurishima, N. Matsuda, N. Tamura and T. Ito, *J. Chem. Soc., Dalton Trans.*, (1991) 1135.
156. R.H. Cayton, M.H. Chisholm, J.C. Huffman and E.B. Lobkovsky, *Angew. Chem., Int. Ed. Engl.*, 30 (1991) 862.
157. R.H. Cayton, M.H. Chisholm, J.C. Huffman and E.B. Lobkovsky, *J. Am. Chem. Soc.*, 113 (1991) 8709.
158. J.M. Giraudon, J. Sala-Pala, J.E. Guerchais and L. Toupet, *Inorg. Chem.*, 30 (1991) 891.
159. T. Ito, T. Tokunaga, M. Minato and T. Nakamura, *Chem. Lett.*, (1991) 1893.
160. R.S. Herrick, M.S. George, R.R. Duff Jr, F. Henry, H. D'Aulnois, R.M. Jarret and J.L. Hubbard, *Inorg. Chem.*, 30 (1991) 3711.
161. P.K. Baker and D. ap Kendrick, *Polyhedron,* 10 (1991) 433.
162. P.K. Baker, M.A. Beckett and L.M. Severs, *J. Organomet. Chem.*, 409 (1991) 213.
163. M. Green, M.F. Mahon, K.C. Molloy, C.B.M. Nation and C.M. Woolhouse, *J. Chem. Soc.,Chem. Commun.*, (1991) 1587.
164. H. Adams, N.A. Bailey, J.T. Gauntlett, I.M. Harkin, M.J. Winter and S. Woodward, *J. Chem. Soc., Dalton Trans.*, (1991) 1117.
165. N.M. Agh-Atabay (in part), L.J. Canoira, L. Carlton and J.L. Davidson, *J. Chem. Soc., Dalton Trans.*, (1991) 1175.
166. E. Lindner, R. Fawzi, H.A. Mayer, K. Eichele and K. Pohmer, *Inorg. Chem.*, 30 (1991) 1102.
167. H. Schumann, J.H. Enemark, M.J. Labarre, M. Bruck and P. Wexler, *Polyhedron,* 10 (1991) 665.
168. W. Abriel, G. Baum, H. Burdorf and J. Heck, Z. *Naturforsch B., Chem . Sci.*, 46 (1991) 841; *Chem. Abstr.*, 114 (1991) 136312d.
169. F.A. Cotton, J. Czuchajowska and R.L. Luck, *J. Chem. Soc., Dalton Trans.*, (1991) 579.
170. F.A. Cotton and K. Weisinger, *Inorg. Chem.*, 30 (1991) 750.
171. P.K. Baker, M. van Kampen and D. Kendrick, *J. Organomet. Chem.*, 421 (1991) 241.
172. M.S. Balakrishna, S.S. Krishnamurthy and H. Manohar, *Organometallics,* 10 (1991) 2522.
173. K-B. Shiu, K-H. Yih, S-L. Wang and F-L. Liao, *J. Organomet. Chem.*, 414 (1991) 165.
174. S.E. Kegley, D.T. Bergstrom, L.S. Crocker, E.P.Weiss, W.G. Berndt and A.L. Rheingold, *Organometallics,* 10 (1991) 567.
175. J-D. Chen and F.A. Cotton, *Inorg. Chem.*, 30 (1991) 6.
176. H. Adams, N.A. Bailey, A.N. Day, M.J. Morris and M.M. Harrison, *J. Organomet. Chem.*, 407 (1991) 247.
177. J.C. Jeffery, D.W.I. Sams and K.D.V. Weerasuria, *J. Organomet. Chem.*, 418 (1991) 395.
178. F. Calderazzo, A. Juris, R. Poli and F. Ungari, *Inorg. Chem.*, 30 (1991) 1274.
179. J. Casas, R.H. Cayton and M.H. Chisholm, *Inorg. Chem.*, 30 (1991) 358.
180. M. McCann, A. Carvill, P. Guinan, P. Higgins, J. Campbell, H. Ryan and M. Walsh, *Polyhedron,* 10 (1991) 2273.
181. M. McCann and P. Guinan, *Polyhedron,* 10 (1991) 2283.
182. R.J. Blau, M.S. Goetz and R-J. Tsay, *Polyhedron,* 10 (1991) 605.
183. J.L. Davidson and F. Sence, *J. Organomet. Chem.*, 409 (1991) 219.
184. P.T. Bishop, J.R. Dilworth, T. Nicholson and J. Zubieta, *J. Chem. Soc., Dalton Trans.*, (1991) 385.
185. K-B. Shiu, K-H. Yih, S-L .Wang and F-L. Liao, *J. Organomet. Chem.*, 420 (1991) 359.
186. P.K. Baker, S.G. Fraser and D. ap Kendrick, *J. Chem. Soc., Dalton Trans.*, (1991) 131.
187. P.K. Baker and D. ap Kendrick, *J. Organomet. Chem.*, 411 (1991) 215.
188. D. Sellmann, F. Grasser and M. Moll, *J. Organomet. Chem.*, 415 (1991) 367.
189. M. Herberhold, G. Jin, W. Kremnitz, A.L. Rheingold and B.S. Haggerty, Z. *Naturforsch., B., Chem. Sci.*, 46 (1991) 500.
190. F. Gloaguen, C. Le Floc'h, F.Y. Pétillon, J. Talmarin, M. El Khalifa and J-Y. Saillard, *Organometallics,* 10 (1991) 2004.
191. R.H. Hill, A. Becalska and N. Chiem, *Organometallics,* 10 (1991) 2104.

192. R.G. Beevor, M.J. Freeman, M. Green, C.E. Morton and A.G. Orpen, *J. Chem. Soc., Dalton Trans.*, (1991) 3021.
193. A.C. Filippou and W.C. Gruenleitner, *Z. Naturforsch., B., Chem. Sci.*, 46 (1991) 216; *Chem. Abstr.*, 114 (1991) 229087d.
194. S.C. Tenhaeff and D.R. Tyler, *Organometallics*, 10 (1991) 473.
195. J.L. Davidson, *J. Organomet. Chem.*, 419 (1991) 137.
196. C.L. Sterzo, *J. Organomet. Chem.*, 408 (1991) 253.
197. N.H. Dryden, P. Legzdins, R.J. Batchelor and F.W.B. Einstein, *Organometallics*, 10 (1991) 2077.
198. M. Fei, S.K. Sur and D.R. Tyler, *Organometallics*, 10 (1991) 419.
199. R.L. Beddoes, C. Bitcon and M.W. Whitely, *J. Organomet. Chem.*, 402 (1991) 85.
200. W. Clegg, N.A. Compton, R.J. Errington, G.A. Fisher, N.C. Norman and T.B. Marder, *J. Chem. Soc., Dalton Trans.*, (1991) 2887.
201. M. Hanaya and M. Iwaizumi, *J. Organomet. Chem.*, 401 (1991) 31.
202. M. Hanaya and M. Iwaizumi, *J. Organomet. Chem.*, 417 (1991) 407.
203. T.A. George and B.B. Kaul, *Inorg. Chem.*, 30 (1991) 882.
204. T.A. George, M.A. Jackson and B.B. Kaul, *Polyhedron*, 10 (1991) 467.
205. G.J. Leigh and M. Jimenez-Tenorio, *J. Am. Chem. Soc.*, 113 (1991) 5862.
206. Y. Mizobe, T. Ishida, Y. Egawa, K. Ochi, T. Tanase and M. Hidai, *J. Coord. Chem.*, 23 (1991) 57; *Chem. Abstr.*, 115 (1991) 125623e.
207. A. Keller, *J. Mol. Catal.*, 64 (1991) 171.
208. A. Keller, *J. Organomet. Chem.*, 407 (1991) 237.
209. A. Keller, *J. Organomet. Chem.*, 415 (1991) 97.
210. T. Yoshida, T. Adachi, K. Kawazu, A. Yamamoto and N. Sasaki, *Angew. Chem., Int. Ed. Engl.*, 30 (1991) 982.
211. J-C. Wang, C-H. Sun, T.J. Chow and L-K. Liu, *Acta Crystallogr ., Sect.C* , 47 (1991) 2459.
212. S.D. Perera, B.L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, (1991) 1183.
213. M.A. Beckett, D.P. Cassidy and A.J. Duffin, *Inorg. Chim. Acta*, 189 (1991) 229.
214. K-B. Shiu, S-L. Wang and F-L. Liao, *J. Organomet. Chem.*, 420 (1991) 207.
215. J.R. Hinchcliffe and M.W. Whitely, *J. Organometal Chem.*, 402 (1991) C50.
216. P.S. Braterman, J-I. Song, S. Kohlmann, C. Vogler and W. Kaim, *J. Organomet. Chem.*, 411 (1991) 207.
217. W. Matheis and W. Kaim, *Inorg. Chim. Acta*, 181 (1991) 15.
218. W. Matheis and W. Kaim, *Z. Anorg. Allg. Chem.*, 593 (1991) 147.
219. J. L. Fourquet, M. Leblanc, A. Saravanamuthu, M.R.M. Bruce and A.E. Bruce, *Inorg. Chem.*, 30 (1991) 3241.
220. W. Kaim, S. Kohlmann, J. Jordanov and D. Fenske, *Z. Anorg. Allg. Chem.*, 598,9 (1991) 217.
221. J.A. Chudek, G. Hunter, R.L. Mackay, P. Kremminger and W. Weissensteiner, *J. Chem. Soc., Dalton Trans.*, (1991) 3337.
222. K. Zhang, A.A. Gonzalez, S.L. Mukerjee, S-J. Chou, C.D. Hoff, K.A. Kulat-Martin, D. Barnhart and G.J. Kubas, *J. Am. Chem. Soc.*, 113 (1991) 9170.
223. D.V. Khasnis, M. Lattman and U. Siriwardane, *Organometallics*, 10 (1991) 1326.
224. C.H. Ueng and R.S. Lee, *J. Chinese Chem. Soc.*, 38 (1991) 155.
225. E.G. Bakalbassis, C.A. Tsipis and A.J.L. Pombeiro, *J. Organomet. Chem.*, 408 (1991) 181.
226. E. Carmona, A.K. Hughes, M.A. Muñoz, D.M. O'Hare, P.J. Pérez and M.L. Poveda, *J. Am. Chem. Soc.*, 113 (1991) 9210.
227. C-H. Ueng and G-Y. Hwang, *J. Chem. Soc., Dalton Trans.*, (1991) 1643.
228. W.A. Herrmann, C.W. Kohlpaintner, E. Herdtweck and P. Kiprof, *Inorg. Chem.*, 30 (1991) 4271.
229. J.L. Bookham and W. McFarlane, *Polyhedron*, 10 (1991) 2381.
230. B.L. Shaw and J.D. Vessey, *J. Chem. Soc., Dalton Trans.*, (1991) 3303.
231. M. Herberhold, S. M. Frank and B. Wrackmeyer, *J. Organomet. Chem.*, 410 (1991) 159.
232. M.F.M. Al-Dulaymmi, P.B. Hitchcock and R.L. Richards, *Polyhedron*, 10 (1991) 1549.
233. M.R. Mason and J.G. Verkade, *J. Am. Chem. Soc.*, 113 (1991) 6309.
234. M.R. Mason, Y. Su, R.A. Jacobson and J.G. Verkade, *Organometallics*, 10 (1991) 2335.
235. A.M. Bond, R. Colton, S.W. Feldberg, P.J. Mahon and T. Whyte, *Organometallics*, 10 (1991) 3320.
236. M. Garcia-Basallote, P. Valerga, M.C. Puerta-Vizcaino, A. Romero, A. Vegas and M. Martinez-Ripoll, *J. Organomet. Chem.*, 420 (1991) 371.
237. M. Baudler and T. Etzbach, *Angew. Chem., Int. Ed. Engl.*, 30 (1991) 580.
238. H.S.O. Chan, T.S.A. Hor, L-T. Phang and K.L. Tan, *J. Organomet. Chem.*, 407 (1991) 353.

239. T.S.A. Hor and L.T. Phang, *Thermochimica Acta,* 178 (1991) 287; *Chem. Abstr.*, 115 (1991) 63416d.
240. W.A. Schenk and C. Neuland-Labude, *Z. Naturforsch. B., Chem. Sci.*, 46 (1991) 573; *Chem. Abstr.*, 115 (1991) 71809z.
241. J. Szymoniak, M.M. Kubicki, J. Besançon and C. Moise, *Inorg. Chim. Acta,* 180 (1991) 153.
242. M. Ogasa, M.D. Rausch and R.D. Rogers, *J. Organomet. Chem.*, 403 (1991) 279.
243. O. Heyke, W. Hiller and I-P. Lorenz, *Chem.Ber.*, 124 (1991) 2217.
244. A. Varshney and G.M. Gray, *Inorg. Chem.*, 30 (1991) 1748.
245. W. Clegg, N.A. Compton, R.J. Errington, G.A. Fisher, D.C.A. Hockless, N.C. Norman and A.G. Orpen, *Polyhedron,* 10 (1991) 123.
246. T. Schmidt, C. Krüger and P. Betz, *J. Organomet. Chem.*, 402 (1991) 97.
247. C. Jegat, M. Fouassier and J. Mascetti, *Inorg. Chem.*, 30 (1991) 1521.
248. A.E. Sánchez-Peláez and M.F. Perpiñán, *J. Organomet. Chem.*, 405 (1991) 101.
249. W. Kläui and H. Hamers, *Z. Anorg. Allg. Chem.*, 595 (1991) 151.
250. H.J. Kim, Y.K. Do, H.W. Lee, J.H. Jeong and Y.S. Sohn, *Bull. Korean Chem. Soc.*, 12 (1991) 257; *Chem. Abstr.*, 115 (1991) 125617f.
251. R.A. Henderson and K.E. Oglieve, *J. Chem. Soc., Chem. Commun.*, (1991) 584.
252. K.E. Oglieve and R.A. Henderson, *J. Chem. Soc., Dalton Trans.*, (1991) 3295.
253. M.C. Ghosh and E.S. Gould, *Inorg. Chem.*, 30 (1991) 483.
254. M.C. Ghosh and E.S. Gould, *Int. J.Chem. Kinetics,* 23 (1991) 807.
255. A.A. Eagle, M.F. Mackay and C.G. Young, *Inorg. Chem.*, 30 (1991) 1425.
256. U. Bossek, P. Knopp, C. Habernicht, K. Wieghardt, B. Nuber and J. Weiss, *J. Chem. Soc., Dalton Trans.*, (1991) 3165.
257. M. Herberhold, G.X. Jin, A. Mueller and M. Penk, *Z. Naturforsch, B. Chem. Sci.*, 46 (1991) 25; *Chem. Abstr.*, 114 (1991) 198500b.
258. R. Alvarez, J.L. Atwood, E. Carmona, P.J. Pérez, M.L. Poveda and R.D. Rogers, *Inorg. Chem.*, 30 (1991) 1493.
259. R. Poli, J.C. Gordon, J.U. Desai and A.L. Rheingold, *J. Chem. Soc., Chem. Commun.*, (1991) 1518.
260. B. Zhuarg, L. Huang, L. He, P. Yu, A. Lan and J. Lu, *Inorg. Chim. Acta,* 179 (1991) 179.
261. L. Li, G.D. Yang, G.R. Zhang, Z.K. Tang, G.Q. He, X.B. Qu, C.T. Sun and Q.J. Huang, *Chinese Science Bulletin,* 36 (1991) 464; *Chem. Abstr.*, 115 (1991) 293481a.
262. A. Berry, M.L.H. Green, J.A. Bandy and K. Prout, *J. Chem. Soc., Dalton Trans.*, (1991) 2185.
263. D. Perrey, J.C. Leblanc, C. Moise and J. Martin-Gil, *J. Organomet. Chem.*, 412 (1991) 363.
264. H-J Haupt, U. Flörke, G. Disse and C. Heinekamp, *Chem. Ber.*, 124 (1991) 2191.
265. S.A. Brew, N. Carr, M.D. Mortimer and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1991) 871.
266. N. Carr, J.R. Fernandez and F.G.A. Stone, *Organometallics,* 10 (1991) 2718.
267. G.H. Young, M.V. Raphael, A. Wojcicki, M. Calligaris, G. Nardu and N. Bresciani-Pahar, *Organometallics,* 10 (1991) 1934.
268. J-C Tsai, R.A. Wheeler, M.A. Khan and K.M. Nicholas, *Organometallics,* 10 (1991) 1344.
269. M. Cano, J.V. Heras, P. Ovejero, E. Pinilla and A. Monge, *J. Organomet. Chem.*, 410 (1991) 101.
270. J.M. McFarland, M.R. Churchill, R.F. See, C.H. Lake and J.D. Atwood, *Organometallics,* 10 (1991) 3530.
271. M.J. Chetcuti, P.E. Fanwick, S.R. McDonald and N.N. Rath, *Organometallics,* 10 (1991) 1551.
272. P. Braunstein, B. Oswald, A. Decian and J. Fischer, *J. Chem. Soc., Dalton Trans.*, (1991) 2685.
273. M. Cano and J.A. Campo, *Polyhedron,* 10 (1991) 133.
274. M. Cano and J.A. Campo, *Polyhedron,* 10 (1991) 2611.
275. M.M. Kubicki, P. Richard and M. Jannin, *Acta Crystallogr., Sect C,* 47 (1991) 2362.
276. E. Rosenberg, K.I. Hardcastle, M.W. Day, R. Gobetto, S. Hajela and R. Muftikian, *Organometallics,* 10 (1991) 203.
277. V. Saboonchian, G. Wilkinson, B. Hussain-Bates and M.B. Hursthouse, *Polyhedron,* 10 (1991) 595.
278. D.L. Thorn, *J. Organomet. Chem.*, 405 (1991) 161.
279. J. Kim, Y. Do, Y.S. Sohn, C.B. Knobler and M.F. Hawthorne, *J. Organomet. Chem.*, 418 (1991) C1.
280. J.R. Chipperfield, S. Clark, D.E. Webster and H. Yusof, *J. Organomet. Chem.*, 421 (1991) 205.
281. H. Piana, U. Kirchgäßner and U. Schubert, *Chem. Ber.*, 124 (1991) 743.
282. E. Gumaer, K. Lettko, L. Ma, D. Macherone and J. Zubieta, *Inorg. Chim. Acta,* 179 (1991) 47.
283. G. Shikkim, D.A. Keszler and C.W. Dekock, *Inorg. Chem.*, 30 (1991) 574.

284. J. Glerup, A. Hazell and K. Michelsen, *Acta Chem. Scand.*, 45 (1991) 1025.
285. N. Ya. Turova, V.G. Kessler and S.I. Kucheiko, *Polyhedron,* 10 (1991) 2617.
286. H. Ichida and A. Yogasaki, *J. Chem. Soc., Chem. Commun.*, (1991) 27.
287. F.A. Cotton, P.A. Kibala and C.S. Miertschin, *Inorg. Chem.*, 30 (1991) 548.
288. V.P. Fedin, M.N. Sokolov, V.Y. Fedorov, D.S. Yufit and Y.T. Struchkov, *Inorg. Chim. Acta,* 179 (1991) 35.
289. K. Hegetschweiller, T. Keller, W. Amrein and W. Schneider, *Inorg. Chem.*, 30 (1991) 873.
290. H. Zimmermann, K. Hegetschweiller, T. Keller, V. Gramlich, H.W. Schmalle, W. Petter and W. Schneider, *Inorg. Chem.*, 30 (1991) 4336.
291. K. Hegetschweiller, T. Keller, M. Bäumle, G. Rihs and W. Schneider, *Inorg. Chem.*, 30 (1991) 4342.
292. V.P. Fedin, M.N. Sokolov, O.A. Gerasko, A.V. Virovets, N.V. Podberezskaya and V. Ye. Fedorov, *Inorg. Chim. Acta,* 187 (1991) 81.
293. L. Shao-Fang, H. Jian-Quan, Z. Hang-Hui, L. Jun-Gian, W. Ding-Ming, H. Zi-Xiang, L. Con-Zhang, H. Jin-Ling and L. Jia-Xi, *Polyhedron,* 10 (1991) 2203.
294. P. Baird, J.A. Bandy, M.L.H. Green, A. Hamnett, E. Marseglia, D.S. Obertelli, K. Prout and J. Qin, *J. Chem. Soc., Dalton Trans.*, (1991) 2377.
295. Z. Nianyong, W. Xinato and L. Jiaxi, *J. Chem. Soc., Chem. Commun.*, (1991) 235.
296. N. Zhu, Y. Zheng and X.Wu, *Polyhedron,* 10 (1991) 2743.
297. T. Shibahara and M. Yamasaki, *Inorg. Chem.*, 30 (1991) 1678.
298. T. Shibahara, M. Yamasaki, H. Akashi and T. Katayama, *Inorg. Chem.*, 30 (1991) 2693.
299. T. Shibahara, H. Akashi, M. Yamasaki and K. Hasimoto, *Chem. Lett.*, (1991) 689.
300. T. Shibahara, T. Asano and G. Sakane, *Polyhedron,* 10 (1991) 2351.
301. U. Riaz, O. Curnow and M.D. Curtis, *J. Am. Chem. Soc.*, 113 (1991) 1417.
302. O.J. Curnow, J.W. Kampf and M.D. Curtis, *Organometallics,* 10 (1991) 2546.
303. T. Saito, T. Tsuboi, Y. Kajitani, T. Yamagata and H. Imoto, *Inorg. Chem.*, 30 (1991) 3575.
304. L. Jiguo, X. Xinquan, Z. Zhangyuan and Y. Kaibei, *J. Chem. Soc., Chem. Commun.*, (1991) 249.
305. F. Sécheresse, F. Robert, S. Marzak, J-M Manoli and C. Potvin, *Inorg. Chim. Acta.*, 182 (1991) 221.
306. M.A. Greaney, C.L. Coyle, R.S. Pilato and E.I. Stiefel, *Inorg. Chim. Acta,* 189 (1991) 81.
307. F.A. Cotton, M. Shang and Z.S. Sun, *J. Am. Chem. Soc.*, 113 (1991) 3007.
308. F.A. Cotton, M. Shang and Z.S. Sun, *J. Am. Chem. Soc.*, 113 (1991) 6917.
309. A. Burini, F.A. Cotton and J. Czuchajowska, *Polyhedron,* 10 (1991) 2145.
310. K. Harder, G. Peters and W. Preetz, *Z. Anorg. Allg. Chem.*, 598 (1991) 139.
311. S. Böschen and H-L. Keller, *Z. Kristallogr.*, 196 (1991) 159.
312. N. Perchenek and A. Sumon, *Acta Crystallogr., Sect C,* 47 (1991) 2354.
313. P.A. Eldredge, K.S. Bose, D.E. Barber, R.F. Bryan, E. Sunn, A. Rheingold and B. Averill, *Inorg. Chem.*, 30 (1991) 2365.
314. P. Braunstein, C. de Méric de Bellefon, S-E. Bouaoud, D. Grandjean, J-F Halet and J-Y Saillard, *J. Am. Chem. Soc.*, 113 (1991) 5283.
315. J. Granifo and M.E. Vargas, *J. Organomet. Chem.*, 408 (1991) 357.
316. R. Reina, O. Rossell, M. Seco and A. Perales, *J. Organomet. Chem.*, 415 (1991) 101.
317. L.M. Clarkson, W. Clegg, D.C.R. Hockless, N.C. Norman and T.B. Marder, *J. Chem. Soc., Dalton Trans.*, (1991) 2229.
318. L.M. Clarkson, W. Clegg, D.C.R. Hockless, N.C. Norman, L.J. Farrugia, S.G. Bott and J.L. Atwood, *J. Chem. Soc., Dalton Trans.*, (1991) 2241.