4.   Molybdenum   1993

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CONTENTS

INTRODUCTION

This review surveys the coordination chemistry of molydenum reported in 1993, and follows the same format as the one which covered 1992 [1]. The references have been located by a search of volumes 118, 119 and 120 of *Chemical Abstracts*, together with use of the Current Contents and

BIDS databases; in addition all the major inorganic chemistry journals have been examined individually. Where appropriate, late references from 1992 have also been included. The review is restricted to coordination complexes, including carbonyls but excluding organometallic compounds and solid-state chemistry. Synthetic models of Mo centres and clusters in biological systems are covered, but biochemical studies of the enzymes themselves are not.

A major review on the synthesis of sulfur-bridged molybdenum and tungsten complexes which covers dinuclear species, cubanes and related clusters has appeared [2]. General reviews which contain some relevant material include those on poly(pyrazolyl)borate chemistry [3], *N*-halogenoimido complexes [4] and developments in the chemistry of selenide and telluride ligands [5]. A re-evaluation of the controversial phenomenon of bond-stretch isomerism also deals extensively with molybdenum complexes [6].

4.1   MOLYBDENUM(VI)

#### 4.1.1   Complexes with halide ligands

A recent paper includes calculations of the optimised geometries of MoF_6 and hypothetical $MoCl_6$ [7]. Under conditions of rapid cooling, MoF_6 vapour has been induced to crystallise in a previously unobserved monoclinic form, which was studied by electron diffraction [8]. Salts such as $[CpFe(\eta-C_5H_4X)][MoF_6]$ (X = Br, I) and $[CoCp_2.2MeCN]_2[MoF_6]$ have been prepared by the use of MoF_6 as a strong oxidant with various metallocenes [9].

4.1.2   Complexes with nitrogen donor ligands

The adduct $[Mo(N)Cl_3(dme)]$ has been prepared by adding dme to the nitrido complex $[Mo(N)Cl_3]$; its crystal structure was determined and the W analogue was also made [10]. The reaction of $[Mo(N)Cl_3]$ with the phosphine imine $Me_3SiN=PPh_3$ produced the unusual salt $[Mo(NPPh_3)_4][Mo(N)Cl_3(NPPh_3)]_2$ which contains a homoleptic tetrahedral dication and two square pyramidal anions with the nitrido ligand in the axial position [11].

The phosphoniomethylene complex $[Mo(N^tBu)_2Cl(=CHPPh_3)]$, made by addition of $Ph_3P=CH_2$ to $[Mo(N^tBu)_2Cl_2]$, has been shown to undergo insertion of CO, MeNC and $Ph_2C=C=O$ into the Mo–C bond; it has also been used in the ring expansion reactions of lactones [12, 13]. In the case of $[Mo(N^tBu)_2(NH^tBu)_2]$ insertion of ^tBuNCO into the two amide ligands occurs to give the ureate complex $[Mo(N^tBu)_2(N^tBuCONH^tBu)_2]$ (1) [14]. Reduction of the readily accessible $[Mo(NR)_2Cl_2(dme)]$ (R = 2,6-$C_6H_3^iPr_2$) with magnesium in the presence of PMe_3 affords $[Mo(NR)_2(PMe_3)_2]$; the two PMe_3 ligands can be replaced by PMe_2Ph [15]. The transfer of imido groups from Mo to Os has been achieved in the reaction of $[Mo(NR)_2(O^tBu)_2]$ (same R) with OsO_4 to give $[OsO_2(NR)_2]$; if an excess of the molybdenum reagent was used, $[OsO(NR)_3]$ was formed as well [16]. Treatment of MoO_2Cl_2 with $HN(SiMe_3)_2$ produced the imido-siloxide species $[Mo(NSiMe_3)_2(OSiMe_3)_2]$ [17]. The mixed imido-oxo complex $[MoO(N^tBu)(OSiMe_3)Cl]$ can be arylated with MesMgBr to give $[Mo(N^tBu)Mes_3(OSiMe_3)]$,

which is trigonal bipyramidal with the mesityl ligands in the equatorial sites. At 1.786(10) Å, the Mo=N bond is one of the longest recorded for a linear imido group [18]. The reaction of [MoO$_2$(Et$_2$dtc)$_2$] with ArNCO (Ar = 2,6-C$_6$H$_3$^{i}Pr$_2$) gave [Mo(NAr)$_2$(Et$_2$dtc)$_2$] as expected; however the crystal structure shows that both imido ligands are linear, in contrast to the archetypal complex [Mo(NPh)$_2$(Et$_2$dtc)$_2$] which contains one linear and one bent imido ligand [19]. The reaction of [MoO$_2$(Et$_2$dtc)$_2$] with only one equivalent of PhNCO causes disintegration of the dithiocarbamate ligand, with formation of [Mo(NPh)(S$_2$)(Et$_2$dtc)$_2$] (2) and the Mo(V) dimer [Mo$_2$O$_2$(μ-NPh)$_2$(Et$_2$dtc)$_2$]; obviously a redistribution of the available ligands is also involved [20]. Photolysis of [Mo(=NNRPh)$_2$(Et$_2$dtc)$_2$] (R = alkyl, Ph) in tetrachloroethane resulted in transfer of the hydrazide ligand to the solvent, giving dichloroacetohydrazides and dichloroacetamides; this was shown not to involve free nitrenium ions [21].
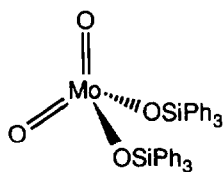

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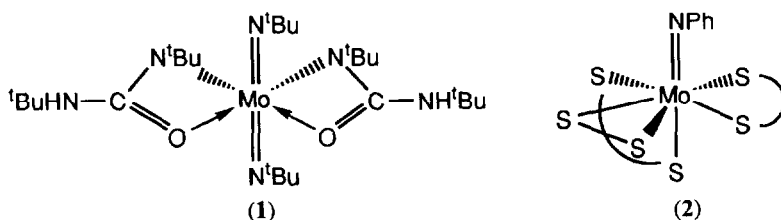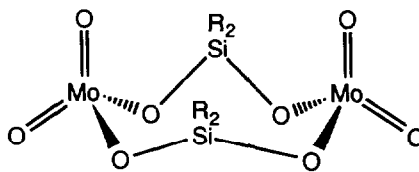
4.1.3   Complexes with oxygen donor ligands

An *ab initio* study of [M$_2$O$_7$]$^{2-}$ where M = Cr, Mo or W has obtained optimised geometries, atomic populations, electron densities and electronic spectra which show good agreement with the experimentally observed ones [22]. The speciation of Mo(VI) in acid solution has been investigated by EXAFS and XANES analysis; monomeric MoO$_2$$^{2+}$ is present in HClO$_4$, HNO$_3$ or H$_2$SO$_4$, but in HCl chloride coordination occurs and [MoO$_2$Cl$_2$] can be isolated from these solutions by ether extraction [23]. Complex formation between molybdate and lactate in the pH range 2–7.5 has been studied by potentiometry and analysed with the Superquad program; a complex of the type [MoO$_2$L$_2$]$^{2-}$ where H$_2$L = lactic acid was observed [24]. A similar study with aspartate in the pH range 1.2–7.5 identified a total of nine species, including [MoO$_3$L]$^{2-}$ and [MoO$_2$L$_2$]$^{2-}$ [25]. A ^{95}Mo and ^{13}C NMR study of the interaction of aqueous molybdate with the ligands EDDA (RNHCH$_2$CH$_2$NHR where R = CH$_2$COOH), DTPA (R$_2$NCH$_2$CH$_2$NRCH$_2$CH$_2$NR$_2$) and TTHA (R$_2$NCH$_2$CH$_2$NRCH$_2$CH$_2$NRCH$_2$CH$_2$NR$_2$) has appeared; both 1:1 and 2:1 complexes were detected [26]. Stability constants for the complexation of Mo(VI) by salicyldoxime and 2-hydroxybenzophenone oxime have also been calculated [27]. The reduction of acetylene by a catalyst system derived from molybdate, homocitric acid and N-methyl imidazole led to the proposal of a similar active site for nitrogenase [28].

    Treatment of Ag$_2$MoO$_4$ with Ph$_3$SiCl gave air-stable [MoO$_2$(OSiPh$_3$)$_2$] (3) in >90% yield. Addition of PPh$_3$ then gave [MoO$_2$(OSiPh$_3$)$_2$(PPh$_3$)], the first example of a Mo(VI) phosphine complex [29]. The unusual 8-membered ring complex (4) was prepared by the reaction of

[MoO2Br2] with ^{t}Bu2Si(OH)2 and BuLi [30]. The interaction of Na2MoO4 with Me3SnCl produced [MoO2(OSnMe3)2]; crystals of this compound were isolated as a by-product in the reaction of [Mo(CN)8]$^{4-}$ with Me3SnCl and shown to have a complicated polymeric structure [31]. The synthesis and structure of [Fe2(μ-O)(μ-MoO4)(L)2] (L = tris-2-pyridylamine) have been reported; similar compounds were made with bridging sulfate, phosphate or vanadate groups [32]. Refluxing a solution of Cr(CO)6 with sodium molybdate in propionic anhydride for 2 days produced dimeric Na2[CrMo3O4(O2CEt)8]2 [33]. The synthesis and crystal structure of the salt [Pd(NH3)4][MoO4] has been reported, and the structure of [NH4]2[Cu(NH3)2(MoO4)2] has also been determined; there is a square planar geometry at Cu with a *trans* arrangement of the ammine and molybdate ligands [34, 35].
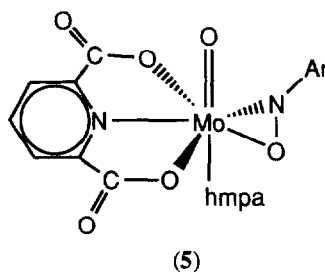

(3)   (4)

Reduction of [MoO3(tacn)].3H2O with Zn produced a green solution containing [Mo2(μ-OH)2(H2O)2(tacn)2]$^{4+}$ which was oxidized on exposure to air to the known [Mo2O4(tacn)2]$^{2+}$; adding more [MoO3(tacn)] to the green solution gave a low yield of [Mo3(μ-O)3(μ3-O)(tacn)3]$^{4+}$, though if the solution is too acidic this decomposes to [Mo3(μ-O)3(μ3-O)(H2O)9]$^{4+}$ [36]. Starting from the complex [LMoOI2]$^+$, a range of Mo(IV), Mo(V) and Mo(VI) complexes can be prepared where L = 1,4,7-trimethyl-1,4,7-triazacyclononane; these include [LMoOI2], [LMoO(OMe)2]$^+$ and [LMoO2(OMe)]$^+$ as well as the mixed valence Mo(IV)/Mo(VI) species [LMoO(I)(μ-O)MoO2L]$^+$ and its dicationic oxidation product [37]. Anodic oxidation of Mo metal in MeOH containing LiCl produced [MoO(OMe)4]2; its X-ray structure shows pseudo-centrosymmetric dimers with two bridging methoxide ligands [38].

Numerous publications have appeared on the synthesis and application of molybdenum peroxo complexes. Several papers deal with the immobilisation of Mo complexes on polymer supports, usually by treatment with [MoO2(acac)2]. One approach consists of functionalising chloromethylated styrene-divinylbenzene copolymer with acac [39], but polymers with other suitable chelating groups such as Schiff's bases can also be used [40, 41]. Such species have then been examined in catalytic epoxidation reactions with ^{t}BuOOH [42, 43]. Both the rate and yield of epoxidation reactions catalysed by [MoO2Cl2L], where L is a derivative of 3-diethoxyphosphoryl camphor, were found to be improved by addition of molecular sieves; for example, a 25% conversion of styrene was improved to 96% with 94% selectivity [44].

A battery of techniques, including ^{95}Mo, ^{1}H and ^{17}O NMR and EPR spectroscopies, has been used to study the epoxidation of cyclohexene by ^{t}BuOOH or cumene hydroperoxide catalysed by [MoO2(acac)2]. They revealed the initial formation of species such as [MoO2(OOR)2],

[MoO$_2$(OR)$_2$] and [MoO(O$_2$)(acac)$_2$], which are gradually replaced by complexes of the type [MoO$_2$(diol)$_2$] and [MoO$_2$(diol)(OOR)], with the latter thought to be the active epoxidation agent [45, 46]. A similar study of the epoxidation of cyclohexene by H$_2$O$_2$ suggested the formation of [MoO(O$_2$)(acac)$_2$], [Mo$_6$O$_{19}$]$^{2-}$, and [{MoO$_2$(acac)}$_2$(μ-O)], and a species formulated as [MoO(O$_2$)$_2$L] or [MoO(O$_2$)$_2$L(H$_2$O)] where L is H$_2$O$_2$. The same paper showed that in reactions catalysed by [MoO(O$_2$)$_2$(hmpa)(H$_2$O)], coordination of the alkene is probably not an important step in the epoxidation process [47]. A separate study of the epoxidation of 2-methyl-2-pentene with cumene hydroperoxide and [MoO$_2$(acac)$_2$] also suggested the formation of a hydroperoxide-catalyst complex [48].

The formation of nitroso compounds (RNO) from primary aromatic amines RNH$_2$ and H$_2$O$_2$ is catalysed by the complex [MoO(O$_2$)$_2$(hmpa)(H$_2$O)] at room temperature over 14–72 hours [49]. The same authors reported that cyclohexylamine could be oxidised to cyclohexanone, its oxime, and nitrocyclohexane by the same means, and isolated the complex [MoO$_3$(CyNH$_2$)$_2$(H$_2$O)] from a stoichiometric reaction [50]. With benzylic amines, the species [MoO$_2$(O$_2$)(PhCH$_2$NH$_2$)$_2$] could be isolated, and proved to be a catalyst for the oxidation of benzylamine to its oxime [51]. The first examples of Mo complexes with side-bound nitosoarene ligands (5) have been prepared by treatment of [MoO$_2$(dipic)(hmpa)] (H$_2$dipic = 2,6-pyridine dicarboxylic acid) either with aromatic hydroxylamines, or with H$_2$O$_2$ and the corresponding amine. Treatment of the product with further H$_2$O$_2$ gives free nitrosoarenes and regenerates [MoO(O$_2$)(dipic)], and a catalytic cycle for the conversion of amines to the corresponding nitrosoarenes was again developed [52].

(5)

The correlation between O–O bond length, as measured by vibrational frequency, and the ability of the complex to accept an electron, as measured by reduction potential, has been studied for a number of Mo(VI) peroxo species including [MoO(O$_2$)$_2$(hmpa)(H$_2$O)] and [MoO(O$_2$)$_2$L]$^-$ where HL = PhCO$_2$H, 2-picolinic acid, or 2-picolinic acid N-oxide [53]. These complexes, together with [MoO(O$_2$)(dipic)], were also investigated in the oxidation of cyclohexanol and 1-octanol; anionic complexes were found to be more effective than neutral ones, and a vacant apical coordination site was also important [54]. Although usually very stable in dichloroethane solution, the same complexes were found to release oxygen when treated with [Co(acac)$_2$], with anionic ones most susceptible to this decomposition [55]. The same group have also studied the oxidation of *meso*- and *d, l*-hydrobenzoin with [MoO(O$_2$)$_2$(hmpa)(H$_2$O)] and [MoO(O$_2$)$_2$(pic-*O*)]$^-$; the former complex gives largely benzaldehyde from both isomers whereas the second gives mainly benzil

from the *meso* form, possibly *via* a glycol complex intermediate [56]. The Baeyer-Villiger oxidation of cyclopentanone to valerolactone has also been examined; in this case the reaction appears to be effected by free H_2O_2 with [MoO(O_2)(dipic)] acting as a catalyst due to its strongly acid nature [57]. Attempts to insert oxygen into the Pd–C bonds of cyclopalladated complexes with [MoO(O_2)$_2$(hmpa)(H_2O)] were largely unsuccessful and instead products were obtained resulting from attack of alkoxide or halide (from the CH_2Cl_2 solvent); this does however allow the conversion of a C–H bond to an ether function by palladation then alkoxylation [58].
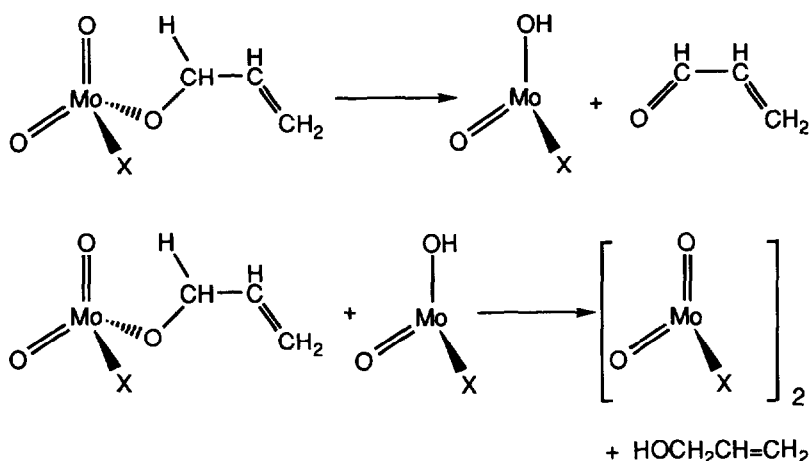
A number of synthetic routes to peroxo species have been described. The use of a sacrificial metal anode in H_2O_2 allowed the synthesis of [MoO(O_2)$_2$L$_2$] (L$_2$ = bpy, phen) [59] and K_2[MoO(O_2)F_4] was produced by a similar technique in a H_2O_2/HF mixture [60]. The formation of a compound [MoO(O_2)(TMP)] by reversible oxidation of the porphyrin complex [MoO(TMP)] with O_2 has been reported; the dioxygen unit appears to be bound side-on as a peroxo ligand [61]. Other species prepared include [MoO(O_2)$_2$(L)(H_2O)] where L = adenine or adenosine [62] and [MoO(O_2)L$_2$] where HL = glycine or leucine [63]. A short report on the oxidation of bromide with [MoO(O_2)$_2$(ox)]$^{2-}$ has also appeared [64].

Density functional theory calculations have been carried out on the ground state energies of [MO$_2$X$_2$] where M = Cr, Mo and X = F, Cl [65]. Addition of diglyme to [MoO$_2$Cl$_2$] affords the adduct [MoO$_2$Cl$_2$(diglyme)] in which one of the terminal oxygen atoms of the ether ligand is uncoordinated; there is a rapid exchange between the coordinated and uncoordinated ends, observable by variable temperature NMR methods [66]. Adducts of [MoO$_2$Cl$_2$] with ^{t}BuDAB (i.e. ^{t}BuN=CHCH=N^{t}Bu) and *N,N*-dimethylpiperazine have also been characterised; this paper also contains the structure of [MoO$_2$Cl$_2$(tmen)], which displays the unusual *cis*-dioxo, *cis*-dichloro geometry [67]. Another example of this is found in the adduct with tetramethylcyclam (1,4,8,11-tetramethyl-1,4,8,11-tetrazacyclotetradecane); on the other hand the reaction of [MoO$_2$Cl$_2$] with [15]aneN$_4$ (1,4,8,12-tetrazacyclopentadecane, H$_4$L) produced a compound of the type [MoO$_2$(H$_3$L)][Cl] in which the ligand is tetradentate and uninegative [68].

Complexes with 2,2'-biimidazole (H$_2$bim) such as [MoO$_2$Cl$_2$(H$_2$bim)] and [MoO$_2$(Hbim)$_2$] have been prepared [69]. Crystallisation of Mo(VI) in HCl containing Et$_4$NCl produced [MoO$_2$Cl$_2$(H$_2$O)$_2$].H$_2$O.Et$_4$NCl, which has the more normal *cis*-dioxo, *trans*-dichloro arrangement; with hydrogen bonding interactions with the water of crystallisation; vibrational spectra confirm that this is also the major species in solution [70].

The synthesis and crystal structure of [MoO$_2$Cl$_2$L$_2$] where L$_2$ is the chelating phosphine oxide (MeOCH$_2$CH$_2$)$_2$P(=O)CH$_2$CH$_2$P(=O)(CH$_2$CH$_2$OMe)$_2$, have also been reported [71].

Further studies on chemistry related to the oxidation of propene to acrolein and acrylonitrile (the SOHIO process) have appeared. Treatment of [MoO$_2$Cl$_2$] with LiOCH$_2$CH=CH$_2$ and bpy gave [MoO$_2$(OR)(X)(bpy)] where X = Cl or OR, which decomposes at 65°C to acrolein, allyl alcohol and [MoO$_2$Cl(bpy)]$_2$. Similar imido species could be prepared from [Mo(N^{t}Bu)$_2$Cl$_2$]. The decomposition is a two step process, involving firstly 1,4 hydrogen-transfer to an oxo ligand, followed by dimer formation, illustrated in Scheme 1 [72].

$$+ \; HOCH_2CH=CH_2$$

Scheme 1. Coordination of the bpy ligand is ignored

Two groups have reported the alkylation of [(HBpz*$_3$)MoO$_2$Cl] to complexes of the type [(HBpz*$_3$)MoO$_2$R]; in one instance AlMe$_3$ was used, and in the other either MeMgI or Me$_3$SiCH$_2$MgCl [73, 74]. Reproducible routes to [Cp*MoO$_2$Cl] and [Cp*MoOCl$_2$] have been published [75].

The complex [MoO$_2$(acac)$_2$] has been shown to be an effective catalyst for the protective formation of tetrahydropyran derivatives of alcohols and phenols, and also for the methoxymethylation of alcohols [76, 77]. Two groups have described the preparation of salicylate complexes of the MoO$_2^{2+}$ core. In one case [MoO$_2$(sal)$_2$]$^{2-}$ (H$_2$sal = salicylic acid) was prepared as its 1-methylimidazolium salt by heating [Mo(CO)$_6$] in molten [1-MeIm][Hsal] [78]; the same anion was made and crystallographically characterised as its [NMe$_4$]$^+$ salt by the more convenient reaction of molybdate with salicylate. Dimeric, insoluble [Mo$_2$O$_5$(sal)$_2$]$^{2-}$ was also prepared [79]. The complexes [MoO$_2$(ox)$_2$(OC$_6$H$_4$OH)$_2$]$^{4-}$ and [MoO(ox)$_2$(OC$_6$H$_4$OH)$_4$]$^{4-}$ have been made from oxalate and 1,3-dihydroxybenzene [80]. The reaction of molybdate or [MoO$_2$(acac)$_2$] with 2-aminophenol (H$_2$amp) produced [MoO$_2$(Hamp)$_2$] [81]. Further studies on the complexation of molybdate with 1-hydroxyethylidenediphosphonic acid (H$_4$L) have led to the isolation of K$_6$[MoO$_2$L$_2$].12H$_2$O [82]. Complexes of MoO$_2^{2+}$ with 2-mercapto-3-phenylquinazoline-4-one and with 1-substituted 2-tetrazoline-5-thiones have been prepared [83, 84] and a species with hexamethyleneimine carbodithioate as a ligand has also been characterised [85]. The synthesis and IR spectra of [NH$_4$][MoO$_2$(OH)$_3$L] where L = S(CH$_2$Ph) or Se(CH$_2$Ph)$_2$ have been reported [86]. An IR, ^{1}H and ^{95}Mo NMR study of compounds of the type [Mo$_2$O$_5$(OH)$_2$L] where L is various amino acids has appeared [87].

Numerous complexes of the MoO$_2^{2+}$ unit containing Schiff's base ligands have been prepared and studied. For uninegative ligands (from HL) they usually take the form [MoO$_2$L$_2$] or [Mo$_2$O$_5$L$_2$], and for dianionic ones (from H$_2$L) they tend to be [MoO$_2$L(S)] where S = solvent. One unusual example arose from the reaction of hexamethylenetetramine and salicylaldehyde in the

presence of $[NBu_4]_4[Mo_8O_{26}]$, which gave the dimeric species $[Mo_2O_5(\mu-OMe)(OC_6H_4CH=NCH_2N=CHC_6H_4O)]$, **(6)**, derived from decomposition of the amine ligand into NH_3 and HCHO due to adventitious water [88]. Details of the derivation of the other Schiff's bases and the complexes formed are summarised in Table 1.
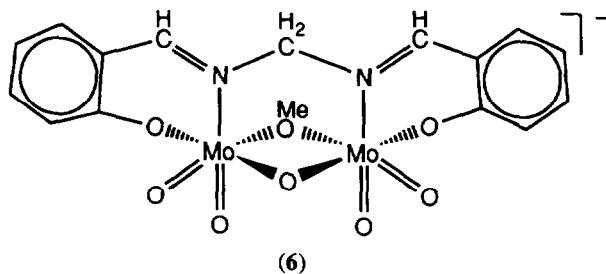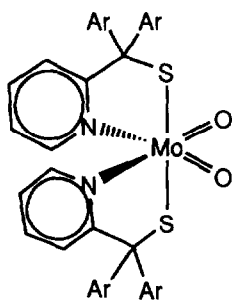

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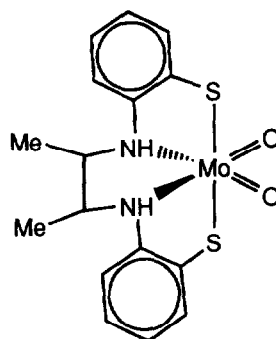**Table 1. Dioxomolybdenum (VI) complexes with Schiff's base ligands**

Carbonyl compound	Amine	Complex type	Reference
Salicylaldehyde o-hydroxyacetophenone	$H_2NNHCOC_6H_4$-4-NO_2	$[MoO_2(HL)_2]$	[89]
Salicylaldehyde o-hydroxyacetophenone	2-hydroxy-1,3-diaminopropane	$[MoO_2L]$	[90]
Salicylaldehyde o-hydroxyacetophenone and others	2-aminoethanol	$[MoO_2L]$ $[MoO_2L(EtOH)]$	[91]
5-X-salicylaldehyde (X = H, Me, Cl, Br, NO_2)	$H_2NNHC(S)SMe$	$[MoO_2L]_n$ $[MoO_2(L)(S)]$ S = py, dmso, dmf	[92]
Methylene bis(5- salicylaldehyde) Dithio bis(5- salicylaldehyde)	o-aminophenol 2-aminoethanol 2-amino-2-methylpropanol 1-amino-2-methylpropanol	$[\{MoO_2\}_2L]$ $[\{MoO_2(py)\}_2L]$	[93]
1-phenyl-3-methyl- 4-benzoylpyrazolone	p-anisidine m-toluidine m-phenetidine o-, m- and p-phenylene- diamine	$[MoO_2(HL)_2]$ $[Mo_2O_4(L)(OEt)_x]$	[94]
Benzil Biacetyl Glyoxal	Semicarbazide Thiosemicarbazide	$[MoO_2L]$	[95]

Only one paper has appeared this year on the interaction of [MoO$_2$(acac)$_2$] with aryl hydrazines to give [Mo(NNAr)$_2$(acac)$_2$]; the crystal structures of the complexes with Ar = *p*-tol and *p*-C$_6$H$_4$OMe were determined, showing singly bent diazenido ligands [96].

Several papers deal with complexes which are designed to mimic the action of oxotransferase enzymes. In connection with this, a short review deals with the thermodynamics of oxygen transfer reactions, including a section on molybdenum complexes [97]. A second, more general review of atom transfer reactions has also appeared [98]. The reaction of [MoO$_2$(acac)$_2$] with Ar$_2$C(2-pyridyl)EH where E = O or S and Ar = Ph or *p*-C$_6$H$_4$^{t}Bu, gave [MoO$_2$(ECAr$_2$C$_5$H$_4$N)$_2$]; the complex with E = S and Ar = *p*-C$_6$H$_4$^{t}Bu (7) transfers oxygen to PEt$_3$ or various other substrates to give the corresponding Mo(IV) complex [MoO(SCAr$_2$C$_5$H$_4$N)$_2$] [99]. The kinetics of a number of these transfer reactions have been examined in detail and shown to be substrate-sensitive, a feature not previously observed in related systems [100]. The complex [MoO$_2$(H$_2$L)] (H$_4$L = HSC$_6$H$_4$NHCHMeCHMeNHC$_6$H$_4$SH) (8), which has a highly distorted octahedral structure, has been studied electrochemically. In the presence of *N*-methyl imidazole, one electron reduction is accompanied by dehydration to give [MoO(L)]$^-$, which then undergoes a fast second reduction to [MoO(L)]$^{2-}$; under neutral conditions this sequence appears as a single two-electron process. The Mo(V) species can also be obtained by adding PPh$_2$Me, presumably by conproportionation of the Mo(IV) complex with further Mo(VI) species [101]. The complex [MoO$_2$(H$_2$mpe)] has also been prepared (H$_4$mpe = HSCMe$_2$CH$_2$NHCH$_2$CH$_2$NHCH$_2$CMe$_2$SH); it can be reduced to the [MoO(H$_2$mpe)]$^+$ cation [102]. Seven-coordinate compounds of the type [MoO(cat)(aet)$_2$] where H$_2$cat = catechol or substituted catechols and Haet = 2-aminoethanethiol, have been characterised [103].

(7)   (8)

4.1.4   Complexes with sulfur donor ligands

The chemical shielding of the ^{95}Mo nucleus in [MoO$_n$S$_{4-n}$]$^{2-}$ has been calculated by semiempirical finite perturbation theory techniques [104]. Replacement of one or two oxo ligands of [MoO$_3$L]$^{2-}$ where H$_2$L = MeSCH$_2$CH$_2$N(CH$_2$COOH)$_2$ by sulfides can be achieved by treatment with B$_2$S$_3$; the method was also used for complexes of related ligands such as iminodiacetate [105].

The synthesis of crown ether dithiolene ligands H_2L such as (9) and their complexation to $MoCl_5$ to give complexes of the type $[MoL_3]$ has been described; the binding of Li^+, Na^+ and K^+ to the crown ether moieties was then studied by UV-visible spectroscopy and electrochemistry [106, 107].

(9)

4.2   MOLYBDENUM(V)

4.2.1   Complexes with halide ligands

Electron diffraction studies in the gas phase have shown that $MoCl_5$ possesses a distorted trigonal bipyramidal structure and does not undergo a Berry pseudo-rotation process through a square pyramidal C_{4v} intermediate. Molecular orbital c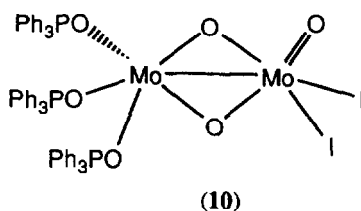alculations were carried out at three different levels to rationalise the structure [108]. The Raman spectra of $MoCl_5$ dissolved in liquid Cl_2 show the presence of monomeric species [109]. The replacement of the chlorides in $MoCl_5$ dispersed in poly(acrylic acid) matrices by oxygen ligands of the polymer has been monitored by EPR spectroscopy [110]. The solid state metathesis reaction of $MoCl_5$ or $MoCl_3$ with Li_2O at 400-500°C for 10 hours resulted in the formation of MoO_2 [111].

As with $MoCl_5$, addition of two equivalents of MeLi to $[MoOCl_3(thf)_2]$ produces a reagent which is useful for chemoselective in situ carbonyl methylenation reactions; a complex with bridging methylene groups is assumed to be involved [112, 113]. The interaction of $[MoOCl_5]^{2-}$ with macrocycles has been studied in detail. In the case of crown ethers such as 18-crown-6 and dibenzo-18-crown-6, octahedral complexes of the type $[MoO(Cl)L]Cl_2 \cdot H_2O$ can be isolated [114, 115]. With L = diaza-18-crown-6, the initial product is the protonated macrocycle salt $[H_2L][MoOCl_5]$, but this undergoes thermal conversion into $[MoO(L)Cl_3]$ [116]. For the same ligand complexes of the type $[MoOL_2X_3]$ (X = Cl, Br) have been made and shown to undergo a thermal isomerisation from a mer, cis structure to a mer, trans one [117]. When H_2L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetrazacyclotetradecane the initial product is $[H_4L][MoOCl_5]$ but this again loses HCl thermally to give $[MoOCl_3(H_2L)]$ and ultimately $[MoO(L)Cl]$ and $[MoO_2L]$ [118, 119]. The reaction of $[NH_4]_5[P_3O_{10}]$ with $[NH_4]_2[MoOCl_5]$ gave $[NH_4]_8[Mo_2O_4(P_3O_{10})_2]$ [120].

The reaction of $MoCl_5$ with 15-crown-5 and $AlCl_3$ in MeCN solution deposited crystals of $[AlCl_2(15-crown-5)][MoOCl_4(MeCN)] \cdot MeCN$ in which the MeCN ligand is trans to the oxo group [121]. Treatment of Mo(V) oxohalide complexes with 2-cyanopyridine (L) gave an assortment of products including $[HL][MoOCl_4]$, $[Mo_2O_3Cl_4(L)_2]$, and $[Mo_2O_4Cl_2(L)_2]$ [122]. Interaction of $[NEt_4][MoOI_4(H_2O)]$ with $Ph_3P=O$ produced $[MoOI_3(O=PPh_3)_2]$ and unexpectedly the

unsymmetrical dinuclear species [(Ph3P=O)3Mo(μ-O)2MoOI2] (10) [123].The reaction of MoCl5 with chlorobenzene and benzoyl peroxide has resulted in the isolation of a double salt in which two trityl-like [PhC(C6H4Cl)2] cations are associated with two anions; one is [Mo2O2(μ-Cl)3Cl4]$^-$ and the other is [Mo2O2(μ-Cl)2(μ-O2CPh)Cl4]$^-$, in which one of the bridging chlorides is replaced by a benzoate ligand [124]. The complex [Mo2OCl2L4]$^{2+}$ where HL = thiovanol has been prepared [125].

$$\begin{array}{c}
\text{Ph}_3\text{PO}_{\prime\prime\prime\prime\prime\prime} \qquad\qquad \text{O} \qquad\qquad \text{O} \\
\text{Ph}_3\text{PO}-\text{Mo}=\!=\!=\text{Mo}-\text{I} \\
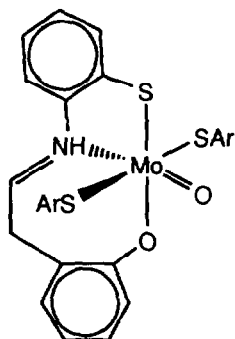\text{Ph}_3\text{PO} \qquad\qquad \text{O} \qquad\qquad \text{I}
\end{array}$$

(10)

The interaction of [MoCl4(OEt2)2] with the redox-active ligand 9,10-phenanthrene quinone produced the Mo(V) semiquinonate complex [MoCl4(L)], and [MoOCl3(dme)] also gave a Mo(V) product, [MoOCl3(L)], in which the ligand is in its quinone form. In both cases the analogous tungsten species gave complexes of W(VI). However MoCl5 reacted with tetrachlorobenzoquinone to give the Mo(VI) catecholate complex [MoCl4(OC6Cl4O)] [126].
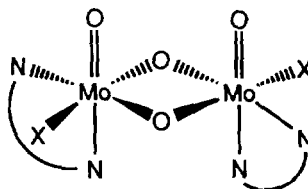
4.2.2 Complexes with oxygen and sulfur donor ligands

Doping MoO3 into zeolites such as H-SAPO-5 and H-SAPO-11 followed by dehydration eventually results in Mo(V) species, probably involving MoO2$^+$ cations, which can be studied by EPR spectroscopy. The coordination differs in the two types of zeolite. On admission of oxygen, the Mo(V) signal diminishes and a signal due to the superoxide radical appears [127]. A series of dimetallic Mo-Mg alkoxide complexes have been isolated, including both Mo(V) species e.g. [MoO(OMe)5Mg(MeOH)2]2 and some Mo(VI) ones, e.g. [MoO2(OMe)4Mg(MeOH)2]2; when reduced to the Mo(III) state they are catalysts for dinitrogen reduction by sodium amalgam [128]. Further investigations have appeared on the hydrolysis of alkoxides derived from MoCl5 and simple alcohols [129]. The correlation of the energies of the ligand field and lowest energy charge transfer bands in complexes of the type [(HBpz*3)MoO(OC6H4R)2] with the Hammett parameter of R has been established for a wide range of substituents [130].

The synthesis of two complexes [NMe4][MoO(SC6H4CH=NC6H4O)(SR)2] (11) (R = Ph, p-tol) with S3NO2 coordination spheres as models for the enzyme sulfite oxidase has been reported. They have EPR spectra almost identical to that of the enzyme. They react with water to give a dimeric Mo(V) μ-oxo complex, and with air to produce [MoO2(SC6H4CH=NC6H4O)(solvent)] where solvent = MeCN or dmso; this Mo(VI) species can also be prepared from [MoO2(acac)2] and the ligand [131]. Treatment of [MoOCl3(thf)2] with o-HOC6H4SH and NaOMe produced [NBu4][Mo2O2(OMe)(OC6H4S)]; one of the o-hydroxythiophenol ligands and the methoxide group act as bridging ligands [132].

(11)   **(12)**
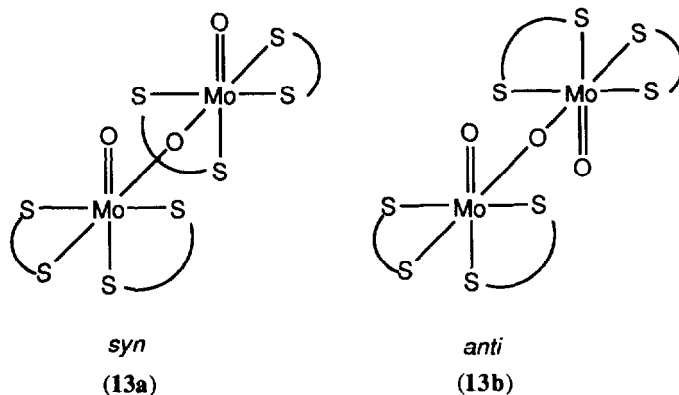
Flash photolysis of $[Mo_2O_2(\mu-O)_2(H_2O)_6]^{2+}$ in aqueous perchloric acid proceeds *via* the intermediates $[Mo_2O_3(H_2O)_8]^{4+}$ and $[Mo_2O_3(Cl)(H_2O)_7]^{3+}$ and ultimately produces hydrogen and Mo(VI) species [133]. Similar treatment of $[Mo_2O_4(cys)_2]$ in aqueous solution also gave H_2 *via* an intermediate identified as $[Mo_2O_5(H_2O)_2]$ [134].

A number of complexes containing the $Mo_2O_4{}^{2+}$ and $Mo_2O_3{}^{4+}$ cores have been prepared, including $Na_2[Mo_2O_4(pen)_2].3MeOH.3H_2O$ where H_2L = penicillamine (i.e dimethylcysteine) [135]. The unusual bis(3,5-dimethylpyrazolyl)methane complexes $[Mo_2O_4(X)_2(CH_2pz*_2)_2]$ **(12)** (X = Cl, Br) were prepared serendipitously by the reaction of $[MoX(\eta\text{-allyl})(CO)_2(MeCN)_2]$ with CH_2pz*_2 in the presence of air [136].

A range of compounds of the type $[Mo_2O_4(dtc)_2]$ in which the dithiocarbamate ligands are derived from amino acids have been made either from $MoCl_5$ or from molybdate in the presence of dithionite [137]. Complexes of the type $[Mo_2O_3(dtc)_4].2H_2O$ were isolated when molybdate was treated with the same ligands in acid solution; in organic solvents they change into $[MoO(dtc)_2]$ [138]. Labelling the compound $[Mo_2O_3(dtc)_4]$ [dtc = $S_2CN(CH_2Ph)_2$] with ^{13}C at the dithiocarbamate ligand revealed an interesting fluxionality, which has activation parameters typical of an intramolecular process, i.e. mechanisms involving a dissociative equilibrium were ruled out. The compound consists of two isomers, *syn* and *anti*, **(13a, b)** each of which contains two different dtc ligands; the proposed mechanism involves bridge-terminal exchange of the oxo ligands *via* an intermediate with two μ-O ligands. A similar process also operates in $[Mo_2O_3(S_2COEt)_4]$ [139]. The electronic spectra of the analogous dithiophosphate complexes $[Mo_2O_3\{S_2P(OR)_2\}_4]$ (R = Me, Et, Ph) show unusual Beer's law plots suggestive of a dissociative equilibrium in solution involving disproportionation into mononuclear $[MoO_2\{S_2P(OR)_2\}_2]$ and $[MoO\{S_2P(OR)_2\}_2]$ fragments. This was proven for R = Et, where both mononuclear species could be prepared independently, and suggests that the photoreactivity of the dimers actually reflects the photochemistry of their monomeric constituents [140].

Treatment of $[Mo_2O_3(acac)_4]$ with $[Sacac]^-$ produced $[Mo_2O_3(acac)_3(Sacac)]$ and $[Mo_2O_3(acac)_2(Sacac)_2]$, which were both crystallographically characterised [141]. Several complexes of the type $[Mo_2O_3L_4]$ where HL is a hydroxamic acid RCONHOH (R = various aryl) have also been prepared [142].
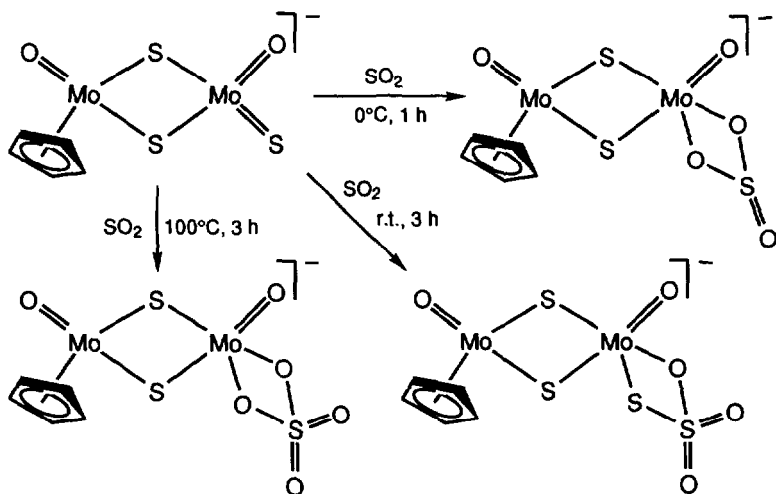
syn

(13a)

anti

(13b)

Heating the imido complex $[Mo_2O_2(\mu\text{-}NPh)_2(dtc)_2]$ (dtc = S_2CNEt_2) with PhNCO produces the ureato complex $[Mo_2(NPh)_2(\mu\text{-}NPh)(\mu\text{-}PhCONPh)(dtc)_2]$, which arises through substitution of the oxo ligands followed by insertion of further isocyanate into one of the bridging imido ligands. Heating the product alone indeed expels this PhNCO and gives the tetraimido complex $[Mo_2(NPh)_4(dtc)_2]$, which reacts rapidly and quantitatively with PhNCO to reform the ureato compound (Scheme 2) [143]. The reaction of $[NH_4]_2[MoS_4]$ with dtc⁻ (dtc = $S_2CNC_4H_8$) and PPh₃ produced $[Mo_2S_4(dtc)_2]$; its reaction with Cu⁺ produced $[Cu(dtc)_2]$ and $[Mo_3S_7(dtc)_3]^+$ [144]. The mixed ligand species $[Mo_2O_2(\mu\text{-}S)_2(dtc)_2]$ and $[Mo_2O(S)(\mu\text{-}S)(dtc)_2]$ were also made [145].

Scheme 2

The reactivity of the Mo=S bond in $[CpMoO(\mu\text{-}S)_2MoO(S)]^-$ towards SO_2 has been explored under a variety of conditions, giving rise to complexes with didentate SO_3, S_2O_3 and SO_4 ligands (Scheme 3) [146]. Crystal structure determinations of $[Mo_2O_2(SO_4)_2(\mu\text{-}S)_2]^{2-}$ with various counter-ions have shown that dimerisation through a bridging sulfate group can be stabilised by intramolecular hydrogen bonding, for example in the $Me_2NH_2^+$ salt [147].

The macrocyclic metal complex (14) (M = Ni, Co) can be used as a catecholate ligand in Mo(V) complexes; thus reaction with $[Mo_2O_2S_2(S_2)(dmf)_3]$ afforded $[Mo_2O_2(\mu\text{-}S)_2(S_2)(cat)]^{2-}$ while use of $[Mo_2O_2S_2(dmf)_6]^{2+}$ gave rise to $[Mo_2O_2(\mu\text{-}S)_2(cat)_2]^{2-}$ [148]. The polyselenide anion $[Mo_2Se_2(\mu\text{-}Se)_2(Se_2)_2]^{2-}$ has been prepared by treatment of $[Mo_2(OAc)_4]$ with K_2Se_4 and structurally characterised; the related oxo species $[Mo_2O_2(\mu\text{-}Se)_2(Se_2)_2]^{2-}$ was also made [149].

Scheme 3

(14)

The first example of a Mo(V) tetrathiometallate complex has been made and characterised spectroelectrochemically in an OTTLE cell. The dianion $[(NC)(OC)_3ReS_2MoS_2Re(CO)_3(CN)]^{2-}$ can be reduced to the corresponding trianion, which shows hypsochromically-shifted charge transfer absorptions, bathochromically-shifted CN, CO and MoS stretching frequencies, and shows an EPR signal with $g_{\parallel}$ of 2.019 and $g_{\perp}$ of 1.965 [150].

4.3   MOLYBDENUM(IV)

4.3.1   Complexes with halide and cyanide ligands

A gas phase electron diffraction study of $MoBr_4$ shows that it is not tetrahedral but instead has C_{2v} symmetry [151]. Good yields of $MoBr_4$ can be obtained by halide exchange from $MoCl_5$

using dry HBr between −50 and +20°C. Similar reactions with HI gave only mixed halides. The adduct [MoBr$_3$(thf)$_3$] was formed by treatment of MoBr$_4$ with thf [152]. Reduction of MoCl$_5$ with alkenes, usually Me$_3$SiCH$_2$CH=CH$_2$, in the appropriate solvent provides high yield routes to the useful starting materials [MoCl$_4$(dme)] and [MoCl$_4$(OEt$_2$)$_2$] [153]. Reduction of various metal halides, including MoCl$_4$ and MoCl$_3$, with LiBHEt$_3$ in toluene produced reactive metal powders, but if the solvent was changed to thf, high yields of the metal carbides M$_2$C were obtained [154]. The complex [Cl$_4$Mo(μ-dppf)MoCl$_4$] has been prepared from [MoCl$_4$(MeCN)$_2$] [155].

Salts of [Mo(CN)$_8$]$^{4-}$ have been obtained in which the counter-ion is diprotonated 4,4'-bipyridine. The ion pairs exhibit outer sphere electron transfer between adjacent redox sites, and an EPR spectroscopic signal due to Mo(V) can be detected [156]. The thermal or photochemical decomposition of [Hbpy]$_3$[H$_3$O][Mo(CN)$_8$] in aqueous solution produces amorphous salts which contain the [Mo$_3$O$_4$(CN)$_{9-x}$(H$_2$O)$_x$]$^{(5-x)-}$ ions [157]. A kinetic study of the reduction of [Mo(CN)$_8$]$^{4-}$ and its W analogue in aqueous NaOH has shown that the reaction is second order in complex and first order in both Na$^+$ and OH$^-$ [158]. Adducts of [Mo(CN)$_8$]$^{4-}$ with 8-hydroxyquinoline have been prepared by a photochemical reaction which proceeds *via* [Mo(CN)$_7$]$^{2-}$ [159]. A short survey of the photochemistry of octacyanomolybdates has appeared [160].

The kinetics of the replacement of the water ligand in [MoO(H$_2$O)(CN)$_4$]$^{2-}$ by CN$^-$ or HCN have been studied; this is an important step on the way to [Mo(CN)$_8$]$^{4-}$ [161]. The reaction between K$_3$Na[MoO$_2$(CN)$_4$].6H$_2$O, KCN and H$_2$SO$_4$ in the presence of PPh$_4$Cl affords the complex [PPh$_4$]$_2$[MoO(NCH)(CN)$_4$].5H$_2$O in which a HCN ligand is coordinated through the nitrogen atom [162].

4.3.2   Complexes with nitrogen and phosphorus donor ligands

The autoxidation of [MoO(L)], where H$_2$L is tetrakis-4-^{t}butyl phthalocyanine, has been studied by EPR spectroscopy; the species formed are [MoO(L)]$^+$ and [MoO(O$_2$)(L)]$^-$ [163].

The interaction of [MoCl$_4$(MeCN)$_2$] with 2,6-diacetylpyridine bis(benzoylhydrazone) (H$_2$L) produced the complex [MoCl$_2$L] in which the ligand acts as a pentadentate N_3O_2-donor [164]. The reaction of [MoOCl$_2$(PPh$_2$Me)$_3$] with *o*-phenylenediamine produced the monodentate Mo(V) imido complex [Mo(=NC$_6$H$_4$NH$_2$)Cl$_3$(PPh$_2$Me)$_2$] [165]. A kinetic study of the deprotonation of *trans*-[MoCl(=NCH$_2$CO$_2$Me)(dppe)$_2$]$^+$ with OH$^-$ demonstrated not only that both methylene protons can be removed, but also that their pK$_a$ values are remarkably similar (*viz* 11.2 and 11.5) [166].

4.3.3   Complexes with oxygen and sulfur donor ligands

Full details have appeared of the reaction of the Mo(VI) complex [MoO$_2$(SCPh$_2$COO)$_2$]$^{2-}$ with further thiobenzilic acid. This results initially in reduction to Mo(V) and the isolation of [MoO(SCPh$_2$COO)$_2$]$^-$, which on neutralisation is converted into the tris-chelate complex [Mo(SCPh$_2$COO)$_3$]$^{2-}$ [167]. The monomeric Mo(IV) oxo complex [MoO(SR)$_4$]$^{2-}$ (R = *p*-C$_6$H$_4$Cl) was prepared by sodium borohydride reduction of [MoO(SR)$_4$]$^-$ and isolated as its PPh$_4$$^+$ salt. Molecular orbital calculations on the model species [MoO(SH)$_4$]$^{2-}$ were used to explain the torsion angles of the chlorophenyl groups [168]. The reaction of [Mo(CO)$_4$(dtc)]$^-$ (dtc = S$_2$CNEt$_2$) with SPh$^-$ in MeCN in the presence of air produced [MoO(SPh)$_2$(dtc)]$^-$; two forms of the NEt$_4$$^+$

salt were structurally characterised [169]. A diamagnetic host matrix of [(HBpz*$_3$)MoO(dtc)] was used to record the EPR spectrum of the isostructural vanadium analogue [170]. The presence of adventitious oxygen in the reaction of [MoCl$_3$\{PhP(CH$_2$CH$_2$PPh$_2$)$_2$\}] with NaSeR (R = Mes) caused the isolation of [MoO\{Ph$_2$P(=O)CH$_2$CH$_2$PPhCH$_2$CH$_2$PPh$_2$\}(SeR)$_2$], in which the *fac-P,P,O*-chelate ligand is formed by oxidation of one arm of the tris(phosphine) [171].

The dimeric complex [Mo$_2$(μ-S)(S4)$_2$] (**15**), where the "S4" ligand is $^-$SC$_6$H$_4$CH$_2$CH$_2$SC$_6$H$_4$S$^-$ or its bulkier 3,5-^{t}Bu substituted analogue, can be prepared by treatment of [MoCl$_4$(MeCN)$_2$] with H$_2$S4 and H$_2$S or by the reaction of preformed [MoCl$_2$(S4)] with H$_2$S. An analogous complex could also be prepared from HSC$_6$H$_4$NHCH$_2$CH$_2$NHC$_6$H$_4$SH, but attempts to make anionic derivatives led only to disintegration of the ligand and isolation of the NBu$_4$$^+$ salt of the [Mo$_3$S$_6$(μ_3-S)(μ-S$_2$)$_3$]$^{2-}$ cluster [172]. The reaction of MoCl$_5$ with Na$_2$[C$_3$S$_5$] produced the distorted trigonal prismatic tris-chelate complex [NBu$_4$]$_2$[Mo(C$_3$S$_5$)$_3$], which can be oxidised by FeCp*$_2$ into [FeCp*$_2$][Mo(C$_3$S$_5$)$_3$] [173]. Protonation of *trans*-[Mo(S)$_2$(*syn*-Me$_8$[16]-aneS$_4$)] with HBF$_4$ results in loss of H$_2$S and formation of [Mo$_2$(S)$_2$(μ-S)(Me$_8$[16]aneS$_4$)$_2$][BF$_4$]$_2$ and [Mo(S)(F)(Me$_8$[16]aneS$_4$)][BF$_4$]; the first of these contains a linear S=Mo–S–Mo=S unit [174].
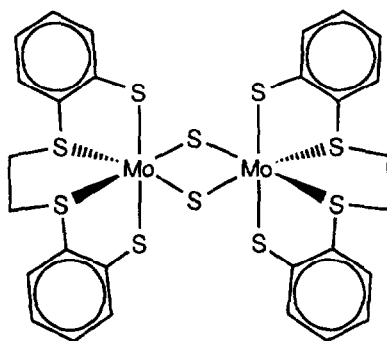
(15)

The reaction of [MoCl$_4$(SMe$_2$)$_2$] with SR$^-$ (R = *p*-C$_6$H$_4$X where X = Me, F, Cl, Br) and [CuCl(PPh$_3$)]$_4$ produced [(Ph$_3$P)Cu(μ-SR)$_3$Mo(μ-SR)$_3$Cu(PPh$_3$)]. The X-ray structure of the *p*-tolyl complex showed an octahedral Mo^{IV}(SR)$_6$ core capped on two faces; a Mo-Cu distance of 2.691(1)Å is probably indicative of some direct bonding between the metals [175]. The electrochemistry of these complexes shows a reversible one-electron reduction; the *p*-tolyl complex also shows a reversible one-electron oxidation based at the molybdenum [176].

4.4   MOLYBDENUM(III)

### 4.4.1   Complexes with halide and phosphine ligands

The X-ray structures of the salts [MeNH$_3$]$_4$[MoCl$_6$][Cl] and its [Me$_2$NH$_2$]$^+$ analogue have been determined; each consists of alternating layers of cation/[MoCl$_6$]$^{3-}$ and cation/Cl$^-$ [177]. The structure of [NBu$_4$]$_2$[MoCl$_2$(dppe)$_2$][BF$_4$]$_3$ has been discussed in relation to some similar rhenium

complexes [178]. The structure of *trans*-[pyH][MoBr4(py)2] has also been determined; it reacts with 4-picoline (L) to give [MoBr3L3] and [MoBr3(py)2L] [179]. The reaction of [MoCl4(thf)2] with triphos afforded [MoCl3(triphos)], the first example of a Mo(III) trihalide with a *fac*-P3 coordination [180]. Decarbonylation of [LMo(CO)3] (L = 1,4,7-triisopropyl-1,4,7-triazacyclononane) in nitric acid provided a route to [LMoO3]; alternatively treatment with SOCl2 or Br2 gave the Mo(III) complexes [LMoX3] (X = Cl, Br) [181]. Treatment of [LMoCl3] with bpy in aqueous methanol in aerobic conditions produced the mixed valence complex [{LMoO(μ-O)2}2Mo(bpy)][PF6]2; the central Mo atom is formally Mo(IV) while the two terminal ones are formally Mo(V) [182].

The magneto-optical properties of Cs3[Mo2X9] (X = Cl, Br) have been investigated by single crystal absorption spectra and MCD spectra; the results were described using an exchange coupled pair model [183].

Further molecular orbital calculations on edge-sharing bioctahedral complexes with the general formula [M2X6L4] have appeared; this paper, which contains a useful table of such species, shows that the absence of a metal-metal bond in [Mo2Cl6(PEt3)4] compared with its PMe2Ph analogue may be a consequence of the larger cone angle of PEt3 producing steric hindrance in the equatorial positions, which in turn reduces the angles made by the bridging chlorides, termed a reverse scissoring effect [184].

(16)
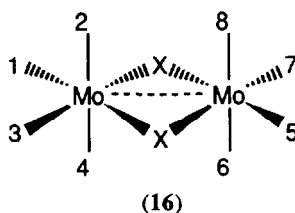
Synthetic investigations of complexes of the type [Mo2X6L4] have revealed some new structural isomers (the numbering scheme is shown in diagram **16**). The mixed-metal species [MoWCl6(dmpe)2] was isolated as two isomers, the 1,2,5,6-isomer with a metal-metal distance of 2.695(1)Å, and the 1,3,5,7-isomer which has a Mo–W distance of 2.7028(5)Å. The compound 1,2,5,8-[MoWCl6(tetraphos-1)] (tetraphos-1 = Ph2PCH2CH2PPhCH2CH2PPhCH2CH2PPh2) was also made, and has an apparent Mo–W bond length of 2.718(2)Å, though it is contaminated with a small percentage of the Mo2 analogue [185]. Attempts to prepare Mo(II) complexes of the chelating tetraphosphine ligand Et2PCH2CH2PPhCH2PPhCH2CH2PEt2 were only partially successful; from one preparation the complex 1,2,7,8-[Mo2Cl6(*meso*-L)].C6H6 was isolated as a result of oxidation, while in another 1,2,5,6-[Mo2Cl4(Et2PCH2CH2PPhCH2PPh)2] was formed by P-C cleavage of L to give a mixed diphosphine-phosphido ligand [186]. The complexes [Mo2Cl4(μ-OAc)2L2] have been structurally characterised for L = PMe3 and PEt3; the Mo–Mo distances are 2.5932(7)Å and 2.612(1)Å respectively. Analysis of the PEt3 complex by paramagnetic 1H NMR spectroscopy gave a singlet-triplet state energy gap smaller than that found for [Mo2Cl6(dppm)2] [187].

4.4.2   Complexes with oxygen and nitrogen donor ligands

The hydrolysis reactions of several possible precursors have been investigated with a view to the sol-gel preparation of Mo(III) oxide, Mo(O)(OH). Of these, compounds of the type [$Mo_2(OR)_6$] (R = ^iPr, ^tBu) were of little use, but [$Mo_4(OEt)_{12}$] gave a product formulated as [$Mo_2(OH)_5(OEt)$] which did give the correct product when heated with hydrogen at 250°C [188]. The conformation of the water molecules in the [$Mo(H_2O)_6$]$^{3+}$ cation in the alum salt [$CsMo(SO_4)_2$].$12H_2O$ has been studied by neutron diffraction at 15K; the analogous Ru complex was examined too [189]. The reaction of [$Mo_2(OCH_2^tBu)_6$] with $KOCH_2^tBu$ and 18-crown-6 produced the [$K(18-C-6)$]$^+$ salt of the [$Mo_2(OCH_2^tBu)_7$]$^-$ anion; the X-ray crystal structure shows six terminal alkoxides and one bridging, with a Mo≡Mo bond of length 2.218(3)Å [190].

Treatment of *mer*-[$MoCl_3(thf)_3$] with NH_3 and then triflic acid produced *fac*-[$Mo(NH_3)_3(OTf)_3$], which acts as a useful precursor to a range of classical Mo(III) ammine complexes since the triflates can be easily replaced by halides [191]. The reaction of [$Mo_2(NMe_2)_6$] with Me_3SiI gave [$Mo_2I_2(NMe_2)_4$] or [$Mo_2I(NMe_2)_5$] depending on the stoichiometry employed; the iodide ligand can then be replaced by a range of organic groups with Grignard reagents, organolithiums, organo-tin reagents etc. [192]. The reaction of [$Mo_2Cl_2(NMe_2)_4$] with $LiEPh_3$ (E = Si, Ge, Sn) gave [$Mo_2(EPh_3)_2(NMe_2)_4$], which have an ethane-like structure with an *anti*-conformation [193].

4.5   MOLYBDENUM(II)

4.5.1   Complexes with halide and phosphine or carbonyl ligands

Quadruply-bonded complexes of the the type [$Mo_2X_4L_4$] have remained an active area of research. Two molecular orbital studies have appeared on these systems. Fenske-Hall calculations have been used to study the electronic spectrum and metal-metal bond length in [$M_2X_4(PH_3)_4$] (M = Mo, W) as a function of halide; as X is changed from Cl to Br to I, the $\delta \rightarrow \delta^*$ transition is red shifted, but there is little change in M-M distance [194]. Cotton has studied the properties of the δ bond in [$Mo_2Cl_4(PH_3)_4$] as a function of the rotation angle by *ab initio* methods; the δ bond energy was calculated to be 70.2 kJ mol^{-1} and the electronic contribution to the rotational barrier was found to be 51.8 kJ mol^{-1} [195]. In relation to the latter paper, a series of [$M_2X_4(L_2)_2$] complexes (M = Mo, W; X = Cl, Br, I; L_2 = various chelating phosphines) have been studied by variable temperature ^{31}P NMR spectroscopy, which enables calculation of the singlet-triplet energy gap, the diamagnetic shift, and the hyperfine coupling constant. Even at a torsion angle of 45° (i.e staggered) the δ^2 $^1A_{1g}$ state remained the ground state, with the $\delta\delta^*$ $^3A_{2u}$ state approximately 1230 cm^{-1} above it. The δ bond energy was estimated as 57.8 ± 2.1 kJ mol^{-1} and the electronic barrier to rotation as 43.0 ± 2.1 kJ mol^{-1}, in reasonable agreement with the calculated figures above [196].

What was previously thought to be a green isomer of [$Mo_2Cl_4(PPh_2Me)_4$] has now been found to consist of the blue isomer contaminated with varying amounts of [$MoOCl_2(PPh_2Me)_3$], [$MoOCl_3(OPPh_2Me)_2$], and *trans*-[$MoCl_4(PPh_2Me)_2$]$^-$, depending on the purity of the starting

materials [197]. Depending on L-L, complexes of the type $[Mo_2X_4(L-L)_2]$ exist either as α-isomers with chelating phosphines, or β-isomers with bridging phosphines. The complexes $[Mo_2X_4(\mu\text{-}dmpm)_2]$ have been structurally characterised for X = Br [Mo–Mo 2.1271(8)Å] and I [2.132(2)Å] [198]. The complex $[Mo_2Cl_4(\mu\text{-}Ph_2PCH_2PMe_2)_2]$ has also been prepared; the Mo–Mo distance is 2.1523(9)Å and there is a torsion angle of 17.56° about the Mo–Mo axis. The termini of the unsymmetrical diphosphine alternate – each Mo atom bears one PPh_2 and one PMe_2 ligand [199].

The X-ray structures of both the *rac* and *meso* isomers of $[Mo_2X_4L]$ have been determined where X = Cl and Br; L is tetraphos-1 i.e. $Ph_2PCH_2CH_2PPhCH_2CH_2PPhCH_2CH_2PPh_2$. In the *rac* isomers (**17**), the two central phosphorus atoms of the tetraphosphine ligand are on different Mo atoms and the ligand is doubly chelating, singly bridging; in the *meso* forms (**18**) the two central phosphorus atoms are on the same Mo atom and the ligand is singly chelating, doubly bridging. These are the first examples of enantiomeric 1,2,5,8/1,2,6,7 and 1,2,5,7/1,2,6,8 isomers. The average Mo-Mo distances for the *rac* and *meso* isomers are 2.154 and 2.190Å respectively [200]. The reaction of $[Mo_2Cl_4(PEt_3)_4]$ with tetraphos-2, i.e. $P(CH_2CH_2PPh_2)_3$ gave *rac*-$[Mo_2Cl_4(PEt_3)(L)]$ (**19**) in which the tetraphosphine acts as a tridentate ligand [201].

The reaction of $[WBr_4(PPh_3)_2]$ with $[Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3]$ provides a route to the mixed-metal complex $[MoWBr_4(PMe_2Ph)_4]$; it is contaminated with a small amount of the corresponding Mo_2 species, but the Mo-W distance of 2.209(1)Å was determined from the X-ray structure [202]. The related $[MoWCl_4(\mu\text{-}dmpm)_2]$, which has a metal-metal distance of 2.193(2)Å, has also been made [198].

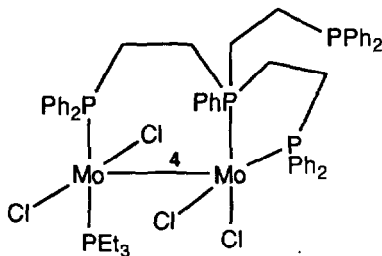Desilylation of $[Mo_2(C\equiv CSiMe_3)_4(PMe_3)_4]$ with $[NBu_4][HF_2]$ afforded the parent acetylide complex $[Mo_2(C\equiv CH)_4(PMe_3)_4]$, which has a Mo–Mo bond length of 2.134(1)Å [203].
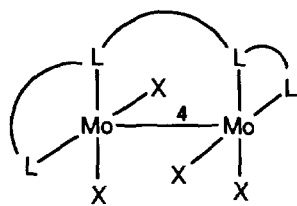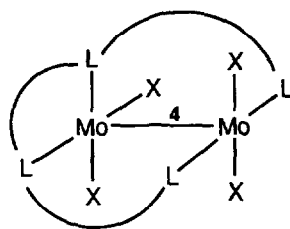
(17)   (18)

(19)

The reaction of [MoCl$_2$(PPh$_2$Me)$_4$] with ammonia or primary amines gives amine complexes of the type [MoCl$_2$(NH$_2$R)(PPh$_2$Me)$_3$] (R = H, alkyl, allyl). With en, two phosphines can be displaced to give [MoCl$_2$(en)(PPh$_2$Me)$_2$]. The amine complexes do not go on to form imido species [204]. Treatment of [MoCl$_2$(CO)$_2$(PMe$_3$)$_2$] with LiBHEt$_3$ produces only the monohydride [MoH(Cl)(CO)$_2$(PMe$_3$)$_2$]; the second halide can however then be replaced by ligands such as S$_2$CNMe$_2$, S$_2$COMe and acac [205]. The halide ligands in [MoBr$_2$(CO)$_2$L$_2$] (L = PPh$_3$, PPh$_2$Me, PMe$_2$Ph) can be replaced stepwise by NaO$_2$CCF$_3$; initially [MoBr(O$_2$CCF$_3$)(CO)$_2$L$_2$] with a didentate carboxylate is formed, but addition of a second equivalent gives [Mo(O$_2$CCF$_3$)$_2$(CO)$_2$L$_2$] which has one didentate and one monodentate. The same starting materials react with oxalate to give [{MoBr(CO)$_2$L$_2$}$_2$(μ-ox)] [206]. Halide abstraction from [MoBr$_2$(CO)$_2$(PPh$_3$)$_2$] with AgBF$_4$ gave [(Ph$_3$P)$_2$(CO)$_2$Mo(μ-F)$_3$Mo(CO)$_2$(PPh$_3$)$_2$][BF$_4$] which was structurally characterised [207]. The complex [Mo(NHC$_6$H$_4$NH)(CO)$_2$(PPh$_3$)$_2$] was isolated from the reaction of *o*-phenylenediamine with [MoBr$_2$(CO)$_2$(PPh$_3$)$_2$]; the PPh$_3$ ligands can be replaced by other phosphines [208].

Oxidative addition of IBr to [Mo(CO)$_3$(MeCN)$_3$] affords [MoI(Br)(CO)$_3$(MeCN)$_2$]; the two MeCN ligands can then be replaced by various phosphines [209]. The reaction of one equivalent of L (L = Im, 2-Meim, 4-Meim) with [MoI$_2$(CO)$_3$(MeCN)$_2$] gave [MoI(μ-I)(CO)$_3$L]$_2$; alternatively two equivalents gave [MoI$_2$(CO)$_3$L$_2$] [210]. The oxidative addition of RSnCl$_3$ (R = Ph, Bu, Me) to [Mo(CO)$_3$(MeCN)$_3$] produces [MoCl(SnCl$_2$R)(CO)$_3$(MeCN)$_2$] [211]; the MeCN ligands can be replaced by phosphines or phosphites [212, 213] and the chloride ligand can be replaced by S$_2$P(OEt)$_2^-$, which then gives [Mo(SnCl$_2$R){S$_2$P(OEt)$_2$}(CO)$_2${P(OMe)$_3$}$_2$] on addition of phosphite [214]. The reaction of [MoCl(GeCl$_3$)(CO)$_3$(MeCN)$_2$] with didentate ligands such as bpy, phen, dppm results either in replacement of the MeCN ligands or one MeCN and one CO [215]. Addition of alkynes RC≡CR (R = Me, Ph) to [MoCl(GeCl$_3$)(CO)$_2$(MeCN)$_2$(PPh$_3$)] displaced one MeCN ligand and gave a rare example of a complex with six different ligands [216].

4.5.2   Complexes with nitrogen donor ligands

A review article has appeared on multiply-bonded porphyrin dimers, including those of molybdenum [217].

Further developments in the extensive chemistry of the tris(3,5-dimethylpyrazolyl)borate complex [(HBpz*$_3$)Mo(NO)X$_2$] (X = Cl, Br, I) have been reported. This redox-active 16-electron complex reacts with alcohols and amines with elimination of HX and formation of [(HBpz*$_3$)Mo(NO)(X)(OR)] or [(HBpz*$_3$)Mo(NO)(X)(NHR)], or the corresponding disubstituted species. The sugars D-glucofuranose and D-galactopyranose, suitably protected as acetals, react in this way to give diastereomers of the monosubstituted product; their absolute configuration was assigned by crystal structure and then related to their CD spectra [218]. Attempts to produce metal-containing liquid crystals with amines such as H$_2$NC$_6$H$_4$CH=CHC$_6$H$_4$OR or phenols such as HOC$_6$H$_4$C$_6$H$_4$OR, where R is a long chain alkyl group, were unsuccessful; complexes were formed, but displayed no liquid crystal properties [219, 220].

Several papers deal with the interaction between two linked Mo centres. The diphenolate complexes [{(HBpz*$_3$)Mo(NO)(X)}$_2$(μ-OQO)] (X = Cl, I) have been made where the linking

group Q is p-C_6H_4, $C_6H_4COC_6H_4$, $C_6H_4SO_2C_6H_4$, or $C_6H_4CO(C_6H_4)_2COC_6H_4$. Reduction of each Mo atom to a 17-electron centre reveals fast exchange between them, though this is slower for longer ligands. When Q = p-C_6H_4, the mixed-valence 16/17-electron species can be made and is valence-trapped [221]. Similar studies on complexes where Q = $C_6H_4(CH_2)_n$ (n = 1-3) confirm the insulating effect of aliphatic spacers, as there is now only a weak interaction between the two metals [222]. The same group have prepared a series of ligands with both pyridine and phenol functionalities, e.g. 4-$NC_5H_4C_6H_4$-4-OR, the 3- and 4-pyridyl isomers of NC_5H_4CH=CHC_6H_4-4-OR and 4-NC_5H_4CH=CHC_6H_4-3-OR, where R = H or Me. Reaction of the ligands with R = Me with [(HBpz*$_3$)Mo(NO)Cl$_2$] affords 17-electron complexes attached through the pyridyl ring, whereas with R = H the ligands act as phenols. In the latter case, reaction with a second equivalent of Mo complex occurs at the pyridine ring to produce the mixed dinuclear 16 electron, 17 electron species. In these the odd electron is localised, but on reduction to a 17 electron, 17 electron system, fast exchange is observed [223]. A similar study was carried out with the two Mo centres linked by ligands with two pyridine functionalities, such as 4,4'-bpy, bis(4-pyridyl) acetylene, 4,4'-azopyridine, and 1,4-bis(4-pyridyl) benzene. The reduction potentials of these compounds vary with the degree of ligand unsaturation, implying that the redox orbital is ligand based; there is a strong interaction between the Mo centres, as the reduction potentials of the two differ by 0.16 to 0.56V. The EPR spectra of these 17-electron, 17-electron complexes again show fast exchange [224]. An overview of the electrochemistry of (HBpz*$_3$)Mo complexes has appeared [225].

The μ-oxo complex [{(HBpz*$_3$)Mo(NO)(Cl)}$_2$(μ-O)] has been synthesized as a mixture of diastereomers by treating [(HBpz*$_3$)Mo(NO)Cl$_2$] with water in refluxing toluene [226]. Treatment of the dichloride with S(SnPh$_3$)$_2$ gave low yields of the analogous sulfide-bridged complex [{(HBpz*$_3$)Mo(NO)(Cl)}$_2$(μ-S)], which could also be made by the reaction of sulfur with the reduced species [NHEt$_3$][(HBpz*$_3$)Mo(NO)Cl$_2$]; in this case the disubstituted complex [{(HBpz*$_3$)Mo(NO)}$_2$(μ-S)$_2$] was also formed [227]. The influence of hydrogen bonding on the redox properties of complexes of the type [{(HBpz*$_3$)Mo(NO)(I)(SR)] has been briefly discussed [228].

In a complex reaction, treatment of [(HBpz*$_3$)Mo(NO)Cl$_2$] with BuLi and then Bu$_3$SnCl produced [(HBpz*$_3$)Mo(NO)Cl(Hpz*)]; the analogous Hpz complex [(HBpz*$_3$)Mo(NO)(I)(Hpz)] could be made by stirring the diiodide with Hpz [229]. Disintegration of the borate ligand was also observed when trying to make the initial [LMo(CO)$_2$(NO)] complex with HB(3-^{i}Pr-5-Me-C$_3$HN$_2$)$_3$; one of the pyrazole groups was replaced by an O^{i}Pr [230].

Starting from 1-H-1,2,4-triazole, the tris(triazolyl)borate ligands RBtz$_3^-$ (R = H, Ph) have been prepared, and from them [(RBtz$_3$)Mo(CO)$_3$]$^-$, [(RBtz$_3$)Mo(CO)$_3$X] (X = Br, I) and other similar species were made [231]. Reaction of [LMo(CO)$_3$I] where L = RBtz$_3$ or HBpz$_3$ with Agdtc (dtc = S$_2$CNEt$_2$, S$_2$CNC$_5$H$_{10}$) gave [LMo(CO)$_3$(dtc)] in which the dtc is didentate [232].

### 4.5.3   Complexes with oxygen donor ligands

A survey of some 350 compounds of the type M_2X_8, M_2X_8L, and $M_2X_8L_2$, including Mo(II) complexes such as [Mo$_2$(O$_2$CR)$_4$], has revealed correlations between the metal-metal

distance and both the M-M-X angle and the internal rotation angle [233]. The reaction of [Mo$_2$(OAc)$_4$] with [NR$_4$][CN] (R = Et, Bu) in chlorinated solvents gave [NR$_4$]$_4$[Mo$_2$(CN)$_8$] which has a Mo-Mo bond of length 2.122(2)Å, the shortest yet reported for a homoleptic Mo$_2$X$_8$ species. If the reaction is carried out in thf, the main product is [NBu$_4$]$_3$[Mo$_2$(OAc)(CN)$_6$], which has a bond length of 2.114(2)Å [234].

The reaction of β-MoCl$_2$ with NHEt$_2$ and CO$_2$ gave good yields of the complex [Mo$_2$(O$_2$CNEt$_2$)$_4$], which has a Mo-Mo distance of 2.067(2)Å [235]. Addition of [NBu$_4$][O$_2$C^{t}Bu] to [Mo$_2$(O$_2$C^{t}Bu)$_4$] affords [NBu$_4$][Mo$_2$(O$_2$C^{t}Bu)$_5$] in which the extra carboxylate ligand is monodentate on one Mo atom, though there is rapid exchange of environments in solution; in the solid state the Mo-Mo distance is 2.1035(7)Å [236]. The complexes [Mo$_2$(O$_2$CH)$_4$L$_2$] have been made where L = 4-aminopyridine and diethylnicotinamide [237], and the CD spectra of didentate complexes of [Mo$_2$(OAc)$_4$] with cholestane 1,3-diols have been used to assign absolute configurations [238]. The activity of [Mo$_2$(OAc)$_4$] in the liquid phase hydrogenation of acetophenone was found to be increased by the use of a zeolite support [239].

The reaction of [Mo$_2$(O$_2$CCF$_3$)$_4$] with the unsymmetrical diamine Me$_2$NCH$_2$CH$_2$NH$_2$ (= L) affords [Mo$_2$(O$_2$CCF$_3$)$_3$(L)$_2$][O$_2$CCF$_3$] (20), in which the two amines act as chelating ligands, with the NMe$_2$ groups in the axial sites; the metal-metal bond length is 2.132(2)Å [240]. The macrocycle H$_2$tmtaa, 5,7,12,14-tetramethyl-dibenzo[b,i]-1,4,8,11-tetrazacyclotetradecine, reacts with [Mo$_2$(O$_2$CR)$_4$] (R = Me, ^{t}Bu) to produce [Mo$_2$(tmtaa)(O$_2$CR)$_2$] (21) in which it acts as a bis-didentate ligand [241]. Treatment of [Mo$_2$(O$_2$CCF$_3$)$_4$] with 4,4'-bpy gave a compound whose X-ray crystal structure revealed [Mo$_2$(O$_2$CCF$_3$)$_4$(bpy)$_2$] units and linear chains of [Mo$_2$(O$_2$CCF$_3$)$_4$(μ-bpy)]$_n$ in the same crystal [242]. Linkage of two Mo$_2$ units was also achieved by reaction of [Mo$_2$(O$_2$C^{t}Bu)$_3$(MeCN)$_2$]$^+$ with Na$_2$(dop) where H$_2$dop = dioxypyridazine. The same starting material reacted with Na(imt) where Himt = 2-imidazolinethione to give [Mo$_2$(O$_2$C^{t}Bu)$_3$(μ-imt)]; the ligand is coordinated as a bridging N,S-donor with a Mo-Mo distance of 2.116(1)Å [243].

(20)   (21)
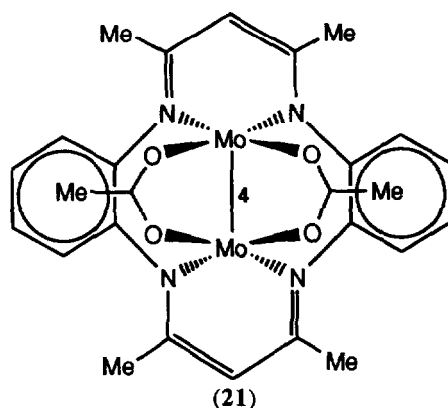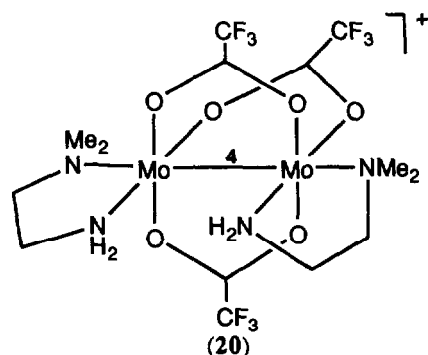
Protonolysis of [Mo$_2$^{i}Bu$_2$(NMe$_2$)$_4$] with ^{i}PrOH or cyclopentanol produced [Mo$_2$(OR)$_4$(ROH)$_4$], while ^{t}BuCH$_2$OH gave [Mo$_2$(OR)$_4$(NHMe$_2$)$_4$]; all three show typical Mo-Mo distances in the range 2.11-2.13Å. Further reaction of the ^{i}PrOH complex with py gave

[Mo$_2$(O^{i}Pr)$_4$py$_4$], and displacement of the amine ligands from the neopentoxide by PMe$_3$ yielded [Mo$_2$(OCH$_2^t$Bu)$_4$(PMe$_3$)$_4$]; these have longer Mo-Mo bonds of 2.195(1) and 2.218(1)Å respectively [244].

Reaction of [Mo$_2$(μ-OAc)$_4$] with the anion of 6-diphenylphosphino-2-hydroxypyridine (pyphos$^-$) affords [Mo$_2$(μ-pyphos)$_4$] in which the ligand is bonded through N and O; the four pendant phosphines can then be coordinated to [PdCl$_2$(PhCN)$_2$] to give [ClPdMo$_2$(pyphos)$_4$PdCl] (22) which contains a linear four metal chain. The reaction of [PdCl$_2$(Hpyphos)$_2$] with [Mo$_2$(OAc)$_4$] instead gives [Cl$_2$PdMo$_2$(μ-pyphos)$_2$(μ-OAc)$_2$]$_2$ (23); the two pyphos ligands are situated *cis* around the metal-metal axis, and the two trimeric units are loosely associated through the acetate ligands [245].
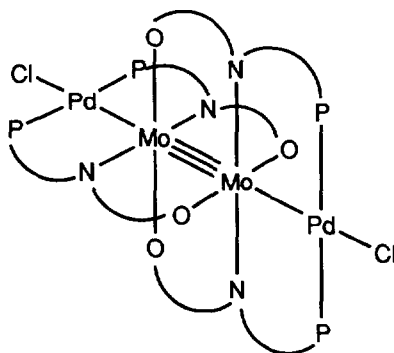
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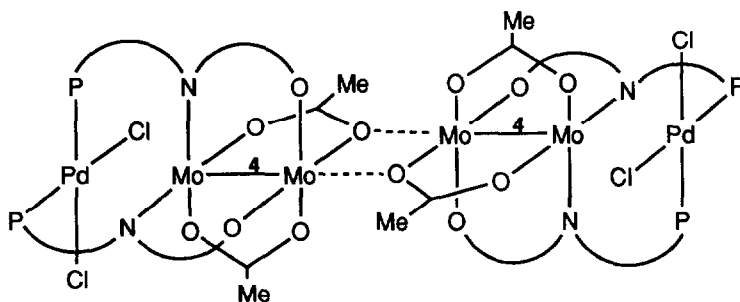
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4.5.4   Complexes with sulfur donor ligands

A mass spectroscopic study of [Mo$_2$(S$_2$PF$_2$)$_4$] and [Mo$_2$(S$_2$PMe$_2$)$_4$] has been published [246]. The synthesis and X-ray structures of [Mo$_2$(CO)$_2$(μ-SR)$_2$Cp$_2$] (R = Ph, ^{t}Bu) and [CpMo(MeCN)(μ-SPh)$_3$Mo(CO)$_3$] have been described [247].

4.6   MOLYBDENUM(I)

The X-ray structure of the 17-electron species [(HBpz*$_3$)Mo(CO)$_3$] has been determined, along with that of [(HBpz*$_3$)Mo(CO)$_3$H]. The availability of both these compounds, as well as the

anion [NBu₄][(HBpz*₃)Mo(CO)₃], has allowed the determination of the rates of electron transfer, proton transfer, and H-atom transfer in this system by mixing two of the three. Electron transfer is fastest and H-atom transfer slowest [248]. The energetics of deprotonation and of Mo-H bond homolysis in this system have also been explored; pK_a values and bond dissociation energies decrease in the order [CpMo(CO)₃H] > [(HBpz₃)Mo(CO)₃H] > [(HBpz*₃)Mo(CO)₃H] [249]. Full characterisation of a range of 17-electron [LMo(CO)₂L¹] complexes, where L = HBpz₃, HBpz*₃, or Bpz₄, has been achieved. For L¹ = CO, the compounds exhibit a Jahn-Teller distortion; they are EPR-silent except in frozen glasses. One carbonyl can be replaced by a phosphine ligand, but the reaction is not clean and the formation of hydrides and disproportionation products is observed [250].

4.7   MOLYBDENUM(0)

4.7.1   Complexes with carbonyl ligands

This section deals largely with complexes of the type [Mo(CO)₆₋ₙLₙ] (n = 1-3), derived from [Mo(CO)₆], arranged according to donor atom, though reactions in which [Mo(CO)₆] or derivatives such as [Mo(CO)₃(NCMe)₃] are used as routine starting materials are not included.

A theoretical study of the M–CO bonds lengths and dissociation energies in [M(CO)₆] (M = Cr, Mo, W) has produced results which show good agreement with observed gas phase values; the derived values are 155 ± 8, 163 ± 8 and 192 ± 8 kJ mol⁻¹ for the three metals [251]. Several papers deal with the behaviour of [Mo(CO)₆] on supports or loaded into zeolites. Variable temperature ⁹⁵Mo NMR relaxation measurements made on [Mo(CO)₆] encapsulated into dry Na-Y zeolite have shown that the molecule exhibits rotational freedom within the supercage with an activation energy of 40 ± 4 kJ mol⁻¹ [252]. The adsorption of [Mo(CO)₆] in the same zeolite and its subsequent substitution reaction with PMe₃ have been studied by solid state ²³Na double rotation NMR spectroscopy [253]. A detailed kinetic and mechanistic study of this reaction, which gives cis-[Mo(CO)₄(PMe₃)₂], has shown that both dissociative and associative pathways are in operation, whereas substitution with ¹³CO occurs only by a dissociative route, though this is much faster than in solution [254]. Oxidation of [Mo(CO)₆] in this zeolite with O₂ gave an identical Mo(VI) product whether carried out under thermal or photochemical conditions [255].

The decomposition of [Mo(CO)₆] on dehydroxylated alumina has been followed by EXAFS; typical species detected were Mo(CO)₅, Mo(CO)₂.₅, and Mo₂C [256]. The formation of subcarbonyl species by partial decarbonylation of [Mo(CO)₆] on MgAl₂O₄ spinel has been followed by IR spectra [257]. A range of Mo carbonyl species were formed by photoreduction with CO of the Mo(VI) moieties produced by adsorption of various Mo complexes on a silica support and were characterised by FTIR spectra [258]. Sonoluminescence has been observed on ultrasonic irradiation of [Mo(CO)₆] and other metal carbonyls in silicone oil; it arises by atomic emission from metal atom excited states [259].

A mixture of [Mo(CO)₆] and and a large excess of phenol has been shown to catalyse the polymerisation of phenylacetylene at elevated temperatures [260]. The use of stoichiometic quantities of [Mo(CO)₆] as a reagent in cyclisation reactions of enynes to cyclopentenones has also

been reported [261]. Cyclisation of alkynyl alcohols to 2,3-dihydrofuran derivatives is promoted by [Mo(CO)$_5$(NMe$_3$)], prepared *in situ* [262].

The crystal structure of [PPN]$_2$[Mo$_2$(CO)$_{10}$] has been determined [263], as has that of [NEt$_4$][Mo(CO)$_5$I] [264]. The reaction of [HMo$_2$(CO)$_{10}$]$^-$ with sodium nitrite in acid conditions produces [HMo$_2$(CO)$_9$(NO)], which undergoes substitution reactions with phosphine ligands to give mono- or disubstituted products [265]. Anionic Mo carbonyl complexes, particularly [NHEt$_3$][Mo$_2$(CO)$_{10}$(SEt)], were found to be effective in the hydrodesulfurisation of dibenzothiophene when adsorbed on a support [266].

The reaction of [M(CO)$_3$(EtCN)$_3$] (M = Mo, W) with Na$_2$[*nido*-7,9-Me$_2$-7,9-C$_2$B$_{10}$H$_{10}$] gave the dianions [M(CO)$_3$(η^6-cage)]$^{2-}$, isolated as the PPN salts; these were then employed in the synthesis of MPt complexes [267]. The reaction of [PPN][*closo*-1,2-Me$_2$-3-allyl-3,3-(CO)$_2$-3,1,2-MoC$_2$B$_9$H$_9$] with HI under CO produced initially the tricarbonyl iodo complex of the same carborane, which then underwent a slow polytopal rearrangement to [PPN][*closo*-1,8-Me$_2$-2-I-2,2,2-(CO)$_3$-2,1,8-MoC$_2$B$_9$H$_9$] [268]. The reactions of the carbaborane anion Na$_2$[Mo(CO)$_3$(η^5-7,8-C$_2$B$_9$H$_9$Me$_2$)] with [CpRh(MeCN)$_3$]$^+$ to give trinuclear clusters has also been reported [269].

A comparative ^{13}C NMR spectroscopic study has been carried out on the acetonitrile species {M(CO)$_5$(MeCN)} for M = Cr, Mo, W [270]. A range of [M(CO)$_5$L] complexes (M = Cr, Mo, W; L = NMe$_3$, PMe$_3$, AsMe$_3$, PCl$_3$ and PBr$_3$) have been studied by IR and ^{13}C NMR spectroscopies, and their dipole moments and optical polarisabilities have been measured; the trends provide some evidence for a π–component in the bonding of PMe$_3$ and AsMe$_3$ [271].

The spectroelectrochemistry of *trans, mer*-[L$_2$(CO)$_3$Mo(μ-pyr)Mo(CO)$_3$L$_2$]$^+$ (L = P^{i}Pr$_3$, pyr = pyrazine) indicates that it is a completely delocalised system with an average oxidation state of 0.5, as shown by EPR, electronic and vibrational spectra, and is thus an analogue of the famous Creutz-Taube ion [272]. A photophysical study of [W(CO)$_4$(bpym)] and [{M(CO)$_4$}$_2$(μ-bpym)] (M = Mo, W; bpym = 2,2'-bipyrimidine) has established that the two lowest energy transitions are both MLCT ones to different π^* orbitals of the ligand; surprisingly it is the second of these which involves the LUMO, which explains the unusual band intensities and the low g values observed in the EPR spectra of the anion radicals [273]. The complexes [Mo(CO)$_4$(dpq)] and [{Mo(CO)$_4$}$_2$(μ-bpq)] where bpq = 2,3-bis(2-pyridyl) quinoxaline have been prepared [274]. The reaction of [Mo(CO)$_3$(MeCN)$_2$(PPh$_3$)] with 8-azidoquinoline produced the phosphoramine chelate complex (**24**), by insertion of a nitrene into the Mo-P bond. The reaction also occurs with [Mo(CO)$_3$(dppm)(MeCN)] and results in an analogous *P,N,N*-chelate ligand [275].
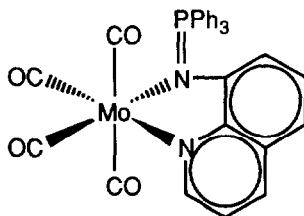
(24)

The synthesis of the pyrazolylmethane species [Mo(CO)$_4$(CH$_2$pz$_2$)] and its CH$_2$pz*$_2$ analogue has been reported [276]. However complexation of Ph$_2$Cpz*$_2$ to [Mo(CO)$_6$] produced [Mo(CO)$_3$(Ph$_2$Cpz*$_2$)] which is stabilised by an η^2-interaction of one phenyl group. This compound reacts with [PhN$_2$][BF$_4$] to give [Mo(CO)$_2$(N$_2$Ph)(Ph$_2$Cpz*$_2$)], but P(OMe)$_3$ displaces the pyrazolylmethane ligand to give [Mo(CO)$_3$\{P(OMe)$_3$\}$_3$] [277]. The synthesis of [Mo(CO)$_4$L] where L = bis(2-pyridyl)amine has been reported [278] and the crystal structure of the chelate complex [Mo(CO)$_4$(tmen)] has been determined [279]. Oxidations of the Schiff's base complexes [Mo(CO)$_4$L] (L = RCH=NCH$_2$CH$_2$N=CHR where R = various aryl) with halogens gave [MoX$_2$(CO)$_3$L], and NOCl gave [MoCl(NO)(CO)$_2$L] [280]. The reaction of [Mo(CO)$_6$] with [Ru(NHC$_6$H$_4$NH)(PPh$_3$)$_3$] gave [Mo(CO)$_2$\{(μ-NHC$_6$H$_4$NH)Ru(CO)$_2$(PPh$_3$)\}$_2$] [281].

An ingenious method of selectively functionalising one end of the tetramine ligand H$_2$N(CH$_2$)$_3$NH(CH$_2$)$_3$NH(CH$_2$)$_3$NH$_2$ has been devised by des Abbayes and coworkers. Coordination to an M(CO)$_3$ fragment occurs as a tridentate ligand, leaving one terminal amine group uncoordinated. Reaction with aldehydes or ketones (R^{1}R^{2}C=O) in refluxing dmf converts this end to its Schiff's base, and subsequent reductive decomplexation with NaBH$_4$ affords the monoalkylated amine ligand H$_2$N(CH$_2$)$_3$NH(CH$_2$)$_3$NH(CH$_2$)$_3$NHCHR^{1}R^2 [282]. However if RCHO is used where R = 2-furyl or 2-thienyl, both ends of the amine were alkylated; moreover if a donor solvent such as thf was added, the same happened with PhCHO. The conclusion is that the tridentate complex is in equilibrium with a didentate one in which the other end is also freed for reaction, and this allows the preparation of unsymmetrically substituted tetramines by addition of the first carbonyl compound in dmf, then a different one in thf (Scheme 4) [283].

Scheme 4
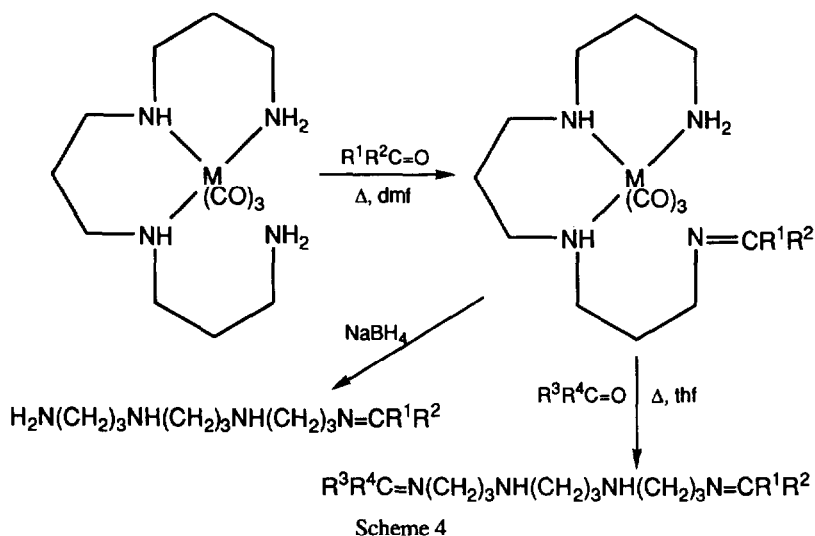
A number of phosphine ligands have been synthesized and characterised as complexes of the type [Mo(CO)$_5$L], [Mo(CO)$_4$L$_2$], and [Mo(CO)$_3$L$_3$]. These include PRH$_2$ and PR$_2$H where R = adamantyl [284], Me$_2$PCH$_2$P^{t}Bu$_2$ and ^{t}Bu$_2$PCH$_2$PMeCH$_2$P^{t}Bu$_2$ [285], and the silylated

triphosphites $R^1Si\{OP(OR)_2\}_3$ (R = Me, Et; R^1 = Ph, vinyl) which were made into [Mo(CO)$_4$(η^2-L)] and *fac*-[Mo(CO)$_3$L] [286]. The tetraphosphites Si$\{OP(OR)_2\}_4$ were also prepared, and can bridge two Mo(CO)$_4$ units [287]. A ^{31}P and ^{95}Mo NMR spectroscopic study of all three types of complex was carried out for L = 1,3,5-triaza-7-phospha-adamantane; this showed a strong σ-interaction and also a strong nephelauxetic effect [288]. The electrospray mass spectra of a number of Mo carbonyl phosphine complexes, including both anionic and cationic examples, have been recorded; in each case the dominant peak corresponds to the main ion in solution [289]. X-ray structures have been reported for *fac*-[Mo(CO)$_3$(PPh$_2$H)$_3$] [290] and the chelate complex *cis*-[Mo(CO)$_4$\{(PPh$_2$O)$_2$P(O)R\}] where R = Me, *p*-C$_6$H$_4$OMe [291]. The barrier to rotation about the P–C bonds in [M(CO)$_5$\{P(*o*-tolyl)$_3$\}] (M = Cr, Mo, W) has been studied by VT-NMR spectra; it is in the range 36–42 kJ mol^{-1} [292].

Coordination of the functionalised macrocycle 1,4,8,11-tetrakis(diphenylphosphinomethyl)-1,4,8,11-tetrazacyclotetradecane to [Mo(CO)$_6$] occurs through the four phosphines to produce [(CO)$_4$Mo(μ-L)Mo(CO)$_4$] (25) [293]. Coordination of an M(CO)$_5$ (M = Cr, Mo, W) unit to the phosphorus atom of the side-bound phospha-alkyne complex [Pt(dppe)(PC^{t}Bu)] has been achieved [294]. The reaction of [Cr(CO)$_5$\{AsPhH$_2$\}] with P^{t}Bu(C≡CH)$_2$ affords the six-membered ring complex [Cr(CO)$_5$\{P^{t}Bu(CH=CH)$_2$AsPh\}], which in turn reacts with [Mo(CO)$_5$(thf)] by attachment through the As centre [295].

(25)
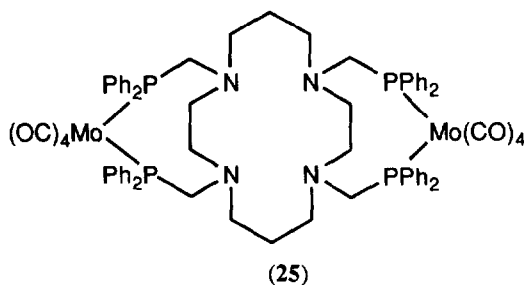
Improved syntheses of the secondary diphosphine ligands PhPH(CH$_2$)$_n$PHPh (n = 2, 3, 4 and 6) have been developed; those with n = 2 and 3 were made into [Mo(CO)$_4$L] complexes [296]. Cleavage of one aryl group from each arm of Me(CH$_2$PPh$_2$)$_3$ with lithium occurs cleanly enough to allow the synthesis of Me(CH$_2$PPhR)$_3$ where R = H, Me, Et, ^{i}Pr, CH$_2$Ph. Complexation of these to [Mo(CO)$_3$(MeCN)$_3$] gives [Mo(CO)$_3$L] as two pairs of diastereomers (*SSR/RRS* and *SSS/RRR*) in the statistically-expected 3:1 ratio, except for R = CH$_2$Ph where only the first pair is formed [297]. Base-catalysed rearrangement of [M(CO)$_4$\{(Ph$_2$PCH$_2$)$_2$C=CH$_2$\}] (M = Cr, Mo, W) gave [M(CO)$_4$\{*cis*-Ph$_2$PCH=C(Me)CH$_2$PPh$_2$\}], while base-catalysed addition of PPh$_2$H to the same complex produced *fac*-[Mo(CO)$_3$\{(Ph$_2$PCH$_2$)$_2$C(Me)PPh$_2$\}] [298]. Addition of an N–H bond of the diamines Me$_2$N(CH$_2$)$_n$NH$_2$ (n = 2, 3) to [M(CO)$_4$\{(Ph$_2$P)$_2$C=CH$_2$\}] (M = Cr, Mo, W) gave [M(CO)$_4$\{(Ph$_2$P)$_2$CHCH$_2$NH(CH$_2$)$_n$NMe$_2$\}]. The pendant diamine can then be used to form complexes with Zn, Cd, Hg, Cu and Ni; the structure of the ZnCl$_2$ complex (26) (n = 2) was reported [299, 300]

(26)
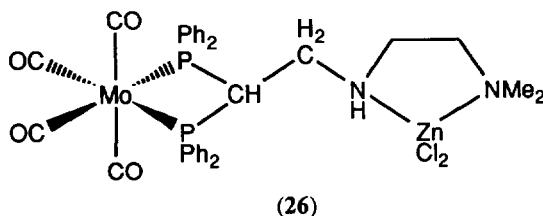
Deprotonation of the phosphine ligand in [M(CO)$_5$(PPh$_2$H)] (M = Cr, Mo, W) followed by reaction with [CpFe(CO)$_2$I] gave [CpFe(CO)$_2$(μ-PPh$_2$)M(CO)$_5$]; when M = W, photochemical CO loss and Fe–W bond formation could be induced, but not for M = Mo [301]. Two equivalents of the same deprotonated species react with [M(CO)$_5$(PCl$_3$)] (M = Cr, Mo) to produce the triphosphine complex [(CO)$_5$M(PH{PPh$_2$M(CO)$_5$}$_2$)] [302]. Coupling of [M(CO)$_5$(PPhHCl)] (M = Cr, Mo, W) was achieved on dehydrohalogenation with NEt$_3$ to give [(CO)$_5$M(PPhH–PPhCl)M(CO)$_5$] [303]. Lithiated dibenzophosphole reacts with [Mo(CO)$_6$] in thf to give Li[Mo(CO)$_5$(dbp)], which can be derivatised at the phosphorus atom by treatment with electrophiles such as H$^+$, BrCH$_2$C≡CH, and BrCH$_2$CH$_2$Br; this last causes formation of a direct P–P bond. Base-catalysed addition of the P–H bond of [Mo(CO)$_5$(dbpH)] to the alkyne of [Mo(CO)$_5$(dbpCH$_2$C≡CH)] occurs to produce initially [(CO)$_5$Mo{dbpCH$_2$C(=CH$_2$)dbp}Mo(CO)$_5$], which then undergoes a hydrogen shift with loss of one Mo centre to yield [Mo(CO)$_4${*cis*-dbpCH=C(Me)dbp}] [304].

The unsaturated derivatives [Mo(CO)(R$_2$PCH$_2$CH$_2$PR$_2$)$_2$] have been prepared for R = Et, ^{i}Bu and Ph, and their reactions with H$_2$ studied. For the first two, oxidative addition occurs to give a dihydride, but with dppe a dihydrogen complex is formed; a neutron diffraction study was carried out on [Mo(H$_2$)(CO){(C$_6$D$_5$)$_2$PCH$_2$CH$_2$P(C$_6$D$_5$)$_2$}].4.5C$_6$D$_6$. Inelastic neutron scattering measurements indicated a low barrier to rotation of the H$_2$ ligand of 5.85 kJ mol^{-1} [305].

The thermodynamics of the protonation of the pendant phosphine in [M(CO)$_5$(η^1-dppm)] have been examined by titration calorimetry; all are exothermic and they vary in the order Cr < Mo < W. The related compounds *fac*-[Mo(CO)$_3$(L$_2$)(η^1-dppm)] (L$_2$ = bpy, phen) were also studied [306]. The identification of the bonding modes of the dppm ligand in [Mo(CO)$_4$(dppm)] and [Mo(CO)$_3$(phen)(η^1-dppm)] by spectroscopy has been adapted as an undergraduate experiment [307]. The X-ray structure of [Mo(CO)$_5$(dppf)] has been determined, and the pendant phosphine in [M(CO)$_5$(dppf)] (M = Cr, Mo, W) has been coordinated to other metals e.g. with [AuCl(SMe$_2$)], *trans*-[PdCl$_2$(PhCN)$_2$] and *cis*-[PdCl$_2$(dmso)$_2$] [308]. Di- and trinuclear chain complexes of the type [(CO)$_5$M(μ-L-L)M(CO)$_5$] and [(CO)$_5$M(μ-L-L)M(CO)$_4$(μ-L-L)M(CO)$_5$] have also been prepared where the bridging ligand L-L = dppf, dppe or dppp [309, 310].

The complex [Mo(CO)$_3$(dppm)(η^1-dppm)] has also been used to construct dimetallic species by reaction with [PdCl$_2$(CN^{t}Bu)$_2$]. In benzene the product is [MoCl(CO)$_2$(CN^{t}Bu)(μ-dppm)$_2$PdCl], whereas in more polar CH$_2$Cl$_2$, [Mo(CO)$_3$(CN^{t}Bu)(μ-dppm)$_2$PdCl][Cl] is formed; the former can be converted into the latter by treatment with CO [311]. The related complex [MoCl(CO)$_3$(μ-PPh$_2$py)$_2$PdCl] can be used for alkene hydrogenation, and the X-ray structure of the analogous iodide derivative has been reported [312, 313]. The reaction of [Mo(CO)$_6$] with [Fe(CO)$_3$(PPh$_2$py)$_2$] gave [MoFe(CO)$_6$(μ-PPh$_2$py)$_2$] with a Fe to Mo donor bond [314].

Treatment of the tetraphosphoxane cage compound [(CO)$_4$Mo{P(N^{i}Pr$_2$)O}$_4$Mo(CO)$_2$I$_2$] with NaS$_2$CNEt$_2$ causes loss of the Mo(II) vertex to give [Mo(CO)$_4${P(N^{i}Pr$_2$)O}$_4$]; the two uncoordinated phosphorus atoms can then be attached to suitable metal fragments e.g. [W(CO)$_4$(nbd)], [Fe$_2$(CO)$_9$], [Cu(MeCN)$_4$]$^{2+}$ to give complexes of the type (27) [315]. Heating (EtAsO)$_n$ with [M(CO)$_6$] (M = Cr, Mo, W) produced [{M(CO)$_3$}$_2${EtAsO}$_6$] [316].

Complexes of hybrid *P,N*-ligands have been explored extensively. Phenylbis(2-pyridyl) phosphine, PPhpy$_2$, reacts with [Mo(CO)$_5$(MeCN)] by coordination through P; two equivalents react with [Mo(CO)$_4$(nbd)] in the same way to give [Mo(CO)$_4$L$_2$]. However if only one equivalent is used, the *N,N*-bonded complex [Mo(CO)$_4$L] is formed [317]. Treatment of [Mo(CO)$_4$(nbd)] with *trans*-[EtNP(OC$_6$H$_3$-2,6-Me$_2$)]$_3$ gave a complex of formula [Mo(CO)$_4$L], whereas the closely related *cis*-[EtNP(OCH$_2$CF$_3$)]$_3$ gave [(CO)$_4$Mo(μ-L)Mo(CO)$_4$] [318].

(27)   (28)
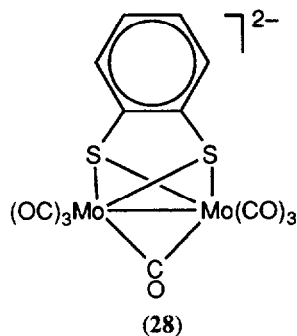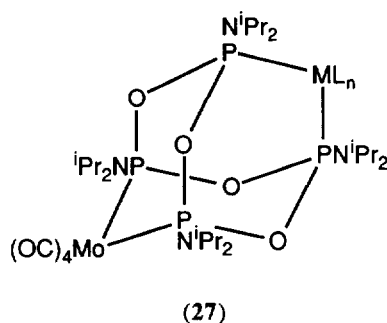
The reaction of [Mo(CO)$_3$(MeCN)$_3$] with Ph$_2$PN^{i}PrPPhpz* gave initially *P,P*-bonded [Mo(CO)$_3$(MeCN)(L)]; the MeCN ligand could be replaced by PPh$_3$ or P(OPh)$_3$ to give *fac*-tris-phosphine complexes which slowly isomerised to *mer*. The complex [Mo(CO)$_3$L], where the pyrazolyl group is also coordinated, was successfully prepared from [Mo(CO)$_4$(L)] [319]. Complexes of Ph$_2$PNPhP(=E)Ph$_2$ (E = O, S), including the Mo(CO)$_4$ one, have also been made; the ligand acts as a *P,E*-chelate [320]. The ligand *o*-Ph$_2$PC$_6$H$_4$CH=NCH$_2$CH$_2$N=CHC$_6$H$_4$-*o*-PPh$_2$ forms complexes such as [{Mo(CO)$_4$}$_2$(μ-L)], where it acts as a bis-*P,N*-chelate, and *fac*-[Mo(CO)$_3$L]; in the latter it is bonded through P, N, N, and its monoxide also forms a similar compound [321]. The ligand MeN(CONMe)$_2$PNMeCH$_2$CH$_2$NMe$_2$ reacts with [Mo(CO)$_4$(nbd)] to give two isomers of [Mo(CO)$_4$L]; one is bonded through P and NMe$_2$, the other through the NMe and NMe$_2$ groups of the diamine moiety [322].

The complexes *cis*-[M(CO)$_4$(EMe$_3$)(E'Me$_2$SiMe$_3$)] where M = Cr, Mo, W and E, E' = P or As have been made; they are open-chain analogues of the previously prepared chelates [M(CO)$_4${Me$_2$E(CH$_2$)$_n$SiMe$_2$EMe$_2$}] [323]. The stibine ligands SbPh$_2$Cl and E(SbPh$_2$)$_2$ (E = O, S) have been used to make compounds of the type [M(CO)$_5$L], {M(CO)$_4$L}, and [M(CO)$_4$(μ-L)]$_2$ [324].

The ligand 2,5-bis(diphenylphosphinoethyl)thiophene has been synthesized; it acts as a *P,S,P*-donor in its *fac*-[Mo(CO)$_3$L] complex [325].

The reaction of [Mo(CO)$_3$(MeCN)$_3$] with the dianions derived from o-C$_6$R$_4$(SH)$_2$ (R = H, Me, Cl) or HSCH$_2$CH$_2$SH in MeCN initially gives complexes [Mo(CO)$_3$(S-S)]$^{2-}$, which gradually add another carbonyl fragment to give [Mo$_2$(CO)$_7$(μ-S-S)]$^{2-}$ (**28**). The yield of the latter can be improved by adding [Mo(CO)$_4$(nbd)] [326]. Treatment of [Mo(CO)$_4$(pip)$_2$] with dtc$^-$ (dtc is derived from pyrrolidine or piperidine) produced [PPN][Mo(CO)$_4$(dtc)] [327]. The reaction of [Mo(CO)$_6$] with 1,3-diphenyltetrazolium 5-thiolate or selenolate gave [Mo(CO)$_5$L] [328].

Protonation of [Mo(S$_2$CPMe$_3$)(CO)$_2$(PMe$_3$)$_2$] produces [Mo(S$_2$CHPMe$_3$)(CO)$_2$(PMe$_3$)$_2$]$^+$, whereas methylation occurs at sulfur to give a S-alkyl phosphonio-thioester ligand. It is suggested that protonation probably occurs initially at the metal [329]. The reaction of [Mo(CO)$_3$(MeCN)$_3$] with [MnBr(S$_2$CPR$_3$)(CO)$_3$] (R = Cy, ^{i}Pr) gave [(CO)$_3$Mn(μ-Br)(μ-S$_2$CPR$_3$)Mo(CO)$_3$]; both sulfurs and the carbon atom are bonded to Mo [330]. Reduction of this complex with sodium amalgam gives an anion which on quenching with Ph$_3$SnCl gave [(CO)$_3$Mn(μ-S$_2$CPR$_3$)Mo(CO)$_3$(SnPh$_3$)], in which the bonding mode of the ligand has reversed: the sulfur and carbon atoms are now all bonded to Mn (Scheme 5) [331].
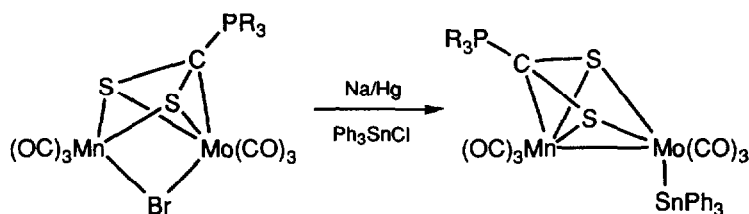
Scheme 5

Due to the bending back of the alkyne substituents, the complexes [Co$_2$(CO)$_4$(μ-dppm)(μ-RSCH$_2$C≡CCH$_2$SR)] (R = various alkyl) are able to act as chelate complexes through the sulfur atoms to a Mo(CO)$_4$ fragment [332]. The complex [Ni(SCH$_2$CH$_2$PPh$_2$)$_2$] is able to do likewise, giving (**29**) [333].

(29)
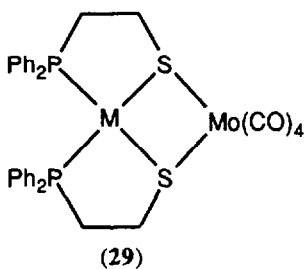
Three interesting Mo carbonyl clusters were prepared. Treatment of NaBiO$_3$ with [Mo(CO)$_6$] and NEt$_4$Br in MeOH produced [NEt$_4$]$_2$[BiMo$_4$(CO)$_{12}$(μ_3-OMe)$_3$]; the structure consists of a Mo$_3$ triangle with a capping Bi atom and a Mo(CO)$_3$ unit joined underneath through the bridging methoxides [334]. Incorporation of Mo(CO)$_3$ vertices into Co-As clusters has been

achieved by reaction with [Mo(CO)5(thf)]; thus [Cp*Co(μ-As6)Mo(CO)3CoCp*] (**30**) was formed from [Cp*Co(μ-As6)CoCp*] and [Cp*3Co3(μ-As2)3] gave [Cp*3Co3(μ-As6)Mo(CO)3] (**31**) [335].

(**30**)   (**31**)
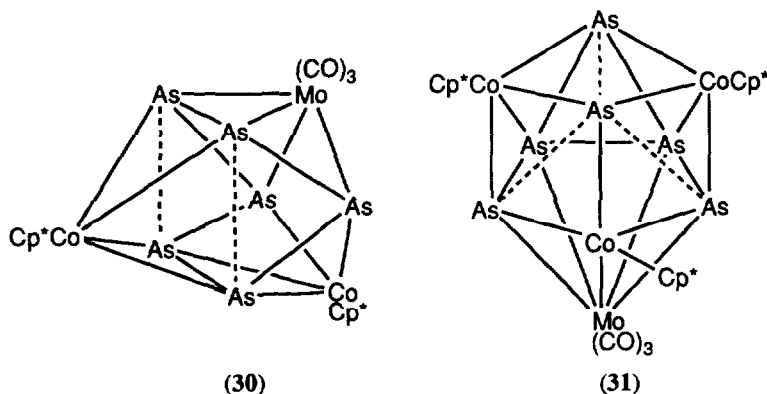
4.7.2 Complexes with nitrogen and phosphorus donor ligands

An overview of the reactions of the dinitrogen ligands in *trans*-[Mo(N2)2(dppe)2] and *cis*-[Mo(N2)2(PMe2Ph)4] has appeared [336]. Reduction of [MoCl3L] where L = N(CH2CH2PPh2)3 with sodium dispersion under N2 gave the unstable complex *cis*-[Mo(N2)2L], which reacts with CO, PMe3, MeI and CF3CO2H to give [Mo(CO)3L], [Mo(PMe3)3L], [MoI2L] and [Mo(O2CCF3)2L] respectively. Reduction of the analogous trichloride with L = P(CH2CH2PPh2)3 gave *trans*-[Mo(N2)2L] but this was also unstable [337]. The reaction of the compound *trans*-[Mo(N2)2(PS-dppe)(PPh2Me)2], where the diphosphine ligand is attached to a polystyrene support, with HBr produced more ammonia than usual if SnBr2 was added; the free complex *trans*-[Mo(N2)2(dppe)(PPh2Me)2] also reacted similarly. In the presence of 6 mole equivalents of HBr the product was the Mo(V) hydrazido compound [MoBr3(NNH2)(dppe)], whereas with 10 mole equivalents of HBr (but without SnBr2) the initial product was [MoBr(NNH2)(dppe)(PPh2Me)2]+ which then lost one phosphine to give [MoBr2(NNH2)(dppe)(PPh2Me)] [338]. Treatment of [Mo(N2)2(PMe2Ph)4] with Me3SiCl and Na in thf resulted in the catalytic conversion of N2 into silylamines; the analogous *cis*-[W(N2)2(PMe2Ph)4] produced *trans*-[WI(NNSiMe3)(PMe2Ph)4] [339]. The protonolysis of [MoH(η-C3H5)(dppe)2] with HCl produces [MoH2Cl2(dppe)2]; at high acid concentrations propyne is formed, whereas under more dilute conditions propene is observed, a fact rationalised by the operation of two parallel mechanisms, one of which involves loss of H2 [340].

Treatment of the dinitrosyls [Mo(NO)2(CN)4]$^{2-}$ with donor ligands such as various pyrazolinones, pyridines and drugs, gives complexes of the type [Mo(NO)2(CN)2L2].2H2O [341, 342]. A number of Schiff's base complexes of the type [Mo(NO)2(HL)2] have been prepared from [Mo(NO)2(acac)2]; the ligands are derived by the condensation of salicylaldehyde, *o*-hydroxyacetophenone or *o*-vanillin with benzoylhydrazides or nicotinoylhydrazide [89, 343]. The

products can be compared to the well-known [MoO$_2$(HL)$_2$] compounds. The reaction of [Mo(NO)$_2$(acac)$_2$] with picolinic acid in refluxing methanol produced [Mo(NO)$_2$(pic)$_2$], with a small amount of [Mo(NO)(pic)$_3$] [344]. The synthesis of [MoCl$_2$(NO)$_2$(phen)] has been reported; halide abstraction with AgClO$_4$ in acetone gave a solvent stabilised cation which was used to prepare complexes with bridging pyrazine ligands [345]. After treatment with silanes such as Me$_3$SiCl, the polymeric species [Mo(NO)$_2$(OEt)$_2$(EtOH)]$_n$ acts as a catalyst for alkene oligomerisation [346].

4.8   MOLYBDENUM CLUSTERS

4.8.1   Polyoxomolybdates

The following brief discussion deals first with homonuclear species and then with heteropolymolybdates. A review article on high nuclearity Mo(V) oxo species contains much that is relevant to this section [347], and reviews on the incorporation of organometallic fragments into polyoxometalates [348], the incorporation of organic fragments into polyoxomolybdates [349], and electron transfer reaction of heteropolyoxometalates [350] have appeared. A series of articles on various aspects of polyoxometalate chemistry have been published in Japanese [351]. A hydrophobicity scale for a range of heteropolyanions has been proposed on the basis of their standard ion transfer potentials, determined by electrochemical studies of their behaviour at a nitrobenzene-water interface [352].

The hydrothermal reaction of Na$_2$MoO$_4$.2H$_2$O, MoO$_3$, en.2HCl, and HCl in a 6:6:10:300 ratio at 160°C gave [H$_2$en][Mo$_3$O$_{10}$], which consists of infinite chains of MoO$_6$ octahedra linked in a complex way by face, edge and corner sharing. The structure is different to that of the known ammonium and potassium salts [353]. A stopped-flow kinetic study of the reaction of [Mo$_4$O$_{12}$(O$_2$)$_2$]$^{4-}$ with HSO$_3^-$ has appeared [354]. Polynuclear oxomolybdenum complexes of various *N*-alkyl phenothiazine drugs with formulae such as [Mo$_4$O$_9$(H$_2$O)$_2$L$_2$], [Mo$_5$O$_{10}$(H$_2$O)$_2$L$_2$] and [Mo$_6$O$_{12}$(H$_2$O)$_2$L$_2$] have been prepared [355].

The reaction of hydroxylamine with various isopolyoxomolybdates in MeOH or EtOH produced the nitrosyl compounds [Mo$_5$O$_{13}$(OR)$_4$(NO)]$^{3-}$ (32) (R = Me, Et) which can be viewed as a defect structure derived from the as yet unknown Lindqvist ion [Mo$_5$O$_{18}$]$^{6-}$ [356].

Addition of [NBu$_4$][ClO$_4$] to the filtrate remaining after the synthesis of [Mo$_2$(OAc)$_4$] from [Mo(CO)$_6$], AcOH and Ac$_2$O produced [NBu$_4$]$_2$[Mo$_6$O$_{19}$] after exposure to air [357]. A single crystal of this salt was then used in conjunction with EtAlCl$_2$ as an initiator for the ROMP polymerisation of norbornene; it acts as a heterogeneous catalyst and can be recovered unchanged at the end of the polymerisation [358]. The thermal behaviour of this salt has been examined [359] and the crystal structure of a second polymorph has been determined [360].

The synthesis and crystal structure of the derivatives [NBu$_4$]$_3$[Mo$_6$O$_{18}$(N$_2$R)] where R = C$_6$H$_3$-2,4-(NO$_2$)$_2$ have been described [361, 362]. The reaction of [NBu$_4$]$_2$[Mo$_2$O$_7$] with NH$_2$OH.HCl in refluxing MeCN affords the nitrosyl species [NBu$_4$]$_3$[Mo$_6$O$_{18}$(NO)], which in turn reacts with Me$_2$SO$_4$ to give [NBu$_4$]$_2$[Mo$_6$O$_{17}$(NO)(OMe)] as well as [SMo$_{12}$O$_{40}$]$^{2-}$ [363].

(32)
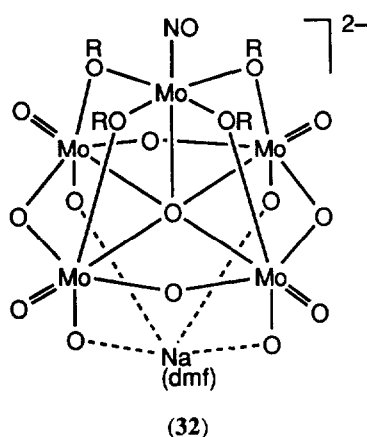
The kinetics and thermodynamics of the epimerisation of the aldopentoses D-xylose and D-lyxose, catalysed by ammonium heptamolybdate, have been studied; the kinetics conform to a Michaelis-Menten model, and the binding affinity for these sugars is greater than for the related aldohexoses glucose and mannose [364].

The X-ray structures of $[NMe_4]_4[Mo_8O_{26}].2H_2O$ and $[NH_3Bu]_4[Mo_8O_{26}].6H_2O$ have been determined [365, 366]; the mixed $[NH_2Me_2]_2[NBu_4]_2$ salt has also been studied [367]. All three contain the β-polyoxomolybdate. A further TTF radical cation salt of the same anion, $[TTF]_7[Mo_8O_{26}]$, which is a semiconductor, has been made by electrooxidation [368, 369]. The thermal behaviour of $[H_2dien]_2[Mo_8O_{26}]$, as well as $[MoO_3(dien)]$ and $[H_3dien]_2[Mo_7O_{24}]$, has been studied by TGA; mixtures of MoO_2 and Mo_2C are formed, with the ratio depending on the starting material [370]. Octamolybdate ions of the type $[Mo_8O_{26}L_2]^{4-}$ where L = imidazole, 1- or 2-methyl-imidazole have been prepared from MoO_3 and L in dmf/water; the structures consist of two $MoNO_5$ and six MoO_6 edge-sharing octahedra [371].

Molten pyrazole reacts with Mo oxides to give octamolybdates with pyrazole ligands i.e. $[Mo_8O_{18}(pz)_6(Hpz)_6].2Hpz$ (33) and the related $[Mo_8O_{21}(pz)_6(Hpz)_6].3Hpz.0.5H_2O$; the former contains Mo(V) and Mo(VI), the latter just Mo(VI) [372]. Treating $[NBu_4]_4[\alpha-Mo_8O_{26}]$ with 4 equivalents of NH_2OH and 4-6 equivalents of the amide oximes $RC(NH_2)=NOH$ (R = Ph, p-tolyl, 2-thienyl) gave the new complexes $[Mo_5O_{12}(NO)_2\{RC(NH)NO\}_2\{RC(NH_2)NHO\}_2]^{2-}$ (34) in which a central $Mo(NO)_2$ unit is bonded to two Mo_2O_5 units through a bridging oxo and the nitrogen of one of the oxime groups [373].

The inclusion of cations into mixed valence polyoxoanions has been observed in the case of $[NH_4]_7[NaMo_{16}(OH)_{12}O_{40}]$ and $[NH_2Me_2]_6[H_2Mo_{16}(OH)_{12}O_{40}]$, which both contain four Mo(V) and twelve Mo(VI) centres. These compounds are unusual in that they contain the ε-Keggin structure [374].

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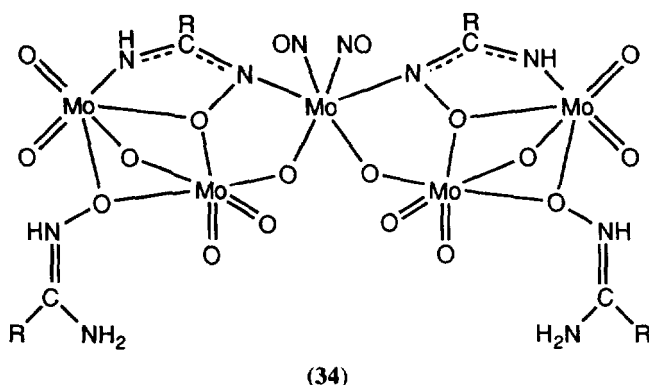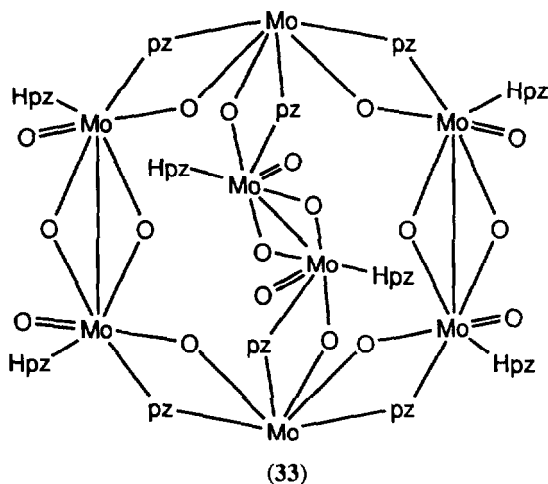
Two groups have reported the synthesis of $Q_3[XO_4\{MO(O_2)_2\}_4]$ where X = P or As, M = Mo or W, and Q is a large counterion such as PPN^+ or NR_4^+. Typically they can be made from MoO_3, H_2O_2, Na_2HPO_4 and the appropriate counterion in benzene. Their ability to effect catalytic epoxidation reactions was also examined [375, 376]. A third group has studied them as catalysts for the oxidation of aniline to nitrosobenzene [377].

Two groups have also reported the synthesis of the $[Na\{Mo_6O_{15}(O_3PPh)(HO_3PPh)_3\}_2]^{9-}$ anion; both involve hydrothermal reactions. In the first case, heating Na_2MoO_4, Mo metal, NEt_4OH, $PPh(O)(OH)_2$ and H_2O in a 2:1:2:6:300 produced the $[NEt_4]_2Na_3(H_3O)_4$ salt, while in the other the $Na_4[NH_4]_5$ salt was formed from a 6:6:10:10:5:300 mixture of $Na_2MoO_4.2H_2O$, MoO_3, $PPh(O)(OH)_2$, KCl, NH_4Cl and H_2O at 180°C for 4 days [378, 379]. The X-ray structure of a salt of the $[Mo_6O_{18}(H_2O)(O_3AsR)]^{4-}$ anion (R = C_6H_3-4-OH-3-NHCOMe) has been reported [380].

The behaviour of the $K_3[PMo_{12}O_{40}]$ catalyst during the oxidation of acrolein has been studied by Raman spectroscopy [381]. Calorimetric measurements have also been made by the same workers [382]. Reduction of α-$[P_2Mo_{18}O_{62}]^{6-}$, or its conproportionation with α-$[P_2Mo_{18}O_{62}]^{8-}$,

generates the corresponding hepta-anion in solution. The monoprotonated octa-anion shows intramolecular migration of the proton between two sites on the Dawson-type structure with an activation energy of around 25 kJ mol^{-1} [383]. The syntheses and structures of eight heteropoly blues of the type $[Ln\{P_2Mo_{17}O_{61}\}_2]^{n-}$ (Ln = Lu, Pr, Sm. Yb; n = 19, 21) as mixed K$^+$/H$^+$ salts have been described [384].

The reaction of As_2O_3, MoO_3, NaCl and H_2O in a 5:10:10:380 ratio at 150°C for 50 hours produced $[As_3Mo_{12}O_{40}]^{5-}$ as its $Na_{0.5}H_{4.5}$ salt. The structure consists of a Keggin-type $AsMo_{12}O_{40}$ core capped on opposite faces by As(III) units. The complex is a mixed-valence $Mo^{VI}_4Mo^V_8$ species [385]. The reaction of $Na_2MoO_4.2H_2O$, Mo metal, MnO_3, $H_5As_3O_{10}$, NaCl and H_2O in a 6:6:6:3:10:166 ratio at 180°C for 110 hours gave crystals of the Na salt of the $[As_6Mo_4O_{20}(OH)_2]^{4-}$ anion (35); the crystal structures of the $9H_2O$ and $10H_2O$ solvates were both determined, but they differ only slightly due to the different cation environments [386, 387]. From a mixture of Mo(VI), AsO_3^{3-} and HCl in MeCN at room temperature, the new green anion $[H_6AsMo_{11}O_{39}]^{3-}$ was isolated as its NBu_4^+ salt [388].

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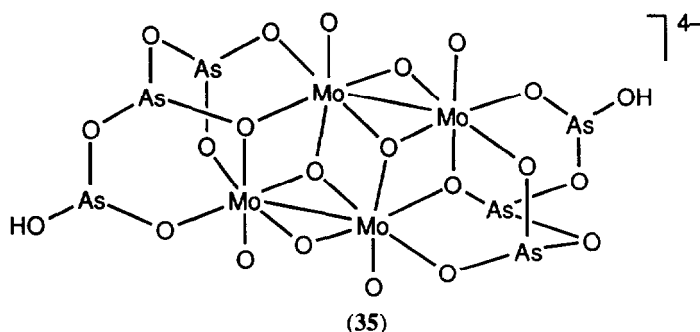
An electrochemical study of the α-$[S_2Mo_{18}O_{62}]^{4-}$ anion in MeCN revealed four reversible one-electron reduction processes; the green penta-anion and blue hexa-anion were both isolated. In acid the penta-anion disproportionates, but not in neutral solution. The EPR spectra of this species showed complete delocalisation of the extra electron [389]. The X-ray structures of $K_2[SeMo_3O_{13}].3.5H_2O$ and $K_2[SMo_3O_{13}].4H_2O$ have been determined; they are chain-like structures made up of MoO_6 and EO_4 units. The Se complex decomposes between 460–470°C to K_2MoO_4, but the sulfur analogue is stable up to 500°C [390]. The reaction of MoO_3, K_2CO_3, H_2SO_4 and SeO_2 in aqueous solution gave the new polyanion $[SeS_3Mo_6O_{33}]^{8-}$, which has an SeO_3 unit in the centre of a ring of MoO_6 octahedra alternately linked by corners and edges, with three SO_4 groups above them [391].

Several papers deal with crystal structure determinations of salts of the $[TeMo_6O_{24}]^{6-}$ anion. These include $Na_6[TeMo_6O_{24}].22H_2O$ [392], $Cs_6[TeMo_6O_{24}].2Te(OH)_6.4H_2O$ [393], $Li_6[TeMo_6O_{24}].18H_2O$ and $Li_6[TeMo_6O_{24}].Te(OH)_6.18H_2O$ [394], $Rb_6[TeMo_6O_{24}].10H_2O$ and $Rb_6[TeMo_6O_{24}].Te(OH)_6.6H_2O$ [395], and $Na_4[NH_4]_2[TeMo_6O_{24}].16H_2O$ [396]. The interest in these structures centres on the capabilities of the different types of oxygen atom to engage in

hydrogen bonding with the water of crystallisation or included telluric acid. Other workers have prepared the Eu^{3+} and Nd^{3+} salts of this anion [397].

The complex $[Mo_2V_2O_8(OMe)_2\{(OCH_2)_3CCH_2OH\}_2]^{2-}$ (36) was produced by reaction of $[VO_2Cl_2]^-$ with $C(CH_2OH)_4$ and then $[NBu_4]_2[Mo_2O_7]$ [398]. The crystal structure of $Na_3[VMo_{12}O_{40}].19H_2O$ has been determined [399]. The reaction of molybdate with Mn^{2+} and HOCl gave $[MnMo_9O_{32}]^{6-}$; speciation studies on the Mn^{2+} showed that $[Mn(H_2O)_6]^{2+}$ was involved as the active species. The kinetics of the formation of the polymolybdate were studied, and the X-ray structure of $Na_4[MnMo_8O_{27}].20H_2O$ was also included [400]. Luminescence from the LMCT triplet states of various polyoxoanions, especially those of the formula $[MMo_6O_{24}]^{9-}$, (M = Cr, Fe, Co) has been observed below 100K [401]. The anion $[H_2W_{11}MoO_{40}]^{6-}$, which probably has the α-Keggin structure, has been identified in solution by its ^{183}W NMR spectrum [402].

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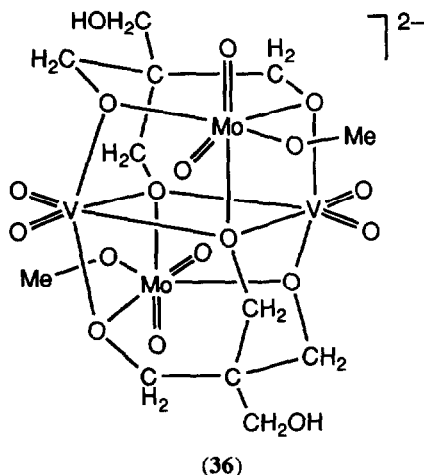
The hydrothermal reaction between Na_2MoO_4, Mo metal, $FeCl_3$, $(NH_4)_2HPO_4$, NMe_4OH, H_3PO_4 and H_2O produced $[NMe_4]_2[NH_4]_2[Fe_2Mo_{12}O_{30}(H_2PO_4)_6(HPO_4)_2].11H_2O$; a different ratio of the same reagents gave $Na_4[NMe_4]_2[Fe_3Mo_{12}O_{30}(H_xPO_4)_8].16H_2O$ [403]. From a mixture of $[Mo_2O_7]^{2-}$, H_3PO_4, $NiCO_3$ and citric acid, $[NH_4]_8[NiMo_{10}O_{30}(HPO_4)_2(PO_4)_2]$ was obtained [404].

The reaction of $Na_2MoO_4.2H_2O$ with NH_4VO_3 and $NH_2OH.HCl$ in boiling water for 2 hours was reported to give the giant cluster $[H_3O]_6[Mo_{57}V_6O_{183}(NO)_6(H_2O)_{18}].89H_2O$, which consists of three subunit clusters each containing 17 edge sharing MoO_6 octahedra, two VO_6 octahedra, and two $Mo(NO)O_6$ pentagonal bipyramids [405]. In the related cluster $Na_6[H_6Mo_{57}Fe_6O_{183}(NO)_6(H_2O)_{18}]$, the Mo_{17} units were linked by FeO_6 octahedra and Mo_2O_9 units [406]. Later investigations reformulated the vanadium cluster as $[H_8Mo_{57}V_6(NO)_6O_{183}(H_2O)_{18}]^{16-}$; if the vanadate was omitted from the reaction, the new species $[H_6Mo_{36}(NO)_4O_{108}(H_2O)_{16}]^{6-}$ was formed, while addition of As_2O_3 to the reagents resulted in the isolation of $[NMe_4]_5[As_3Mo_8V_4O_{40}].3H_2O$. The presence of the Mo_{17} structural motif in some of these clusters was commented on [407].

The synthesis of some new polyoxometalates containing disilicate units has been reported, including $[\alpha\text{-}SiW_9Mo_2(MeSiOSiMe)O_{39}]^{4-}$ and $[\alpha\text{-}PW_9Mo_2(MeSiOSiMe)O_{39}]^{3-}$ [408]. A route to free molybdovanadophosphoric acid $[H_4PMo_{11}VO_{40}]\cdot32H_2O$ has been described [409], and a salt with protonated melamine as the counterion has also been reported [410]. A solid state ^{31}P MAS NMR spectroscopic study of various anions, including $[PMo_{11}VO_{40}]^{4-}$, adsorbed on silica has appeared [411]. The oxidative dehydrogenation of hydrazodicarboxamide, $H_2NCONHNHCONH_2$, to azodicarboxamide, $H_2NCON{=}NCONH_2$, can be catalysed by compounds of the type $H_{3+n}[PMo_{12-n}V_nO_{40}]$ (where n = 4, 6 or 8) in the presence of O_2 [412]. Single crystal structures and powder diffraction studies on a range of molybdovanadophosphoric acid catalysts have been reported [413], and the behaviour of such catalysts in the oxidation of butadiene and n-butane has also been investigated [414]. The synthesis of a mixed Na^+/H^+ salt of $[PMo_{10}V_2O_{40}]^{5-}$ has been achieved [415]. This anion was used to catalyse the oxidation of alkylaromatics to acetates or alcohols with H_2O_2 [416] and the formation of Schiff's bases from benzylamine in the presence of O_2 [417]. The influence of composition on catalytic efficiency in the oxidative dehydrogenation of isobutyric acid to methacrylic acid has been studied for a range of mixed-metal Keggin ions of the type $[H_4PMo_{11-n}W_nO_{40}]$ (n = 0-6) [418].

4.8.2   Halide clusters

The reaction of $MoCl_2$ with NaOH and then $[NBu_4][NCS]$ and HBF_4 gave $[NBu_4]_2[Mo_6Cl_8(NCS)_6]$, which was structurally characterised. It was also isolated as the salt of the radical cation of tetrakis(methylthio)TTF and characterised by EPR spectra [419]. The radical cation of diphenyl (4',5,5'-trimethyl-1,1',3,3'-tetrathiafulvalenyl)phosphine oxide has similarly been studied as its $[Mo_6Br_{14}]^{2-}$ salt [420].

Heating $[Mo_6Cl_8Br_4]$ produces mixed halides $[Mo_6Br_nCl_{8-n}]^{4+}$, which were converted to $[Mo_6Br_nCl_{8-n}Cl_6]^{2-}$. Further treatment with $AgBF_4$ and NBu_4F replaced the outer-sphere halides to give $[Mo_6Br_nCl_{8-n}F_6]^{2-}$ (n = 0-8) as a mixture of 22 compounds, characterised by ^{19}F NMR spectra [421]. A similar process starting from $[Mo_6Cl_8I_4]$ gave $[Mo_6I_nCl_{8-n}F_6]^{2-}$, but in this case the compound with n = 8 was absent so there are only 21 of them in the mixture. The distribution is not entirely statistical: those with n = 3 and 4 are predominant. The n = 8 species $[Mo_6I_8F_6]^{2-}$ was made separately [422].

The compound $[NBu_4]_2[Mo_6Cl_8(OAc)_6]$ was made by treating $[Mo_6Cl_{14}]^{2-}$ with silver acetate [423]. The reaction of $[Mo_6Cl_{12}]$ with 2 equivalents of NaOMe in the presence of 2,2,2-crypt produced $[Na(crypt)]_2[Mo_6Cl_{12}(OMe)_2]$; the methoxides could be exchanged with 9-anthracenyl methanol [424]. Starting from $[Mo_6Cl_8(OMe)_6]^{2-}$, the methoxides could be exchanged for phenoxides in the presence of the same crypt ligand to give $[Na(crypt)]_2[Mo_6Cl_8(OPh)_6]$ [425]. The labile triflate groups in $[Mo_6Cl_8(OTf)_6]^{2-}$ can be displaced by metal cyanide complexes such as $[CpMn(CO)_2(CN)]^-$, $[CpMn(CO)(NO)(CN)]$, and $[CpRu(PPh_3)_2(CN)]$. The resulting dodecanuclear compounds are highly coloured due to vibronic coupling between the metal-cyanide charge transfer absorptions and the cluster bands [426].

The luminescence quenching of $[Mo_6Cl_{14}]^{2-}$ by $[IrCl_6]^{2-}$ has been studied in MeCN and HCl; in MeCN the rate constant depends on the cation present, suggesting that the association between anions and cations is important. Both electron transfer and energy transfer processes are occurring [427]. The oxidation of alcohols by $[Mo_6Cl_{14}]^-$, generated electrochemically from the dianion, has been studied; for example, $PhCH_2OH$ gave a mixture of benzaldehyde and benzyl chloride [428].

4.8.3   Other clusters, including cubanes

The reaction of $[MoCl_3(H_2O)_3]$ with AcOH, Ac_2O and $[NBu_4][BF_4]$ in acetone produced $[NBu_4][Mo_3Cl_3(\mu_3\text{-O})(\mu\text{-Cl})_3(\mu\text{-OAc})_3]$ as an acetone solvate; the analogous bromide could be prepared in the same way [429]. A different group has also reported the isolation and X-ray analysis of the $[NEt_4]^+$ salt of the chloride cluster [430]. Two by-products were isolated from the preparation of the bromide cluster. One of these was the capped butterfly cluster $[NBu_4]_2[Mo_4(\mu_4\text{-O})Br_{12}]$ (37); six of the bromide ligands are terminal, four edge-bridging and two face-capping [431]. The other was the dianionic species $[NBu_4]_2[Mo_3Br_3(\mu_3\text{-O})(\mu\text{-Br})_3(\mu\text{-OAc})_3]$, which could also be prepared by zinc reduction of the mono-anion. If the reduction was carried out in the presence of PMe_3 and $[NBu_4][BF_4]$ the substituted cluster $[Mo_3(\mu_3\text{-O})(\mu\text{-Br})_3(\mu\text{-OAc})_3(PMe_3)_3][BF_4]$ was formed. Reduction of the chloride mono-anion with zinc afforded the neutral cluster $[Mo_3Cl(\mu_3\text{-O})(\mu\text{-Cl})_3(\mu\text{-OAc})_3(thf)_2]$ [432]. Reaction of the tetraethylammonium salt of the chloride mono-anion with Me_3SiCl and PMe_3 afforded $[NEt_4][Mo_3Cl_3(\mu_3\text{-O})(\mu\text{-Cl})_3(\mu\text{-OAc})_2(PMe_3)_2]$. This paper also contains a survey of the structural types found in capped triangular Mo and W complexes with bridging carboxylate ligands [433].

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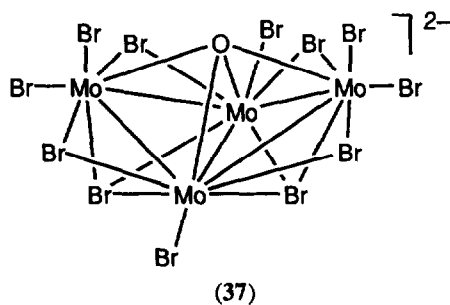
The compounds $[Mo_4Cl_4(\mu\text{-Cl})_2(\mu\text{-OMe})_2(\mu\text{-dppm})_2]$ (38) and $[Mo_4Cl_4(\mu_4\text{-O})(\mu\text{-Cl})_3(\mu\text{-OMe})_3(\mu\text{-dmpm})_2]$ (39) have been prepared by refluxing $K_2[Mo_2Cl_8]$ in MeOH followed by addition of the phosphine ligand. These clusters have square metal frameworks and have been described as cyclotetramolybdenum diynes; they are the first examples with didentate phosphine ligands [434].

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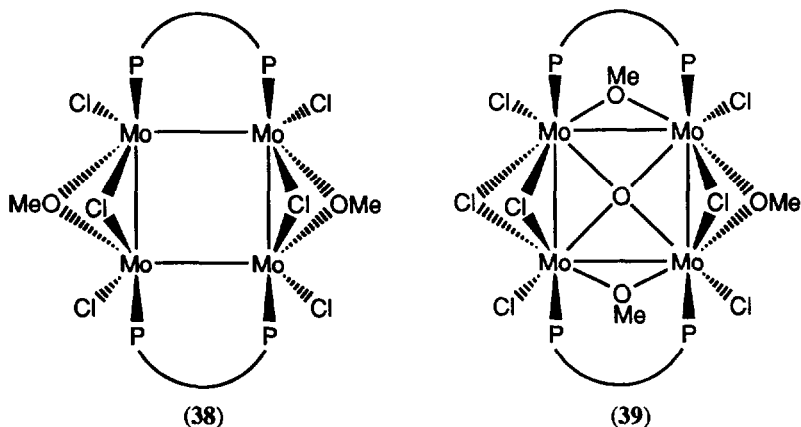
Two tetranuclear alkoxide clusters with butterfly structures have been reported. The complex $[Mo_4(\mu_4\text{-}O)(OCH_2{}^tBu)_{10}(py)]$ is formed by exposure of $[Mo_2(OCH_2{}^tBu)_6]$ to 0.5 equivalents of water in toluene in the presence of pyridine [435]. The reaction of $[Mo_2(p\text{-tol})_2(NMe_2)_4]$ with ${}^tBuOH$ and hydrogen produced the unusual hydride cluster $[Mo_4H_3(O^tBu)_7(NHMe_2)]$ (40); it is proposed that two of the hydride ligands are bridging edges and the third capping one wing of the butterfly, though they were not located directly in the X-ray analysis. The reaction proceeds in two distinct stages; alcoholysis with ${}^tBuOH$ followed by exposure to D_2 gave the analogous trideuteride cluster with a $NDMe_2$ ligand, indicating that this arises by hydrogenolysis [436].

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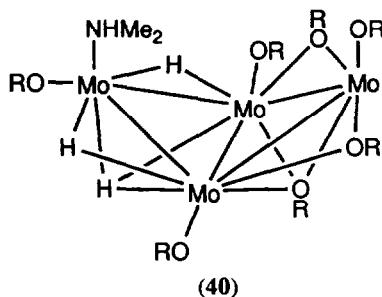
The use of $[MoS_4]^{2-}$ for the construction of heteronuclear complexes and clusters continues to find extensive application. The reaction of $[NEt_4][Mo(CO)_4(dtc)]$ with $[MoS_4]^{2-}$ affords $[NEt_4]_2[(CO)_4Mo(\mu\text{-}S)_2MoS_2]$, a complex which contains two molybdenum atoms in very different oxidation states [437]. The related species $[NEt_4]_2[(CO)_4Mo(\mu\text{-}S)_2Mo(\mu\text{-}S)_2Mo(CO)_4]$ has also been prepared, together with its MoWMo analogue [438]. The osmium nitrido complex $[Os(N)R_2Cl_2]^-$ (R = Me, CH_2SiMe_3) reacts with $[MoS_4]^{2-}$ to produce $[R_2Os(N)(\mu\text{-}S)_2MoS_2]^-$ [439]. The reaction between $[MoO_nS_{4-n}]^{2-}$ (n = 0, 2) with CuCl and Na[dtc] has been followed by dynamic ${}^{95}Mo$ NMR spectroscopy [440]. From $[NH_4]_2[MoS_4]$ and AgI in the presence of methylpyridines, polymeric compounds of the composition $[AgMoS_4.pyH]_n$ were isolated which consist of MoS_2AgS_2 chains with methylpyridinium counterions [441].

A review on the synthesis of Mo/S/Cu and Mo/S/Ag cubanes by low-temperature reactions has appeared [442]. The reaction between $[NH_4]_2[MS_4]$ (M = Mo, W) with CuX (X = Br, I) and PPh_3 occurs in the solid state to give the cubanes $[M(=S)Cu_3(X)S_3(PPh_3)_3]$ [443]. Analogous Ag clusters were made in the same way from AgX (X = Cl, Br, I, CN, SCN) and the structure of $[Mo(=S)Ag_3(I)S_3(PPh_3)_3]$ was determined [444]. The related $[NBu_4]_3[Mo(=S)Ag_3(Br)S_3I_3]$ was also made by a solid state reaction and structurally characterised [445]. A mixture of $[NH_4]_2[MS_4]$, CuBr and NEt_4I in the solid state yielded the new clusters $[NEt_4]_4[MS_4Cu_4I_6]$ [446], while the reaction of $[NH_4]_2[MoS_4]$ with CuI and pyridine gave $[MoS_4Cu_4I_2(py)_6]$ [447]. The bonding mode of the ligands in $[MoS_4M_4X_2(py)_4]$ and $[MoS_4M_4X_2(phen)_2]$ (M = Cu, Ag) has been analysed; a bridging mode is ascribed when X is azide while OCN^- is terminally bound through the oxygen [448].

Another copper-containing cubane, $[Mo(=O)Cu_3(S_2COEt)S_3(PPh_3)_3]$, has been made by treating the incomplete cubane $[Mo(=O)Cu_2S_3(PPh_3)_3]$ with $Cu(S_2COEt)$; with CuS^tBu the double cubane $[Mo_2O_2Cu_6(S^tBu)_2S_6(PPh_3)_4]$, linked through the S^tBu groups, is formed [449]

The compounds $[L_2Fe(\mu-S)_2MoS_2]$ (L = bpy, phen) have been prepared and characterised; magnetism and Mössbauer studies of the L = bpy complex suggest that the iron is in a distorted octahedral environment with an intermediate spin state [450]. Similar species have been prepared from $[MoO_4]^{2-}$ [451]. The reaction of $[Cl_2Fe(\mu-S)_2MoS_2]^{2-}$ with $[Ag(NO_3)(PPh_3)]$ or $[CuCl(PPh_3)]$ and PPh_3 affords the trinuclear chain species $[Cl_2Fe(\mu-S)_2Mo(\mu-S)_2M(PPh_3)_2]^-$, isolated as NEt_4^+ salts [452, 453].

Coucouvanis and co-workers have prepared a series of double cubanes containing $MoFe_3$ units linked by a variety of different ligands. The starting point for most of these reactions is the tetrachlorocatecholate cluster $[MoFe_3S_4Cl_3(cat)L]^{2-}$ where $H_2cat = C_6Cl_4(OH)_2$ and L = MeCN, dmf or dmso. Reaction of this cluster with oxalate affords $[\{MoFe_3S_4Cl_4\}_2(\mu-ox)]^{4-}$, and addition of further oxalate then gives the single cubane $[MoFe_3S_4Cl_4(ox)]^{3-}$. Similar complexes can be made from suitable acids such as citric acid [454]. Reaction of the initial catecholate with hydrazine replaces the labile solvent ligand to give $[\{MoFe_3S_4Cl_3(cat)\}_2(\mu-N_2H_4)]^{4-}$; an analogous species was prepared from pyrazine [455]. Some of the cubanes are active catalysts for the reduction of hydrazine to ammonia using $[CoCp_2]$ as reducing agent and lutidine hydrochloride as a source of H^+. The $[MoFe_3S_4Cl_3(cat)(NCMe)]^{2-}$ cluster is one of the most active ones. The integrity of the cubane is evidently maintained during the reaction [456]. The synthesis of the double cubane $[\{MoFe_3S_4Cl_2(cat)\}_2(\mu-S)(\mu-NH_2OH)]^{4-}$ has also been achieved, but it slowly degrades to the dinuclear $[(cat)MoO(\mu-S)_2FeCl_2]^{2-}$ and $[NEt_4][MoO(S)(\mu-S)_2FeCl_2][FeCl_4]$ [457].

Kinetic studies on the acid-catalysed substitution reactions of $[\{MFe_3S_4(SR)_3\}_2(\mu-SR)_3]^{3-}$ (M = Mo, W; R = Et, Ph) have shown that these clusters exhibit an additional associative pathway compared to the homonuclear $[Fe_4S_4(SR)_4]^{n-}$ clusters, demonstrating that the incorporation of Mo or W does have an effect on the Fe centres [458]. The reaction of $[\{MoFe_3S_4(SEt)_3(\mu-SEt)_3\}_2Fe]^{3-}$ with the hydrochloride of ethyl cysteinate results in the replacement of the terminal thiolate ligands by cysteinates; the reaction evidently proceeds *via* the chloride-substituted species $[\{MoFe_3S_4Cl_3(\mu-SEt)_3\}_2Fe]^{3-}$; this can be isolated separately and was found to react with methyl tyrosinate by replacement of the chlorides [459].

The reaction of [MoCl3(thf)3] with two equivalents of [FeCl2(PEt3)2] and 4-7 equivalents of S(SiMe3)2 produced the unusual cluster [MoFe4(Cl)S6(PEt3)4] (41). The Mo and Fe EXAFS spectra of the compound were also analysed. An analogous complex could be prepared for vanadium [460]. Dirac molecular orbital calculations have been carried out on compounds of the type [M6S8L6] where M = Mo or W and L = a two-electron donor ligand; the results were compared with the photoelectron spectra of [Mo6S8(PEt3)6] [461].

(41)
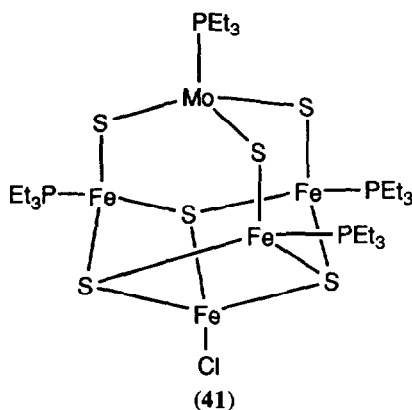
The Mo(IV) cluster [Mo3O4(H2O)9]$^{4+}$ is reduced by zinc in *p*-TsOH to the corresponding species with three Mo(III) centres. This reacts with one-electron oxidants such as Co(III) ammine complexes to produce a mixed valence Mo(III)2Mo(IV) species, which then reverts to the starting Mo(IV) cluster with no evidence for a Mo(III)Mo(IV)2 intermediate. This agrees with a structural assignment of [Mo3(μ-OH)4(H2O)9]$^{5+}$ for the Mo(III) complex [462]. The synthesis of the mixed-metal cluster [Mo2WO4(H2O)9]$^{4+}$ has been achieved; the derivative [NMe4]5[Mo2WO4(NCS)9] was structurally characterised. A kinetic study of the replacement of the aquo ligands by NCS$^-$ showed that it occurs initially on molybdenum at the two more labile sites *trans* to the μ-O ligands [463]. A similar effect has been noted in [Mo3S4(H2O)9]$^{4+}$, where the water molecules *trans* to the μ-S ligands exchange 10^5 times faster than those *trans* to μ3-S due to a conjugate base mechanism involving a mono-hydroxo intermediate [464]. The rate constants for the replacement of the first two water molecules by NCS$^-$ in [Mo2WS4(H2O)9]$^{4+}$ and its MoW2 analogue have been evaluated; substitution at Mo is about 10 times faster than at W, but overall the characteristics of these mixed-metal clusters resemble those of their homonuclear counterparts [465].

The synthesis of [Mo2O2(μ-Se)2(cys)2]$^{2-}$ and [Mo2O2(μ-Se)2(H2O)6]$^{2+}$ has enabled the subsequent preparation of [Mo3OxSe4-x(H2O)9]$^{4+}$ where x = 0-3 as well as [Mo4Se4(H2O)12]$^{n+}$ where n = 4-6 [466]. Kinetic studies on the replacement of aquo ligands in the trinuclear clusters again show that positions *trans* to μ-Se ligands are labile compared with the positions *trans* to the μ3-Se atom, which can be confirmed by studying the tetranuclear species. The order of labilising effects is μ-Se > μ-S > μ-O, whereas the substitution rates for water molecules *trans* to the capping ligands run in the order μ3-O > μ3-S > μ3-Se [467]. Kinetic studies of the rate of complexation of

NCS⁻, oxalate, and methanol compared to the rates of water exchange in the cluster $[M_3(\mu_3\text{-}O)_2(\mu\text{-}OAc)_6(H_2O)_3]^{2+}$ (M = Mo, W) indicate an I_d mechanism for Mo but an I_a process for W [468].

The reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with indium metal in 4M p-TsOH affords the cubane cluster $[Mo_3InS_4(OTs)_2(H_2O)_{10}]^{3+}$, which reverts to the starting materials on exposure to air. The oxidation states have been tentatively assigned as two Mo(III), one Mo(IV), and In(III) [469]. The reaction of acetylene with $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_2(\mu\text{-}O)(H_2O)_9]^{4+}$ or $[Mo_3S_4(H_2O)_9]^{4+}$ produces the dithiolene complexes $[Mo_3(\mu_3\text{-}S)(\mu\text{-}E)(\mu\text{-}SCH=CHS)(H_2O)_9]^{4+}$ (42) (E = O, S) by insertion of the alkyne into two of the bridging sulfur ligands [470].

(42)
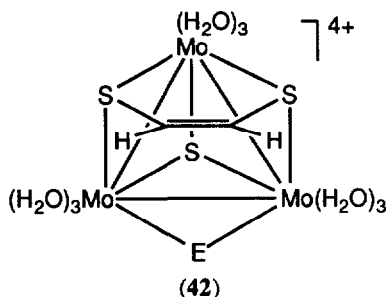
The synthesis of $[Mo_4S_4(H_2O)_{12}]^{5+}$ by $NaBH_4$ reduction of $[Mo_2O_2(\mu\text{-}S)_2(H_2O)_6]^{2+}$ has been detailed, as well as its reaction with ammonia to give $[Mo_4S_4(NH_3)_{12}]^{5+}$. The reduction of $[Mo_2O_2(\mu\text{-}S)_2(edta)]^{2-}$ with $NaBH_4$ similarly gave $[Mo_4S_4(edta)_2]^{3-}$, which can be oxidised or reduced to the corresponding 2– and 4– clusters [471]. The oxidation of $[Mo_4S_4(H_2O)_{12}]^{5+}$ with two equivalents of VO_2^+ in p-TsOH affords the corresponding 6+ cluster as well as another unidentified product. Substitution reactions in the product are faster than in the analogous 4+ and 5+ clusters, but it shows a tendency to fragment into $[Mo_3S_4(H_2O)_9]^{4+}$ [472].

The X-ray structures of nine products arising from the replacement of the aquo ligand in $[Mo_3S_4\{S_2P(OEt)_2\}_4(H_2O)]$ with species such as PPh_3, thiourea, py and cyanide have been determined [473]. The reaction of $[Mo_3(\mu_3\text{-}O)(\mu\text{-}S)_3\{S_2P(OEt)_2\}_4(H_2O)]$ with $NaOCH_2Ph$ in pyridine produced $[Mo_3(\mu_3\text{-}O)(\mu\text{-}S)_3(\mu\text{-}OCH_2Ph)_2\{S_2P(OEt)_2\}_2(py)]$, and the related compound $[Mo_3(\mu_3\text{-}O)(\mu\text{-}S)_3(\mu\text{-}OAc)_2\{S_2P(OEt)_2\}_2(py)]$ was also made and structurally characterised [474, 475]. The reaction of $[Mo_3S_4(S_2PR_2)_4]$ (R = Et, Pr) with CuI in pyridine affords the cubane clusters $[Mo_3Cu(I)S_4(S_2PR_2)_4(py)]$ which have one bridging dithiophosphinite ligand [476]. Similar complexes $[Mo_3Cu(I)OS_3(\mu\text{-}OAc)\{S_2P(OEt)_2\}_3(L)]$ (L = py or dmf) have been prepared by the reaction of $[Mo_3S_4\{S_2P(OEt)_2\}_4(H_2O)]$ with CuI in the presence of L [477].

Replacement of the two bridging dithiophosphate ligands in $[Mo_4S_4\{S_2P(OEt)_2\}_6]$ occurs when it is treated with nickel acetate to give $[Mo_4S_4(\mu\text{-}OAc)_2\{S_2P(OEt)_2\}_4]$ [478]. Electrochemical studies of $[Mo_4OS_3\{S_2P(OEt)_2\}_6]$ have shown that it undergoes two one-electron reductions and one one-electron oxidation, all of them reversible [479]. The cubane-type mixed-metal clusters $[Mo_2W_2S_4(S_2PR_2)_6]$ and $[Mo_2Co_2S_4(CO)_2(S_2PR_2)_2]$ (R = Et, Pr) have been prepared; in the former there are bridging and chelating S_2PR_2 ligands and the compound exists as four isomers

which differ in the arrangement of bridging ligands. The second compound has only chelating S_2PR_2 ligands on each Mo atom [480].

The formation of $[NH_4]_2[Mo_3S_{13}].H_2O$ by the reaction of MoS_3 with hydroxide in aqueous ammonia has been reported; an improved crystal structure determination of the compound was also carried out [481]. Two groups have reported the synthesis and X-ray structure of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(S_2CNEt_2)_3][I]$ and the preparation of related complexes with other dtc ligands [482, 483]. Other complexes containing the $[Mo_3S_7]^{4+}$ core have been made starting from $[NEt_4]_2[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_6]$, including $[Mo_3S_7L_3]^+$ where HL = 6-mercaptopurine or 8-hydroxyquinoline. However degradation of the $\mu\text{-}S_2$ groups to $\mu\text{-}S$ also occurs in some cases, such as reactions with 1,3,5-trideoxy-1,3,5-triaminoinositol which gives $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3L_3]^{4+}$ [484].

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