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6. Molybdenum 1992

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CONTENTS

INTRODUCTION

This chapter surveys the coordination chemistry of molydenum reported in 1992, and follows the review of this element covering the literature of 1991 [1]. The references have been located by a search of volumes 116, 117 and 118 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. The review is restricted to coordination complexes, including carbonyls

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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.

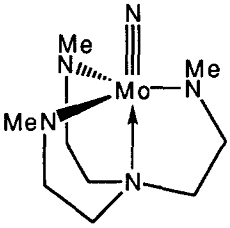
6.1 *MOLYBDENUM(VI)*

6.1.1 *Complexes with halide ligands*

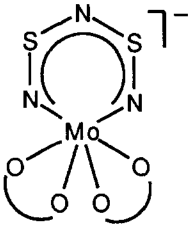
The structure of volatile MoF_6 has been investigated in the solid state at 10K by Mo K-edge EXAFS; a Mo-F bond length of 1.81Å was found, in agreement with a previous neutron diffraction study [2]. Procedures for the synthesis of $K[MoF_6]$ and $K_2[MoF_6]$ from MoF_6 in anhydrous HF have appeared [3]. Oxidation of tellurium with MoF_6 produced a compound formulated as $[TeF_3(NCMe)][MoF_6][MoF_5(NCMe)]_3$ [4].

6.1.2 *Complexes with nitrogen donor ligands*

The nitrido complex $[Mo(N)Cl_3]$ is converted into $[Mo(N)(O^tBu)_3]$ by reaction with LiO^tBu; the product can be alkylated with $ZnMe_2$ to the tetrameric $[Mo(N)(Me)_2(O^tBu)]_4$ [5]. It can also be transmetallated with the stannatrane $BuSn\{N(CH_2CH_2NMe)_3\}$ to give the corresponding complex $[Mo(N)\{N(CH_2CH_2NMe)_3\}]$ (**1**) [6]. Treatment of $\{Mo(N)(O^tBu)_3]$ with ethylene glycol or pinacol produces the distorted octahedral tris-chelates $[Mo(OCR_2CR_2O)_3]$ (R = H, Me) which were both structurally characterised. The same compounds can be made from $[Mo(N)Cl_3]$ and the diols in the presence of a base. However, anionic $[Mo(N)Cl_4]^-$ reacts with NaOPh to give $[Mo(N)(OPh)_4]^-$ with retention of the nitride ligand [7]. The compound $[Mo(N_3S_2)Cl_3]_n$ reacts with the sodium salt of 3,5-di-^{t}Bu-catechol to give $[Mo(N_3S_2)(cat)_2]^-$ (**2**) [8]. Oxidation of $[Mo(NSiMe_3)Cl_2(PMe_3)_2]$ with Cl_2 affords the unusual Mo(VI) phosphiniminato complexes $[Mo(NPMe_3)Cl_5]$ as well as PMe_3Cl_2 and Me_3SiCl. The same starting material reacted with PMe_3Cl_2 to produce the Mo(IV) complex $[Mo(NPMe_3)Cl_2(PMe_3)_3][Cl]$ containing the same ligand [9].

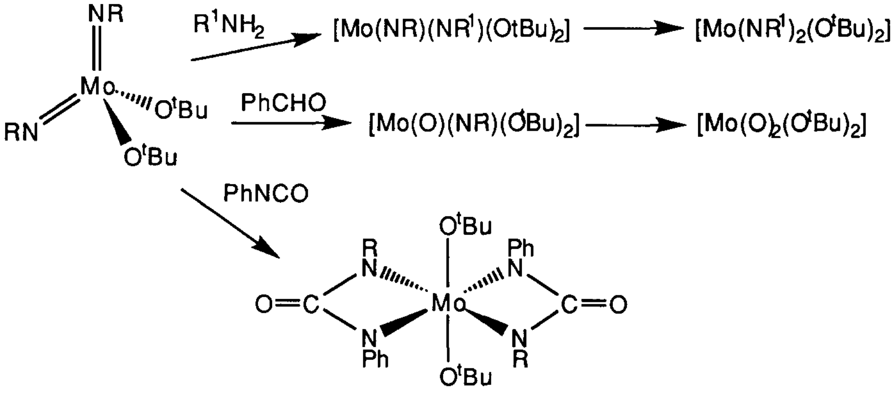


(**1**)



(**2**)

A convenient synthesis of $[Mo(NR)_2Cl_2(dme)]$ (R = aryl, ^{t}Bu *etc.*) has been devised; reaction of $[NH_4]_2[Mo_2O_7]$ with RNH_2 in dme in the presence of 8 equivalents of NEt_3 and 17 equivalents of Me_3SiCl gives the product in 97% yield [10]. These complexes are valuable precursors to the Schrock-type alkene metathesis catalysts and other high-valent organometallic compounds. For example the N^{t}Bu compound reacts with RCH_2CH_2MgCl and PMe_3 to give the alkene complexes [Mo(N^{t}Bu)$_2$(η-RCH=CH$_2$)(PMe)$_3$]; the structure of the propene complex (R = Me) was determined [11]. Unsolvated [Mo(N^{t}Bu)$_2$Cl$_2$] is also a useful starting material, serving as a source of [CpMo(N^{t}Bu)$_2$Cl] and [Cp*Mo(N^{t}Bu)$_2$Cl]; the latter is readily hydrolysed to [Cp*MoO$_3$]$^-$ [12, 13]. Reaction of [Mo(N^{t}Bu)$_2$Cl$_2$] with the ylid $Ph_3P{=}CH_2$ gives the reactive phosphoniomethylidene complex [Mo(N^{t}Bu)$_2$(=CHPPh$_3$)$_2$] [14]. The reactions of the related [Mo(NR)$_2$(O^{t}Bu)$_2$] with amines and aldehydes result in the exchange of the imido groups for other imido groups or Mo=O functionalities; the imido groups also undergo cycloaddition with PhNCO to give (3) [15]. In fact a series of oxo, imido, and carbene transfer reactions between metal centres [ME$_2$(O^{t}Bu$_2$] (M = Mo, W; E = NR, O, =CHR), as well as between these complexes and related Nb and Ta species, have been studied by Gibson, who has established that the reactions proceed through a four-centre transition state and has drawn up an order of reactivity [16].



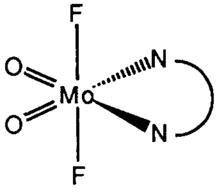
(3)

Scheme (i)

6.1.3 Complexes with oxygen donor ligands

The unusually high nucleophilicity of the molybdate ion, $[MoO_4]^{2-}$, has been recognised. Even though it is 1000 times less basic than the phosphate dianion, it is over 35 times as effective at catalysing the hydrolysis of *p*-nitrophenyl acetate. Although the reasons for this are not entirely clear, the authors suggest that the lower degree of solvation may be at least partly responsible [17, 18]. Interest in bismuth molybdate catalysts has prompted the synthesis of caesium bismuth molybdate [19]. Two papers deal with the catalytic decomposition of H_2O_2 by molybdate, and show that it involves the production of singlet oxygen, detected by its IR phosphorescence at 1270 nm; decomposition of sodium peroxomolybdate also forms $^1O_2$ [20, 21]. The oxidation of thioethers, sulfoxides and alkenes with $[N(C_6H_{13})_4]_3[Mo(O)(O_2)_2(PO_4)]_4$ has been studied [22]. The use of $[MoO_2Cl_2(L)]$ (L = 3-diethoxyphosphoryl camphor) in the functionalisation of polybutadiene by epoxidation with ^{t}BuOOH has been described [23], and the catalytic properties of the triketonate complexes $[Mo_2O_5(PhCOCHCOCHCOCPh)L_2]$ (L = dmso or EtOH) in the epoxidation of cyclooctene and 1,5-cod by ^{t}BuOOH have been studied; they catalysed monoepoxidation with good selectivity [24]. The synthesis of the peroxo complexes $[MoO_2(O_2)(L_3)]$ where L_3 is a tridentate amine such as dien or tren, and $[MoO(O_2)(L_2)(N\text{-}N)]$ where L_2 is the dianion of diphenic acid or homophthalic acid and N-N = bpy or phen, have been described.[25, 26]

A large number of complexes containing the *cis*-MoO_2 grouping have been described. The X-ray structure of $[MoO_2F_2(bpy)]$ (4) shows that the F-Mo-F axis is quite non-linear at 154.4(1)°, though not so much as in $[MoO_2(Me)_2(bpy)]$ [27]. The related $[MoO_2Cl_2(tmed)]$ (5) has been made by addition of tmed to $[MoO_2Cl_2]$ or its dme adduct. Uniquely for this type of compound it adopts an all-*cis* structure [28]. The reagent $(C_2F_5)_2P(Cl){=}NSiMe_3$ attacks the oxygen of $[MoO_2Cl_2]$ to give tetrameric oxide-bridged $[MoOCl_3\{OP(NSiMe_3)(C_2F_5)_2\}]_4$ whereas with $[MoOCl_4]$ elimination of Me_3SiCl occurs, leading to $[MoOCl_3\{\text{-}N{=}P(Cl)(C_2F_5)_2\}]$ [29].



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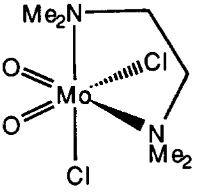
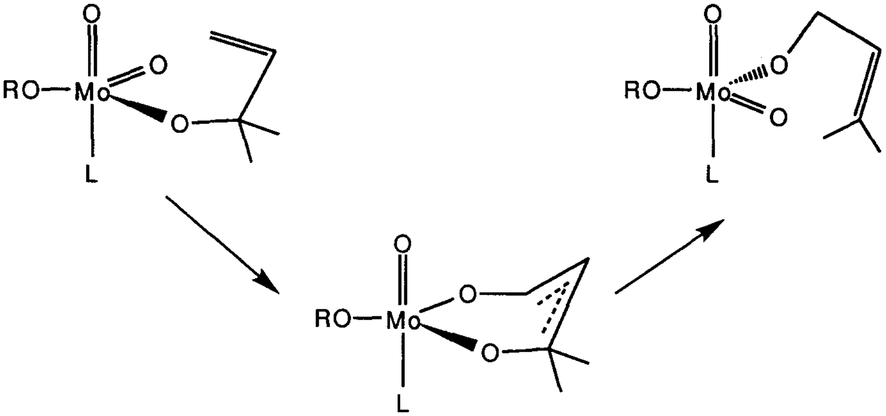


(5)

Procedures for the synthesis of the useful starting materials $[MoO_2(acac)_2]$ and $[Mo_2O_3(acac)_4]$ involving the reaction of acacH in aqueous ammonia with $[NH_4]_6[Mo_7O_{24}]$ and $[MoO(OH)_3]$ respectively have been published; a procedure for the Mo(V) complex by electrochemical reduction of $[MoO_2(acac)_2]$ was also given [30]. Displacement of one or both of the acac ligands occurs readily on reaction with anions; for example deprotonation of $[CpFe(\eta\text{-}C_5H_4CH_2NMe_2)]$ with BuLi, then reaction with $[MoO_2(acac)_2]$ gives the C,N-bound chelate $[MoO_2(acac)\{(\eta\text{-}Me_2NC_5H_3)FeCp\}]$ [31].

The isomerisation of allyl alcohols, related to the industrial SOHIO process, has been studied in the complexes $[MoO_2(OCMe_2CH{=}CH_2)_2L_2]$ (L = MeCN, py or L_2 = bpy). Stepwise isomerisation of the allyloxo ligands occurs to give firstly the mixed complex $[MoO_2(OCMe_2CH{=}CH_2)(OCH_2CH{=}CMe_2)L_2]$ and then $[MoO_2(OCH_2CH{=}CMe_2)_2L_2]$. This also occurs in the related complex with one oxo and one imido ligand, but more slowly. The process involves transfer of the allyl group to the oxo ligands and a five-coordinate intermediate such as that shown below in Scheme (ii) was invoked [32]. The compounds $[MoO_2(dipic)(HMPA)]$ (dipic = pyridine 2,6-dicarboxylate) or $[MoO_2(Et_2dtc)_2]$ catalyse the allylic amination of various alkenes $R^1R^2C{=}CHCH_2R^3$ with PhNHOH to give $PhNHCR^1R^2CH{=}CHR^3$ and H_2O with a high degree of regioselectivity engendered by the double bond migration. The reaction appears to proceed *via* an η^2-PhNO complex which can be detected in the mixture [33].



Scheme (ii)

The reduction of the complexes *fac*-$[MoO_3(L)]^{2-}$ (H_2L = aspartic acid or iminodiacetic acid) has been investigated electrochemically; it occurs in two steps to give initially an oxo-bridged Mo(V) dimer and ultimately the Mo(III) dimer $[Mo_2O_2L_2(H_2O)_2]^{2-}$ [34]. The synthesis of $[MoO_3L]^{3-}$ where $H_3L = N(CH_2COOH)_2(CH_2CH_2COOH)$ has been described [35]. The thermal behaviour of the alkoxide complex $[MoO(OCH_2CH_2OMe)_4]$ has been studied; decomposition occurred *via* $[MoO_2(OR)_2]$ [36].

The complexes $[MoO_2(esc)_2]^{2-}$ and $[Mo_2O_5(esc)_2]^{2-}$ have been prepared by reaction of the catechol esculetin (H_2esc) with ammonium or sodium molybdate respectively [37]. Reports of the synthesis and thermal behaviour of compounds of the type $[MoO_2(HL)_2]$ where H_2L = 1,2-propanediol or 2,3-butanediol have also appeared [38, 39]. The synthesis of $[MoO_2L_2]$ where HL = 3-hydroxypyridine-2-one of 1,2-dimethyl-3-hydroxypyridine-4-one has also been described [40]. Treatment of $[MoO_2(acac)_2]$ with amino acids replaced only one acac ligand and produced $[Mo_2O_5(L)(acac)]$ [41].

A number of complexes of Schiff's base ligands have been prepared; for uninegative ligands (from HL) they take the form $[MoO_2L_2]$ and for dianionic ones (from H_2L) they are $[MoO_2L(S)]$ where S = solvent. Details of the derivation of the Schiff's bases and the complexes formed are given below in Table 1.

Many of these complexes act as oxygen transfer reagents towards phosphines, and the rate constant for this reaction can be correlated to the IR spectral ν(Mo=O) value and the Hammett σ_p constant for the substituent X. In some cases the reduced form of the complex can reoxidised with dmso, enabling a catalytic oxygen transfer from dmso to PPh_3 to be carried out.

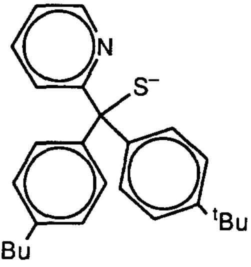
Several other model systems for oxotansferase enzymes have been synthesised. The complex $[MoO_2L_2]$ where L is the didentate *N,S*-ligand (**6**) shown below, transfers one oxo ligand to PEt_3; the resulting $[MoOL_2]$ can be reoxidised with a range of substrates including amine oxides, sulfoxides, selenoxides, and $[MoO_2(Et_2dtc)_2]$ [42]. Treatment of $[(HBpz^*_3)MoO_2Br]$ with PhSH and NEt_3 produces $[(HBpz^*_3)MoO_2(SPh)]$, which transfers oxygen to PPh_3; the resulting mono-oxo species can again be reoxidised with dmso and can be trapped as a py adduct or as dinuclear $[\{(HBpz^*_3)MoO(SPh)\}_2(\mu\text{-}O)]$. Reduction of $[(HBpz^*_3)MoO_2(SPh)]$ with $CoCp_2$ produces the corresponding anion which displays lower values of ν(Mo=O) in its IR spectrum (864 and 767 cm^{-1} as opposed to 922, 889 cm^{-1} for the neutral species); it can be reoxidised with O_2, and reacts with Me_3SiCl to give $[(HBpz^*_3)MoO(OSiMe_3)(SPh)]$ [43]. Treatment of $[(HBpz^*_3)MoO(\eta^2\text{-}S_2P^iPr_2)]$ with oxygen or sulfur transfer agents produces the related compounds $[(HBpz^*_3)Mo(O)(E)(\eta^1\text{-}S_2P^iPr_2)]$. The X-ray structure for E = S shows a relatively short distance of 2.396(3)Å between the Mo=S sulfur and the P=S sulfur, indicating a weak stabilising interaction [44].

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

Aldehyde/ketone	*Amine*	*Complex type*	*Reference*
Salicylaldehyde	Isonicotinylhydrazone	$[MoO_2L(MeOH)]$	[45]
Salicylaldehyde	*S*-methyl thiosemicarbazide	$[MoO_2L(S)]$ S = MeOH, EtOH, py	[46, 47]
5-X-salicylaldehyde (X = H, NO_2, Cl, Br, or OMe)	*o*-$H_2NC_6H_4EH$ $H_2NCH_2CH_2EH$ (E = O, S)	$[MoO_2L(dmf)]$	[48]
5-X-salicylaldehyde (X = H, Me, Cl, Br)	$H_2NNHC(S)SCH_2Ph$	$[MoO_2L(S)]$ S = py, dmf, dmso	[49]
2,3-dihydroxy-benzaldehyde	Aniline + various substituted anilines	$[MoO_2L_2]$	[50]
2-acetylpyridine 2-acetylfuran 2-acetylthiophene 2-acetylindole	semicarbazide thiosemicarbazide	$[MoO_2L_2]$	[51]

Treatment of $[MoO_2(acac)_2]$ with the lithium salt of the '$^{Bu}S_4$' ligand affords $[MoO_2($'$^{Bu}S_4$'$)]$ (7), which also undergoes reversible oxygen transfer (to PPh_3, and from dmso). Reaction with $PhNHNH_2$ gives $[Mo(NNPh)_2($'$^{Bu}S_4$'$)]$, while cleavage of the ligand is observed with PMe_3 (see section 6.3.2 below) [52]. The reaction of $[MoO_2(Et_2dtc)_2]$ with Me_3SiCN gives $[MoO(OSiMe_3)(CN)(Et_2dtc)_2]$ as an isolable compound whereas that from Me_3SiCl could not be characterised; the silylated species was still able to transfer oxygen to PPh_3 [53]. The dithiolene complex $[MoO_2\{S_2C_2(CN)_2\}_2]^{2-}$ mimics the activity of sulfite oxidase using SO_3^{2-} as electron donor and hexacyanoferrate(III) as acceptor [54]. Protonation of $[MoO_2(Racda)_2]$ (Racda = 2-alkylaminocyclopent-1-ene-1 carbodithioate, R = Pr, Bu) produces $[MoO(Racda)_3]^+$; if Hacda (R =

H) or *o*-$H_2NC_6H_4SH$ is added, release of the second oxygen affords the Mo(V) complexes $[Mo(Hacda)(Racda)_3]^+$ or $[Mo(SC_6H_4NH_2)(Racda)_3]^+$ are formed instead [55].



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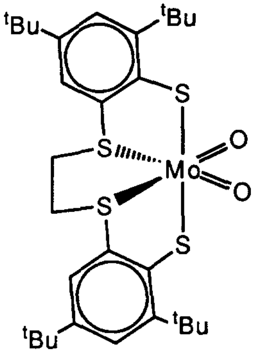
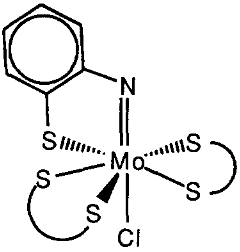


(7)

The replacement of Mo=O groups by hydrazide or imido groups in *cis*-MoO_2^{2+} species is a well established methodology. Thus, reaction of $[MoO_2(SCH_2CH_2NH_2)_2]$ with a range of hydrazines produced $[Mo(NNAr)_2(SCH_2CH_2NH_2)_2]$ (Ar = *p*-C_6H_4X where X = H, Me, OMe, F, or NO_2). The X-ray structure shows that the aryldiazenide ligands are bent at the N-N-C angle of 118.4(2)° but virtually linear at the Mo-N-N angle [56]. The reaction of $[MoO_2(acac)_2]$ with the same hydrazines in alcohols gave either dinuclear $[Mo(NNAr)_2(acac)(\mu\text{-}OR)]_2$ or tetranuclear $[Mo(NNAr)_2(\mu\text{-}OR)(\mu\text{-}MoO_4)]_2^{2-}$ [57]. With $PhMeNNH_2$ only one oxo ligand is replaced, giving the hydrazide $[MoO(NNMePh)(acac)_2]$, which transforms into a similar alkoxide-bridged dimer, $[MoO(NNMePh)(acac)(\mu\text{-}OR)]_2$, on refluxing in ROH [58]. The reaction of $[MoOCl_2(Et_2dtc)_2]$ with 2-aminothiophenol in MeOH gives complex (**8**), whereas if $[MoOBr_2(Et_2dtc)_2]$, $[MoO(Et_2dtc)_3]$ or $[Mo_2O_3(Et_2dtc)_4]$ are used as starting materials, the imido bridged Mo(V) dimer (**9**) is formed instead [59].



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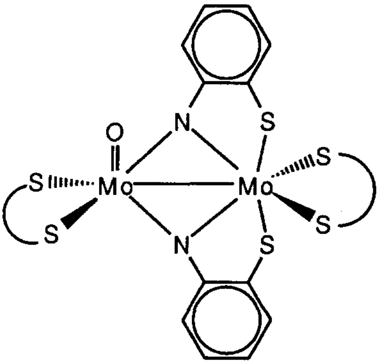

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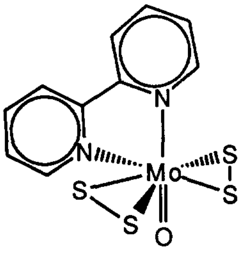
6.1.4 Complexes with sulfur donor ligands

The stepwise replacement of the oxo ligands in $[MoO_4]^{2-}$ with sulfides from S^{2-} was found to be accelerated by the presence of relatively large quantities of thiols (*e.g.* a 50 fold excess of $HSCH_2CH_2OH$ increased the rate by a factor of 10^4). Based on this a method for the preparation of $[MoS_4]^{2-}$ by the reaction of $[MoO_4]^{2-}$ with Li_2S and 2-mercaptoethanol in NH_3/NH_4^+ buffer at pH 9.6 was devised 60]. The presence of Fe(II) was also found to accelerate the reaction, and a one-pot route to $[Fe(MoS_4)_2]^{3-}$ was proposed [61]. The reaction of molybdate with polysulfide S_x^{2-} in the presence of bpy produced $[MoO(S_2)_2(bpy)]$ (**10**), shown to be pentagonal bipyramidal [62]. The reaction of $[MO_2S_2]^{2-}$ (M = Mo, W) with S_8 and $H_2NNH_2.2HCl$ in DMF gave the unusual $[M_2(S_2)_4(\mu\text{-}S_7)(\mu\text{-}H_2NNH_2)]^{2-}$ ion (**11**), crystallographically characterised for both metals. Two different conformations of the S_7 chain were observed [63].



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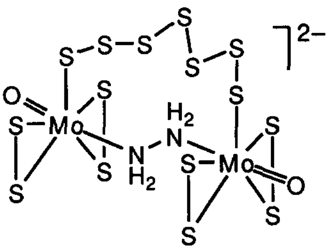


(11)

The photoreduction of acetylene by $[MoS_4]^{2-}$ or $[Mo_2S_4(SC_2H_4S)_2]^{2-}$ supported on colloidal TiO_2 has been reported, and the same workers observed photocatalytic evolution of hydrogen from the same colloids in an aqueous medium, though this was not as efficient as other catalysts *e.g.* Pt [64, 65].

The reaction of $[MoS_4]^{2-}$ with barium salts of dithiocarbamates derived from glycine, alanine, or 2-aminobutyric acid produced $Ba[Mo_2S_4(dtc)_2]$ [66]. Treatment of $[MoS_4]^{2-}$ with $[BiCl_2(Et_2dtc)]$ produced $[(Et_2dtc)BiMoS_4]$ [67]. The reaction of tetrathiomolybdate with copper or silver acetylides is claimed to give polymeric materials of the formula $[NH_4]_{2n}[\text{-}MoS_4MC{\equiv}CM\text{-}]_n$ [68]. Other reactions of $[MoS_4]^{2-}$ and related species with various metal halides to give cubanes and other clusters are dealt with in the final section of this review.

6.2 MOLYBDENUM(V)

6.2.1 Complexes with halide or cyanide ligands

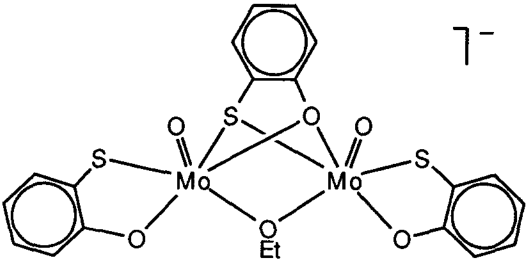
Attempts to use $MoCl_5$ as a chlorinating agent for alcohols were only partially successful [69]. However treatment of $MoCl_5$ with two equivalents of MeLi at –70°C gives, on warming, a complex, tentatively formulated as $[Cl_3Mo(\mu\text{-}CH_2)_2MoCl_3]$, which is capable of the methylenation of ketones [70].

The use of $^tBuOSiMe_3$ as an oxygen transfer reagent has been explored. With $MoCl_5$ in dme, it produces $[MoOCl_3(dme)]$ in 91% yield, and on further reaction this is converted to $[\{MoOCl_2(dme)\}_2(\mu\text{-}O)]$; the other products are ^tBuCl and $O(SiMe_3)_2$ [71]. The halide complex $[MoOBr_3(18\text{-crown-}6)]$ has been made, and reacts with HBr to give $[MoOBr_4(H_2O)]^-$ [72]. The synthesis and crystal structure of the diethyl phthalate adduct $[MoOCl_3\{o\text{-}C_6H_4(CO_2Et)_2\}]$ have been described [73], and $[MoOX_3(L_2)]$ where L_2 is the didentate phosphine oxide $RP\{CH_2P(O)Ph_2\}_2$ (R = Ph, OEt) have also been prepared [74]. The fluorescence properties of $[MoOX_4(NCMe)]^-$ (X = Cl, Br) have been studied in solution; the fluorescence is quenched by electron acceptors such as TCNE, showing that the excited states produced by absorption have sufficient lifetimes for photoredox reactions to occur [75]. The preparation of salts of $[MoOX_5]^{2-}$ (X = Cl, Br) with protonated amines as the counter-ions, and their spectra, magnetism, and thermal behaviour have been described [76].

An improved route to $Cs_3[Mo(CN)_8]$ has appeared [77]. The thermal behaviour of the 8-hydroxyquinoline adduct of $[Mo(CN)_8]^{3-}$ has been investigated [78].

6.2.2 *Complexes with oxygen and sulfur donor ligands*

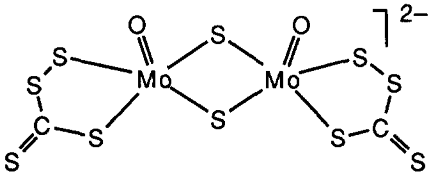
The Mo(V) complexes $[Mo(O)(SC_6H_4\text{-}2\text{-}NHCOR)]^-$ (R = Me, ^tBu, CF_3) and their dianionic Mo(IV) analogues have been synthesised by thiol exchange of $[MoO(SPh)_4]^-$ with the *o*-acylaminothiophenols. The X-ray structures of monoanion and dianion were both determined for R = Me. The structure is distorted square pyramidal; all the NHCOR groups point towards the Mo=O unit as a consequence of N–H···S hydrogen bonding within each thiolate ligand [79]. The reaction of $[MoOCl_3(thf)_2]$ with the disodium salt of $o\text{-}HSC_6H_4OH$ in the presence of ethanol gave complex (**12**), as well as a related species where the bridging ligand is $\mu\text{-}ONa(EtOH)_3$ [80].



(**12**)

Reaction of $[Mo_2O_3(OAc)_4]$ with various β-diketonates and their thio analogues produced the $[Mo_2O_3(\beta\text{-dik})_4]$ complexes where β-dikH = $R^1C(X)CH_2C(X)R^2$ (R^1, R^2 = Ph, Me, ^tBu; X = O or S). All have the familiar structure with one μ-O ligand. In the case of $^tBuC(S)CH_2C(S)^tBu$, the mononuclear $[MoO(SH)_3(\beta\text{-dik})]^-$ was also prepared [81]. A redox reaction between the Cr(IV) complex [Cr(O)(TPP)] (H_2TPP = tetraphenylporphyrin) and $[MoO(Et_2dtc)_2]$ produced $[(TPP)Cr(\mu\text{-}O)MoO(Et_2dtc)_2]$ [82]; similarly interaction of $CdMoO_4$ with $Et_2NCS_2^-$ formed a complex thought to be $[(dtc)_2Mo(O)(\mu\text{-}O)Cd(dtc)(OH_2)]$ [83]. The complex $[Mo_2O_4L_2]$ (HL = dithiooxamidic acid) has been reported [84]. The Mo(V) porphyrin complex [MoO(OMe)(L)] where H_2L is 5,15-diphenyl-2,8,12,18-tetrabutyl-3,7,13,17-porphyrin, has been prepared and structurally characterised; the complexes *cis*-$[MoO_2(L)$ and $[Mo(O_2)_2L]$ were also made [85].

Flash photolysis of the dimer $[(H_2O)_3Mo(O)(\mu\text{-}S)_2Mo(O)(H_2O)_3]^{2+}$ at 200-220 nm in aqueous $HClO_4$ (pH 0.1-2.5) resulted in production of hydrogen and oxidation of the metal to Mo(VI) as $[Mo(OH)_6]$, $[MoO_3S]^{2-}$, and $[MoO_2S_2]^{2-}$ [86]. The X-ray structure, Raman spectrum and thermal analysis of $[NH_4]_2[Mo_2(S_2)_6]$ have been reported [87]. Addition of CS_2 to *syn*-$[Mo_2(S)_2(\mu\text{-}S)_2(\eta^2\text{-}S_4)(\eta\text{-}S_2)]^{2-}$ produced the perthiocarbonate complex *syn*, *cis*-$[Mo_2(S)_2(\mu\text{-}S)_2(\eta^2\text{-}CS_4)_2]^{2-}$ (**13**), whereas a similar reaction with $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_4)(\eta\text{-}S_2)]^{2-}$ gave a related complex with one CS_4 and one CS_3 ligand. Complexes (**14**) with two CS_3 ligands were also prepared from CS_2 and $[Mo_2S_6]^{2-}$ (E = S) or $[Mo_2O_2S_2(dmf)_6]^{2+}$ and CS_3^{2-} (E = O) [88].



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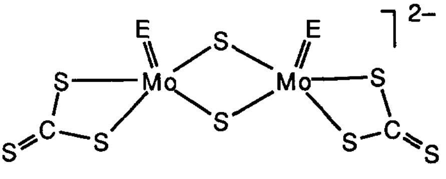


(14)

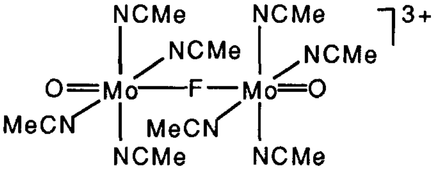
Further chemistry of dimeric Mo(V) imido complexes with dithiophosphate ligands has appeared. The bridging SNH_2 group in $[Mo_2(Ntol)_2\{S_2P(OEt)_2\}_2(\mu\text{-}S)(\mu\text{-}OAc)(\mu\text{-}SNH_2)]$ reacts with aldehydes RCHO (R = H, Me, ${}^tBu$, *p*-tol) to produce sulfenimine ligands in $[Mo_2(Ntol)_2\{S_2P(OEt)_2\}_2(\mu\text{-}S)(\mu\text{-}OAc)(\mu\text{-}SN{=}CHR)]$. Isomers caused by inversion at the S and N centres were observed in solution [89]. The related $[Mo_2(Ntol)_2\{S_2P(OEt)_2\}_2(\mu\text{-}S)_2(\mu\text{-}OAc)]^-$ reacts with diazonium salts ArN_2^+ to give $[Mo_2(Ntol)_2\{S_2P(OEt)_2\}_2(\mu\text{-}S)(\mu\text{-}SNNAr)]$ with a bridging diazosulfide ligand. An exchange reaction occurs between the aryl groups of the imido ligands and the diazo group. The compounds decompose thermally with formation of aryl radicals [90]. The tetramer $[Mo(Ntol)\{S_2P(OEt)_2\}(\mu_3\text{-}S)]_4$ dissociates in solution to dimeric fragments, as shown by the production of a mixed Mo_2W_2 species when Mo_4 and W_4 analogues are mixed [91].

6.3 MOLYBDENUM(IV)

6.3.1 Complexes with halide and phosphine ligands

The reduction of $MoCl_5$ with one equivalent of Ph_2SiH_2 in thf is a useful route to $[MoCl_4(thf)_2]$ [92]. Oxidation of $[MoCl_3(thf)_3]$ with three equivalents of $AgBF_4$ in MeCN produced the dimeric Mo(IV) species $[Mo_2O_2(\mu\text{-}F)(NCMe)_8][BF_4]_3$ (**15**) [93].

Two papers have appeared which discuss the occurrence of bond stretch isomerism in *cis*, *mer*-$[Mo(O)Cl_2L_3]$ (L = PMe_3, PMe_2Ph). Compounds of this type were originally isolated as blue and green isomers with different values of ν(Mo=O) in the IR spectrum and different Mo=O bond lengths in their X-ray structures. Parkin and Rheingold have proposed that this can be rationalised by the presence of varying proportions of isostructural *mer*-[$MoCl_3L_3$] as a contaminant [94]. On the other hand Gibson and McPartlin managed to isolate two forms of the complex with L = PMe_2Ph with ν(Mo=O) of 943 and 955 cm^{-1}; both have identical solution spectra. Their X-ray structures show that the two forms are distortional isomers with larger variations in bond angles than lengths, and that the higher frequency compound has C_s symmetry whereas the other has C_1 symmetry [95].



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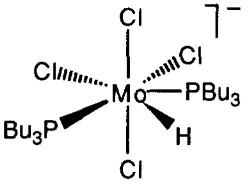
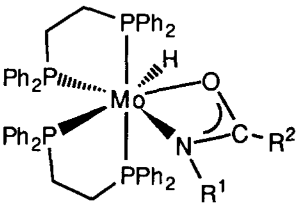
Reaction of [$MoCl_4(thf)_2$] with $LiBHEt_3$ and phosphines produces the useful hydride complexes [MoH_4L_4], which undergo a number of interesting protonation reactions. Reaction with HX produces the anionic, paramagnetic hydride [$MoH(X)_4L_2$]$^-$ (X = Cl, Br; L = PEt_3, PMe_2Ph, PBu_3) as the phosphonium salt. The crystal structure of [PBu_3H][$MoH(Cl)_4(PBu_3)_2$] (**16**) shows a distorted pentagonal bipyramid with the hydride situated slightly out of the central plane [96]. Protonation of [MoH_4L_4] with HBF_4 under CO gives [$(OC)_2(L)_2Mo(\mu\text{-}F)_3Mo(CO)_2(L)_2$][$BF_4$], and a similar product is obtained from [$WH_6(PMe_2Ph)_3$] [97]. The reaction of [$MoH_4(dppe)_2$] with the N-alkylamides R^1NHCOR^2 (R^1 = Me, Ph; R^2 = Me, Ph, H) yields [$MoH(\eta^2\text{-}R^1NCR^2O)(dppe)_2$] (**17**) in which the anionic ligand is bound through N and O; the complex again has a distorted pentagonal bipyramidal structure [98].





(16) (17)

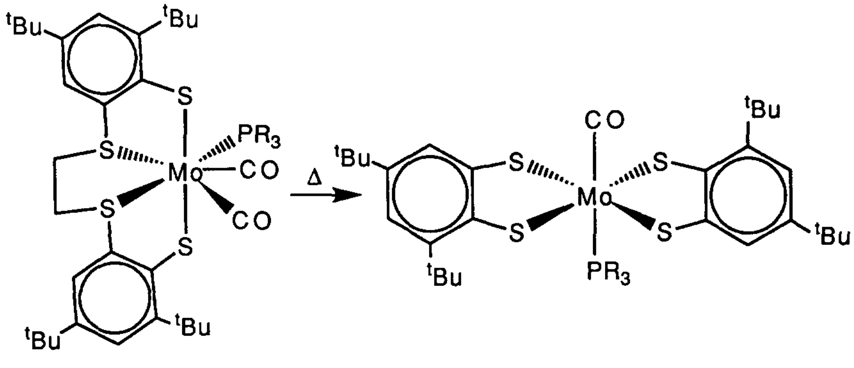
The protonation of *trans*-[$Mo(N_2)_2L_4$] (L = PMe_2Ph) with HCl produces the hydrazide complex [$MoCl_2(=N\text{-}NH_2)L_3$] which reacts with ketones to give the diazoalkane complexes [$MoCl_2(N_2CR^1R^2)L_3$] (R^1, R^2 = Ph, Me). Addition of ligands such as CO, C_2H_4, or ^{t}BuNC then produces [$MoCl_2(N_2CR^1R^2)L_2(L')$] [99]. Addition of $Ph_2C=C=O$ to [$MoCl_2(=N\text{-}NH_2)L_3$] gives the acylhydrazide complex *cis*, *mer*-[$MoCl_2(=N\text{-}NHCOCHPh_2)L_3$], which is diamagnetic as a solid but paramagnetic in solution; it reacts with py by displacement of one chloride [100].

The nitride ligand in *trans*-$[Mo(Cl)(\equiv N)(dppe)_2]$ can be alkylated with ICH_2CO_2Me to give the cationic complex $[Mo(Cl)(NCH_2CO_2Me)(dppe)_2]^+$; this cation can be deprotonated to form $[Mo(Cl)(N{=}CHCO_2Me)(dppe)_2]$ and then methylated to give $[Mo(Cl)(NCHMeCO_2Me)(dppe)_2]^+$. The cationic species are electroactive and on controlled potential electrolytic reduction in AcOH release the resulting esters of glycine or alanine. The metal can be recovered as $[Mo(H)_2(\eta^2\text{-}OAc)(dppe)_2]^+$ [101].

6.3.2 Complexes with oxygen and sulfur donor ligands

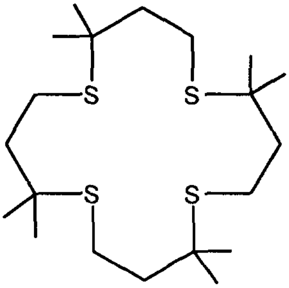
Treatment of the Mo(VI) complex $[MoO_2(SCPh_2COO)_2]^{2-}$ with further thiobenzilic acid resulted in reduction to Mo(IV) and the isolation of $[Mo(SCPh_2COO)_3]^{2-}$ as a mixed salt of NBu_4^+ and Na^+. The X-ray structure shows a trigonal prismatic arrangement with very short Mo-S bonds of 2.291(4)Å. The dianion can be reversibly oxidised to the corresponding Mo(V) monoanion [102]. A series of salts of the anions $[MoO(SCN)_4]^{2-}$ and $[MoO(SCN)_6]^{4-}$ have been prepared [103].

Sellman has reported a series of complexes of the type $[MoO('S_4')]$ where the $'S_4'$-ligand is *o*-$^-SC_6H_4SCH_2CH_2XCH_2CH_2SC_6H_4$-*o*-$S^-$ for X = S, O, and NH. These were prepared by ligand transfer from nickel salts (either $[Ni('S_4')]$ or $[Ni('S_4')]_2$ depending on X) in reactions with $[MoCl_4(thf)_2]$ [104]. A bulkier ligand of the same type features in the reaction shown below. Thermolysis of the Mo(II) complex $[MoCO)_2(L)('^{Bu}S_4')]$ (**18**) (L = PPh_3, PMe_3, CO) releases ethylene and forms the Mo(IV) species *trans*-$[Mo(CO)_2(SC_6H_2{}^tBu_2S)_2]$ (**19**) [105] The related *trans*-$[Mo(PMe_3)_2(SC_6H_2{}^tBu_2S)_2]$ has been made in a similar cleavage reaction from $[MoO_2('^{Bu}S_4')]$ and PMe_3 [52]. The complex $[Mo(S)_2(Me_8[16]aneS_4)]$, in which the macrocyclic ligand (**20** below) has an all-up conformation, undergoes alkylation by MeI or $PhCH_2Br$ stereoselectively at the uncongested terminal sulfur, giving a compound in which the molybdenum is ligated by S, SR, and SR_2 groups [106].



(18) **(19)**

In an obviously complex reaction, treatment of $MoCl_5$ with four equivalents of $NC_5H_3\text{-}2\text{-}SH\text{-}3\text{-}SiMe_3$ afforded complex (**21**) which acts as a precursor for the catalytic disproportionation of hydrazine to N_2 and NH_3, and for the reduction of hydrazine to NH_3. The bridging ligand is present as the neutral pyridine-2-thione form with a proton on the nitrogen; this evidently plays an important role in the catalysis since methylation of the nitrogen produces an inactive complex [107]. Reaction of $MoCl_5$ with $Na_2[C_3S_5]$ gave distorted trigonal prismatic $[Mo(C_3S_5)_3]^{2-}$, together with $[MoO(C_3S_5)_2]^{2-}$ as a by-product [108]. Addition of CS_2 to the $Mo(S_2)$ groups of $[Mo(S)(S_2)_2]^{2-}$ produces *cis* and *trans* isomers of $[Mo(S)(CS_4)_2]^{2-}$ (22) and (23) [88].



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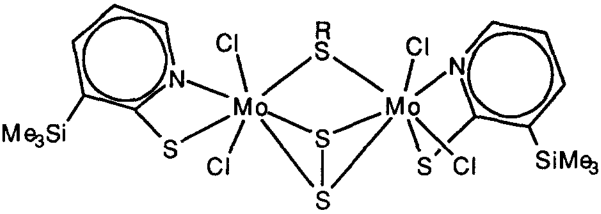

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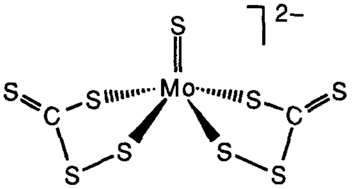

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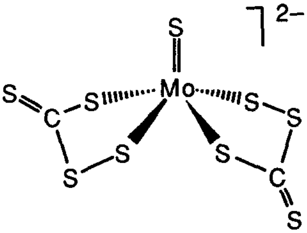

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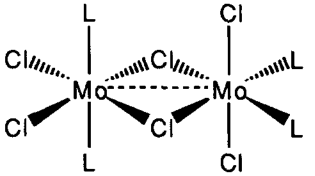
6.4 MOLYBDENUM(III)

6.4.1 Complexes with halide and phosphine ligands

Reduction of $MoCl_5$ with two equivalents of Ph_2SiH_2 in thf produces $[MoCl_3(thf)_3]$; the same complex is formed by reduction of $[MoCl_4(thf)_2]$ with $SnCl_2$. These methods avoid the problem of over-reduction sometimes experienced with other reagents [92]. The material formulated as "$MoCl_3(dme)$", made by reducing $[MoCl_4(dme)]$ with tin, is actually thought to be $[Mo_2Cl_6(dme)_2]$. It serves as a good starting material for compounds such as $[Mo_2(CH_2{}^tBu)_6]$, $[Mo_2(CH_2SiMe_3)_6]$, and fluoroalkoxides of the type $[Mo_2(OR)_6]$ (see following section) [109].

Changing the phosphine ligand in $[Mo_2Cl_6L_4]$ (24) from PEt_3 to PMe_2Ph has a dramatic effect on the Mo-Mo distance [3.730(1)Å compared to 2.8036(8)Å respectively] and magnetic properties (three unpaired electrons per Mo compared to virtually diamagnetic). This can be explained in terms of a delicate balance between stabilisation without Mo-Mo bonding or by direct interaction in a $\sigma^2\pi^2\delta^{*2}$ ground state [110]. A paramagnetic ^1H NMR spectroscopic study of the mixed species $[Mo_2Cl_6(L)_{4-n}(L')_n]$, prepared by addition of L' to the face-sharing bioctahedral $[Mo_2Cl_6L_3]$ has rationalised the isomers produced on the basis of the larger *trans*-effect of L with respect to Cl at the Mo(III) centre. Attack of L' initially results in $[Mo_2Cl_6(L)_3(L')]$ in which L' occupies an axial site; other processes, including ligand exchange, then produce a single isomer of $[Mo_2Cl_6(L)_2(L')_2]$ [111]. Oxidative addition of halogens to $[MoWCl_6(L\text{-}L)_2]$ (L-L = dppe, dppm, dmpm, dmpe) gives the corresponding Mo(III), W(III) dimers $[MoWCl_6(L\text{-}L)_2]$, the first examples of heteronuclear edge-sharing bioctahedral complexes, in which the L-L ligands can be chelating or bridging [112]. A theoretical study of the face-sharing bioctahedral complexes $[Mo_2Cl_9(SH_2)_n]^{n-3}$ (n = 2-5) and $[(H_2S)Cl_2Mo(\mu\text{-}Cl)_2(\mu\text{-}SR_2)MoCl_2(SH_2)]$ where R = H, F, or CF_3, predicts that the former, with a $(\mu\text{-}Cl)_3$ arrangement, will have a high-spin configuration with a long Mo-Mo bond, whereas the latter will be low spin with a shorter Mo-Mo distance [113].



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6.4.2 Complexes with oxygen and nitrogen donor ligands

The new fluoroalkoxide complexes $[Mo_2\{OCMe_{3-n}(CF_3)_n\}_6]$ (n = 1, 2) have been prepared from $[Mo_2Cl_6(dme)_2]$. The X-ray structure for n = 2 shows a Mo-Mo distance of 2.230(3)Å, typical for a $\sigma^2\pi^4$ triple bond [109]. The reaction of $[Mo_2(NMe_2)_6]$ or $[Mo_2(O^tBu)_6]$ with optically pure (+)- or (–)-menthol produced isomers of $[Mo_2(OC_{10}H_{19})_6]$ which were studied by CD and ORD spectra [114]. The silanol complex $[Mo_2(OSiMe_2{}^tBu)_6]$ reacts with NO to produce $[Mo_2(NO)_2(OSiMe_2{}^tBu)_2(\mu\text{-}OSiMe_2{}^tBu)_2]$ [115]. The mixed amide-phosphide complex $[Mo(NMe_2)_4(P^tBu_2)_2]$ has been reported; the phosphide ligands are terminal [116].

6.5 MOLYBDENUM(II)

6.5.1 Complexes with halide and phosphine ligands

Quadruply-bonded complexes of the the type $[Mo_2X_4L_4]$ continue to attract much interest. Analysis of the fluorescence excitation spectra of a number of these (X = Cl, Br, I for L = PMe_3, and X = Cl when L = $AsMe_3$, as well as some tungsten analogues), monitoring the $^1(\delta\delta^*)$ excited state, has allowed the assignment of virtually all the bands in the UV region to excitations from the Mo-Mo (σ, π, δ), M-L (σ) and M-X (σ, π) orbitals to the δ^* level [117]. Their far-IR spectra have also been recorded, but proved more difficult to assign than expected due to interference from the internal deformation modes of the ligands [118]. Protonolysis of $[Mo_2Me_4L_4]$ (L = PMe_3, PMe_2Ph) with py.xHF (Olah's reagent) yields $[Mo_2F_4L_4]$, the first examples where X = F [119].

Depending on L-L, complexes of the type $[Mo_2X_4(L\text{-}L)_2]$ exist either as α-isomers with chelating phosphines, or β-isomers with bridging phosphines. The isomerisation of α-$[Mo_2Cl_4(dppe)_2]$ to the β-form has been studied in the solid state by ^{31}P NMR spectroscopy, and found to have much higher activation parameters than in solution [120]. Cotton has used the temperature dependence of the ^{31}P chemical shift in solution to calculate the energy gap between the δ^2 ground state and the thermally-accessible ($\delta\delta^*$) triplet excited state, and has determined that the δ-electronic contribution to the barrier to rotation along the Mo-Mo bond is around 41 kJ mol^{-1} [121].

The mixed metal species $[MoWCl_4(L\text{-}L)_2]$ (L-L = dppe, dppm, dmpm, dmpe) have been prepared by phosphine exchange from $[MoWCl_4(PMePh_2)_4]$. The Mo-W distances in the β-dmpm and α-dmpe complexes were 2.193(2)Å and 2.243(1)Å respectively. Although crystal structures of the others were also done, they were found to co-crystallise as solid solutions with the Mo_2 species, and consequently the M-M distance could not be accurately determined [122]. In the corresponding Mo(III), W(III) dimers $[MoWCl_6(L\text{-}L)_2]$, the Mo-W bonds lengthen to 2.7123(9)Å for L-L = dppe, and 2.682(1)Å for L-L = μ-dmpm [112].

A comparative study of the reactions of $[MCl_2L_4]$ (M = Mo, W; L = PMe_3, PPh_2Me) with sources of O, S and NR fragments, which give $[M(=X)Cl_2(L)_3]$, has shown that the mechanism involves phosphine dissociation and the trapping of the unsaturated intermediate; in the absence of any other reagents the Mo complexes slowly produce $[Mo_2Cl_4L_4]$ at 80°C [123]. Intermetallic oxygen transfer occurs from $[ReOCl_3(PPh_2Me)_2]$ to $[MCl_2(PPh_2Me)_4]$ (M= Mo, W); the Mo oxo complex transfers oxygen to the tungsten (II) species, enabling the order of M=O bond strengths Re < Mo < W to be drawn up [124].

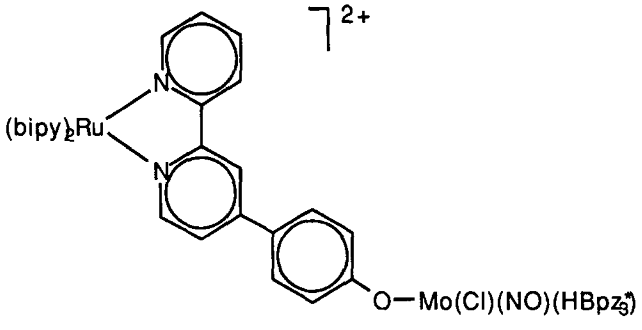
Deprotonation of $[MoF(NN{=}CHCH_2Me)(dppe)_2]^+$ with LDA occurs at the β-carbon to produce the diazenido complex $[MoF(NNCH{=}CHMe)(dppe)_2]$, which reacts with alkyl halides or heterocumulenes such as PhNCO or $Ph_2C{=}C{=}O$ at the same carbon to give substituted diazoalkane complexes [125]. Reaction of $[Mo(CO)_3(NCMe)_3]$ with ICl produces $[Mo(I)(Cl)(CO)_3(NCMe)_2]$, which in turn reacts with one equivalent of L (L = PPh_3, $AsPh_3$) or L_2 (L_2 = bpy, phen, dppe) to give $[Mo(\mu\text{-}I)Cl(CO)_3(L)]_2$ or $[Mo(I)(Cl)(CO)_3(L_2)]$ respectively [126].

6.5.2 Complexes with nitrogen donor ligands

The barriers to rotation about the M-M bond in $[M_2(porph)_2]$ (porph = mono-*meso*-*p*-tolyl-octaethylporphyrin) have been measured as 45.1 ± 0.4 kJ mol^{-1} for M = Mo and 53.9 ± 0.1 kJ mol^{-1} for M = W; this implies that the W-W δ-bond is 8.8 kJ mol^{-1} stronger than that of the dimolybdenum unit [127].

An extensive chemistry of the tris(3,5-dimethylpyrazolyl)borate complex $[(HBpz^*_3)Mo(NO)X_2]$ (X = Cl, Br, I) has been developed by the groups of McCleverty and Jones. 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. Recently more elaborate alcohols and amines have been used, including cholesterol [128], a protected form of the saccharide β-D-fructopyranose [129], the complex $[(HBpz^*_3)Re(O)(OH)(SC_6H_4\text{-}4\text{-}OH)]$ [130], and an amine derived from retinal [131]. Treatment of oxacyclobutane with $[(HBpz^*_3)Mo(NO)X_2]$ causes ring opening and formation of $[(HBpz^*_3)Mo(NO)(X)(OCH_2CH_2CH_2X)]$, but larger cyclic ethers do not ring open [132, 133]. The monosubstituted $[(HBpz^*_3)Mo(NO)(X)(OC_{10}H_{19})]$ derived from optically active (+)- or (–)-menthol, exists as diastereomers which can be separated by chromatography, studied by circular dichroism, and crystallised to determine the absolute configuration [134]. The diastereomers from the optically active benzylamine $PhCHMeNH_2$ can also be separated [135]. Other developments include the preparation of $[(HBmppz_3)Mo(NO)X_2]$ where mppz is 3-*p*-methoxyphenyl pyrazole [136].

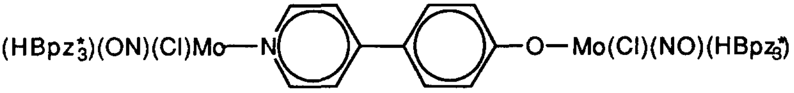
The redox properties of the $Mo(NO)^{3+}$ centre have been used to examine the communication between the Mo atom and other redox active centres. For example, the crown-ether-like complexes $[(HBpz^*_3)Mo(NO)\{OCH_2(CH_2OCH_2)_nCH_2O\}]$ ($n = 2$-5) are reduced at a potential of around –1.3V relative to the SCE, which moves to more anodic potentials in the presence of one equivalent of Na^+; when n = 3, 1:1 complexes with Li^+, Na^+ and K^+ could be isolated [137]. Picosecond laser spectroscopy of $[(HBpz^*_3)Mo(NO)(Cl)(L)]$ where L = 5-Ar-10,15,20-triphenylporphyrin (Ar = *o*-, *m*-, or *p*-C_6H_4O, *p*-C_6H_4NH) shows that fluorescence quenching of the porphyrin is due to a fast intramolecular charge separation, producing species with lifetimes of 120-290 ps [138]. Similarly attaching the $(HBpz^*_3)Mo(NO)(X)$ fragment to a derivative of $[Ru(bpy)_3]^{2+}$ (complex **25**) results in complete quenching of the luminescence which normally results from the Ru to bpy π^* MLCT excited state transition; the conclusion is that the charge transfer is probably passed on to the molybdenum *i.e.* oxidative quenching [139].



(25)

The communication between two molybdenum units can also be studied. The complex $[\{(HBpz^*_3)Mo(NO)(Cl\}_2(\mu\text{-}NHC_6H_4NH)]$ shows two reduction potentials separated by 770 mV when the *o*-isomer of the phenylenediamine ligand is employed, implying that the two metals are strongly interacting; the interaction is somewhat less for the *m*- and *p*-isomers [140].

By treating $[(HBpz^*_3)Mo(NO)Cl_2]$ with reducing agents such as 1,4-dithiane-2,5-diol in the presence of NEt_3, the reduced 17-electron $[NHEt_3][(HBpz^*_3)Mo(NO)Cl_2]$ could be isolated and characterised by ESR spectroscopy. Further reduction to an 18-electron complex was not possible, but reaction with py gave $[(HBpz^*_3)Mo(NO)(Cl)(py)]$, which could be reduced further [141]. The linked complexes $[\{(HBpz^*_3)Mo(NO)(Cl)\}_2\{\mu\text{-}4,4'\text{-}NC_5H_4(CH{=}CH)_nC_5H_4N\}]$ ($n = 2$-4) can be reduced in two one-electron processes with the separation between them decreasing by about 166 mV for each additional *trans*-ethenyl unit. The ESR spectra are consistent with rapid exchange between the metal centres [142]. The mixed ligand NC_5H_4-4-C_6H_4OH is also of interest; after attachment to one Mo centre through the alcohol functionality, the pyridine unit can be either methylated or attached to a second Mo centre to produce the mixed 16-electron, 17-electron complex (26). Reduction of the methylated species with $[CoCp_2]$ gives a localised ESR spectrum, but reduction of (26) gives a delocalised species with fast exchange between the centres [143].



(26)

A further development on this theme is $[LMo(NO)Cl_2]^+$ where L = the neutral ligand 1,4,7-trimethyl-1,4,7-triazacyclononane. This cation reacts with MeOH in the same way as the $HBpz^*_3$ complexes above, but 4-ferrocenylphenol caused reduction instead. Attachment of an amine occurred by simple addition rather than substitution [144].

The kinetics of the reaction $[Mo(CN^tBu)_7]^{2+} + X^- \rightarrow [Mo(CN^tBu)_6X]^+ + {}^tBuNC$, where X = Cl, Br or I, have been measured by conductance in MeCN. The reaction is reversible, with equilibrium constants of 3.5, 1.3 and 0.12 for the three halides at a halide concentration of 5.6×10^{-3} M. A dissociative process involving both ion-paired and non-ion-paired intermediates was proposed [145].

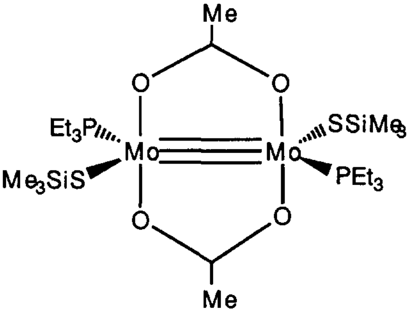
6.5.3 *Complexes with oxygen donor ligands*

The photoelectron spectrum of a $[Mo_2(\mu\text{-}OAc)_4]$ film has been recorded at variable photon energy; in the 40-50 eV range the ionisations from metal σ, π, and δ orbitals are enhanced relative to those of the acetates. The π orbitals have the largest amount of metal 4*d* character, but the σ and δ levels have some, as do the acetate ligands due to orbital mixing [146].

The carboxylate complexes, most commonly the acetate, are useful starting materials as they undergo ligand exchange; new examples of $[Mo_2(\mu\text{-}O_2CR)_4]$ prepared in this way include those with R = adamantyl [147] and $CH_2OC_6H_3$-2,4-Cl_2 [148]. A particularly interesting example involves the cluster acid $[Co_3(CO)_9(\mu_3\text{-}CCO_2H)]$, which forms $[Mo_2(\mu\text{-}O_2CR)_4]$, the adduct $[Mo_2(\mu\text{-}O_2CR)_4(RCO_2H)_2]$, and the mixed ligand species $[Mo_2(\mu\text{-}O_2CR)_3(\mu\text{-}O_2CMe)]$ [149]. The formation of axial adducts of donors such as phen and bpy with $[Mo_2(O_2CH)_4]$ has been reported [150], and addition of anthraquinone to the trifluoroacetate complex produces a chain-type polymer $[Mo_2(\mu\text{-}O_2CCF_3)_4.AQ]_n$ [151].

Exchange also occurs with other ligands. The β-diketonate complexes $[Mo_2(R^2COCR^1COR^2)_4]$ (R^1 = H, R^2 = Me, C_8H_{17}, ${}^tBu$; $R^1 = R^2$ = Me) are prepared this way; crystallography of the R^1 = H, R^2 = ${}^tBu$ complex shows that the β-diketonates are all chelating and there is an unsupported Mo-Mo bond of length 2.1467(5)Å [152]. The reaction of $[Mo_2(\mu\text{-}OAc)_4]$

with $S(SiMe_3)_2$ and PEt_3 produces $[Mo_2(\mu\text{-}OAc)_2(PEt_3)(SSiMe_3)_2]$ (**27**) in 83% yield; the Mo-Mo bond length is 2.110(1)Å [153]. Displacement of two of the benzoate ligands in $[Mo_2(\mu\text{-}O_2CPh)_4]$ by $[WS_4]^{2-}$ gives $[Mo_2(\mu\text{-}O_2CPh)_2(\mu\text{-}WS_4)_2]^{2-}$ (**28**); the X ray structure shows a Mo-Mo distance of 2.144(1)Å and the WS_4 units tilted slightly in opposite directions [154].



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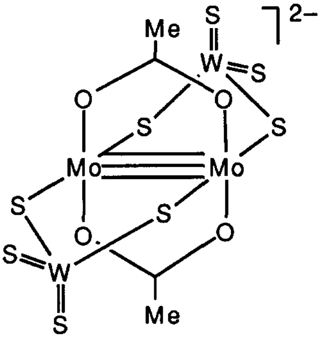

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The various acetonitrile complexes derived from $[Mo_2(\mu\text{-}O_2CR)_4]$ provide another useful source of the Mo_2^{4+} core. Reaction of $[Mo_2(\mu\text{-}O_2C^tBu)_3(NCMe)]^+$ with anions from 6-hydroxy-2-methylpyridine or 2,6-dimethylpyridine gives $[Mo_2(\mu\text{-}O_2C^tBu)_3(\mu\text{-}L)]$ in which the pyridines are bound as N,O- or N,C-bridges. However reaction of the same substrate with $NC_5H_4\text{-}2\text{-}PPh_2$ results in the production of $[Mo_2(\mu\text{-}O_2C^tBu)_2(dppy)_2]^{2+}$ and $[Mo_2(\mu\text{-}O_2C^tBu)_4]$ by a carboxylate scrambling process [155]. Reaction of $[Mo_2(\mu\text{-}OAc)_4]$ with the anion of 6-diphenylphosphino-2-hydroxypyridine affords $[Mo_2(\mu\text{-}L)_4]$ in which the ligand is bonded through N and O; the pendant phosphines can then be coordinated to $[Mo(CO)_3(NCMe)_3]$ [156].

Replacement of the acetate ligands in $[Mo_2(\mu\text{-}OAc)_2(NCMe)_6]^{2+}$ with (–)-menthoxyacetic acid gives $[Mo_2(\mu\text{-}O_2CR)_2(NCMe)_4]^{2+}$ which acts as a ROMP catalysts for nbd [148]. A synthetic procedure for the homoleptic complex $[Mo_2(NCMe)_{10}][BF_4]_4$ has been published [157]; it acts as the Mo_2^{4+} source in reactions with $[Mo_2(\mu\text{-}OAc)_4]$ and L-L (L-L = dppm, dppe) to give $[Mo_2(\mu\text{-}OAc)_2(\mu\text{-}L\text{-}L)_2][BF_4]_2$; the mononuclear complex $[Mo(O)(F)(L\text{-}L)_2][BF_4]$, formed by fluoride abstraction from the anion, is isolated as a by-product [158]. Intercalation of $[Mo_2(NCMe)_8]^{4+}$ into layered V or Nb phosphates has been reported to give a mixed valence Mo_2^{5+} centre coordinated to the oxygens in the tetragonal holes [159].

6.5.4 Complexes with sulfur donor ligands

Reaction of $[Mo_2Br_4(CO)_8]$ with the ligand $Me_8[16]aneS_4$ (**20**) produced $[MoBr(CO)_2(Me_8[16]aneS_4)]^+$ as its $[MoBr_3(CO)_4]^-$ salt; the X-ray structure showed a previously unobserved conformation for the macrocycle [160]. The electrochemical properties of the related $[MoX_2(Me_8[16]aneS_4]$ (X = Cl, Br) have been reassessed, with the reversible process occurring at –0.52V, previously thought to be a reduction wave, reassigned as the Mo(II)/Mo(III) couple. The true reduction occurs at –2.87V (relative to ferrocene) and gives a species which reacts with CO or N_2. The neutral Mo(II) and oxidised Mo(III) products display a fluxional process involving motion of the metal in or out of the plane, together with a deformation of the macrocycle; in the solid state the neutral complex has an all-up arrangement of the $CMe_2CH_2CH_2$ groups, whereas the cation has an up, up, down, down conformation [161].

6.6 *MOLYBDENUM(I)*

The ESR spectrum of the 17-electron complex $[(HBpz^*_3)Mo(CO)_3]$ doped into single crystals of its diamagnetic manganese analogue has been recorded for comparison with the related chromium compound [162].

6.7 *MOLYBDENUM(0)*

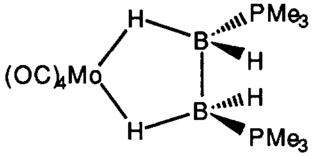
6.7.1 *Complexes with carbonyl ligands*

This section deals largely with complexes of the type $[Mo(CO)_{6-n}L_n]$ (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 new addition to the series of labile trisubstituted complexes is $[Mo(CO)_3(dmf)_3]$, in which substitution of the dmf ligands occurs readily under mild conditions, and is facilitated by addition of BF_3 [163]. The thermodynamic stabilities of a range of *fac*-$[M(CO)_3L_3]$ species have been ordered into the following series: C_6H_6 < cht < NCMe < py < PPh_2Me < PBu_3 < triphos < PEt_3 < PMe_2Ph < $P(OMe)_3$ < CyNC < PMe_3 [164]. Several ^{95}Mo NMR spectroscopic studies of $[Mo(CO)_{6-n}L_n]$ complexes where L = isonitriles, amines, substituted pyridines or phosphines, have appeared [165, 166, 167]. In general some degree of correlation is observed between ^{95}Mo spectral shift, structural type, and π-donor ability of L. The linewidths of the isonitrile complexes are < 10Hz, smaller than usual for such unsymmetrical structures. This is presumably a consequence of the similarity of CO and RNC ligands, and indeed the line is somewhat broadened due not to the electric field gradient but to ^{95}Mo-^{14}N coupling, the magnitude of which is inversely proportional to n. In *fac*-$[Mo(CO)_3(PR_3)_3]$ the ^{95}Mo nucleus is a good probe of ligand nature and is able to show that unlike PF_3, PCl_3 is only a poor π-acceptor.

An interesting growth area in recent times has been the intercalation of the volatile $[Mo(CO)_6]$ into the cavities of zeolites, and a useful review has appeared [168]. The incorporation of $[Mo(CO)_6]$ into Na-Y zeolite has been studied by ^{129}Xe NMR spectroscopy; initially approximately two hexacarbonyl molecules are absorbed per supercage, and on evacuation produce a subcarbonyl species which acts as adsorption site for ^{129}Xe. On further heat treatment complete decarbonylation occurs and the Mo is able to migrate into the sodalite cages and/or the hexagonal prisms of the zeolite, where it is inaccessible to the Xe [169].

The reaction of $[Mo(CO)_6]$ with the phosphine-borane adduct $B_2H_4.(PMe_3)_2$ gives complex (29) in which the ligand is bound through the BH bonds [170].

The anion $[Mo(CO)_5(CN)]^-$ can itself be used as a ligand for metal ions, allowing the preparation of complexes such as $[CrL_6]^{3-}$ and $[CoL_4]^{2-}$ [171]. The reaction of $[Mo(CO)_5I]^-$ with the phosphonium isonitrile ligands *o*-$CNC_6H_4CH_2PR_3^+$ and $AgBF_4$ produces $[Mo(CO)_5(L)]^+$, which can be cyclised to carbene-like species on treatment with base [172]. The tripodal isonitrile ligand *o*-tarc, *i.e.* $N(CH_2CH_2CH_2OC_6H_4\text{-}2\text{-}NC)_3$ has been prepared and coordinated to the $Mo(CO)_3$ fragment as a *fac*-tridentate ligand [173].



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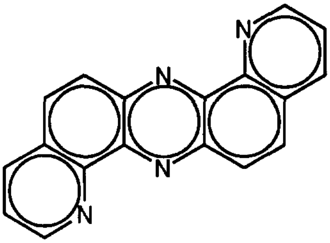


(30)

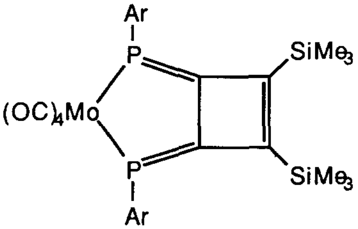
A comparative analysis of the IR spectra, dipole moments, and anisotropic molecular polarisabilities of a number of $[M(CO)_5(L)]$ complexes, (M = Cr, Mo, W; L is a substituted pyridine) has demonstrated a large increase in polarisability along the M-L axis [174].

Laser flash photolysis of $[Mo(CO)_6]$ in the presence of didentate nitrogen donors such as phen or bpy initially produces $[Mo(CO)_5(\eta\text{-L-L})]$. The kinetics of the subsequent CO elimination reaction to give $[Mo(CO)_4(L\text{-}L)]$ have been studied as a function of temperature and pressure. In both cases small negative values of the entropy and volume of activation indicate an associative interchange (I_a) mechanism; however for the bulkier 4,4'-diphenyl-2,2'-bipyridyl, a dissociative interchange (I_d) mechanism is indicated by the positive value of $\Delta V^\ddagger$ [175, 176].

The crystal structures of $Mo(CO)_4$ complexes of 3,3'-dimethyl-2,2'-bipyridyl and 6,6'-dimethyl-2,2-bipyridyl have been determined as benzene solvates. In each case the rings of the bpy ligand are forced to adopt distorted boat-like conformations to maximise the Mo-N bonding and reduce repulsions between the methyl groups [177, 178]. The mono- and bis-$Mo(CO)_4$ complexes of dipyrido-[2,3-*a*: 2',3'-*h*]-phenazine (**30**) have been prepared and show lower energy MLCT absorptions than a comparable uncyclised bis-pyridyl pyrazine ligand [179]. Complexation of the Schiff's bases $R^1R^2C{=}NCH_2CH_2N{=}CR^1R^2$ (R^1 = H, Me; R^2 = *p*-tol, *p*-C_6H_4OMe) also gives simple tetracarbonyl chelate compounds [180].

A photoelectron spectroscopy study of $[Mo(CO)_5(\eta^1\text{-dmpe})]$ and its dmpm analogue has shown that the π-backbonding capability of both ligands is about the same as that of PMe_3 (approximately 25% that of CO) [181]. The laser Raman spectra of $[MoCO)_4(dppe)]$ and its dppm analogue have been recorded, from which it was concluded that they have different crystal structures [182]. The ^{31}P chemical shift tensors of a number of complexes of the type $[Mo(CO)_4\{Ph_2P(CH_2)_nPPh_2\}]$ (n = 1-5) have been studied by solid state and solution spectroscopy; in solution the ^{31}P NMR spectral shift shows a dependence on chelate ring size when n =1-3, but this relationship breaks down for larger rings [183].

The diphosphene ArP=PCp* (Ar = 2,4,6-$C_6H_2{}^tBu_3$) forms a complex with the $Mo(CO)_5$ unit in which the organic groups are initially *trans*, but which changes to the *cis* isomer [184]. The related ArP=PAr where Ar = 2,4,6-$C_6H_2(CF_3)_3$ has also been complexed to $Mo(CO)_5$ [185]. The $Mo(CO)_4$ complex of a diphosphinidenecyclobutene (**31**) (Ar = 2,4,6-$C_6H_3{}^tBu_3$) has been structurally characterised [186].



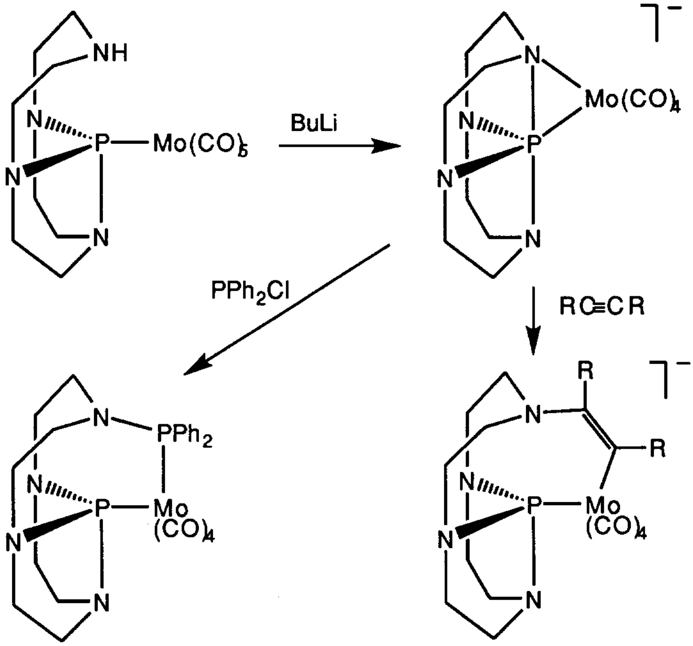
(31)

Deprotonation of $[Mo(CO)_5(Hcyclen)]$ with BuLi forms the corresponding anion in which the ligand is bound through P and N in a strained 3-membered ring. Reaction with PPh_2Cl or the electron-deficient alkyne DMAD causes their insertion into the Mo-N bond (Scheme iii) [187].

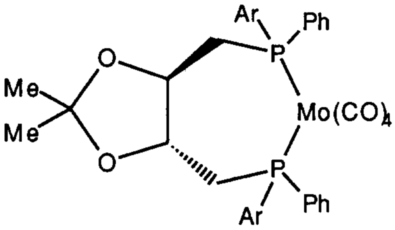
Other monodentate phosphines which have been coordinated to molybdenum carbonyl fragments include $PPh_2C_5H_5$, which can then be deprotonated with TlOEt, and the dioxaphosphorinanes $XP(OCH_2CMe_2CH_2O)$ which undergo nucleophilic halide displacement on reaction with amines, alcohols, or thiols [188, 189].

A variety of interesting new didentate phosphine ligands have been characterised as $Mo(CO)_4$ complexes *e.g.* the chelating silylated diphosphites $R^2R^3Si\{P(O)(OR^1)_2\}_2$ (R^1 = Me, Et; R^2, R^3 = Me, Ph), in which the six-membered chelate rings adopt twist-boat conformations [190, 191]. The ligands $Me_2ESiMe_2(CH_2)_2E'Me_2$ also give six-membered chelates with $[Mo(CO)_4(nbd)]$ when E and E' are P or As, but not when either is nitrogen [192]. A number of chiral phosphine complexes such as (**32**) have been prepared as mixtures of *R,R*-, *R,S*-, and *S,S*-diastereomers; when Ar = *o*-$C_6H_4NMe_2$ the complex rearranges from a *P,P'*-bound chelate to a *P,N*-bound one [193]. The bis-$Mo(CO)_4$ complex of the tetradentate ligand $[CH(CH_2PPh_2)_2]_2$ has also been made [194]. Addition of alkyl lithium reagents to the crown ether phosphite complex (**33**) produces acylate complexes in which the Li^+ ion is held in the crown [195]. The phosphine $CH(PMe_2)_3$ acts as a didentate ligand in its $Mo(CO)_4$ complex, leaving one arm pendant [196]. Thermal reaction of $[Mo(CO)_6]$ with *cyclo*-$As_3P_3Ph_6$, in which the pnictogen atoms alternate, leads to $[Mo(CO)_4(As_3P_3Ph_6)]$, where the ligand adopts a boat conformation with prow and stern bonded to molybdenum. Interestingly, complete scrambling of the P and As atoms occurs during the reaction [197].

In the complex $[W(CO)(S_2CNEt_2)_2(Ph_2PC{\equiv}CPPh_2)]$ the phosphine substituents of the alkyne ligand are bent back as a consequence of its coordination to tungsten through the triple bond. This allows them to act as a didentate ligand to $M(CO)_4$ fragments; the Cr, Mo, and W complexes were all found to be isostructural by X-ray crystallography [198]. Two isomers of the phosphaferrocene (**34**) and (**35**) have also been characterised as chelate ligands to $Mo(CO)_4$ units [199].



Scheme (iii)



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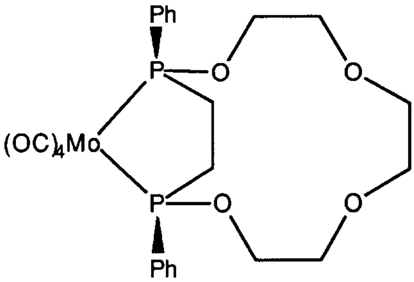

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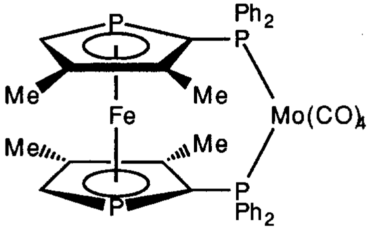

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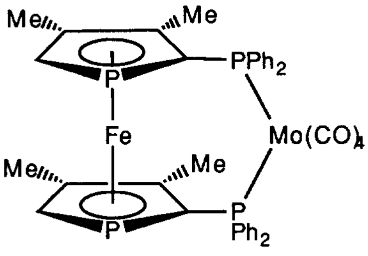


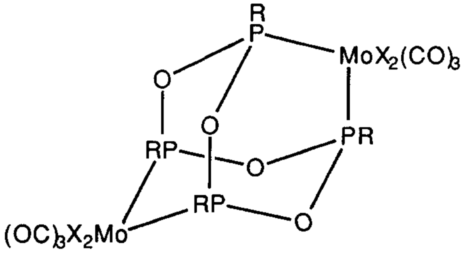
(35)

Oxidation of $[Mo_2(\mu\text{-}PPh_2)_2(CO)_8]$ with $AgPF_6$ gave unstable cationic species, whereas the substituted complex $[Mo(\mu\text{-}PPh_2)_2(CO)_6(PPh_2H)_2]$ produced isolable monocations [200]. Phosphido-bridged heteronuclear complexes have been prepared by 'bridge-assisted' reactions between *cis*-$[Mo(CO)_4(PPh_2H)_2]$ and $[Ru(CO)_3Cl_2(THF)]$ or $[MCl_2(PPh_3)_2]$ (M = Pd, Pt) in the presence of base [201]. Similarly *cis*-$[Mo(CO)_4(PPh_2CH_2OH)_2]$ reacts with $[(HBpz^*{}_3)TiCl_3]$ to give $[(HBpz^*{}_3)TiCl\{OCH_2PPh_2\}_2Mo(CO)_4]$, though in this case the X-ray crystal structure shows that the two metals are separated by over 5.3Å [202].

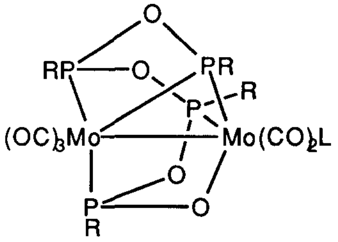
Complexes with pendant phosphines are also useful for synthesising dinuclear species. The reaction between *mer*-$[Mo(CO)_3(dppm)(\eta^1\text{-}dppm)]$ and $[AuCl(PPh_3)]$ is solvent-dependent; in benzene the product is $[(OC)_3(Cl)Mo(\mu\text{-}dppm)_2Au]$, whereas in dichloromethane, $[Mo(CO)_2(dppmO)_2(AuPPh_3)]^+$ is formed. Both the dppm ligands are oxidised to monoxides and both chelate to the molybdenum; there is a direct MoAu bond [203]. In a similar reaction, $[Mo(CO)_3(phen)(\eta^1\text{-}dppm)]$ reacts with $[Rh(CO)_2(S_2CNEt_2)]$ to give $[(OC)(phen)Mo(\mu\text{-}CO)_2(\mu\text{-}dppm)Rh(S_2CNEt_2)]$; however the pendant arm is not a prerequisite since $[Mo(CO)_4(dppm)]$ also reacts to give $[(OC)_4Mo(\mu\text{-}dppm)Rh(CO)(S_2CNEt_2)]$ [204]. The complex $[Mo(CO)_3(L)(\eta^1\text{-}L)]$ where L = $MeN(PF_2)_2$ has also been used to make dinuclear complexes with two μ-L groups in reactions with $[M(Cl)(CO)(PPh_3)_2]$ (M = Rh, Ir), $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$, and $[Ni(CO)_2(PPh_3)_2]$ [205].

Further reactions of the tetraphosphoxane cage complex $[(OC)_4Mo(^iPr_2NPO)Mo(CO)_4]$ have been reported. Halogenation occurs stepwise at both molybdenum atoms to produce the corresponding Mo(II), Mo(II) complex (**36**) [206]. Under mild conditions stepwise substitution also occurs with $P(OMe)_3$; however on heating with this ligand or PPh_2R (R = Ph, Me, H), cage rearrangement and formation of Mo-Mo and Mo-O bonds occurs to give the complex $[(OC)_3Mo(^iPr_2NPO)_4Mo(CO)_2L]$ (**37**) [207].

The heats of protonation of $[M(CO)_2(L\text{-}L)_2]$ (M = Cr, Mo or W; L-L = a didentate ligand such as dppm, dppe, dppe, dmpe, or arphos) have been studied by titration calorimetry. Protonation occurs at the metal, and becomes less exothermic as the chelate ring size increases [208]. Irradiation of $[Mo(PMe_3)_4(CO_2)]$ produces *cis*-$[Mo(CO)_2(PMe_3)_4]$ and $O{=}PMe_3$ as major products with minor amounts of *mer*- and *fac*-$[Mo(CO)_3(PMe_3)_3]$ and $[Mo(CO)_5(PMe_3)]$. A species formulated as *trans*-$[Mo(CO)_2(PMe_3)_4]$ was also detected but not isolated [209].



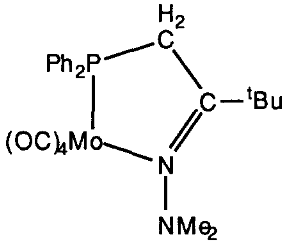
(**36**)



(**37**)

A number of ligands with phosphorus and nitrogen donor atoms have also been studied. The ligand (o-OC_6H_4O)$PN(Me)CH_2CH_2NMe_2$ acts as a monodentate *P*-donor in its reaction with $[Mo(CO)_3(\eta^6\text{-cht})]$ to give *fac*-$[Mo(CO)_3L_3]$, but from $[Mo(CO)_4(nbd)]$ the *P,N*-chelate complex $[Mo(CO)_4(L)]$ is obtained as well as $[Mo(CO)_4(L)_2]$ [210]. The aminophosphine *erythro*-$PhP(Cl)N(^iPr)PPh(NH^iPr)$ forms a four-membered chelate ring bonding though both P atoms [211]. The course of the reaction of the cyclodiphosphazanes $(R^1NPR^2)_2$ with $[Mo(CO)_6]$ or $[Mo(CO)_4(nbd)]$ depends on the stereochemistry of the ring; $[^tBuNP(OPh)]_2$ and [PhNP(O-*p*-tol)]$_2$, which both exist predominantly as *cis* isomers in the free ligand, form monodentate P-bound complexes $[Mo(CO)_4(L)_2]$, whereas $[PhNP(OCH_2CF_3)]_2$, which is mainly *trans*, forms $[Mo_2(CO)_8(\mu\text{-}L)_2]$ in which the ligand is didentate through both P atoms [212, 213].

The ligand *Z*-$Ph_2PCH_2C(^tBu)=N\text{-}NMe_2$ produces two isomeric complexes of formula $[Mo(CO)_4(L)]$. Thermal reaction with $[Mo(CO)_6]$ produces the five-membered chelate complex (**38**) of the *E*-form of the ligand, whereas from $[Mo(CO)_4(nbd)]$ the six-membered chelate (**39**) is formed. Heating the latter in diglyme causes cleavage of the NMe_2 unit. Oxidation of these and related complexes with bromine produces $[MoBr_2(CO)_3(L)]$ [214].



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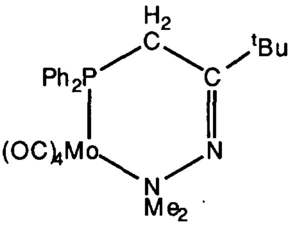

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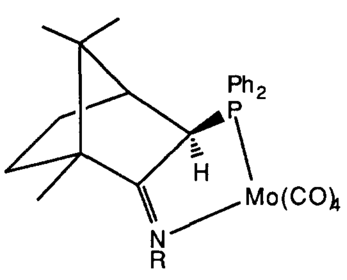
By deprotonation of $MeC(^tBu)=NN=C(^tBu)Me$ and treatment with PPh_2Cl, Shaw and co-workers have prepared the azine diphosphine *Z, Z*-$Ph_2PCH_2C(^tBu)=N\text{-}N=C(^tBu)CH_2PPh_2$. This ligand reacts with $[Mo(CO)_4(nbd)]$ to give $[Mo(CO)_4(L)]$ in which it is bound though both P atoms, but on heating decarbonylation occurs, giving *fac*-$[Mo(CO)_3(L)]$, where it acts as a tridentate *P,N,P'*-ligand. Oxidation of any of these with bromine gives $[MoBr_2(CO)_2(L)]$ [215].

Reaction of the camphor hydrazone complex (**40**) (R = NMe_2) with bromine also produces the corresponding Mo(II) complex. With HCl, however, the hydrazone is cleaved as well to produce the Mo(II) complex of the related ligand with R = H. This in turn can be reduced back to (**40**) (R = H) [216].

The $Mo(CO)_3$ complex (**41**) of the hybrid tridentate *P,P',O*-ligand shown above undergoes reaction with added ligands (MeCN, py, phosphite) by replacement of the weak oxygen donor interaction to give two diastereomers of $[Mo(CO)_3(L)(P\text{-}P)]$; the major one is that in which L occupies the same position as the oxygen, but the minor one has L *trans* to this site. Isomerisation of a five coordinate intermediate is proposed. The addition is reversible in the case of MeCN leading to an equilibrium in solution [217].



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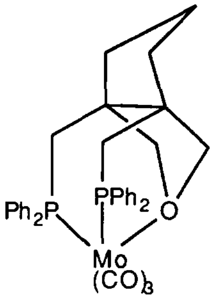

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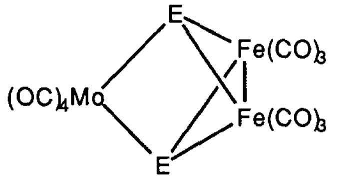
The reaction of $[Mo(CO)_6]$ with KOH in hot ethanol was previously assumed to produce a dimeric species, $K_3[Mo_2(\mu\text{-}OH)_3(CO)_6]$ by analogy with the tungsten complex, which was structurally characterised some years ago. Now, however, by adding Cs^+ to the anion-containing solution, crystals of the cubane-like cluster $Cs_4[M_4(\mu_3\text{-}OH)_4(CO)_{12}].nH_2O$ have been obtained for both Mo and W [218].

The ligands 1,6-bis(2-thienyl)-2,5-dithiahexane and 1,9-bis(2-thienyl)-2,5,8-trithianonane both coordinate to the $Mo(CO)_4$ fragment in a simple didentate manner, with the thienyl groups remaining unattached; the complexes are fluxional by sulfur inversion [219]. Protonation of $[Mo(CO)_2(PMe_3)_2(S_2CPMe_3)]$ with HBF_4 occurs at the carbon of the S_2CPMe_3 ligand, whereas alkylation occurs at sulfur, giving η^3-bound phosphonothioester complexes [220]. The same ligand functions as a bridge in $[(\eta\text{-}C_6Me_6)Ru(\mu\text{-}Cl)(\mu\text{-}S_2CPMe_3)Mo(CO)_3]^+$, prepared by addition of $[(\eta\text{-}C_6Me_6)Ru(S_2CPMe_3)(Cl)]^+$ to $[Mo(CO)_3(NCMe)_3]$ [221], and in $[BuCl_2Sn(\mu\text{-}S_2CPMe_3)Mo(Cl)(CO)_2(PR_3)]$ (R = Cy, Et, Bu) which can be made by oxidative addition of $BuSnCl_3$ to dimeric $[Mo(CO)_2(PMe_3)(S_2CPR_3)]_2$ [222].

Several heterodinuclear complexes with μ-SR ligands have been prepared. These include $[Cp_2Ti(\mu\text{-}SPh)_2Mo(CO)_4]$, which shows two reversible waves in its cyclic voltammogram corresponding to Ti(IV)-Ti(III) and Mo(0)-Mo(I) couples, and $[Cp(\eta\text{-}C_2Ph_2)Nb(\mu\text{-}S^iPr)_2Mo(CO)_4]$; both have planar $MoMS_2$ cores [223, 224]. A three-component reaction between $[Fe(CO)_4Br_2]$, $[Mo(CO)_4(nbd)]$, and $NEt_4[SPh]$ produced a 34% yield of $[NEt_4][(OC)_3Fe(\mu\text{-}SPh)_2Mo(CO)_3(SPh)]$ [225].

Reaction of $[Mo(CO)_5(thf)]$ with $[Fe_2(\mu\text{-}E)_2(CO)_6]$ (E = S, Se) produced $[MoFe_2(\mu_3\text{-}E)_2(CO)_{10}]$ (**42**), and a related cluster, $[NEt_4][MoFe_2(\mu_3\text{-}S)_2(CO)_8(S_2CNEt_2)]$ was made by treatment of $[Mo(CO)_4(S_2CNEt_2)]^-$ with $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$ in a mixture of THF, MeCN and MeOH [226, 227, 228]. None of these compounds has a direct Mo-Fe bond.

The reaction of $[M(CO)_6]$ (M = Mo, W) with K_2Te_2 produces the $[M_4(CO)_{18}(Te)_2]^{2-}$ dianion (**43**); the tungsten complex was structurally characterised [229]. The hexacarbonyls also reacted with $As_2Se_6{}^{2-}$ and $As_4Se_6{}^{2-}$ to give $[M(AsSe_5)_2]^{2-}$ (**44**) and $[M(CO)_2(As_3Se_3)_2]^{2-}$ (**45**) respectively, the X-ray structures of both tungsten salts again being determined [230]. Oxidative decarbonylation of $[Mo(CO)_6]$ with *o*-HSC_6H_4OH produces $[Mo_2(CO)_3(OC_6H_4S)_3]^{2-}$ and $[Mo_3(CO)_7(OC_6H_4S)_3]^{2-}$; these consist of a trigonal prismatic $Mo(OC_6H_4S)_3$ tris-chelate dianion with a $Mo(CO)_3$ unit ligated by the three oxygen atoms; in the latter compound a $Mo(CO)_4$ group is additionally coordinated to two of the sulfur atoms [231].



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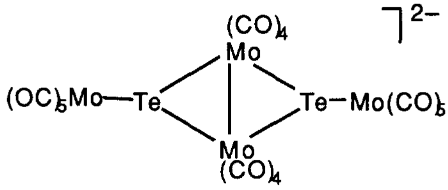

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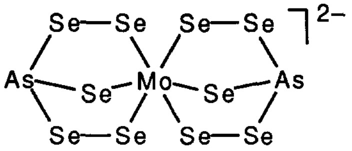

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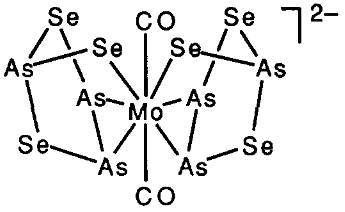

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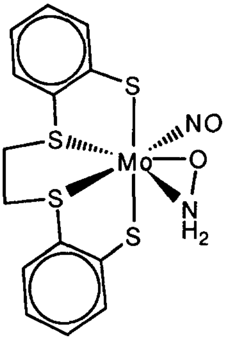
Molybdenum carbonyl clusters are not numerous, but two interesting examples reported this year are triangular $[MoOs_2(CO)_{11}\{P(OMe)_3\}_2]$, formed by irradiation of $[(OC)_5MoOs(CO)_4\{P(OMe)_3\}]$, and $[(OC)_4Mo\{Au(PPh_3)\}_5]^+$, produced by photolysis of $[Mo(CO)_6]$ with $[(Ph_3P)AuN_3]$ [232, 233]. Reaction of $[Mo_2(\mu\text{-}H)(\mu\text{-}dppm)(CO)_8]^-$ with $[(Ph_3P)MCl]$ (M = Au, Cu, Ag) also gives triangular clusters [234].

6.7.2 Complexes with nitrogen and phosphorus donor ligands

The most common starting materials are the dinitrogen complexes $[M(N_2)_2L_4]$ where L = a phosphine (or two didentate phosphines), and two recent reviews on the protonation of coordinated dinitrogen and the reaction of dinitrogen complexes with nitriles such as $NCNH_2$ both contain some relevant material [235, 236]. Electrochemical reduction of $[MoCl_3(L_3)]$ (L_3 = $Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2$) in the presence of PPh_3 occurs initially by one electron and gives ultimately either $[Mo(\eta^6\text{-}PPh_3)(L_3)]$ or in an N_2 atmosphere, unstable *cis*-$[Mo(N_2)_2(L_3)(PPh_3)]$ [237]. The decomposition of *trans*-$[Mo(N_2)_2(PPh_2Me)_4]$ to Mo, N_2 and free phosphine has been studied in benzene; two consecutive steps with comparable rates are proposed, with the first being phosphine dissociation, detected by NMR spectroscopy and in the reaction with py [238]. The complex *trans*-$[Mo(N_2)_2(dppe)_2]$ reacts with N_2CHCO_2Et by replacement of both nitrogen ligands, giving *trans*-$[Mo(NNCHCO_2Et)_2(dppe)_2]$ [239]. The same compound reacts with terminal alkynes to afford the alkyne complexes $[Mo(HC{\equiv}CR)_2(dppe)_2]$, the alkynyl hydrides $[Mo(H)_2(C{\equiv}CR)_2(dppe)_2]$, or the bis-alkynyls *trans*-$[Mo(C{\equiv}CR)_2(dppe)_2]$ (R = Ph, CO_2Me, CO_2Et) depending on the conditions [240].

The preparation of a complex of phenyldiazene has been achieved by Hillhouse and co-workers. The synthetic route starts from *trans, trans*-$[Mo(Cl)(CO)_2(NO)(PPh_3)_2]$, which is first converted to the corresponding hydride with $LiBHEt_3$, then to the triflate with TfOH. Subsequent reaction with the diazonium cation PhN_2^+ produces *trans, trans*-$[Mo(PhN{=}NH)(CO)_2(NO)(PPh_3)_2][BF_4]$, which on treatment with bromide releases the unstable PhN=NH at −40°C instead of 0°C for the tungsten analogue, with the advantage that the half-life of the free ligand is much longer at the lower temperature [241]. Reduction of $[Mo_7O_{24}]^{6-}$ with hydroxylamine in ^iPrOH gives mainly dinitrosyl species, whereas in MeOH mononitrosyls are formed; addition of ligands such as phen allows isolation of compounds of the type $[MoCl_2(NO)_2L_2]$ and $[MoCl(NO)(OMe)_2L_2]$ [242]. Carbene complexes for alkene metathesis can be prepared from $[Mo(NO)_2(OAc)_2]$ by reaction with $EtAlCl_2$ [243].



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The complex $[Mo(NO)_2('S_4')]$ ($'S_4' = {}^-SC_6H_4SCH_2CH_2SC_6H_4S^-$) undergoes a 2-electron reduction, acquiring $2H^+$, to give complex (**46**). On protonation with HCl gas, the ligand is released as $[N_2H_5][Cl]$ and NH_4Cl. The complex is recovered as $[MoCl(NO)('S_4')]$, which can be reconverted to $[Mo(NO)_2('S_4')]$ by reduction with zinc in the presence of NO [244].

6.8 MOLYBDENUM CLUSTERS

6.8.1 Polyoxomolybdates

An extensive review of the chemistry of polyoxomolybdates and polyoxovanadates has appeared [245]. The following brief discussion deals first with homonuclear species and then with heteropolymolybdates.

The complex series of equilibria involving $[MoO_4]^{2-}$, H^+ or M^+ (M= Na, K, NH_4, or guanidinium), and the ligand $MeC(OH)\{P(O)(OH)_2\}_2$ (= H_5L) have been investigated by Russian workers [246, 247]. By varying the counter-ion they were able crystallise out $[Mo_2O_6(L)]^{5-}$, $[Mo_3O_9(L)]^{5-}$, and $[Mo_6O_{17}L_2]^{8-}$ and determine their X-ray structures [248, 249].

Oxidation of $[Cp^*{}_2Mo_2(CO)_4]$ with molecular oxygen causes a most unusual reaction; the product is $[C_5Me_5O][Cp^*Mo_6O_{18}]$ in which a pyrylium cation formed by insertion of O into the five-membered ring of a Cp* ligand is associated with the novel polyoxoanion in which one vertex has a MoCp* unit instead of the usual MoO. Irradiation of the starting complex in chloroform with oxygen present gives two dimeric compounds, $[Mo_2Cl_2(\mu\text{-}Cl)_2(\mu\text{-}O)Cp^*{}_2]$ and $[Mo_2Cl_2(\mu\text{-}CO_3H)(\mu\text{-}O)(\mu\text{-}Cl)Cp^*{}_2]$ [250]. One of the terminal Mo=O units in $[Mo_6O_{19}]^{2-}$ can also be replaced by a terminal imido group by treatment with $Ph_3P{=}N\text{-}p\text{-}tol$ in pyridine, yielding $[Mo_6O_{18}(NR)]^{2-}$ [251].

The anion $[Mo_6O_{19}]^{2-}$ has been used as a large counter-ion to crystallise $[Re_2(NCMe)_8]^{4+}$ for X-ray determination [252]. The synthesis of some tetrathiafulvalene (TTF) salts of various polyoxoanions has been reported, including $[TTF]_3[Mo_6O_{19}]$, which contains stacked trimeric $[TTF]_3{}^{2+}$ cations [253]. The crystal structure of $[NEt_4]_2[Mo_6O_{19}H_4]$ has been determined [254]. The reaction of $[Mo_6O_{19}]^{2-}$ with the electron donor $p\text{-}Me_2NC_6H_4NMe_2$ (tmpd) gave a mixed salt $[tmpd]_2[tmpdH]_2[\beta\text{-}Mo_8O_{26}]$; two of the counterions are tmpd radical cations and two are monoprotonated tmpd [255]. The reaction of MoO_3 with dien gives four products: two polymorphs of $[H_3dien]_2[Mo_7O_{24}].4H_2O$, $[H_2dien]_2[Mo_8O_{26}].6H_2O$, and the simple adduct $[MoO_3(dien)]$ [256]. The $[{}^tBuNH_3]^+$ salts of these anions have been investigated by TGA; they all ultimately yield MoO_3 [257]. The photolysis of the same anions at 255 or 355 nm produces transient species arising from LMCT absorptions similar to those in the tungsten analogues [258]. The isomerisation of $[NBu_4]_4[\alpha\text{-}Mo_8O_{26}]$ to the β-form can be achieved by treatment with NEt_3 and salicylaldehyde; the product is isolated as the $[NBu_4]_2[NHEt_3]_2$ salt, and it appears that a small cation facilitates the transformation [259]. Reaction of MoO_3 with pyrazole (Hpz) gives $[H_2pz]_4[Mo_8O_{26}(Hpz)_2]$ which contains six edge sharing MoO_6 octahedra and two MoO_5pz octahedra [260]. The synthesis and thermal analysis of $[Mo_{14}O_{42}(C_2O_4)_7]^{14-}$ has been described; on heating, loss of oxalate occurs [261].

Evidence for the participation of two large polyoxoanions, $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ and $[Mo_{18}O_{56}]^{4-}$, was obtained in the extraction of Mo(VI) in 1M $HClO_4$ with $P(OBu)_3$ [262]. The hydrothermal reaction of MoO_3, $Na_2[MoO_4].2H_2O$, pentaerythritol ($H_4L = C(CH_2OH)_4$), Et_4NCl, Me_3NHCl and H_2O in a 6:6:10:10:10:300 ratio produces the $Mo^V{}_{36}Mo^{VI}{}_6$ complex $[Me_3NH]_2[NEt_4]_2Na_4[Na(H_2O)_3H_{15}Mo_{42}O_{109}(HL)_7].7H_2O$ in 30% yield. The structure consists of a central Mo_6O_{24} ring, four $Mo_6O_{22}(HL)$ units, and three $Mo^V{}_2Mo^{VI}{}_2O_{15}(HL)$ units, with a $Na(H_2O)_3$ encapsulated within the giant anion [263].

The X-ray structure of $Na[NMe_4]_3[S_2Mo_5O_{23}].4H_2O$ has confirmed the existence of this anion, which consists of a ring of five MoO_6 octahedra capped above and below by two SO_4 tetrahedra [264]. By heating MoO_3, $SeO_3{}^{2-}$, H_2SeO_3 and K_2CO_3 in boiling water, the novel species $K_2[Se_2MoO_8].3H_2O$ was obtained; it has a unique infinite chain structure in which MoO_6 octahedra are linked by pseudo-tetrahedral SeO_3 groups. This structure is evidently lost on dissolution in hot water since on cooling crystals of $K_4[Se_2Mo_5O_{21}].2H_2O$ are formed [265]. The new ion $[Te_6Mo_{12}O_{60}]^{12-}$ has been synthesised from $Te(OH)_6$ and MoO_3 in a 1:1.8 ratio at 60°, pH 7.5. The structure shows a puckered ring of corner-sharing TeO_6 octahedra, to each of which are attached two MoO_6 octahedra sharing corners and edges [266].

A number of other main-group polyoxomolybdates have been studied, mainly based on the $[EMo_{12}O_{40}]^{n-}$ structure, including $[PMMo_{11}O_{39}(H_2O)]^{5-}$ where M = Mn, Co, Ni, Cu, Zn [267]. The crystal structure of $[NEt_4]_4[PMo_{12}O_{40}]$ has been determined [268], and a laser Raman spectroscopic study of the thermal behaviour of $[H_3PMo_{12}O_{40}]$ supported on silica has shown a reversible change to an unidentified species on heating [269]. The crystal structure of $[H_6SiMo_{12}O_{40}].10H_2O$ has been determined [270], and the mixed metal species $[\alpha\text{-}SiMo_{3-x}V_xW_9O_{40}]^{(4+x)-}$ (x = 1, 2) have been prepared from $[SiMo_2W_9O_{39}]^{8-}$ [271]. In a similar way $[PMo_3W_9O_{40}]^{3-}$ has been made from $[PW_9O_{34}]^{9-}$ [272]. A ^{31}P and ^{51}V NMR spectroscopic study of $[PMo_{12-n}V_nO_{40}]^{(3+n)-}$ has appeared [273] and the aerobic dehydrogenation of α-terpinene to *p*-cymene has been used to investigate the mechanism of oxidation by $[PV_2Mo_{10}O_{40}]^{5-}$; the reaction is zero order in substrate, first order in O_2, and second order in the anion, which is explained by the formation of a substrate-catalyst complex in the first stage and of a μ-peroxo intermediate during reoxidation of the catalyst [274]. Reoxidation is also the key process in photocatalytic oxidation by $[P_2Mo_{18}O_{62}]^{n-}$ (n = 6, 8, 10); oxidation of the 10^- anion is much slower than in the W analogue, and reoxidation of the 8^- anion requires H_2O_2, not just O_2 [275]. The anion $[(RAs)_2Mo_6O_{25}]^{6-}$ (R = C_6H_3-3-NO_2-4-OH) has been structurally characterised [276].

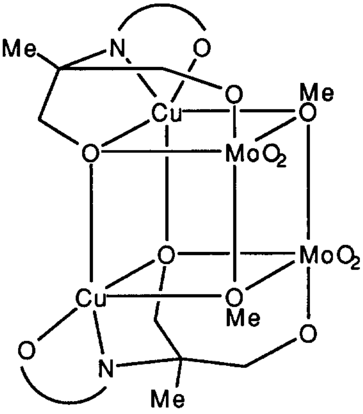
The X-ray structures of $[NH_4]_6[MMo_9O_{32}].6H_2O$ where M = Ni(IV) or Mn(IV) have been determined; they are isomorphous [277]. The X-ray structure of the $[Nd(GeMo_{11}O_{39})_2]^{13-}$ ion has also been determined [278]. The hydrothermal reaction of $[Cp^*{}_2Rh_2(\mu\text{-}OH)_3][Cl]$ and $MoO_3.2H_2O$ produced $[(Cp^*Rh)_8Mo_{13}O_{40}]^{2+}$ [279]. The $[Zn_3Mo_{12}O_{30}(HPO_4)_2(H_2PO_4)_6]^{2-}$ anion has also been produced by hydrothermal synthesis from $Na_2[MoO_4]$, Mo, ZnO, Me_4NOH, and H_3PO_4 [280].

6.8.2 *Halide clusters*

By reaction with AgOTf in CH_2Cl_2, the outer sphere halides in the cluster $[Mo_6Cl_{14}]^{2-}$ can be replaced with OTf groups to give $[Mo_6Cl_8(OTf)_6]^{2-}$; the labile triflate ligands can then be replaced by NCS^-, OMe^-, OAc^-, $O_2CCF_3{}^-$ *etc*., and also by solvent, either totally (*e.g.* dmf) or partially (*e.g.* acetone) [281]. Direct reaction of $[Mo_6Cl_{14}]^{2-}$ with CF_3CO_2H also replaces the outer-sphere chlorides [282]. Structural investigations on the series $[NBu_4]_2[Mo_6Cl_8(X)_6]$ (X = F, Cl, Br, I) have shown an expansion of the Mo_6 octahedron but a compression of the Cl_8 cube as X is changed progressively from F to I [283]. The structures of $Pb[Mo_6X_{14}]$ (X = Cl, Br, I) have also been determined [284]. Reaction of ^{15}N-labelled $[Mo_6Cl_8(NCS)_6]^{2-}$ with $[Mo_6Cl_8(X)_6]^{2-}$ (same X) can be followed by ^{15}N and ^{19}F NMR spectroscopies, and produces an equilibrium mixture of the mixed species $[Mo_6Cl_8(X)_n(NCS)_{6-n}]^{2-}$ in about 10 hours at room temperature [285]. Reduction of a mixture of $MoCl_5$ and WCl_6 with Al in an $AlCl_3$/NaCl melt gives the mixed-metal clusters $[Mo_nW_{6-n}Cl_{14}]^{2-}$, identified by their secondary ion mass spectra (SIMS) [286]. Oxidation of the $Mo_6{}^{12+}$ clusters $[Mo_6(X)_7E(X')_6]^{3-}$ (X, X' = Cl, Br; E = S, Se) gives the corresponding $[Mo_6(X)_7E(X')_6]^{2-}$ cluster; crystallography shows that the Mo-Mo bonds lengthen slightly on oxidation [287].

6.8.3 *Other clusters, including cubanes*

The exchange of all the bridging OAc groups in $[Mo_3(\mu_3\text{-}CMe)(\mu_3\text{-}O)(\mu\text{-}OAc)_6(H_2O)_3]^+$ has been reported; this enables the preparation of compounds in which the bridging ligands bear a different R group to that on the capping carbyne [288]. The synthesis of the cubane-like cluster $[Mo_2Cu_2O_4(saladhp)_2(OMe)_2]$ (**47**) ($H_3saladhp$ is $MeCH(CH_2OH)_2N{=}CHC_6H_4\text{-}2\text{-}OH$, derived from salicylaldehyde) has been reported [289].



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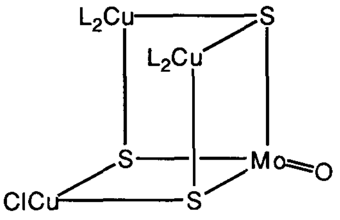
The use of $[MoS_4]^{2-}$ in the preparation of polynuclear species is well established, and a number of new examples have appeared. The reaction of $MnBr_2$ with $[MS_4]^{2-}$ (M = Mo, W) in MeOH produced $[PPh_4]_2[Mn(MS_4)_2]$, which had previously defied isolation. The structure of the W complex was determined [290]. Treatment of $[LRu(CO)(PPh_3)_2Cl]$ (L = $CH_2CH_2CO_2Me$, CH_2CH_2-2-pyridyl) with $[MoS_4]^{2-}$ gives $[\{LRu(CO)(PPh_3)_2\}_2MoS_4]$ [291].

The reaction of $[MoS_4]^{2-}$ with CuCl is already known to give a large variety of cubane clusters. The ultimate stage in this addition, $[NMe_4]_5[MoS_4(CuCl)_6Cl_3]$, in which a CuCl bridges each edge of the tetrahedron, has now been isolated and crystallographically characterised [292]. The reaction of $[MS_4(CuCl)_4]^{2-}$ (M = Mo, W) with $[Fe(bpy)_3]^{2+}$ gave the incomplete cubane $[MoOS_3Cu_3(Cl)(bpy)_2]$ (**48**); the X-ray structures of $[Cu(bpy)_2][MS_4(CuCl)_3]$ were also reported [293]. The preparations of the clusters $[MoS_4Cu_2(S_2CPh)_2]$ and $[MoOS_3Cu_2(PPh_3)_3]$, and the double incomplete cubane $[Mo_2S_6O_2Cu_5(Et_2dtc)_3]$ have also been described [294, 295].

A number of cubanes containing silver have also been prepared. Reaction of $[MoS_4]^{2-}$, AgCl, and PPh_3 produced $[Mo(=S)Ag_3S_3(Cl)(PPh_3)_3]$ (**49**), and a similar procedure starting from $[Mo_2O_2(S)(S_2)_4]^{2-}$ produced the analogous $[Mo(=O)Ag_3S_3(Cl)(PPh_3)_3]$ cluster [296, 297]. Treatment of $[MoS_4Cu(CN)]^{2-}$ with $Ag(PPh_3)_2^+$ led to the linear cluster (**50**), whereas $[MoOS_3Cu(CN)]^{2-}$ gave the butterfly cluster (**51**) with the same reagent [298]. Heating $[NH_4]_2[MoS_4]$, AgCl and NBu_4Br in the solid state unexpectedly gave $[NBu_4]_3[Mo_4S_4Cl_4]$ [299].



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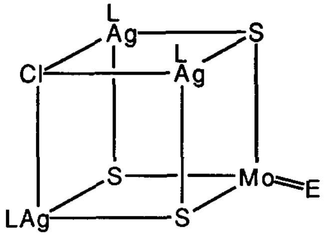

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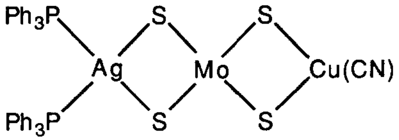

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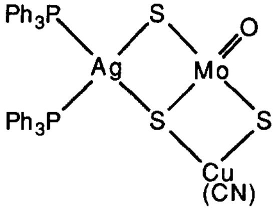

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The reaction of $[MoOS_3Cu_2(PPh_3)_3]$ with $CuSCH_2CH_2OH$ gave the double cubane $[Mo_2O_2Cu_6S_6(PPh_3)_4(SCH_2CH_2OH)_2]$ in which the two cubane fragments are bridged by the mercaptoethanol ligand [300]. A similar reaction of $[MoOS_3Ag_2(PPh_3)_3]$ with AgS^tBu gave the analogous thiolate-bridged $[Mo_2O_2Ag_6S_6(PPh_3)_4(S^tBu)_2]$ [301].

The effect of Lewis bases on the synthesis of linear $[Cl_2FeMoS_4FeCl_2]^{2-}$ and the electronic structure of the products have been investigated [302, 303]. Treatment of the linear complexes $[Fe_3S_4L_4]^{3-}$ (L = SEt, SCH_2Ph, OPh, Cl *etc.*) with $[M(CO)_3(NCMe)_3]$ (M = Mo, W) affords cubane-type clusters $[Fe_3S_4L_3M(CO)_3]^{3-}$. If heated with Et_2S_2 they convert into the double cubanes $[Fe_6Mo_2S_8(SR)_9]^{3-}$ which are linked by a $Mo(\mu\text{-}SR)_3Mo$ bridge [304]. A survey of routes to homonuclear cubanes of the type $[Mo_4S_4L_6]$ where L = a sulfur chelate such as dtc, S_2COR, S_2CSR, or $S_2P(OR)_2$, has appeared [305].

Synthetic routes to the incomplete cubane cluster $[Mo_3(\mu\text{-}S)_3(\mu_3\text{-}S)(H_2O)_9]^{4+}$ from $[NH_4]_2[MoS_4]$ or $Na_2[Mo_2O_2S_2(cys)_2]$ have been detailed. Other clusters with the same core can then be prepared by replacement of the aquo ligands, including $[Mo_3S_4(Hnta)_3]^{2-}$ ($H_3nta = N(CH_2COOH)_3$). This cluster undergoes three successive reductions in alkaline solution (at −0.64V, −1.08V, and −1.39V) as the $Mo(IV)_3$ core is reduced to $Mo(III)_3$ [306]. The second stage of the substitution reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with NCS^- has been studied by UV-VIS spectroscopy; replacement of the first H_2O had been reported previously [307]. The conversion of a μ-S ligand in $[Mo_3S_4(H_2O)_9]^{4+}$ to a μ-O can be achieved by treatment with $NaBH_4$; this strategy also works with the analogous $MoOS_3$ and MoO_2S_2 clusters, but with the MoO_3S cluster the trinuclear structure is destroyed, and with $[Mo_4S_4(H_2O)_{12}]^{5+}$ simple reduction to the tetracation occurs [308]. Substitution reactions of $[Mo_4S_4(H_2O)_{12}]^{4+}$ with NCS^- have also been examined, and proceed in two steps with large and small associated absorbance changes respectively. A slower overall reaction is seen for $[Mo_4S_4(H_2O)_{12}]^{5+}$, with attack occurring at one of the Mo(III) centres; this provides the first evidence that Mo(III) and Mo(IV) sites are different [309].

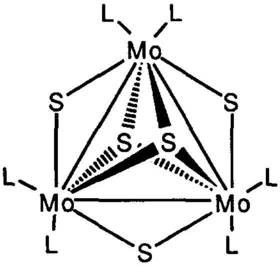
Treatment of $[Mo_3S_4(H_2O)_9]^{4+}$ with palladium black produces a species formulated as $[Mo_3PdS_4(Cl)(H_2O)_9]^{3+}$, which could not be crystallised; however, displacement of the aquo ligands by addition of tacn (1,4,7-triazacyclononane) gave the cubane $[Mo_3Pd(Cl)(tacn)_3]^{3+}$ and anion exchange with tosylate produced the double cubane $[Mo_6Pd_2S_8(H_2O)_{18}]^{8+}$. Anion exchange of the tacn cluster with ClO_4^- followed by reaction with the alkene $HOCH_2CH{=}CHCH_2OH$ gave $[Mo_3PdS_4(tacn)_3(\eta\text{-alkene})]^{4+}$ in which the alkene is bonded to the palladium atom [310].

The aquo ligand in $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3\{S_2P(OEt)\}_4(H_2O)]$ can be replaced with allylthiourea, whereas reaction with NaOAc and $Na(S_2CNC_4H_8)$ produced the unusual cluster $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_2(\mu\text{-}OAc)(O)_2(dtc)_3]$ with only two Mo-Mo bonds [311, 312].

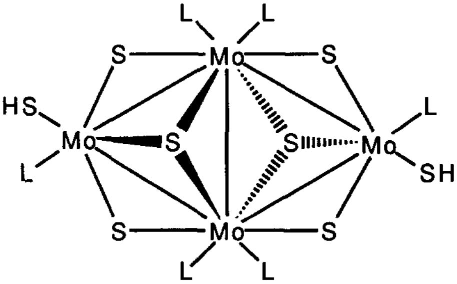
Heating the cluster $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(Et_2dtc)_3][Et_2dtc]$ in $ClCH_2CH_2Cl$ results in replacement of the outer sphere dtc anion by chloride [313]. The same cluster forms charge transfer salts with the electron acceptor tcnq [314]. Reaction with KSeCN converts the $\mu\text{-}S_2$ groups into μ-SSe ligands, producing $[Mo_3(\mu_3\text{-}S)(\mu\text{-}SSe)_3(Et_2dtc)][SeCN]$, in which there are short contacts between these ligands and the counter-ion [315]. Reaction of the related $[Mo_3S_7Br_6]^{2-}$ with aniline yields $[Mo_3S_7(HN_2Ph)_3Br_3]^+$, which in the crystal is associated with two Br^- ions and one NEt_4^+ cation [316].

Treatment of MoS_3 with 5% aqueous KOH produced $K_2[Mo_3S_{13}]$, which was isolated by conversion to $[Mo_3S_7(Et_2dtc)_4]$; elegant mass spectrometry studies proved that the Mo_3 clusters are already present in the solid MoS_3 rather than being assembled in solution [317]. The collision induced decomposition of mixed S/Se clusters, including a liquid SIMS and FTMS study of $[Mo_3S_{7\text{-}n}Se_n(Et_2dtc)_4]$ ($n = 0, 3, 7$) has been studied in related work; similar fragmentation patterns were observed for all three [318]. The nuclear quadrupole interaction of $^{99}Mo(\beta^-)^{99}Tc$ has been measured in several Mo-S clusters including $[Mo_3S_{13}]^{2-}$, $[Mo_3S_4(CN)_9]^{5-}$, $[Mo_2(S_2)_6]^{2-}$, and $[Mo_2S_2(CN)_8]^{6-}$ [319].

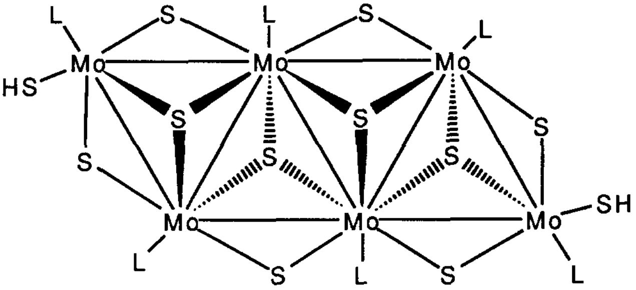
Three interesting clusters have been synthesised by addition of phosphines to $[NH_4]_2[Mo_3S_{13}]$. With PMe_3 in excess, the equilateral triangular Mo(III)$_2$Mo(IV) cluster $[Mo_3(\mu_3\text{-}S)_2(\mu\text{-}S)_3(PMe_3)_6]$ (**52**) is formed [320]. However larger clusters with fused triangles are also produced, and $[Mo_4S_6(SH)_2(PMe_3)_6]$ (**53**) and $[Mo_6S_{10}(SH)_2(PEt_3)_6]$ (**54**) have been isolated and structurally characterised. In the first, the wing-tip Mo atoms are Mo(IV) and the hinge Mo atoms are Mo(III); in the latter the two central Mo atoms are Mo(III) while the others are all Mo(IV) [321].



(52)



(53)



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