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3 MOLYBDENUM (1981)

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CONTENTS

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INTRODUCTION

The material included in this review was obtained from the reports published in primary research journals during 1981 and/or volumes 94 and 95 of Chemical Abstracts. The material follows on from the review [1] of the 1980 literature, and is organised into sections following a similar scheme. The major classification is by the oxidation state of molybdenum, with several sections at the end dealing with specific areas which cut across a simple oxidation state classification.

A review of molybdenum compounds containing 37 references has been published, dealing with the technological applications of molybdenum [2]. The 1976 annual survey of the organometallic chemistry of chromium, molybdenum and tungsten has been compiled [3].

Thermodynamic data have been used to estimate the metal-halogen, metal-oxygen and metal-metal bond energies in a number of molybdenum complexes including $MoCl_4$, $MoCl_6$, $MoCl_5$, $MoO_2Cl_2.H_2O$, $(MoOCl_3)_n$, $(MoOBr_3)_n$, MoO_3, Mo_3O_9 and $MoOCl_4$. Relations were established between bond energies and interatomic distances [4].

3.1 MOLYBDENUM(VI)

3.1.1 Molybdenum(VI) fluoride

The reaction of $[Me_4N][N_3]$ with $[MoF_6]$ leads to the formation of $[Me_4N][MoF_6]$ and N_2. $[Me_3Si][N_3]$ reacts with $[MoF_6]$ at room temperature to give Me_3SiF and N_2, with no other fluorinated species detected. The reaction at -70 °C yields $[MoF_5(N_3)]$ and *cis*-$[MoF_4(N_3)_2]$, identified by ^{19}F NMR spectroscopy [5]. The fluorides in $[MoF_6]$ can be replaced by $(F_5TeO)^-$ groups by means of $B(OTeF_5)_3$. Rearrangement reactions and internal fluorination give compounds of the general formulae $[MoF_n(OTeF_5)_{6-n}]$ and $[MoOF_n(OTeF_5)_{4-n}]$ [6].

3.1.2 *Oxo complexes*

The infrared and electronic spectra of matrix isolated $[MoOF_4]$ and $[MoOCl_4]$ have been recorded and interpreted [7]. The adduct $MoOF_4.SbF_5$ has been obtained from the reaction of $[MoOF_4]$ with excess SbF_5, and characterised by observation of the reaction stoichiometry, Raman and mass spectra, and by X-ray diffraction. The crystal structure shows the adduct to be polymeric with a zig-zag chain of alternate Sb and molybdenum atoms linked through fluorine bridges. Some evidence was obtained of a second adduct, $MoOF_4.2SbF_5$ [8]. The reaction of KrF_2 with $[MoOF_4]$ in SOClF at low temperatures yields adducts $KrF_2.nMoOF_4$ (n = 1-3) in solution, shown by ^{19}F NMR spectroscopy to contain Kr---F---Mo bridges. Raman spectra of the solid $KrF_2.MoOF_4$ and of $XeF_2.2MoOF_4$ were reported and interpreted in terms of covalent fluorine-bridged structures [9].

The crystal structure of the adduct $MoO_2Cl_2.POCl_3$ has been obtained and shows the molybdenum atoms in a distorted octahedral environment forming extended interlocking chains [10]. The reaction was reported of $[MoO_2Cl_2]$ with H_2SO_4 to give $[MoO_2(SO_4)]$, which reacts with $[MoCl_5]$ to produce $[MoOCl_4]$, $[MoOCl_3]$ and SO_2, and with $[WCl_6]$ to produce $[WOCl_2]$, $[MoOCl_4]$ and SO_3 [11].

The ^{95}Mo NMR spectra of a number of dioxomolybdenum(VI) complexes have been recorded, and demonstrate the usefulness of the technique for characterisation of molybdenum compounds [12]. $[MoO(O_2)_2(Hacac)]$, a peroxo compound of molybdenum with neutral acetylacetone, was prepared by the reaction of MoO_3 with H_2O_2 in the presence of Hacac. It was characterised by chemical analysis, electrical conductivity, and electronic and IR spectroscopy. Hacac is bonded *via* the two ketonic oxygen atoms to the molybdenum atom in the complex, which readily decomposes to give molybdenum blue [13]. The compound dioxobis(ferrocenedithiocarboxylato)molybdenum(VI) has been synthesised and some of its properties investigated [14].

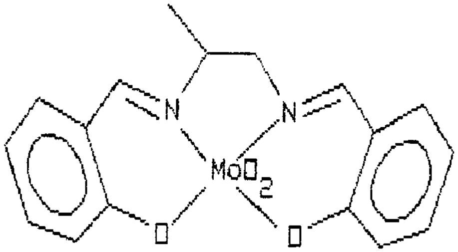
Polarography was used to study the formation of complexes of molybdenum(VI) in ethanoic acid [15] and malic acid [16]. The stoicheiometry and degree of condensation is dependant on pH and the relative concentrations of molybdenum and the acid. Aqueous solutions of $Na_2[MoS_4]$ and (L)-malic acid have also been investigated in pH range 3.9-6.6 by ^1H and ^{13}C NMR spectroscopy; four complexes were observed [17]. In aqueous solutions of oxalic acid molybdenum(VI) forms three stable complexes, $[MoO_2(OH)_2(C_2O_4)]^{4-}$,

$[Mo_2O_5(OH)_2(C_2O_4)_2]^{4-}$, and $[Mo_2O_5(OH)(C_2O_4)_2]^{3-}$. These have been isolated as salts of $[Co(en)_3]^{3+}$ and characterised by X-ray powder diffraction and IR spectra [18]. The solid state photochemistry and photochromism of several oxalate complexes of molybdenum(VI) have been reported. All the complexes studied developed colours on exsposure to light, and IR spectra showed that CO_2 was formed, with reduction of molybdenum(VI) to molybdenum(V) shown by EPR spectra [19]. Ammonium paramolybdate reacts with citric acid to give a complex $K_2[Mo_2O_5(OH)(C_6H_5O_7)(H_2O)].\frac{1}{2}H_2O$, identified by EPR and IR spectroscopy, and X-ray diffraction. On irradiation with UV light the complex loses CO_2 and the molybdenum is reduced to molybdenum(V) [20].

Chloranilic acid (2,5-dichloro-3,6-dihydroxy-4-benzoquinone; H_2L) forms a complex with molybdenum(VI) in aqueous solution at pH 8 of stoicheiometry 1:1 (Mo:L) [21]. Potentiometric titration was used to investigate the molybdenum(VI)-histidine system in the pH range 4-7; formatiom of a 1:1 complex was demonstrated [22]. Raman and resonance Raman spectra have been collected for a series of oxomolybdenum complexes of cysteine-containing oligopeptides and bands were identified due to Mo=O, Mo-S-Mo, and Mo-S-CH_2 vibrations [23]. The electrochemical properties and stability in solution of complexes $[MoOL_2]$ {L = diethyldithiocarbonate (ddtc) or cysteamine} were studied, and it was demonstrated that reduction to $[MoOL_2]$ occurred *via* molybdenum(V) intermediates. With ddtc a molybdenum(III) complex was also detected [24]. X-ray photoelectron spectra were used to determine the sulfur 2p binding energies in a series of molybdenum(VI) complexes with cysteamine-type ligands. The result showed no evidence that the complexes contain coordinated partial disulfide bonds [25].

Equilibria and kinetics of the reactions of $Na_2[MoO_4]$ with 1,2-dihydroxyanthraquinone-3-sulfonate and nitrilotriacetate have been studied spectrophotometrically in aqueous solution of pH 6-8. Formation constants were determined and a reaction mechanism was proposed [26]. Several new *cis*-dioxomolybdenum (VI) complexes have been synthesised incorporating dibasic tridentate Schiff-base ligands derived from 5-substituted salicylaldehydes and *o*-aminophenol, 2-aminoethanol or anthranilic acid. Cyclic voltammetry was used to determine the effects of substituents and of structure on the cathodic reduction potentials for the irreversible reduction of the complexes, and the trends were discussed [27]. Complexes of dioxomolybdenum(VI) with tetradentate Schiff-base ligands have been isolated as solids, and shown to contain *cis* oxygen atoms [28]. Infrared data of complexes MoO(L), where L is a tridentate dianionic Schiff-base ligand, suggest that oligomerisation occurs *via* a $Mo{=}O \longrightarrow Mo$ bridge which can be cleaved by a wide variety of donors (D) to give $MoO_2(L)(D)$. The electron transfer characteristics of a number of

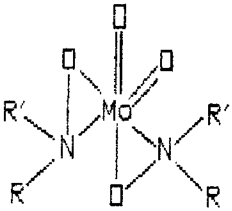
$MoO_2(L)(dmf)$ species were studied [29]. The crystal structure of dioxo[(2R)-propane-1,2-diyl-bis(salicylideniminato)]molybdenum(VI), a complex containing a chiral Schiff-base ligand, has been determined, (1). The



(1)

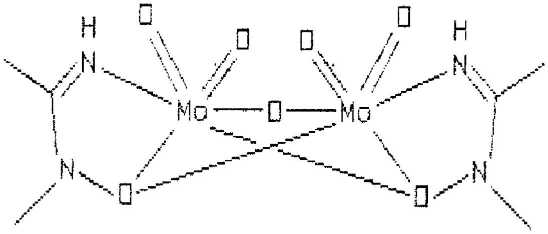
confirmations of this and related compounds in solution have been investigated using ^1H and ^{13}C NMR, and circular-dichroism spectra [30].

The oxo groups in *N,N*-disubstituted analogues of *cis*-dioxobis-(hydroxylamido-*O,N*)molybdenum(VI), (2), can be replaced stepwise by thio



(2)

groups using H_2S, giving first the oxothio then the dithio complexes. ^1H NMR spectroscopy provides evidence of two isomers in solution for the oxothio complexes, but only one for the dithio and dioxo compounds [31]. The reaction of (2), (R = H, R'= Me), with R"CN in the presnce of $[MeNH_2OH]^+$ yields compounds containing bidentate ligands $\{ON(Me)C(R'')=NH\}^-$. The structures of bis{*N*-hydroxy-*N*-methylacetamidinato(1-)-*O,N'*}{*N*-methylhydroxylamido(1-)-*O,N*}-oxomolybdenum(VI) perchlorate and of μ-oxo-bis[{*N*-hydroxy-*N*-methylacetamidinato(1-)-*O,N'*$\longrightarrow$$Mo^1$;*O*$\longrightarrow$$Mo^2$}-*cis*-dioxo]dimolybdenum(VI), **(3)**, have



(3)

been determined [32]. Oxalic acid reacts with **(2)**, (R = R' =Et), in ethanol yielding yellow crystals of $[Et_2HNOH]_2[Mo_2O_4(Et_2NO)_2(C_2O_4)_2]$. The crystal structure shows that in the anions the molybdenum(VI) atoms are in a distorted pentagonal-bipyramidal environment containing an *O,N*-coordinated *N,N*-diethyl hydroxylamido ligand, a bidentate oxalato anion, and a terminal and two bridging oxo ligands [33]. Complexes of the type **(2)** react with benzohydroxamic acid in trichloromethane to afford monomeric neutral products containing benzohydroximato(2-) and benzohydroximato(1-) ligands, and a terminal oxo group. The complex $[MoO(Me_2NO)(BzH)Bz]$ (BzH = benzohydroxamate, Bz = benzohydroximate) has been characterised by X-ray diffraction . The structure consists of monomeric molybdenum(VI) in a distorted pentagonal-bipyramidal environment. The reaction of molybdenum(VI) anions with benzohydroxamic acid in pH ≈ 9 yields the bis (benzohydroximato)-*cis*-dioxomolybdate(VI) anion. The caesium salt of this has been isolated and the structure dtermined. The molybdenum(VI) atoms are in a distorted octahedra environment [34]. In aqueous and aqueous-organic media molybdenum(VI) reacts with propriohydroxamic acid (HL) to give $[MoO_2L_2]$, characterised by spectrophotometry. The maximum optical density is at pH = 1-3 [35].

Oxodiperoxo(hexamethylphosphoramide)molybdenum(VI) has been used to oxidise phenacetin and related amides to their respective hydroxamic acids, which were isolated as the stable dioxomolybdenum(VI) salts. The complexes formed by the hydroxamato ligands derived from phenacetin and acetanilide have been characterised by X-ray diffraction. Both compounds contain molybdenum(VI) atoms in a distorted octahedral environment, and no conjugation is apparent between the phenyl rings and the hydroxamic acid groups [36].

3.1.3 Complexes with ligands derived from $[MoO_4]^{2-}$

A review has been published on transition metal thiometallates, including the role of thiomolybdates as ligands in complex chemistry and in bioinorganic chemistry [37]. Preparations and ^1H NMR and IR spectra were reported for several mixed valence compounds of molybdenum, including $[\{(\eta\text{-}C_5H_4R)Mo(\mu\text{-}O)_2MoO_2\}_2]$ (R = H, Me or Bu), $[\{(\eta\text{-}C_5H_4R)_2Mo(\mu\text{-}S)_2MoS_2\}_2]$ (R = H, Me or Bu), and $[\{(\eta\text{-}C_5H_5)_2W(\mu\text{-}S)_2MoS_2\}_2]$ [38]. The complex $[(PPh_3)(Me_2NN)Mo(\mu\text{-}S)_2MoS_2]$ has been prepared and the crystal structure determined [39]. Resonance Raman spectra have been used to identify coordinated $[MoS_4]^{2-}$ anions in systems of bioinorganic interest such as $[Cl_2Fe(\mu\text{-}S)_2MoS_4]^{2-}$, $[Cl_2Fe(\mu\text{-}S)_2Mo(\mu\text{-}S)_2FeCl_2]^{2-}$, $[(Ph_3P)Cu(\mu\text{-}S)_2Mo(\mu\text{-}S)_2Cu(PPh_3)_2]$, and $[(Ph_3P)Ag(\mu\text{-}S)_2Mo(\mu\text{-}S)_2Ag(PPh_3)_2]$. The resonace effect is a very sensitive probe for $[MoS_4]^{2-}$ attached to iron and copper centres, and can be used to determine the type of coordination [40].

Complexes of nickel(II), palladium(II) and platinum(II) with the ligand $[MoOS_3]^{2-}$ of the form $[OSMo(\mu\text{-}S)_2M(\mu\text{-}S)_2MoOS]$ have been prepared and characterised. Mixed ligand complexes $[(Et_2NCS_2)M(\mu\text{-}S)_2MoS_2]$ were also investigated [41]. The synthesis of $[PPh_4]_2[O_2Mo(\mu\text{-}S)_2M(\mu\text{-}S)_2MoO_2]$, (M = Co or Ni) have been described in detail, and their IR and electronic spectra, and redox behaviour were discussed in relation to molecular and electronic structure of the compounds [42]. ^{95}Mo NMR data was published for a number of $[MoO_nE_{4-n}]^{2-}$ species (E = S or Se; n = 0-4), and for the complexes $[MoO_2(SCH_2CH_2N(Et)CH_2CH_2N(Et)CH_2CH_2S)]$, $[MoO_3\{HN(CH_2CO_2)_2\}]^{2-}$, and $[MoO_2\{OC(CMe_3)CHC(CMe_3)O\}_2]$ [43]. The complexes $[PPh_4]_2[(CuCN)(MoS_4)]$ and $[NMe_4]_2[(CuCN)_2(MoS_4)]$ have been investigated. The former complex contains thiomolybdate coordinated to the copper in discrete molecules, whereas the copper forms infinite zig-zag chains in the latter [44].

3.1.4 Oxides, sulfides and homonuclear polyanions

MoO_3 forms layered compounds with pyridine and 4,4'-bipyridine which consist of inorganic layers separated by organic layers in which the heterocyclic nitrogen is directly coordinated to the metal atom of the oxide layer [45]. EPR spectroscopy has been used to study the irreversible decomposition of MoS_3 to MoS_2. Three paramagnetic species were observed, including MoS^{3+}. These results correlate well with X-ray diffraction and analytical data [46]. X-ray photoelectron spectroscopic analysis of the mixed valence molybdenum oxides $Mo_{18}O_{52}$, Mo_5O_{14}, $Mo_{17}O_{47}$ and Mo_4O_{11} show that they contain tetrahedrally coordinated molybdenum(VI), with considerable molybdenum(V)–molybdenum(VI) mixing in octahedral and pentagonal bipyramidal coordination sites [47].

The photolysis of $[NH_3(CHMe_2)]_6[Mo_7O_{24}].3H_2O$ in solution of pH = 5.4 leads to reduction to molybdenum(V) with involvement of hydroxy-radicals, followed by decomposition to yellow and blue species. Irradiated single-crystal EPR spectra show the formation of $Mo^{V}O_3(OH)$ in an octahedral site. EPR, and Raman spectroscopy, and flash photolysis, were used to elucidate the reaction mechanism [48]. The dye-sensitised reduction of $[Mo_7O_{24}]^{6-}$ has also been investigated. The nature of the cation and the addition of edta as an electron donor make no significant difference to the quantum yield of molybdenum(V) [49]. The extraction of molybdenum(VI) from weak acid aqueous solution by tetraalkylammonium salts has been studied. The molybdenum is obtained as complexes $[NR_4]_{2m}[Mo_nO_{3n+m}]$, with n and m depending on pH [50].

$[MoO_2S_2]^{2-}$ polymerises after protonation in aqueous solution under physiological conditions, forming polymeric compounds containing $[S_2]^{2-}$-ligands such as $[Mo_2O_2S_2(S_2)_2]^{2-}$. From the solution other di-sulfido molybdenum(V) complexes can be easily obtained [51]. The reaction of $Na_2[MoS_4]$ with sulfuric acid produces various polyanions which can be identified using electrochemical techniques. The stoicheiometry depends on pH, the stable species at pH 6.5, 4.5 and 2.8 being $[Mo_4S_{15}]^{6-}$, $[Mo_2S_7]^{2-}$, and $[Mo_4S_{13}]^{2-}$ respectively. At a pH of less than 2.5, $MoS_3.H_2O$ is formed [52].

3.1.5 Heteronuclear polyatomics and various ternary phases

Heteronuclear compounds of molybdenum can be reduced by multielectron reduction yielding blue products. The methods appear to involve excitation at the O-Mo charge transfer band, followed by internuclear electron or hydrogen transfer [53]. The Raman spectra of phases obtained by cooling molten mixtures of $Na_2Mo_2O_7$ and $Na_2W_2O_7$ are in agreement with expectations for formation of substitutional phases $Na_2Mo_{2-x}W_xO_7$, with statistical distribution of molybdenum and tungsten atoms [54]. In systems containing $[MoO_2Cl_2]$ and WCl_4 or WCl_5, it has been shown by differential thermal analysis that exchange, oxidation-reduction and disproportionation reactions all occur, with formation of molybdenum(V) and molybdenum(III) species [55].

Stereospecific preparations have been reported of new *n*-molybdo-(18-*n*)-tungsto-2-phosphates and related compounds of general formulae $[P_2W_{18-n}Mo_nO_{62}]^{6-}$ and $[P_2W_{17-n}Mo_nO_{61}]^{10-}$. Constants of formation and degradation kinetics were investigated [56]. Quantitative IR studies of the reduction of $K_3[PMo_{12}O_{40}]$ with H_2 demonstrated that the initial stage proceeded by consuming two bridging oxygen atoms per Keggin anion. The process was accompanied by stoicheiometric formation of molybdenum(V), detected by X-ray photoelectron spectroscopy [57]. The alkylation of $[N(C_6H_{13})_4]_3[PMo_{12}O_{40}]$ using $[Me_3O][BF_4]$ yields $[N(C_6H_{13})_4]_2[PMo_{12}O_{39}(OMe)]$. The product was examined by IR, and ^1H and ^{31}P NMR spectroscopy. A crystal structure determination showed that the prefered alkylation site is a bridging, rather than terminal, oxygen atom [58]. Several salts of the anions $[(RAs)_4Mo_{12}O_{46}]^{4-}$, (R = Me, Ph, $4\text{-}C_6H_4NH_3^+$ or C_2H_4OH), have been prepared and characterised. The structure of $[(4\text{-}H_3NC_6H_4As)_4Mo_{12}O_{46}].6H_2O.10MeCN$ has been determined. The complex contains octahedrally coordinated arsenic atoms [59].

Studies have to be carried out on the fibrillar form of trimolybdate $Rb_2[Mo_3O_{10}].H_2O$. The structure was discussed on the basis of X-ray, thermogravimetric, IR and NMR measurements [60]. Alkali metal chlorides react with molten $MoOCl_4$ to give free chlorine and $M_2[MoOCl_5]$ (M = Li, Na, K, Rb or Cs) or $MCl.2MoOCl_3$ (M = Rb or Cs). The reactions were followed by differential thermal analsis and the products characterised by IR spectroscopy [61]. The preparation of $[AlMo_6O_{21}]^{3-}$ has been monitored by ^{27}Al NMR spectroscopy. It was possible using this technique to distinguish between aluminium in octahedral and tetrahedral environments [62].

Crystals have been synthesised of a monoclinic form of a mixed metal molybdate $K_5[In(MoO_4)_4]$. A structure determination showed it to have a palmierite type of structure [63]. The reaction of $[NH_4]_6[Mo_7O_{40}]$ with $InCl_3$

in the presence of NH_4OH and NaOH yields heteropoly complexes $[NH_4]_6[Mo_7O_{40}]$, $[NH_4]_6[Mo_7O_{24}]$ and $[In_2(MoO_4)_3]$. These were characterised by IR and UV spectroscopy, and by thermal analytical methods [64]. The formation and reduction of molybdenum heteropoly complexes of indium in solution has been studied photometrically [65]. Double sulfate-molybdates of potassium, rubidium and caesium with indium were prepared by heating the alkali metal sulfide with MoO_3 and In_2O_3 at 450-500 °C. The products were compounds of the form $M_2In_2(SO_4)(MoO_4)_3$, (M = K, Rb or Cs), characterised by derivatographic analysis and X-ray diffraction [66]. The interaction of potassium sulfatomolybdate with bismuth oxide was studied by X-ray diffraction, DTA and IR spectroscopy. A product $KBi[(MoO_4)_{1.5}(SO_4)_{0.5}]$ was obtained and an equilibrium diagram constructed [67]. A number of ammonium salts of nitrate-molybdate complexes of bismuth were prepared by addition of $Na_2[MoO_4]$ to a solution of $Bi(NO_3)_3$ in nitric acid followed by precipitation by NH_4OH. Chemical analysis and vibrational spectra were used to identify the product [68].

The phase equilibrium diagram of the mixed oxide system TeO_2-MoO_3 has been studied by DTA. A new congruently melting phase, Te_2MoO_7 is formed [69]. IR and Raman spectra of α-Te_2MoO_7 have been recorded and discussed in relation to the crystal structure. Comparison of the spectra with those of telluromolybdates $M^{II}TeMoO_6$ allowed a proposal to be made for those phases [70]. Structural models for glasses in the TeO_2-MoO_3 system have been proposed based on X-ray and IR studies comparing the known structures of TeO_2, MoO_3 and Te_2MoO_7 with the mixed phases. Glasses in the range TeO_2-$TeMoO_7$ possess $\{TeO_4\}$ and $\{MoO_5\}$ groups as basic units, but in MoO_3-rich glasses $\{TeO_3\}$ and $\{MoO_6\}$ polyhedra are found [71]. Some properties of glasses in systems TeO_2-MoO_3-V_2O_5 have been studied [72].

The synthesis has been reported of the adducts formed by $\{MoO_2Cl\}^+$ and $\{Mn(CO)_3\}^+$ with the complex anion $[(\eta^5\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-}$. The anion consist of an octahedron formed by the titanium and five molybdenum atoms bridged by the oxygen atoms. In the adducts bonds are formed between three of the doubly-bridging oxygen atoms of the anion and the metal atom of the cation [73]. The double-molybdate $K_3[Sc(MoO_4)_3]$ has been prepared and the crytsal structure was determined. Some differences were found between this and the structure of other double salts with a tetrahedral EO_4 anion [74]. X-ray photoelectron spectroscopy and magnetic moment measurements were used to investigate some heteropoly complexes of zinc with molybdates and tungstates, and the binding energies of electrons in the oxygen 1s, molybdenum 3d and zinc 2p orbitals calculated [75]. The solid-phase reactions of Cs_2MoO_4 with $M(MoO_4)$, (M = Zr or Hf) at 450-600 °C for 50-100 h yield products,

$Cs_2M(MoO_4)_3$ and $Cs_8M(MoO_4)_6$. The crystal structures were determined and compared [76].

The vibrational spectra have been recorded and interpretated for a series of lanthanide molybdates Ln_2MoO_6 (Ln = Sm, Eu, Tb, Dy, He, Er, Lu or Pr) [77]. The lanthanide molybdates α-$Ln_2Mo_3O_{12}$, (Ln = La, Pr, Nd, Sm, Gd, Tb or Dy), can be reduced hydrogen yielding $Ln_2Mo_3O_9$. The reaction is topologically controlled with both parent and product phases having Scheelite-related structures. IR spectra and magnetic properties of the metastable product phases were reported [78]. $K_2[SO_4]$ reacts with $Ln_2(MnO_4)_3$ (Ln = Dy, Mo, Eu or Tm) to give $K_2Ln_2(MnO_4)_3(SO_4)$. Crystal structures were obtained of the products, and their thermal stabilities determined [79].

The Na_2MO_4-UO_3 diagram has been studied and interpreted within the context of the ternary system UO_3-MoO_3-Na_2O, and confirms previous results concerning $Na_2U_2O_7$-$Na_2Mo_2O_7$-Na_2O [80]. The UO_2MoO_4-Na_2MoO_4 line in the same ternary mixture was investigated, and is not a true binary system. The X-ray phase analysis and DTA data were discussed in terms of the equilibrium in the UO_3-MoO_3-Na_2O system [81]. The reduction of UO_2MoO_4 by hydrogen has been found to proceed in two stages. Initially UO_2 and MoO_2 were formed, then the molybdenum(IV) was reduced furthur to the metal. The reduction of Na_2MoO_4 is more complicated, although similar processes occur. A model showing three phase fields within Mo-MoO_3-Na_2O space explains the observations, and also accounts for the reduction process in a UO_3-MoO_3-Na_2O system [82]. Complexes $M_2[UO_2(MoO_4)_2]$, (M = Na, K, Rb or Cs), have been prepared and characterised by thermogravimetry, X-ray diffractometry, luminescence and IR spectroscopy. The presence of $[MoO_4]^{2-}$ groups was indicated [83]. The vibrational and luminescence spectra of a number of anhydrous and hydrated uranyl sulfates and molybdates have been recorded, and the possibility discussed of detecting changes in the bond lengths of the uranyl ions from analysis of this data [84]. The interaction of the $[UMo_{12}O_{42}]^{8-}$ anion with Th^{4+} results in the formation of an infinite chain complex $\{Th(H_2O)_3UMo_{12}O_{42}\}_n^{4n-}$. A crystal structure of the salt $[NH_4]_3H[Th(H_2O)_3UMo_{12}O_{42}].12H_2O$ showed that the thorium atom has tricapped trigonal-prismatic geometry [85]. In aqueous solution containing phosphorus(V), uranium(IV), molybdenum(VI) and tungsten(VI), stable heteropolyacids are formed having ratios P:U:Mo:W of 1:1:3:8 and 2:1:6:16. Reduced species have ratios 2:1:10:20, and a new heteropolyacid with ratio 2:1:2:20 has been isolated and characterised by UV, IR and EPR spectroscopy [86].

The superconducting ternary phase $PbMo_6S_8$ has been prepared by chemical transport reactions [87].

3.1.6 Nitride Complexes

Several new complexes containing $Mo\equiv N$ triple bonds have been prepared, including $MoNCl_3(bipy)$ and [MoN(tetraphenylporphyrin)]Br_3. Their properties and IR spectra have been examined [88]. The reaction of $[MoCl_4(py)_2]$ with $Me_3Si(N_3)$ yields two complexes, $[MoN(N_3)Cl_2(py)]$ and $[MoN(N_3)_3(py)]$. The crystal structure of the latter shows that the molybdenum atom has square pyramidal coordination with the nitride ligand at the apex [89]. $[MoN(S_2CNR_2)_3]$ (R_2 = Me_2 or Et_2) reacts with R'X (R' = PhCO, $PhSO_2$, 2,4-$(NO_2)_2C_6H_3$ or 2,4-$(NO_2)_2C_6H_3S$, X = Cl; R' = Me, X =I), $[R'_3O][BF_4]$ (R' =Me or Et), or $[Ph_3C][BF_4]$ to give the amido complexes $[Mo(NR')(S_2CNR_2)_3]^+$. The X-ray crystal structures of $[Mo(NCPh)(S_2CNMe_2)_3][BF_4]$ and $[Mo(NSO_2Ph)(S_2CNMe_2)_3][PF_6]$ have been determined, and show that the molybdenum atoms have pentagonal bipyramidal geometry [90].

3.1.7 Complexes with Mo-C bonds (excluding carbonyls)

From the reaction between $MoCl_5$ and $LiCH_2SiMe$ at -78 °C a yellow distillate can be obtained of the carbyne complex $[(Me_3SiCH_2)_3Mo\equiv CSiMe_3]$, characterised by analysis and by IR, ^1H and ^{13}C NMR, and mass spectroscopy [91]. The complex $[Mo(\eta^5\text{-}C_5H_5)(dmpe)H_4][PF_6]$ has been prepared after a series of reactions from $[Mo(\eta^5\text{-}C_5H_5)_2I_2]$. The ^1H NMR spectrum shows the MoH_4 system as a single triplet, which indicates the molecular ion to be fluxional. The ^{31}P NMR spectrum showed a broad singlet for the two phosphorus nuclei of the dmpe ligand [92].

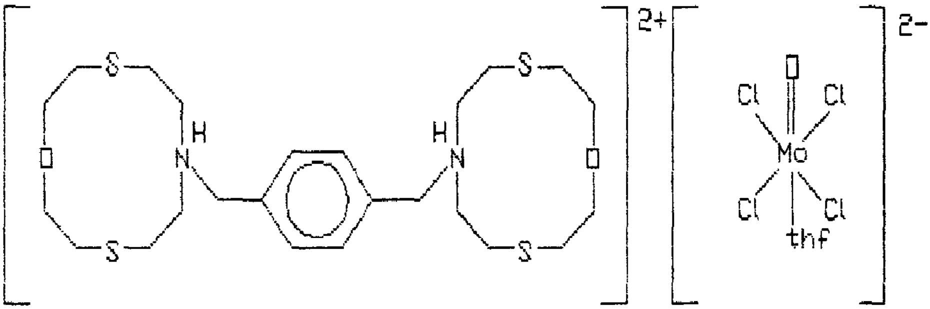
3.2 MOLYBDENUM(V)

3.2.1 Molybdenum(V) chloride

$MoCl_5$ reacts with 2,5-dimercapto-1,3,4-thiadiazole (H_2dmt) to give $[Mo(Hdmt)_2Cl_3].H_2O$ or a disulfide oxidation product $(Hdmt)_2$ and a polymeric molybdenum(III) product [93]. The reactions of $MoCl_5$ with $(SCN)_2$, $(SeCN)_2$, or ICN give $[MoCl_5(NCS)]$, $[MoCl_5(NCSe)]$ or $[MoCl_5(NCI)]$ respectively. IR and EPR indicate that each pseudohalogen is bound by the nitrogen atom [94]. $MoCl_5$ can be oxidised by WO_2SO_4 to yield $MoOCl_4$, WO_2Cl_2 and SO_2 [11]. In the presence of $POCl_3$ the reaction of $MoCl_5$ with CCl_3NO_2 yields $[Mo(NO)(O)Cl_3(POCl_3)]$, which in CH_2Cl_2 decomposes to give $[\{MoOCl_3(POCl_3)\}_2]$. The crystal structure of this complex shows it to contain two bridging chloride ligands, with each molybdenum atom octahedrally coordinated [95].

3.2.2 Oxo compounds

The interaction of molybdenum lower fluorides with water vapour and the disproportionation of the hydrolysis products were studied by thermogravimetric methods. Conditions were determined for the formation and isolation of $MoOF_3.½H_2O$ [96]. The EPR spectra of $[MoOF_4]^-$ and $[MoOCl_4]^-$, in a single crystal of $[NH_4]_2SbF_5$ and $[NH_4]_2SbCl_5$ respectively, have been obtained. The experimentally derived molecular orbital parameters were compared with values calculated by the MS-SCF-Xα method [97]. The crystal structure of 1,4-bis(1-oxa-4,10-dithia-7H-7-azoniacyclododecan-7-ylmethyl)benzene tetrachlorooxo(tetrahydrofuran)molybdate(V), (4), shows the $[MoOCl_4(thf)]^{2-}$ anions to have *trans* octahedral coordination around the molybdenum [98]. A novel route has been reported for the synthesis of 1,2-bis(diphenylphosphine)-ethane (dppe) complexes of molybdenum(V). $[MoOCl_5]^{2-}$ reacts with dppe in 2*M*

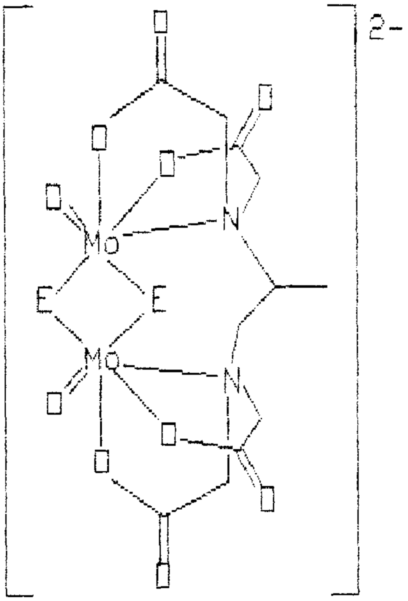


(4)

hydrochloric acid to give the salt [$dppeH_2$][$MoOCl_5$], which in dry methanol loses HCl to form [$MoOCl_3$(dppe)]. A similar method can be used to prepare the 2,2'-bipyridine complex [99]. The potentially bidentate ligand 2,2'-biquinoline (biquin) has been used to stabilise the oxomolybdenum(V) cation in various complexes and salts, including [$MoOX_3$(biquin)], [$biquinH_2$][$MoOX_5$] and [biquinH][$MoOX_4$] (X = Cl or Br) [100]. Other organic ligands such as 2-picolylamine can also stabilise molybdenum(V) oxohalide anions by forming salts [101].

The complexes formed by molybdenum(V) and its chlorinated derivatives in ethanoic acid have been studied by electrochemical methods. The composition of the mixture depends on pH, concentration and temperature [15,102]. The synthesis and structure have been reported of a complex of molybdenum(V) with malonic acid (H_2mal), $K_6[\{Mo_2O_4(mal)_2\}_2(mal)].4H_2O$. The complex contains two {(mal)MoO(μ-O)$_2$MoO(mal)} units bridged by a malonate dianion, each molybdenum having an octahedral coordination geometry [103].

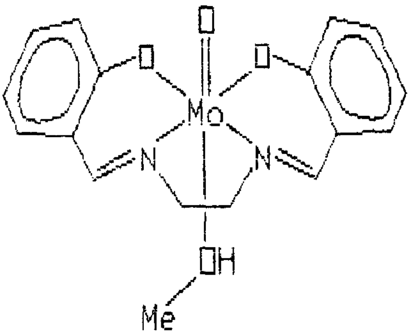
(R)-propylenediaminetetracetic acid (R-$pdtaH_4$) acts as a bridging hexadentate ligand in the complexes $Na_2[Mo_2O_4(R\text{-}pdta)].3H_2O$, $Na_2[Mo_2O_4S(R\text{-}pdta)].4H_2O$, and $Na_2[Mo_2O_2S_2(R\text{-}pdta)].4H_2O$, (5). In each compound



(5; E = O or S)

the two molybdenum atoms are coordinated to one nitrogen atom, two carboxylate oxygen atoms, one terminal oxygen atom and two bridging oxygen or sulfur atoms [104]. The outer sphere redox reaction between $[Mo_2O_4(R,S\text{-pdta})]^{2-}$ and $[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}O_2)Co(en)_3]$ exhibits stereoselectivity in aqueous solutions of pH 3.5 and 4.6 at 25 °C [105]. The electron transfer reaction between $[Mo_2O_4(edta)]^{2-}$ and $[(NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5]$ is affected by changes in pressure. There is a large positive activation volume for both the ion-pair formation constant and the first-order electron-transfer rate constant, interpreted as being due to the changes in solvation state in each process [106].

Many new oxomolybdenum(V) complexes have been prepared with tri- and tetra-dentate Schiff bases, and the first example of a mononuclear oxothiolate Schiff base complex of molybdenum(V) was reported [28]. The chemistry and electrochemistry of a dinuclear molybdenum(V) species resulting from hydrazine reduction of $[MoO_2(L)]$ (H_2L = *N*-(2-hydroxypphenyl)salicylidenimine) were investigated [29]. Several compounds of tetradentate Schiff bases with oxomolybdenum(V) have been prepared, and the crystal structure determined of *trans*-[*N*,*N*'-ethylenebis(salicylidenimine)](methanol)oxomolybdenum(V), (6) [107]. Absorption spectra of some new oxomolybdenum(V) complexes of tetraphenylporphyrin (TPP) with univalent ligands, [MoO(TPP)X], have been recorded. IR and EPR spectra show the presence of a central $Mo^V{=}O$ group [108].



(6)

Complexes $[MoO_2L]$ ($HL = 1\text{-}HO\text{-}2\text{-}R\text{-}5\text{-}ClC_6H_2NNC_6H_2\text{-}2',4'\text{-}(OH)_2$) ($R = H$ or AsO_3H_2) were prepared and characterised by ^1H NMR and IR spectroscopy. Intramolecular hydrogen bonding was observed [109]. 8-hydroxyquinoline (HL) forms a dimeric complex $[Mo_2L_2O_4]$ with molybdenum(V). This was characterised using IR, UV and mass spectroscopy, magnetic susceptibility, thermogravimetry and differential thermal analysis [110]. The preparation has been reported of $[HR]_2[MoO(NCS)_5]$ (R = benzoylpyridine or lutidine). Magnetic susceptibility measurements show that the magnetic moments are close to the spin only values [111].

Room-temperature single crystal EPR spectra of $[MoO(S_2CNEt_2)_3]$ and $[MoOCl(S_2CNEt_2)_2]$ diluted in isomorphous host lattices have been recorded. In both compounds the principal axes systems for the *g* and metal hyperfine tensors are non-coincident [112]. The disproportionation reaction of $[Mo_2O_3(S_2CSCHMe_2)_4]$ with $[MoO(S_2CSCHMe_2)_2]$ and $[MoO_2(S_2CSCHMe_2)_2]$ has been investigated by concentration-jump relaxation experiments. The slow decomposition of the molybdenum(V) product to $[Mo_2O_4(S_2CSCHMe_2)_2]$ and $\{SC(S)CHMe_2\}_2$ was followed potentiometrically and a reaction mechanism for this was proposed [113]. The oxygen-bridged complex $[(FeS_2)_2MoO(\mu\text{-}O)MoO(FeS_2)_2]$ (FeS_2 = ferrocenedithiocarboxylate) has been prepared. In solution it disproportionates yielding $[(FeS_2)_2MoO_2]$ and $[MoO(FeS_2)]$ [14]. A number of oxomolybdenum(V) complexes of cysteine and related thiolate ligands were prepared and investigated using Raman and resonance Raman spectroscopy. The vibrations due to Mo=O, Mo-S-Mo, and $Mo\text{-}S\text{-}CH_2$ bonds were detected by the resonance technique even in dilute solutions [23]. Magnetic susceptibility and EPR spectroscopic measurements have been made of a series of mononuclear and triply-bridged binuclear thiolate compounds of oxomolybdenum(V) and their selenium analogues. ^{98}Mo and ^{95}Mo isotope substitution and computer simulation permitted extraction of the *g* and hyperfine tensor anisotropies [114]. The electrochemistry of these complexes in MeCN and dmf has been explored in the temperature range +25 to -60 °C. Interconversion between the mononuclear $[MoO(XR)_4]^-$ and binuclear $[Mo_2O_2(XR)_6Z]^{n-}$ {X = S or Se; R = aryl; Z = uninegative (n = 1) or neutral (n = 0) ligand} forms occurs *via* redox processes involving the metal and ligand centres [115].

3.2.3 Sulfur complex

The polynuclear anion $[Mo_2S_{10}]^{2-}$ has been isolated from the reaction between $[NH_4]_2[Mo_2S_{12}]$ and $[PhS]Na$. The crystal structure of $[AsPh_4]_2[Mo_2S_{10}].\frac{1}{2}MeCN$ shows that the anion has a terminal sulfido group bonded to each of the molybdenum atoms which are bridged by two μ-sulfido groups: one of the molybdenum atoms is also coordinated to a persulfido group, whereas the other is bonded to a tetrasulfido group [116].

3.2.4 Nitride complex

The complex $[MoNBr_2(2,2'\text{-bipyridine})]$ has been prepared and its properties investigated. The IR spectrum shows an absorption for the $Mo\equiv N$ triple bond [88].

3.2.5 Complexes with Mo-C bonds (excluding carbonyls)

The new compounds $[Mo(\eta\text{-}C_6H_4Me)Cl_4]$, $[Mo(\eta\text{-}C_6H_4R)Cl_3(CH)]$ (R = $CHMe_2$ or CMe_3), $[\{Mo(\eta\text{-}C_6H_4R)(\mu\text{-}O)O\}_2]$ (R = Me, $CHMe_2$ or CMe_3) and $[\{Mo(\eta\text{-}C_6H_4)OI\}_2(\mu\text{-}O)]$ have been prepared and characterised [117]. The reaction between $MoCl_5$ and $LiCH_2SiMe_3$ at 0 °C yields a purple distillate which contains the carbene complex $[(Me_3SiCH_2)_3Mo{=}CHSiMe_3]$, identified by its analytical data, and by IR, ^1H and ^{13}C NMR, and mass spectroscopy [91].

3.3 MIXED MOLYBDENUM(V)/MOLYBDENUM(IV) COMPLEX

The reaction of $[MoO(S_2CNEt_2)_3][BF_4]$ and PPh_3 in methanol under anaerobic conditions results in the formation of $[Mo_2O(S_2CNEt_2)_6][BF_4]$, an X-ray crystal structure of which shows a new type of μ-oxo-bridging between two molybdenum atoms, each having a formal oxidation state of 4.5 [118].

3.4 MOLYBDENUM(IV)

3.4.1 Molybdenum(IV) chloride

The crystal structure of the β-form of $MoCl_4$ has been redetermined and was found to consist of $(MoCl_4)_6$ molecules. Each molybdenum atom is octahedrally coordinated to two terminal and four bridging chlorine atoms [119]. The thermolysis of $[MoCl_4(MeCN)_2]$ leads to formation of multiphased products, which have been studied by X-ray diffraction [120]. Several trihalostannate complexes of molybdenum $[NR_4]_2[MoCl_4(SnX_3)_2]$ (R = Et, X = Cl or Br; R = Me or H, X = Cl) and $[NMe_4]_6[MoCl_4(SnCl_3)_6]$ have been prepared and their vibrational spectra studied. All are easily oxidised to molybdenum(VI) species [121].

3.4.2 Oxo complexes

The reversible electrolytic reduction of molybdenum(IV) aqua trimer, $\{Mo_3O_4\}^{4+}$, in acidic solution yields first an orange pink $\{Mo_3^{III,III,IV}\}$ complex then a green $\{Mo_3^{III}\}$ aqua ion. The latter can also be obtained by reduction of $\{Mo_3O_4\}^{4+}$ with Zn/Hg [122]. The oxidations of $\{Mo_3O_4\}^{4+}$ with $[IrCl_6]^{2-}$ and $[Fe(phen)_3]^{3+}$ (phen = 1,10-phenanthroline) have been studied under various conditions. With $[IrCl_6]^{2-}$, the initial oxidation to molybdenum(V) is faster than the subsequent oxidation yielding molybdenum(VI) products, whereas the opposite effect is observed for $[Fe(phen)_3]^{3+}$. This is because $[IrCl_6]^{2-}$ can react by an inner-sphere mechanism but oxidation using $[Fe(phen)_3]^{3+}$ is an outer-sphere reaction [123]. The trinuclear cluster $[Mo_3O_4F_9]^{5-}$ has been isolated from acid solution as the salt $[NH_4]_5[Mo_3O_4F_9].[NH_4]F.H_2O$: it was characterised by analysis, IR and VIS spectra, and by an X-ray crystal structure determination [124].

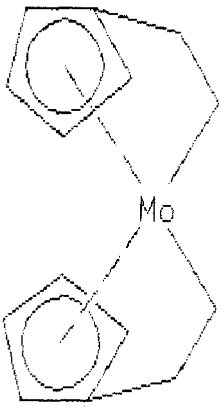
Monomeric non-ionic $[MoO(O_2CMe)_2(H_2O)]$ and $[MoO(O_2CCH_2CO_2)(H_2O)]$ were prepared by the reactions of glacial ethanoic acid and malonic acid on the reduced brownish-black product of the reduction of $[NH_4][MoOCl_5]$ with hydazine. The molybdenum(IV) products were characterised by analysis, electrical conductivity, IR and ^1H NMR spectra, and magnetic suscaptibility measurements [125]. A new bridging ligand, $[H_3O_2]^-$, has been identified in the complexes $[M_3O_2(O_2CEt)_6(H_2O)_2$-$(H_3O_2)$-$M_3O_2(O_2CEt)_6(H_2O)_2]Br_3.6H_2O$ (M = Mo or W). The $[H_3O_2]^-$ ligand was found from a crystal structure determination to contain a short, symmetric hydrogen bond between the two oxygen atoms [126]. Some new compounds with substituted cyclopentadiene ligands have been prepared and investigated including $[Mo(\eta\text{-}C_5H_5)_2(\mu\text{-}O)_2WO_2]_2$, $[Mo(\eta\text{-}C_5H_4R)_2X_2]$ (R = Me or Bu; X = H or Cl), and $[Mo(\eta\text{-}C_5H_4R)_2(\mu\text{-}O)(\mu\text{-}X)SO_2]$ (R = Me or Bu; X = O or S) [38]. $MoO(S_2CSCHMe_2)_2$ reacts with $MeOOCC{\equiv}CCOOMe$ (dmac) to give a 1:1 adduct having a pentagonal bipyramidal configuration with dmac in the equatorial plane and the terminal oxo group in an axial position. Kinetic studies indicate that the reaction proceeds *via* a mono-capped trigonal prismatic intermediate [127].

3.4.3 Sulfur compounds

The reaction between MoS_2 and $[NH_4][NO_3]$ has been studied by differential thermal analysis and the products identified by IR spectroscopy and X-ray diffraction [128]. $[Et_4N]_2[MoS_9]$ has been prepared and characterised by X-ray crystallography. The molybdenum atom of the anion is bonded to one terminal thio group and two bidentate $(S_4)^{2-}$ ligands [129]. The crystal structure has been determined of the mixed metal cluster $[\{Mo(SCH_2CH_2SCH_2CH_2S)_2\}_2Ag][PF_6]\cdot\frac{1}{2}dmf$. Each molybdenum atom is octahedrally coordinated to two tridentate thiol ligands, and the silver atom is tetrahedrally coordinated to one of the terminal sulfur atoms of each ligand [130]. $[Mo(Me_3CS)_4]$ has been prepared from the reaction of $MoCl_4$ with Me_3CSLi. The crystal structure showed that the geometry of sulfur atoms around molybdenum(IV) has approximately D_{2d} configuration [131]. The reactions of $[Mo(Me_3CS)_4]$ with Me_3CNC, CO or PMe_2Ph yield *cis*-$[Mo(Me_3CS)_2(CNCMe_3)_4]$, $[Mo_2(\mu\text{-}Me_3CS)_2(CO)_8]$ or $[Mo_2(\mu\text{-}S)_2(Me_3CS)_4(PMe_2Ph)_2]$, respectively [132]. Reaction-solution calorimetry has been used to determined standard enthalpies of formation of $[Mo(\eta\text{-}C_5H_5)_2(SR)_2]$ complexes (R = Pr, $CHMe_2$, Bu or CMe_3) [133]. The kinetics of the reaction of $[(\eta\text{-}C_5H_4Me)Mo(S)SH]$ with $PhCH_2NC$, which forms H_2 and $[(\eta\text{-}C_5H_4Me)MoS_2(CNCH_2Ph)]$, have been studied by the method of initial rates. The results suggest that the reaction proceeds by an associative mechanism. Extended Hückel calculations have been completed for a series of molybdenum dimers with bridging sulfur ligands, and the mechanism discussed with respect to the energies of the frontier molecular orbitals [134].

3.4.4 Compounds with Mo–C bonds (excluding carbonyls)

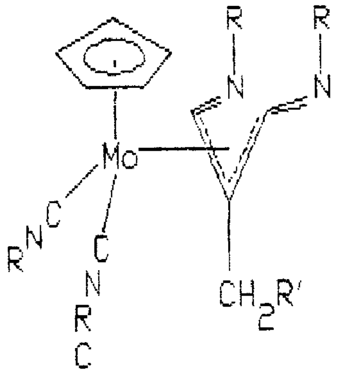
$[(\eta^5\text{-}C_5H_5)_2MoH_2]$ forms stable complexes with a large number of transition metal halides. IR spectra suggest that the hydride ligands participate in formation of a bond to the metal [135]. Kinetic studies of the equilibrium between $[(\eta^5\text{-}C_5H_5)_2Mo(NCPh)I][PF_6]$ and $[(\eta\text{-}C_5H_5)_2Mo(NCMe)I][PF_6]$ in solutions containing excess MeCN and PhCN indicate a dissociative mechanism for both the thermal and photosubstitutional reactions [136]. Cocondensation of molybdenum atoms with spiro[4,4]nona-1,3-diene or spiro[2,4]hepta-4,6-diene gives the compounds $[Mo(\eta^5\text{-}C_5H_4(CH_2)_3CH_2)_2]$ and $[Mo(\eta^5\text{-}C_5H_4CH_2CH_2)_2]$ respectively. The latter reacts with iodine giving $[Mo(\eta^5\text{-}C_5H_4CH_2CH_2I)_2I_2]$; the structures of $[Mo(\eta^5\text{-}C_5H_4CH_2CH_2)_2]$, (7), and $[Mo(\eta^5\text{-}C_5H_4CH_2CH_2I)_2I_2]$ have been determined by X-ray crystallography [137]. Several new compounds of molybdenum containing cyclopentadienyl and 1,2-bis(dimethylphosphino)ethane (dmpe) have been prepared and characterised by IR, ^1H NMR, and mass spectra. These include $[Mo(\eta^5\text{-}C_5H_5)(dmpe)Cl_3]$, $[Mo(\eta^5\text{-}C_5H_5)(dmpe)H_3]$, and $[Mo(\eta^5\text{-}C_5H_5)(dmpe)O][PF_6]$ [92].



(7)

The carboxylic acid group of the amino-acid ligand in $[Mo(\eta^5\text{-}C_5H_5)_2(GlyO)]^+$ (GlyO = glycinate) has been esterified by alkylation with dimethylsulfate, with methyltoluene-4-sulfonate and by acid-catalysed esterification in methanol. The product contains a chelated amino-acid ester, which slowly de-chelates in the presence of chloride ions to give $[Mo(\eta^5\text{-}C_5H_5)_2(GlyOMe)Cl]^+$ [138]. The standard enthalpies of formation of

$[Mo(\eta^5\text{-}C_5H_5)_2(O_2CR)_2]$ (R = Ph or CF_3) have been determined by reaction-solution calorimetry, in order to investigate the influence of the nature of chemical groups in the ligands on the metal-ligand bond strength [139]. Reaction of the alkylidyne complex $[Mo(CCH_2CMe_3)\{P(OMe)_3\}_2(\eta^5\text{-}C_5H_5)]$ with 2,6-dimethylphenylisocyanide affords initially the adduct $[Mo(CCH_2CMe_3)(CN\text{-}2,6\text{-}Me_2C_6H_3)\{P(OMe)_3\}(\eta^5\text{-}C_5H_5)]$, then the allyl $[Mo\{\eta^3\text{-}RN{=}C\cdots C(CH_2CMe_3)\cdots C{=}NR\}(CNR)_2(\eta^5\text{-}C_5H_5)]$ (R = 2,6-$Me_2C_6H_3$), (**8**),



(**8**; R = 2,6-$Me_2C_6H_3$, R' = CMe_3)

identified by X-ray crystallography. The reaction with CO proceeds by displacing the phosphine ligands to give $[Mo(CCH_2CMe_3)(CO)\{P(OMe)_3\}(\eta^5\text{-}C_5H_5)]$ and $[Mo(CCH_2CMe_3)(CO)_2(\eta^5\text{-}C_5H_5)]$ [140]. Addition of BuLi-thf or BuLi-OEt_2 to the alkylidyne complex $[Mo(CCH_2CMe_3)(CO)\{P(OMe)_3\}(\eta^5\text{-}C_5H_5)]$ yields the deprotonated salt $[Mo(CCHCMe_3)(CO)\{P(OMe)_3\}(\eta^5\text{-}C_5H_5)]Li$, which on quenching with D_2O affords a mixture of $[Mo(CCHDCMe_3)(CO)\{P(OMe)_3\}(\eta^5\text{-}C_5H_5)]$ and $[Mo(CCD_2CMe_3)(CO)\{P(OMe)_3\}(\eta^5\text{-}C_5H_5)]$ [141].

3.4.5 Chalcogenide phases

Specific chemical treatments of *n*-$MoSe_2$ and *n*-WSe_2 photoanodes have led to an improvement in their energy conversion efficiency [302]. In strong acid solution, *n*-type $MoSe_2$ or MoS_2 can be used as photoanodes to effect the oxidation of SO_2 to $[SO_4]^{2-}$: the oxidation can be driven by visible light [303].

3.5 MOLYBDENUM(III)

3.5.1 Chloride complexes

$[MoCl_3(thf)_3]$ reacts with diazadienes or diamines N-N (N-N = RN=CHCH=NR, R = C_6H_4-4-OMe; N-N = $Me_2NCH_2CH_2NMe_2$) and MeNC to give $[MoCl_2(CNMe)(N\text{-}N)]$ and $[MoCl_3(CNMe)(N\text{-}N)]$. The IR and magnetic measurements were interpreted on the basis of the electronic properties of the ligand [142]. Complexes $[MoCl_3L_2]$ (L = pyridoxine, phthivazide, saluzide or laruson) were precipitated by the reaction of $MoCl_5$ with L in pyridine, in the presence of $SnCl_2$. The products were characterised by IR spectrometry, X-ray diffraction and electrical conductivity measurements [143]. The preparation and electronic spectra were reported of *cis*-$[MoCl_2(1,10\text{-phenanthroline})_2]X$ (X = Cl, Br or $[MeC_6H_4SO_3]$) and *cis*-$[MoCl_2(2,2'\text{-bipyridine})_2]Cl$. The salts are stable in an inert atmosphere, but sensitive to dioxygen and water [144].

3.5.2 Oxo and sulfur complexes

The binuclear molybdenum(III) complex $[Mo_2O(C_2O_4)(L)_2(H_2O)_4]$ (HL = phenylalanine) has been prepared. The magnetic properties of this compound suggest that it contains an angular oxygen bridge and an oxalate bridge. Radioisotope exchange with $[^{14}C_2O_4]^{2-}$ proceeds *via* an S_N2 mechanism. The activation energy and activation entropy were determined and a reaction mechanism proposed [145]. A new binuclear cysteine complex of molybdenum has been prepared. UV-VIS spectra suggest that the complex is $[Mo_2O_2(Hcys)_4]^{2-}$ (H_2cys = cysteine) [146].

EPR spectroscopy has been used to investigate reactions of RR'P(S)SH (R = MeO, R' = Me; R = PrO, R' = 4-chlorocyclohexyl or cyclohexyl; R = R' = EtO, $CHMe_2$ or Ph; R = Bu, R' = C_7H_{15} or $C_8H_{17}O$) with a molybdenum oxide surface. Two series of molybdenum(II) complexes were formed which differ in denticity of the ligand in the axial position [147].

3.5.3 Organometallic complex

$[Mo(\eta^5\text{-}C_5H_5)_2(dmpe)][PF_6]$ {dmpe = 1,2-bis(phosphino)ethane} has been prepared and characterised by IR, ^{1}H NMR and mass spectroscopy [92].

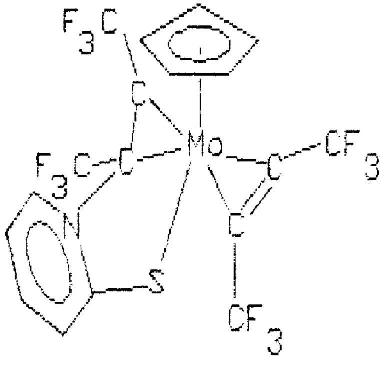
3.6 MOLYBDENUM(II)

3.6.1 Halide complexes

Crystals of MoI_2 have been grown by a chemical transport reaction in a closed ampoule. An X-ray crystal structure determination showed it to be isostructural with $MoCl_2$, with some minor differences [148]. The complex *trans*-$[MoCl_2(dppe)_2].CH_2Cl_2$ {dppe = 1,2-bis(diphenylphosphino)ethane} has been isolated from the reaction between *trans*-$[Mo(N_2)_2(dppe)_2]$ and $P(OEt)_3$ in CH_2Cl_2. An X-ray crystal structure determination has been carried out; the complex is the first structurally characterised example of a *trans* $Cl-Mo^{II}-Cl$ geometry [149].

3.6.2 Complexes with Mo-C bonds

The reduction of $[Mo(TTP)Cl_2]$ ($TTPH_2$ = *meso*-tetra-4-tolylporphyrin) by $Li[AlH_4]$ in the presence of excess $PhC{\equiv}CPh$ yields a molybdenum(II) product $[Mo(TTP)(PhC{\equiv}CPh)].PhMe$. The structure of the complex was determined by X-ray crystallography, and the short molybdenum-alkyne bond distance interpreted as implying that the alkyne acts as a four electron donor [150]. $[(\eta^5-C_5H_4Me)Mo\{C_2(CF_3)_2\}]$ has been prepared and characterised by spectroscopic and X-ray diffraction methods to examine the influence of the orbital occupancy of the HOMO on the nature of the molybdenum-alkyne interaction. The complex contains a central metallopropane ring, with the carbon-carbon multiple bond being lengthened by *ca.* 0.08 Å compared with free alkyne [151]. The bidentate monoanionic ligands, pyridine-2-thiolato, pyrimidine-2-thiolato and thiazoline-2-thiolato, react with the coordinated alkyne in $[Mo(\eta^5-C_5H_5)(CF_3C{\equiv}CCF_3)_2Cl]$ to form novel η^2-vinyl complexes. The crystal structure of $[Mo\{SC_5H_4NC(CF_3)C(CF_3)\}(CF_3C{\equiv}CCF_3)(\eta^5-C_5H_5)]$, (9), has been determined [152]. The reaction of $[Mo(\eta-MeC_2Me)(SC_6H_4-4-SPh)(\eta^5-C_5H_5)]$ with 3,3-dimethylcyclopropene leads to displacement of the alkyne and the novel migration of the phenyl group from the sulfur atom to the carbon atom of the ring-opened cyclopropene, with formation of the η^3-allylic complex of molybdenum(IV) $[Mo(\eta^3$-*syn*-$1-Ph-3,3-Me_2C_3H_2)(1,2-C_6H_4S_2)(\eta^5-C_5H_5)]$, identified by X-ray crystallography [153]. $[Mo\{P(OMe)_3\}_2(PhC{\equiv}CPh)(\eta^5-C_5H_5)]^+$ reacts with $K[BH(CHMeEt)_3]$ to give $[MoH\{P(OMe)_3\}_2(PhC{\equiv}CPh)(\eta^5-C_5H_5)]$ which rearranges to



(9)

give the η-vinyl complex $[Mo\{P(OMe)_3\}_2(\eta^1\text{-}PhHC{=}CPh)(\eta\text{-}C_5H_5)]$. This coordinatively saturated species can undergo transformatiom into the stable three-electron η^2-bonded cyclic alkylidene complex $[Mo\{P(OMe)_3\}_2(\eta^2\text{-}PhHC{-}CPh)(\eta\text{-}C_5H_5)]$, characterised by X-ray crstallography [154]. The complexes $[Mo(\eta^5\text{-}C_5H_5)(dmpe)(RC{\equiv}CR)][PF_6]$ (dmpe = 1,2-bis(dimethylphosphino)ethane; R = Me or Ph) have been prepared and characterised by IR, ^{1}H NMR and mass spectra [92].

The reaction of heptacoordinate $[Mo(CNCMe_3)_7]^{2+}$ with zinc in ethanol produces $[Mo(CNCMe_3)_4(Me_3CHNCCNHCMe_3)(CN)]^+$. The crystal structure of the $[BPh_4]^-$ salt of this cation has been determined, and the molecular geometry analysed according to Kepert's ligand-ligand repulsion model for seven-coordinate stereochemistries [155]. The reductive coupling of adjacent isocyanide ligands in $[Mo(CNCMe_3)_6X]^+$ complexes produce $[Mo(CNCMe_3)_4(Me_3CHNCCNHCMe_3)X]^+$ (X = Br or I). Crystal structures have been determined of $[Mo(CNCMe_3)_4(Me_3CHNCCNHCMe_3)I]Y$ (Y = I or $[PF_6]$) and $[Mo(CNCMe_3)_4(Me_3CHNCCNHCMe_3)Br]_2[ZnBr_4]$. In all of these compounds the coupled ligand may be formally considered as a four-electron-donating (dialkyldiamine)alkyne [156]. Bulk electrolysis of dichloromethane solutions of $[Mo(CNR)_7][PF_6]_2$ and $[Mo(CNR)_6(PR_3)][PF_6]_2$ generates the molybdenum(III) cations, which then decomposes *via* ligand loss (RNC or PR_3) to a complex reported to be $[Mo(CNR)_6]^{3+}$ [157]. Furthur research showed that the molybdenum(III) product was $[Mo(CNR)_6Cl]^{2+}$, possibly produced by reaction of $[Mo(CNR)_6]^{3+}$ with dichloromethane. A complex previously reported as $[\{Mo(CNCMe_3)_4Cl\}_2]$ was also reformulated as $[Mo(CNCMe_3)_6Cl]Cl$ [158]. The structures of $[Mo(CNC_6H_{11})_7][PF_6]$ and $[Mo(CNCMe_3)_6(CN)][PF_6]$ have been reported. Comparison with the structures of related seven-coordinate complexes demonstrated that the crystal packing forces are the dominant factor in determining the geometry adopted by each complex in the solid state [159]. $SnCl_2$ reacts with $[Mo(CNCMe_3)_6Cl]Cl$ to give $[Mo(SnCl_3)(CNCMe_3)_6]^+$, which has been crystallised as the $[(Ph_3B)_2CN]^-$ salt, and the crystal structure determined. The cation does not react with zinc to give reductive coupling of two of the isonitriles [160]. The structure of *cis*-$[Mo(Me_3CS)_2(CNCMe_3)_4]$ has been determined by X-ray crystallography. The six-coordinate molecule is substantially deformed from ideal octahedral geometry, which was shown by a molecular orbital analysis of a model to be due to the coordinative unsaturation of the molecule. ^1H and ^{13}C NMR, UV-VIS, and IR spectra were recorded [161].

3.7 MOLYBDENUM(0)

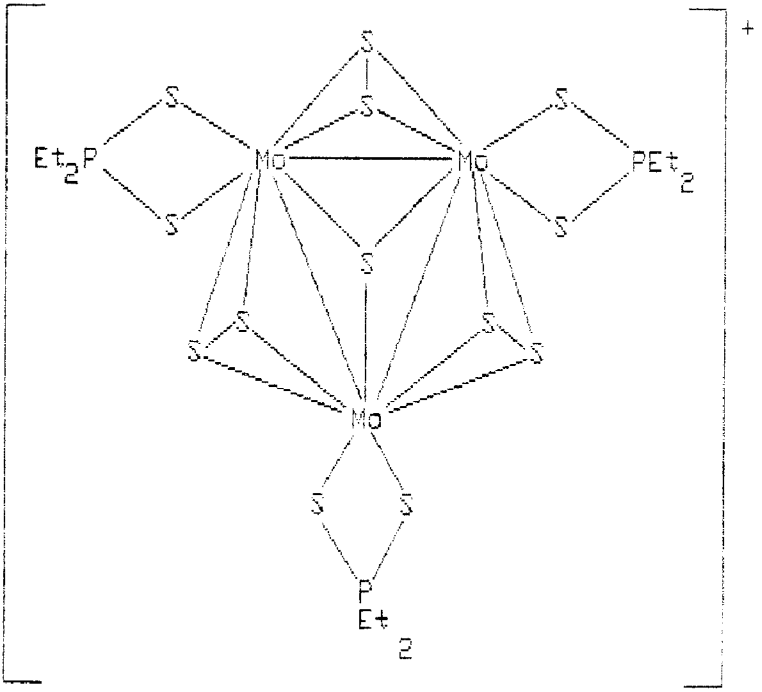
The isonitrile complex $[Mo(CNCMe_3)_6]$ has been prepared and characterised by IR, and ^1H and ^{13}C NMR spectroscopy [162]. The electrochemical and chemical oxidation of $[Mo(CNPh)_6]$ to $[Mo(CNPh)_7]^{2+}$ has been investigated. The product could be obtained in 80% yield as the $[PF_6]^-$ salt [163]. Microcalimetric measurements at 520-523 K of the heats of decomposition and iodination of $[Mo(C_6H_6)_2]$ were used to calculate the enthalpy of formation of the molybdenum-benzene bond as 247 ± 6 kJ mol^{-1} [164]. $[Mo(\eta^5\text{-}C_5H_4Me)(N_2C_6H_4\text{-}4\text{-}F)_2Cl]$ has been isolated from the reaction of $[F\text{-}4\text{-}C_6H_4N_2][BF_4]$ with $Na[Mo(\eta^5\text{-}C_5H_4Me)(CO)_3]$. A crystal structure determination showed the molybdenum coordination to be distorted octahedral with three facial sites occupied by the $\eta^5\text{-}C_5H_4Me$ ligand and the remaining sites occupied by the chloride and two arenediazo ligands. The Mo-N-N angles are slightly distorted from 180 ° by intermolecular packing effects [165].

3.8 COMPOUNDS CONTAINING METAL-METAL BONDS

A book containing reviews of the reactivity of metal-metal bonds in various systems has been published, and includes references to a large number of molybdenum complexes [166].

3.8.1 Higher oxidation state complexes

The reaction of $[MoCl_2O_2]$ with ethanoic anhydride yields $[\{Mo_2ClO_3(O_2CMe)_3\}_2].(MeCO_2)O$. The crystal structure shows the complex to have four molybdenum atoms bridged through two oxo groups and six bidentate ethanoate ligands. Two of the molybdenum atoms are bonded together with Mo-Mo 2.609 Å [167]. Complexes $[Mo_3(\mu_3\text{-}O)_2(\mu_2\text{-}O_2CMe)_6(H_2O)_3]Y_2.xH_2O$ (Y = Br, $x = 1$; $Y = CF_3SO_3$, $x = 0$), which contains a triangle of molybdenum(IV) atoms joined by Mo-Mo bonds, can be isolated from the reaction of $[Mo(CO)_6]$ with ethanoic acid - ethanoic anhydride in the presence of dioxygen. Average bond lengths are 2.767 Å (Y = Br) and 2.757 Å ($Y = CF_3SO_3$) [168]. The *triangulo*-Mo_3 complex $[Mo_3(\mu_3\text{-}O)(\mu_3\text{-}OCH_2CMe_3)(\mu_2\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6]$ has been isolated from the reaction between $[Mo_2(OCH_2CMe_3)_6]$ and molecular oxygen, and characterised by X-ray crystallography ($\bar{r}$(Mo-Mo) = 2.529 Å). The complex, and the analogous $OCHMe_2$ complex, can also be prepared form the reaction between $[Mo_2(OR)_6]$ and $[MoO(OR)_4]$ ($R = CH_2CMe_3$ or $CHMe_2$) [169]. The reaction of $[Mo(CO)_6]$ with $R_2P(S)\text{-}S_2\text{-}P(S)R_2$ affords the *triangulo* complexes $[Mo_3S_7(R_2PS_2)_3]^+[R_2PS_2]^-$ (R = Et or Pr). The crystal structure of the diethyldithiophosphinate compound shows the cation to contain three $\mu_2\text{-}(S_2)^{2-}$ ligands, one $\mu_3\text{-}S^{2-}$ ligand and three bidentate phosphinate ligands, (10). The Mo-Mo bond lengths average to 2.737 Å [170].



(10)

The electronic structure and bonding interactions in the *syn*, *anti*, and closed isomers of $[Mo_2S_4(S_2C_2H_4)_2]^{2-}$ were examined and compared through extended Hückel and Fenske-Hall molecular orbital calculations. A molybdenum-molybdenum bond was found to be important in determining the relative stability of the isomers, which was predicted to be *syn* > closed > *anti* [171]. The structure of the cubane-like compound $[\{Mo(NC_6H_4Me)(\mu\text{-}S)[S_2P(OEt)_2]\}_4]$ has been determined. Two molybdenum-molybdenum bonds are present of bond lengths 2.862 and 2.861 Å. Molecular orbital calculations account for the binding of the ligands to the core, including four $Mo\equiv N$ bonds [172].

3.8.2 Complexes with a metal-metal triple bond and their derivatives

$[Mo_2(NMe_2)_6]$ reacts with 2-hydroxy-6-methylpyridine (mhpH) in hydrocarbon solvents to give $[Mo_2(NMe_2)_4(mhp)_2]$. In the solid state each molybdenum atom is coordinated to two amido nitrogen atoms and an oxygen and nitrogen atom from mhp^-, which form *cis* bridges across the $Mo\equiv Mo$ triple bond (bond length 2.211 Å). In solution ^1H NMR spectroscopy shows that a second isomer is also present which is not bridged. Furthur addition of Hmhp yields an insoluble product thought to be $[Mo_2(NMe_2)_2(mhp)_4]$ [173]. 1,3-di-4-tolyltriazine, $Me\text{-}4\text{-}C_6H_4NNNHC_6H_4\text{-}4\text{-}Me$, (Hdtt) reacts with $[Mo_2(NMe_2)_6]$ yielding red crystals of $[MO_2(NMe_2)_4(dtt)_2]$. The crystal structure showed that each molybdenum is coordinated to four nitrogen atoms which lie in a plane; there is an unbridged molybdenum-to-molybdenum triple bond with a Mo-Mo distance of 2.212 Å. ^1H NMR spectroscopy demonstrate that the structure remains the same in solution [174]. $[MoCl_2(NMe_2)_4]$ reacts in hydrocarbon solvents with a suspension of (6-methyl-2-pyridyl)methyllithium to give $[Mo_2(NMe_2)_4(CH_2pyMe)_2]$. In the solid state each molybdenum atom is coordinated to two amido nitrogen atoms and the carbon atom of a (6-methyl-2-pyridyl)methyl ligands. The $Mo\equiv Mo$ bond length is 2.204 Å. In solution two isomers were observed by ^1H NMR spectroscopy [175]. Alkylithium reagents can be used to substitute alkyl ligands for chlorides in $[MoCl_2(NMe_2)_4]$. Several complexes $[MoR_2(NMe_2)_4]$ have been made and spectroscopically characterised, and X-ray diffraction studies have been carried out on the ethyl and isopropyl compounds. The crystal structure of $[MoEt_2(NMe_2)_4]$ reveals that it adopts a gauche configuration with $Mo\equiv Mo$ 2.203 Å. Crystalline samples of $[Mo(CHMe_2)_2(NMe_2)_4]$ were disordered and it was not possible to distinguish between NMe_2 and $CHMe_2$ groups [176].

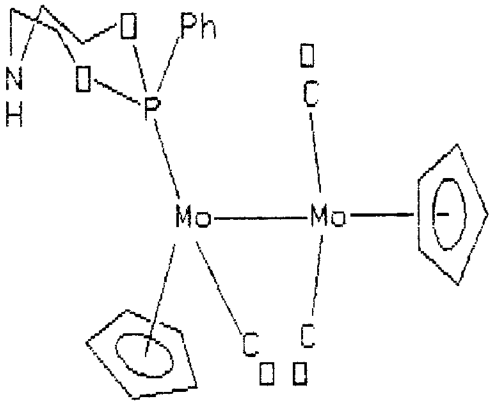
$[MoMe_2(NMe_2)_4]$ reacts with 1,3-di-4-tolyltriazine (Hdtt) to give $[MoMe_2(NMe_2)_2(dtt)_2]$. The crystal structure was determined and showed that the $Mo\equiv Mo$ bond (2.174 Å) is bridged by a *cis* pair of triazenido ligands which afford sufficient flexibility to allow a non-eclipsed geometry [177].

Hydrocarbon solutions of $[Mo_2(OCHMe_2)_6]$ react with 1,3-diphenyltriazine or 2-hydroxy-6-methylpyridine (Hmhp) to give $[Mo_2(OCHMe_2)_4(PhN_3Ph)_2]$ and $[Mo_2(OCHMe_2)_4(mhp)_2]$ respectively. In both reactions two $OCHMe_2$ groups are replaced by two bidentate ligands which form *cis* bridges across the $Mo\equiv Mo$ bond. The complexes were characterised by analysis, IR and ^1H NMR spectroscopy. A crystal structure of the mhp complex showed that each molybdenum was coordinated to three nitrogen and one oxygen atom with a $Mo\equiv Mo$ bond length of 2.206 Å [178]. $[Mo_2(OCHMe_2)_6]$ and $Me_2CHOOCHMe_2$ react to give $[Mo_2(OCHMe_2)_8]$, which contains a Mo=Mo double bond. $[Mo_2(OCMe_3)_6]$ does not react with either $Me_2CHOOCHMe_2$ or $Me_3COOCMe_3$, and $[Mo_2(OCHMe_2)_6]$ does not react with $Me_3COOCMe_3$. A reaction pathway involving an initial association reaction has been proposed. $[Mo_2(OCHMe_2)_6]$ reacts with Cl_2, Br_2 and I_2 to give $[Mo_2(OCHMe_2)_6X_4]$, which have a Mo-Mo single bond. X-ray diffraction studies on the chloro and bromo compounds showed that both contain central $Mo_2O_6X_4$ units that have virtual D_{2h} symmetry. Each molybdenum atom is octahedrally coordinated to two *cis* terminal halide ligands, two *trans* $OCHMe_2$ ligands, and two *cis*-bridging $OCHMe_2$ ligands, with Mo-Mo 2.73 Å [179]. Careful addition of alkynes ($R'C\equiv CR''$) to solutions of $[Mo_2(OR)_6]$ ($R = CHMe_2$, $R'C\equiv CR'' = HC_2H$, MeC_2H or MeC_2Me; $R = CH_2CMe_3$, $R'C\equiv CR'' = HC_2H$) in hexane-pyridine solvent mixtures precipitated crystalline adducts $[Mo_2(OR)_6(py)_2(R'C_2R'')]$. A crystal structure of $[Mo_2(OCHMe_2)_6(py)_2(HC_2H)]$ was determined and showed that the alkyne bridges the two molybdenum atoms in a crosswise manner. ^1H NMR spectroscopy of the complexes demonstrated that they were all fluxional on the NMR time scale [180]. The reaction between $[Mo_2(OCHMe_2)_6]$ and O_2 in pyridine yields as a minor product $[Mo_4O_8(OCHMe_2)_4(py)_4]$, characterised by X-ray crystallography. The complex contains four terminal, two μ_2- and two μ_3-bridging oxo ligands, two terminal and two μ_2-bridging $OCHMe_2$ ligands, and four terminal pyridine ligands. There are two localised Mo-Mo single bonds [181].

In the reaction of $[Mo_2(OCHMe_2)_6]$ with 2,2'-bipyridine (bipy), the $Mo\equiv Mo$ triple bond is cleaved, yielding $[Mo(OCHMe_2)_2(bipy)_2]$. A crystal structure of this complex showed that the Mo-N bond lengths were short (2.12 Å) compared with those in other molybdenum-pyridine systems (2.35 Å). It was suggested from this and spectroscopic evidence that there was some molybdenum-pyridine π^* back-bonding involved in the Mo-N bond [182]. Hydrocarbon solutions of $[Mo_2(OCMe_3)_6]$ react with aryl azides and O_2 to form $[\{Mo(OCMe_3)_2(NAr)_2\}_2]$ and

$[Mo(O)_2(OCMe_3)_2]$ (Ar = Ph or Me-4-C_6H_4). A crystal structure of $[\{Mo(OCMe_3)_2(NC_6H_4\text{-}4\text{-}Me)_2\}_2]$ showed that the two molybdenum atoms were bridged by the two NR ligands, but there was no Mo-Mo bond {*r*(Mo...Mo) = 3.247 Å} [183]. The addition of diphenyldiazomethane to $[Mo_2(OR)_6]$ (R = $CHMe_2$ or CH_2CMe_3) in the presence of pyridine leads to the formation of $[Mo_2(OR)_6(N_2CPh_2)_2(py)]$ which contains mixed-valence $\{Mo\text{-}Mo\}^{10+}$ units. The crystal structure of $[Mo_2(OCHMe_2)_6(N_2CPh_2)_2(py)]$ shows that there are three $OCHMe_2$ ligands bridging a Mo-Mo single bond. One of the molybdenum atoms is also coordinated to two terminal $OCHMe_2$ and one Ph_2CN_2 ligands, whereas the other is coordinated to two terminal $OCHMe_2$, one Ph_2CN_2, and one pyridine ligand [184].

The complex $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)(C_{12}H_{20})]$, which contains a metallocycle derived from the coupling of two hex-3-yne ligands, has been prepared by a thermal reaction. Its chemistry and spectroscopic properties were investigated and discussed [185]. The synthesis and molecular structure were reported of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3\{PhP(OCH_2CH_2)_2NH\}]$, a dissymmetric Mo≡Mo compound. One of molybdenum atoms is coordinated to a cyclopentadienyl ligand and two CO ligands, and the other to a cyclopentadienyl ligand, one CO ligand, and to the phosphorane which acts as a monodentate *P*-donor ligand, (**11**) [186].



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Two species have been identified in aqueous solution which contain Mo≡Mo triple bonds. They are $[Mo_2Cl_n(H_2O)_{8-n}]^{(6-n)+}$, prepared by dissolving $[Mo_2(SO_4)]^{3-}$ salts in 1 *M* HCl, and $[Mo_2(HPO_4)_4]^{2-}$, prepared by dissolving its salt in aqueous H_3PO_4 [187].

3.8.3 Complexes with a metal-metal quadruple bond

The complex $[Mo_2(\eta\text{-allyl})_4]$ exists in solution as a mixture of two isomers. Each isomer has two inequivalent allyl groups which are *trans* to one another and bridge the $Mo\underline{\equiv}Mo$ quadruple bond. The other allyl groups are bonded to each one of the metals. In the major isomer (90%), these two allyls are *cis*, and in the minor *trans*. At temperatures greater than 80 °C, ^1H NMR spectroscopy showed that interconversion takes place *via* exchange of the anti protons of the non-bridging allyl group of the major isomer with the anti protons of the non-bridging allyl group of the minor isomer [188]. The gas phase core-electron ionisation energies of $[M_2L_4]$ (M = Cr, L = O_2CMe or mhp; M = Mo, L = O_2CH, O_2CMe or mhp; Hmhp = 2-hydroxy-6-methylpyridine) were reported. It was found that the charge distribution was the same within $[Cr_2(O_2CMe)_4]$ and $[Mo_2(O_2CMe)_4]$ and within $[Cr_2(mhp)_4]$ and $[Mo_2(mhp)_4]$ despite the large variations in the metal-metal bond lengths for these pairs of molecules [189].

Unit cell parameters have been calculated from X-ray powder diffraction data of $[Mo_2Br_4(py)_4]$, $[Mo_2I_4(pic)_4]$, $[Mo_2I_4(py)_4]$, $[Mo_2(SCN)_4(4\text{-Mepy})_4]$ and $[Mo_2(SCN)_4(py)_4]$ (py = pyridine, 4-Mepy = 4-methylpyridine) [190]. The structure of $[Mo_2Cl_4(PMe_3)_4]$ has been reported {$r(Mo\underline{\equiv}Mo) = 2.130$ Å}. The UV-VIS spectrum has been recorded and comparisons of bond lengths with tungsten analogues discussed as a function of stereochemistry [191]. The complexes $[Mo_2(ambt)_3(O_2CMe)].2thf$, $[Mo_2(ambt)_4].thf$ and $[Mo_2(acbt)_4].2thf$ (Hambt = 2-amino-4-methylbenzothiazole; Hacbt = 2-amino-4-chlorobenzothiazole) have been prepared and their crystal structures determined. The $Mo\underline{\equiv}Mo$ bond lengths were found to be 2.093, 2.103, and 2.117 Å [193]. The structures of the mixed ligand complexes $[Mo_2\{[(2,6\text{-}Me_2C_6H_3)N]_2CMe\}_2(O_2CMe)_2].4thf$ and $[Mo_2\{(PhN)_2CMe\}_3(O_2CMe)]$ have been reported: the $Mo\underline{\equiv}Mo$ bond lengths were 2.107 and 2.082 Å [193]. The structure of $[Mo_2\{(2,6\text{-}Me_2C_6H_3)NC(Me)O\}_4].2CH_2Br_2$ has been determined; $r(Mo\underline{\equiv}Mo) = 2.085$ Å [194]. The reaction of $[Mo_2(O_2CMe)_4]$ with $Li[1,2\text{-}Me_2NCH_2C_6H_4]$ yields crystals of $[Mo_2(1,2\text{-}Me_2NCH_2C_6H_4)_4]$. The structure of this showed that the steric requirements of chelate ring formation lead to distortion of the conformation about the Mo-Mo of 11° from the usual eclipsed geometry. The $Mo\underline{\equiv}Mo$ bond is 2.145 Å [195]. The compound $[Mo_2(O_2Cbiph)_4]$ (HO_2Cbiph = 2-phenylbenzoic acid) has been prepared and structurally characterised by X-ray crystallography. The bulky ligands prevent any axial ligation; the $Mo\underline{\equiv}Mo$ bond length was found to be 2.082 Å [196]. The reaction between $[Mo_2(O_2CMe)_4]$ and $[Et_2B(pzl)_2]^-$ (pzl = pyrazolyl) yields several products. A complex $[Mo_2\{Et_2B(pzl)_2\}_2\{Et_2B(OH)(pzl)\}_2]$ has been isolated and the crystal structure determined. Each molybdenum is chelated by one $[Et_2B(pzl)_2]^-$ ligand and one $[Et_2B(OH)(pzl)]^-$ ligand; the Mo$\underline{\equiv}$Mo bond length is 2.156 Å [197]. $[Mo_2(O_2CCF_3)_4]$ readiliy forms adducts with various phosphines. The crystal structure of $[Mo_2(O_2CCF_3)_4(PR_3)_2]$ (R_3 = Ph_3, $PhEt_2$ or Ph_2Me) have been determined, though that of the triphenylphosphine adduct was not fully refined. The Mo$\underline{\equiv}$Mo bond lengths of the other two adducts are 2.100 Å (R_3 = $PhEt_2$) and 2.107 Å (R_3 = Ph_2Me) [198]. Molybdenum alkyl xanthates form adducts $[Mo_2(xanthate)_4L_2]$ with Lewis bases, L = pyridine, methylpyridines or dimethylsulfoxide. In solution, adduct formation can also be seen with L = propanone, nitriles, thf, or dimethylsulfide. No adducts are formed with CO or hexene [199].

The reaction of $A[O_2CH]$ (A = NH_4, K, Rb or Cs) with $K_4[Mo_2Cl_8]$, $[NH_4]_5[Mo_2Cl_9].H_2O$ or $[NH_4]_4[Mo_2(SO_4)_4].2H_2O$ yields complexes $A_2[Mo(O_2CH)_3Cl_2]Cl.xH_2O.yHCl$, $Cs[Mo_2(O_2CH)_3(SO_4)].2H_2O$, $Cs_2[Mo_2(O_2CH)_2(SO_4)_2].2H_2O$, $Cs_3[Mo_2(O_2CH)(SO_4)_3].2H_2O$ or $[Mo_2(O_2CH)_4].H_2O$ [200]. The crystal structures of $[NH_4]_2[Mo_2(O_2CH)_3Cl_2]Cl.2H_2O.2HCl$ and its rubidium analogue have been determined [201]. All of these mixed methanoate/chloride/sulfate complexes have been characterised using IR spectroscopy [202]. The compounds $[Mo_2(O_2CH)_4L_2]$ (L = 1,4-dioxane, *N,N*-dimethylmethanamide, *N,N*-dimethylethanamide, dimethylsulfoxide, pyridine, or 2- or 3-methylpyridine) and $[Mo_2(O_2CH)_4L']$.H_2O (L' = 2,2'-bipyridine or 1,10-phenathroline) have been prepared and characterised by IR and thermal decomposition studies [203].

The quadruple metal-metal bonds in $[Mo_2(O_2CMe)_4]$, $[Mo_2(O_2CCF_3)_4]$ and $K_4[Mo_2Cl_9]$ can be cleaved by $CNCMe_3$ to give $[Mo(CNCMe_3)_5(O_2CMe)_2]$ or $[Mo(CNCMe_3)_6X]X$ (X = O_2CCF_3 or Cl). These can be converted into $[Mo(CNCMe_3)_7][PF_6]_2$ by the action of $[NH_4][PF_6]$ and excess $CNCMe_3$, or into $[Mo(CNCMe_3)_7][Mo_6O_{19}].2Me_2CO$ by recrystallisation from propanone in air [204]. The reactivity of $[Mo_2Cl_4(PEt_3)_4]$ with CO, N_2 and H_2 was screened using high pressure IR spectroscopy. The irreversible reaction of the molybdenum complex with CO under pressure was described [205]. The reaction of $[Mo_2Cl_4(PR_3)_4]$ (R = Et or Bu) with CO at atmospheric pressure in toluene at 70 °C cleaves the metal-metal bond yielding $[Mo(CO)_3(PR_3)_2Cl_2]$ and *trans*-$[Mo(CO)_4(PR_3)_2]$ [206]. The electrochemistry of complexes $[Mo_2X_4L_4]$ {X = Cl, Br or NCS; L = PEt_3, PPr_3 or L_2 = 1,2-bis(diphenylphosphino)ethane or bis(diphenylphosphino)methane} has been investigated. The compounds may be oxidised reversibly to $[Mo_2X_4L_4]^+$, but reductions were only observed for the isocyanate complexes, which suggests that these processess do not utilise the metal-based orbitals [207]. The reduction of $[Mo_2(O_2CMe)_4]$ by sodium amalgam in thf in the presence of PMe_3 under H_2 yields $[Mo_2H_2(\mu\text{-}H)_2(PMe_3)_6]$, characterised by X-ray crystallography.

Each molybdenum atom is coordinated to three phosphines, one terminal and two bridging hydides. The metal-metal bond length is 2.194 Å [208].

3.8.4 *Molybdenum clusters*

The luminescence and redox photochemistry of the molybdenum(II) cluster $[Mo_6Cl_{14}]^{2-}$ has been investigated. The phosphorescence lifetimes are amongst the longest known for any transition metal complex [209]. SCF-MS-Xα calculations have been performed on the complexes $GaMo_4S_8$, $PbMo_6S_8$ and $Tl_2Mo_2Se_6$, which contain tetrahedra, octahedra and infinite chains of triangles respectively made up of molybdenum atoms. The calculations were used to interpret the various modes of interaction and the nature of the molybdenum-chalcogen and molybdenum-molybdenum bonds [210]. New clusters containing Mo_9, Mo_{12} and $(Mo_{6/2})_\infty$ groups have been synthesied by condensation of octahedral Mo_6 clusters in molybdenum(II) chalcognides [211].

3.8.5 *Carbonyl and organometallic complexes*

Kinetic studies of the reactions of $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2]$ in decalin have shown that it undergoes reversible homolytic fission and that the activation enthalpy is 135.9 ± 2.2 kJ mol^{-1} [212]. The reaction of $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2]$ with PhC≡CPh has been investigated, and it was found to involve successive dissociation of two CO ligands before reaction with the alkyne. This dissociative mechanism is considerably slower than homolytic Mo-Mo fission [213]. The kinetics of halogenation of $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2]$ with I_2, ICl, Br_2 $CHBr_3$ or $C_2H_2Cl_4$ to yield mononuclear halogeno complexes have been studied. The results suggested that the halogen molecules react *via* transition states involving adduct formation with the halogen attached to oxygen atoms around the periphery of the complex. Reactions with $CHBr_3$ and $C_2H_2Cl_4$ proceed cleanly to form $[(\eta^5\text{-}C_5H_5)Mo(CO)_3X]$ *via* a reaction involving direct attack by two molecules of hydrocarbon competing with homolytic fission as the rate-determining step [214].

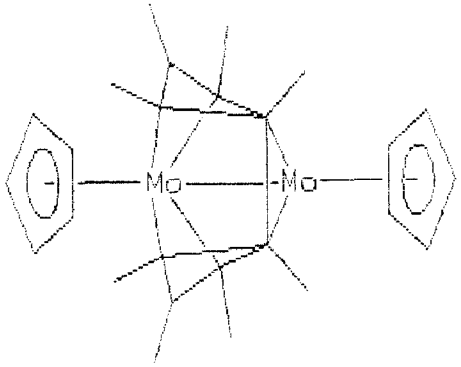
The complexes $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_{6-n}(CNR)_n]$ (n = 1, R = Me, $PhCH_2$, 2,4-dimethylphenyl or CMe_3; n = 2, R = CMe_3) have been prepared from the reaction of $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2]$ with CNR, and were found to catalyse the reaction between $[(\eta^5\text{-}C_5H_5)Mo(CO)_{3-n}(CNR)_nI]$ and $[(\eta^5\text{-}C_5H_5)Mo(CNR)_4]I$. A reaction pathway involving a fast non-chain radical mechanism and a slower chain radical reaction was proposed [215]

X-ray diffraction studies on $[Et_4N]^+$, $[(Ph_3P)_2N]^+$, and $[K(crypt\text{-}222)]^+$ salts of $[Mo_2(CO)_{10}(\mu\text{-}H)]^-$ have demonstrated that the anion can adopt a linear, eclipsed conformation ($[Et_4N]^+$) or bent, staggered with dihedral angles 15.4° {$[(Ph_3P)_2N]^+$} or 29.9° {$[K(crypt\text{-}222)]^+$} [216]. UV irradiation of $[Mo(CO)_6]$, $Na_2S.9H_2O$ and 18-crown-6 ether yields $[Mo_2(CO)_{10}(\mu\text{-}SH)]^-$ and $[Mo(CO)_5(SH)]^-$, isolated as $[Na(crown)]^+$ salts. The crystal structures of the analogous tungsten complexes are polymeric with Na–OC linkages, and the stability of the molybdenum compounds imply that a similar interaction occurs in these [217]. The reaction of $[\{Mo(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2]$ with $C_7H_7\text{-}7\text{-}SCMe_3$ yields $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_2(\mu\text{-}S\text{-}Me_3C)_2]$, characterised by analysis and NMR spectroscopy [218]. Thiolato-bridged dimolybdenum complexes $[Mo_2(CO)_3(\mu\text{-}SR)_3(\eta^7\text{-}C_7H_7)]$ are formed by treating $[MoI(CO)_2(\eta^7\text{-}C_7H_7)]$ with RSH (R = Me, Et, $CHMe_2$ or CMe_3) in the presence of NEt_3. IR and variable temperature NMR spectroscopy revealed that the two isomers exist in solution with different orientations of the R group on the bridging sulfurs. Interconverting isomers were also observed for the monosubstituted derivatives $[Mo_2(CO)_2\{P(OMe)_3\}(\mu\text{-}SCMe_3)_3(\eta^7\text{-}C_7H_7)]$ and showed the phosphorus ligand *trans* to one bridging sulfur and CO *trans* to the other two. The molybdenum-molybdenum single-bond length is 2.946 Å [219]. The structure has been determined of the first triply selenato bridged complex $[Mo_2(CO)_3(\mu\text{-}SePh)_3(\eta^7\text{-}C_7H_7)]$. The Mo-Mo bond length is 2.946 Å [220]. $[(\eta^5\text{-}C_5H_5)MoH(CO)_3]$ reacts with disulfides to give dimeric and trimeric products, depending on the reaction conditions. The complexes $[\{Mo(\eta^5\text{-}C_5H_5)(SMe)(\mu\text{-}CO)(CO)\}_3]$, $[Mo_2(\eta^5\text{-}C_5H_5)(\mu\text{-}SMe)_3(CO)_4]$ and $[Mo_2(\eta^5\text{-}C_5H_5)_2(SR)_2(CO)_2(\mu\text{-}SR)(\mu\text{-}Br)\}$ (R = Me or Ph) have been prepared and characterised [221]. Irradiation of $[Mo(CO)_6]$ in thf gives solutions which react with R_2SbSbR_2 (R = Me, Et or Ph) to give products including $[\{Mo(CO)_4(\mu\text{-}SbR)\}_2]$, which contains a molybdenum-molybdenum bond [223].

The reaction of $[Mo(CO)_6]$ with HO_2CMe and $O(OCMe)_2$ yields several products according to the reaction conditions. The hydrated ethylidene complexes $[Mo_3(\mu_3\text{-}O)(\mu_3\text{-}CMe)(\mu_2\text{-}O_2CMe)_6(H_2O)_3][BF_4].9H_2O$ and $[Mo_3(\mu_3\text{-}CMe)_2(\mu_2\text{-}O_2CMe)_6(H_2O)_3]X_x.yH_2O$ (X = $[SbF_6]$, x = 1, y = 3; X = $[CF_3SO_3]$, x = 2, y = 0; X = $[C_7H_7SO_3]$, x = 2, y = 10) have been isolated and characterised by X-ray crystallography. The three molybdenum atoms form a triangle capped on the top and bottom by an oxo and an ethylidene, or by two ethylidene ligands; each molybdenum-molybdenum bond is bridged by two ethanoate ligands, and the water ligands are terminally bound to the molybdenum atoms [168]. The salt $[Mo_3(\mu_3\text{-}O)(\mu\text{-}CMe)(\mu_2\text{-}O_2CMe)(H_2O)_3][BF_4].9H_2O$

has been investigated by a variety of physical measurements including ^1H and ^{13}C NMR spectroscopy which are consistent with the crystallographic data. A ^{13}C tracer study showed that the ethylene arises from reduction of an ethanoate group [223]. ^1H NMR studies have been carried out on the three bis(ethylidene) complexes, $[Mo_2(\mu_3\text{-}CMe)_2(\mu_2\text{-}O_2CMe)_6(H_2O)_3]X_x.yH_2O$. The $[SbF_6]^-$ complex (x = 1) has one unpaired electron according to bulk susceptibility measurements but shows no EPR spectrum; its ^1H NMR spectroscopy is sharp, with a peak for the ethanoate protons shifted to 14 ppm downfield and that of the ethylidene protons broadened and shifted 85 ppm downfield. The cations in the $[CF_3SO_3]^-$ and $[C_7H_7SO_3]^-$ complexes (x = 2) appear to be paramagnetic and give a ^1H NMR spectrum with lines at 15.6 and 27.1 ppm for the ethanoate and ethylidene protons respectively [224].

The complex $[Mo(NCMe)(MeC_2Me)(\eta^5\text{-}C_5H_5)][BF_4]$ reacts with $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ affording $[Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$ and a complex which analyses as $[Mo_2(MeC_2Me)_4(\eta^5\text{-}C_5H_5)_2]$. A single crystal X-ray diffraction study established that the molybdenum compound contains octamethyl-substituted molybdenacyclononatetraene bonded to a second molybdenum atom, (12) [225].



(12)

^{13}C NMR spectroscopy has been used to show that the complex $[(\eta^5\text{-}C_5H_5)_2Zr(Me)Mo(CO)_3(\eta^5\text{-}C_5H_5)]$ contains two different carbonyl peaks in solution at −80 °C of relative intensity 2:1. It was suggested that one of the carbonyl acts as a four-electron μ-η^1,η^2-CO bridge, and interconverts with the other carbonyls at room temperature. The complex reacts with CO which inserts into the Zr-Me bond, and the resulting ethanoyl ligand migrates from the zirconium to the molybdenum, yielding an ethanoyl bridged dimer [226]. Infrared and Raman spectra of $[(CO)_5Re\text{-}Mo(CO)_4(CPh)]$ have been recorded and interpreted by comparison with chromium and tungsten analogues. The vibrational features of the phenyl group and the $Mo\equiv C$ vibration are identical to those of $[XMo(CO)_4(CPh)]$ (X = Cl, Br or I) [227]. The fluxional behaviour of $[(CO)_4Fe(\mu\text{-}AsMe_2)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ has been investigated by ^1H and ^{13}C NMR spectroscopy. Three different fluxional processes were identified: (a) an interchange between square pyramidal and trigonal pyramidal geometry of the molybdenum exchanges the methyl groups on the arsenic, (b) the same process exchanges the carbonyl groups on the molybdenum, and (c) a high temperature exchange process occurs between the carbonyls on the iron and those on the molybdenum [228]. Full synthetic procedures have been reported for a number of heteronuclear metal carbide clusters, including $[Et_4N]_2[Fe_5MoC(CO)_{17}]$, $[Fe_4MoC(CO)_{16}]$ and $[Ph_3PNPPh_3][Fe_4Mo_2C(CO)_{18}]$ [229]. The metallocarbonylate $K[Mo(\eta^5\text{-}C_5H_5)(CO)_5]$ reacts with $[H_2Os_3(CO)_{10}]$ in a manner analogous to the reaction of a halide ion to yield $[H_2Os_3(CO)_{10}Mo(\eta^5\text{-}C_5H_5)(CO)_3]^-$, which contains a triangle of osmium atoms, one of which is bonded to the $\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}$ group, three carbonyls and a bridging hydride to a second osmium. This is coordinated to three carbonyls, one terminal and one bridging hydride, whilst the third osmium is coordinated to four carbonyls [230].

The reaction between $[(\eta^5\text{-}C_5H_5)Co(cot)]$ and $[(digly)Mo(CO)_3]$ (cot = cyclooctatetraene, digly = diglyme) yields $[(\eta^5\text{-}C_5H_5)Co(\mu\text{-}cot)Mo(CO)_3]$, which contains a bridging, fluxional cot ligand. The electron deficiency of the $\{Mo(CO)_3\}$ group relative to $\{(C_5H_5)Co\}$ is balanced by a π-donor Co-Mo bond, indicated by a low absorption band in the IR spectrum and a shortened Mo-CO bond in the structure *trans* to the Mo-Co bond. Reaction with CO yields $[(\eta^5\text{-}C_5H_5)Co(\mu\text{-}cot)Mo(CO)_4]$ in which the cot is non-fluxional. The reaction between $[(cot)Fe(CO)_3]$ and $[(digly)Mo(CO)_3]$ also yields a product with a fluxional bridge, $[(CO)_3Fe(\mu\text{-}cot)Mo(CO)_3]$ [231]. Triangular Co_2Mo clusters with μ_3-RSi and μ_3-RGe bridging ligands have been prepared by two different methods. The construction method yields $[(\eta^5\text{-}C_5H_5)(CO)_2Mo(\mu_3\text{-}SiMe)\{Co(CO)_3\}_2]$ from the reaction betweeen $[(\eta^5\text{-}C_5H_5)(CO)_3Mo\text{-}\{SiH_2Me\}]$ and $[Co_2(CO)_8]$. A metal exchange reaction between $[(\mu_3\text{-}GeR)\{Co(CO)_3\}_3]$ (R = Me or Ph) and $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2]$ yields the GeR analogue [232].

The synthesis, crystal structure, cyclic voltametry and spectroscopic characterisation have been reported of $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}PMe_2)_2Mo(CO)_4]$, which contains a Rh-Mo bond of length 2.9212 Å. NMR studies demonstrated that the complex is highly fluxional with a facile axial to equatorial carbonyl interchange mechanism [233]. The heterodimetallic complex

[$(\eta^5\text{-}C_5H_5)(CO)_3$MoPd($PMePh_2$)(8-methylquinoline-*C,N*)] has been prepared and the crystal structure determined. The palladium has square planar coordination geometry, with the phosphine *trans* to the nitrogen of the quinoline ligand. The complex [$(\eta^5\text{-}C_5H_5)(CO)_3$MoPd(4-methylpyridine)(8-methylquinoline-*C,N*)] was also prepared in which the molybdenum is *trans* to the nitrogen of the quinoline ligand [234]. The reaction between [$PtHCl(PPh_3)_2$] and Na[$(\eta^5\text{-}C_5H_5)Mo(CO)_3$] affords [$(\eta^5\text{-}C_5H_5)(CO)_3MoPtH(PPh_3)_2$]. The crystal structure shows that the two phosphine ligands are *cis* to each other [235]. The tetrahydrothiophen group (tht) in [$Au(C_6F_5)_3$(tht)] can be replaced by [$(\eta^5\text{-}C_5H_5Mo(CO)_3]^-$ to give [$(\eta^5\text{-}C_5H_5)(CO)_3MoAu(C_6F_5)_3]^-$, which reacts with PPh_3 to cleave the metal-metal bond [236]. [$(\eta^5\text{-}C_5H_5)_2Mo(HgSEt)_2$] crystallises in two forms, a red insoluble isomer and an orange soluble isomer. The molecular geometry is nearly identical, but the overall structure is different. Dimeric units are found in the red form, with the shortest Hg-S distance between molecules of 3.17 Å. An infinite system of Hg-S interactions exists in the orange compound, with Hg-S distances of 3.32-3.33 Å. The electronic structure has been discussed on the basis of ^{1}H, ^{13}C, ^{95}Mo and ^{199}Hg NMR spectra. A relationship between X in [$(\eta^5\text{-}C_5H_5)_2MoX_2$] (X = O, Cl, S, H or Hg), the (C_5H_5)-Mo-(C_5H_5) angle and the ^{1}H chemical shift of the C_5H_5 ring was evident [237].

3.9 MOLYBDOENZYMES AND RELATED CHEMICAL STUDIES

A review has been published on metal ion transportation and complexation in biological systems, including molybdenum containing enzymes [238].

3.9.1 Oxo enzymes

EPR signals due to monomeric molybdenum(V) species formed by mild reduction of [MoO_2(cys-OR)$_2$] (R = Me, Et or CH_2Ph) have been observed at 298 K and 77 K. EPR parameters of these complexes, which have catalytic activity for oxidation of PPh_3, are similar to those of reduced xanthine oxidase [239]. The enzymes sulfite oxidase and xanthine dehydrogenase have been investigated by fluorescence-detected EXAFS using synchrotron radiation, and the results interpreted with improved EXAFS analysis procedures. For oxidised sulfite oxidase the analysis revealed two oxygens at 1.68 Å and two or three sulfurs at 2.41 Å, changing to one oxygen at 1.69 Å and three sulfurs at 2.38 Å upon reduction. For oxidised intact xanthine dehydrogenase, one oxygen at 1.70 Å, one sulfur at 2.15 Å and two sulfurs at 2.47 Å were found changing to one oxygen at 1.68 Å and three sulfurs at 2.38 Å upon reduction. In cyanolysed xanthine dehydrogenase two oxygens at 1.67 Å and two sulfurs at 2.46 Å were found, which on reduction changed to one oxygen at 1.66 Å and two or three sulfurs at 2.33 Å. In all cases there may be extra ligands which only contribute weakly to the EXAFS [240].

3.9.2 Iron-molybdenum-sulfur clusters

A review has been published of Fe-M-S (M = Mo or W) complexes derived from $[MS_4]^{2-}$ anions, and their relavence to nitrogenase [241]. The compounds $[(FeCl_2)_2MoS_4]^{2-}$ and $[(MoS_4)_2Fe]^{2-}$ have been studied by Mössbauer spectroscopy and magnetic determinations. The results implied a high electron affinity of $[MoS_4]^{2-}$ group and intramolecular spin coupling. These properties and the structural features of the complexes suggested these molecular groups as possible building blocks of the Fe-Mo-cofacter in nitrogenase [242]. The complexes $[(FeCl_2)MoS_4]^{2-}$, $[\{Fe(SPh)_2\}MoS_4]^{2-}$ and $[Fe_4S_4(MoS_4)_4]^{6-}$ have been prepared as possible models of the nitrogenase cofacter. The structure of the two $[(FeX_2)MoS_4]^{2-}$ complexes is based on tetrahedral $[MoS_4]^{2-}$ acting as a bidentate ligand to the iron, with no metal-metal bond. In $[Fe_4S_4(MoS_4)_4]^{6-}$ the $\{Fe_4S_4\}$ group forms a cubane-like structure with the $(MoS_4)^{2-}$ groups acting as bidentate terminal ligands [243]. The reaction of $[(FeCl_2)MoS_4]^{2-}$ with Na[OPh] yields $[\{Fe(OPh)_2\}MoS_4]^{2-}$, which has been investigated and compared with the SPh analogues using UV-VIS, magnetic susceptibility, ^{57}Fe Mössbauer and ^{1}H NMR spectroscopy, and electrochemical studies [244]. The nitrosyl complex $[\{Fe(NO)_2\}MoS_4]^{2-}$ has been prepared and isolated as its $[Ph_3PNPPh_3]^+$ salt, and the crystal structure determined [245].

The reaction of $[NH_4]_2[MoS_4]$ and $Na_2[SCH_2CH_2S]$ with iron(III) chloride, followed by addition of $[NMe_4]Br$, yielded the trinuclear complex $[NMe_4]_3[\{(SCH_2CH_2S)MoS_3\}_2Fe]$. An X-ray crystal structure determination showed the molybdenum atoms to have distorted square pyramidal geometry, and the iron atom to be tetrahedrally coordinated to four μ-sulfido ligands [246]. Reaction of the iron(III)-bridged complex anion $[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$ with catechol cleaves the "double-cubane" cluster, yielding a complex $[Et_4N]_3[MoFe_4S_4(SEt)_3(C_6H_4O_2)_3]$. Its crystal structure has been determined, and showed that the anion consists of a single $\{MoFe_3S_4(SEt)_3\}$ cluster with the molybdenum coordinated *via* three Mo–O–Fe bridges to a $\{Fe(C_6H_4O_2)_3\}$ group acting as a tridentate ligand. Cyclic voltammetry revealed three redox processes. One corresponds to cluster electron transfer and the other two have been tentatively ascribed to $\{Fe(C_6H_4O_2)_3\}$ sub-unit metal centre reduction and ligand based oxidation [247].

A plot of the average magnetic moment, μ_m, against temperature in the range 300–1.8 K, and the variation of μ_m with applied magnetic field between 0.125 and 2.0 T have been reported for the salts $[Et_4N]_3[Fe_6M_2S_8(SPh)_6(OMe)_3]$ (M = Mo or W). The results were interpreted in terms of antiferromagnetic spin coupling between iron atoms in the separate $\{Fe_3MS_4\}$ cubane-like clusters [248]. The electrochemical behaviour of $[Fe_6M_2S_8(SEt)_9]^{3-}$ (M = Mo or W) in ethanenitrile has been reported. The 3-/4- and 4-/5- couples showed good electrochemical reversibility for both complexes, unlike the behaviour in dimethylsulfoxide in which the tungsten complex couples appear to be irreversible [249]. The reduced cluster complexes $[Fe_4S_4(SPh)_4]^{n-}$ (n = 3 or 4) and $[Mo_2Fe_6S_9(SPh)_8]^{m-}$ (m = 4 or 5) can be produced by controlled-potential electrolysis of $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_9(SPh)_8]^{3-}$, and have been found to catalyse the reduction of C_2H_2 to C_2H_4. This reaction has been suggested as a model reaction for the reduction of dinitrogen catalysed by nitrogenase [250]. The reaction of $[Et_4N]_3[Mo_2Fe_7S_8(SEt)_{12}]$ with 3,6-$Pr_2C_6H_2$-1,2-$(OH)_2$ (Pr_2catH_2 = 3,6-dipropylcatechol) yields $[Et_4N]_3[Mo_2Fe_7S_8(SEt)_6(Pr_2cat)_2]$. The stucture of this consists of two $\{MoFe_3S_4\}$ cubane-like units, with each molybdenum chelated by a $[Pr_2cat]^{2-}$ ligand, two of the irons of each cube terminally coordinated to one $[SEt]^-$ ligand, and the third iron bridged to the molybdenum atom of the other cube *via* a $[SEt]^-$ bridge. The ^{1}H NMR spectrum has been assigned, and changes of this on addition of RSH (R = 4-MeC_6H_4 or Ph) demonstrate the loss of a signal due to bridging $[SEt]^-$ ligands. The product formed has a similar EPR spectrum to those of the native Fe–Mo proteins and the Fe-Mo-cofactor of nitrogenase [251].

3.9.3 Dinitrogenyl chemistry

Several reviews have been published dealing with the chemical reduction of dinitrogen with inorganic complexes acting as catalysts [252-255].

$[Mo(N_2)_2(dppe)_2]$ {dppe = 1,2-bis(diphenylphosphino)ethane} reacts with RI (R = Me, Bu, C_6H_{11} or C_8H_{17}) to form $[MoI(N_2R)(dppe)_2]$ with loss of one equivalent of N_2. The carbon bound nitrogen atom can be protonated by strong Lewis acids yielding $[MoI(N_2HR)(dppe)_2]^+$. $[MoI(N_2C_6H_{11})(dppe)_2]$ can be converted to $[MoI(OH)(N_2C_6H_{11})(dppe)_2]$ when eluted on an aluminium column with thf. The preparation, characterisation and spectroscopic properties of these complexes have been reported and discussed [256]. The reaction of $[Mo(N_2)_2(dppe)_2]$ with PhCl affords molybdenum-chlorine complexes and a variety of phenylated organic products which suggests radical attack after homolytic fission of the Ph–Cl bonds. In the presence of $P(OEt)_3$ under mild conditions $[Mo(N_2)\{P(OEt)_3\}(dppe)_2]$ is formed, but at higher temperatures the phosphite is attacked yielding $PhP(O)(OEt)_2$ [257-258]. $[Mo(N_2)_2(dppe)_2]$ may be alkylated using trifluoroethanoic anhydride giving trifluoroethanoyldiazenide complexes in high yield. A non-radical mechanism analogous to protonation has been suggested [259]. The reactions of $HCONR^1R^2$, $HCOOR^3$ and R^4CHO with $[Mo(N_2)_2(dppe)_2]$ yield decarbonylated products (HNR^1R^2, HOR^3, and R^4H) and molybdenum-carbonyl complexes. A reaction mechanism was proposed involving oxidative addition of the molybdenum complex with cleavage of the methanoyl C-H bond, followed by decarbonylation. Primary alcohols RCH_2OH yield RH and a mixture of molybdenum-carbonyl complexes and molybdenum-hydride compounds. Secondary alcohols yield ketones and molybdenum hydrides [260]. $RCOOCH_2Ph$ (R = Me or Et) reacts with $[Mo(N_2)_2(dppe)_2]$ to give RH, benzene and molybdenum-carbonyl complexes. When R = Et, C_2H_4 and H_2 are also formed. This has been accounted for by assuming the oxidative addition of the ester to the molybdenum with cleavage of the acyl-oxygen bond, followed by elimination of CO. Reactions of phenyl carboxylates occur similarly by way of acyl-oxygen cleavage. The reactions of allyl ethanoate and vinyl carboxylates with $[Mo(N_2)_2(dppe)_2]$ occur *via* cleavage of the allyl-oxygen bond or vinyl-oxygen bonds yielding propene or ethene and a molybdenum-carboxylate complex containing an orthometallated phosphine [261].

Several molybdenum bis(dinitrogen) complexes containing mixed tertiary phosphine ligands of the form $[Mo(N_2)_2LL']$ (LL' = PPh_2Me, $PPhMe_2$; dppe or bis(2-diphenylphosphinoethyl)phenylphosphine {triphos}) have been prepared and characterised by analysis, IR, ^{31}P NMR and mass spectroscopy [262]. An investigation of the mechanism of the reaction of *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ with HCl, HBr or H_2SO_4 in MeOH to yield $[Mo(N_2H)(OMe)_2(PMe_2Ph)_3]$ has shown that protic solvents play an important part [263]. The formation of hydazido(2-) complex intermediates in solution during the reaction of *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ with H_2SO_4 in thf has been established by ^{15}N NMR spectroscopy, and the isolation of $[Mo(NNH_2)(HSO_4)_2(PMe_2Ph)_3]$ from the solution. When treated with H_2SO_4 in MeOH, the complexes $[MoX_2(NNH_2)(PMe_2Ph)_3]$, $[MX(NNH_2)(PMe_2Ph)_3L]^+$ and $[Mo(NNH_2)(quin\text{-}8\text{-}O)(PMe_2Ph)_3]X$ (X = Cl, Br or I; L = tertiary phosphine or substituted pyridine; quin-8-O = quinolin-8-olate) yield ammonia or hydrazine.

Treatment of $[MoX_2(NNH_2)(PMe_2Ph)_3]$ with $Na[BH_4]$ in thf or MeOH also yields ammonia and a hydride complex $[MoH_x(PMe_2Ph)_3]$ [264]. Crystal structure studies of five complexes of formula $[M(NNH_2)(quin)(PMe_2Ph)_3]X$ (M = Mo, W; X = Cl, Br, I) have shown that in each case the metal is found in almost identical octahedrally coordinated environments. Slight differences were found in the extended hydrogen bonding schemes, the position of the anion, and the orientations of the phosphine ligands [265]. The reaction of *trans*-$[Mo(N_2)_2\{(S,S)\text{-chiraphos}\}_2]$ {chiraphos = $Ph_2PC^*H(Me)C^*H(Me)PPh_2$} with an excess of RX (RX = racemic 2-bromooctane) affords the products $[MoBr(NNR)\{(S,S)\text{-chiraphos}\}_2]$. The formation of the C–N bond occurs *via* an enantioselective mechanism, leaving an excess of the S isomer in the unreacted ligand [266]. The complex $[MoBr(NNBu)(dppe)_2]$ reacts with MeX (X = FSO_3 or I) to yield $[MoBr(NNMeBu)(dppe)_2]X$, with secondary alkyl bromides to yield $[MoBr(NNHBu)(dppe)_2]^+$, but does not react at room temperature with primary alkyl bromides. At 60 °C, alkylation followed by decomposition was observed with primary alkyl bromides [267].

The complexes $[MoF(NN{=}CRR')(dppe)][BF_4]$ undergo consecutive one- and two-electron oxidations and reductions under cyclic voltametric conditions at a platinum electrode. EPR spectra of species generated by controlled potential electrolysis have shown that primary oxidation occurs on the metal atom and reduction on the two nitrogen atoms [268]. Complexes $[Mo(N_2RR')(S_2CNMe_2)_3]^+$ (R = alkyl or aryl) undergo two successive reversible one-electron reductions in non-aqueous electrolytes at platinum or vitreous carbon electrodes. The initial product, $[Mo(N_2RR')(S_2CNMe_2)_3]^0$, disproportionates to $[Mo(N_2RR')(S_2CNMe_2)_3]^+$ and $[Mo(N_2RR')(S_2CNMe_2)_3]^-$. Two-electron reduction of the cation leads to electroactivation of the N_2RR' ligand to attack by electrophiles, and reduction-protonation has been shown to liberate NH_2NRR'. A mechanism for this activation has been proposed and it was suggested that the redox orbitals of the cation are associated with the Mo=N-N function [269]. Electrochemical reduction, at a platinum electrode, of *trans*-$[MoBr(N_2CH_2\{CH_2\}_3CH_2)(dppe)_2]^+$ under N_2 yields the free organohydrazine and *trans*-$[Mo(N_2)_2(dppe)_2]$, under CO yields *cis*- and *trans*-$[Mo(N_2)(dppe)_2]$ and *N*-aminopiperidine, and under Ar yields *trans*-$[Mo(N_2CH_2\{CH_2\}_3CH_2)(dppe)_2]$. The complex *trans*-$[Mo(N_2)_2(dppe)_2]$ is readily converted into the starting material, suggesting a possible cyclic pathway for the fixation of dinitrogen as organohydrazine [270].

At ambient temperatures in MeOH, the complexes *trans*-$[Mo(NH)X(dppe)_2]^+$ (X = F, Cl, Br or I) are inert to acid, but give ammonia in high yield on treatment with $[OMe]^-$. A kinetic study has shown that the initial step is a rapid deprotonation, followed by loss of halide to give $[MoN(dppe)_2]^+$ which reacts with $[OMe]^-$ to yield $[MoN(OMe)(dppe)_2]$. This rapidly accepts a proton from the solvent giving $[Mo(NH)(OMe)(dppe)_2]^+$. When X = Cl, Br or I, the halide is liberated rapidly, but with X = F loss of fluoride is the rate-limiting step. $[Mo(NH)(OMe)(dppe)_2]^+$ reacts in basic MeOH with rate-limiting phosphine-chelate ring opening to give ammonia [271].

3.10 MOLYBDENUM CATALYSTS AND RELATED COMPLEXES

Molybdenum porphyrin complexes [OMo(TPP)X] (X = Cl, OMe or O; $TPPH_2$ = 5,10,15,20-tetraphenylporphyrin) catalyse the epoxidation of cyclohexene by Me_3COOH with a selectivity of up to 85% epoxide formation on total conversion of the hydroperoxide. Epoxidation of *cis*- and *trans*- 2-hexene catalysed by [OMe(TPP)Cl] gives 97% and 99% of *cis*- and *trans*-epoxides respectively. Comparison of relative reaction rates with this catalyst and with $[Mo(CO)_6]$ suggests that the reaction is sterically controlled, with the macrocycle affecting epoxidation of the *trans* isomer more than that of the *cis* [272,273]. $[Mo(\eta^5\text{-}C_5H_5)_2X_2]$ (X = Cl, Br) are highly efficient catalyst in the synthesis of cycloaliphatic diepoxides by oxidation of alkenes with Me_3COOH, giving practically 100% yields. An intermediate species $[Mo(\eta^5\text{-}C_5H_5)_2X_2]^+A^-$ {A^- = $(Me_3COO^-)(Me_3COOH)$} has been identified by EPR, IR, kinetic studies and analysis [274].

The complexes $[(bipy)_2Ru(\mu\text{-}S)_2MoS_2]$ (bipy = 2,2'-bipyridine) and $[(bipy)_2Ru(\mu\text{-}S)_2Mo(\mu\text{-}S)_2Ru(bipy)_2]^{2+}$ have been prepared and investigated as catalysts for ethyne reduction. No reaction was observed between the clusters and ethyne in the presence of MeOH or a proton source, but electrochemically reduced species of the clusters react to give ethene and ethane [275]. A polymeric reagent formed by fixing cysteine by its carbonyl group on an insoluble polymer giving the 1,2-aminethiol forms a complex with molybdenum(VI) which catalysis the reduction of ethyne to ethene [276]. The reaction of molybdenum atoms with thf leads to the formation of molybdenum hydrides, which may be used to effect hydrogenations of added alkenes [277]. $[Mo(\eta^5\text{-}C_5H_5)(dmpe)H_3]$ {dmpe = 1,2-bis(dimethylphosphino)ethane} catalyses the photo-induced hydrogen-deuterium exchange in deuteriobenzene solutions of hydrocarbons such as 1,4-dimethylbenzene and ethylbenzene, dimethyl ether, or 4-methylanisole [278]. A Mo(0)/PDA (PDA = partially dehydrogenated alumina) species generated by heating $[Mo(CO)_6]$/PDA in flowing helium has been shown to be catalytically active for the hydrogenation of carbon monoxide, the isotropic exchange between alkanes and deuterium at 20 °C, the hydrogenolysis of cyclopropane at 0 °C, and the hydrogenation of propene at -46 °C [279].

Gas-phase π-allyl radicals, detected by EPR, were produced when propene reacted over Bi_2O_3 and γ-bismuth molybdate catalysts at 723 K. No radicals were detected using α-bismuth molybdate, and MoO_3 was found to act as a sink for radicals produced elsewhere in the system [280]. The essential role played by an excess of MoO_3 in Fe_2O_3-MoO_3 catalysts (bulk composition Mo/Fe = 1.5) has been found on the basis of a photoelectron study to be the production of stoicheiometric iron(III) molybdate at the catalyst surface; this was found to be the active phase for the oxidation of methanol to methanal [281]. Three crystals of MoO_3 which have the same catalytic activity for the oxidation of ethanol were found to give different products for the non-catalytic reaction with no dioxygen added, depending on the crystal shape. This was due to the different distribution of crystal faces exposed in each crystal [282]. An ^{18}O labelling experiment has shown that hydrogen peroxide exchanges oxygen with the molybdenum species $[MoO(O_2)_2L_2]$ (L = neutral ligand). This complex acts as a catalyst for the oxidation of sulfides and alkenes by hydrogen peroxide [283].

A new dimolybdenum(II) compound has been prepared and characterised by physical measurements: it can coordinate O_2 directly and use the activated molecule to oxidise various organic ligands [284]. Irradiation of [OMo(TPP)OMe] yields the molybdenum(IV) complex [OMo(TPP)]. This reacts with O_2 in methanol reforming [OMo(TPP)OMe] and producing H_2O_2, forming a catalytic route for the photo-assisted reduction of molecular oxygen to hydrogen peroxide [255].

A kinetic study has been carried out on the water gas shift reaction at 200 °C and lower using $[M(CO)_6]$ (M = Cr, Mo or W) as catalyst precursors in basic methanol-water solutions. The overall kinetics were explained by a mechanism involving methanoate decomposition rather than activation of carbon monoxide [286]. The addition of CCl_4 to oct-1-ene is catalysed by $[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$, and proceeds by a redox catalysed mechanism. Gradual decomposition of the catalyst was found to lead to the intervention of a radical pathway [287]. The hydroformylation and carboxylation of alkenes is catalysed by $[Mo(CO)_5(SnCl_2)]$, $[Mo(CO)_5(SnO)]$ and $[Mo(CO)_6]/SnCl_2$ mixtures, although $[Mo(CO)_6]$ itself is not a catalyst for these reactions [288]. Furan reacts with Me_3CCl at 130 °C in the presence of $[(arene)Mo(CO)_3]$ to yield 2-*t*-butylfuran and 2,5-di-*t*-butylfuran. The catalyst was largely deactivated after twelve hours. Using furan:Mo of 1000:1, yields of the 2-*t*-butylfuran were high, but fell sharply with increasing catalyst concentration [289].

3.11 NITROSYL COMPLEXES

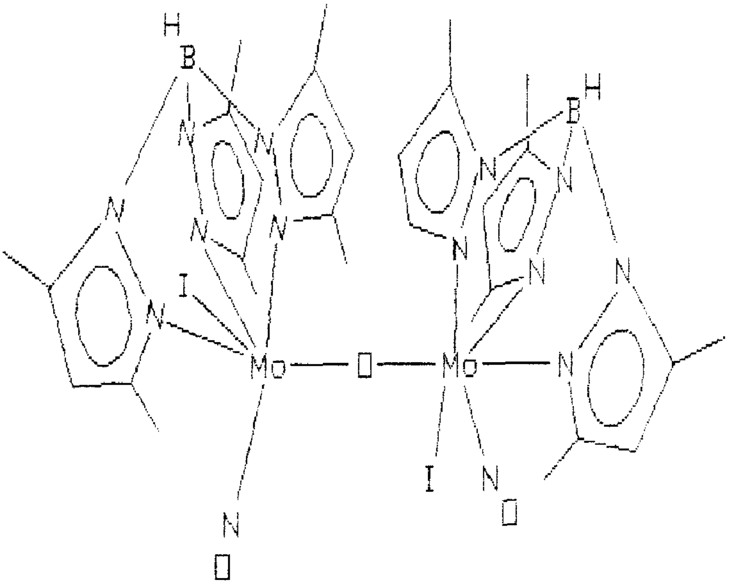
Gas-phase core electron binding energies of organometallic nitrosyl complexes of chromium, molybdenum, and tungsten have been reported. On going from chromium to tungsten in the series $[(\eta^5\text{-}C_5H_5)M(NO)_2Cl]$, back-bonding to the NO group increases and electron density is withdrawn from the chlorine atoms. The data for these complexes and for $[(\eta^5\text{-}C_5H_5)M(CO)_2(NO)]$ indicate a significant difference in the back-bonding to the molybdenum and tungsten compounds from the first row transition-metal nitrosyls, in that the electron density is mainly transferred to the nitrosyl oxygen atom, whereas in the first row nitrosyls approximately equal amounts of electron density are transferred to the oxygen and nitrogen atoms [290].

The polymeric complex $\{[Mo(NO)_2Cl_2]\}_n$ reacts with neutral ligands L (L = RCN, py, PPh_3, ½bipy or ½dppe) to give $[Mo(NO)_2L_2Cl_2]$. The stereochemistries of the products have been established by IR, ^1H and ^{31}P NMR spectroscopy. An X-ray crystal study of the $[Mo(NO)_2(bipy)_2Cl_2]$ showed it to be *cis*-dinitrosyl, *trans*-dichloride, with two linear Mo-N-O units where the nitrosyls act as three-electron donors. The $[Mo(NO)_2(PPh_3)_2Cl_2]$ complex was found to be *cis*-dinitrosyl, *cis*-dichloride, *trans*-diphosphine. The correlation between the structural parameters of the $Mo(NO)_2$ group and the values of ν(N-O) found in the IR spectra was discussed [291]. The pyrolysis of complexes *cis*-$[Mo(NO)_2Cl_2L_2]$, *cis*-$[Mo(NO)_2Cl_2L']$ and *cis*-$[Mo(NO)_2(L')_2]$ (L = monodentate ligand, L' = bidentate ligand) has been studied using thermogravimetric and gas chromatographic techniques. The pyrolysis of the nitrosyls were found to yield mixtures of N_2, N_2O and NO [292].

Solutions of $MoCl_5$ in $POCl_3$ react with NOCl forming $[Mo(NO)Cl_3(POCl_3)_2]$, which in CH_2Cl_2 dimerises with loss of one $POCl_3$ group, giving $[\{Mo(NO)Cl_3(POCl_3)\}_2]$. This reacts with $[AsPh_4]Cl$ in dichloromethane yielding $[AsPh_4][Mo(NO)Cl_4].CH_2Cl_2$ and $[AsPh_4][Mo(NO)Cl_5].2CH_2Cl_2$. The IR spectra have been recorded and assigned, and crystal structures obtained of $[AsPh_4]_2[Mo(NO)Cl_5].2CH_2Cl_2$ and $[Mo(NO)Cl_3(POCl_3)]$. Both structures contain linear Mo-N-O bonds [293]. The reaction of $[AsPh_4][Mo(NO)Cl_4]$ with $[AsPh_4][PO_2Cl_2]$ in dichloromethane yields $[AsPh_4]_2[Mo(NO)Cl_4(PO_2Cl_2)]$, characterised by IR spectroscopy and X-ray crystallography. The NO is *trans* to the $[PO_2Cl_2]^-$ ligand, and acts as a three-electron donor with a linear Mo-N-O arrangement [294].

$[(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)]$ reacts with PMe_3 with loss of CO to form $[(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(PMe_3)]$. The tungsten analogue reacts more slowly, and an intermediate has been identified as $[(\eta^5\text{-}C_5H_5)W(CO)_2(NO)(PMe_3)]$ when the reaction is carried out in pure PMe_3. This suggests an associative mechanism for the substitution reaction [295]. The reaction between propanone and $[Ph_4P]_2[Mo(NO)(ONH_2)(NCS)_4]$ produces $[Ph_4P]_2[Mo(NO)(ONCMe_2)(NCS)_4]$. The crystal structure has been determined, and shows the molybdenum to have a pentagonal coordination geometry with a side-on oximato ligand in the equatorial plane and NO and one NCS in the axial positions [296,297].

Reaction of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I_2]$ with boiling propanone leads to formation of $[\{Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I\}_2(\mu\text{-}O)]$ and the bicyclic cation $[C_6H_3Me_6N_2(OH)]^+$, isolated as the I^- or mixed $I^-/[I_3]^-$ salt. The crystal structure of the molybdenum complex, (13), revealed a slightly bent Mo-O-Mo bond [298]. The complexes $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I\{O(CH_2)_nR\}]$ (R = OH, n = 2-6; R = Cl or OMe, n = 2) and $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)\{O(CH_2)_2OH\}_2]$ have been prepared by the reaction of $[\{Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I\}_2]$ with appropriate α,ω-alkanediol, 2-chloro- or 2-methoxy-ethanol; no evidence was found for the existence of chelating complexes of the type $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)\{O(CH_2)_nO\}]$ [299]. $[\{Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I\}_2]$ reacts with alcohols, primary amines, hydrazines or thiols to give $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(I)_2Q]$ (Q = OR, NHR or SR). Reduction of the starting material to the mono anion can be achieved electrochemically remarkably easily, followed by dissociation of I^- affording paramagnetic $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I]$. These reduction products are important intermediates in the formation of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(I)Q]$ [300,301].



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3.12 CARBONYL COMPLEXES

The ^{95}Mo NMR spectra have been reported and discussed of a large number of molybdenum carbonyl complexes including compounds containing PPh_3, $AsPh_3$, $SbPh_3$, PCl_3, dppe, Br^-, I^-, pyridine, $[C_5H_5]^-$, $[C_7H_7]^-$, norbornadiene or S_2CNMe_2 ligands [304]; $[C_5H_5]^-$, $[SMe]^-$, $[C(O)C(CF_3)=C(CF_3)C(O)SMe]^{2-}$ (S,C-chelate), $[C(CF_3)=C(CF_3)C(O)SMe]^{2-}$ (S,C-chelate), [ethylxanthate]$^-$, [ethylthioxanthate]$^-$, [diethylthiophosphate]$^-$, [diethyldithiocarbanate]$^-$, $[C(Me)=C(Me)_2]^-$, Cl^-, Br^-, I^-, Me^-, H^-, Hg^{2-} or $SnMe_3^-$ ligands [305]; and C_7H_8, mesitylene, 1,2-, 1,3-, and 1,4-dimethylbenzene, toluene or $[C_5H_5]^-$ ligands [306]. The bidentate ligand derived from the condensation of pyridine-2-carbaldehyde with (S)(-)-1-phenylethylamine forms a complex $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)][PF_6]$ of molybdenum(II) which exists as two diastereomers with opposite molybdenum configuration. These have been directly detected using ^{95}Mo NMR spectroscopy [307].

^{13}C NMR spectroscopy has been used to investigate CO ligand rearrangement processes in molybdenum carbonyl derivatives. The complex *cis*-$[Mo(CO)_4(^{13}CO)(PMe_2Ph)]$ gave one signal split into a doublet due to ^{31}P in the ^{13}C NMR spectrum. After heating to 75 °C in heptane for 12 hours a second doublet was observed from the *trans* isomer. At high resolution $^{13}C\text{-}^{13}C$ coupling could be resolved, which showed that an intermolecular mechanism was involved in the isomerisation [308]. The site of bond breaking in the stereospecific introduction of ^{13}CO into the substrate $[Mo(CO)_4(phen)]$ (phen = 1,10-phenanthroline), and the extent of fluxionality in the intermediate produced, have been determined using ^{13}C NMR and UV-VIS spectroscopy. The results obtained were consistent with a mechanism involving loss of CO *cis* to the phen ligand, followed by complete scrambling of the five-coordinate intermediate [309].

The stable radical anionic species $[(CO)_5Mo\text{-}L\text{-}Mo(CO)_5]^{\cdot-}$ (L = pyrazine or 4,4'-bipyridine) have been prepared from the reaction of $K^+L^{\cdot-}$ with $[Mo(CO)_6]$, and characterised by EPR spectroscopy [310]. Redox reactions of *cis*-$[Mo(CO)_2(bipy)_2]$ (bipy = 2,2'-bipyridine) produce $[Mo(CO)_2(bipy)_2]^{z}$ (z = ±1 or ±2). These ions have been found to react with isocyanides to substitute CO or bipy, or both, depending on z [311]. Kinetic studies have been reported for reactions of $[Mo(CO)_4(bipy)]$ with cyanide in several non-aqueous solvents, with methoxide in dimethylsulfoxide/water mixtures, and with azide. The reaction of $[Mo(CO)_4(5\text{-nitrophenanthroline})]$ with cyanide was also investigated. Solvent effects in the reaction of $[Mo(CO)_4(bipy)]$ with cyanide were dissected into initial state and transition state components which showed that an important role is played by cyanide solvation. Preliminary results were presented for the reaction of $[Mo(CO)_4(diimine)]$ with phosphines, diethyldithiocarbamates and ether peroxides [312]. The solid and solution IR spectra of $[Mo(CO)_4(dipyam)]$ (dipyam = di-2-pyridylamine) have been studied and found to be significantly different. The solution spectrum is similar to that of the bipyridine analogue, but the solid spectrum shows evidence of intermolecular interaction, suggesting an associated or polymeric structure [313].

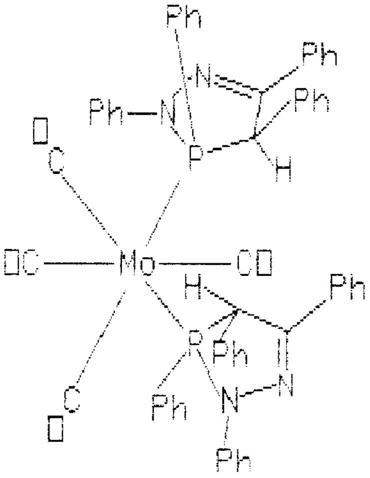
The crystal structure has been determined of the complex $[\{HB(Me_2pz)_3\}Mo(CO)_6(S\text{-}4\text{-}C_6H_4Cl)].(Me_2CO)_x$ (Me_2pz = 3,5-dimethylpyrazole). The molybdenum atom has slightly distorted octahedral coordination with the pyrazolylborate ligand occupying three facial sites. The Mo-S distance is short (2.305 Å), indicating considerable double bond character [314]. The ambidentate ligand $Ph_2P(Me_2pz)$ reacts with $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene) under mild conditions to give an equilibrium mixture of products $[\{Ph_2P(Me_2pz)\}Mo(CO)_4]$ and *cis*-$[\{Ph_2P(Me_2pz)\}_2Mo(CO)_4]$. In the former complex the ligand is coordinated to the molybdenum *via* the phosphorus and nitrogen forming a four-membered metallocycle. The latter complex contains two monodentate *P*-donor ligands, and is favoured by use of an excess of phosphine ligand [315]. The compound $[\{PhP(Me_2pz)_2\}Mo(CO)_3]$, in which the pyrazolylphosphine ligand is coordinated *via* two nitrogen atoms forming a six-membered metallocycle in boat configuration, reacts reversibily with CO to give $[\{Ph_2P(Me_2pz)\}Mo(CO)_4]$ with the phosphine ligand coordinated *via* the phosphorus and nitrogen atoms in a four-membered metallocycle. The tricarbonyl complex also reacts reversibly with H_2, C_2H_4, $P(OMe)_3$ or PF_3, but not with PPh_3 or N_2. The product of the reaction with PF_3 is $[\{Ph_2P(Me_2pz)\}_2Mo(CO)_4(PF_3)_2]$, containing a four-membered metallocycle, *trans* dicarbonyl and *cis*-(bis-triflurophosphine) coordination [316].

In CH_2Cl_2 solution, the complex *cis,trans*-$[Mo(CO)_2(PPh_3)_2(py)(\eta^2\text{-}SO_2)]$ loses PPh_3 to give a dimeric species $[\{Mo(CO)_2(PPh_3)(py)(\mu\text{-}SO_2)\}_2]$. The crystal structure of this complex has been determined and showed that the molybdenum atoms are bridged by two SO_2 ligands that are coordinated to one metal through the sulfur atom and one oxygen atom, and to the second metal *via* the remaining oxygen atom [317]. The complexes $[Mo(CO)_2(PPh_3)(S_2COR)_2]$ (R = Et, $PhCH_2$ or CMe_3) have been prepared and characterised by IR and UV-VIS spectroscopy. The xanthates act as bidentate ligands, and the stability of the complexes decreases in the order Et > $PhCH_2$ > CMe_3 [318].

MCD spectra have been reported and discussed for $[M(CO)_5L]$ complexes (M = Cr, Mo or W; L = PCl_3, PPh_3, PMe_3, thiazole, pyridine, pyrazine, pyradizine, piperidine or NMe_3), and results used to assign absorption spectra of $[M(CO)_5L]$ compounds. It was deduced the lowest ligand field transition is directed to the d_{z^2} orbital, which is significant in understanding the photochemistry of these complexes [319]. A series of complexes $[M(CO)_{6-n}L_n]$ (M = Mo or W; n = 1-3; L = bicyclic aminophosphane) have been synthesised and the coordination abilities of the *P*-donor ligands evaluated using IR and ^{31}P NMR spectroscopy. The main characteristics of these constrained ligands were found to be low steric requirements and good π-accepting abilities. No evidence of coordination through the nitrogen atom was found [320]. X-ray crystal structures and IR spectra have been reported of the compounds $[Mo(CO)_5\{P(CH_2CH_2(N)_3\}]$ and $[Mo(CO)_5(PPh_3)]$. On the basis of the structural data and the $\nu(CO)$ infrared data, tris(2-cyanoethyl)phosphine was described as a good π-acceptor ligand [321].

The principal of electrochemical substitution of metal carbonyls was applied to $[Mo(CO)_5(PR_3)]$ in an attempt to prepare selectively di- and tri-substituted products $[Mo(CO)_4(PR_3)(PR'_3)]$ and $[Mo(CO)_3(PR_3)(PR'_3)_2]$. However as a result of simultaneous replacement of CO and PR_3 mixtures of products were formed [322]. A new ligand $Ph_2PCH_2CH_2NMe_2$, L, has been made and used to prepare $[Mo(CO)_5L]$ in which it acts as monodentate, *P*-donor ligand. The complex reacts with MeI to form $[Mo(CO)_5(amphos)]I$ (amphos = $[Ph_2PCH_2CH_2NMe_3]^+$), characterised by analysis, conductivity, IR, ^1H and ^{31}P NMR measurements [323]. The electrochemistry of both the *cis*- and *trans*-isomers of $[Mo(CO)_4(PR_3)_2]$ (R = Bu, Et or Ph) has been investigated as an example to illustrate the type of interactions that occur on electrochemical reduction/oxidation of systems which can exist in isomeric forms with similar redox potentials. It was demonstrated that the structural rearrangements between *cis*- and *trans*- isomers occurring *via* an intramolecular mechanism do not lead to the observation of slow electron transfer [324].

Thermal substitution reactions of $[Mo(CO)_5L_c^1]$ with *cis*-diazaphosphole derivatives (L^1 = 3,4-dihydro-2,3,4,5-tetraphenyl-2H-1,2,3-diazaphosphole; L_c^1 and L_t^1 denote *cis* and *trans* L^1 respectively) have yielded a mixture of *cis* and *trans* $[Mo(CO)_4(L_c^1)_2]$. The reactions of $[Mo(CO)_5L_t^1]$ with the bulkier *trans* diazaphospholes L_t^1 and L_t^2 (L^2 = 5-benzyl-3,4-dihydro-2,3,4-triphenyl-2H-1,2,3-diazaphosphole) afforded only the *trans*-$[Mo(CO)_4(L_t^1)_2]$ or $[Mo(CO)_4(L_t^1)(L_t^2)]$ isomers. $[Mo(CO)_4L_c^1]$ reacts with L_t^1 or L_t^2 giving the *trans* products. $[Mo(CO)_4(norbornadiene)]$ reacts with L_c^1 to form *cis*-$[Mo(CO)_4(L_c^1)_2]$ but with L_t^1 no tetracarbonyl complexes were observed. These results show that steric effects play an important part in the substitution reactions of these bulky ligands. IR and ^1H NMR spectra of the complexes were reported, together with an X-ray study on *cis*-$[Mo(CO)_4(L_c^1)_2]$, (14) [325].



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The hydrolysis under basic conditions of *trans*-$[Mo(CO)_4(PPh_2Cl)_2]$ was found to give the anionic *cis*-$[Mo(CO)_4(Ph_2P\text{-}O\text{-}H\text{-}O\text{-}PPh_2)]^-$, identified by IR, ^1H and ^{31}P NMR spectra, and by analysis. The *trans*⟶*cis* isomerisation occurs because of the thermodynamically very favourable intramolecular proton bridging available only in the *cis* product [326]. A novel tridentate chelating strong π-acceptor ligand has been reported formed in the reaction between $C_6H_5N(PF_2)_2$ and *fac*-$[Mo(CO)_3(MeCN)_3]$. The product was identified by X-ray crystallography as *fac*-$[Mo(CO)_3\{P[N(Ph)PF_2]_3\}]$. A mechanism for the reaction was proposed involving the initial formation of *fac*-$[Mo(CO)_3\{PF_2N(Ph)PF_2\}_3]$, followed by elimination of two molecules of PF_3 to form the bicyclo[2.2.2]octane-like cage structure of the product [327]. A series of complexes *cis*-$[M(CO)_4\{Ph_2P(OCH_2CH_2)_nOPPh_2\}]$ (M = Cr, Mo or W; n = 2, 3, 4 or 5) have been prepared from the reaction between the bis(diphenylphosphinite) ligands and $[M(CO)_4(\text{norbornadiene})]$. ^{13}C NMR spectroscopy was used to show that the molybdenum compound (n = 5) will complex Li^+ and Na^+ in a crown-ether-like interaction, but the compound (n = 4) will only complex Li^+. The ^{13}C carbon chemical shifts for the compounds (n = 2 or 3) were unaffected by the presence of the Group 1 cations, showing no or only weak complexation. The compounds (n = 2, 4 and 5) do not react with RLi (R = Me, Ph, CMe_3 or Et_2N) but with (n = 3) rapid reactions occur, yielding $[Mo(CO)_3(RCO)\{Ph_2P(OCH_2CH_2)_3OPPh_2\}Li]$. A crystal structure of the benzoylate complex (R = Ph) showed the benzoylate oxygen and the diphosphinite "backbone" oxygens forming a cage in which the Li^+ cation is situated. The reaction is made thermodynamically favourable by the preferential cation binding by the basic groups on the diphosphinite ligand together with the benzoylate-acylate-type oxygen in the product molecule. The equilibrium in the reaction between PhLi and [Mo(CO)$_4$(R$_2$P-X-PR$_2$)] (X = {OCH$_2$CH$_2$N(Me)CH$_2$}$_2$, OCH$_2$CH$_2$N(Me)(CH$_2$)$_3$N(Me)CH$_2$CH$_2$O, O(CH$_2$)$_3$O(CH$_2$)$_3$O, N(Me)(CH$_2$)$_3$N(Me)(CH$_2$)$_3$N(Me); R = Et or Ph) was studied using IR spectroscopy to establish the degree of stabilisation of the product due to Li$^+$ binding [328].

Several complexes of *N*-(diphenylphosphino)pyrrole (lp) and *N*-(diphenylphosphino)-2,5-dimethylpyrrole (lm) have been prepared, including *cis*-[Mo(CO)$_4$(lp)$_2$], [Mo(CO)$_5$(lm)] and [Mo(CO)$_2$(lp)$_2$Br$_2$]. The structures were assigned from IR spectra. The ligand lp was found to resemble PPh$_3$ in coordination ability, whilst lm is a weaker ligand, and successive replacements of the phenyl groups in PPh$_3$ by pyrrole groups decreases the donor properties of the phosphorus [329].

The preparation has been reported of [(CO)$_5$Mo(PMe$_2$-PMe$_2$)], [{(CO)$_5$Mo(PMe$_2$-PMe$_2$)}$_2$Cr(CO)$_4$], and [(CO)$_3$Mo(PMe$_2$-PMe$_2$)Cr(CO)$_5$]. Thermolysis of the molybdenum-chromium complexes resulted in the formation of Mo(PMe$_2$-PMe$_2$)Cr six-membered rings, which decompose at higher temperatures [330]. Directed synthesis were used to prepare a series of complexes [L$_n$M(EMe$_2$-E'Me$_2$)M'L$_m$] (M,M' = Cr, Mo, W, Mn, Fe, Co or Ni; E,E' = P or As; *n*,*m* = 2, 3 or 4), characterised by IR and ^{31}P NMR spectroscopy [331].

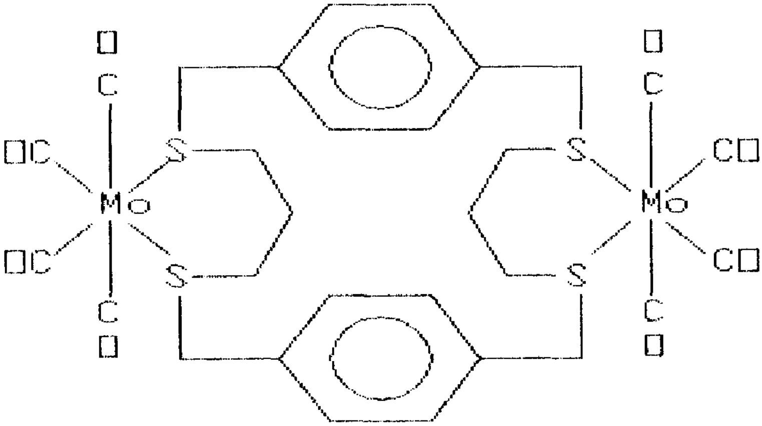
The methylarsine complex [Mo(CO)$_5$(MeAsH$_2$)] has been prepared, but decomposed with loss of CO and H$_2$ to form an insoluble oligomer [332]. A bulky arsine ligand As(SiMe$_3$)$_3$ has been synthesised and reacted with [Mo(CO)$_6$] to form [Mo(CO)$_5${As(SiMe$_3$)$_3$}]. NMR, IR, Raman and He I PE data have been reported [333]. 4-R-λ^3-arsenines and 2-phenyl-4-R-λ^3-arsenines (R = Ph, CMe$_3$, cych or Et) react smoothly with [Mo(CO)$_3$(MeCN)$_3$] to give stable [{η^6-(λ^3-arsenine)}Mo(CO)$_3$] products. IR, ^{1}H and ^{13}C NMR, UV and mass spectra have been recorded and discussed [334]. The adamantane structured MeC(CH$_2$AsO)$_3$ reacts with [Mo(CO)$_6$] on UV irradiation to give [{MeC(CH$_2$AsO)$_3$}Mo(CO)$_4$]. The ligand can also behave as a tridentate chelate, and reacts with [Mo(CO)$_3$(C$_7$H$_8$)] to give {*fac*-[MeC(CH$_2$AsO)$_3$Mo(CO)$_3$]}$_n$, which was thought to have a polymeric structure. IR, Raman, ^{1}H and ^{13}C NMR, and mass spectra were recorded, and the vibrational spectra discussed in detail [335].

Irradiation of [Mo(CO)$_6$] in thf gives a solution which reacts with R$_2$SbSbR$_2$ (R = Me or Et) to give [(CO)$_5$MoSbR$_2$SbR$_2$Mo(CO)$_5$] [222]. [Mo(CO)$_6$] reacts with Sb(SiMe$_3$)$_3$ to form [Mo(CO)$_5${Sb(SiMe$_3$)$_3$}], which acts as an initiator for the polymerisation of thf. IR, ^{1}H NMR and mass spectra of this and related complexes have been recorded and discussed [336]. The chelating ligands dimethyl(α-picolyl)stibine (picstib) and dimethyl(8-quinolyl)stibine (quinstib) have been prepared and characterised. They react with $[Mo(CO)_6]$ in thf under UV irradiation to produce $[Mo(CO)_4$(picstib)] and $[Mo(CO)_4$(quinstib)] [337].

$[Mo(CO)_4$(norbornadiene)] reacts with $Me_2XGeMe_2(CH_2)_2X'Me_2L$, to give $[Mo(CO)_4L]$ (X,X' = P or As, but not N), characterised by IR, NMR and mass spectra [338]. The chemical and spectroscopic results obtained during the synthesis of $[Mo(CO)_4L]$ complexes with chelating phosphine and arsine complexes have been critically discussed and compared with results for analogous five-membered ring chelates of the form $[Mo(CO)_4R_2XGeMe_2CH_2XR_2]$ (X,X' = P or As; R = alkyl) [339].

The reaction of [PNP]$[Mo(CO)_5Cl]$ ($[PNP]^+ = [Ph_3PNPPh_3]^+$) with $Ag[O_2CMe]$ or $Ag[O_2CCF_3]$ readily affords the complexes [PNP]$[Mo(CO)_5(O_2CMe)]$ or [PNP]$[Mo(CO)_5(O_2CCF_3)]$. The crystal structures have been determined and show short Mo-CO bond distances *trans* to the monodentate ethanoate ligands [340]. Photolysis of $[Mo(CO)_6]$ in a toluene solution containing phenanthroquinone, PQ, yields stable metal carbonyl quinone radical complexes $[PQ^{\cdot}\text{-}Mo(CO)_4]$. These can undergo furthur ligand exchange reactions between CO and ER_3 (ER_3 = PPh_3, $AsPh_3$ or NEt_3) to give $[PQ^{\cdot}\text{-}Mo(CO)_3(ER_3)]$. EPR spectroscopy has been used to study the mechanisms and dynamics of these reactions [341].

The reaction between $[Mo(CO)_6]$ and imidazolethione molecules, L, forms $[Mo(CO)_5L]$ complexes which have been shown by IR and UV-VIS spectroscopy to contain *S*-bonded ligands with weak π back-bonding [342]. $[Mo(CO)_6]$ yields $A[Mo(CO)_5(XH)]$ (A = Li or Na; X = S, Se or Te) on photochemical or thermal reaction with chalcogenides or alcohol. These compounds have been isolated as $[(Ph_3P)_2N]^+$ and $[AsPh_4]^+$ salts. Furthur reaction with $[Mo(CO)_5(thf)]$ gives the dimers $[(CO)_5Mo(\mu\text{-}XH)Mo(CO)_5]^-$. The reaction of $[Mo(CO)_6]$ with LiS in ethanol/thf in the presence of $[(Ph_3P)_2N]Cl$ yields $[(Ph_3P)_2N][(CO)_4Mo(\mu\text{-}SH)_2Mo(CO)_4]$ [343]. The cation [Na(18-crown-6-ether)]$^+$ has also been used to isolate the complexes $[Mo(CO)_5(SH)]^-$ and $[(CO)_5Mo(\mu\text{-}SH)M(CO)_5]^-$ (M = Cr, Mo or W), formed by irradiation of $[Mo(CO)_6]$ in the presence of $[SH]^-$ [344]. The macrocyclic tetradentate sulfur ligand 2,6,15,19-tetrathia[7.7]paracyclophane, L_4, reacts with $[Mo(CO)_6]$ to give $[(CO)_4Mo(L_4)Mo(CO)_4]$, which has been isolated and characterised by X-ray crystallography, (**15**). This type of complex is believed to be an intermediate in the metal carbonyl catalysed 1,3-dithiapropane elimination from L_4 [345]. The electron-rich closed-shell molybdenum(II) complexes $[Mo(CO)(S_2CNEt_2)_2L_2]$ {L_2 = $(PMe_2Ph)_2$, $(PMePh_2)_2$ or dppe, 1,2-bis(diphenylphosphine)ethane} have been prepared and characterised by analysis and IR spectroscopy. $[Mo(CO)(S_2CNEt_2)_2(dppe)]^+$ has been prepared form the molybdenum(II) complex by

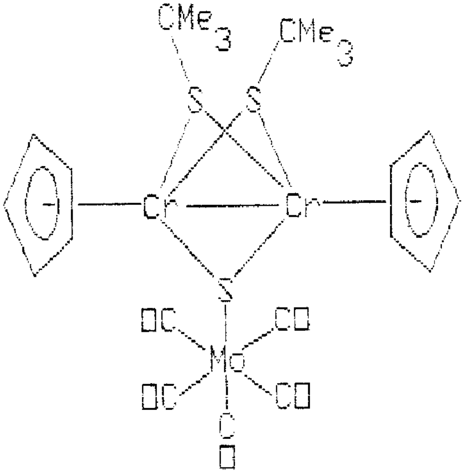


(15)

low-temperature controlled-potential electrolysis, and was found to be stable in thf at 0 °C. All three molybdenum(II) complexes undergo two successive one-electron oxidations in solution, but no other molybdenum(III) or molybdenum(IV) complex is stable [346]. Et_3PCS_2 reacts with $[Mo(CO)_6]$ or $[Mo(C_7H_8)(CO)_3]$ to give $[\{Mo(CO)_2(PEt_3)(\mu_2\text{-}S_2CPEt_3)\}_2]$. Both the Et_3PCS_2 zwitterions coordinate one metal atom through an $\eta^3\text{-}S_2C$ linkage and the second metal atom through a single sulfur [347].

The stannylene complexes $[Mo(CO)_5(SnCl_2)].thf$, $[Mo(CO)_5\{Sn(OH)_2\}]$, $[Mo(CO)_5(SnO)]$ and $[Mo(CO)_5\{Sn(OCOMe)_2O(COMe)_2\}]$ have been prepared and characterised [348]. $Me_2Si(NCMe_3)_2Sn$ reacts under UV irradiation with $[Mo(CO)_6]$ to give $[\{Me_2Si(NCMe_3)_2Sn\}Mo(CO)_5]$ and $[\{Me_2Si(NCMe_3)_2Sn\}_2Mo(CO)_4)]$, presumed to be *cis*. The ligand was also found to react with $[Mo(CO)_3(thf)]$ yielding only $[\{Me_2Si(NCMe_3)_2Sn\}Mo(CO)_5]$ [349]. The iron complex ferrocenylphenylthioketone can replace one CO ligand in $[Mo(CO)_6]$. A ^{13}C NMR study of this ligand has shown that the carbon nuclei in the cyclopentadienyl rings are deshielded on coordination to the $\{Mo(CO)_5\}$ fragment [350]. The ferrocene analogue $[Fe\{C_5H_4Si(Me)_2CH_2PPh_3\}_2]$ acts as a bidentate phosphorus-donating ligand, forming cyclic oligomeric complexes with the $\{Mo(CO)_4\}$ moiety. Steric constraints prevent the formation of a dinuclear complex [351]. Addition of salicylaldehyde to *cis*-$[Mo(CO)_4(Ph_2PNHCH_2CH_2NH_2)_2]$ yields the condensation product *cis*-$[Mo(CO)_4\{Ph_2PNHCH_2CH_2N{=}CH(C_6H_4\text{-}2\text{-}OH)\}_2]$.

This can act as a tetradentate *N,N′,O,O′* ligand with other metals: the synthesis and structure of *trans*-[*cis*$(CO)_4Mo\{Ph_2PNHCH_2CH_2N{=}CH(C_6H_4\text{-}2\text{-}O)\}_2Ni]$ have been reported [352]. The complex $[\{(\eta^5\text{-}C_5H_5)Cr(\mu_2\text{-}SCMe_3)\}_2(\mu_2\text{-}S)]$ reacts with $[Mo(CO)_6]$ in thf to yield $[\{(\eta^5\text{-}C_5H_5)Cr(\mu_2\text{-}SCMe_3)\}_2(\mu_2\text{-}S)Mo(CO)_5]$. An X-ray crystal structure showed that the Cr-Cr bond length is very little changed by coordination of the ligand to molybdenum, showing that most of the interaction is through the metal-metal bond, not *via* the sulfur bridge, (**16**) [353].



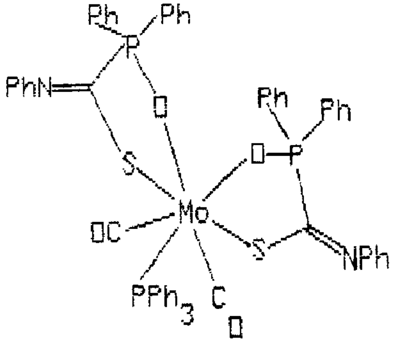
(**16**)

The anion $[HCr(CO)_5]^-$ has been isolated and spectroscopically identified. It forms hydride-bridged dimers with $\{Mo(CO)_5\}$ and $\{Mo(CO)_4(PPh_3)\}$ fragments, of the form $[(CO)_5Cr(\mu\text{-}H)Mo(CO)_4L]$, characterised by NMR spectroscopy [354]. An improved method has been reported of the synthesis of $[HMo(CO)_5]^-$, using sodium naphthalenide in thf to reduce $[Mo(CO)_6]$ [355]. The reduction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ by quaternary ammonium borohydrides in phase transfer catalyse reactions yields $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$. Reducing $[Mo(CO)_6]$ gives $[NR_4][(CO)_5Mo(\mu\text{-}H)Mo(CO)_5]$. In the presence of Ph_3SnCl, both $[(CO)_5Mo(\mu\text{-}H)Mo(CO)_3Cl]$ and $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ are reduced to produce $[(\eta^5\text{-}C_5H_5)_2Mo(CO)_3(SnPh_3)]$ [356,357].

The rate of reduction and mechanism of hydrogenation of α-methylstyrene by $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ have been studied. A mechanism which involved a rate limiting step of H atom transfer to the β carbon atom was proposed on the basis of the observed rate law, isotope effect and absence of CO inhibition

[358]. $[(\eta^5\text{-}C_5H_5)MoH(CO)_3]$ reacts with $[MeMn(CO)_5]$ or $[(\eta^5\text{-}C_5H_5)Mo(CO)_3R]$ (R = Me, Et or CH_2Ph) producing aldehydes and the dimers $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2]$ or $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_2\}_2]$. Reaction with ethene produces ethane and diethylketone. The suggested mechanism is by hydrogen transfer to a vacant coordination site, and the hydride/alkyl reaction is related to the final step in hydroformylation [359]. The reaction of elemental sulfur with $[(\eta^5\text{-}C_5H_5)MoH(CO)_3]$ yields $[\{(\eta^5\text{-}C_5H_5)Mo_2\}_2]$ and $[\{(\eta^5\text{-}C_5H_5)MoS_5\}_2]$. The former product contains a planar $\{Mo_2(\mu\text{-}S)_2\}$ unit with terminal sulfide ligands in the anti configuration, and can be oxidised to $[\{(\eta^5\text{-}C_5Me_5)MoOS\}_2]$ with oxo ligands replacing the terminal sulfurs. In the $[\{(\eta^5\text{-}C_5H_5)MoS_5\}_2]$ complex, the molybdenum atoms are each coordinated to a single sulfur atom of a bridging disulfide ligand, and to two $\eta^2\text{-}S_2$ ligands and a C_5Me_5 ligand. The complex $[\{(\eta^5\text{-}C_5H_5)MoS_2\}_2]$ was also prepared and found to be an *anti* isomer of a $[\{MoS(\mu\text{-}S)\}_2]$ dimer. The complexes all react with dihydrogen to form compounds containing hydrosulfido ligands, and with ethene or ethyne to produce species containing dithiolate-bridges [360].

The crystal structures have been reported of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3HgCl]$. The average metal-carbon ring distances are 2.304 and 2.305 Å, and the Mo-Hg bond length is 2.683 Å, with a Mo-Hg-Cl angle of 160.02 Å [361]. In the presence of Et_3N, $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ reacts with $Ph_2P(O)C(S)NHR$ (R = Me or Ph) to give $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(Ph_2(O)C(S)NR)]$ in which the deprotonated ligands coordinate through the nitrogen and sulfur to give a four-membered ring. The ligand also reacts with $[Mo(CO)_3(PPh_3)_2Cl_2]$ in the presence of NEt_3 to give a seven-coordinate product with the molybdenum bonded to one PPh_3, two CO, and two deprotonated ligands bonded through oxygen and sulfur to give five-membered rings, (17). The complexes were



(17)

characterised by IR, ^{1}H and ^{31}P NMR spectroscopy, and X-ray crystallography [362]. Oxidation of $[\{(\eta^5\text{-}C_5H_4Me)Mo(CO)_3\}_2]$ with I_2 yields the molybdenum(IV) complex $[(\eta^5\text{-}C_5H_4Me)Mo(CO)_2I_3]$. The crystal structure of this has been obtained and reported [363].

The electrochemistry of a series of molybdenum(II) complexes $[(\eta^5\text{-}C_5H_5)Mo(CO)_n(XYCNMe_2)]$ {*n* = 2, XY = SeSe (*I*), SeS (*II*), SS (*III*), SeO (*IV*), SO (*V*); *n* =3, XY = SeO (*VI*), SO (*VII*)} has been studied using DC cyclic voltammetry and coulometry in MeCN and CH_2Cl_2. (*I*)-(*III*) undergo one-electron reversible oxidation-reduction in both solvents. Oxidised species of (*IV*) and (*V*) in MeCN are stabilised by formation of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(XC(O)NMe_2)]^+$ (X = Se or O), which lose MeCN on reduction to regenerate (*IV*) and (*V*). Oxidation of (*VI*) and (*VII*) is irreversible with loss of one molecule of CO accompanied by coordination of MeCN [364]. The structure has been determined of one of the diastereoisomers and of the racemic pairs having the composition $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(SC(Me)NR)]$ (R = $CH\{CH(Me)_2\}Ph$ or S-$CH\{CH(Me)_2\}Ph$). The enantiomorphic crystal has S configuration at the optically active carbon and at molybdenum. Both complexes have square-planar coordination geometry around the molybdenum with the ligand sulfur and nitrogen bound [365].

$Na[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ reacts with Ph_2PCl to give $[(\eta^5\text{-}C_5H_5)MoPPh_2(CO)_3]$, which exchanges with Me_3P to produce *trans*-$[(\eta^5\text{-}C_5H_5)MoPPh_2(CO)_2(PMe_3)]$. Both complexes react with HCl, MeI or Br_2 to yield $[(\eta^5\text{-}C_5H_5)Mo(PPh_2R)(CO)_2L]X$ (L = CO or PMe_3; R = H, Me or Br; X = Cl, I or Br). Reaction with sulfur or selenium leads to the formation of $[(\eta^5\text{-}C_5H_5)Mo(PPh_2E)(CO)_2L]$ (L = CO or PMe_3; E = S or Se). Analytical, NMR and IR data were recorded [366]. The ligands $Ph_2PC(X)N(H)R$ (LH; X = S, R = Ph or Me; X = O, R = Ph; X = NC_6H_4-4-Me, R = C_6H_4-4-Me) were found to behave as neutral monodentate ligands in substitution reactions with $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$, giving $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(LH)Cl]$ with the ligand *P*-bonded to molybdenum. Deprotonation using Et_3N occurs only when X = S, to yield the chelated complexes $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)]$ with the ligand *P,S*-bonded. $Me_2NC(S)N(H)R$ (HL'; R = Me or Ph) reacts with $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl]$ in the presence of NEt_3 to produce $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(L')]$. With the ligand $Me_2NC(S)N(H)C(S)NMe_2$, the reaction occurs only in the presence of Et_3N to yield a product with a six-membered ring [367].

UV irradiation of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3SiR_3]$ (R = H, alkyl or Cl) in the presence of $P(XPh)_3$ (X = O, S, CH_2), or phosphines containing allyl, 1-naphthyl or tolyl groups, gives cyclometalated compounds, with elimination of R_3SiH. Five-membered rings are formed in preference to six-membered rings and the reactions occurs more easily at sp^2 than sp^3 hybridised carbon atoms

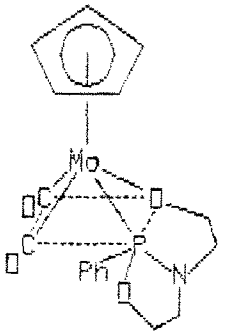
[368]. The kinetics of the reaction between $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(SnMe_3)]$ and I_2 have been investigated to illustrate the influence of an intermediate on reactions kinetics in organometallic systems [369]. Complexes $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(PbR_3)]$ (R = Me or Et) have been prepared and characterised. The trimethyllead complex is photochemically and thermally unstable, decomposing to give $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(Me)]$. The triethyllead rearranges to give $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_2\}_2PbEt_2]$. Both complexes react with SO_2 to yield $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(SO_2R)]$ (R = Me or Et) [370].

The ethene bridged complexes $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(\mu\text{-}C_2H_4)M(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) and $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(\mu\text{-}C_2H_4)Re(CO)_5]$ have been obtained by nucleophilic addition of $[M(CO)_3(\eta^5\text{-}C_5H_5)]^-$ (M = Mo or W) and $[Re(CO)_5]^-$ to coordinated ethene in $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(\mu\text{-}C_2H_4)]^+$. The cations $[M(CO)_3(\eta^7\text{-}C_7H_7)]^+$ react with carbonyl metalates to give C–C coupling with formation of $[(CO)_3M(C_{14}H_{14})M'(CO)_3]$ (M,M' = Cr, Mo or W) [371]. The reaction of $[Et_4N][(R_3P)Mo(CO)_4Cl]$ (R = Et, Bu, $CHMe_2$ or Ph) with alkenes yields *cis*-$[(R_3P)Mo(CO)_4(alkene)]$ (alkene = maleic anhydride, dimethylmaleate, dimethylfumurate, bis(trimethylsilyl)fumurate or ethene). The alkenes are readily displaced from these complexes by amines or phosphines under mild conditions [372]. $[(\eta^5\text{-}C_5H_5)(CO)_2(L)MoFBF_3]$ reacts with various alkynes to give $[(\eta^5\text{-}C_5H_5)(CO)Mo(RCCR')_2][BF_4]$ and $[(\eta^5\text{-}C_5H_5)(CO)(L)Mo(RCCR)_2][BF_4]$ complexes (L = CO, $P(OPh)_3$, PEt_3 or PPh_3; R = R' = H, Me or Ph; R = H, R' = Ph). The crystal structure has been determined for the mono-alkyne complex $[(\eta^5\text{-}C_5H_5)(CO)(PPh_3)Mo(PhCCPh)][BF_4]$ [373]. The reaction of $[(L_5')(CO)(L)Mo(RCCR')_2][BF_4]$ (L_5' = $\eta^5\text{-}C_5H_5$ or $\eta^5\text{-}C_9H_7$) with ethanenitrile in the presence of an excess of alkyne yields $[(L_5')(MeCN)(L)Mo(RCCR')_2][BF_4]$ (R,R' = H, Me, CMe_3, Ph or $CHMe_2$). The reaction with PR''_3 (R" = Et, Ph or cyclohexyl) yields $[(L_5')(CO)(PR''_3)Mo(RCCR')][BF_4]$ (R,R' = Me, CMe_3, H, $CHMe_2$, Ph or C_6H_4-4-Me). The ethanenitrile complex reacts with phosphines, L (L = PEt_3, PMe_3, $PMePh_2$, $Ph_2PCH{=}CHPPh_2$, dppe or dmpe) to form $[(L_5')L_2Mo(RCCR')][BF_4]$. The crystal structures were determined of $[(\eta^5\text{-}C_9H_7)(CO)(PEt_3)Mo(MeCCMe)][BF_4]$ and $[(\eta^5\text{-}C_9H_7)(PMe_3)_2Mo(MeCCMe)][BF_4]$. Variable temperature ^1H and ^{13}C NMR spectroscopy showed the alkyne ligands to be rotating, and the ^{13}C chemical shifts suggested that the alkyne ligands could act as four-electron donors [374].

The kinetics of the insertion of CO into the Mo-Me bond in the reaction of $PMePh_2$ with $[(\eta^5\text{-}C_5H_5)(CO)_3Mo\text{-}Me]$ yielding $[(\eta^5\text{-}C_5H_5)(CO)_2(PMePh_2)Mo\text{-}COMe]$ have been investigated in thf and thf-substituted solvents. The results provide direct evidence for solvent coordination in this reaction [375]. Infrared spectroscopy has been used to investigate the species formed by irradiation of $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(Me)]$ isolated in polymer films at 12-293 K:

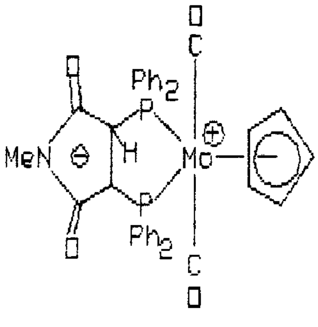
both CO dissociation and Mo-Me bond homolysis reactions were observed [376]. UV irradiation of $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(C_2H_5)]$ has been found to yield $[\{(\eta^5\text{-}C_5H_5)(CO)_3Mo\}_2]$, $[(\eta^5\text{-}C_5H_5)(CO)_3MoH]$, C_2H_6 and C_2H_4. In the presence of PMe_3, irradiation yields $[(\eta^5\text{-}C_5H_5)(CO)(PMe_3)_2Mo\text{-}Mo(CO)_3(\eta^5\text{-}C_5H_5)]$, $[(\eta^5\text{-}C_5H_5)(CO)_2(PMe_3)Mo(C_2H_5)]$ and $[(\eta^5\text{-}C_5H_5)(CO)_2(PMe_3)MoH]$. The thermal reaction gave the insertion product $[(\eta^5\text{-}C_5H_5)(CO)_2(PMe_3)Mo(COC_2H_5)]$ [377]. The first-order rate-constants in the reaction of $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2C_6H_4X)]$ with PPh_3 to yield *trans*-$[(\eta^5\text{-}C_5H_5)(CO)_2(PPH_3)Mo(COCH_2C_6H_4X)]$ have been found to tend to a limiting value at high PPh_3 concentration. The reactivity of the $Mo\text{-}CH_2$ bond was enhanced by electron donating substituents, X, and could be analysed in terms of Hammett substitution parameters [378].

The synthesis and structures of $[(\eta^5\text{-}C_5H_5)(CO)_2Mo\{PhP(\mu\text{-}OCH_2CH_2)_2N\}]$, which contains a pentacoordinate phosphorus atom acting as a phosphoranide ligand, and a coordinated nitrogen atom forming a Mo-P-N metallocycle [379]. The bicyclic phosphorane $PhHP(\mu\text{-}OCH_2CH_2)_2N$ forms a complex with molybdenum $[(\eta^5\text{-}C_5H_5)(CO)_2Mo\{PhP(\mu\text{-}OCH_2CH_2)_2NH\}]^+$ which can be deprotonated with LiMe to give $[(\eta^5\text{-}C_5H_5)(CO)_2Mo\{PhP(\mu\text{-}OCH_2CH_2)_2NCH_2CH_2O\}]$. The crystal structure shows the ligand to be coordinated *via* phosphorus and oxygen atoms, forming a six-membered metallocycle, (**18**), [380]. $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2]$ reacts with the ligand $(Ph_2P)_2\{\mu\text{-}CC(O)\}_2NMe$, L, to give $[(\eta^5\text{-}C_5H_5)(CO)_2MoL]$. This can be oxidised by iodine giving $[(\eta^5\text{-}C_5H_5)(CO)_2MoL]^+I^-$, or hydrogenated by toluene to produce the radical complex $[(\eta^5\text{-}C_5H_5)(CO)_2Mo(LH)]$. The crystal structure



(**18**)

has been determined of this radical, and shows the molybdenum to be coordinated to the C_5H_5 ligand, two CO ligands, and the two phosphorus atoms of the LH radical, (19), [381].



(19)

$[(\eta^5\text{-}C_5H_5)(CO)_3Mo\{C(O)C(O)OMe\}]$ reacts with $Li[Et_3BH]$ to give $[(\eta^5\text{-}C_5H_5)(CO)_2Mo(CHO)\{C(O)C(O)OMe\}]^-$, a kinetically unstable anionic methanoyl complex [382]. The reaction of $[(\eta^5\text{-}C_5H_5)(CO)_5Mo\{C(O)Me\}]$ with $R_3P{=}CH_2$ (R_3 = Me_3, $EtMe_2$, Et_3 or Bu_3) yields $[PR_4][(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ and $R_3P{=}CR'C(O)Me$ *via* heterolysis of the Mo–C σ bond and transylidisation. The products were characterised by IR and NMR spectroscopy [383].

^1H NMR spectroscopy has been used to investigate the isomerisation of $[(\eta^5\text{-}C_5H_5)(CO)_2Mo(\text{benzamidinato})]$ complexes containing bidentate *N,N'*-donor ligands with various substituents on the nitrogen atoms. The preferred conformations of the thermodynamically more stable isomers were established by means of NOE difference spectroscopy [384]. The reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(LL)][PF_6]$ with RLi (LL = $C_5H_4N\text{-}2\text{-}CH\text{-}NCHMePh$, R = Me; LL = $C_5H_4N\text{-}2\text{-}CH{=}NCHMe_2$, R = Ph) yields the complexes $[(\eta^5\text{-}C_5H_5)(CO)_2Mo\{NH(R')C(NC_5H_4)R''\}]$ (R' = CHMePh, R'' = Me; R' = $CHMe_2$, R'' = Ph). The crystal structures show both compounds to contain a three membered ring with a η^2-aminomethylene ligand bonded to molybdenum through carbon and nitrogen atoms [385]. The rotational isomerisation of methylaminofulvene, L, has been investigated in the complex $[LMo(CO)_3]$ using ^1H NMR spectroscopy. It was found that coordination to the metal increased the barrier to rotation about the C-N bond with respect to the free ligand, *i.e.* in the coordinated ligand the C-N bond has more double bond character. Protonation of the complex yields $[LMoH(CO)_3]$ in which the barrier to rotation was found to be higher than in the parent compound [386,387].

The *N,O,S*-chelating ligands $\{Me_2Ga(N_2C_5H_7)(OCH_2CH_2SR)\}^-$ (L; R = Et or

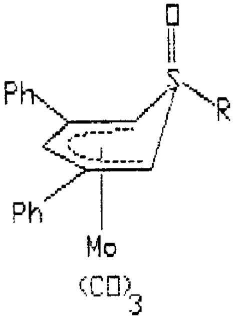
Ph) have been synthesised and used to prepare $[(\eta^3\text{-}C_3H_5)(CO)_2MoL]$, $[(\eta^3\text{-}C_7H_7)(CO)_2MoL]$ and $[(NO)(CO)_2MoL]$ complexes, in which it binds in a *fac* geometry to the octahedrally coordinated molybdenum [388]. The crystal structure has been determined of $[(\eta^3\text{-}C_7H_7)(CO)_2MoL]$ {L = $Me_2Ga(N_2C_5H_7)(OCH_2CH_2NH_2)$} in which the ligand L acts as a *fac-N,O,N'* tridentate ligand with NH_2 *trans* to the C_7H_7 ligand [389]. The bidentate ligand $\{Me_2Ga(N_2C_3H_3)_2\}^-$ and the pyrazolyl ligand $N_2C_3H_4$ adopt a *fac* arrangement in the complex $[Et_4N][\{Me_2Ga(N_2C_3H_3)_2\}(N_2C_3H_4)Mo(CO)_3]$ which has been synthesised and characterised by ^1H NMR spectroscopy and X-ray crystallography [390].

The reaction between triphenylcyclopropenyl bromide and $[Mo(CO)_4L_2]$ {L = 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), or di(2-pyridyl)amine (bipyam)} yields $[(\eta^3\text{-}C_3Ph_3)Mo(CO)_2L_2Br]$ and $[(\eta^3\text{-}C_4Ph_3O)Mo(CO)_2L_2Br]$. The crystal structures of $[(\eta^3\text{-}C_3Ph_3)Mo(CO)_2(bipy)Br].MeCN$ and $[(\eta^3\text{-}C_4Ph_3O)Mo(CO)_2(bipy)Br].thf$ showed that in both complexes the molybdenum is octahedrally coordinated to two *cis* CO ligands in the same plane as the bipy, with *trans* bromine and η^3-cyclopropenyl or η^3-oxocyclobutenyl groups [391]. The reactions of L (L = $PHPh_2$ or $PMePh_2$) with $[(\eta^3\text{-}C_3H_4R)Mo(CO)_2(MeCN)_2Cl]$ (R = H or Me) in MeOH give $[(\eta^3\text{-}C_3H_4R)Mo(CO)_2L_2Cl]$. In MeCN, an excess of phosphine caused reductive elimination of the allyl chloride with formation of *mer*-$[Mo(CO)_2(MeCN)L_3]$. This complex is also formed from the reaction of $PMePh_2$ with $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(MeCN)_3]^+$ or $[(\eta^3\text{-}C_3H_5)_2Mo_2(CO)_4Cl_3]^+$, during which $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(PMePh_2)Cl_2]^-$ anions were formed and could be isolated as σ-allylphosphonium salts. Under forcing conditions, $PHPh_2$ also reacts with elimination of the allyl group to yield *cis*-$[Mo(CO)_2(PHPh_2)_4]$ [392]. $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl]$ reacts with PR'_3 (R = Me, CMe_3 or C_6H_{11}; R' = Et_3, Pr_3, $MePh_2$ or $EtPh_2$) to give $[Mo(CO)_2(CNR)_2(PR'_3)_2]$, characterised by IR and ^1H, ^{13}C and ^{31}P NMR spectroscopy. The reaction between $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl]$ and CNR in the presence of $PMePh_2$ yields *cis*-$[Mo(CO)_2(CNR)_4]$ and $[(\eta^3\text{-}C_3H_5)Mo(CO)(CNR)_4]^+$. X-ray photoelectron spectra of the neutral complexes were recorded and discussed [393].

Complexes $[(\eta^3\text{-}C_3H_4R)Mo(CO)_2(bipy)(O_2CR')]$ (R = H, R' = Me, Ph, CF_3, C_2F_5 or C_3F_7; R = Me, R' = CF_3, C_2H_5 or C_3F_7) have been prepared and their solution properties investigated using ^1H and ^{19}F NMR, and IR spectroscopy. Each β-methylallyl compound contains a symmetrical trihapto ligand and adopts a pseudo octahedral structure. The allyl derivatives exist in two isomeric forms, one similar to the methylallyl analogues and a second dynamic form. At high temperatures the isomers interconvert *via* an intramolecular trigonal twist rearrangement [394].

[(π-allyl)Mo(CO)$_2$(L)$_2$Br] (L = MeCN or py) react with xanthates or dithiocarbamates A[L$_2$] (A = Na or K) to form the disubstituted products A[(π-allyl)Mo(CO)$_2$(L$_2$)$_2$] from the MeCN complex and the monosubstituted [(π-allyl)Mo(CO)$_2$(py)(L$_2$)] from the pyridine starting material [395]. The complexes [(π-allyl)Mo(CO)$_2$(bipy)Br] react with alkylxanthates, A[S$_2$COR] (R = Me, Et, CMe$_3$ or CH$_2$Ph; A = Na or K), and *N*-alkyldithiocarbamates, A[S$_2$CNHR] (R = Me or Et; A = Na or K), yielding [(π-allyl)Mo(CO)$_2$(bipy)(L$_2$)] (L$_2$ = S$_2$COR or S$_2$CNHR). Monodentate coordination of the sulfur ligand was deduced from spectral data. The reactions of [(π-allyl)Mo(CO)$_2$(bipy)Br] with [S$_2$CNHMe]$^-$ and [S$_2$COMe]$^-$ gave the same products in the presence of pyridine [396].

Stable molybdenum carbonyl complexes of sulfur ylide ligands 1-alkyl-3,5-diphenylthiabenzene-1-oxides of the form [(π-C$_5$H$_3$Ph$_2$S(O)R)Mo(CO)$_3$], **(20)**, can be isolated when the R substituents are bulky electron releasing groups such as CH(CH$_2$Ph)$_2$ or CH(SiMe$_3$)$_2$ [397].



(**20**; R = CH(CH$_2$Ph)$_2$ or CH(SiMe$_3$)$_2$)

The photochemical reaction of [Mo(CO)$_6$] with 3-*t*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene yields [Mo(CO)$_5${F$_2$SiC(CMe$_3$)CHSiF$_2$}]. A crystal structure determination has shown the molybdenum to be seven coordinate, with a strained five-membered molybdodisilabutene ring in which there may be some direct silicon-silicon transannular interaction [398].

The nucleophilic attack of [Mo(CO)$_5$]$^{2-}$ on the imminium ion [Ph$_2$C=NMe$_2$]$^+$, followed by protonation yields the alkylidene complex [Mo(CO)$_5$(CPh$_2$)], which has been spectroscopically characterised [399]. The crystal structure has been reported of *trans*-[Mo(CO)$_4${CN(Me)CH$_2$CH$_2$NMe}$_2$], which contains two cyclic alkylidene ligands. A kinetic study of the *cis-trans* isomerisation was made using differential scanning calorimetry [400].

The crystal structure of $[Mo(CO)_3(C_6Et_6)]$ showed the ethyl groups to project alternately above and below the plane of the benzene ring, with the three ethyl groups which project away from the molybdenum eclipsed by the carbonyl groups. Dynamic NMR spectroscopy was used to determine the barrier to site exchange of the ethyl groups [401]. The IR spectrum of $[Mo(CO)_5(mch)]$ (mch = methylcyclohexane) has been reported, and compared with the solution IR spectrum in CH_2Cl_2 in which the dichloromethane replaces the alkane [402].

Extended Hückel calculations have been used to derive molecular orbital descriptions of six types of monomeric molybdenum carbonyl complexes, $[(\eta^5\text{-}C_5H_5)Mo(CO)(RCCR)(R')]$, $[Mo(CO)(RCCR)(S_2CNR'_2)]$, $[Mo(O)(RCCR)(S_2CNR'_2)_2]$, $[Mo(RCCR)_2(S_2CNR'_2)_2]$, $[Mo(CO)_2(OR)_2L_2]$ and $[Mo(CO)_2(S_2CNR'_2)_2]$. Each of these compounds is formally electron deficient, and is stabilised by π-donation which raises the energy of the LUMO which would be filled if the compounds obeyed the inert gas formalism [403].

The reaction $[Mo(CO)_6]$ with sulfur or selenium and Br_2 or I_2 in boiling benzene gives MoS_4I_2, MoS_4Br_2 and $MoSe_4Br_2$, identified by analysis and IR spectroscopy. When MoS_4I_2 was heated in air, it decomposed stepwise to give MoO_3. MoS_4Br_2 and $MoSe_4Br_2$ were converted to $Mo_3S_7Br_4$ and $Mo_3Se_7Br_4$ by heating under vacuum in sealed ampoules [404].

Neutron and gamma-ray bombardment of $[^{98}Mo(CO)_6]$ produces $[^{99}Mo(CO)_6]$, which is radioactive and decomposes to form the technetium complexes $[^{99m}Tc(CO)_5]\cdot$, $[^{99m}Tc_2(CO)_{10}]$ and $^{99m}Tc^{n+}$, depending on whether the reaction takes place in the solid or in the pentane solution [405].

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