



Molybdenum 1996

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1. Introduction

This review surveys the coordination chemistry of molybdenum reported in 1996, and follows the same format as those which covered 1994 and 1995 [1,2]. The references have been located by a search of volumes 124, 125 and 126 of Chemical Abstracts, together with use of the Current Contents and BIDS databases; in addition, all the major inorganic chemistry journals have been examined individually. Where appropriate, late references from 1995 have also been included. The review is restricted to coordination complexes, including carbonyls but excluding organo-metallic compounds and solid-state chemistry. Synthetic models of Mo centres and clusters in biological systems are covered, but biochemical studies of the enzymes themselves are not. A thematic issue of Chemical Reviews dedicated to bioinorganic enzymology provides a useful overview of the current state of molybdoenzyme chemistry, including articles on nitrogenase [3] and its crystal structure [4], alternative nitrogenases [5], and on mononuclear molybdenum enzymes [6] and their newer tungsten counterparts [7]. These articles include details of important recent advances in the crystallography of oxomolybdoenzymes, including the solution of the crystal structure of the dmsO reductase enzyme from *Rhodobacter sphaeroides*, which revealed that two pterin ligands are coordinated to the molybdenum centre through dithiolene linkages [8]. This ties in with an EXAFS study of the same enzyme which showed that in the oxidized form the molybdenum is coordinated by four sulfur atoms, one oxo group and a further N or O donor [9].

Two further reviews deal with the structure and mode of action of the oxomolybdoenzymes with emphasis on the pterin fragment [10] and the chemistry of the oxomolybdenum centre [11]. Three further accounts of the use of molecular complexes in modelling and understanding nitrogenase have also appeared [12–14].

The book "Transition Metal Sulfur Chemistry: Biological and Industrial Significance", edited by Stiefel and Matsumoto, contains much pertinent material [15]. Arising from a symposium in Hawaii in December 1995, it contains an overview [15a], followed by relevant chapters on the reduction of hydrazine and acetylene by MoFe_3 cubane clusters [15b], hydrodesulfurisation catalysts and model MoCo clusters [15c], C–S bond making and breaking reactions in molybdenum and tungsten complexes [15d,15e], incorporation of heterometals into the incomplete $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ cubane [15f,15g], raft type molybdenum chalcogenide clusters [15h], the chemistry of dinuclear cyclopentadienyl molybdenum complexes with bridging sulfur ligands [15i], and heterometallic Cu/Ag Mo/W clusters [15j]. A separate general article by Stiefel deals with the importance of molybdenum–sulfur chemistry in geology, biology and technology [16].

Other reviews published this year include further articles on the chalcogenide clusters of the Group 6 metals and Re [17] and on Cu/Ag Mo/W clusters [18], a review of mixed octahedral complexes and clusters including some related to $[\text{Mo}_6\text{Cl}_{14}]^{2-}$ [19], and a comprehensive account of halocarbonyl complexes of Mo(II) and W(II) [20]. The coordination chemistry of the Group 6 metals in 1995 has been reviewed in an annual report [21]. Some relevant material can also be

found in reviews on metal sulfoxide complexes [22], metal oxoalkoxides [23], complexes of heterocyclic thionates [24], alkanes [25] and CO_2 [26], and the theoretical relationship between metal–metal distance and force constants in homodinuclear complexes [27]. An analysis of the MAM' angle in 283 compounds of the type $\text{L}_m\text{M}(\mu\text{-A})\text{M}'\text{L}_n$, where M and M' are d- or f-block metals and A is a p-block element, includes many oxo-bridged Mo(V) dimers, which are usually linear in form [28].

2. Molybdenum(VI)

2.1. Complexes with halide ligands

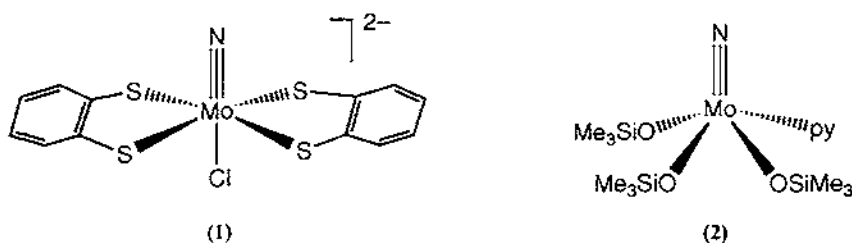
The second virial coefficient and viscosity of gaseous MoF_6 have been measured [29]. Theoretical ab initio calculations have been carried out to explain the fact that $[\text{MoF}_7]^-$ and $[\text{WF}_7]^-$ adopt capped octahedral structures whereas $[\text{TeF}_7]^-$, IF_7 and $[\text{XeF}_7]^-$ all prefer a pentagonal bipyramidal geometry. In fact, for $[\text{MoF}_7]^-$ the capped octahedral and capped trigonal prismatic structures are of approximately the same energy [30].

2.2. Complexes with nitrogen donor ligands

Electrochemical studies of a number of high oxidation state molybdenum complexes have shown that $[\text{Mo}(\equiv\text{N})\text{Cl}_4]^-$ was the most stable of those studied, followed in order by $[\text{MoCl}_3(\text{NPPH}_2\text{NPPH}_2\text{N})]$, $[\text{MoCl}_4(\text{NSNSN})]^-$, $[\text{MoOCl}_5]^{2-}$, $[\text{MoF}_6]^-$ and $[\text{MoCl}_6]^-$. The geometries of these d^1 and d^0 species and the trends in their redox properties were successfully reproduced by theoretical studies [31]. The reaction of $[\text{NEt}_4][\text{Mo}(\equiv\text{N})\text{Cl}_4]$ with two equivalents of $\text{Li}_2(\text{SC}_6\text{H}_4\text{S})$ gave $[\text{NEt}_4]_2[\text{Mo}(\equiv\text{N})(\text{SC}_6\text{H}_4\text{S})_2\text{Cl}]$ (1). This compound is much more air- and water-sensitive than the starting halide and reacts rapidly with O_2 or H_2O to afford $[\text{MoO}(\text{SC}_6\text{H}_4\text{S})_2]^{2-}$. The lower $\text{Mo}=\text{N}$ stretching frequency (1010 cm^{-1}) and an upfield shift in the ^{14}N NMR spectroscopic signal both suggest that π -donation from the thiolate ligands is competing with that from the nitrido group [32]. The reaction of $[\text{Mo}(\equiv\text{N})\text{Cl}_3]$ with $\text{Me}_3\text{SiN}=\text{PMe}_3$ gave the homoleptic phosphiniminate complex $[\text{Mo}(\text{NPM}_3)_4][\text{Cl}]_2$, an unusual example of a dicationic, tetrahedral Mo(VI) species [33]. Fluorination of $[\text{Mo}(\equiv\text{N})\text{Cl}_3]$ with elemental F_2 afforded $[\text{Mo}(\equiv\text{NCl})\text{F}_4]$ which coordinates thf to give $[\text{Mo}(\equiv\text{NCl})\text{F}_4(\text{thf})]$ and then slowly converts into $[\text{MoO}_2\text{F}_2(\text{thf})_2]$; the X-ray structure of this compound revealed a *trans* disposition of the fluoride ligands [34].

The complex $[\text{MoO}_2\text{Cl}_2(\text{dme})]$, prepared in situ by reaction of Na_2MoO_4 with Me_3SiCl in dme, reacted with hexamethyldisilazane to give an unidentified material which on treatment with pyridine produced $[\text{Mo}(\equiv\text{N})(\text{OSiMe}_3)_3(\text{py})]$ (2). The crystal structure showed a monomeric square-based pyramidal structure with an

Mo≡N distance of 1.627 Å [35]. A molecularly defined alkene metathesis catalyst has been prepared from $[\text{Mo}(=\text{N})(\text{CH}_2^t\text{Bu})_3]$ by grafting onto a silica support. In reactions designed to model its interaction with the support, treatment of the complex with the disilanol $\text{HOSiPh}_2\text{OSiPh}_2\text{OH}$ afforded the imido species $[(\text{HN}=\text{})\text{Mo}(\text{CH}_2^t\text{Bu})_3(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{O})\text{Mo}(\text{CH}_2^t\text{Bu})_3(=\text{NH})]$ [36].



The reaction of $[\text{Mo}(=\text{N})(\text{O}^t\text{Bu})_3]$ with $[\text{Ti}(\text{N}(\text{R})\text{Ar})_3]$ ($\text{R}=\text{C}(\text{CD}_3)_2\text{Me}$, $\text{Ar}=3,5\text{-C}_6\text{H}_3\text{Me}_2$), gave an unstable intermediate thought to be $[(^t\text{BuO})_3\text{Mo}(\mu\text{-N})\text{Ti}(\text{N}(\text{R})\text{Ar})_3]$, which rearranges by loss of ^tBu radical in a first order process to give $[(\text{N}=\text{})\text{Mo}(\text{O}^t\text{Bu})_2(\mu\text{-O})\text{Ti}(\text{N}(\text{R})\text{Ar})_3]$. The product reacts with more $[\text{Ti}(\text{N}(\text{R})\text{Ar})_3]$ in the same way, via a second observable intermediate, to give the final product $[(\text{N}=\text{})\text{Mo}(\text{O}^t\text{Bu})\{(\mu\text{-O})\text{Ti}(\text{N}(\text{R})\text{Ar})_3\}_2]$. A similar reaction occurs between $[\text{MoO}_2(\text{O}^t\text{Bu})_2]$ and $[\text{Ti}(\text{N}(\text{Ph}^t\text{Bu})_3)]$ to give $[\text{MoO}_2\{(\mu\text{-O})\text{Ti}(\text{N}(\text{Ph}^t\text{Bu})_3)_2\}]$, whereas in contrast the related μ -nitrido complex $[(\text{Me}_2\text{N})_3\text{Mo}(\mu\text{-N})\text{Ti}(\text{N}(\text{Ph}^t\text{Bu})_3)]$ is stable [37].

The ^{31}P NMR chemical shielding tensors for the terminal phosphide complexes $[\text{Mo}(=\text{P})(\text{N}(\text{R})\text{Ar})_3]$ (R^tBu , $\text{Ar}=\text{Ph}$, $3,5\text{-C}_6\text{H}_3\text{Me}_2$) and $[\text{Mo}(=\text{P})\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3\}]$ have been measured from solid state MAS spectra. The chemical shift occurs at over 1000 ppm and the anisotropy is over 2000 ppm, one of the largest ever. These effects arise through paramagnetic shielding in directions perpendicular to the $\text{Mo}=\text{P}$ bond [38]. The Raman spectra of $[\text{M}(=\text{E})\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3\}]$ ($\text{M}=\text{Mo}$, W ; $\text{E}=\text{P}$, As) have been measured with the peaks due to $\text{Mo}=\text{E}$ being assigned as 521 and 374 cm^{-1} for P and As respectively. The force constants for Mo are slightly larger than those for W [39].

The readily available complexes $[\text{Mo}(\text{NR})_2\text{Cl}_2(\text{dme})]$ continue to provide a convenient entry into $\text{Mo}(\text{VI})$ imido chemistry. The reaction of Na_2MoO_4 with Me_3SiCl and a mixture of $^t\text{BuNH}_2$ and 2,6-diisopropylaniline gave the mixed imido complex $[\text{Mo}(\text{N}^t\text{Bu})(\text{N}(\text{Ar})\text{Cl}_2(\text{dme}))]$ [40]. However, with very bulky amines the bis-imido product is not formed; thus adamantylamine gave $[\text{Mo}(\text{O})(\text{NAd})\text{Cl}_2(\text{dme})]$ [40] and the corresponding mono-imido complex was produced from 2,4,6-triphenylaniline [41]; both of these compounds were structurally characterised. Reaction of $[\text{Mo}(\text{N}^t\text{Bu})_2\text{Cl}_2]$ with LiN^tBuSPh afforded $[\text{Mo}(\text{N}^t\text{Bu})_2\{\text{N}^t\text{BuSPh}\}_2]$; the corresponding dioxo species was prepared from $[\text{MoO}_2\text{Cl}_2(\text{dme})]$ [42].

The diamines 2,2'-H₂NC₆H₄(CH₂)_nC₆H₄NH₂ (*n*=1 or 2) have been used to make complexes with chelating bis-imido ligands. In the case of the *p*-substituted diamine CH₂{C₆H₂-3,5-ⁱPr₂-4-NH₂}₂, dinuclear [(dme)Cl₂Mo{μH=NC₆H₂ⁱPr₂CH₂C₆H₂ⁱPr₂N=}₂MoCl₂(dme)] was formed [43]. The complex [LMo(NAr)₂], where L=NC₅H₃-2,6-(CH₂CPh₂O)₂²⁻ and Ar=C₆H₃-2,6-ⁱPr₂ contains one linear and one bent imido group (Mo–N–Ar angle 144.8°); comparison with the corresponding alkylidene complex supports the view that this nitrogen is sp² hybridised [44].

Two routes to the complexes [(HBpz³)MoO₂(S₂PR₂)] (R=Me, Et, ⁱPr, Ph) have been described: reaction of [(HBpz³)MoO₂(Cl)] with the NaS₂PR₂ or oxidation of the Mo(IV) complexes [(HBpz³)MoO(S₂PR₂)] (q.v.) [45]. Further details on the extensive interconversions of Mo(IV), Mo(V) and Mo(VI) tris-pyrazolylborate complexes can be found in Sections 3.2 and 4.2.

2.3. Complexes with oxygen donor ligands

The structures of [MoO₄]²⁻, [HMoO₄]⁻ and [H₂MoO₄] in aqueous solution have been modelled by DV-Xα calculations, giving good agreement with their observed UV-visible spectra. It was proposed that the first two species are tetrahedral but the last is octahedral and is the key species in molybdate build-up reactions; a sequence of changes from [H₂MoO₄] to [H₂MoO₄]·2H₂O to [Mo(OH)₆] was suggested [46]. The ⁹⁵Mo NMR spectra of [MoO_nS_{4-n}]²⁻ⁿ⁻ (*n*=0–4) has been modelled theoretically by semi-empirical, CNDO and ab initio methods; the calculated values agree well with the observed ones when p- and d-orbital electron populations are taken into account [47]. The relationship between the ⁹⁵Mo chemical shift in *cis*-dioxo Mo(VI) species and their oxygen atom transfer capability has also been examined [48].

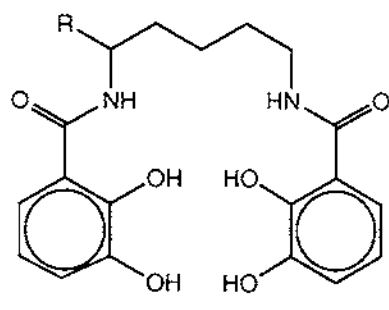
Complex formation between molybdate (or tungstate) and D-galacturonic acid or D-glucuronic acid in aqueous solution has been studied by NMR spectroscopic methods; evidence for complexes with 1:2 and 2:1 stoichiometry was obtained, with the latter species thought to play an important role in the oxidation of these acids by Mo(VI) [49]. The formation of dinuclear complexes of molybdate with D-fructose, L-sorbose and D-glycero-L-mannoheptose has also been studied by multinuclear NMR spectroscopy [50,51]. The ¹H and ¹³C NMR spectra of dinuclear complexes of molybdate with EDTA and with EGTA [3,12-bis(carboxymethyl)-6,9-dioxo-3,12-diazatetradecanedioic acid] have been recorded at various temperatures [52]. The interaction of [MoO₄]²⁻ with the enzyme purple acid phosphatase has been examined over a range of pH conditions. Similar experiments with [WO₄]²⁻, [VO₄]³⁻ and [AsO₄]³⁻ were undertaken, and showed that the rates are independent of the concentration of oxoanion, suggesting that loss of water from the Fe(III) centre in the enzyme may be the rate determining step [53].

The kinetics of the formation of the known complex [(H₃N)₅CoOMoO₃][ClO₄] from [Co(NH₃)₅(H₂O)]³⁺ and molybdate have been studied by stopped flow methods and are consistent with a mechanism involving substitution at Mo

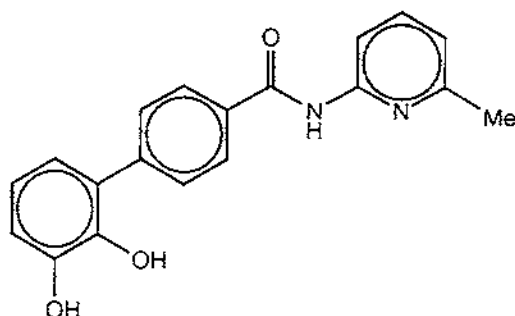
rather than at Co [54]. The complex $[\text{LCr}(\mu\text{-O})(\mu\text{-MoO}_4)\text{CrL}][\text{ClO}_4]_2$, where $\text{L} = \text{tris}(2\text{-pyridylmethyl})\text{amine}$, has been prepared from molybdate and $[\{\text{LCr}(\text{OH})_2\}_2]$ and characterised by electronic spectra and electrochemistry [55]. A similar reaction between molybdate and $[\text{Cu}(\text{acpa})]^+$ [$\text{Hacpa} = \text{N}-(1\text{-acetyl-2-propylidene})(2\text{-pyridylmethyl})\text{amine}$] afforded $[\{\text{Cu}(\text{acpa})\}_2(\mu\text{-MoO}_4)] \cdot 4\text{H}_2\text{O}$ in which the copper atoms are antiferromagnetically coupled with $2J = -5.1 \text{ cm}^{-1}$; the analogous compound with a $\mu\text{-CrO}_4$ unit exhibited ferromagnetic coupling [56,57]. A large number of double salts of the type $[\text{M}^1\text{M}^2\{\text{MoO}_4\}_2]$, where M^1 = a monovalent cation such as NH_4^+ and M^2 = a trivalent cation such as a rare earth, Fe, In, Bi, Cr, etc., have been prepared by interaction of ammonium molybdate with M^2 acetate [58–61].

A system for the aerobic hydroxylation of benzene to phenols using Fe(II) and Mo(VI) has been described [62]. The reduction of hydroxyiminophosphonates to 1-aminophosphonates has been accomplished with NaBH_4 in the presence of MoO_3 [63]. Reduction of potassium molybdate with aqueous KBH_4 at room temperature gave a variety of lower valent oxides such as MoO_2 and Mo_4O_{11} , as well as nonstoichiometric bronzes K_xMoO_3 [64].

The catecholate ligand $\text{N,N}'\text{-bis}(2,3\text{-hydroxybenzoyl})\text{-1,5-diaminopentane}$ (H_4L ; **3**; $\text{R} = \text{H}$), which is an analogue of a naturally occurring siderophore from *A. vinelandii* (**3**; $\text{R} = \text{COOH}$), reacted with $[\text{MoO}_4]^{2-}$ to give $[\{\text{MoO}_2(\text{L})\}_2]^{4-}$ which has a double helical structure [65]. A study of the solubilisation of Fe(III) hydroxide by the siderophore in the presence of stoichiometric amounts of molybdate also revealed the instantaneous formation of such a complex, with a consequent slowing of the iron dissolution [66].



(3)



(4)

Coordination of two of the catecholate ligands (**4**) to a MoO_2 unit to give $[\text{MoO}_2\text{L}_2]^{2-}$ produced a species which can act as a receptor for dicarboxylic acids [67]. Dinuclear complexes of the type $[\text{Mo}_2\text{O}_5(\text{cat})_2]^{2-}$ containing two co-facially oriented catecholate groups have been prepared by a new route from $[\text{Mo}_2\text{O}_7]^{2-}$; this has been applied to elaborate catechols which incorporate secondary metal binding sites as well as simpler species such as the Cl_4cat ligand ($\text{HOC}_6\text{Cl}_4\text{OH}$). The weak intramolecular coordination of the Cl_4cat ligands can be released by

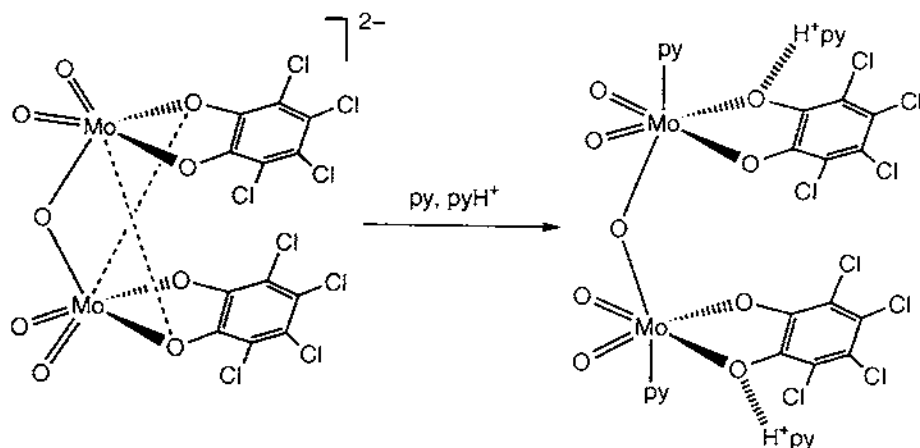
addition of py and pyH^+ , which results in an opening up of the central MoOMo angle to give $[\text{pyH}]_2[\text{Mo}_2\text{O}_5(\text{py})_2(\text{Cl}_4\text{cat})_2]$, as shown in Scheme 1 [68].

The (*R*)- and (*S*)-isomers of 2-diphenylphosphinoyl-2'-hydroxy-1,1'-binaphthalene, abbreviated as Hbinappo, have been prepared. Reaction with $[\text{MoO}_2(\text{acac})_2]$ gave $[\text{MoO}_2(\text{acac})(\text{binappo})]$, whereas with $[\text{MoO}_2\text{Cl}_2]$ in the presence of TIOEt, the disubstituted $[\text{MoO}_2(\text{binappo})_2]$ was produced [69]. The crystal structure of a 3:1 disordered solid solution of $[\text{Mo}_2\text{O}_2(\text{OMe})_8]$ and $[\text{Mo}_2\text{O}_2(\text{OMe})_6\text{Cl}_2]$ has been determined [70]. The photochemistry of the complex $[\text{MoO}(\text{L})]$, where H_4L = tetrakis-(phenyldiazanyl)calix-4-arene, has been studied by extended Hückel calculations and spectroscopy; the lowest energy excited states involve the azobenzene moieties [71].

The synthesis of 2-(diphenylphosphinoyl)propanoic acid, $\text{Ph}_2\text{P}(=\text{O})\text{CHMeCOOH}$, and its coordination to a number of metals have been described; in the case of molybdenum, reaction of $[\text{MoO}_2\text{Cl}_2]$ with the thallium salt gave $[\text{MoO}_2\text{L}_2]$ [72]. The related enantiomerically pure chiral alcohols (1*S*)-2-(diphenylphosphoryl)-1-methylethanol, $\text{Ph}_2\text{P}(=\text{O})\text{CH}_2\text{CHMeOH}$, and (1*R*)-2-(diphenylphosphoryl)-1-phenylethanol, $\text{Ph}_2\text{P}(=\text{O})\text{CH}_2\text{CHPhOH}$, have been prepared; reaction with $[\text{MoO}_2(\text{acac})_2]$ gave $[\text{MoO}_2(\text{acac})(\text{L})]$ or $[\text{MoO}_2\text{L}_2]$ depending on the stoichiometry used [73].

The catalytic oxidation of alcohols to carbonyl compounds by an oxygen atom transfer reaction from dmsO or Ph_2SO using $[\text{MoO}_2(\text{acac})_2]$ as catalyst has been reported [74], and the same catalyst system has been used for the Meyer-Schuster rearrangement of α -acetylenic alcohols to α,β -unsaturated carbonyl compounds [75].

Much effort continues to be devoted to the investigation and application of molybdenum complexes, especially peroxo species, in oxidation reaction. The oxidation of organic compounds with H_2O_2 catalysed by peroxo complexes of Mo, W and V has been reviewed [76]. Alcohol oxidation by sodium perborate or sodium percarbonate and $[\text{MoO}_2(\text{acac})_2]$ has been described [77], and the oxidation of



Scheme 1.

aniline to azobenzene by H_2O_2 can also be catalysed by Mo(VI) species [78]. The bromination of alkenes and aromatics can be achieved with a system consisting of H_2O_2 , KBr, and Na_2MoO_4 or NH_4VO_3 in a two-phase water–chloroform mixture [79]. The kinetics of the oxidation of the anthocyanidin colouring agent malvin chloride by H_2O_2 have been studied; bleaching was found to be catalysed by Mo(VI) species such as $[\text{MoO}(\text{O}_2)_2(\text{C}_5\text{H}_5\text{NO})_2]$ [80].

The ^{17}O NMR spectra of a range of peroxo and diperoxo complexes have been recorded and the chemical shifts correlated with $\nu(\text{O}-\text{O})$ and the O–O bond length. Monoperoxo complexes have chemical shifts in the range 500–660 ppm, with the IR frequency at $>900\text{ cm}^{-1}$ and a bond length of 1.43–1.46 Å, whereas the corresponding values for diperoxo complexes are 350–460 ppm, $<900\text{ cm}^{-1}$ and 1.46–1.53 Å [81]. Molybdenum peroxo complexes, particularly $[\text{MoO}(\text{O}_2)(\text{dipic})(\text{hmpa})]$ ($\text{H}_2\text{dipic} = 2,6\text{-dipicolinic acid}$) have been used to catalyse allylic amination by aryl amines in the presence of tBuOOH . The first stage in this reaction involves formation of the aryl nitroso compound (which can be trapped by the addition of 2,3-dimethylbutadiene); this adds to the alkene to give an N-allylhydroxylamine, which is reduced to the N-allylamine, possibly by a Mo(IV) species [82]. The same $[\text{MoO}(\text{O}_2)(\text{dipic})(\text{hmpa})]$ complex catalyses the formation of oxazines (hetero Diels–Alder adducts of aryl nitroso compounds with dienes) from aromatic amines, H_2O_2 , and the diene [83]. A study of the oxidation of aryl amines to nitro compounds with H_2O_2 showed that yields were better with $[\text{MoO}(\text{O}_2)_2(\text{hmpa})(\text{H}_2\text{O})]$ than with Fe or Mn porphyrin complexes [84]. Oxidation of N,N-benzylalkylamines to nitrones has been carried out with the Mo(VI) and W(VI) polyperoxo complexes $[\text{PO}_4\{\text{M}(\text{O})(\text{O}_2)_2\}_4]^{3-}$; the intermediacy of a hydroxylamine was again suggested [85].

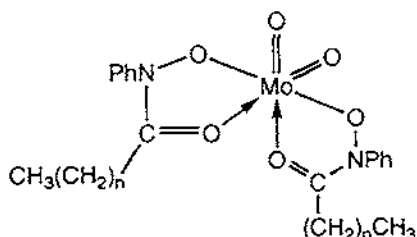
In the reaction of $[\text{MoO}(\text{O}_2)_2(\text{L}-\text{L})]$ ($\text{L}-\text{L} = \text{N-octyl-3-pyrazolylpyridine}$) with strong Brønsted acids such as $\text{CF}_3\text{CO}_2\text{H}$, NMR spectroscopic studies have shown that protonation occurs at a peroxo ligand and not on the terminal oxo group, a result backed up by extended Hückel calculations [86]. The reaction of $[\text{MoO}(\text{O}_2)_2(\text{hmpa})]$ with dialkyl tartrates produced complexes of the type $[\text{Mo}_4\text{O}_{14}(\text{O}_2)_8(\text{hmpa})_4(\text{L})]$, or in the case of N,N-dibenzyltartramide $[\text{Mo}_2\text{O}_7(\text{O}_2)_4(\text{hmpa})_2(\text{L})]$. The different diastereomers of 1-benzyl-3,4-dihydroxy-2,5-pyrrolidine diol gave either dinuclear or tetranuclear species [87]. A key step in the total synthesis of (\pm)-mitomycin K involved the oxidation of a double bond in mitosene with $[\text{MoO}(\text{O}_2)_2(\text{hmpa})]$ [88]. The sulfoxidation of thianthrene-5-oxide by $\text{Me}_3\text{SiOOSiMe}_3$ has been studied with a range of Mo, W and V catalysts, the most effective being $[\text{MoO}(\text{O}_2)_2(\text{OP}^t\text{Bu}_3)]$ [89]. Treatment of $[\text{MoO}(\text{O}_2)_2(\text{hmpa})]$ with $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{NH}_2$ (L) gave $[\text{MoO}_2(\text{O}_2)(\text{L})]$ which was characterised by thermal analysis [90]. Peroxo complexes of the type $[\text{MoO}_2(\text{O}_2)(\text{L})]$ have been prepared from tetraazamacrocyclic ligands such as 1,4,8,12-tetraazacyclopentadecane [91].

Chiral β -hydroxyphosphoryl ligands derived from camphor have been prepared and used to make complexes of the type $[\text{MoO}(\text{O}_2)_2(\text{L})(\text{H}_2\text{O})]$ [92]. The reaction of MoO_3 with glycylglycine or aspartic acid (H_2L) in aqueous H_2O_2 gave complexes of the type $[\text{MoO}(\text{O}_2)_2(\text{H}_2\text{L})(\text{H}_2\text{O})]$; if copper powder was included dimetallic

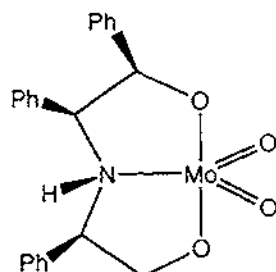
species could be isolated [93]. The complex $[\text{MoO}(\text{O}_2)(\text{L})_2]$, where $\text{HL} = 2$ -(2-hydroxyphenyl)benzimidazole, has been prepared from MoO_3 , H_2O_2 and the ligand; the species $[\text{MoO}_2\text{L}_2]$ and $[\text{MoOL}_2]$ were also made [94].

The X-ray structures of $[\text{NMe}_4][(\text{R}_2\text{EO}_2)\{\text{MoO}(\text{O}_2)_2\}_2]$, where $\text{E} = \text{As}$, $\text{R} = \text{Me}$ and $\text{E} = \text{P}$, $\text{R} = \text{Ph}$ have been determined; both contain peroxo groups which act as bridging ligands by coordinating to the axial site of the other molybdenum of the dimeric unit. The structure of $[\text{NH}_4][(\text{Ph}_2\text{PO}_2)\{\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})\}]$ is similar, with the water occupying the axial site [95]. The related sulfate species $[\text{NBu}_4]_2[(\text{SO}_4)\{\text{MoO}(\text{O}_2)_2\}_2]$ was formed from molybdate and sulfate in the presence of H_2O_2 and structurally characterised [96]. A compound of the formula $[\text{NMe}_4]_3[\text{H}(\text{SO}_4)_2\{\text{MoO}_2(\text{O}_2)\}_3] \cdot 3\text{H}_2\text{O}$ was isolated from the reaction of strongly acidic molybdate solution with sulfate [97]. The structure of $\text{K}_4[\text{Mo}_3\text{O}_7(\text{O}_2)_4] \cdot 2\text{H}_2\text{O}$ has also been determined [98].

Complexation reactions between N-arylmonohydroxamic acids $\text{CH}_3(\text{CH}_2)_n\text{CON}(\text{R})\text{OH}$ (H_2L^1 : $\text{R} = \text{Ph}$, $n = 4-6, 8$; $\text{R} = p\text{-tol}$, $n = 5$) and $[\text{NH}_4]_2[\text{MoOCl}_5]$ or Na_2MoO_4 gave species of the type $[\text{MoO}_2(\text{L}^1)_2]$ (5); the crystal structures of those with $\text{R} = \text{Ph}$ and $n = 4$ and 5 were determined. Similar reactions employing dihydroxamic acids $\text{HON}(\text{R})\text{CO}(\text{CH}_2)_n\text{CON}(\text{R})\text{OH}$ (H_2L^2 : $\text{R} = \text{Ph}$ or $p\text{-tol}$, $n = 2-4, 7$; $\text{R} = p\text{-C}_6\text{H}_4\text{Et}$, $n = 5$) gave analogous compounds $[\text{MoO}_2\text{L}^2]$ [99]. The ligand $\text{HOCH}_2\text{-(R)-CHPhNH-(S)-CHPh-(R)-CHPhOH}$ (H_2L), prepared by reaction of (*R*)-phenylglycinol and *rac-trans*-stilbene oxide, has been complexed to molybdenum in the form of $[\text{LMoO}_2]$ (6); the absolute stereochemistry was established by NOESY NMR spectroscopic studies and crystal structure analysis. The solid state structure is polymeric with one $\text{Mo}=\text{O}$ group coordinated to the neighbouring molecule [100]. A related ligand has been prepared by the reaction of (*R*)-phenylglycinol with cyclohexene oxide and separated from its diastereomer by crystallisation; the $[\text{LMoO}_2]$ complex was again synthesized [101]. The UV stabilizer Tinuvin P, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, has been used as a didentate monoanionic ligand in a complex of the type $[\text{MoO}_2(\text{acac})(\text{L})]$ [102]. The crystal structure of *cis*- $[\text{MoO}_2\text{L}_2]$, where $\text{HL} = 2$ -methyl-8-hydroxyquinoline, has been determined [103]. The reaction of $[\text{MoO}_2(\text{acac})_2]$ with PhRRNNH_2 ($\text{R} = \text{Ph}$, Me) gave $[\text{Mo}(\text{NNRPh})_2(\text{acac})_2]$, both of which were shown to have linear hydrazido groups by crystallography [104].



(5)



(6)

Treatment of $[\text{MoO}_2(\text{acac})_2]$ with 1,1-dimethyl-1-(2-pyridyl)-methanol produced $[\text{MoO}_2(\text{NC}_5\text{H}_4\text{CMe}_2\text{O})_2]$ which selectively catalyses alkene epoxidation with air [105]. Chiral diol ligands derived from (2*S*,4*R*)-4-hydroxyproline have been complexed to Mo(VI) centres and in some cases grafted to zeolites, then used for the epoxidation of allylic alkenes with $^t\text{BuOOH}$ [106]. Complexation of $[\text{MoO}_2(\text{acac})_2]$ by a triazole unit bonded to a polyimide support in the form of spherical particles gave a catalyst which was active for the epoxidation of cyclohexene by $^t\text{BuOOH}$ with good activity and recycling properties [107]. A short review of alkene epoxidation with Mo(VI) peroxo species has appeared [108].

A theoretical study of the oxygen atom transfer reaction between $[\text{MoO}_2(\text{SH})_2(\text{NH}_3)_2]$ and PMe_3 has proposed that the substrate approaches the *cis*- MoO_2 unit from a perpendicular direction and rotates to be in the plane in the $\text{MoO}(\text{OPMe}_3)$ grouping of the product. This direction of attack leaves two electrons in an orbital which is of δ symmetry with respect to the remaining $\text{Mo}=\text{O}$ group, allowing further overlap to form a $\text{Mo}\equiv\text{O}$ unit which is not possible in the original *cis*-dioxo arrangement. Displacement of the $\text{O}=\text{PMe}_3$ by H_2O is followed by reaction with further starting material to give a Mo(V) species which is reoxidized by O_2 to complete the model catalytic cycle [109]. The structure of the thiobenzilate complex $[\text{MoO}_2(\text{O}_2\text{CCPh}_2\text{S})_2]^{2-}$ intercalated into a Zn(II)–Al(III) double hydroxide host has been studied by XANES and EXAFS methods, which reveals that it changes to a novel structure with three $\text{Mo}=\text{O}$ groups, a coordinated water molecule, and the thiobenzilate ligands bonded in a monodentate fashion through the sulfur atom [110].

The reaction of $[\text{MoO}_2(\text{NCS})_4]^{2-}$ with bpy afforded initially $[\text{MoO}_2(\text{NCS})_2(\text{bpy})]$, but this was unstable and underwent a redistribution reaction to give $\{[\text{MoO}_2(\text{NCS})(\text{bpy})]_2(\mu\text{-O})\}$ and $[\text{MoO}(\text{NCS})_4(\text{bpy})]$. Increasing the steric bulk of the bipyridyl ligand by employing 4,4'-di- ^tBu -bpy stops the reaction at the first stage, and $[\text{MoO}_2(\text{NCS})_2(4,4\text{'-di-}^t\text{Bu-bpy})]$ is an extremely active oxygen transfer catalyst [111]. The synthesis of some Mo(VI) and Mo(V) complexes of α -nitroso- β -naphthol, including $[\text{MoO}_2(\text{L})_2(\text{NCS})(\text{Cl})]$ and $[\text{MoO}(\text{L})_2(\text{NCS})_2(\text{Cl})]$, has been described [112].

A theoretical study of the topology of the electron density distribution in various halides and oxyhalides which do not possess the structure expected by VSEPR, including square pyramidal $[\text{MoOF}_4]$, has attributed these variations to the non-spherical nature of the electron cloud [113]. Several papers have appeared on the electronic structure and thermal stability of oxohalides of Mo and W compared to those of element 106, seaborgium [114–116]. A density functional theory investigation of the activation of C–H or O–H bonds in MeOH by a variety of d^0 metal complexes, including $[\text{MoO}_2\text{Cl}_2]$, has appeared. Geometries were optimised for the possible products including $[\text{M}(\text{O})\text{Cl}_2(\text{OH})]$, $[\text{M}(\text{O})\text{Cl}_2(\text{OH})(\text{OMe})]$ and $[\text{M}(\text{O})\text{Cl}_2(\text{OH})(\text{CH}_2\text{OH})]$; the oxidative addition of O–H was found to be more favourable than that of C–H or H-abstraction by the $\text{M}=\text{O}$ unit [117]. Treatment of $[\text{MoO}_2\text{Cl}_2]$ with the free stable carbene 1,3-dimethylimidazoline-2-ylidene gave $[\text{MoO}_2(\text{Cl})(\text{L})_3][\text{Cl}]$, a rare example of cationic Mo(VI) species, whereas the tungsten analogue gave $[\text{WO}_2\text{Cl}_2(\text{L})_2]$ [118]. The reaction of $[\text{MoO}_2\text{Cl}_2]$ with

diethyl (2-phenyl-2-oxoethyl)phosphonate gave $[\text{MoO}_2\text{Cl}_2(\text{L})]$ in which the β -ketophosphonate acts as a didentate ligand [119]. The ROMP polymerisation of norbornene can be catalysed by $[\text{MoO}_2\text{Br}_2(\text{bpy})]$ and by the organic derivatives $[\text{MoO}_2\text{R}_2(\text{bpy})]$ ($\text{R} = \text{Me}, \text{Et}$) in the presence of MeMgBr . The methyl complex is also a catalyst when supported on montmorillonite clays, and the polymer formed has a higher *cis*-content [120].

Numerous complexes of the MoO_2^{2+} unit containing Schiff base ligands have been prepared, mostly from $[\text{MoO}_2(\text{acac})_2]$. For uninegative ligands (from HL) they usually take the form $[\text{MoO}_2\text{L}_2]$ or $[\text{Mo}_2\text{O}_5\text{L}_2]$, and for dianionic ones (from H_2L) they tend to be $[\text{MoO}_2\text{L}(\text{S})]$, where $\text{S} = \text{solvent}$. Tetradentate ligands H_4L form dinuclear complexes. Further details of some of the compounds prepared are given in Table 1.

2.4. Complexes with sulfur donor ligands

Two methods for the deposition of MoS_2 from $[\text{MoS}_4]^{2-}$ by either acidification or cathodic electrodeposition have been described [132,133].

The unsymmetrical tris-dithiolene complexes $[\text{Mo}(\text{SCH}=\text{CRS})_3]$ ($\text{R} = \text{Ph}, p\text{-C}_6\text{H}_4\text{OMe}$) have been prepared. Solution NMR spectroscopic studies show that they retain a trigonal prismatic structure in solution and are non-rigid, with the *trans* isomer favoured. Calculations show that the rotation of one ligand is a low energy process [134]. The non-planarity of the dithiolene ligands in complexes of the type $[\text{M}(\text{S}_2\text{C}_2\text{H}_2)_3]$ can be attributed to a second-order Jahn–Teller distortion which should be greatest for d^0 species, according to Fenske–Hall calculations [135]. The electrochemical properties of $[\text{Mo}(\text{mnt})_3]^{n-}$, where $\text{mnt} = \text{S}_2\text{C}_2(\text{CN})_2$, have been examined by FTIR and potential modulation techniques for $n=0$ to the highly reduced species with $n=4$, for which the redox process is only partially reversible. A plot of $\nu(\text{CN})$ against n shows the increasing π -interaction with the ligand [136].

Three dioxo Mo(VI) complexes with dithiolene-type ligands have been prepared, structurally characterised and compared to the known $[\text{MoO}_2(\text{mnt})_2]^{2-}$. The first, $[\text{PPh}_4]_2[(\text{MoO}_2(\text{SC}_6\text{H}_4\text{S})_2)]$, has two long Mo–S bonds *trans* to the $\text{Mo}=\text{O}$ linkages and two shorter ones due to the *trans* effect of the oxo ligands; reduction with PPh_3 gave the corresponding Mo(IV) species $[\text{MoO}(\text{SC}_6\text{H}_4\text{S})_2]^{2-}$ without formation of dinuclear Mo(V) complexes. In the related $[\text{MoO}_2(\text{S}_2\text{C}_6\text{H}_3\text{-4-Me})_2]^{2-}$ and $[\text{MoO}_2(\text{S}_2\text{C}_6\text{H}_3\text{-3-SiPh}_3)_2]^{2-}$, the presence of the methyl substituent accelerates oxo transfer reactions whereas the triphenylsilyl group retards them [137].

A theoretical study of a selection of four-, five- and six-coordinate model species for the active site of xanthine oxidase has been undertaken using the local density approximation of density functional theory, with a view to determining whether a hydroxide ligand is present on the Mo centre. This is considered unlikely in four- and six-coordinate systems, but the optimised geometry of a species of the type $[\text{Mo}(\text{O})(\text{OH})(\text{S})(\text{SR})_2]^-$ gives good agreement with the observed EXAFS data [138].

Thermolysis of $[\text{MoO}_2(\text{dtc})_2]$ ($\text{dtc} = \text{S}_2\text{CNMe}_2, \text{S}_2\text{CNEt}_2$) with RNCO ($\text{R} = \text{Ph}, t\text{-Bu}, 2,6\text{-C}_6\text{H}_3\text{Pr}_2$ and others) gave moderate yields of $[\text{Mo}(\text{NR})(\text{S}_2)(\text{dtc})_2]$, which

Table 1
Dioxomolybdenum(VI) complexes with Schiff base ligands

Carbonyl compound	Amine	Complex type	Reference
Salicylaldehyde	<i>p</i> -Hydroxybenzoic hydrazide	$[\text{MoO}_2(\text{L})(\text{S})]$ where $\text{S} = \text{H}_2\text{O}, \text{MeOH}, \text{py}, \text{dmsO}, \text{dmf}$	[121]
Salicylaldehyde	Thiosemicarbazide	$[\text{MoO}_2(\text{HL})(\text{H}_2\text{O})]^+$	[122, 123]
Salicylaldehyde	S-methylisothio-semicarbazide	$[\text{MoO}_2(\text{L})(\text{MeOH})]$	[124, 125]
Salicylaldehyde	Benzimidazole-2-hydrazide	$[\text{MoO}_2(\text{L})(\text{S})]$ where $\text{S} = \text{dmf}, \text{dmsO}$	[126, 127]
α -Hydroxyacetophenone	Isonicotinamide	[not stated in abstract]	[128, 129]
2-Hydroxynaphthaldehyde	Isonicotinic hydrazide	$[\text{MoO}_2(\text{L}) \cdot 2\text{H}_2\text{O}]$	[130, 131]
2-Hydroxynaphthaldehyde	Oxalic dihydrazide	$[\text{MoO}_2(\text{L})(\text{H}_2\text{O})]$	[132, 133]
2-Hydroxynaphthaldehyde	Benzothiazole-2-hydrazide	$[\text{MoO}_2(\text{L})(\text{S})]$ where $\text{S} = \text{dmf}, \text{dmsO}$	[134, 135]
Benzoylacetone	1-Naphthylhydrazide	$[\text{MoO}_2(\text{L})(\text{MeOH})]$	[136]
2-Aminobenzaldehyde	1,2-Diaminopropane	$[\text{MoO}_2(\text{L})]$	[137, 138]
Pyridine 2-carboxaldehyde	N-oxide	$[\text{MoO}_2(\text{L})]$	[139, 140]
	Thiosemicarbazide		

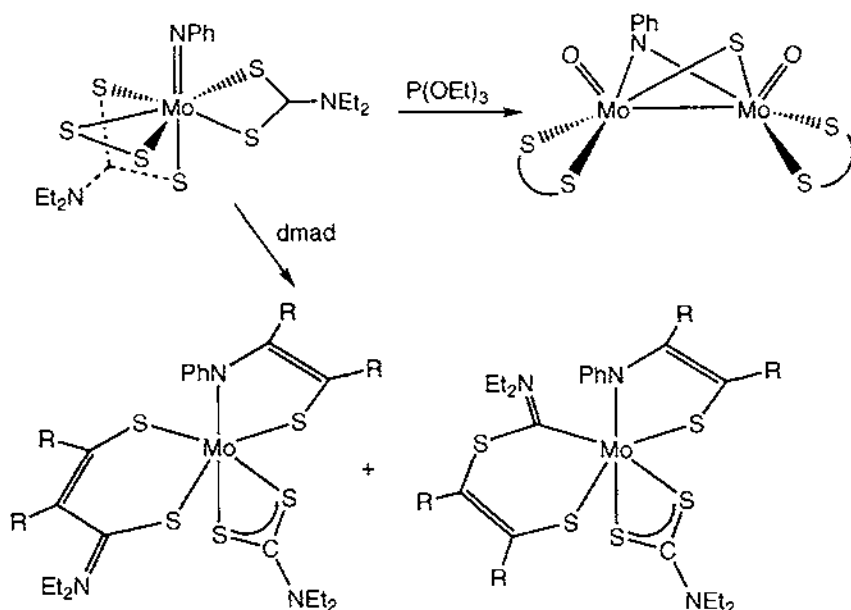
has a pentagonal bipyramidal structure with a side-bound S_2 ligand. Separate experiments showed that $[\text{MoO}(\text{NR})(\text{dte})_2]$ is a probable intermediate in this transformation. The reactivity of one of the product complexes towards $\text{P}(\text{OEt})_3$ and the electron-deficient alkyne *dmad* ($\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$) was explored (Scheme 2) [139].

3. Molybdenum(V)

3.1. Complexes with halide ligands

The diffusion of MoCl_5 in dmf solutions of polyacrylic acid has been studied by two-dimensional spatial-spectral EPR imaging [140]. A similar study was undertaken using MoCl_5 in ethanol solution and in perfluorinated (Nafion) membranes; the sulfonic acid groups of the membrane are thought to be coordinated to the molybdenum centre [141,142]. Alkyne polymerisation reactions of $^t\text{BuC}\equiv\text{CH}$ and of 1-chloro-2-naphthylacetylene have been catalysed by MoCl_5 -based catalysts. In the first case, the stereoregularity of the polymer was examined; directly after polymerisation the polymer is all *cis*, but the regularity decreases if it is allowed to stand. Use of $[\text{Mo}(\text{CO})_6]$, a less Lewis acid catalyst, slows down this isomerisation process [143,144].

Further details of reactions of the compound $[\text{Cl}_2(\text{O})\text{Mo}(\mu\text{-OEt})_2(\mu\text{-EtOH})\text{Mo}(\text{O})\text{Cl}_2]$, formed by treating MoCl_5 with



Scheme 2.

ethanol in chloroform, have appeared. Its reaction with NEt_3 followed by $[\text{PN}][\text{Cl}]\cdot 2\text{H}_2\text{O}$ afforded $[\text{PPN}][\text{NHEt}_3][\text{Cl}_2(\text{O})\text{Mo}(\mu\text{-O})_2\text{Mo}(\text{O})\text{Cl}_2]$ in 90% yield; an intermediate complex is formed and then hydrolysed to the isolated product by the water present in the PPN chloride. Reactions of the starting dimer with allyltrimethylsilane or SbF_3 gave $[\text{Mo}_6\text{O}_6(\mu_3\text{-O})_2(\mu\text{-OEt})_6(\mu\text{-Cl})_2]$ and $[\text{Mo}_8\text{O}_8\text{Cl}_6(\mu_3\text{-O})_4(\text{OH})_2(\mu\text{-OH})_4(\mu\text{-OEt})_4(\text{EtOH})_4]$ respectively, which simulates the build-up of molybdenum oxides from alkoxides in the sol-gel process [145]. Treatment of MoCl_5 with $\text{Me}_3\text{SiOC}_6\text{H}_4\text{-4-'Bu}$ gave a complex of the type $\{[\text{MoCl}_2(\text{OAr})_3]_2\}$ [146]. Oxidation of $[\text{LMo}(\text{CO})_2\equiv\text{Ctol}]$ [$\text{L}=\text{CpCo}\{\text{P}(\text{O})(\text{OR})_2\}^-$ where $\text{R}=\text{Me}$, ^iPr] with PhICl_2 produced $\{[\text{LMoCl}_2]_2\}$ at -78°C and $[\text{LMoCl}_4]$ at $40\text{--}50^\circ\text{C}$ [147].

The reaction of tellurium bromide with MoOBr_3 or of TeCl_4 with MoNCl_2 and MoOCl_3 gave crystals of $[\text{Te}_{15}\text{X}_4][\text{MoOX}_4]_2$ [148], while treatment of MoOCl_4 with elemental sulfur in the presence of ICl_3 at 100°C gave $[\text{SCl}_3][\text{MoOCl}_4]$ [149]. The EPR spectra of $[\text{MoOBr}_5]^{2-}$ and $[\text{MoOCl}_4(\text{H}_2\text{O})]^-$ have been recorded in solution and also doped into a diamagnetic host crystal [a salt of the corresponding $\text{Nb}(\text{V})$ anion]. The electronic structure was also studied by theoretical methods to simulate the EPR parameters [150]. The reaction of $[\text{Mo}(\text{CO})_6]$ with HCl gas, water and a crown ether in toluene led to the rapid formation of liquid clathrates, from which the crown ether oxonium salts $[\text{H}_3\text{O}\cdot 18\text{C}6][\text{MoOCl}_4(\text{H}_2\text{O})]$ and $[\text{H}_2\text{O}\cdot \text{aza-18C}6\text{-H}][\text{MoOCl}_4(\text{H}_2\text{O})]$ were crystallised [151]. The reaction of MoCl_5 with thioldipivaloylmethane gave the first structurally characterised example of a salt of the 3,5-di- ^iBu -1,2-oxathiolium cation, $[\text{BuCOCHCS}^+\text{Bu}][\text{MoOCl}_4(\text{H}_2\text{O})]$ [152]. A spectrophotometric and mathematical modelling study of the formation of thiocyanate complexes of $\text{Mo}(\text{V})$ in aqueous HCl , HBr or H_2SO_4 has been carried out. Species such as $[\text{MoO}(\text{NCS})_2]^{+}$, $\text{H}_3[\text{MoOCl}_3(\text{NCS})_2]^{+}$, $\text{H}_4[\text{MoOCl}_4(\text{NCS})_2]^{2+}$, $\text{H}_4[\text{MoOCl}_5]^{2+}$, $\text{H}_4[\text{MoOCl}_3(\text{NCS})]^{3+}$ and $\text{H}_2[\text{MoOCl}_2]^{3+}$ are involved in HCl ; chloride has a greater ability to compete with NCS^- for $\text{Mo}(\text{V})$ [153].

3.2. Complexes with nitrogen donor ligands

The reaction of $[\text{Mo}(\text{O})(\text{OEt})(\text{TPP})]$ with hydroquinone afforded the catecholate-bridged species $[(\text{O})\text{Mo}(\text{TPP})(\text{OC}_6\text{H}_4\text{O})\text{Mo}(\text{TPP})(\text{O})]$ in which there is fast exchange of electrons as shown by EPR spectroscopy. The compound is in equilibrium with $[\text{Mo}(\text{O})(\text{TPP})]$ and 1,4-benzoquinone [154]. The crystal structure of $\{[\text{Mo}(\text{O})(\text{TPP})]_2(\mu\text{-O})\}\cdot 1.5\text{H}_2\text{O}\cdot 0.5\text{CH}_2\text{Cl}_2$ has been determined [155]. The oxidation of cysteine by chemically modified graphite electrodes containing the phthalocyanine species $[\text{Mo}(\text{O})(\text{OH})(\text{Pc})]$ has been compared to that in solution using the analogous tetrasulfonatophthalocyanine complex $[\text{Mo}(\text{O})(\text{OH})(\text{Pc-SO}_3)]^{4-}$ [156].

Compounds of the type $[\text{Mo}_2\text{O}_3(\text{L})_2\text{Cl}_2]\cdot \text{H}_2\text{O}$ and $[\text{Mo}_2\text{O}_3(\text{L})_2(\text{OH})_2(\text{H}_2\text{O})_2]$ have been made from the Schiff base ligands HL, derived by reaction of benzo-thiazole 2-hydrazide with substituted salicylaldehydes [157]. The complexes $[\text{MoO}(\text{HL})\text{X}_3]$ ($\text{X}=\text{Cl}$, Br) where HL is 1,1-dihydro-1,5-dimethyl-2-phenyl-4-(2-hydroxynaphthylazo)3H-pyrazol-2-one have been prepared [158].

Several papers deal with the redox properties of Mo(IV), Mo(V) and Mo(VI) complexes containing the HBpz₃⁺ (i.e. Tp⁺) ligand, denoted for the next two paragraphs by L. The EPR properties of complexes containing chelating dithiolates, [LMo(O)(S–S)], have been examined, where S–S=S(CH₂)_nS (*n*=2–4) and SC₆H₄S. The presence of the sulfur atoms appears to result in large *g* values, attributed to low energy charge transfer transitions from sulfur to molybdenum. The EPR spectrum of the low pH and high pH forms of sulfite oxidase were also studied, as was that of [MoO(SCH₂CH₂S)₂][–] [159]. Reduction of [LMoO₂(SPh)] by Cp₂Co in py occurs stepwise to give [LMo(O)(SPh)(py)], which can be oxidized by [FeCp₂]⁺ to the cationic Mo(V) species; in wet solvents this is rapidly hydrolysed to [LMo(O)(OH)(SPh)], which in turn is oxidized by air back to Mo(VI) [160]. If Me₃SiCl is present during the initial reduction, air-stable species [LMo(O)(OSiMe₃)(X)] (X=Cl, Br, NCS, OPh, SPh, SCH₂Ph) can be isolated [161]. The X-ray structure of [CoCp₂][(HBtz₃⁺)Mo(O)₂(SPh)], containing the related tris(3,5-dimethyltriazolyl)borate ligand, has been determined. Comparison with the corresponding Mo(VI) complex shows that in the reduced form the Mo–O bonds are longer and the O–Mo–O angle is slightly opened up [162]. Reduction of [LMo(O)₂(S₂PR₂)] with SH[–] afforded initially [LMo(O)₂(SPR₂S)][–] in which the dithiophosphate ligand is monodentate, then [LMo(O)(S)(SPR₂S)][–], which could be oxidized by air to [LMo(O)(S)(S₂PR₂)] [45]. This complex contains an S...S interaction between the P=S group of the monodentate dithiophosphinate ligand and the Mo=S group, which is thought to break on reduction to [LMo(O)(S)(SPR₂S)][–]. Oxidation of [LMo(S)(S₂PR₂)] to Mo(V) is proposed to be accompanied by S–S bond formation [163]. An EPR study of LMo(V) centres weakly coupled to low spin Fe(III) porphyrin substituents has appeared [164].

The recent exploration of the interaction of LMo(NO)(X) metal centres through bridging ligands undertaken by McCleverty has now been extended to analogous Mo(V) species. The complexes [{LMo(O)(Cl)}₂(μ-O–O)] have been prepared, where O–O=1,4-O(C₆H₄)_nO (*n*=1–4), 1,3-OC₆H₄O, and O(C₆H₃-2-Me)O. Electrochemical measurements show that each Mo(V) centre can undergo a one-electron oxidation or a one-electron reduction. Large separations between the two oxidation waves were noted, e.g. 990 mV for the *n*=1 complex, but less so for the reduction waves; EPR spectra showed magnetic interactions between the two metals. The interactions could be related to *n*, the substitution pattern of the ligand, and its dihedral twist angle [165].

3.3. Complexes with oxygen and sulfur donor ligands

The reaction of [Mo(CO)₆] with chrysene semiquinone gave five products, of which two were proposed to contain Mo(V) centres: *cis* and *trans* isomers of [Mo₂O₄(CO)₂(L)₂] and [Mo₂O₅(L)₂][–]L; the other species isolated included [Mo₂O₂(CO)₄(L)₂] and [Mo₂O₄(L)₄] [166]. A similar reaction with chrysene semiquinone monooxime was also reported [167]. An EPR spectroscopy study of Mo(V) complexes containing salicylaldoxime, 2-hydroxyacetophenone oxime and 2-hydroxybenzophenone oxime in the solid state and in solution has been carried

out [168]. The photoinduced oxidation of $\text{Na}_2[\text{Mo}_2\text{O}_4(\text{edta})]$ in aqueous KBr or $\text{K}_2\text{S}_2\text{O}_8$ has been investigated [169].

The synthesis of $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{dtp})_2]$ [$\text{dtp} = \text{S}_2\text{P}(\text{OR})_2$; $\text{R} = \text{Et}, \text{Ph}, ^i\text{Pr}$ or the cyclic analogues where $(\text{OR})_2 = \text{OCMe}_2\text{CMe}_2\text{O}$ or $\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O}$] has been achieved by addition of $\text{Na}[\text{dtp}]$ to MoCl_5 ; an alternative route involves heating $[\text{Mo}_2\text{O}_3(\text{dtp})_4]$ in glacial acetic acid [170]. The reaction of $[\text{Mo}(\text{CO})_6]$ with Na_2MoO_4 in $(\text{CF}_3\text{CO}_2)_2\text{O}$ gave initially $\text{Na}_4[\text{Mo}_2\text{O}_2(\text{O}_2\text{CCF}_3)_{10}]$ which reacted with P_2S_5 in ethanol to give $[\text{NEt}_4][\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\mu\text{-O}_2\text{CCF}_3)\{\text{S}_2\text{P}(\text{OEt})_2\}_2]$ [171]. Oxidation of the dinuclear imido complex $[\text{Mo}_2(\text{NAr})_2\{\text{S}_2\text{P}(\text{OEt})_2\}_2(\mu\text{-S})(\mu\text{-Stol})(\mu\text{-OAc})]$ with *m*-CPBA occurred at the bridging sulfur atom to give corresponding species with $\mu\text{-SO}$ and $\mu\text{-SO}_2$ ligands; irradiation of the latter with visible light caused the release of SO with formation of a $\mu\text{-oxo}$ ligand [172]. The X-ray structures of three compounds which contain the metalloligand $[\text{Fe}_2(\mu\text{-S})_2(\text{CO})_6]^{2-}$ (L^{2-}) coordinated to the $\text{Mo}_2\text{O}_2(\mu\text{-E})_2^{2+}$ core have been determined: $[\text{AsPh}_4]_2[\text{Mo}_2\text{O}_2(\mu\text{-S})_2\text{L}_2]$, $[\text{PPh}_4]_2[\text{Mo}_2\text{O}_2(\mu\text{-O})(\mu\text{-S})\text{L}_2]$ and $[\text{PPh}_4]_2[\{\text{LMo}_2\text{O}_2(\mu\text{-O})_2\}_2(\mu\text{-OMe})_2] \cdot \text{thf}$ [173].

A new high yield preparation of $[\text{NH}_4]_2[\text{Mo}_2(\text{S}_2)_6] \cdot 2\text{H}_2\text{O}$ has been described. Its reaction with eight equivalents of PhSH afforded $[(\text{S}_2)\text{Mo}(\text{S})(\mu\text{-S})_2\text{Mo}(\text{S})(\text{S}_2)]^{2-}$, which can also be obtained from $[\text{MoS}_4]^{2-}$ and Ph_2S_2 . If a large excess of PhSH was used, $[\text{Mo}_2\text{S}_4(\text{SPh})_4]^{2-}$ was formed instead. Reaction with didentate ligands gave $[\text{Mo}_2\text{S}_2(\mu\text{-S})_2\text{L}_2]^{n-}$ ($\text{L} = \text{S}_2\text{CNEt}_2$, $\text{SC}_6\text{H}_4\text{NH}_2$, $n=0$; $\text{L} = \text{SC}_6\text{H}_4\text{S}$, $\text{SC}_6\text{H}_4\text{NH}$, $\text{SCH}_2\text{CH}_2\text{S}$, $n=2$) [174].

The synthesis of $[\text{Mo}(\text{dte})_4][\text{Ln}(\text{dte})_4]$ ($\text{dte} = \text{S}_2\text{CNEt}_2$) where $\text{Ln} = \text{La}$ to Er , excluding Pm , from MoCl_5 , LnCl_3 and $\text{Na}[\text{dte}]$ has been described; X-ray structures were determined for the Nd , Sm , Ho and Er complexes [175,176]. The dinuclear complexes $[\text{MnMoO}_2(\text{dte})_4(\text{H}_2\text{O})]$ and $[\text{HgMoO}_2(\text{dte})_3(\text{H}_2\text{O})]$ [$\text{dte} = \text{S}_2\text{CNEt}_2$, $\text{S}_2\text{CN}(\text{CH}_2)_4$, $\text{S}_2\text{CN}(\text{CH}_2)_5$] have been prepared; both contain distorted octahedral $\text{MoO}(\text{dte})_2$ centres linked through an oxo bridge to the second metal [177].

4. Molybdenum(IV)

4.1. Complexes with halide and cyanide ligands

Heating $[\text{MoCl}_4]$ with SeCl_4 in a sealed ampoule produced $[\text{SeCl}_3]_2[\text{MoCl}_6]$, consisting of pyramidal selenium cations and octahedral $\text{Mo}(\text{IV})$ anions [178]. The analogous reaction of $[\text{MoCl}_4]$ with TeCl_4 at 150°C gave $[\text{TeCl}_3]_2[\text{MoCl}_6]$ [179]; from a similar reaction the related compound $[\text{TeCl}_3]_3[\text{MoCl}_6][\text{Cl}]$ was also isolated [180].

The reaction of $[\text{MoCl}_4(\text{SEt}_2)_2]$ with $\text{PhC}\equiv\text{CSeBu}$ gave the alkyne complex $[\text{MoCl}_4(\text{SEt}_2)(\text{PhC}\equiv\text{CSeBu})]$, which was structurally characterised [181].

The electron transfer reaction between $[\text{Mo}(\text{CN})_8]^{4-}$ and *cis*- $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ has been studied in a number of different solvent mixtures and analysed by Marcus theory; this paper also includes an evaluation of the

formal redox potential of the cyanide complex [182]. The kinetics and mechanism of the reaction of $[\text{Mo}(\text{CN})_8]^{4-}$ with $[\text{Cr}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ to give $[\{\text{Cr}(\text{H}_2\text{O})_4(\text{OH})\}_2\{\text{Mo}(\text{CN})_8\}]$ have also been studied [183]. The thermal properties of the compounds $\text{K}_3[\text{MoO}(\text{O}_2)(\text{OH})(\text{L})] \cdot 3\text{L}$ and $\text{K}_3[\text{Mo}(\text{CN})_3(\text{OH})_4\text{L}] \cdot 2\text{L} \cdot 3\text{H}_2\text{O}$ have been studied; the compounds were made from the photoproduct of $[\text{Mo}(\text{CN})_8]^{4-}$ with en by reaction with 8-hydroxyquinoline (L) [184].

4.2. Complexes with nitrogen and phosphorus donor ligands

Interaction of $[\text{MoO}(\text{TMP})]$ (TMPH_2 = tetramesitylporphyrin) with O_2 in the solid state has enabled the detection of a dioxo species, $[\text{Mo}(\text{O})_2(\text{TMP})]$, by in situ UV–visible spectroscopy. The reaction is reversible: irradiation reforms the starting $\text{Mo}(\text{IV})$ complex [185].

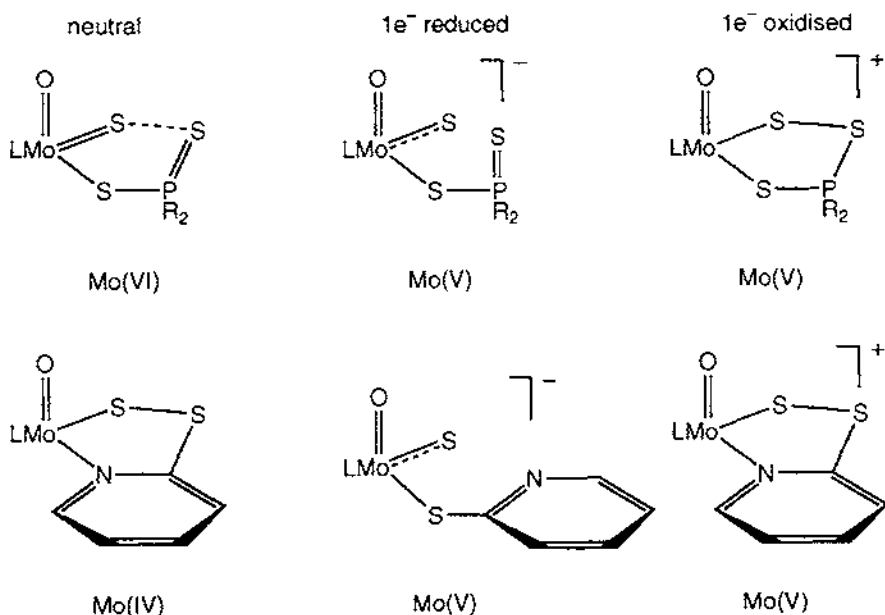
Two short review accounts have appeared concerning the reactivity of the compounds *trans*- $[\text{MX}(\text{NNH}_2)(\text{dppe})_2]^+$ and *cis,mer*- $[\text{MX}_2(\text{NNH}_2)(\text{PMe}_2\text{Ph})_3]$ ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{F}, \text{Cl}$) towards aldehydes, ketones and thf derivatives, which ultimately enables the formation of pyrrole or N-aminopyrrole from molecular nitrogen [186,187]. The hydrazido complexes $[\text{MCl}_2(\text{NNR}_2)(\text{PMe}_2\text{Ph})_3]$, $[\text{MCl}_2(\text{NNPh}_2)(\text{dppe})(\text{PMe}_2\text{Ph})]$ and $[\text{MCl}(\text{NNPh}_2)(\text{dppe})_2]^+$ ($\text{M} = \text{Mo}, \text{W}$; $\text{R} = \text{Me}, \text{Ph}$) have been prepared and their reactions with acid were studied; in some cases ammonia was formed [188]. Controlled potential electrolysis of the hydrazido complexes $[\text{MoX}(\text{NNH}_2)(\text{triphos})(\text{PPh}_3)] [\text{Y}]$ [$\text{X} = \text{Y} = \text{Br}, \text{Cl}$; or $\text{X} = \text{F}, \text{Y} = \text{BF}_4$; $\text{triphos} = \text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$] in thf at a mercury pool electrode in the presence of H_3PO_4 also gave ammonia, quantitatively so for the chloride complex [189]. Displacement of the alkene ligand in $[\text{Mo}(\text{N}^i\text{Bu})_2(\text{PMe}_3)(\text{CH}_2=\text{CHMe})]$ or $[\text{Mo}(\text{NAr})_2(\text{PMe}_3)_2(\text{CH}_2=\text{CH}_2)]$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{Pr}_2$) by the diphosphene $\text{RP}=\text{PR}$ [$\text{R} = 2,4,6\text{-C}_6\text{H}_2(\text{CF}_3)_3$] gave the corresponding species $[\text{Mo}(\text{N}^i\text{Bu})_2(\text{PMe}_3)(\text{RP}=\text{PR})]$ and $[\text{Mo}(\text{NAr})_2(\text{PMe}_3)(\text{RP}=\text{PR})]$ in which the phosphorus ligands are side-bound, as shown by X-ray analysis of the former product [190].

Several papers deal with the redox properties of $\text{Mo}(\text{IV})$, $\text{Mo}(\text{V})$ and $\text{Mo}(\text{VI})$ complexes containing the HBpx_3^+ (i.e. Tp^+) ligand, denoted for this paragraph by L; see also Section 2.2 and Section 3.2. Reduction of $[\text{LMo}(\text{O})_2\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}, \text{NCS}, \text{OPh}, \text{SPh}$) to $[\text{LMo}(\text{O})(\text{X})]$ can be accomplished by reaction with PPh_3 ; dmso effects the reverse reaction [160]. The reaction of $[\text{MoO}(\text{S}_2\text{PR}_2)_2]$ ($\text{R} = \text{Me}, \text{Et}, ^i\text{Pr}, \text{Ph}$) with KL gave the $\text{Mo}(\text{IV})$ complexes $[\text{LMo}(\text{O})(\text{S}_2\text{PR}_2)]$ which could be oxidized to $\text{Mo}(\text{VI})$ dioxo analogues. The rates of oxygen atom transfer from dmso or pyridine-N-oxide to the $\text{Mo}(\text{IV})$ species were determined (this being an associative process), as was the rate of transfer from the $\text{Mo}(\text{VI})$ complex to PPh_3 ; both compounds catalyse oxidation of PPh_3 by dmso [45]. The reaction of $[\text{MoO}(\text{S}_2\text{PR}_2)_2]$ ($\text{R} = \text{Ph}, ^i\text{Pr}$) with the related KL^* , where $\text{L}^* = \text{hydridobis}(3\text{-}^i\text{Pr-pyrazolyl})(5\text{-}^i\text{Pr-pyrazolyl})\text{borate}$, $\text{HB}(3\text{-}^i\text{Prpz})_2(5\text{-}^i\text{Prpz})$ gave $[\text{L}^*\text{Mo}(\text{O})(\text{S}_2\text{PR}_2)]$, which reacts with B_2S_3 to give $[\text{L}^*\text{Mo}(\text{S})(\text{S}_2\text{PR}_2)]$. Both of these can be converted into the $\text{Mo}(\text{VI})$ species $[\text{L}^*\text{Mo}(\text{O})(\text{S})(\text{SPR}_2\text{S})]$ in which

the dithiophosphinate ligand is monodentate [191]. The reaction of ethylene sulfide with $[\text{LMo}(\text{O})(\text{NC}_5\text{H}_4\text{S})]$ results in insertion of a sulfur atom into the Mo–S bond of the pyridine-2-thiolate ligand to give $[\text{LMo}(\text{O})(\text{NC}_5\text{H}_4\text{SS})]$. Reduction of this complex gave $[\text{LMo}(\text{O})(\text{S})(\text{SC}_5\text{H}_4\text{S})]^-$. The structure of this compound was compared to that of $[\text{LMo}(\text{O})(\text{S})(\text{SPR}_2\text{S})]$ which contains a S...S interaction between the monodentate dithiophosphinate and the Mo=S bond; the proposed relationship between the oxidized and reduced forms of these two complexes is shown in Scheme 3 [163].

The compound $[\text{MoH}_2\text{F}_2(\text{PMe}_3)_4]$ can be prepared by the reaction of $[\text{MoH}_2(\text{PMe}_3)_5]$ with aqueous HF. However, if the reaction is stopped at an intermediate stage, the interesting species $[\text{Mo}(\text{H})_2(\text{F})(\text{FHF})(\text{PMe}_3)_4]$ can be isolated, which contains a molecule of HF hydrogen-bonded to the Mo–F bond as shown by X-ray analysis; the FHF angle is 134° . The IR spectrum shows that this interaction is weaker than in $[\text{HF}_2]^-$. A bis-HF adduct could also be detected [192].

The reaction of $[\text{MoH}_4(\text{dppe})_2]$ with the N-alkylamides R^1NHCOR^2 ($\text{R}^1 = \text{Me}, \text{Ph}$; $\text{R}^2 = \text{Me}, \text{Ph}, \text{H}$) yields the distorted pentagonal bipyramidal species $[\text{MoH}(\eta^2\text{-R}^1\text{NCR}^2\text{O})(\text{dppe})_2]$ (7) in which the anionic ligand is bound through N and O. The reactivity of the complex with $\text{R}^1 = \text{R}^2 = \text{Me}$ was explored: treatment with MeOH gave $[\text{MoH}_2(\text{OMe})_2(\text{dppe})_2]$ which gradually converted into $[\text{MoH}_2(\eta^2\text{-CH}_2\text{O})(\text{dppe})_2]$ while reaction with catechol gave $[\text{MoH}_2(\text{OC}_6\text{H}_4\text{O})(\text{dppe})_2]$ which was crystallographically characterised [193]. The mechanism of the reaction of $[\text{MoH}_3(\text{C}\equiv\text{C}^t\text{Bu})(\text{dppe})_2]$ with HCl to give

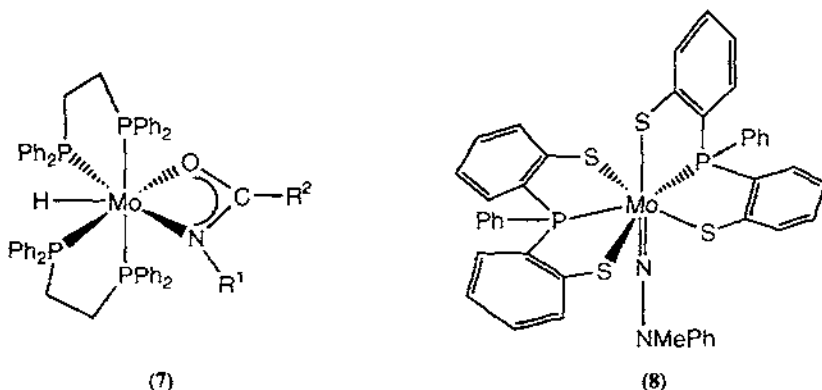


Scheme 3.

$[\text{MoH}_2\text{Cl}_2(\text{dppe})_2]$, H_2 and alkyne has been elucidated; protonation can occur either at the acetylide ligand to give a cationic vinylidene or at the metal; while the former is the predominant initial product, the latter is more reactive, eliminating first H_2 then the alkyne [194].

4.3. Complexes with oxygen and sulfur donor ligands

The reaction of $[\text{Mo}(\text{PMe}_3)_6]$ with phenol itself gave *trans*- $[\text{Mo}(\text{OPh})_4(\text{PMe}_3)_2]$, whereas with more hindered phenols (ArOH , where $\text{Ar} = \text{mes}$ or $2,6\text{-C}_6\text{H}_3\text{Pr}_2$) the $\text{Mo}(\text{II})$ complexes, $[\text{MoH}(\text{OAr})(\text{PMe}_3)_4]$ were formed. The analogous reactions with W complexes gave cyclometallated species; labelling studies showed that cyclometallation of the *o*-Me groups does take place in the Mo case, but that the hydride-aryloxide complex is the most thermodynamically stable product [195].



Complexes of the type $[\{\text{MoO}\}_2\text{L}_2]$ have been prepared from the doubly didentate amide ligands $\text{HO}_2\text{C-A-CONH}-(p\text{-C}_6\text{H}_4)_n\text{-NHCO-A-CO}_2\text{H}$ where $n=1$ or 2 and the spacer group A can be CH_2CH_2 or *o*- C_6H_4 . The ligands were prepared by condensation of benzidine or *p*-phenylene diamine with phthalic anhydride or succinic anhydride, then complexed to the metal with $[\text{MoO}_2(\text{acac})_2]$, followed by phosphine reduction to $\text{Mo}(\text{IV})$ [196].

The X-ray structure of $[\text{NBu}_4][\text{MoO}(\text{mnt})_2]$ [$\text{mnt} = \text{S}_2\text{C}_2(\text{CN})_2$] has been determined. The NBu_4^+ cation was exchanged for various bipyridinium salts and the energy of the ion pair charge transfer band was plotted against the redox potential; this produced a linear graph, but with a gradient of 0.45 rather than 1 which suggests a deviation from Hush–Marcus theory [197]. As part of a paper about tungsten mnt derivatives, it was shown that $[\text{WO}(\text{mnt})_2]^{2-}$ reacted with $[\text{MoO}_4]^{2-}$ to give $[\text{MoO}(\text{mnt})_2]^{2-}$ by a dithiolene transfer reaction which possibly involves a $\text{W}(\text{V})$ intermediate [198]. The complex $[\text{NPr}_4][\text{MoO}(\text{S}_2\text{WS}_2)_2]$ was obtained as an unexpected side product in the known reaction of $[\text{Mo}_2(\text{O}_2\text{CPh})_4]$ with $[\text{WS}_4]^{2-}$ [199].

A variety of complexes have been prepared from the ligand $\text{PhP}(\text{C}_6\text{H}_4\text{-2-SH})_2$ (H_2L); its reaction with $[\text{MoCl}_4(\text{PPh}_3)_2]$ gave unstable $[\text{MoL}_2]$ or, if carried out in MeCN, air-stable $[\text{MoL}_2(\text{MeCN})]$. From the reaction with

[MoCl₂(CO)₂(PPh₃)₂], the compound [MoL₂(CO)] was isolated, and from [MoCl(NNMePh)(PPh₃)₂][Cl], [MoL₂(NNMePh)] (**8**) was formed. Its crystal structure showed a distorted pentagonal bipyramidal structure in which one L spans the axial and equatorial positions whereas the other is all equatorial. The compound [MoL₂(NO)] was also made from [Mo(NO)(SPh)₄][−] [200].

Protonolysis of [Mo(*o*-tolyl)₄] with the highly hindered tellurol HTeSi(SiMe₃)₃ afforded the homoleptic tellurolate [Mo{TeSi(SiMe₃)₃}₄], shown by crystallography to be a slightly flattened tetrahedron with Te–Mo–Te angles of about 114.9°. The main pathway observed in the reactivity of the product appeared to involve elimination of RTe–TeR [201].

A theoretical study of the electronic structure and spectra of the complexes [Mo(=E)₂(PH₃)₄] (E=O, S, Se, Te) using X α and ab initio calculations has appeared. The ab initio calculations suggest that the HOMO is a π lone pair rather than the Mo d_{xy}, and for the three heavier chalcogens the lowest energy transition is calculated to be from the π lone pairs into the Mo=E π^* orbitals; however, both the calculated and observed spectra are different for E=O [202].

5. Molybdenum(III)

5.1. Complexes with halide and phosphine ligands

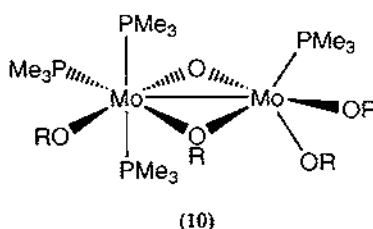
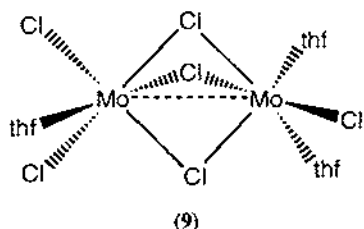
The reaction of [MoX₃(thf)₃] with X[−] (X=Cl, Br) afforded [MoX₄(thf)₂][−], isolated as NBu₄⁺, PPN⁺ or PPh₄⁺ salts. Dissolution of these compounds in CH₂Cl₂ caused loss of thf and formation of [Mo₃X₁₂]^{3−}, which has a linear structure consisting of three face-sharing octahedra. The long Mo–Mo distances are consistent with bond orders of 0.5 between the metals [203]. By treatment of *fac*-[Mo(OTf)₃(NH₃)₃] with lithium halides in EtOH or thf, the new species *fac*-[MoX₃(NH₃)₃] (X=Cl, Br, I) were obtained. The spectrochemical parameters for Mo(III) were calculated by analysis of the electronic spectra and comparison to [MoX₆]^{3−}. Their magnetic moments are all close to the d³ spin only value [204].

As well as the expected *mer*-[MoX₃(py)₃], the reaction of [NH₄]₂[MoX₅(H₂O)] (X=Cl, Br) with py in methanol was found to give 10–20% of the double salt *trans,trans*-[MoX₂(py)₄][MoX₄(py)₂] as a side product; both compounds were structurally characterised. The anionic component can be oxidized with Br₂ to *trans*-[MoX₄(py)₂], allowing isolation of the cation as [MoX₂(py)₄][Br₃] [205]. The X-ray structure of the compound with X=Cl was subsequently determined [206]. The reaction of [MoCl₃(triphos)] [triphos=PhP(CH₂CH₂PPh₂)₂] with NaCp or NaInd has been used to prepare [CpMoCl(triphos)] and its indenyl analogue [207].

The complex [Mo₂Cl₆(tht)₃] is an active catalyst for the polymerisation and cyclotrimerisation of alkynes; [MoCl₃(tht)₃] exhibits similar behaviour, and the process probably occurs at a mononuclear centre. Two alkyne complexes, [MoCl₃(tht)₂(PhC \equiv CR)] (R=Me, Et), were isolated and structurally characterised; they were also found to be active catalysts [208]. The X-ray structure of [Mo₂Cl₆(thf)₃] (**9**) has been determined; the compound has an *anti*-(1,2,6) arrangement of the thf ligands. The rate constants for the interconversion of *anti* and *gauche* forms were also evaluated [209].

The electronic structure of edge- and face-sharing bioctahedral complexes of Mo has been explored by ab initio calculations. The metal–metal interaction in such species was found to have a dual nature: formation of direct metal–metal bonds and antiferromagnetic coupling of remaining electrons. The experimentally observed magnetism can be explained on the basis of low-lying magnetic excited states due to weak exchange coupling [210].

Density functional theory calculations have been carried out on the electronic structure of $[M_2Cl_9]^{3-}$ ($M = Cr, Mo, W$) under full- and broken-symmetry regimes; it was found that for Cr, where overlap of the magnetic orbitals is weaker (i.e. electrons are more localised), the broken symmetry model was more accurate, but where overlap is strong, both methods gave the same result [211]. Optimised geometries for the ground state and for excited spin states up to $S = 3$ have been obtained for the Mo and W compounds from further calculations, which predict an increase in M–M distance with increasing S [212]. The magneto-optical properties of $Cs_3[Mo_2Br_9]$ have been studied by single crystal absorption, Zeeman and MCD spectroscopy; seven band regions were resolved and show that the Mo–Mo π -bonding in this compound is weaker than in the corresponding chloride [213]. The compound $[H_3O^+ \cdot 18C6]_2[(H_5O_2) \cdot Mo_2Cl_9]$ has been crystallised from a liquid clathrate produced by treating $[Mo(CO)_6]$ in toluene/ H_2O with HCl gas in the presence of the crown ether [214].

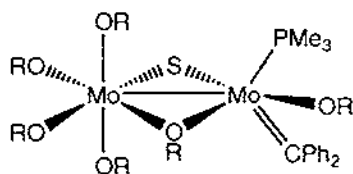


5.2. Complexes with oxygen and nitrogen donor ligands

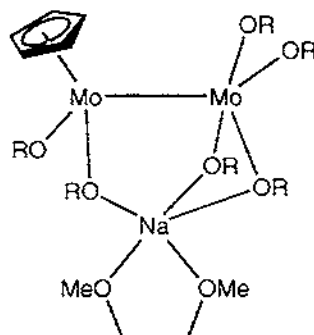
Partial hydrolysis of $[Mo_2(OR)_6]$ ($R = CH_2^tBu$) in the presence of an excess of PMe_3 gave $[Mo_2(\mu-O)(\mu-OR)(OR)_3(PMe_3)_4]$ (10). The bridging oxo ligand is asymmetrically bonded and it is proposed that the octahedral metal centre is formally Mo(II), whereas the trigonal bipyramidal one is formally Mo(IV); there is a metal–metal bond distance of 2.4931(9) Å. In solution it reacts with CO to give a 1:1 adduct which could be considered as the formal cleavage product of CO_2 by $[Mo_2(OR)_4(PMe_3)_4]$; in reality this reaction proceeds by insertion into the Mo–O bonds instead [215].

The reaction of $[Mo_2(OR)_6]$ (same R) with $Ph_2C=S$ results in cleavage of the C=S bond with formation of the terminal alkylidene complex $[Mo_2(OR)_5(\mu-OR)(\mu-S)(=CPh_2)]$. The structure of the PMe_3 adduct (11) of this species was determined. The activation parameters for the reaction were calculated for various aryl groups. The analogous tungsten compound reacts differently, giving

$[\text{W}(\text{OR})_4(\eta^2\text{-SCPh}_2)]$ and $[\text{W}(\text{S})(=\text{CPh}_2)(\text{OR})_2]$ [216]. The reaction of $[\text{Mo}_2(\text{OR})_6]$ (same R) with NaCp in dme gave $[\text{Na}(\text{dme})(\mu\text{-OR})_3\text{Mo}_2(\text{OR})_3\text{Cp}]$ (12) with a Mo–Mo bond of 2.276(1) Å; in polar solvents it dissociates back to the starting materials [217].



(11)



(12)

Further developments in the chemistry of the complex $[\text{Mo}(\text{NRAr})_3]$, where $\text{R}=\text{C}(\text{CD}_3)_2\text{Me}$ and $\text{Ar}=3,5\text{-C}_6\text{H}_3\text{Me}_2$, have been reported by Cummins and coworkers. Full details of the synthesis and characterisation of the amide complex, the nitrogen-bridged species $[\{\text{Mo}(\text{NRAr})_3\}_2(\mu\text{-N}_2)]$ and the cleavage product $[\text{Mo}(=\text{N})(\text{NRAr})_3]$ have appeared, as well as those of analogous compounds derived from $[\text{Mo}(\text{N}^i\text{BuPh})_3]$; X-ray structures and EXAFS data for some complexes were included [218]. In the absence of N_2 , $[\text{Mo}(\text{NRAr})_3]$ was shown to undergo a N-atom transfer reaction with $[\text{Mo}(=\text{N})(\text{O}^i\text{Bu})_3]$ to give $[\text{Mo}(=\text{N})(\text{NRAr})_3]$ and $[\text{Mo}_2(\text{O}^i\text{Bu})_6]$. In the presence of N_2 , however, both nitrido complexes are formed, and if $^{15}\text{N}_2$ is used, both are labelled, i.e. N_2 is cleaved by the amide complex and can be transferred to the alkoxide. An unobserved intermediate, presumably $[(^i\text{BuO})_3\text{Mo}(\mu\text{-N}_2)\text{Mo}(\text{NRAr})_3]$, was postulated [219].

The ammoniolysis reactions of a range of metal amides have been studied with a view to obtaining metal carbides and nitrides; the product from $[\text{Mo}_2(\text{NMe}_2)_6]$ analysed as $\text{MoCNH}_{2.5}$ [220]. The structure of the thionitrosyl complex $[\text{Mo}(\text{NS})(\text{dtc})_3]$ ($\text{dtc}=\text{S}_2\text{CNEt}_2$) has been determined and shows a distorted pentagonal bipyramidal geometry with the NS ligand in an axial position [221]. The compounds $[\text{L}_3\text{Mo}\{\text{M}(\text{SCN})_2\}_3]$ [$\text{L}=\text{py}$, nicotinamide, PPh_3 ; $\text{M}=\text{Cu}(\text{I})$ or $\text{Ag}(\text{I})$] have been reported; the first two contain bridging and terminal S-bound thiocyanates, whereas the last contains N-bound ligands [222].

6. Molybdenum(II)

6.1. Complexes with halide and phosphine or carbonyl ligands

The geometry of $[\text{Mo}_2\text{Cl}_8]^{4-}$ in the lowest excited state (the $\delta\delta^*$) has been determined by application of the sum-over-states method to resonance Raman band

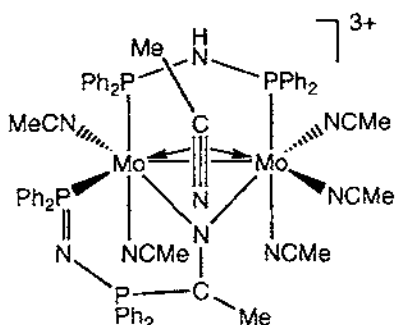
intensities [223]. The electronic, IR and Raman spectra of $[\text{Mo}_2\text{X}_6(\text{H}_2\text{O})_2]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$ and also some mixed ligand species) have been recorded [224]. The electronic spectra show broad bands attributable to the $\delta \rightarrow \delta^*$ transition. An experimental and theoretical study of anomalous intensity variations in the resonance Raman excitation profile of the totally symmetric Raman bands in these complexes has also appeared [225].

The compound $[\text{MoCl}_2(\text{PMe}_3)_2]$, which was previously reported as the product of the reaction of $[(\eta\text{-C}_5\text{Me}_4\text{Et})\text{MoCl}_2(\text{PMe}_3)_2]$ with Li_2Pmes , has now been reformulated as the zinc complex $[\text{ZnCl}_2(\text{PMe}_3)_2]$ and its identity confirmed by independent synthesis from ZnCl_2 and PMe_3 . Its presence in the original reaction presumably arises from zinc used as a reductant at some point in the synthesis, thus producing zinc chloride [226,227]. The reactions of compounds of the type $[\text{MCl}_2\text{L}_2]$ with various substrates, leading to $[\text{M}(=\text{E})\text{Cl}_2\text{L}_2]$ ($\text{M} = \text{Mo}, \text{W}$; $\text{E} = \text{O}, \text{Se}$; $\text{L} = \text{a phosphine}$), have been reviewed [228].

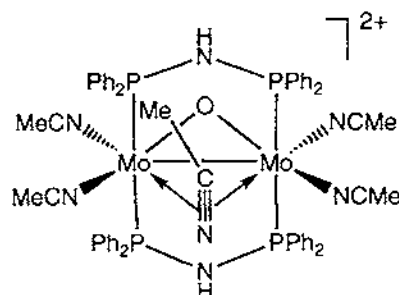
A number of papers describe the synthesis of Mo(II) complexes containing bis(diphenylphosphino)amine, $(\text{Ph}_2\text{PNHPPH}_2)$, abbreviated as *dppa*. Treatment of $[\text{Mo}_2(\text{OAc})_4]$ with Me_3SiX and *dppa* at reflux afforded $[\text{Mo}_2\text{X}_4(\mu\text{-dppa})_2]$ ($\text{X} = \text{Cl}, \text{Br}$). The Mo-Mo distances in these compounds are quite short [2.134(1) and 2.137(2) Å respectively], even though there are significant torsion angles (14.4 and 15.2° respectively) around the Mo-Mo bond [229]. Under milder conditions, the intermediate complexes $[\text{Mo}_2\text{X}_2(\mu\text{-OAc})_2(\mu\text{-dppa})_2]$ could be isolated for $\text{X} = \text{Cl}, \text{Br}, \text{I}$; the Mo-Mo distances in these three complexes are 2.158(1), 2.176(1), and 2.164(1) Å respectively [230]. A similar compound with the related ligand $\text{Ph}_2\text{PNMePPh}_2$, *dppma*, was also prepared; the structure of $[\text{Mo}_2\text{Cl}_2(\mu\text{-OAc})_2(\mu\text{-dppma})_2]$ again showed some degree of torsional strain and had a Mo-Mo distance of 2.1719(8) Å [231]. Another related complex, $[\text{Mo}_2(\text{MeCN})_2(\mu\text{-OAc})_2(\mu\text{-dppa})_2][\text{BF}_4]_2$, was made from $[\text{Mo}_2(\mu\text{-OAc})_2(\text{MeCN})_6][\text{BF}_4]_2$ and *dppa* [232]. However, an unexpected result was obtained from the reaction of $[\text{Mo}_2(\text{NCMe})_8]^{4+}$ with *dppa*; crystals of $[\text{Mo}_2(\mu\text{-NCMe})(\mu\text{-dppa})(\mu\text{-NCMePPh}_2\text{NPPH}_2)(\text{NCMe})_5][\text{BF}_4]_3 \cdot 0.5\text{MeOH} \cdot 3\text{MeCN}$ (**13**) were obtained. If water was also present, the complex $[\text{Mo}_2(\mu\text{-NCMe})(\mu\text{-O})(\mu\text{-dppa})_2(\text{NCMe})_4][\text{BF}_4]_2 \cdot \text{MeCN} \cdot 0.5\text{C}_6\text{H}_{14}$ (**14**) was obtained instead. Both of these contain unusual transverse bridging MeCN ligands, and the first also contains a ligand formed by coupling of MeCN with one of the *dppa*'s [233].

Reaction of $[\text{Mo}_2(\text{OAc})_4]$ with Me_3SiCl and PR_3 ($\text{R} = \text{CH}_2\text{CH}_2\text{CN}$) affords a blue material assumed to be $[\text{Mo}_2\text{Cl}_4(\text{PR}_3)_2]_x$, which dissolved in $\text{R}'\text{CN}$ ($\text{R}' = \text{Me}, \text{Et}, \text{Pr}$) to give the unusual 1,1,2,2 isomers of $[\text{Mo}_2\text{Cl}_4(\text{PR}_3)_2(\text{NCR}')_2]$ (**15**) in which the phosphines occupy *trans* positions on one metal and the nitriles *trans* positions on the other [234]. The reaction of $[\text{Mo}_2(\mu\text{-OAc})_2\text{Cl}_2(\text{PPh}_3)_2]$ with the phosphines $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ (tetraphos-2) or $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ (triphos) gave $[\text{Mo}_2(\mu\text{-OAc})\text{Cl}_3(\text{L})]$ (**16**) in which the phosphine ligand is tridentate; both compounds were structurally characterised [235].

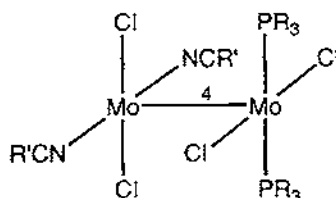
Treatment of $[\text{Mo}_2(\text{OAc})_4]$ with Me_3SiCl in the presence of didentate ligands *L* such as *bpy*, 4,4'- Me_2bpy , 2,2'-bipyrazine, 2,2'-bipyrimidine, *phen* or 3,3'-bipyridazine gave the compounds $[\text{Mo}_2\text{X}_4\text{L}_2]$ which contain an unbridged Mo-Mo bond.



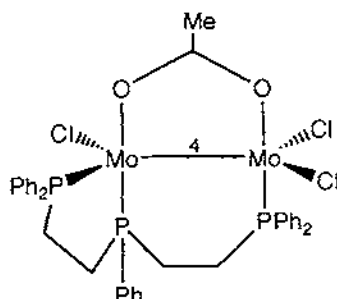
(13)



(14)



(15)



(16)

The products react slowly with oxygen to give initially $[\text{Mo}_2\text{O}_4\text{Cl}_4\text{L}_2]$ and then $[\text{MoO}_2\text{Cl}_2(\text{L})]$; the crystal structure of the latter with $\text{L}=4,4'\text{-Me}_2\text{bpy}$ was determined [236].

Interaction of $[\text{Mo}_2\text{Cl}_4(\mu\text{-dmpm})_2]$ with $\text{LiC}\equiv\text{CSiMe}_3$ in *dme* in the presence of $\text{HC}\equiv\text{CSiMe}_3$ gave the highly unusual complex $[\text{Li}(\text{dme})][\text{Mo}_2(\text{C}\equiv\text{CR})_3(\mu\text{-HC}\equiv\text{CR})(\mu\text{-C}=\text{CR}-\text{C}\equiv\text{CR})(\mu\text{-dmpm})_2]$ which contains a transversely bridging alkyne ligand and a bridging alkynylvinylidene ligand formed by acetylide coupling [237].

The reaction of $[\text{MoBr}_2(\text{CO})_2(\text{PPh}_3)_2]$ with one equivalent of *N*-acyl- α -amino acids in the presence of NaOMe gave the carboxylate species $[\text{MoBr}(\text{O}_2\text{CCH}_2\text{NHCOR})(\text{CO})_2(\text{PPh}_3)_2]$ ($\text{R}=\text{Me}, \text{Ph}$), whereas the use of two equivalents led to the disubstituted species $[\text{Mo}(\text{O}_2\text{CCHR}^1\text{MHCOR}^2)(\text{CO})_2(\text{PPh}_3)_2]$ ($\text{R}^1=\text{H}, \text{R}^2=\text{Ph}; \text{R}^2=\text{CH}_2^i\text{Pr}, \text{R}^2=\text{Me}; \text{R}^1=\text{Me}, \text{CH}_2\text{OH}, \text{R}^2=\text{CH}_2\text{Ph}$). In the first of these the carboxylate ligand is didentate, whereas the second contains one didentate and one monodentate ligand; both are thus seven-coordinate species [238].

Treatment of $[\text{Ml}_2(\text{CO})_3(\text{NCMe})_2]$ ($\text{M}=\text{Mo}, \text{W}$) with the thiamacrocyclic [9]ane S_3 gave $[\text{Ml}(\text{CO})_3\text{L}]^+$; the X-ray structure of the *W* complex as the BPh_4^- salt showed a capped octahedral structure. A similar reaction with

$[\text{MoI}_2(\text{CO})_3(\text{NCMe})(\text{PPh}_3)]$ gave $[\text{MoI}(\text{CO})_2(\text{PPh}_3)\text{L}][\text{MoI}_3(\text{CO})_4]$. Similar compounds could be prepared from 2,5,8-trithia[9]orthocyclophane, $\text{C}_6\text{H}_4\text{CH}_2(\text{SCH}_2\text{CH}_2)_2\text{SCH}_2$ [239]. Coordination of dppm disulfide, $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{S})\text{Ph}_2$, to $[\text{MoI}_2(\text{CO})_3(\text{NCMe})_2]$ has also been achieved [240]. The pendant phosphine arm of $[\text{WI}_2(\text{CO})(\eta^2\text{-triphos})(\eta\text{-C}_2\text{R}_2)_2]$ [triphos = $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$, $\text{R} = \text{Me, Ph}$] can be used as a ligand to displace one or both of the acetonitrile ligands in $[\text{MoI}_2(\text{CO})_3(\text{NCMe})_2]$, $[\text{MoI}_2(\text{CO})_3(\text{NCMe})\text{L}]$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3$) and $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_2(\text{NCMe})_2(\text{PPh}_3)]$ to give di- or trinuclear species [241].

6.2. Complexes with nitrogen donor ligands

A series of diarylformamidinate complexes $[\text{Mo}_2(\text{ArNCHNAr})_4]$ have been prepared and their quasi-reversible oxidation potentials correlated with the Hammett constants of the aryl substituents. Four of the complexes were structurally characterised and show virtually identical geometries in the solid state, with the Mo–Mo distance varying between 2.0949(8) and 2.0965(5) Å [242]. The formation of Mo(II) dimers with substituted 1,8-naphthyridine ligands (HL) has been explored. With 2-benzylamino-7-methyl naphthyridine, the complex *trans*- $[\text{Mo}_2\text{L}_4]$ was formed in which the *trans*-ligands are oriented the same way, whereas 7-phenylnaphthyridine-2-one gave *cis*- $[\text{Mo}_2\text{L}_4]$. The reaction of $[\text{Mo}_2(\text{OAc})_4]$ with 2-acetamido-7-phenylnaphthyridine gave *cis*- $[\text{Mo}_2(\mu\text{-OAc})_2(\mu\text{-L})_2]$ while the intermediate complex $[\text{Mo}(\text{CO})_4(\text{HL})]$ could be isolated from the reaction between $[\text{Mo}(\text{CO})_6]$ and the 7-methyl analogue [243]. The compound $[\text{Mo}_2(\text{OAc})_2(\text{HBpz}_3)_2]$ reacted with Me_3SiX to give $[\text{Mo}_2\text{X}_2(\text{HBpz}_3)_2]$ ($\text{X} = \text{Cl, Br}$); X-ray structures of both products revealed Mo–Mo distances of 2.155(1) and 2.156(1) Å respectively. As in the starting materials, the pyrazolylborate ligands bridge the two metals [244]. The compounds *cis*- $[\text{Mo}_2\text{Cl}_2(6\text{-mhp})_2\text{L}_2]$ (6-mhpH = 6-methyl-2-hydroxypyridine; $\text{L} = \text{PMe}_3, \text{PEt}_3, \text{PMe}_2\text{Ph, PPh}_2\text{Me}$) undergo a ligand redistribution process when irradiated with visible or near-UV light to give $[\text{Mo}_2\text{Cl}_3(6\text{-mhp})\text{L}_2]$ and $[\text{Mo}_2\text{Cl}(6\text{-mhp})_3\text{L}_2]$. By carrying out the reaction in different solvents in which one of the products decomposes or reacts further, it was possible to isolate each one. The photoreactions do not occur from the first excited state, but from higher ones [245].

Many papers report further extensive chemistry of the tris(3,5-dimethylpyrazolyl)borate complexes $[(\text{HBpz}_3^*)\text{Mo}(\text{NO})\text{X}_2]$ ($\text{X} = \text{Cl, Br, I}$). These redox-active 16-electron compounds react with alcohols and amines with elimination of HX and formation of $[(\text{HBpx}_3^*)\text{Mo}(\text{NO})(\text{X})(\text{OR})]$ or $[(\text{HBpz}_3^*)\text{Mo}(\text{NO})(\text{X})(\text{NHR})]$, or the corresponding disubstituted species, but also react with neutral donors such as pyridines to give 17-electron compounds $[(\text{HBpz}_3^*)\text{Mo}(\text{NO})(\text{X})(\text{L})]$. The nitrile complexes $[(\text{HBpz}_3^*)\text{Mo}(\text{NO})(\text{I})(\text{NCR})]$ ($\text{R} = \text{Me, Pr, CH}_2\text{CH}_2\text{CH}_2\text{CN}$) have been made by the reaction of $[(\text{HBpz}_3^*)\text{Mo}(\text{NO})\text{I}_2]$ with RCN. They are paramagnetic and display one irreversible electrochemical reduction [246]. Treatment of $[(\text{HBpz}_3^*)\text{Mo}(\text{NO})\text{I}_2]$ with $(\text{NH}_4)_2\text{S}_{10}$ or $(\text{NH}_4)_2\text{Se}_6$ gave $[(\text{HBpz}_3^*)\text{Mo}(\text{NO})(\text{E}_5)]$; the X-ray structure of the

selenium complex showed a chair-like configuration of the MoSe_5 ring. In the presence of H_2E (from slow hydrolysis of Al_2E_3) the dimers $[\{(\text{HBpz}^*)\text{Mo}(\text{NO})(\mu\text{-E})\}_2]$ were formed [247].

The *o*-, *m*- and *p*-isomers of 5- $\{(\text{HBpz}^*)\text{Mo}(\text{NO})(\text{Cl})(\text{NHC}_6\text{H}_4)\}$ -10,15,20-tetraphenylporphyrin have been prepared. Electrochemical studies revealed two porphyrin-centred oxidations and three reductions, two of which were on the porphyrin and one at the molybdenum; the redox potentials of the porphyrin or the metal centre are only slightly different to their normal values. However, the compounds do undergo a photoinduced electron transfer from the ring to the metal to give an excited state with a lifetime of approximately 300–340 ps [248].

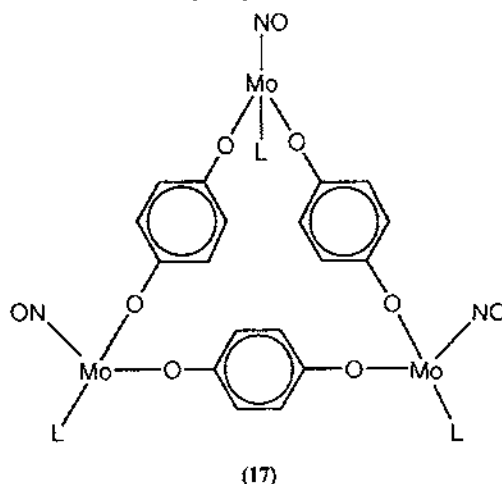
A number of papers deal with the interaction between two metal centres linked by different types of ligand. The complexes $[\{(\text{HBpz}^*)\text{Mo}(\text{NO})(\text{X})\}_n(\mu\text{-N-N})]$ ($\text{X} = \text{Cl}$, I ; $n = 1$ or 2) have been prepared for a large number of difunctional ligands N–N. These include 3,3'-bpy, 4,4'-bpy, 4,4'- $\text{NC}_5\text{H}_4\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4\text{N}$, 4,4'- $\text{NC}_5\text{H}_4(\text{CH}=\text{CH})_m\text{C}_5\text{H}_4\text{N}$ ($m = 0\text{--}4$), and 4,4'- $\text{NC}_5\text{H}_4\text{CH}=\text{CHCMe}=\text{CHCH}=\text{CHCH}=\text{CMeCH}=\text{CHC}_5\text{H}_4\text{N}$; the X-ray structure of the latter complex with $\text{X} = \text{Cl}$ confirmed that the chain has an all-*trans* configuration. Cyclic voltammetry shows a one-electron reduction for the monometallic species, and for the dimetallic ones two one-electron reductions separated by an amount which depends on the chain length of N–N, varying from 36 mV for the longest to 765 mV in the 4,4'-bpy complex. The EPR spectra show an antiferromagnetic interaction in one case over a distance of approximately 20 Å [249]. The complexes with dipirydyloctatetraene and dipirydyldodecapentaene show a solvatochromic shift of the low energy absorption in the electronic spectrum which has been analysed quantitatively [250]. Complexes in which the N–N ligand is 3,3'-, 3,4'- and 4,4'-bis(pyridyl)ethane have been compared to those of 3,3'-, 3,4'- and 4,4'-bpy; these too show a large electrochemical interaction between the metals. The sign of the magnetic interaction changes with the number of carbon atoms between the metals: the 3,3'- and 4,4'-isomers are antiferromagnetic whereas the 3,4'-isomer is ferromagnetic; this is in accord with a spin polarisation mechanism [251]. The ligand 1,3,5-tris[3,4-bis(4-pyridylethenyl)phenyl]benzene has been prepared by Pd-catalysed crosscoupling. Six $(\text{HBpz}^*)\text{Mo}(\text{NO})(\text{Cl})$ groups can be attached to the pendant pyridyl arms. The resulting complex is EPR active with each nearest neighbour pair of molybdenum centres displaying magnetic interactions [252].

Ligands have been synthesized in which two pyridyl or phenol groups are joined by an oligothiophene chain, as in 4,4'- $\text{NC}_5\text{H}_4(\text{SC}_6\text{H}_4)_n\text{C}_5\text{H}_4\text{N}$ ($n = 1\text{--}4$) and $\text{ROC}_6\text{H}_4(\text{SC}_6\text{H}_4)_2\text{C}_6\text{H}_4\text{OR}$ ($\text{R} = \text{Me}$, H). The ligands are electrochemically active, undergoing two one-electron oxidations, and are also strongly luminescent. When $(\text{HBpz}^*)\text{Mo}(\text{NO})(\text{Cl})$ units were attached to each terminus of the pyridyl ligand, a strong electrochemical interaction was observed between the metal centres: the oligothiophene chain transmits this better than a polyene chain [253].

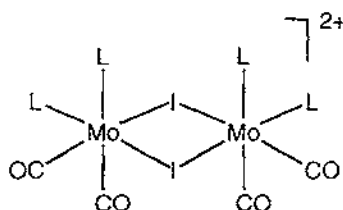
The compounds $[\{(\text{HBpz}^*)\text{Mo}(\text{NO})(\text{Cl})\}_2(\mu\text{-O-O})]$ have been prepared for $\text{O-O} = \text{O}(\text{CH}_2)_4\text{O}$, $\text{OCH}_2\text{CH}=\text{CHCH}_2\text{O}$, and $\text{OCH}_2\text{C}\equiv\text{CCH}_2\text{O}$. The alkenyl bridge gave the largest electrochemical interaction between the two metal centres

[254]. Dimetallic complexes bridged by cyclohexanediolate or cyclopentanediate ligands were prepared, of the type $[(\text{HBpz}_3^*)\text{Mo}(\text{NO})(\text{X})]_2(\mu\text{-O-O})$ where $\text{O-O} = 1, x\text{-OC}_6\text{H}_{10}\text{O}$ ($x = 2-4$) or $1,3\text{-OC}_5\text{H}_8\text{O}$. They exhibit two one-electron reductions separated by a difference which increases with decreasing spatial separation. For 1,3-cyclohexanediolate the difference is only slightly less than for $1,3\text{-OC}_6\text{H}_4\text{O}$, but for the 1,4-isomer it is over 300 times less than in the corresponding $1,4\text{-OC}_6\text{H}_4\text{O}$ species [255]. The reaction of two equivalents of $[(\text{HBpz}_3^*)\text{Mo}(\text{NO})(\text{X})_2]$ with Schiff base ligands derived by condensation of *p*- or *m*-hydroxybenzaldehyde with *p*-phenylene diamine or 1,6-diaminohexane was complicated by hydrolysis of the ligand, the isolated product being $[(\text{HBpz}_3^*)\text{Mo}(\text{NO})(\text{X})(\text{OC}_6\text{H}_4\text{CHO})]$. Reduction of the imine linkage allowed the reaction to proceed smoothly to give $[(\text{HBpz}_3^*)\text{Mo}(\text{NO})(\text{Cl})]_2(\mu\text{-OC}_6\text{H}_4\text{CH}_2\text{NHC}_6\text{H}_4\text{NHCH}_2\text{C}_6\text{H}_4\text{O})$ [256].

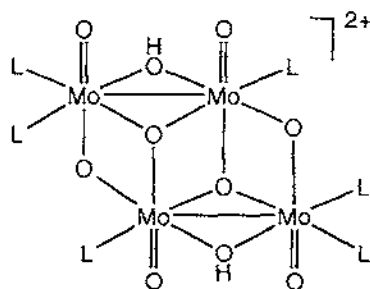
The cyclic oligomeric species $[(\text{HBpz}_3^*)\text{Mo}(\text{NO})(4,4'\text{-OC}_6\text{H}_4\text{OC}_6\text{H}_4\text{O})]_n$ ($n = 3, 4$) have been made as mixtures of isomers. The trimer displays three unresolved one-electron reductions, but the tetramer has two two-electron processes separated by about 120 mV [257]. From the reaction of $[(\text{HBpz}_3^*)\text{Mo}(\text{NO})\text{I}_2]$ with hydroquinone, the cyclic trimer $[(\text{HBpz}_3^*)\text{Mo}(\text{NO})(\text{OC}_6\text{H}_4\text{O})]_3$ (17) could be isolated as the symmetrical *syn,syn* isomer (i.e. all the NO ligands are on the same side of the plane). The analogous W complex was also prepared, and shown by X-ray structure to have a *syn,anti* structure instead [258].



The reaction of $[\text{MoI}_2(\text{CO})_3(\text{NCMe})_2]$ with $\text{K}[\text{HBpz}_3^*]$ proved to be unexpectedly complex, with a range of products formed depending on the solvent and initial concentration of reagents; most of them arise from degradation of the HBpz_3^* ligand to Hpz^* . With CH_2Cl_2 as solvent, $[\{\text{Mo}(\mu\text{-I})(\text{CO})_2(\text{Hpz}^*)_2\}_2][\text{I}]_2 \cdot 2\text{MeCN}$ (18) was produced, whereas in MeCN , the Mo(V) cluster $[\text{Mo}_4\text{O}_8(\text{OH})_2(\text{Hpz}^*)_6][\text{I}]_2 \cdot 4\text{MeCN}$ (19) was formed; X-ray structures of both were determined [259].



(18)



(19)

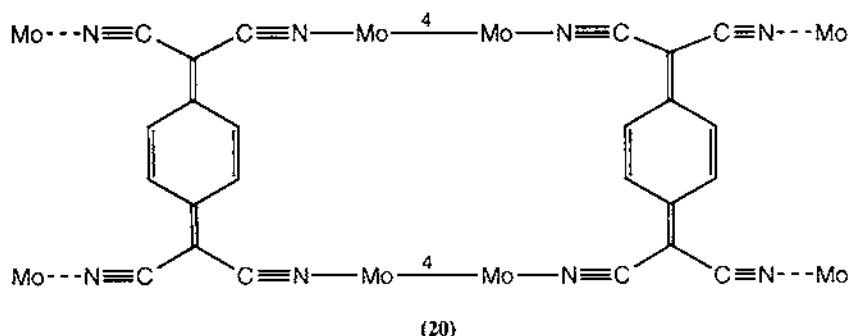
Modification of the pyrazolylborate ligand has also been explored. The complexes $[\text{LMo}(\text{CO})_2(\text{NO})]$ and $[\text{LMo}(\text{NO})\text{Cl}_2]$ have been prepared for $\text{L} = \text{HB}(4\text{-R-dimethylpyrazolyl})_3$, where $\text{R} = \text{Me}, \text{Bu}$, the idea being to create a bowl shaped structure [260].

6.3. Complexes with oxygen donor ligands

A number of complexes of the type $[\text{Mo}_2(\text{O}_2\text{CAr})_4]$ have been prepared for a variety of monosubstituted aryl groups. In certain cases, the MLCT band is red shifted (e.g. $\text{Ar} = p\text{-C}_6\text{H}_4\text{NO}_2$) whereas in others (e.g. $\text{Ar} = m\text{-C}_6\text{H}_4\text{NO}_2$) only a slight shift is observed. Cyclic voltammetry was used to study the influence of the substituents on the ease of oxidation [261]. The complex $[\text{Mo}_2(\text{O}_2\text{CC}_{12}\text{H}_9)_4 \cdot \text{thf}]$ and the corresponding bis(pyridine) adduct have been prepared from biphenyl-4-carboxylic acid; the first of these has a polymeric chain structure with a Mo–Mo distance of $2.0955(1) \text{ \AA}$ and the second has $\text{Mo–Mo} = 2.112(7) \text{ \AA}$ [262]. The complex $[\text{Mo}_2\{(R)\text{-C}_{13}\text{H}_{17}\text{O}_2\}_2\{(S)\text{-C}_{13}\text{H}_{17}\text{O}_2\}_2]$ in which the ligand is the drug ibuprofen, 4-isobutyl- α -methylphenylacetic acid, has also been prepared; it is a centrosymmetric dimer in the solid state with $\text{Mo–Mo} = 2.085(2) \text{ \AA}$ [263]. Molybdenum acetate has been used as a reagent for determining the absolute configurations of diols derived from monosaccharides by the sign of the Cotton effect in the CD spectra [264].

The reaction of $[\text{Mo}_2(\text{O}_2\text{CCF}_3)_4]$ with 2,5-dimethyl- N,N' -dicyanoquinone diimine gave a one-dimensional polymeric species $[\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{dm-dcnqi}) \cdot \text{C}_6\text{H}_6]$ which forms a zigzag chain with $\text{Mo–Mo} = 2.127(2) \text{ \AA}$. There is a π -stacking motif between the quinone imine and the benzene of crystallisation [265]. Treatment of the same carboxylate complex with TCNQ gave $[\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{TCNQ})_{0.5}(m\text{-xylene})]_2 \cdot [\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(m\text{-xylene})]$. This consists of an unprecedented one-dimensional polymer in which the four cyano groups of each TCNQ ligand bridge between four different Mo_2 units to form a 24-membered ring, shown in (20); the Mo–Mo bond length in this portion of the crystal is $2.1126(8) \text{ \AA}$, and in the Mo_2 units which do not bear TCNQ units it is $2.1131(11) \text{ \AA}$, both of these being longer than in $[\text{Mo}_2(\text{O}_2\text{CCF}_3)_4]$. There is a π -stacking interaction between the TCNQ units and m -xylenes [266].

The reaction of $[\text{Mo}_2(\text{NCMe})_8]^{4+}$ with RCO_2H and $(\text{RCO})_2\text{O}$ provides a route



to the compounds $[\text{Mo}_2(\mu\text{-O}_2\text{CR})_2(\text{NCMe})_6]^{2+}$ ($\text{R} = \text{Me}, \text{CH}_2\text{Cl}, \text{tBu}, \text{CF}_3$) [231]. The reaction of $[\text{Mo}_2(\mu\text{-OAc})_2(\text{NCMe})_6]^{2+}$ with 9-ethylguanine in MeCN afforded $[\text{Mo}_2(\mu\text{-OAc})_2(\mu\text{-9-EtG})_2(\text{NCMe})_2][\text{BF}_4]_2$, which was structurally characterised as its 2MeCN solvate. The two ethylguanine ligands are attached through N7 and O6 in a head-to-head arrangement, with a Mo–Mo distance of 2.1371(6) Å [267]. The catalytic activity of $[\text{Mo}_2(\text{NCMe})_8]^{4+}$ and $[\text{Mo}_2(\mu\text{-OAc})_2(\text{NCMe})_6]^{2+}$ for the polymerisation of neat cyclopentadiene or its dimer has been assessed; species supported on silica showed much reduced activity [268].

Further details have appeared of complexes containing the anion of 6-diphenylphosphino-2-hydroxypyridine, pyphos^- . Reaction of $[\text{PtX}_2(\text{Hpyphos})_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with $[\text{Mo}_2(\text{OAc})_4]$ or $[\text{Mo}_2(\text{OAc})_2(\text{NCMe})_6]^{2+}$ gave $[\text{Cl}_2\text{PtMo}_2(\mu\text{-pyphos})_2(\mu\text{-OAc})_2]_2$ in which there appears to be some direct interaction between the Pt and the Mo_2 unit; the molecules are dimers by virtue of a loose interaction between the oxygen of one acetate group and the axial coordination site of a second Mo_2 unit, as observed in the structure of the analogous Pd complex reported previously [269]. A second approach involves the reaction of $[\text{Mo}_2(\text{pyphos})_4]$ with $[\text{MX}_2(\text{PhCN})_2]$ ($\text{M} = \text{Pd}, \text{Pt}; \text{X} = \text{Cl}, \text{Br}, \text{I}$) to give linear tetranuclear complexes $[\text{X}_2\text{MMo}_2(\text{pyphos})_4\text{MX}_2]$ in which there is also a weak interaction between M and the quadruply bonded Mo_2 core. Reduction of these compounds with Et_4NBH_4 or by heating or irradiation gave $[\text{XMMo}_2(\text{pyphos})_4\text{MX}]$ in which there is a direct M–Mo bond and the Mo–Mo bond order has been reduced to three ($\pi^2\delta$ bond) [270]. A theoretical study of direct exchange coupling in dinuclear complexes of Cr(II) and Mo(II) has appeared from the same group [271].

The thiobenzoate compound $\text{cis-}[\text{Mo}_2(\text{SOCPh})_4(\text{O}=\text{PPh}_3)_2]$ has been structurally characterised; the Mo–Mo distance is 2.152(1) Å and the triphenylphosphine oxide ligands are only loosely bound [272].

6.4. Complexes with sulfur donor ligands

Protonation of $[\text{Mo}(\text{S}_4)(\text{NO})(\text{X})]$ ($\text{S}_4 = ^-\text{SC}_6\text{H}_4\text{SCH}_2\text{CH}_6\text{H}_4\text{S}^-$) occurred at one sulfur of the S_4 ligand when $\text{X} = \text{SPh}$ or NO , but where $\text{X} = \text{PMe}_3$, decomposition occurred to give $[\{\text{Mo}(\text{S}_4)(\text{NO})\}_2]$ and $[\text{HPMe}_3]^+$. Alkylation of $[\text{Mo}(\text{S}_4)(\text{NO})\text{Cl}]$ with R_3O^+ occurs on one of the terminal sulfur atoms of the S_4 ligand in

all cases [273]. This starting material reacts with $\text{LiSC}_6\text{H}_4\text{SMe}$ to give $[\text{Mo}(\text{S4})(\text{NO})(\text{SC}_6\text{H}_4\text{SMe})]$ in which the SMe group is not coordinated. This paper also reports the decarbonylation of $[\text{Mo}(\text{CO})_3(\text{S4})]$ to $[\{\text{Mo}(\text{CO})(\text{S4})\}_2]$ [274].

The coordination chemistry of 2,2'-dipyridyl diselenide has been explored. Its reaction with $[\text{Mo}(\text{CO})_4(\text{nbd})]$ resulted in Se–Se bond cleavage to give seven-coordinate $[\text{Mo}(\text{CO})_3(\text{SeC}_5\text{H}_4\text{N})_2]$ [275]. The reaction of $[\text{Mo}(\text{dtc})_2(\text{CO})_2]$ ($\text{dtc} = \text{S}_2\text{CNMe}_2$) with the thiacycloalkyne 1,4,7-trithiacycloundec-9-yne gave a compound of the type $[\text{Mo}(\text{dtc})_2(\text{alkyne})_2]$ [276].

7. Molybdenum(I)

The reaction of $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ with pyridine-2-thione (pySH) and PPh_3 gave three complexes. The main products were $[\text{Mo}_2(\mu\text{-pyS})_2(\text{CO})_4(\text{PPh}_3)_2]$ and $[\text{Mo}_2(\mu\text{-pyS})_2(\text{CO})_5(\text{PPh}_3)]$, but traces of the trinuclear complex $[\text{Mo}_3(\mu\text{-pyS})_2(\mu_3\text{-pyS})_2(\text{CO})_6]$ were also found; the first and third of these were subjected to X-ray analysis [277]. The complex $[(\text{OC})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{Mo}(\text{CO})_4]$ was produced from the reaction of *trans*- $[\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})_2]$ with $[\text{Mo}(\text{CO})_6]$ in benzene; although some degree of metal–metal bonding is implied, the Fe–Mo distance is quite long, 2.854(1) Å [278]. The compound $[\{\text{LMo}(\text{CO})_2\}_2]$, where $\text{L} = [\text{CpCo}\{\text{P}(\text{OMe})_2\text{O}\}_3]^-$, has been crystallographically characterised; it contains a $\text{Mo}\equiv\text{Mo}$ triple bond [2.467(1) Å] and is an analogue of the well-known $[\text{Mo}_2(\text{CO})_4\text{Cp}_2]$ [279].

8. Molybdenum(0)

8.1. Complexes with carbonyl ligands

A review of the use of *ab initio* calculations in studies of M–L interactions in metal carbonyls has appeared [280]. The geometries of complexes of the type $[\text{M}(\text{CO})_5\text{L}]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{L} = \text{CO}, \text{SiO}, \text{CS}, \text{N}_2, \text{NO}^+, \text{CN}^-, \text{HCCH}; \text{C}=\text{CH}_2, \text{CH}_2, \text{CF}_2, \text{H}_2$) have been optimised by *ab initio* calculations at the MP2 and CCSD(T) level; good agreement with experimental values was achieved. A charge decomposition method was used to determine the amount of backbonding between M and L, which was correlated with the bond length of the CO ligand *trans* to L [281]. A paper modelling the geometries and H_2 dissociation energies of $[\text{M}(\text{CO})_5(\text{H}_2)]$ (same M) by the same method was inadvertently omitted from last year's review [282]. As part of a study of the coordination of CO to cationic species such as $[\text{Au}(\text{CO})_2]^+$, calculations were also carried out on other species, including $[\text{Mo}(\text{CO})_6]$ in order to show that the amount of σ -donation does not correlate with the force constant of the CO bond [283].

The use of organometallic complexes for the synthesis of other species in zeolite matrices; e.g. preparing MoO_3 from molybdenum carbonyl, has been reviewed [284]. A combined DRIFTS and molecular simulation study of the coadsorption

of $[\text{Mo}(\text{CO})_6]$ and benzene into faujasitic zeolites has appeared. In Na_{56}FAU the reagents undergo rapid reaction on warming to give $[\text{Mo}(\text{CO})_3(\eta\text{-C}_6\text{H}_6)]$ trapped inside the zeolite supercage; in a more sodium-rich zeolite the two molecules are not in close proximity and warming results in decarbonylation to $\text{Mo}(\text{CO})_3$ groups coordinated to the zeolite oxygen atoms [285]. The reversible photodissociation of $[\text{Mo}(\text{CO})_6]$ adsorbed onto NaY zeolite under vacuum, giving $\text{Mo}(\text{CO})_3$ groups, has also been reported [286]. Thin layers of zeolite Y loaded with $[\text{Mo}(\text{CO})_6]$ have been prepared [287]. When adsorbed into faujasitic zeolites, $[\text{Mo}(\text{CO})_6]$ reacted with H_2S to give MoS_2 [288].

A study of the adsorption of $[\text{Mo}(\text{CO})_6]$ onto the (110) surface of TiO_2 has been undertaken using temperature programmed desorption, FT-RAIRS and XPS techniques. It revealed some dissociation to $\text{Mo}(\text{CO})_3$ units and the formation of small Mo particles above 220 K [289]. The decomposition of $[\text{Mo}(\text{CO})_6]$ on a Ni(100) surface has also been examined [290]. A comparison of the EXAFS spectra of MgO-supported PtMo catalysts prepared either from $[\text{PtCl}_2(\text{PhCN})_2]$ and $[\text{Mo}(\text{CO})_6]$ or from $[\text{Pt}\{\text{Mo}(\text{CO})_3\text{Cp}\}_2(\text{PhCN})_2]$ showed no evidence for Pt–Mo interactions in the first case but some in the second [291]. Sonochemical treatment of $[\text{Mo}(\text{CO})_6]$ gave molybdenum carbide, Mo_2C [292].

A time resolved IR spectroscopic study of the laser flash photolysis of $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) in supercritical Ar, Kr, Xe or CO_2 allowed the detection of the transient $[\text{M}(\text{CO})_5\text{L}]$ species (for Cr and Mo, $\text{L} = \text{Kr}, \text{Xe}, \text{CO}_2$; for W, $\text{L} = \text{Ar}$ too). The second order rate constants for the back-reaction of these species with CO were evaluated, with the result that $\text{Kr} > \text{Xe}$ and CO_2 , and Cr and $\text{Mo} > \text{W}$ [293]. The influence of the size of R on the rates of epoxidation of 1-octene and cyclohexene by ROOH catalysed by $[\text{Mo}(\text{CO})_6]$ has been explored; large variations were observed, implying that the reaction is performed by an intact alkylperoxo species [294]. Molybdenum carbonyl has found application as a catalyst in organic chemistry for the ring opening of isoxazoles [295,296] and the cyclisation of alkynols to dihydrofuran derivatives [297].

The carborane complex $[\text{LMo}(\text{CO})_3]^{2-}$ ($\text{L} = \eta^5\text{-C}_2\text{B}_9\text{H}_{11}$) reacted with S_2Ph_2 to afford $\text{cis-}[\text{LMo}(\text{CO})_2(\text{SPh})_2]^{2-}$, which in turn reacted with iodosylbenzene to give either $[(\eta^1\text{-L})\text{MoO}_3]^{2-}$ or $[\text{LMoO}_2(\mu\text{-O})\text{MoO}_2\text{L}]^{2-}$ depending on the counterion present [298].

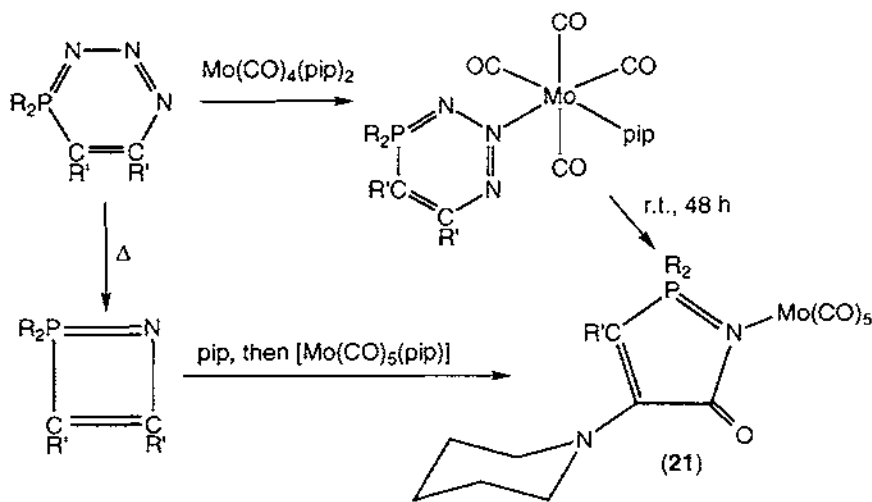
The reaction of $[\text{Mo}(\text{CO})_6]$ with $\text{RNH}(\text{CH}_2)_n\text{N}=\text{PPh}_3$ ($\text{R} = \text{H}, \text{Et}, \text{Ph}; n = 2\text{--}4$) gave initially the isonitrile complexes $[\text{M}(\text{CO})_5\{\text{CN}(\text{CH}_2)_n\text{HNR}\}]$ which then underwent cyclisation to the carbene complexes $[\text{Mo}(\text{CO})_5\{\text{C}=\text{N}(\text{CH}_2)_n\text{NH}\}]$; the NH bond in the product could be deprotonated and then alkylated [299]. The synthesis of the chelating isonitrile ligand $\text{CH}_2(\text{OC}_6\text{H}_4\text{-}o\text{-NC})_2$ and its coordination to $[\text{Mo}(\text{CO})_4(\text{nbd})]$ to give $\text{cis-}[\text{Mo}(\text{CO})_4(\text{L})]$, which contains a 12-membered chelate ring, have been described [300]. The reaction of $[\text{Mo}(\text{CO})_5(\text{thf})]$ with the stable stannylene SnArR , where $\text{Ar} = 2,4,6\text{-C}_6\text{H}_2\text{Bu}_3$ and $\text{R} = \text{CH}_2\text{CMe}_2\text{-}3,5\text{-C}_6\text{H}_3\text{Bu}_2$, gave the base-free complex $[\text{Mo}(\text{CO})_5(\text{C}=\text{SnArR})]$; the X-ray structure showed a Mo–Sn bond of length 2.765(1) Å [301].

Complexation of a 1,2,3,4- λ^5 -triazaphosphinine to $[\text{Mo}(\text{CO})_4(\text{pip})_2]$ occurs to give $[\text{Mo}(\text{CO})_4(\text{pip})(\text{L})]$; however, this slowly converts into (21) in which a piperidyl

group has migrated onto the ring and a CO insertion reaction has occurred. The same product could be obtained by ring contraction of the heterocycle followed by complexation (Scheme 4) [302].

A laser flash photolysis study has been conducted of the ring closing substitution reaction of $[\text{Mo}(\text{CO})_5(\text{L-L})]$ to give chelated $[\text{Mo}(\text{CO})_4(\text{L-L})]$, where L-L = phen or a number of substituted derivatives. The activation parameters are sensitive to the nature of the solvent and the steric and electronic properties of the ligand; this is consistent with an I_a mechanism which gradually changes to I_d with increasing steric bulk of L-L [303]. The nature of the low-lying unoccupied molecular orbitals in phen, 3,4,7,8-tetramethyl phen and four symmetrical diaza-1,10-phenanthroline (dap) derivatives has been investigated by ab initio calculations. The radical anion produced by reduction of one of these derivatives, 4,7-dap, or its $\text{M}(\text{CO})_4$ complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) was shown by EPR spectroscopy to have the extra electron in an orbital whose nature is predicted only by high-level calculations [304].

Complexes of the type $[\text{Mo}(\text{CO})_4\text{L}]$ have been prepared from 2-phenylazopyridine, $\text{NC}_5\text{H}_4\text{N}=\text{NPh}$, and derivatives with a variety of substituents on the py ring. The ^{95}Mo NMR spectroscopic shifts of the compounds were correlated with the lowest energy electronic transition, with the sum of the $\nu(\text{CO})$ frequencies, with the oxidation potential, and with the Hammett parameter for the substituents. The effect of the substituents operates through an inductive mechanism [305]. Several new complexes of pyridine 2-carbaldehyde azine, $\text{NC}_5\text{H}_4\text{CH}=\text{NN}=\text{CHC}_5\text{H}_4\text{N}$, have been prepared, including $[\text{Mo}(\text{CO})_3(\text{PPh}_3)\text{L}]$, $[\text{Mo}_2(\text{CO})_{8-n}(\text{PPh}_3)_n(\mu\text{-L})]$ ($n = 1, 2$) and $[\text{Mo}_2(\text{CO})_6(\mu\text{-dppe})(\mu\text{-L})]$; they all show strong solvatochromism [306]. The complexes $[\text{Mo}(\text{CO})_4(\text{NC}_5\text{H}_4\text{CR}=\text{NCHR}'\text{Ph})]$ and $[\text{Mo}(\text{CO})_3(\text{L})(\text{NC}_5\text{H}_4\text{CH}=\text{NCHMePh})]$ [$\text{R}, \text{R}' = \text{H}, \text{Me}; \text{L} = \text{PET}_3, \text{PPh}_3, \text{P}(\text{OEt})_3$ or $\text{P}(\text{OCH}_2\text{CCH}_2)_3\text{Ct}$] have been obtained from Schiff bases derived from pyridine-



Scheme 4.

2-carbaldehyde. For the phosphine complexes, separate ^{95}Mo NMR spectroscopic signals could be observed for the *mer* isomer and two diastereomers of the *fac* isomer [307].

The reaction of $[\text{Mo}(\text{CO})_6]$ with tris(3,5-dimethyltriazolyl)borate, KHBtz_3^+ , gave the crystallographically characterised $[\text{NEt}_4][\text{LMo}(\text{CO})_3]$; the iodide derivative $[\text{LMo}(\text{CO})_3\text{I}]$ was also made [308]. Complexation of mono-N-alkyl cyclen or cyclam to an $\text{M}(\text{CO})_3$ fragment ($\text{M} = \text{Cr}, \text{Mo}$) occurs to give a single isomer in which the tertiary nitrogen is not coordinated. However, an equilibrium between two forms of the complex is suggested by the formation of 1,7-dialkylated cyclen derivatives on reaction with alkyl iodides [309].

A re-examination of the use of $\nu(\text{CO})$ and other parameters such as phosphine basicity in the evaluation of σ - and π -bonding components in $\text{M}-\text{P}$ bonding has appeared [310]. A method for calculating the force field of compounds of the type $[\text{M}(\text{CO})_5\text{L}]$ has been devised [311]. The ^{95}Mo NMR spectra of a wide range of complexes $[\text{Mo}(\text{CO})_{6-n}(\text{PR}_3)_n]$ ($\text{R} = \text{aryl}, \text{alkyl}, \text{OR}, \text{NR}_2, \text{Cl}, \text{H}; n = 1-3$) have been recorded. There is a reasonable correlation between the steric bulk of the ligand and the chemical shift [312]. A solid state ^{31}P NMR spectroscopic study of 5-phenyldibenzophosphole, its chalcogenides, and their $[\text{M}(\text{CO})_5\text{L}]$ and $[\text{M}(\text{CO})_4\text{L}_2]$ complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) has been undertaken in order to determine the ^{31}P chemical shift tensors. The most shielded part of the tensor lies along the $\text{M}-\text{P}$ axis and is virtually independent of M [313]. A study of the rates of intramolecular ligand exchange in $[\text{M}(\text{CO})_{6-n}\{\text{P}(\text{OMe})_3\}_n]$ has shown that they increase in the order $n = 3 < 1 < 2$, and $\text{Mo} < \text{W} < \text{Cr}$. The rates of *fac-mer* isomerisation of the triphosphite complexes were also examined; computational simulations suggested a trigonal twist mechanism [314].

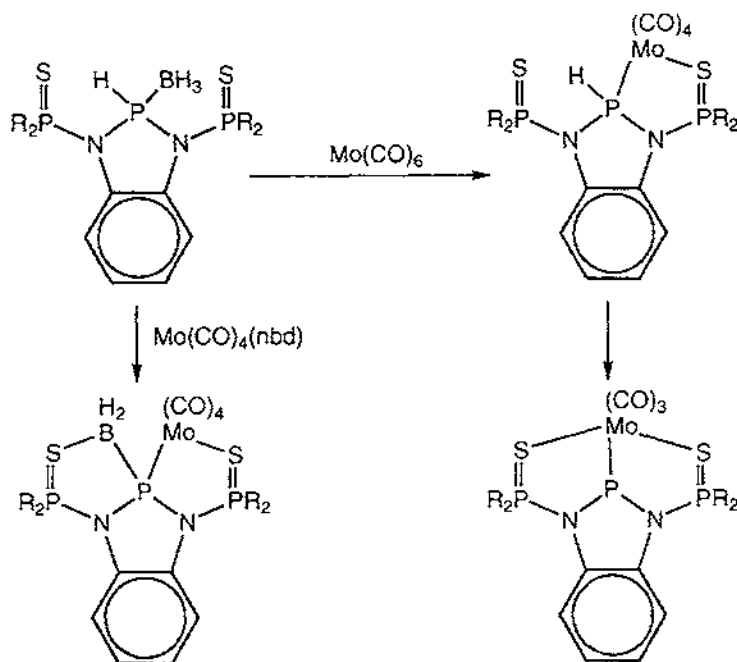
The effect of the *trans* ligand in $[\text{ML}(\text{CO})_4(\text{H}_2)]$ and its dihydride isomer has been modelled by *ab initio* calculations at the MP2 level for a range of L ($\text{CO}, \text{SiO}, \text{CS}, \text{N}_2, \text{NO}^+, \text{CN}^-, \text{H}^-, \text{Cl}^-, \text{F}^-, \text{PH}_3$); the optimised geometries and H_2 dissociation energies were calculated, and the donor-acceptor properties of L were assessed using charge decomposition analysis. Strong σ -donors were found to enhance $\text{M}-\text{H}_2$ bonding [315]. A density functional theory study has been carried out on the dihydrogen and dihydride isomers of $[\text{Mo}(\text{CO})_n(\text{PH}_3)_{5-n}\text{H}_2]$ ($n = 1, 3, 5$); for the $n = 3$ case, a comparison between Cr, Mo and W was also performed. The optimised geometries are in close agreement with experimental data, and existing dihydrogen complexes were found to be more stable than their dihydride isomers. For $n = 3$ the H_2 bond dissociation energy exhibits a minimum at molybdenum, with relativistic effects becoming important for tungsten [316].

Complexation of the unsymmetrical diphosphene $\text{ArP}=\text{POAr}'$ ($\text{Ar} = 2,4,6\text{-C}_6\text{H}_2\text{Bu}_3$, $\text{Ar}' = \text{C}_6\text{H}_2\text{-2,6-Me}_2\text{-4-Bu}$) with $[\text{Mo}(\text{CO})_5(\text{thf})]$ gave mainly the isomer with the POAr' terminus bound to the metal, but also some of the isomer with ArP coordinated [317]. The reaction of $[\text{Mo}(\text{CO})_6]$ with LiPPh_2 followed by alkylation with RX gave $[\text{Mo}(\text{CO})_5(\text{PPh}_2\text{R})]$. If propargyl chloride was used as RX , three isomers were formed containing $\text{PPh}_2\text{CH}_2\text{C}\equiv\text{CH}$, $\text{PPh}_2\text{CH}=\text{C}=\text{CH}_2$ and $\text{PPh}_2\text{C}\equiv\text{CMe}$ ligands [318]. Photolysis of $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{Mo}, \text{W}$) with the diphosphaferrocene $[(\eta\text{-C}_5\text{H}_3\text{-1,3-}^i\text{Bu}_2)\text{Fe}\{\eta\text{-P}_2\text{C}_3\text{-3,4-(OSiMe}_3)_2\text{-5-SiMe}_3\}]$

produced a $\text{M}(\text{CO})_5$ adduct [319]. Triphosphaferrocene complexes $[\text{Cp}^*\text{Fe}(\eta\text{-C}_2^t\text{Bu}_2\text{P}_3)\text{M}(\text{CO})_5]$ ($\text{M}=\text{Mo}, \text{W}$) have also been prepared [320]. The crystal structure of $[\text{Mo}(\text{CO})_5\{\text{P}(o\text{-C}_6\text{H}_4\text{OMe})_3\}]$ has been determined [321].

The equilibrium constants for the bonding of Li^+ and Na^+ to the metallomacrocycles *cis*- $[\text{Mo}(\text{CO})_4\{\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{PPh}_2\}]$ ($n=4, 5$) have been determined by NMR spectroscopic titration. For $n=4$ the values are roughly the same for both cations, but for $n=5$ the affinity for Na^+ is much larger than for Li^+ . The X-ray structure of the $n=4$ complex revealed it to be a solvate in which H_2O and MeOH molecules were held inside the ring by hydrogen bonds to the ether groups [322]. Complexes of $\text{Z-Ph}_2\text{PCH}_2\text{C}^t(\text{Bu})=\text{NNHPh}$ have been made by reaction with $[\text{Mo}(\text{CO})_4(\text{nbd})]$; with a 1:1 ratio $[\text{Mo}(\text{CO})_4(\text{L})]$ was formed in which the ligand is a *P,N*-chelate, but with a 2:1 ratio the *P*-bonded $[\text{Mo}(\text{CO})_4\text{L}_2]$ was formed [323]. The pendant phosphine arm of $[\text{Mo}(\text{CO})_4\{(\text{Ph}_2\text{PCH}_2)_2\text{CMe}(\text{CH}_2\text{PPh}_2)\}]$ has been coordinated to gold(I) and gold(III) fragments such as AuL ($\text{L}=\text{Cl}, \text{C}_6\text{F}_5, \text{acac}$) and $\text{Au}(\text{C}_6\text{F}_5)_3$ [324].

The hydridotriphosphazane $\text{C}_6\text{H}_4\{\text{N}(\text{NP}(\text{S})(\text{NET}_2)_2)_2\text{PH}\cdot\text{BH}_3$ reacts with $[\text{Mo}(\text{CO})_6]$ by displacement of the BH_3 to afford $[\text{Mo}(\text{CO})_4\text{L}]$, in which it acts as a *P,S* donor; heating gave $[\text{Mo}(\text{CO})_3(\text{L})]$ in which it is a *P,S,S*-tridentate ligand. Complexation of the original borane adduct with $[\text{Mo}(\text{CO})_4(\text{nbd})]$ gave $[\text{Mo}(\text{CO})_4(\text{L}\cdot\text{BH}_2)]$ (Scheme 5) [325]. The coordination chemistry of the hemilabile ether ligand $\text{PhCH}_2\text{P}(\text{CH}_2\text{CH}_2\text{OEt})_2$ has been explored; from its reaction with

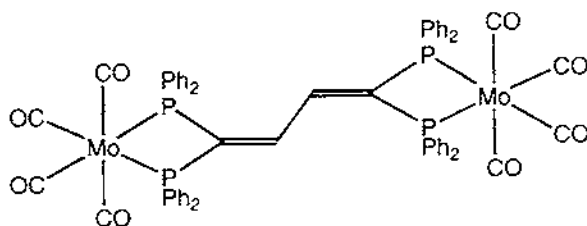


Scheme 5.

[Mo(CO)₃(mesitylene)], the complex *fac*-[Mo(CO)₃(L)₂] was obtained which contains one didentate ligand and one monodentate; the two ligands interchange coordination modes, a process which was studied by VT-NMR spectroscopy [326].

The reaction of [Mo(CO)₄(nbd)] with the four-membered 1,2,3,4-diphosphadiborane ring heterocycle P(^tBu)P(^tBu)B(NMe₂)B(NⁱPr₂) afforded a complex of the rearranged 1,3,2,4-diphosphadiboretane bound through the two P atoms [327]. The synthesis and X-ray structure of the complex *cis*-[Mo(CO)₄(L)₂] has been reported, where L = 1,3,5-triphenyl-1,3,5-diazaphosphorinane [328]. The crystal structures of *trans*-[Mo(CO)₄(L)₂] have been determined for L = PCy₃ [329], P(OMe)₃ [330], and P(O^tBu)₃ [331]. The cone angle of the last ligand is 156°, and that of PCy₃ is 155° in the *trans* isomer compared to 146° in the corresponding *cis* species.

Several papers describe the linking of two molybdenum centres through bridging phosphine ligands. The reaction of [Mo(CO)₄(pip)₂] with Ph₂PC≡CPh₂ gave [(OC)₄Mo(μ-L)₂Mo(CO)₄] which reacted with further L to give *fac, fac*-[(OC)₃Mo(μ-L)₃Mo(CO)₃]. Cyclisation of the three adjacent triple bonds into an arene did not however prove possible [332]. Treating [Mo(CO)₄(pip)₂] with Ph₂PCH₂C≡CCH₂PPh₂ similarly afforded [(OC)₄Mo(μ-L)₂Mo(CO)₄]; however, an unexpected co-product, [Mo(CO){η²-LMo(CO)₄}₃], was obtained in which three Mo(CO)₄L chelates are joined to a fourth Mo through their alkyne moieties, as in the well-known [Mo(CO)(RC≡CR)₃] species [333]. The ligand 1,4-C₆H₂F₂-2,5-(PPh₂)₂ was made from 1,2,4,5-C₆H₂F₄ and LiPPh₂; its reaction with [Mo(CO)₄(pip)₂] gave [(OC)₄Mo(μ-L)₂Mo(CO)₄], and a mixed species [(OC)₄Mo(μ-L)(μ-Ph₂PC≡CPh₂)Mo(CO)₄] was also made [334]. The related ligand 1,2,4,5-C₆H₂(PPh₂)₄ has been used to link two metal centres in [(OC)₄M(μ-L)M(CO)₄] (M = Cr, Mo, W), *fac, fac*-[(L¹)(OC)₃Mo(μ-L)Mo(CO)₃(L¹)] (L¹ = MeCN, PPh₃, monodentate dppe) and [(dppe)₂(OC)₂M(μ-L)M(CO)₂(dppe)₂] (M = Mo, W). However, attempts to make oligomeric or polymeric species were unsuccessful [335]. The highly unusual photochemical reaction between the niobium alkyne complex [Nb(I)(CO)₂(PMe₂Ph)₂(η²-Ph₂PC≡CPh₂)] and [Mo(CO)₆] gave the unexpected product (22), in which two Mo(CO)₄ fragments are bridged by a 1,1,4,4-tetrakis(diphenylphosphino)-1,3-butadiene ligand [336].



(22)

Full details have appeared of a modified synthesis of [Mo(CO)₄(dppe)] and its reaction with NO⁺. The product, *mer*-[Mo(CO)₃(dppe)(NO)][BF₄], reacted with MeCN to give [Mo(CO)₂(NCMe)(dppe)(NO)]⁺ and [Mo(CO)(NCMe)₂

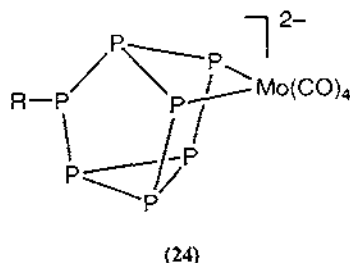
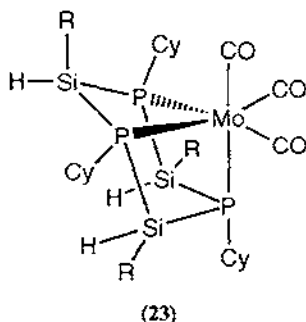
(dppe)(NO)]⁺ from which the acetonitrile ligands can be displaced by phosphines. Treatment of the monoacetonitrile complex with NaSR (R = *o*-tolyl) gave [Mo(SR)(CO)₂(dppe)(NO)]. The reaction of *mer*-[Mo(CO)₃(dppe)(NO)][BF₄] with LiC≡CR (R = H, ^tBu, ⁱPr, Ph, SiMe₃, etc.) gave the acetylide complexes [Mo(C≡CR)(CO)₂(dppe)(NO)] [337]. The complex *trans,mer*-[M(CO)₃(L)₂(pyz-R)]⁺ (M = Mo, W; L = PⁱPr₃, PCy₃) where pyz-R is an N-alkylpyrazinium cation, NC₄H₄NR⁺ (R = Me, C₁₈H₃₇) have been prepared. Oxidation leads to a 17-electron Mo(I) species, but reduction occurs on the pyz-R ligand and is accompanied by dissociation of one phosphine ligand to leave a five-coordinate radical [338]. The complexes [{Mo(CO)₃(L)}₂C₆₀] and [Mo(CO)₂(PPh₃)₂(L)]₂·C₆₀ (L = diacetyldihydrazone) have been reported; in the first the fullerene is bound to the metal, but the second is a co-crystallisation species [339].

A full account of the abstraction of methoxide from *fac*-[Mo(CO)₃(bpy){PXY(OMe)}] [XY = (NEt₂)₂, NEt₂/OMe, NMeCH₂CH₂NMe, NMeCH₂CH₂O, OCM₂Me₂O] with BF₃·OEt₂ to give the cationic phosphonium species *fac*-[Mo(CO)₃(bpy){P(XY)}]⁺ has appeared. A competing reaction in some cases was substitution of F for OMe. Complexes containing cyclic phosphine ligands were found to be more stable [340]. The changes in the ⁹⁵Mo NMR spectra that accompany abstraction from cyclic aminophosphine complexes such as *fac*-[Mo(CO)₃(bpy){P(NMeCH₂CH₂NMe)OMe}] and the subsequent isomerisation to the *mer* isomer of [Mo(CO)₃(bpy){P(NMeCH₂CH₂NMe)}]⁺ have been followed; a deshielding of the doublet resonance is observed, together with an increase in ¹J(MoP) [341]. The carbonyl substitution reaction of *mer*-[Mo(CO)₃(bpy){P(NMeCH₂CH₂O)}]⁺ with further aminophosphine YP(NMeCH₂CH₂NMe) [Y = OMe, OEt, SEt, N(CH₂)₄] is accompanied by the irreversible migration of Y from the incoming ligand to the phosphonium centre and formation of [Mo(CO)₂(bpy){PY(NMeCH₂CH₂O)}{P(NMeCH₂CH₂N)}]⁺ [342]. A short review of this area has been presented at a recent conference [343].

The three- and four-membered ring phosphines PhP(CH₂CH₂) and PhP(CH₂CH₂CH₂) have been prepared from Li₂PPh and Cl(CH₂)_nCl (n = 2, 3). The X-ray structures of *fac*-[Mo(CO)₃L₃] were determined for both ligands [344]. The tripodal ligand N(CH₂PPh₂)₃ has been prepared, together with *fac*-[Mo(CO)₃L]; the complex can be protonated on the nitrogen atom [345]. Oxidation of [Mo(CO)₃{(PRCH₂CH₂CH₂)₃}] (R = ⁱPr, CH₂SiMe₃, Et, CH₂ⁱPr) with halogens gave [MoX₂(CO)₂{(PRCH₂CH₂CH₂)₃}] (X = Cl, Br, I) which can be digested in strong base to release the free macrocycle; unfortunately, this reaction fails when R = H, but this macrocycle can be liberated from the analogous Cr complex. Treatment of the Mo(0) complexes with H₂O₂ or ozone gave the macrocycles trioxides [346,347]. The synthesis and X-ray structure of [Mo(CO)₃(PH₂CMe=CH₂)₃] have been described [348].

Elaboration of the CO₂Me groups in the Mo(CO)₃ complex of 1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane has been carried out by conversion firstly into CO₂H, then reduction to CH₂OH and esterification. The resulting ligands can be released from the metal either with pyridine

N-oxide or N_2O , or with H_2O_2 , in which case the tris(phosphine oxide) is formed [349]. The reaction of RSiHCl_2 with LiPHCy and base gave $(\text{CyPSiHR})_3$ ($\text{R} = \text{Ph}$, mes), which complexed to $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ through the three P atoms to give (23) [350]. Solutions of $[\text{M}(\text{CO})_3(\text{P}_7)]^{3-}$ ($\text{M} = \text{Mo}$, W) in en react with 1 atm of CO to give $[\text{M}(\text{CO})_4(\text{P}_7)]^{3-}$ in which the cage is η^2 -bound. The products lose CO again readily, but can be protonated or alkylated to give $[\text{M}(\text{CO})_4(\text{P}_7\text{R})]^{2-}$ (24); these can also be made by carbonylating $[\text{M}(\text{CO})_3(\text{P}_7\text{R})]^{2-}$ [351].



The structure of $[\text{Mo}(\text{CO})(\text{PH}_3)_4(\text{H}\cdots\text{SiH}_3)]$ has been optimised by ab initio calculations at the MP2 level on *cis* and *trans* isomers. The optimised $\text{Si}\cdots\text{H}$ bond length of 1.813 Å is similar to the 1.769 Å observed experimentally for $[\text{Mo}(\text{CO})(\text{H}\cdots\text{SiHPh}_2)(\text{depe})_2]$ [352]. The homolytic M–H bond dissociation enthalpies have been calculated for a number of cationic hydrides, including $[\text{Mo}(\text{H})(\text{CO})(\text{L}_2)_2]$ ($\text{L}_2 = \text{dppm}$, dppe , arphos), by a thermochemical cycle involving the heat of protonation and the redox potential for the metal fragment; the results fall in the range 234–314 kJ mol^{−1} [353]. The reaction of *trans*- $[\text{Mo}(\text{CO})(\text{dmf})(\text{dppe})_2]$ with alkynes $\text{RC}\equiv\text{CH}$ gave the alkynyl hydride $[\text{Mo}(\text{H})(\text{C}\equiv\text{CR})(\text{CO})(\text{dppe})_2]$ when $\text{R} = \text{CO}_2\text{Me}$ and the vinylidene $[\text{Mo}(=\text{C}=\text{CHR})(\text{CO})(\text{dppe})_2]$ if $\text{R} = \text{Ph}$. Both products can be protonated to form alkylidyne complexes [354].

The tripodal stibine ligand $\text{MeC}(\text{CH}_2\text{SbPh}_2)_3$ has been prepared; its reaction with $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{Cr}$, Mo , W) in the presence of NaBH_4 gave *fac*- $[\text{M}(\text{CO})_3(\text{L})]$ [355]. The reaction of $[\text{M}(\text{CO})_5(\text{thf})]$ with two equivalents of $[\text{NEt}_4]_2[\text{OC}_6\text{H}_2\text{-3,5-}^t\text{Bu}_2\text{O}]$ gave the coordinatively unsaturated catecholate complexes $[\text{NEt}_4]_2[\text{M}(\text{CO})_3(\text{OC}_6\text{H}_2^t\text{Bu}_2\text{O})]$ ($\text{M} = \text{Cr}$, Mo , W) which are stabilised by short M–O bonds. The Mo complex exists in equilibrium with a tetracarbonyl species when placed under 1 atm of CO [356].

The $\text{M}(\text{CO})_5$ complexes ($\text{M} = \text{Cr}$, Mo , W) of 2-chalcogenoimidazolines $\text{RNCMe}=\text{CMeNRC}=\text{E}$ ($\text{E} = \text{S}$, Se , Te ; $\text{R} = \text{Me}$, ^iPr) have been prepared [357]. A theoretical analysis of the fluxionality of $[\text{M}(\text{S}_2\text{CPMe}_3)(\text{CO})_2(\text{PMe}_3)_2]$ ($\text{M} = \text{Mo}$, W) involving rotation of the S_2CPMe_2 fragment has appeared [358]. The reaction of $[\text{Mo}(\text{CO})_6]$ with NaSR ($\text{R} = o\text{-tolyl}$) gave $[\text{NEt}_4]_2[\text{Mo}_2(\mu\text{-SR})_2(\text{CO})_8]$; the X-ray structure of the MeCN solvate showed a folded butterfly core with a long Mo–Mo distance of 3.942(3) Å, whereas the analogous complex with $\text{R} = o\text{-C}_6\text{H}_4\text{OH}$ had a

planar core. The compound exhibited two irreversible electrochemical oxidation waves and two irreversible reductions [359]. The reaction of $[\text{CpMo}(\text{CO})_3\text{H}]$ with Me_2S_2 in the presence of allyl chloride gave $[\text{Mo}_2(\text{CO})_2(\mu\text{-SMe})_3\text{Cp}_2]^+$ as the major product, but a second species, $[\text{CpMo}(\text{CO})(\mu\text{-SMe})_3\text{Mo}(\text{CO})_2(\mu\text{-SMe})\text{Mo}(\text{CO})_2\text{Cp}]$, in which the Cp ligand has been lost from the central Mo, was also formed in 15–20% yield [360]. The attempted coordination of $\text{B}(\text{thienyl})_4^-$ to $[\text{Mo}(\text{CO})_3(\text{cht})]$ was unsuccessful, unlike the related $[\text{B}(\text{CH}_2\text{SMe})_4]^-$ ligand [361].

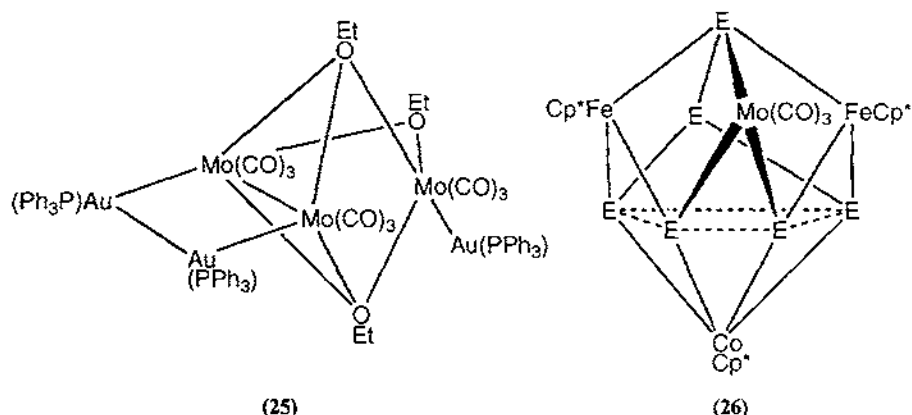
The reaction of $[\text{Fe}(\text{CO})_3(\text{PPh}_2\text{-2-C}_5\text{H}_4\text{N})_2]$ with $[\text{Mo}(\text{CO})_6]$ gave the complex $[(\text{CO})_3\text{Fe}(\mu\text{-Ph}_2\text{P-2-C}_5\text{H}_4\text{N})_2\text{Mo}(\text{CO})_3]$ [362]; an analogous compound containing the $\text{PhMeP-2-NC}_5\text{H}_4$ ligand was also made [363]. The metalloligand $[(\eta\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Ti}(\text{SR})_2]$ ($\text{R} = \text{Et}, \text{Ph}$) reacted with $[\text{Mo}(\text{CO})_4(\text{nbd})]$ to give $[\text{Ti}\{(\mu\text{-SR})(\mu, \eta\text{-C}_5\text{H}_4\text{PPh}_2)\text{Mo}(\text{CO})_4\}_2]$ in which it acts as a *P,S* donor, and $[(\text{OC})_4\text{Mo}(\mu, \eta\text{-C}_5\text{H}_4\text{PPh}_2)\text{Ti}(\text{SR})_2]$ in which it acts as a *P,P* donor; the latter compound can form further adducts with $\text{M}(\text{C}_6\text{F}_5)_2$ ($\text{M} = \text{Pd}, \text{Pt}$) fragments through the thiolate groups [364]. The reaction of $[\text{Mo}(\text{CO})_5(\text{PPh})]^-$ with $[\text{PtCl}_2(\text{L}_2)]$ ($\text{L}_2 = \text{dppe}, \text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ or *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$) gave $[(\text{L}_2)\text{Pt}\{(\mu\text{-PPh})\text{Mo}(\text{CO})_5\}_2]$ as a pair of diastereomers due to the chiral phosphido groups; the Mo–P–Pt angles are wide and the Mo–Pt distances long, indicating the absence of bonding between them. The related $[(\text{OC})_4\text{Mo}(\mu\text{-PPh})_2\text{Pt}(\text{dppe})]$ was also made [365]. Chloride abstraction from $[(\text{OC})_3\text{Mo}(\mu\text{-dppm})_2\text{Pt}(\text{H})\text{Cl}]$ with $\text{Ti}[\text{PF}_6]$ afforded $[(\text{OC})_3\text{Mo}(\mu\text{-dppm})_2\text{Pt}(\text{H})]^+$ in which one of the CO ligands is semibridging [366].

The reaction of $[\text{RuH}_3(\text{PPh}_3)_3]^-$ with $[\text{Mo}(\text{CO})_3(\text{diglyme})]$ gave $[(\text{Ph}_3\text{P})_3\text{Ru}(\mu\text{-H})_3\text{Mo}(\text{CO})_3]^-$; the analogous Cr complex was structurally characterised [367]. A similar reaction employing $[\text{ReH}_9]^{2-}$ as the polyhydride led to the tetrahedral cluster $[\text{H}_4\text{ReMo}_3(\text{CO})_{12}]^{3-}$. NMR spectroscopic studies revealed that the CO ligands are fluxional but the hydrides, which are proposed to be located on the faces, are not [368]. Refluxing a mixture of $[\text{Ru}_3(\text{CO})_{12}]$, $[\text{Mo}(\text{CO})_6]$ and either S_8 or Se_8 in xylene gave a solid which was used to prepare novel catalysts for the electrochemical reduction of O_2 . Monitoring the reaction by IR spectroscopy did not reveal the formation of mixed metal clusters however [369]. Capping the carbido cluster $[\text{PPN}]_2[\text{Re}_6\text{C}(\text{CO})_{19}]$ with $[\text{Mo}(\text{CO})_6]$ under UV irradiation gave $[\text{PPN}]_2[(\text{OC})_4\text{MoRe}_6\text{C}(\text{CO})_{18}]$ in 85% yield [370].

The complex $[\text{NMe}_4][\text{M}_3(\text{CO})_9(\mu\text{-OEt})(\mu\text{-OEt})_2]$ ($\text{M} = \text{Mo}, \text{W}$) reacted with three equivalents of $(\text{PPh}_3)\text{AuCl}$ in the presence of TiPF_6 to give $[\text{M}_3(\text{CO})_9\{\text{Au}(\text{PPh}_3)_3(\mu\text{-OEt})(\mu_3\text{-OEt})_2\}]$ (**25**) in 80% yield [371].

Molybdenum carbonyl units have been incorporated into several iron chalcogenide clusters. The X-ray structure and ^{77}Se NMR spectrum of the previously prepared $[\text{Mo}(\text{CO})_4(\mu_3\text{-Se})_2\text{Fe}_2(\text{CO})_6]$ have been reported [372]. Reaction of equimolar quantities of $[\text{Fe}_2(\mu\text{-SeTe})(\text{CO})_6]$ and $[\text{Mo}(\text{CO})_5(\text{thf})]$ gave the analogous $[\text{Mo}(\text{CO})_4(\mu_3\text{-Te})\text{Fe}_2(\text{CO})_6]$ [373]. However, if two equivalents of the iron reagent were used the double cluster $[\text{Mo}(\text{CO})_2\{(\mu_3\text{-Se})(\mu_3\text{-Te})\text{Fe}_2(\text{CO})_6\}_2]$ was produced instead [374].

The reaction of $[\text{Co}_2(\mu\text{-CO})_2\text{Cp}^*]_2$ with $[\text{Cp}^*\text{Fe}(\eta\text{-E}_5)]$ ($\text{E} = \text{P}, \text{As}$) gave a mixture of compounds including the trinuclear species $[\text{Fe}_2\text{Co}(\mu\text{-P}_2)_3\text{Cp}^*]_3$ or



$[\text{Fe}_2\text{Co}(\mu\text{-As}_3)_2\text{Cp}^*]$. These react further with $[\text{Mo}(\text{CO})_5(\text{thf})]$ to afford tetranuclear clusters $[\text{Fe}_2\text{CoMo}(\mu_3\text{-E})_4(\mu_3\text{-E}_2)(\text{CO})_3\text{Cp}^*]$ (26) [375].

8.2. Complexes with nitrogen and phosphorus donor ligands

Apart from one cited earlier [195], there have been no papers published in this area this year.

9. Molybdenum clusters

9.1. Polyoxomolybdates

The following brief discussion is arranged in order of increasing nuclearity, dealing in each case first with homonuclear species and then with heteropolymolybdates. A special issue of *J. Mol. Catal.* has appeared covering the use of polyoxometalates in catalysis [376] and a review on the photoreactivity of polyoxomolybdates as studied by laser flash photolysis techniques has been published [377].

Aqueous or methanolic solutions of Mo(V) or Mo(VI) oxo species and fluoride react with squaric acid to give oligonuclear species such as $[\text{NET}_4]_3[\text{Mo}_2\text{O}_3\text{Cl}_3(\text{C}_4\text{O}_4)_2]$, $[\text{NET}_4]_3[\text{Mo}_3\text{O}_8(\text{F})(\text{C}_4\text{O}_4)_2]$, and $[\text{NET}_4]_4[\text{Mo}_4\text{O}_{10}\text{F}_6(\text{C}_4\text{O}_4)]$, all of which were structurally characterised [378]. The X-ray structure of $[\text{NBu}_4]_2[\text{Mo}_4\text{O}_{10}\text{L}_2(\text{OMe})_2]$, where L = phenanthrene quinone, has been determined [379]. Clusters such as $[\text{Mo}_3\text{O}_9(\text{OMe})_3(\text{RhCp}^*)_2]$ and $[\text{Mo}_4\text{O}_{16}(\text{RhCp}^*)_4]$ have been impregnated onto silica and then photoreduced under CO to give active species for propene metathesis [380,381].

The reaction of $[\text{MoO}_2(\text{acac})_2]$ or MoCl_4 with REO_3H_2 ($\text{E} = \text{P, As}$; $\text{R} = \text{various}$) has given rise to a large number of Mo_2 to Mo_6 species, 11 of which were structurally characterised, including $[\text{Mo}_2\text{O}_5(\text{O}_2\text{PPh}_2)_4]^{2-}$, four clusters of the type $[\text{Mo}_4\text{O}_{10}(\text{O}_3\text{ER})_4]^{4-}$, two of the type $\text{Mo}_5\text{O}_{15}(\text{O}_3\text{PR})_2]^{4-}$, and two of the type

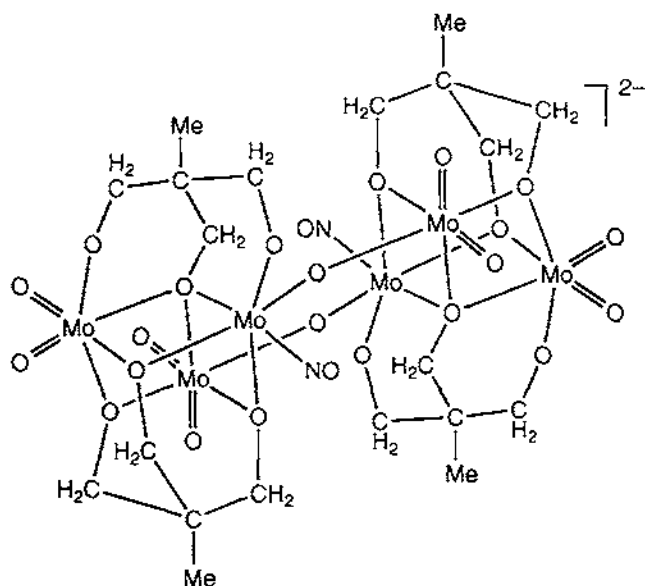
$[\text{Mo}_6\text{O}_{18}(\text{O}_3\text{ER})_2]^{4-}$ [382]. The complex $\text{Na}_2[\text{Mo}_5\text{O}_{15}(\text{Hamp})_2] \cdot 6\text{H}_2\text{O}$ has been prepared by reaction of sodium molybdate with H_2amp , adenosine 5'-monophosphate [383].

The reaction of 2-thienylamidoxime or 2-thienylmethylamidoxime (H_2L) with $[\text{MoO}_2(\text{acac})_2]$ or $\alpha\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$ gave a number of compounds ranging in nuclearity from 1 to 5; addition of NH_2OH to the mixture allowed the introduction of nitrosyl groups. Compounds characterised included $[\text{MoO}(\text{acac})(\text{HL})(\text{L})]$, $[\text{Mo}(\text{NO})(\text{acac})_2(\text{HL})]$, $[\text{Mo}_4\text{O}_{10}(\text{OMe})_2(\text{L})_2]^{2-}$, and salts of $[\text{Mo}_5\text{O}_{13}(\text{OEt})_4(\text{NO})]^{3-}$ [384]. New nitrosyl polyoxomolybdates have been synthesized from $[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{3-}$. Reaction with $\text{MeC}(\text{CH}_2\text{OH})_3$ gave hexanuclear $[\text{NBu}_4]_2[\text{Mo}_6\text{O}_{10}(\text{NO})_2\{(\text{OCH}_2)_3\text{CMe}\}_4]$ (27), whereas with acetylacetone, octanuclear $[\text{NBu}_4]_2\text{Na}_2[\text{Mo}_8\text{O}_{22}(\text{NO})_2(\text{acac})_2] \cdot 2\text{H}_2\text{O}$ (28) was obtained [385]. The pentanuclear species $[\text{NBu}_4]_2[\text{Mo}_4\text{O}_{12}\{\text{Mo}(\text{NO})_2\}(\text{H}_2\text{L})_2\text{L}_2]$ (H_2L = methylthioamidoxime) has been prepared; the Mo_4W and W_4Mo analogues were also made; they consist of two dinuclear $\text{M}_2\text{O}_5(\text{H}_2\text{L})(\text{L})$ units bonded to a central $\text{M}(\text{NO})_2$ core [386].

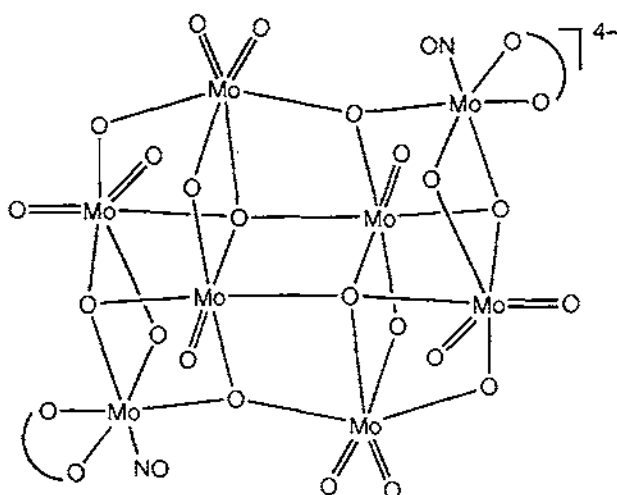
The 2,4,6-triphenylpyrylium salt of $[\text{Mo}_6\text{O}_{19}]^{2-}$ has been prepared and structurally characterised. The cation is a photosensitizer and irradiation causes an immediate reversible photochromism [387]. A solid state reaction between $[\text{NH}_4]_2[\text{Mo}_2\text{S}_2]$, AgI and NBu_4Br gave the mixed salts $[\text{NBu}_4]_4[\text{M}_6\text{O}_{19}][\text{Ag}_2\text{I}_4]$ ($\text{M} = \text{Mo}, \text{W}$) instead of mixed metal species; both compounds were structurally characterised [388]. The crystal structures of the $[\text{Na}(\text{DB18C6})]$ salt of $[\text{Mo}_6\text{O}_{19}]^{2-}$, formed from Na_2MoO_4 and dibenzo-18-crown-6 [389], and of the mixed species $[\text{Na}(\text{DB24C8})]_2[\text{WMO}_5\text{O}_{19}]$ and $[\text{Na}(\text{DB18C6})(\text{MeOH})]_2[\text{Mo}_2\text{W}_4\text{O}_{19}] \cdot \text{DB18C6} \cdot \text{MeOH}$ have also been determined [390]. The synthesis of a range of mixed metal species $[\text{MW}_5\text{O}_{19}]^{n-}$, where M can be $\text{Ti}, \text{Zr}, \text{V}, \text{Nb}$ or Ta as well as Mo or W , has been achieved by hydrolysis of metal alkoxides in the presence of molybdate or tungstate; the reaction can be monitored by ^{17}O NMR spectra and in favourable cases is very specific, for example the reaction of $[\text{MoO}_4]^{2-}$ with an appropriate molar ratio of $[\text{WO}(\text{OMe})_4]$ to give $[\text{MoW}_5\text{P}_{19}]^{2-}$ [391].

The salt $[\text{tmedaH}_2]_3[\text{Mo}_7\text{O}_{24}]$ has been structurally characterised; it is photosensitive and hydrogen bonds from the cation to $\text{Mo}=\text{O}$ groups are thought to play a role in photoreduction and H transfer to give $\text{MoO}_5(\text{OH})$ centres [392]. A new MgO -supported catalyst for alkane dehydrogenation has been prepared from $[\text{PtMo}_6\text{O}_{24}]^{8-}$ and characterised by EXAFS, which shows that the cluster structure is disrupted during adsorption and calcination [393]. The oxidation of $\text{Co}(\text{II})$ by $[\text{HSO}_5]^-$ in the presence of molybdate in weak acid gave primarily $[\text{H}_4\text{Co}_2\text{Mo}_{10}\text{O}_{38}]^{6-}$. The kinetics of the formation of this species revealed three stages, and the formation of an intermediate, $[\text{H}_6\text{CoMo}_6\text{O}_{24}]^{4-}$, which was isolated as its $[\text{NH}_4]^+$ salt and crystallographically characterised [394].

The ROMP polymerisation of norbornene by chiral salts such as $[\text{R}_3\text{NH}]_4[\text{Mo}_8\text{O}_{26}]$, where R_3N is a natural product such as (+)-cinchonine, (+)-hydroquinidine or (–)-quinine, leads to insoluble polymers; addition of 1-hexene as a chain transfer agent gives a better yield [395]. The crystal structure of $[\text{NHEt}_3]_4[\beta\text{-Mo}_8\text{O}_{26}]$ has been determined [396], as have those of the piperazinium



(27)

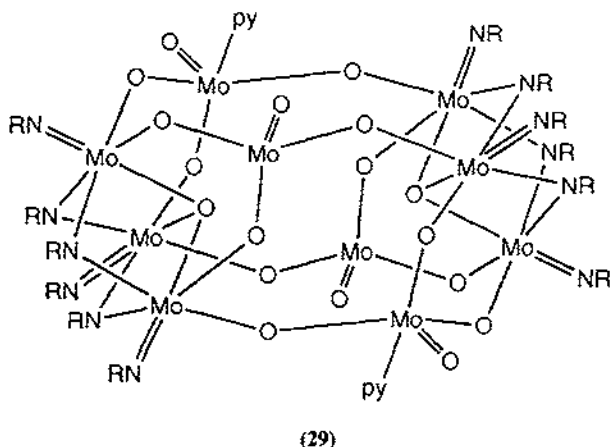


(28)

salt $[\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2]_3[\text{Mo}_8\text{O}_{27}]$ which has infinite chains of anions [397] and $[\text{NH}_4]_6[\text{Mo}_9\text{O}_{30}] \cdot 5\text{H}_2\text{O}$ which has Mo_8 units linked in a zigzag chain structure through additional MoO_4 tetrahedra [398]. Salts of the anion $[\text{AlWMo}_8\text{O}_{32}]^{7-}$ have been isolated [399].

The reaction of $\alpha\text{-}[\text{PMo}_{12}\text{O}_{40}]^{3-}$ with RNCO ($\text{R} = p\text{-tolyl}$) gave several known products, including reduced derivatives of the anion and $\text{RN}=\text{NR}$, but also the

highly functionalised imido complex $[\text{Mo}_{10}(\text{NR})_{12}\text{O}_{18}(\text{py})_2]$ (**29**), which consists of two $\text{Mo}_3(\text{NR})_6\text{O}_7$ units held together by four additional molybdenum atoms [400].



A Mo K-edge EXAFS study has been carried out on solid $[\text{NBu}_4]_3[\text{PMo}_{12}\text{O}_{40}]$ at 80 K; as expected it showed the systematic asymmetry of the Mo–O bonds with distances of 1.81 and 1.97 Å. The structures of $[\text{Mo}_6\text{O}_{19}]^{2-}$ and $[\text{TeMo}_6\text{O}_{24}]^{6-}$ were also studied; the solid state structure appears to be maintained in solution [401]. A spectrophotometric method for determining the coordination ratio of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ has been reported [402].

From a reaction involving the hydrolysis of phenylphosphate, the benzene solvate $[\text{H}_3\text{PMo}_{12}\text{O}_{40}] \cdot 3\text{C}_6\text{H}_6$ was isolated and crystallographically characterised [403]. Salts of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ have been made with counter-ions Ag^+ and Tl^+ [404] and Cs^+ [405]. The thermal dehydration of crystals of $[\text{VO}(\text{H}_2\text{O})_5][\text{H}(\text{PMo}_{12}\text{O}_{40}) \cdot 23\text{H}_2\text{O}]$ was studied by thermogravimetry and EPR spectroscopy; above 75 °C the vanadyl group becomes bound to the surface of the anion and above 320 °C, decomposition of the Keggin structure starts [406]. The effect of using vanadyl or copper counter-ions on the selectivity of the oxidative dehydrogenation of isobutyric acid by $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ or $[\text{PVMo}_{11}\text{O}_{40}]^{4-}$ has been explored [407]. Charge transfer salts have been prepared by reaction of *p*- $\text{Me}_2\text{NC}_6\text{H}_4\text{NH}_2$ with $[\text{H}_3\text{PMo}_{12}\text{O}_{40}]$ or $[\text{H}_7\text{PMo}_{12}\text{O}_{40}]$; their third order non-linear optical response was measured [408]. The reaction of $[\text{LCu}(\text{OAc})_2]$ with $[\text{H}_3\text{PMo}_{12}\text{O}_{40}]$ gave $[\text{LCu}(\text{HPMo}_{12}\text{O}_{40})]$ [$\text{L} = \text{N}, \text{N}, \text{N}', \text{N}'$ -tetrakis(2-benzimidazolylmethyl)-1,2-ethylenediamine] [409].

The catalytic properties of $[\text{H}_3\text{PMo}_{12}\text{O}_{40}]$ for the gas phase partial oxidation of organics have been compared to those of transition metal phosphates [410]. A number of other organic reactions are catalysed by $[\text{H}_3\text{PMo}_{12}\text{O}_{40}]$, including C–C cleavage in diols by H_2O_2 to give carboxylic acids [411], the pinacol rearrangement of diols to carbonyl compounds [412], and the oxidation of alkanes to carboxylic acids [413,414].

The thermal behaviour of $[\text{H}_3\text{PMo}_{12}\text{O}_{40}]$ has been explored by two groups; in

one of these studies, ^{31}P NMR spectroscopic monitoring showed decomposition to species such as $[(\text{MoO}_2)_2(\text{P}_2\text{O}_7)]$ [415,416]. Studies of the adsorption of $[\text{H}_3\text{PMo}_{12}\text{O}_{40}]$ onto alumina from water, water/ethanol or HCl have shown that in water alone depolymerisation to $[\text{PMo}_{11}\text{O}_{39}]^{7-}$ occurs, whereas the anion remains intact in the other two solvent systems; after adsorption the Mo_{11} species is also formed from the HCl solution [417]. The thermal behaviour of silica-supported molybdophosphoric acids has been studied by IR, Raman and XRD techniques, and by catalytic activity in methanol oxidation [418]. Temperature programmed decomposition of 12-molybdophosphoric acid in NH_3 or CH_4/H_2 has given rise to Mo_2N or Mo_2C containing some phosphorus [419].

The polymer derived from *p*-phenylenediamine and terephthalaldehyde can be protonated by $[\text{H}_3\text{PMo}_{12}\text{O}_{40}]$; the cluster remains intact in the polymer matrix [420]. Carbon fibre microelectrodes modified with 12-molybdophosphoric or 12-molybdosilicic acid have been studied [421]. The electrochemistry of a variety of polyanions has been explored by adsorbing them onto the surface of solid gold, graphite or glassy carbon electrodes [422].

The X-ray structure of $[\text{NBu}_4]_2[\text{SMo}_{12}\text{O}_{40}]$ has been determined and its geometry compared with the analogous clusters containing P, Si or Ge [423]. The compounds $[\text{NH}_4]_6[\text{PMo}_{11}\text{SbO}_{40}] \cdot 11\text{H}_2\text{O}$ and $[\text{NH}_4]_6[\text{PMo}_9\text{SbO}_{40}] \cdot 14\text{H}_2\text{O}$ have been prepared and characterised; the first contains Sb(III), the second Sb(V) [424]. The Ce(IV) species $\text{K}_5[\text{PMo}_{11}\text{CeO}_{40}] \cdot 20\text{H}_2\text{O}$ has been characterised [425].

A combinatorial approach has been applied to the synthesis and evaluation of polyoxometalates for the oxidation of tht, this acting as a model reaction for the oxidation of mustard gas. A range of Mo/W compositions between $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ and $[\text{PW}_{12}\text{O}_{40}]^{3-}$ with varying amounts of vanadium was assayed, in particular $[\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}]$ supported on carbon [426,427]. The practical production of PMoV derivatives for oxidation reactions has been discussed [428]. A mixture of molybdovanadophosphate, hydroquinone and O_2 has been used as the reoxidation component for a Pd-catalysed alkene oxidation reaction [429] and $[\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}]$ was found to be effective for the same purpose in Pd-catalysed allylic acetoxylation of cyclohexene [430].

Compounds of the type $[\text{H}_{3+n}\text{PMo}_{12-n}\text{V}_n\text{O}_{40}]$ have been used to catalyse a number of organic reactions, including the oxidation of 2-methyl-1-naphthol to 2-methyl-1,4-naphthoquinone (vitamin K) [431,432], the aerobic oxidation of phenols including 2,3,6-trimethylphenol [433–435], and the oxidative dehydrogenation of α -terpinene to *p*-cymene with $t\text{BuOOH}$ [436]. Palladium salts of $[\text{H}_{3+n}\text{PMo}_{12-n}\text{V}_n\text{O}_{40}]$ supported on silica have been used in the gas phase oxidation of 2-butene. Under the reaction conditions, the cluster becomes reduced by five electrons, but DRIFTS spectra show that the Keggin structure remains intact; however, under steady state conditions, catalyst reoxidation is a problem [437]. The deposition of molybdovanadophosphoric acids on glassy carbon electrodes has been reported [438].

The reaction of Na_2MoO_4 , Na_2WO_4 and KH_2PO_4 in water gave the mixed polyanion $\text{Na}_9[\text{PMo}_6\text{W}_3\text{O}_{34}] \cdot 10\text{H}_2\text{O}$ [439], which on treatment with appropriate metal salts afforded $[\text{NBu}_4]_4\text{H}_n[\text{PMo}_7\text{W}_3\text{M}_2\text{O}_{38}(\text{H}_2\text{O})_2]$ ($n = 3$, $\text{M} = \text{Zn}$, Co , Ni , Cu ; $n = 1$,

M=Cr, Fe) or $[\text{NBu}_4]_4\text{H}_2[\text{PW}_3\text{Mo}_6\text{V}_3\text{O}_{40}]$; X-ray structures determined for the Zn and Cu clusters showed that the metal sites were all disordered [439,440]. Starting from the related anion $\text{Na}_9[\text{PMoW}_8\text{O}_{34}] \cdot 11\text{H}_2\text{O}$, reaction with metal nitrates gave $[\text{NBu}_4]_3\text{H}_n[\text{PMoW}_9\text{M}_2\text{O}_{38}(\text{H}_2\text{O})_2]$ ($n=4$, M=Mn, Co, Cu, Zn; $n=2$, M=Fe) [441].

The electrochemical characterisation of the Keggin ions $\alpha\text{-}[\text{XMo}_{3-x}\text{V}_x\text{W}_9\text{O}_{40}]^{n-}$ has been reported where X=P ($n=3+x$) or Si ($n=4+x$). In each case a one-electron reduction could be observed. The EPR g values for the V(IV) centre depend on the identity of the surrounding atoms; in the V_2 and V_3 cases, electron hopping and delocalisation was evident [442]. Addition of the $\text{M}_2\text{S}_2\text{O}_3^{2+}$ fragment (M=Mo, W) to $\gamma\text{-}[\text{PW}_{10}\text{O}_{36}]^{7-}$ afforded the species $\gamma\text{-}[\text{PW}_{10}\text{M}_2\text{O}_{38}]^{5-}$; they have Keggin type structures capped by the M_2 fragment [443]. A similar approach starting from $\gamma\text{-}[\text{SiW}_{10}\text{O}_{36}]^{8-}$ produced $\gamma\text{-}[\text{SiW}_{10}\text{M}_2\text{S}_2\text{O}_{38}]^{6-}$; the X-ray structure of the Mo derivative was determined [444].

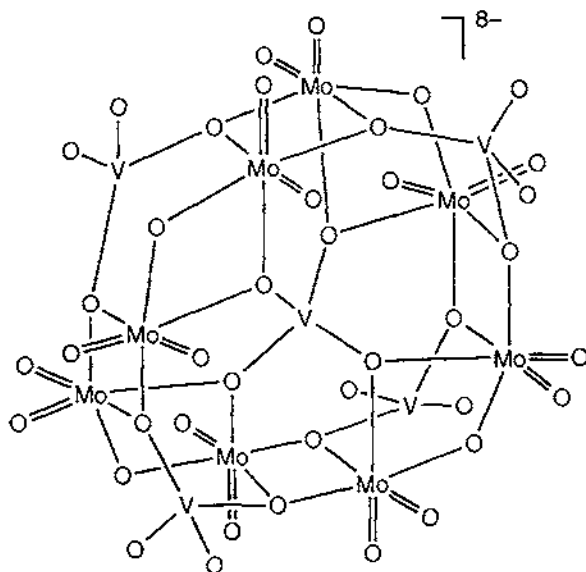
Two papers have described the electrochemical behaviour of $\text{K}_{10}\text{H}_3[\text{Nd}(\text{SiMo}_7\text{W}_4\text{O}_{39})_2]$ in aqueous solution [445,446]. The synthesis and structure of the species $\text{K}_8\text{H}_5[\text{La}(\text{SiW}_2\text{Mo}_9\text{O}_{39})_2(\text{H}_2\text{O})_{17}] \cdot 4\text{H}_2\text{O}$ and $\text{K}_7\text{H}_8[\text{Ln}(\text{Mo}_4\text{V}_6\text{O}_{36})]$ have also been reported [447,448].

The reaction of MoO_3 and $\text{NH}_4[\text{VO}_3]$ gave the cluster $\text{K}_8[\text{Mo}_8\text{V}_5\text{O}_{40}] \cdot n\text{H}_2\text{O}$ (30) in two different crystalline modifications depending on whether $n=9$ or 10. It contains one V(IV) centre as shown by the EPR spectrum. The X-ray structure reveals a central VO_4 tetrahedron surrounded by a puckered ring of eight edge-sharing MoO_6 octahedra and four VO_4 tetrahedra [449]. The bivanadyl capped highly reduced Keggin ion $[\text{NHEt}_3]_5[\text{PMo}_{12}(\text{VO})_2\text{O}_{40}]$ has been produced by a hydrothermal synthesis; it contains six Mo(VI), six Mo(V), and two V(IV) [450].

The assembly of two highly negatively charged clusters into a dimeric structure has been achieved. Crystal structures of $\text{K}_7[(\text{AsOH})_3(\text{MoO}_3)_3\text{AsMo}_9\text{O}_{33}] \cdot 15\text{H}_2\text{O}$ and $\text{K}_{10}[(\text{AsOH})_6(\text{MoO}_3)_2(\text{O}_2\text{MoOMoO}_2)_2(\text{AsMo}_9\text{O}_{33})_2] \cdot 12\text{H}_2\text{O}$ have revealed that the first consists of a Keggin-type fragment capped with a six-membered ring of three MoO_3 and three $\text{As}(\text{OH})^{2+}$ units, and the second is a dimeric assembly of the first through oxo bridges involving four molybdenums of these capping units [451].

The hydrothermal reactions of polyalcohols with molybdate, MoO_3 , Mo metal, NHMe_3Cl and NEt_4Cl gave a number of products. Two polyoxometalate clusters, $[\text{NH}_4]_7[\text{NaH}_{12}\text{Mo}_{16}\text{O}_{52}] \cdot 4\text{H}_2\text{O}$ and $\text{K}_2[\text{NHMe}_3]_4[\text{H}_{14}\text{Mo}_{16}\text{O}_{52}] \cdot 8\text{H}_2\text{O}$, were characterised; each contains four Mo(VI) centres and 12 Mo(V). In addition to these, the bowl shaped giant clusters $[\text{XH}_n\text{Mo}_{42}\text{O}_{109}\{(\text{OCH}_2)_3\text{CR}\}_7]^{m-}$ [$\text{R}=\text{Me}$, CH_2OH ; $\text{X}=\text{Na}(\text{H}_2\text{O})_3^+$, $m=9$, $n=13$ or $m=7$, $n=15$; $\text{X}=\text{MoO}_3$, $m=9$, $n=14$ or $m=10$, $n=13$] were produced; they contain six Mo(VI) and 36 Mo(V) centres and can be readily synthesized from the Mo_{16} species [452]. The preparations of $[\text{P}_2\text{W}_{15}\text{Mo}_2\text{NbO}_{62}]^-$ and $[\text{H}_{6+n}\text{P}_2\text{Mo}_{18-n}\text{V}_n\text{O}_{62}]$ ($n=1-3$), both of which are Dawson-type polyanions, have been described [453,454].

The magnetic properties of the giant clusters $[\text{NH}_4]_{21}\{[\text{VO}(\text{H}_2\text{O})\}_6\{[\text{Mo}_2(\mu\text{-H}_2\text{O})_2(\mu\text{-OH})\}_3\{[\text{Mo}_{17}(\text{NO})_2\text{O}_{58}(\text{H}_2\text{O})_2\}_3\} \cdot 65\text{H}_2\text{O}$, $[\text{NH}_2\text{Me}_2]_{18}[\text{NH}_4]_6\{[\text{VO}(\text{H}_2\text{O})\}_6\{[\text{Mo}_2(\mu\text{-H}_2\text{O})_2(\mu\text{-O})\}_3\{[\text{Mo}_{17}(\text{NO})_2\text{O}_{58}(\text{H}_2\text{O})_2\}_3\} \cdot 14\text{H}_2\text{O}$, and



(30)

$\text{Na}_3[\text{NH}_4]_{12}[\{\text{Fe}(\text{H}_2\text{O})_2\}_6\{\text{Mo}_2(\mu\text{-H}_2\text{O})_2(\mu\text{-OH})\}_3\{\text{Mo}_{17}(\text{NO})_2\text{O}_{58}(\text{H}_2\text{O})_2\}_3] \cdot 76\text{H}_2\text{O}$ have been studied. Each cluster consists of three of the common Mo_{17} structural motifs bridged by paramagnetic V(IV) or Fe(III) centres and arranged in a trigonal prismatic way. There is an efficient exchange pathway between centres located in the triangular faces of the prism and a strong antiferromagnetic coupling even though the distance between V(IV) centres is over 6.5 Å. An analogy was suggested between the metal ions located in these giant clusters and those in metalloproteins [455].

Miller and coworkers claim to have unravelled a 200-year-old mystery, namely the nature of “molybdenum blue”. It is proposed to be a form of molecular MoO_3 , probably with the formula $[(\text{MoO}_3)_{154}(\text{H}_2\text{O})_{70}\text{H}_x]^{y-}$ based on the fact that it bears a strong similarity to the giant cluster $[\text{NH}_4]_{25 \pm 5}[\text{Mo}_{154}(\text{NO})_{14}\text{O}_{420}(\text{OH})_{28}(\text{H}_2\text{O})_{70}] \cdot n\text{H}_2\text{O}$ [456].

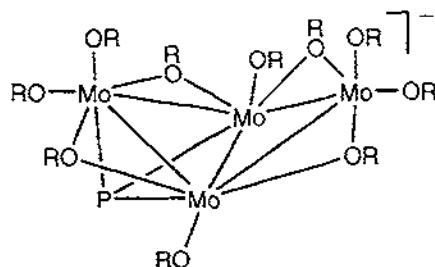
9.2. Halide clusters

A molecular orbital treatment of octahedral clusters including $[\text{Mo}_6\text{Cl}_{14}]^{2-}$ and $[\text{Mo}_6\text{S}_8(\text{PEt}_3)_6]$ has been derived [457]. The resonance Raman spectra of $[\text{Mo}_6\text{X}_8\text{Y}_6]^{2-}$ (X, Y = Cl, Br, I) have been recorded. All three totally symmetric modes were identified, whereas only two had been found previously. It was found that the metal–halide vibrations are largely insensitive to M and to the other ligands present. The spectra of compounds with Y = OMe and SPh were also investigated, and the crystal structure of $[\text{NBu}_4]_2[\text{Mo}_6\text{Cl}_8(\text{SPh})_6]$ was determined [458]. The IR and Raman spectra of $[\text{Mo}_6\text{X}_8\text{Y}_6]^{2-}$ (X = Cl, Br, Y = F, Cl, Br, I) have been

recorded at 10 K on samples isotopically labelled with ^{92}Mo , ^{100}Mo , ^{35}Cl or ^{37}Cl ; significant frequency shifts were observed on labelling the Mo atoms or the halides. The force constants of the Mo–Mo bonds were calculated [459]. Two groups have shown that molybdenum halide clusters can be coordinated intact to poly(4-vinylpyridine) polymers; the degree of crosslinking involved could be controlled by varying the number of labile ligands from six in $[\text{Mo}_6\text{Cl}_8(\text{OTf})_6]^{2-}$ to two in $[\text{Mo}_6\text{Cl}_{12}(\text{EtOH})_2]$; the latter cluster retains its strongly luminescent properties on incorporation into the polymer [460]. The supported clusters can oxidize alkenes under photoexcitation through generation of singlet oxygen [461]. The reaction of CuX with $[\text{Mo}_6\text{X}_{12}]$ gave $[\text{Cu}_2\text{Mo}_6\text{X}_{14}]$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) in which the Mo_6 halide octahedra are linked by trigonal planar $\text{Cu}(\text{I})$ centres [462].

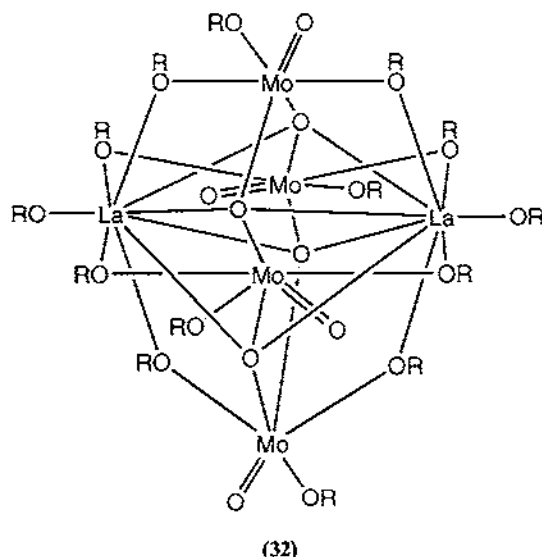
9.3. Other clusters, including cubanes

Treatment of $[\text{M}_2(\text{OCH}_2^t\text{Bu})_6]$ ($\text{M}=\text{Mo}, \text{W}$) with 0.5 equiv. $\text{NaP}(\text{SiMe}_3)_2$ in benzene containing 18-crown-6 gave initially $[\text{M}_4(\mu_3\text{-PSiMe}_3)(\text{OR})_{11}]^-$, which are reactive intermediates on the way to $[\text{M}_4(\mu_3\text{-P})(\text{OR})_{10}]^-$ (31), isolated as $[\text{Na}(\text{18C6})]^+$ salts; two different crystal forms of the Mo complex were X-rayed at two different temperatures. The cluster can also be prepared from $[\text{Mo}_2(\text{OR})_6]$, PH_3 and KOR , and this route was used to make the analogous arsenic compound $[\text{Mo}_4(\mu_3\text{-As})(\text{OR})_{10}]^-$ [463]. The reaction of “ $\text{La}(\text{O}^i\text{Pr})_3$ ”, which is more accurately formulated as $[\text{La}_5\text{O}(\text{O}^i\text{Pr})_{13}(\text{O}^i\text{PrOH})_2]$, with $[\text{MoO}(\text{O}^i\text{Pr})_4]$ in a 1:2 ratio gave $[\text{La}_2\text{Mo}_4(\mu_4\text{-O})_4(\mu\text{-O}^i\text{Pr})_8(\text{O}^i\text{Pr})_6]$ (32) [464].



(31)

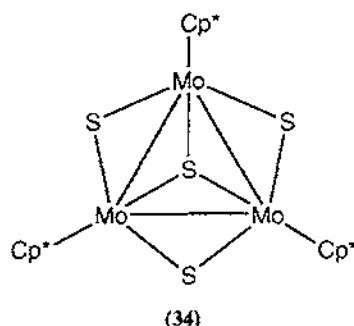
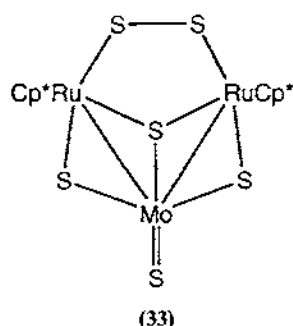
Further clusters of the general type $[\{\text{MMo}_3\text{O}_4(\text{O}_2\text{CR})_8\}_2]^{2-}$, which contain two Mo_3O_4 incomplete cubane units bridged by the M^{3+} ions, have been synthesized; for example, the reaction of sodium molybdate, $[\text{Mo}(\text{CO})_6]$ and AlCl_3 in $(\text{RCO})_2\text{O}$ ($\text{R}=\text{Me}, \text{Et}$) gave $\text{Na}_2[\{\text{AlMo}_3\text{O}_4(\text{O}_2\text{CR})_8\}_2]$ [465]. The same general synthetic method has been employed to make $\text{M}_2[\{\text{CrMo}_3\text{O}_4(\text{O}_2\text{Cet})_8\}_2]$ ($\text{M}=\text{Li}, \text{K}$) from molybdate and $[\text{Cr}(\text{CO})_6]$ [466], $\text{Na}_2[\{\text{VMo}_3\text{O}_4(\text{OAc})_8\}_2]$ from sodium vanadate and $[\text{Mo}(\text{CO})_6]$ [467], and $\text{Na}_2[\{\text{Cr}_{0.5}\text{Fe}_{0.5}\text{Mo}_3\text{O}_4(\text{O}_2\text{Cet})_8\}_2]$ from sodium molybdate and a mixture of $[\text{Cr}(\text{CO})_6]$ and $[\text{Fe}(\text{CO})_5]$ [468]. Heating molybdate with $[\text{W}(\text{CO})_6]$ and CrCl_3 in propionic anhydride gave the mixed species $\text{Na}_2[\{\text{CrMo}_{1.5}\text{W}_{1.5}\text{O}_4(\text{O}_2\text{Cet})_8\}_2]$, whereas from a mixture of tungstate, $[\text{Mo}(\text{CO})_6]$ and AlCl_3 , the complex $\text{Na}_2[\{\text{AlMo}_2\text{WO}_4(\text{O}_2\text{Cet})_8\}_2]$ was obtained



[467]. From a reaction of tungstate with $[\text{Mo}(\text{CO})_6]$ in propionic anhydride, the compound $\text{Na}[\text{MoW}_2\text{O}_2(\text{O}_2\text{C}_2\text{H}_5)_9]$ was formed, which reacts with $[\text{Cr}(\text{CO})_6]$ to give $\text{Na}_2[\{\text{CrMoW}_2\text{O}_4(\text{O}_2\text{C}_2\text{H}_5)_8\}_2]$; it can also be hydrolysed in 2 M HCl and ZnCl_2 to give $[\text{MoW}_2\text{O}_2(\text{O}_2\text{C}_2\text{H}_5)_6(\text{H}_2\text{O})_3][\text{ZnCl}_4] \cdot 2\text{H}_2\text{O}$ [469]. The synthesis and electrochemistry of a series of clusters $[\text{Mo}_3(\mu_3\text{-O})\text{Cl}_6(\text{O}_2\text{CR})_3]^-$ have been studied [470,471]. New tetranuclear clusters $[\text{Mo}_4\text{O}_6\text{X}_2(\text{O}_2\text{C}_2\text{H}_5)_6]$ ($\text{X}=\text{Cl}, \text{Br}$) have been isolated from the reaction of $[\text{MoO}_2\text{X}_2]$ with propionic anhydride [472].

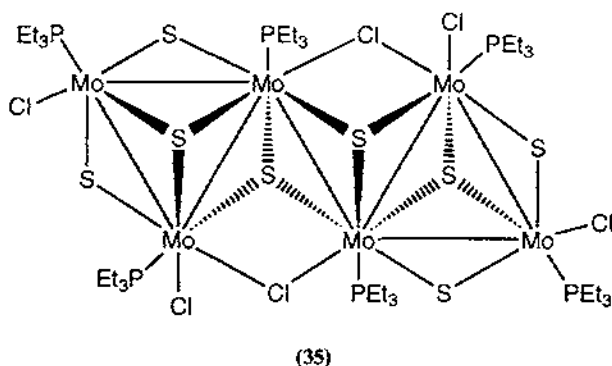
The use of $[\text{Mo}_n\text{S}_{4-n}]^{2-}$ in the construction of heteronuclear complexes and larger cubane-type clusters has continued to be exploited. The reaction of $[\text{Ru}_2\text{Cl}_4\text{Cp}_2^*]$ with $[\text{MS}_4]^{2-}$ ($\text{M}=\text{Mo}, \text{W}$) gave the trinuclear clusters $[\text{Ru}_2\text{M}(=\text{S})(\mu\text{-S})_2(\mu_3\text{-S})(\mu\text{-S}_2)\text{Cp}_2^*]$ (33), both of which were structurally characterised [473]. Microwave irradiation of a well-ground mixture of $[\text{NH}_4]_2[\text{MS}_4]$, TiBr and NBu_4Br ($\text{M}=\text{Mo}, \text{W}$) gave a 25% yield of $[\text{NBu}_4][\text{TiMoS}_4]$ which has a polymeric chain structure and displays some self-focusing non-linear optical properties [474]. The linear clusters $[\text{NBu}_4]_2[\text{M}_2\text{M}'\text{S}_4\text{O}_4]$ ($\text{M}=\text{Mo}, \text{W}$; $\text{M}'=\text{Co}, \text{Ni}, \text{Fe}$) have been prepared from $[\text{MO}_2\text{S}_2]^{2-}$ [475]. The complex $[\text{L}(\text{PPh}_3)\text{Cu}(\mu\text{-S})_2\text{Mo}(\mu\text{-S})_2\text{Cu}(\text{PPh}_3)\text{L}]$, where $\text{L}=\text{S}$ -bound pyridine-2-thione, has been prepared and structurally characterised [476].

Treatment of $[\text{Cp}^*\text{Mo}(\text{S}^i\text{Bu})_3]$ with sodium amalgam gave an 88% yield of the new trinuclear cluster $[\text{Cp}_3^*\text{Mo}_3\text{S}_4]$ (34), which was structurally characterised. Molecular orbital calculations on this seven-electron cluster suggest that the odd electron resides in an orbital of e symmetry, and some evidence for a subtle Jahn–Teller distortion was found in the structure [477]. The compounds $[\text{Mo}_3\text{E}_7\text{L}_3][\text{TCNQ}]$ [$\text{E}=\text{S}, \text{L}=\text{S}_2\text{CNEt}_2, \text{S}_2\text{CNC}_4\text{H}_8, \text{S}_2\text{P}(\text{OEt})_2$; $\text{E}=\text{Se}, \text{L}=\text{S}_2\text{CNEt}_2$] have been prepared; the mixed chalcogen species $[\text{Mo}_3\text{S}_4\text{Se}_3\text{L}_3][\text{TCNQ}]$ have also been made for $\text{L}=\text{S}_2\text{CNEt}_2$ and $\text{S}_2\text{P}(\text{OEt})_2$ [478]. The reaction of $[\text{Mo}_3(\mu_3\text{-E})(\mu\text{-S})_3(\mu\text{-OAc})(\text{dtp})_3(\text{py})]$ [$\text{dtp}=\text{S}_2\text{P}(\text{OEt})_2$]



with BiI_3 (for $\text{E}=\text{O}$) or SbBr_3 (for $\text{E}=\text{S}$) unexpectedly gave the novel hexanuclear cluster $[\{\text{Mo}_3(\mu_3\text{-S})(\mu\text{-S}_2)_2(\text{dtp})_3\}(\mu_3\text{-S})(\mu\text{-S}_2)\{\text{Mo}_3(\mu_3\text{-S})(\mu\text{-S})_3(\mu\text{-OAc})(\text{dtp})_3\}]$ in which two triangular units are linked through S and S_2 bridges [479].

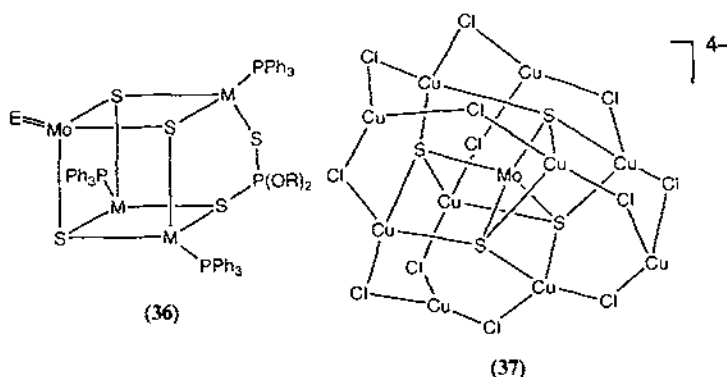
The synthesis of chalcogenide clusters of Mo, Cr, W and Re has been the subject of two short reviews [15h,17], and a new method for the synthesis of chalcogenide clusters from MoO_3 involving electrochemical reduction to MoCl_3 and then reaction with H_2S followed by aerial oxidation has been described [480]. Treatment of $[\text{Mo}_3\text{S}_7\text{Cl}_4]$ with PEt_3 in thf followed by reaction with Mg gave crystals of the raft-like cluster $[\text{Mo}_6\text{S}_8\text{Cl}_6(\text{PEt}_3)_6]$ (35); the $[\text{Mo}_3\text{S}_4\text{Cl}_4(\text{PEt}_3)_x(\text{thf})_{5-x}]$ cluster is thought to be an intermediate in this transformation. The selenium analogue was also prepared [481]. Treatment of $[\text{Mo}_3(\mu_3\text{-S})(\text{S}_2)_6]^{2-}$ with PMe_3 afforded $[\text{Mo}_4(\mu_3\text{-S})_4(\mu\text{-S})_4(\text{SH})_2(\text{PMe}_3)_6]$, which could be converted into $[\text{Mo}_4\text{S}_6\text{X}_2(\text{PMe}_3)_6]$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}, \text{SCN}$) or $[\text{Mo}_4\text{S}_6\text{X}_2(\text{PMe}_3)_4]$ for $\text{X}=\text{S}_2\text{CNEt}_2$ [482]. The crystal structure of $[\text{Mo}_3\text{S}_4(\text{Hox})_2(\text{ox})(\text{H}_2\text{O})_3]$ has been determined; each Mo atom bears a water molecule and a mono- or dianionic oxalate [483]. The electrochemistry of $[\text{Mo}_4\text{S}_4(\mu\text{-OAc})_2(\text{dtp})_4]$, where $\text{dtp}=\text{S}_2\text{P}(\text{OEt})_2$, has been investigated [484].



Much attention has again been given to the synthesis and study of molybdenum chalcogenide clusters containing coinage metals, particularly Cu and Ag, and such compounds have recently been reviewed [15j,18]. The possible mechanisms for cluster

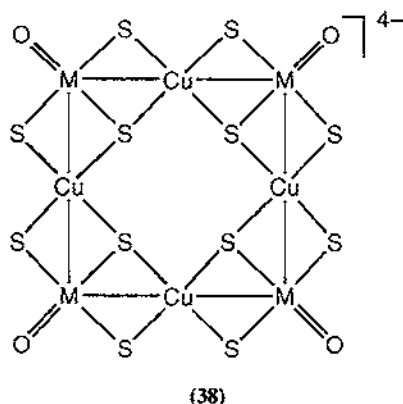
construction during the solid state synthesis of such species have also been discussed [485]. The solid state reaction between $[\text{MoOS}_3]^{2-}$, CuCl , PPh_3 and sodium acetate gave $[\text{MoCu}_2\text{OS}_3(\text{PPh}_3)_2]$ with a butterfly shaped core [486].

The reaction of $[\text{NEt}_4]_2[\text{MoS}_4]$ with $\text{Ag}(\text{dtp})$ [$\text{dtp} = \text{S}_2\text{P}(\text{O}^i\text{Bu})_2$] followed by PPh_3 gave $[\text{MoAg}_3\text{S}_4(\text{PPh}_3)(\text{dtp})]$ (36). A similar species, $[\text{MoCu}_3\text{OS}_3(\text{PPh}_3)_3(\text{dtp})]$, was made from $[\text{MoOS}_3]^{2-}$ and $\text{Cu}(\text{dtp})$ [$\text{dtp} = \text{S}_2\text{P}(\text{OBu})_2$ in this case]. Both clusters have open cubane structures with the dtp ligand acting as a bridge between three metals [487]. The FAB mass spectra of $[\text{MoCu}_3\text{OS}_3(\text{PPh}_3)_3(\text{S}_2\text{COEt})]$ and $[\text{Mo}_2\text{Cu}_6\text{O}_2\text{S}_6(\text{S}^i\text{Bu})_4(\text{PPh}_3)_4]$ have been analysed in attempts to follow the course of cluster interconversion during reactions [488]. The relationship between cluster structure and non-linear optical properties has been explored for the three series $[\text{MM}'_3\text{S}_4(\text{PPh}_3)_3\text{X}]$, $[\text{NBu}_4]_2[\text{MM}'_3\text{OS}_3\text{X}_3]$ and $[\text{NBu}_4]_3[\text{MM}'_3\text{S}_4\text{XX}_3]$ where $\text{M} = \text{Mo}, \text{W}$; $\text{M}' = \text{Cu}, \text{Ag}$; $\text{X} = \text{Cl}, \text{Br}$; and $\text{X}' = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$ [489]. The cluster $[\text{NBu}_4]_3[\text{MoCu}_3\text{OS}_3(\text{Br})\text{I}_3]$ exhibits strong non-linear optical absorption and a large self-defocusing refractive index change [490]. The optical properties of $[\text{NBu}_4]_2[\text{MoCu}_3\text{OS}_3(\text{NCS})_3]$ have also been examined [491].



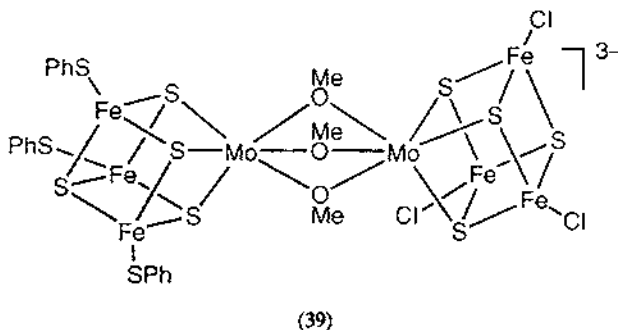
Reaction of $[\text{NH}_4]_2[\text{MoS}_4]$, NEt_4Cl and CuCl in a 1:4:10 ratio gave $[\text{NEt}_4]_4[\text{MoS}_4\text{Cu}_{10}\text{Cl}_{12}]$ (37) in which CuCl units have been added to all six edges and four faces of the MoS_4 tetrahedron; the reaction can be monitored by ^{95}Mo NMR spectroscopy [492]. The reaction of $[\text{NEt}_4]_2[\text{MoO}_2\text{S}_2]$, CuI and NEt_4Cl gave $[\text{NEt}_4]_4[\text{Mo}_2\text{O}_2\text{S}_6\text{Cu}_6\text{I}_6]$, which contains two nest-shaped clusters linked through a $\text{Cu}(\mu\text{-I})_2\text{Cu}$ bridge; reaction with py cleaves it into $[\text{MoOS}_3\text{Cu}_3\text{I}(\text{py})_5]$. The double cluster exhibits strong non-linear optical properties [493].

The compounds $[\text{NEt}_4]_4[\text{M}_4\text{Cu}_4\text{O}_4\text{S}_{12}]$ (38) and $[\text{M}_4\text{Cu}_4\text{O}_4\text{S}_{12}\{\text{Cu}(\text{tmeda})\}_4]$ ($\text{M} = \text{Mo}, \text{W}$) were formed from $[\text{MS}_4]^{2-}$, $[\text{MO}_2\text{S}_2]^{2-}$ and $\text{Cu}(\text{NO}_3)_2$ and KBH_4 . The structure of the first consists of two Cu_2MOS_3 butterfly units joined through MOS_3 groups; the second contains the same basic unit, but is capped alternately up and down on each corner of the ring by additional $\text{Cu}(\text{tmeda})$ moieties [494]. From the reaction of $[\text{NH}_4]_2[\text{MS}_4]$, $[\text{NH}_4]_2[\text{MO}_2\text{S}_2]$ and $\text{Cu}(\text{I})$ in dmf , the eicosanuclear supercubane clusters $[\text{NEt}_4]_4[\text{M}_8\text{Cu}_{12}\text{O}_4\text{S}_{28}]$ ($\text{M} = \text{Mo}, \text{W}$) were isolated. A $\text{M}(\text{=O})$ unit resides at each corner of the cube, and a Cu atom in the middle of each



edge [495]. The non-linear optical properties of the related compound $[\text{NBu}_4]_4[\text{Mo}_8\text{Cu}_{12}\text{O}_8\text{S}_{24}]$ have been investigated [496].

Two types of spectra were obtained in a Mo K-edge EXAFS study of black shales and sediments with a high Mo content. The less common one was consistent with MoS_2 , but the other showed a $\text{Mo}=\text{O}$ contact at around 1.7 Å, Mo–S distances of 2.3–2.38 Å, and in some cases a second shell Mo–Fe interaction. Similar spectra were obtained from molybdate solutions containing humic acid, SH^- , Fe(II) and iron hydroxide, and a cubane-type MoFeS cluster was proposed to be present. A scheme for Mo scavenging was put forward, emphasising its propensity to form complexes with other metals via sulfide bridges [497].



The reaction of $[\text{NH}_4]_2[\text{MoS}_4]$, FeCl_3 , Fe powder, S powder, NaSPh and NEt_4Br in a 1:4:2:2:8:1 ratio in MeOH/dmf afforded a route to the new double cubane cluster $[\text{NEt}_4]_3[\text{Mo}_2\text{Fe}_6\text{S}_8(\mu\text{-OMe})_3(\text{SPh})_3\text{Cl}_3]$ (39). The X-ray structure revealed that ligand positions on Fe are disordered, each one being occupied by Cl and SPh each with half occupancy. Two distinct Fe sites are observed in the Mössbauer spectrum, and it is proposed that one cube of each molecule contains $\text{Fe}(\text{SPh})$ groups and the other FeCl groups [498]. Further details have appeared on the reduction of hydrazine to ammonia by the cubane clusters $[\text{LMoFe}_3\text{S}_4\text{Cl}_3]^{n-}$ ($n=2, 3$) in the presence of $[\text{CoCp}_2]$ and lutidinium hydrochloride. Clusters with

$L = \text{OC}_6\text{Cl}_4\text{O}$, methyliminodiacetate, nta and thiodiglycolate all worked, but that with $L = \text{citrate}$ was most effective. The related $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ cluster was completely inactive, and the reaction was inhibited by CO or PMe_3 , all of which suggests that the Mo atom acts as the binding and reduction site. A mechanism was proposed in which the carboxylate function of L acted as a proton delivery system. The same clusters will also catalyse reduction of acetylene to ethylene [17,499,500]. The temperature dependent magnetism of $[\text{MoFe}_3\text{S}_4(\text{dte})_3]$ ($\text{dte} = \text{S}_2\text{CNMe}_2$, $\text{S}_2\text{CNC}_4\text{H}_8$) has been studied and fitted to a spin coupling model [501].

The reactions of 1,3,5-triamino-1,3,5-trideoxy *cis*-inositol (taci) and its 1,3,5(dimethylamino) derivative (tdci) with the incomplete cubane $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ have been explored. The crystal structures of $[\text{Mo}_3\text{S}_4(\text{tdci})_3][\text{Br}]_4$, in which the ligand is *N,O,O*-bonded, and $[\text{Mo}_3\text{S}_4\text{L}_3] \cdot 20\text{H}_2\text{O}$ were determined. In the latter compound, the ligand L consists of a taci bonded as an anion through O^- , N and N, in which the uncoordinated amine groups have formed a Schiff base with acetone. The reaction of the mixed cubane $[\text{CuMo}_3\text{S}_4(\text{H}_2\text{O})_{10}]^{4+}$ with taci gave crystals of $[\text{Mo}_3\text{CuBrS}_4(\text{tdci})_3][\text{Br}]_3 \cdot 11\text{H}_2\text{O} \cdot \text{EtOH}$. The preference of the Mo_3S_4 core to coordinate a nitrogen donor *trans* to the $\mu_3\text{-S}$ group was noted [502].

Spectroscopic, magnetic and structural investigations have been carried out on the mixed valence clusters $[\text{Mo}_4\text{Se}_4(\text{edta})_2]^{3-}$ and $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$. The ^{77}Se NMR spectrum suggests a trapped Mo(IV)Mo(III)_3 state, but this is not consistent with the ^{95}Mo NMR spectra or the NMR spectra of the analogous 2^- and 4^- clusters; the multiple signals may instead arise from different coordination modes of the edta. A model was proposed to explain the biphasic kinetics of substitution in $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ [503].

The incorporation of additional metals into the incomplete cubane cluster $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ continues to be a subject of interest [15f,15g]. Addition of Sn^{2+} gave $[\text{SnMo}_3\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$ which in the presence of chloride yielded $[\text{Mo}_3\text{SnCl}_3(\text{H}_2\text{O})_9]^{3+}$, which was structurally characterised as its NH_2Me_2^+ salt after treatment with thiocyanate. Reduction of the single cubane gave the corner-sharing double cube $[\text{Mo}_6\text{SnS}_8(\text{H}_2\text{O})_{18}]^{8-}$, which could also be obtained by treating $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ with Sn metal; oxidation of the double cube with Fe^{3+} or $[\text{Co}(\text{dipic})_2]^-$ reformed the single cubane [504]. Combination of $[\text{SnMo}_3\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$ with $[\text{W}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ and NaBH_4 gave the novel mixed double cube $[\text{Mo}_3\text{W}_3\text{SnS}_8(\text{H}_2\text{O})_{18}]^{8-}$ [505].

Treatment of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ with Bi metal or with Bi(III) and NaBH_4 gave $[\text{BiMo}_6\text{S}_8(\text{H}_2\text{O})_{18}]^{8-}$ which reverted to Bi^{3+} and the incomplete cubane on oxidation [506]. Attempted incorporation of thallium by reaction of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ with Tl metal or TlCl and NaBH_4 gave a species thought to contain a $\text{TlMo}_6\text{S}_8^{4+}$ core, but it was thermally unstable and decomposed to Tl(I) and a gas, presumably hydrogen [507]. A similar synthetic procedure with Pb(II) and NaBH_4 or Pb metal gave $[\text{PbMo}_6\text{S}_8(\text{H}_2\text{O})_{18}]^{8-}$ [508]. A second group also claimed the successful incorporation of lead into the incomplete cubane by reaction with Pb powder or with Pb(OAc)_2 in the presence of NaBH_4 to give turquoise solutions, proposed to be $[\text{PbMo}_3\text{S}_4(\text{H}_2\text{O})_{9+x}]^{4+}$, which were rather unstable as attempts to grow crystals

simply resulted in loss of Pb; the UV spectra of both compounds were identical, and a later correction acknowledged that the product was in fact the double cubane [509].

A one-pot synthesis of $[\text{NiM}_3\text{S}_4(\text{H}_2\text{O})_{10}]^{4+}$ ($\text{M} = \text{Mo}, \text{W}$) from $[\text{MS}_4]^{2-}$ has been described. It involves reduction of the tetrathiometalate with Ni at 70 °C followed by air oxidation to $\text{Mo}_3\text{S}_4^{4+}$ and refluxing to achieve nickel incorporation [510]. The compounds $[\text{NiM}_3\text{S}_4(\text{H}_2\text{O})_{10}]^{4+}$ ($\text{M}_3 = \text{Mo}_2\text{W}, \text{MoW}_2, \text{W}_3$) have been prepared from $[\text{M}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ and Ni metal. X-ray structures of the tosylate salts showed that the Mo_2W complex crystallised as a single cubane, but the others were double cubanes $\{[\text{M}_3\text{NiS}_4(\text{H}_2\text{O})_9]_2\}^{8+}$. These clusters react with ethylene to give π -complexes in which the alkene is bound to Ni, as shown by the X-ray structures of $[\text{M}_3\text{NiS}_4(\eta\text{-C}_2\text{H}_4)(\text{H}_2\text{O})_9]^{4+}$ [511].

The kinetics of the substitution of the nickel-bound water molecule in $[\text{NiMo}_3\text{S}_4(\text{H}_2\text{O})_{10}]^{4+}$ with a variety of incoming ligands (NCS^- , Br^- , I^- , CO and two water-soluble phosphines) have been investigated. The narrow spread of rate constants observed suggests an I_d mechanism. For $[\text{NiMo}_3(\text{tacn})(\text{H}_2\text{O})_9]^{4+}$ no substitution occurs at Ni, and a much slower reaction is observed at Mo. No substitution at all by CO was detected on $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$, $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ or $[\text{FeMo}_3\text{S}_4(\text{H}_2\text{O})_{10}]^{4+}$ [512]. The kinetics of the conversion of the double cubane $[\text{Pd}_2\text{Mo}_6\text{S}_8(\text{H}_2\text{O})_{18}]^{8+}$ to $[\text{Mo}_3\text{Pd}(\text{X})(\text{H}_2\text{O})_9]^{4+}$, where $\text{X} = \text{CO}$ or a water-soluble phosphine, have been monitored successfully by stopped-flow methods. With Cl^- , Br^- or NCS^- , slower stages corresponding to substitution at Mo were also observed [513].

The incomplete cubane $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ and $[\text{NiMo}_3\text{S}_4(\text{H}_2\text{O})_9\text{Cl}]^{3+}$ have been incorporated into zeolites NaY, HUSY and KL by ion exchange; UV–visible spectra and EXAFS data indicate that the clusters remained intact. The resulting zeolites showed good activity in the hydrodesulfurisation of benzothiophene, particularly the Ni complex [514]. The cubane $[\text{PdMo}_3\text{S}_4(\text{tacn})_3\text{Cl}][\text{PF}_6]_3$ has been used as a catalyst for the cyclisation of alkynoic acids to enol lactones [515].

References

- [1] M.J. Morris, *Coord. Chem. Rev.* 152 (1996) 309.
- [2] M.J. Morris, *Coord. Chem. Rev.* 164 (1997) 289.
- [3] B.K. Burgess, D.J. Lowe, *Chem. Rev.* 96 (1996) 2983.
- [4] J.B. Howard, D.C. Rees, *Chem. Rev.* 96 (1996) 2965.
- [5] R.R. Eady, *Chem. Rev.* 96 (1996) 3013.
- [6] R. Hille, *Chem. Rev.* 96 (1996) 2757.
- [7] M.K. Johnson, D.C. Rees, M.W.W. Adams, *Chem. Rev.* 96 (1996) 2817.
- [8] H. Schindelin, C. Kisker, J. Hilton, K.V. Rajagopalan, D.C. Rees, *Science* 272 (1996) 1615.
- [9] G.N. George, J. Hilton, K.V. Rajagopalan, *J. Am. Chem. Soc.* 118 (1996) 1113.
- [10] D. Collison, C.D. Garner, J.A. Joule, *Chem. Soc. Rev.* 25 (1996) 25.
- [11] A.G. Wedd, *Coord. Chem. Rev.* 154 (1996) 5.
- [12] R.L. Richards, *Pure Appl. Chem.* 68 (1996) 1521.
- [13] R.L. Richards, *Coord. Chem. Rev.* 154 (1996) 83.
- [14] J.R. Dilworth, *Coord. Chem. Rev.* 154 (1996) 163.

- [15] E.I. Stiefel, K. Matsumoto (Eds.), *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*, ACS Symp. Ser. 653, 1996, American Chemical Society, Washington, DC.
- [15a] E.I. Stiefel, in: E.I. Stiefel, K. Matsumoto (Eds.), *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*, ACS Symp. Ser. 653, 1996, American Chemical Society, Washington, DC, p. 2.
- [15b] D. Coucouvanis, K.D. Demadis, S.M. Malinak, P.E. Mosier, M.A. Tyson, L.J. Laughlin, in: E.I. Stiefel, K. Matsumoto (Eds.), *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*, ACS Symp. Ser. 653, 1996, American Chemical Society, Washington, DC, p. 117.
- [15c] M.D. Curtis, in: E.I. Stiefel, K. Matsumoto (Eds.), *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*, ACS Symp. Ser. 653, 1996, American Chemical Society, Washington, DC, p. 154.
- [15d] P.M. Boorman, X. Gao, H.-B. Kraatz, V. Mozol, M. Wang, in: E.I. Stiefel, K. Matsumoto (Eds.), *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*, ACS Symp. Ser. 653, 1996, American Chemical Society, Washington, DC, p. 197.
- [15e] K. Tatsumi, H. Kawaguchi, in: E.I. Stiefel, K. Matsumoto (Eds.), *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*, ACS Symp. Ser. 653, 1996, American Chemical Society, Washington, DC, p. 336.
- [15f] D.M. Sayse, M.N. Sokolov, A.G. Sykes, in: E.I. Stiefel, K. Matsumoto (Eds.), *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*, ACS Symp. Ser. 653, 1996, American Chemical Society, Washington, DC, p. 216.
- [15g] G. Sakane, T. Shibahara, in: E.I. Stiefel, K. Matsumoto (Eds.), *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*, ACS Symp. Ser. 653, 1996, American Chemical Society, Washington, DC, p. 225.
- [15h] T. Saito, H. Imoto, K. Tsuge, S. Mita, J. Mizutani, S. Yamada, H. Fujita, in: E.I. Stiefel, K. Matsumoto (Eds.), *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*, ACS Symp. Ser. 653, 1996, American Chemical Society, Washington, DC, p. 240.
- [15i] M. Rakowski-Dubois, B. Jagirdar, B. Noll, S. Dietz, in: E.I. Stiefel, K. Matsumoto (Eds.), *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*, ACS Symp. Ser. 653, 1996, American Chemical Society, Washington, DC, p. 269.
- [15j] X. Wu, Q. Huang, Q. Wang, T. Sheng, J. Lu, in: E.I. Stiefel, K. Matsumoto (Eds.), *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*, ACS Symp. Ser. 653, 1996, American Chemical Society, Washington, DC, p. 282.
- [16] E.I. Stiefel, *Sci. Spectra* 7 (1996) 62; *Chem. Abstr.* 126 (1996) 194399a.
- [17] T. Saito, H. Imoto, *Bull. Chem. Soc. Jpn.* 69 (1996) 2403.
- [18] H.-W. Hou, X.-Q. Zin, S. Shi, *Coord. Chem. Rev.* 153 (1996) 25.
- [19] W. Preetz, G. Peters, D. Bublitz, *Chem. Rev.* 96 (1996) 977.
- [20] P.K. Baker, *Adv. Organomet. Chem.* 40 (1996) 45.
- [21] H. Sloan, *Ann. Rep. Progr. Chem.* A92 (1996) 169.
- [22] M. Calligaris, O. Carugo, *Coord. Chem. Rev.* 153 (1996) 83.
- [23] R.C. Mehrotra, A. Singh, *Chem. Soc. Rev.* 25 (1996) 1.
- [24] E.S. Raper, *Coord. Chem. Rev.* 153 (1996) 199.
- [25] C. Hall, R.N. Perutz, *Chem. Rev.* 96 (1996) 3125.
- [26] D.H. Gibson, *Chem. Rev.* 96 (1996) 2063.
- [27] P.D. Harvey, *Coord. Chem. Rev.* 153 (1996) 175.
- [28] F. Bottomley, S.-K. Goh, *Polyhedron* 15 (1996) 3045.
- [29] L. Zarkova, P. Pirgov, *J. Phys. B* 29 (1996) 4411.
- [30] Z. Lin, I. Bytheway, *Inorg. Chem.* 35 (1996) 594.
- [31] K.H. Moock, S.A. Macgregor, G.A. Heath, S. Derrick, R.T. Boeré, *J. Chem. Soc., Dalton Trans.* (1996) 2067.
- [32] M. Kondo, H. Oku, N. Ueyama, A. Nakamura, *Bull. Chem. Soc. Jpn.* 69 (1996) 117.
- [33] M. Rhiel, S. Wocadlo, W. Massa, K. Dehnicke, *Z. Naturforsch.* 51b (1996) 1419.
- [34] M. Rhiel, S. Wocadlo, W. Massa, K. Dehnicke, *Z. Anorg. Allg. Chem.* 622 (1996) 1195.

- [35] H.-T. Chiu, Y.-P. Chen, S.-H. Chuang, J.-S. Jen, G.-H. Lee, S.-M. Peng, *J. Chem. Soc., Chem. Commun.* (1996) 139.
- [36] W.A. Herrmann, A.W. Stumpf, T. Priemer, S. Bogdanovic, V. Dufaud, J.-M. Basset, *Angew. Chem., Int. Ed. Engl.* 35 (1996) 2803.
- [37] J.C. Peters, A.R. Johnson, A.L. Odom, P.W. Wanandi, W.M. Davis, C.C. Cummins, *J. Am. Chem. Soc.* 118 (1996) 10175.
- [38] G. Wu, D. Rovnyak, M.J.A. Johnson, N.C. Zanetti, D.G. Musaev, K. Morokuma, R.R. Schrock, R.G. Griffin, C.C. Cummins, *J. Am. Chem. Soc.* 118 (1996) 10654.
- [39] J.A. Johnson-Carr, N.C. Zanetti, R.R. Schrock, M.D. Hopkins, *J. Am. Chem. Soc.* 118 (1996) 11305.
- [40] R.C.B. Copley, P.W. Dyer, V.C. Gibson, J.A.K. Howard, E.L. Marshall, W. Wang, B. Whittle, *Polyhedron* 15 (1996) 3001.
- [41] G.R. Clark, A.J. Nielsen, C.E.F. Rickard, *J. Chem. Soc., Dalton Trans.* (1996) 4265.
- [42] D.M. Hankin, A.A. Danopoulos, G. Wilkinson, T.K.N. Sweet, M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.* (1996) 1309.
- [43] V.C. Gibson, C. Redshaw, W. Clegg, M.R.J. Elsegood, U. Siemeling, T. Türk, *J. Chem. Soc., Dalton Trans.* (1996) 4513.
- [44] V.C. Gibson, E.L. Marshall, C. Redshaw, W. Clegg, M.R.J. Elsegood, *J. Chem. Soc., Dalton Trans.* (1996) 4197.
- [45] L.J. Laughlin, C.G. Young, *Inorg. Chem.* 35 (1996) 1050.
- [46] T. Ozeki, H. Adachi, S. Ikeda, *Bull. Chem. Soc. Jpn.* 69 (1996) 619.
- [47] H. Teruel, A. Sierralta, *Polyhedron* 15 (1996) 2215.
- [48] H. Teruel, A. Sierralta, *J. Mol. Catal.* 107 (1996) 379.
- [49] M.L.D. Ramos, M.M.M. Caldeira, Gil V.M.S., *Carbohydr. Res.* 286 (1996) 1; *Chem. Abstr.* 125 (1996) 168524x.
- [50] J.-P. Sauvage, J.-F. Verchere, S. Chapelle, *Carbohydr. Res.* 286 (1996) 67; *Chem. Abstr.* 125 (1996) 196111d.
- [51] M. Matulova, J.-F. Verchere, S. Chapelle, *Carbohydr. Res.* 287 (1996) 37; *Chem. Abstr.* 125 (1996) 196112e.
- [52] R.F. Song, F. Li, G.M. Liu, Y.G. Mao, F. Du, *Chin. Chem. Lett.* 7 (1996) 567; *Chem. Abstr.* 125 (1996) 178568d.
- [53] J.-S. Lim, M.A.S. Aquino, A.G. Sykes, *Inorg. Chem.* 35 (1996) 614.
- [54] A.A. Holder, T.P. Dasgupta, *J. Chem. Soc., Dalton Trans.* (1996) 2637.
- [55] R.A. Holwerda, *Inorg. Chim. Acta* 242 (1996) 1.
- [56] H. Oshio, T. Kikuchi, T. Ito, *Inorg. Chem.* 35 (1996) 4938.
- [57] H. Oshio, T. Kikuchi, T. Ito, *Mol. Cryst., Liq. Cryst. Sci. Technol.* A286 (1996) 331; *Chem. Abstr.* 125 (1996) 346138j.
- [58] A.P. Perepelita, *Zh. Prikl. Khim.* 69 (1996) 1252; *Chem. Abstr.* 126 (1997) 180301a.
- [59] O.P. Perepelitsya, *Ukr. Khim. Zh.* 62 (1996) 78; *Chem. Abstr.* 126 (1997) 180303c.
- [60] A.P. Perepelitsa, V.N. Ischenko, V.V. Fomenko, I.Y. Pishchai, *Ukr. Khim. Zh.* 61 (1995) 6; *Chem. Abstr.* 126 (1997) 180305e.
- [61] O.P. Perelitsya, V.M. Ischenko, Z.M. Alekseeva, V.V. Fomenko, *Ukr. Khim. Zh.* 61 (1995) 85; *Chem. Abstr.* 126 (1997) 180307g.
- [62] G.A. Gamidov, M.M. Agaguseinova, U.A. Gasanova, *Zh. Obshch. Khim.* 66 (1996) 974; *Chem. Abstr.* 126 (1997) 7765g.
- [63] A.S. Demir, C. Tanyeli, O. Sesenoglu, S. Demic, O.O. Evin, *Tetrahedron Lett.* 37 (1996) 407.
- [64] C. Tsang, A. Dananjay, J. Kim, A. Manthiram, *Inorg. Chem.* 35 (1996) 504.
- [65] A.-K. Duhme, Z. Dauter, R.C. Hider, S. Pohl, *Inorg. Chem.* 35 (1996) 3059.
- [66] A.-K. Duhme, R.C. Hider, H. Khodr, *Biometals* 9 (1996) 245.
- [67] I. Prévot-Halter, T.J. Smith, J. Weiss, *Tetrahedron Lett.* 37 (1996) 1201.
- [68] S.M. Malinak, D. Coucouvanis, *Inorg. Chem.* 35 (1996) 4810.
- [69] R.J. Cross, L.J. Farrugia, P.D. Newman, R.D. Peacock, D. Stirling, *J. Chem. Soc., Dalton Trans.* (1996) 4449.
- [70] W. Clegg, M.R.J. Elsegood, R.J. Errington, R. Bakri, *Acta Crystallogr.* C52 (1996) 2145.
- [71] P.D. Harvey, J. Gagnon, R. Provencher, B. Xu, T.M. Swager, *Can. J. Chem.* 74 (1996) 2279.

- [72] R.J. Cross, L.J. Farrugia, P.D. Newman, R.D. Peacock, D. Stirling, *J. Chem. Soc., Dalton Trans.* (1996) 1087.
- [73] R.J. Cross, L.J. Farrugia, P.D. Newman, R.D. Peacock, D. Stirling, *J. Chem. Soc., Dalton Trans.* (1996) 1637.
- [74] C.Y. Lorber, I. Pauls, J.A. Osborn, *Bull. Soc. Chim. Fr.* 133 (1996) 755.
- [75] C.Y. Lorber, J.A. Osborn, *Tetrahedron Lett.* 37 (1996) 853.
- [76] V. Conte, F. Di Furia, S. Moro, *J. Phys. Org. Chem.* 9 (1996) 329.
- [77] S. Maignien, S. Ait-Mohand, J. Muzart, *Synlett* (1996) 439.
- [78] C. Karunakaran, P.N. Palanisamy, *Pol. J. Chem.* 70 (1996) 1573.
- [79] V. Conte, F. Di Furia, S. Moro, *Tetrahedron Lett.* 37 (1996) 8609.
- [80] K.M. Thompson, M. Spiro, W.P. Griffith, *J. Chem. Soc., Faraday Trans.* 92 (1996) 2535.
- [81] M.S. Reynolds, A. Butler, *Inorg. Chem.* 35 (1996) 2378.
- [82] R.S. Srivastava, K.M. Nicholas, *J. Chem. Soc., Chem. Commun.* (1996) 2335.
- [83] E.A. Møller, K.A. Jørgensen, *J. Org. Chem.* 61 (1996) 5770.
- [84] F. Porta, F. Colonna, F. Arciprete, S. Banfi, F. Coppa, *J. Mol. Catal.* 113 (1996) 359.
- [85] F.P. Ballistreri, E. Barbuzzi, G.A. Tomaselli, R.M. Toscano, *J. Mol. Catal. A* 114 (1996) 229.
- [86] W.R. Thiel, *Chem. Ber.* 129 (1996) 575.
- [87] A.P. Timosheva, N.G. Mokretsova, N.D. Chichirova, E.K. Kazakova, N.A. Makarova, S.G. Vul'fson, Y.I. Salnikov, *Zh. Obshch. Khim.* 66 (1996) 1769; *Chem. Abstr.* 126 (1997) 165766n.
- [88] Z. Wang, L.S. Jimenez, *Tetrahedron Lett.* 37 (1996) 6049.
- [89] W. Adam, D. Golsch, J. Sundermeyer, G. Wahl, *Chem. Ber.* 129 (1996) 1177.
- [90] C.L. Bianchi, F. Porta, *Vacuum* 47 (1996) 179; *Chem. Abstr.* 124 (1996) 248672p.
- [91] M.T.H. Tarafder, A.R. Khan, *Ind. J. Chem. A* 35 (1996) 781.
- [92] R.J. Cross, L.J. Farrugia, P.D. Newman, R.D. Peacock, D. Stirling, *J. Chem. Soc., Dalton Trans.* (1996) 4149.
- [93] M.S. Sastry, S.S. Gupta, *Trans. Met. Chem.* 21 (1996) 410; *Chem. Abstr.* 125 (1996) 315258u.
- [94] M.R. Maurya, S.A. Bhakare, *J. Chem. Res. (S)* (1996) 390.
- [95] N.M. Gresley, W.P. Griffith, B.C. Parkin, A.J.P. White, D.J. Williams, *J. Chem. Soc., Dalton Trans.* (1996) 2039.
- [96] L. Salles, F. Robert, V. Semmer, Y. Jeannin, J.-M. Brégault, *Bull. Soc. Chim. Fr.* 133 (1996) 319.
- [97] M. Hashimoto, H. Ichida, Y. Sasaki, *J. Coord. Chem.* 37 (1996) 349; *Chem. Abstr.* 125 (1996) 24825y.
- [98] R. Stomberg, S. Olson, *J. Alloys Comp.* 237 (1996) 39; *Chem. Abstr.* 124 (1996) 359163t.
- [99] D.A. Brown, H. Bögge, R. Coogan, D. Dooley, T.J. Kemp, A. Müller, B. Neumann, *Inorg. Chem.* 35 (1996) 1674.
- [100] P. Barbaro, T.R. Belderrain, C. Bianchini, G. Scapacci, D. Masi, *Inorg. Chem.* 35 (1996) 3362.
- [101] P. Barbaro, T.R. Belderrain, C. Bianchini, G. Scapacci, *An. Quim.* 92 (1996) 141.
- [102] T. Carofoglio, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *Polyhedron* 15 (1996) 4435.
- [103] H.-K. Fun, K. Sivakumar, J.-Y. Niu, J.-P. Wang, X.-Z. You, *Acta Crystallogr. C* 52 (1996) 1150.
- [104] C. Manzur, C. Bustos, D. Carrillo, F. Robert, P. Gouzerh, *Inorg. Chim. Acta* 249 (1996) 245.
- [105] B. Scharbert, G. Lobmaier, W.A. Herrmann, *Ger. Offen. DE 4,447,233*; *Chem. Abstr.* 125 (1996) 157016g.
- [106] A. Corma, A. Fuerte, M. Iglesias, F. Sánchez, *J. Mol. Catal. A* 107 (1996) 225.
- [107] J.-H. Ahn, D.C. Sherrington, *J. Chem. Soc., Chem. Commun.* (1996) 643.
- [108] W.R. Thiel, *GIT Fachz. Lab.* 40 (1996) 966; *Chem. Abstr.* 126 (1997) 117579g.
- [109] M.A. Pietsch, M.B. Hall, *Inorg. Chem.* 35 (1996) 1273.
- [110] A. Corma, F. Rey, J.M. Thomas, G. Sankar, G.N. Greaves, A. Cervilla, E. Llopis, A. Ribeiro, *J. Chem. Soc., Chem. Commun.* (1996) 1613.
- [111] H. Arzoumanian, G. Agrifoglio, H. Krentzien, *New J. Chem.* 20 (1996) 699.
- [112] M.L.H.K. Nair, C.P. Prabhakaran, *J. Teach. Res. Chem.* 3 (1996) 25; *Chem. Abstr.* 126 (1997) 206801r.
- [113] R.J. Gillespie, I. Bytheway, J.-H. Tang, R.F.W. Bader, *Inorg. Chem.* 35 (1996) 3954.
- [114] A.B. Yakushev, S.N. Timokhin, M.V. Vedenev, H.G. Xu, I. Zvara, *J. Radioanal. Nucl. Chem. Art.* 205 (1996) 63.

- [115] A. Türlér, B. Eichler, D.T. Jost, R. Dressier, D. Piguet, H.W. Gäggeler, S. Hübener, M. Böttger, M. Grantz, Forschungszent. Rossendorf. FZR (1996) 104; Chem. Abstr. 125 (1996) 103349z.
- [116] G.V. Ionova, V.G. Pershina, G.A. Gerasimova, V.K. Mikhalko, Y.N. Kostrubov, N.I. Suraeva, Zh. Neorg. Khim. 41 (1996) 802; Chem. Abstr. 126 (1997) 11660m.
- [117] L. Deng, T. Ziegler, Organometallics 15 (1996) 3011.
- [118] W.A. Herrmann, G.M. Lobmaier, M. Elison, J. Organomet. Chem. 520 (1996) 231.
- [119] M. Miggins, U.K. Kakarla, D.A. Knight, J.C. Fettingier, An. Quim. 92 (1996) 59; Chem. Abstr. 125 (1996) 124760s.
- [120] M. McCann, A.J. Beaumont, J. Mol. Catal. A 111 (1996) 251.
- [121] I. Ivanovic, K. Andjelkovic, V.M. Leovac, L. Klisarov, M. Lazarevic, D. Minic, J. Therm. Anal. 46 (1996) 1741.
- [122] G. Argay, A. Kalman, V.M. Leovac, V.I. Cesljevic, B. Ribar, J. Coord. Chem. 37 (1996) 165; Chem. Abstr. 125 (1996) 24821u.
- [123] V.L. Abramenko, V.S. Sergienko, Russ. J. Coord. Chem. 22 (1996) 490; Chem. Abstr. 125 (1996) 236834a.
- [124] V.L. Abramenko, V.S. Sergienko, N.V. Dvortsova, Russ. J. Coord. Chem. 22 (1996) 488; Chem. Abstr. 125 (1996) 236833z.
- [125] M.R. Maurya, C. Gopinathan, Ind. J. Chem. A 35 (1996) 701; Chem. Abstr. 125 (1996) 211032z.
- [126] R.A. Lal, M.L. Pal, S. Adhikari, Synth. React. Inorg. Met.-Org. Chem. 26 (1996) 997; Chem. Abstr. 125 (1996) 156961z.
- [127] R.A. Lal, S. Adhikari, Ind. J. Chem. A 35 (1996) 607; Chem. Abstr. 125 (1996) 130763m.
- [128] V.L. Abramenko, V.S. Sergienko, Zh. Neorg. Khim. 41 (1996) 1645; Chem. Abstr. 126 (1997) 83625b.
- [129] B. Prelesnik, I. Ivanovic, V.M. Leovac, K. Andjelkovic, Acta Crystallogr. C52 (1996) 1375.
- [130] P. Subramani, C.N. Krishnan, Ind. J. Chem. A 35 (1996) 151; Chem. Abstr. 124 (1996) 192358w.
- [131] D. Li, Y. Cong, X. Wang, H. Liang, Guangxi Shifan Daxue Xuebao, Ziran Kexueban 14 (1996) 47; Chem. Abstr. 126 (1997) 219905c.
- [132] H.W. Wang, P.S. Skeldon, G.E. Thompson, G.C. Wood, J. Mater. Sci. Lett. 15 (1996) 494.
- [133] E.A. Ponomarev, M. Neumann-Spallart, G. Hodes, C. Levy-Clement, Thin Solid Films 280 (1996) 86.
- [134] D. Argyropoulos, C.-A. Mitsopoulou, D. Katakis, Inorg. Chem. 35 (1996) 5549.
- [135] S. Campbell, S. Harris, Inorg. Chem. 35 (1996) 3285.
- [136] S.P. Best, S.A. Ciniawsky, D.G. Humphrey, J. Chem. Soc., Dalton Trans. (1996) 2945.
- [137] N. Ueyama, H. Oku, M. Kondo, T. Okamura, N. Yoshinaga, A. Nakamura, Inorg. Chem. 35 (1996) 643.
- [138] M.R. Bray, R.J. Deeth, Inorg. Chem. 35 (1996) 5270.
- [139] T.A. Coffey, G.D. Forster, G. Hogarth, J. Chem. Soc., Dalton Trans. (1996) 183.
- [140] K. Kruczala, Z. Gao, S. Schlick, J. Phys. Chem. 100 (1996) 11427.
- [141] K. Kruczala, Z. Gao, K. Dyrek, S. Schlick, J. Phys. Chem. 100 (1996) 2229.
- [142] Z. Gao, S. Schlick, J. Chem. Soc., Faraday Trans. 92 (1996) 4239.
- [143] K. Nanjo, T. Masuda, J. Polym. Sci. A: Polym. Chem. 34 (1996) 2931.
- [144] T. Masuda, H. Izumikawa, Y. Misumi, T. Higashimura, Macromolecules 4 (1996) 1167.
- [145] C. Limberg, A.J. Downs, A.J. Blake, S. Parsons, Inorg. Chem. 35 (1996) 4439.
- [146] K.C. Malhotra, R. Sharma, N. Sharma, S.C. Chaudhry, Proc. Nat. Acad. Sci. Ind. A66 (1996) 87; Chem. Abstr. 125 (1996) 184189x.
- [147] W. Kläui, T. Hardt, J. Organomet. Chem. 526 (1996) 313.
- [148] J. Beck, M.A. Pell, J. Richter, J.A. Ibers, Z. Anorg. Allg. Chem. 622 (1996) 473.
- [149] J. Beck, M. Hengstmann, Z. Naturforsch. 51b (1996) 1415.
- [150] C. Balagopalakrishna, J.T. Kimbrough, T.D. Westmoreland, Inorg. Chem. 35 (1996) 7758.
- [151] J.L. Atwood, S.G. Bott, P.C. Junk, M.T. May, J. Coord. Chem. 37 (1996) 89; Chem. Abstr. 125 (1996) 24817x.
- [152] M. Cindric, D. Matkovic-Calogovic, B. Kamenar, Inorg. Chim. Acta 248 (1996) 103.
- [153] N.D. Chichirova, R.S. Zabbarova, Y.I. Sal'nikov, Zh. Neorg. Khim. 41 (1996) 1666; Chem. Abstr. 126 (1997) 83628e.

- [154] M. Kurihara, I. Saito, Y. Matsuda, *Chem. Lett.* (1996) 1109.
- [155] B. Cheng, W.R. Scheidt, *Acta Crystallogr. C52* (1996) 832.
- [156] T.J. Mafatle, T. Nyokong, *J. Electroanal. Chem.* 408 (1996) 213.
- [157] S.R. Girish, V.K. Revankar, V.B. Mahale, *Trans. Met. Chem.* 21 (1996) 401; *Chem. Abstr.* 125 (1996) 346074k.
- [158] C.P. Prabhakaran, M.L.H.K. Nair, *Ind. J. Chem. A35* (1996) 771; *Chem. Abstr.* 125 (1996) 264174d.
- [159] I.K. Dhawan, J.H. Enemark, *Inorg. Chem.* 35 (1996) 4873.
- [160] Z. Xiao, M.A. Bruck, J.H. Enemark, C.G. Young, A.G. Wedd, *Inorg. Chem.* 35 (1996) 7508.
- [161] Z. Xiao, M.A. Bruck, J.H. Enemark, C.G. Young, A.G. Wedd, *J. Biol. Inorg. Chem.* 1 (1996) 415.
- [162] Z. Xiao, R.W. Gable, A.G. Wedd, C.G. Young, *J. Am. Chem. Soc.* 118 (1996) 2912.
- [163] J.P. Hill, L.J. Laughlin, R.W. Gable, C.G. Young, *Inorg. Chem.* 35 (1996) 3447.
- [164] A.M. Raitsimring, P. Basu, N.V. Shokhirev, J.H. Enemark, *Appl. Magn. Reson.* 9 (1995) 173.
- [165] V.A. Ung, D.J. Bardwell, J.C. Jeffery, J.P. Maher, J.A. McCleverty, M.D. Ward, A. Williamson, *Inorg. Chem.* 35 (1996) 5290.
- [166] R.M. Ramadan, A.S. Attia, M.F. El-Shahat, *Polyhedron* 15 (1996) 301.
- [167] R.M. Ramadan, M.F. El-Shahat, A.S. Attia, *Polyhedron* 15 (1996) 545.
- [168] N. Chenah, S. Djebbar Sid, O. Benali-Baitich, B. Deroide, J.V. Zanchetta, *J. Soc. Alger. Chim.* 6 (1996) 277; *Chem. Abstr.* 126 (1997) 337805t.
- [169] K. Ray, D.C. Mukherjee, S. Basu, P.C. Mandal, *J. Radioanal. Nucl. Chem. Art.* 204 (1996) 349.
- [170] J.E. Drake, A.G. Mirlankar, R. Ratnani, *Inorg. Chem.* 35 (1996) 2665.
- [171] L. Xu, J. Huang, D. Yan, Q. Zhang, *Inorg. Chem.* 35 (1996) 1389.
- [172] R. Wong, M.S. Mashuta, J.F. Richardson, M.E. Noble, *Inorg. Chem.* 35 (1996) 3022.
- [173] D.E. Barber, R.F. Bryan, M. Sabat, K.S. Bose, B.A. Averill, *Inorg. Chem.* 35 (1996) 4635.
- [174] C.C. Lee, T.R. Halbert, W.-H. Pan, M.A. Harmer, L. Wei, M.E. Leonowicz, C.O.B. Dim, K.F. Miller, A.E. Bruce, S. McKenna, J.L. Corbin, S. Wherland, E.I. Stiefel, *Inorg. Chim. Acta* 243 (1996) 147.
- [175] Q. Fu, L. Wu, G. Zhang, C. Sun, *Wuji Huaxue Xuebao* 12 (1996) 208; *Chem. Abstr.* 125 (1996) 184161g.
- [176] Q.-H. Fu, G.-R. Zhang, C.-T. Sun, S.Y. Miu, L.-X. Wu, *Chin. J. Chem.* 14 (1996) 206; *Chem. Abstr.* 125 (1996) 264290p.
- [177] T. Venkataraman, K.S. Nagaraja, *Ind. J. Chem. A35* (1996) 300; *Chem. Abstr.* 124 (1996) 305515r.
- [178] J. Beck, P. Biedenkopf, K. Müller-Buschbaum, J. Richter, K.-J. Schlitt, *Z. Anorg. Allg. Chem.* 622 (1996) 292.
- [179] J. Beck, P. Biedenkopf, K. Müller-Buschbaum, *Z. Naturforsch.* 51b (1996) 727.
- [180] J. Beck, *Z. Naturforsch.* 51b (1996) 1127.
- [181] M. Plate, K. Dehnicke, S. Abram, U. Abram, *Z. Naturforsch.* 51b (1996) 1049.
- [182] M. Galán, M. del Mar Graciani, R. Jiménez, M.L. Moyá, E. Muñoz, A. Rodríguez, F. Sánchez, *Ber. Bunsenges. Phys. Chem.* 100 (1996) 470.
- [183] S.I. Ali, S. Sharma, Z. Khan, *Trans. Met. Chem.* 21 (1996) 222; *Chem. Abstr.* 125 (1996) 68810u.
- [184] S.I. Ali, A.M.A. Ansari, *J. Therm. Anal.* 46 (1996) 1763; *Chem. Abstr.* 125 (1996) 291500p.
- [185] M. Osada, J. Tachibana, T. Imamura, Y. Sasaki, *Chem. Lett.* (1996) 713.
- [186] M. Hidai, Y. Ishii, *Bull. Chem. Soc. Jpn.* 69 (1996) 819.
- [187] M. Hidai, Y. Ishii, *J. Mol. Catal. A* 107 (1996) 105.
- [188] J.D. Niemoth-Anderson, J.R.D. Debor, T.A. George, C.R. Cross, II, J.J. Stezowski, *Polyhedron* 15 (1996) 4031.
- [189] T.A. George, D.N. Kurk, J. Redepennig, *Polyhedron* 15 (1996) 2377.
- [190] K.B. Dillon, V.C. Gibson, J.A.K. Howard, L.T. Sequeira, J.W. Yao, *Polyhedron* 15 (1996) 4173.
- [191] C.G. Young, L.J. Laughlin, S. Colmanet, S.D.B. Scrofan, *Inorg. Chem.* 35 (1996) 5368.
- [192] V.J. Murphy, T. Hascall, J.W. Chen, G. Parkin, *J. Am. Chem. Soc.* 118 (1996) 7428.
- [193] M. Minato, H. Sakai, Z.-G. Weng, D.-Y. Zhou, S. Kurishima, T. Ito, M. Yamasaki, M. Shiro, M. Tanaka, K. Osakada, *Organometallics* 15 (1996) 4863.
- [194] R.A. Henderson, K.E. Oglieve, *J. Chem. Soc., Dalton Trans.* (1996) 3397.
- [195] T. Hascall, V.J. Murphy, G. Parkin, *Organometallics* 15 (1996) 3910.

- [196] D. Kanagavel, C.N. Krishnan, *Trans. Met. Chem.* 21 (1996) 570; *Chem. Abstr.* 126 (1997) 112356x.
- [197] B. Götz, F. Knoch, H. Kisch, *Chem. Ber.* 129 (1996) 33.
- [198] S.K. Das, D. Biswa, R. Maiti, S. Sarkar, *J. Am. Chem. Soc.* 118 (1996) 1387.
- [199] K. Takai, K. Umakoshi, Y. Sasaki, *Chem. Lett.* (1996) 645.
- [200] J.R. Dilworth, A.J. Hutson, J.S. Lewis, J.R. Miller, Y. Zheng, Q. Chen, J. Zubieta, *J. Chem. Soc., Dalton Trans.* (1996) 1093; correction p. 2585.
- [201] C.P. Gerlach, S.P. Waller, J. Arnold, *J. Chem. Soc., Chem. Commun.* (1996) 2565.
- [202] F.A. Cotton, X. Feng, *Inorg. Chem.* 35 (1996) 4921.
- [203] J.C. Fetting, J.C. Gordon, S.P. Mattamana, C.J. O'Connor, R. Poli, G. Salem, *Inorg. Chem.* 35 (1996) 7404.
- [204] M. Brorson, C.J.H. Jacobson, C.M. Jensen, I. Schmidt, J. Villadsen, *Inorg. Chim. Acta* 247 (1996) 189.
- [205] J.V. Brencic, L. Golic, I. Leban, R. Rotar, J. Sieler, *Z. Anorg. Allg. Chem.* 622 (1996) 2124.
- [206] R. Rotar, I. Leban, J.V. Brencic, *Acta Crystallogr. C52* (1996) 2155.
- [207] A.A. Cole, S.P. Mattamana, R. Poli, *Polyhedron* 15 (1996) 2351.
- [208] P.M. Boorman, M. Wang, M. Parvez, *J. Chem. Soc., Dalton Trans.* (1996) 4533.
- [209] F.A. Cotton, J. Su, *Inorg. Chim. Acta* 251 (1996) 101.
- [210] F.A. Cotton, X. Feng, *Int. J. Quantum Chem.* 58 (1996) 671.
- [211] T. Lovell, J.B. McGrady, R. Stranger, S.A. Macgregor, *Inorg. Chem.* 35 (1996) 3079.
- [212] R. Stranger, S.A. Macgregor, T. Lovell, J.E. McGrady, G.A. Heath, *J. Chem. Soc., Dalton Trans.* (1996) 4485.
- [213] R. Stranger, L. Dubicki, E. Krausz, *Inorg. Chem.* 35 (1996) 4218.
- [214] J.L. Atwood, P.C. Junk, M.T. May, K.D. Robinson, *J. Coord. Chem.* 40 (1996) 247; *Chem. Abstr.* 126 (1997) 300951m.
- [215] T.A. Budzichowski, M.H. Chisholm, K. Folting, K.S. Kramer, *Polyhedron* 15 (1996) 3085.
- [216] T.A. Budzichowski, M.H. Chisholm, K. Folting, *Chem. Eur. J.* 2 (1996) 110.
- [217] T.A. Budzichowski, M.H. Chisholm, W.E. Streib, *Can. J. Chem.* 74 (1996) 2386.
- [218] C.E. Laplaza, M.J.A. Johnson, J.C. Peters, A.L. Odom, E. Kim, C.C. Cummins, G.N. George, I.J. Pickering, *J. Am. Chem. Soc.* 118 (1996) 8623.
- [219] C.E. Laplaza, A.R. Johnson, C.C. Cummins, *J. Am. Chem. Soc.* 118 (1996) 709.
- [220] D.V. Baxter, M.H. Chisholm, G.J. Gama, V.F. DiStasi, A.L. Hector, I.P. Parkin, *Chem. Mater.* 8 (1996) 1222.
- [221] T.A. Coffey, G.D. Forster, G. Hogarth, *Acta Crystallogr. C52* (1996) 2157.
- [222] S.B. Sharma, I.N. Tewari, *Synth. React. Inorg. Met.-Org. Chem.* 26 (1996) 1255; *Chem. Abstr.* 125 (1996) 211160q.
- [223] R.J.H. Clark, S.J.R. Owens, C. Svendsen, M.J. Nielsen, O.S. Mortensen, *Inorg. Chim. Acta* 243 (1996) 249.
- [224] V.K. Ceylan, *Spectrosc. Lett.* 29 (1996) 1555.
- [225] V.K. Ceylan, *Spectrosc. Lett.* 29 (1996) 101.
- [226] K. From, M. Plaikner, E. Hey-Hawkins, *Z. Naturforsch.* 51b (1996) 1669.
- [227] F.A. Cotton, G. Schmid, *Polyhedron* 15 (1996) 4053.
- [228] J.M. Mayer, *Adv. Trans. Met. Coord. Chem.* 1 (1996) 105.
- [229] D.I. Arnold, F.A. Cotton, F.E. Kühn, *Inorg. Chem.* 35 (1996) 5764.
- [230] D.I. Arnold, F.A. Cotton, F.E. Kühn, *Inorg. Chem.* 35 (1996) 4733.
- [231] F.A. Cotton, F.E. Kühn, A. Yokochi, *Inorg. Chim. Acta* 252 (1996) 251.
- [232] F.A. Cotton, F.E. Kühn, *Inorg. Chim. Acta* 252 (1996) 257.
- [233] F.A. Cotton, F.E. Kühn, *J. Am. Chem. Soc.* 118 (1996) 5826.
- [234] F.A. Cotton, L.M. Daniels, S.C. Haefner, E.N. Walke, *Inorg. Chim. Acta* 247 (1996) 105.
- [235] C.-T. Lee, S.-F. Chiang, C.-T. Chen, J.D. Chen, C.-D. Hsiao, *Inorg. Chem.* 35 (1996) 2930.
- [236] D.M. Baird, F.L. Yang, D.J. Kavanaugh, G. Finness, K.R. Dunbar, *Polyhedron* 15 (1996) 2597.
- [237] K.D. John, S.J. Geib, M.D. Hopkins, *Organometallics* 15 (1996) 4357.
- [238] K. Severin, D. Koch, K. Polborn, W. Beck, *Z. Anorg. Allg. Chem.* 622 (1996) 562.
- [239] P.K. Baker, S.J. Coles, M.C. Durrant, S.D. Harris, D.L. Hughes, M.B. Hursthouse, R.L. Richards, *J. Chem. Soc., Dalton Trans.* (1996) 4003.

- [240] P.K. Baker, S.D. Harris, M.C. Durrant, R.L. Richards, *Polyhedron* 15 (1996) 3595.
- [241] P.K. Baker, S.J. Coles, D.E. Hibbs, M.M. Meehan, M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.* (1996) 3995.
- [242] C. Lin, J.D. Protasiewicz, E.T. Smith, T. Ren, *Inorg. Chem.* 35 (1996) 6422.
- [243] M. Mintert, W.S. Sheldrick, *Chem. Ber.* 129 (1996) 683.
- [244] C.-T. Lee, J.-D. Chen, L.-S. Liou, J.-C. Wang, *Inorg. Chim. Acta* 249 (1996) 115.
- [245] A.M. Macintosh, D.G. Nocera, *Inorg. Chem.* 35 (1996) 7134.
- [246] S.E.M. Flynn, J.A. McCleverty, M.D. Ward, A. Włodarczyk, *Polyhedron* 15 (1996) 2247.
- [247] M. Herberhold, G.X. Jin, A.L. Rheingold, *Z. Naturforsch.* 51b (1996) 681.
- [248] N.M. Rowley, S.S. Kurek, P.R. Ashton, T.A. Hamor, C.J. Jones, N. Spencer, J.A. McCleverty, G.S. Beddard, T.M. Feehan, N.T.H. White, E.J.L. McInnes, N.N. Payne, L.J. Yellowlees, *Inorg. Chem.* 35 (1996) 7526.
- [249] S.L.W. McWhinnie, J.A. Thomas, T.A. Hamor, C.J. Jones, J.A. McCleverty, D. Collison, F.E. Mabbs, C.J. Harding, L.J. Yellowlees, M.G. Hutchings, *Inorg. Chem.* 35 (1996) 760.
- [250] J.A. Thomas, M.G. Hutchings, C.J. Jones, J.A. McCleverty, *Inorg. Chem.* 35 (1996) 289.
- [251] A.M.W. Cargill Thompson, D. Gatteschi, J.A. McCleverty, J.A. Navas, E. Rentschler, M.D. Ward, *Inorg. Chem.* 35 (1996) 2701.
- [252] A.M.W. Cargill Thompson, J.A. McCleverty, M.D. Ward, *Inorg. Chim. Acta* 250 (1996) 29.
- [253] J. Hock, A.M.W. Cargill Thomson, J.A. McCleverty, M.D. Ward, *J. Chem. Soc., Dalton Trans.* (1996) 4257.
- [254] J.A. Thomas, C.J. Jones, J.A. McCleverty, M.G. Hutchings, *Polyhedron* 15 (1996) 1409.
- [255] S.L.W. McWhinnie, C.J. Jones, J.A. McCleverty, L.J. Yellowlees, *J. Chem. Soc., Dalton Trans.* (1996) 4401.
- [256] S.M. Kagwanja, J.C. Jeffery, C.J. Jones, J.A. McCleverty, *Polyhedron* 15 (1996) 2959.
- [257] F.S. McQuillan, C.J. Jones, *Polyhedron* 15 (1996) 1553.
- [258] F.S. McQuillan, H. Chen, T.A. Hamor, C.J. Jones, *Polyhedron* 15 (1996) 3909.
- [259] M. Cano, J.A. Campo, J.V. Heras, E. Pinilla, A. Monge, *Polyhedron* 15 (1996) 1705.
- [260] A. Włodarczyk, R.M. Richardson, M.D. Ward, J.A. McCleverty, M.B. Hursthouse, S.J. Coles, *Polyhedron* 15 (1996) 27.
- [261] M.H. Chisholm, J.C. Huffman, S.J. Iyer, M.A. Lynn, *Inorg. Chim. Acta* 243 (1996) 283.
- [262] F.A. Cotton, D. de O. Silva, *Polyhedron* 15 (1996) 4079.
- [263] F.A. Cotton, D. de O. Silva, *Inorg. Chim. Acta* 249 (1996) 57.
- [264] J. Frelek, Z. Pakulski, A. Zamojski, *Tetrahedron Asym.* 7 (1996) 1363.
- [265] X. Ouyang, C. Campana, K.R. Dunbar, *Inorg. Chem.* 35 (1996) 7188.
- [266] C. Campana, K.R. Dunbar, X. Ouyang, *J. Chem. Soc., Chem. Commun.* (1996) 2427.
- [267] C.A. Crawford, E.F. Day, V.P. Saharan, K. Folting, J.C. Huffman, K.R. Dunbar, G. Christou, *J. Chem. Soc., Chem. Commun.* (1996) 1113.
- [268] M. McCann, M. Mac Giolla Coda, *J. Mol. Catal. A* 109 (1996) 99.
- [269] H. Nakano, A. Nakamura, K. Mashima, *Inorg. Chem.* 35 (1996) 4007.
- [270] K. Mashima, H. Nakano, A. Nakamura, *J. Am. Chem. Soc.* 118 (1996) 9083.
- [271] M. Nishino, M. Tanaka, S. Takeda, K. Mashima, W. Mori, K. Tani, A. Nakamura, K. Yamaguchi, *Mol. Cryst., Liq. Cryst. Sci. Technol. A* 285 (1996) 515.
- [272] M. Cindric, V. Vrdoljak, D. Matkovic-Calogovic, B. Kamenar, *Acta Crystallogr. C* 52 (1996) 3016.
- [273] D. Sellmann, J.H. Kremitzl, F. Knoch, M. Moll, *J. Biol. Inorg. Chem.* 1 (1996) 127.
- [274] D. Sellmann, B. Hadawi, F. Knoch, *Inorg. Chim. Acta* 244 (1996) 213.
- [275] C.O. Kienitz, C. Thöne, P.G. Jones, *Inorg. Chem.* 35 (1996) 3990.
- [276] F.M. Kerton, G.F. Mohmand, A. Tersteegen, M. Thiel, M.J. Went, *J. Organomet. Chem.* 519 (1996) 177.
- [277] Y. Shi, S. Lu, H. Guo, Q. Wu, N. Hu, *J. Organomet. Chem.* 514 (1996) 183.
- [278] S.-L. Li, Z.Z. Zhang, J.C.C. Chan, S.C.F. Au-Yeung, T.C.W. Mak, *J. Organomet. Chem.* 522 (1996) 155.
- [279] R. Herbst-Irmer, E. Egert, *Acta Crystallogr. C* 52 (1996) 2161.
- [280] G. Frenking, S. Dapprich, A.W. Ehlers, M. Otto, S.F. Vyboishchikov, *NATO ASI Ser. C* 474 (1996) 185; *Chem. Abstr.* 124 (1996) 299098p.

- [281] A.W. Ehlers, S. Dapprich, S.F. Vyboishchikov, G. Frenking, *Organometallics* 15 (1996) 105.
- [282] S. Dapprich, G. Frenking, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 354.
- [283] A.S. Goldman, K. Krogh-Jespersen, *J. Am. Chem. Soc.* 118 (1996) 12159.
- [284] S. Ozkar, NATO ASI Ser. E 297 (1995) 79; *Chem. Abstr.* 125 (1996) 130685n.
- [285] C. Brémard, G. Ginestet, M. Le Maire, *J. Am. Chem. Soc.* 118 (1996) 12724.
- [286] T. Yokota, M. Yaginuma, J.N. Kondo, K. Domen, C. Hirose, F. Wakabayashi, *Catal. Lett.* 40 (1986) 89; *Chem. Abstr.* 125 (1996) 211213j.
- [287] B.R. Müller, G. Calzaferri, *J. Chem. Soc., Faraday Trans.* 92 (1996) 1633.
- [288] Y. Sakamoto, N. Togashi, O. Terasaki, T. Ohsuna, Y. Okamoto, K. Hiraga, *Mater. Sci. Eng. A* 217/218 (1996) 147; *Chem. Abstr.* 126 (1997) 194415c.
- [289] J. Evans, B.E. Hayden, G. Lu, *J. Chem. Soc., Faraday Trans.* 92 (1996) 4733.
- [290] M. Xu, F. Zaera, *J. Vac. Sci. Technol.* 14 (1996) 415; *Chem. Abstr.* 124 (1996) 276946z.
- [291] O. Alexeev, S. Kawi, M. Shelef, B.C. Gates, *J. Phys. Chem.* 100 (1996) 253.
- [292] T. Hyeon, M. Fang, K.S. Suslick, *J. Am. Chem. Soc.* 118 (1996) 5492.
- [293] X.-Z. Sun, M.W. George, S.G. Kazarian, S.M. Nikiforov, M. Poliakov, *J. Am. Chem. Soc.* 118 (1996) 10525.
- [294] H.E.B. Lempers, M.J. van Crey, R.A. Sheldon, *Recl. Trav. Chim. Pays-Bas* 115 (1996) 542.
- [295] R.C.F. Jones, S.H. Dunn, K.A.M. Duller, *J. Chem. Soc., Perkin I* (1996) 1319.
- [296] J. Anderson-McKay, G.P. Savage, G.W. Simpson, *Aust. J. Chem.* 49 (1996) 163.
- [297] F.E. McDonald, M.M. Gleason, *J. Am. Chem. Soc.* 118 (1996) 6648.
- [298] J.-H. Kim, E. Hong, J. Kim, Y. Do, *Inorg. Chem.* 35 (1996) 5112.
- [299] C.-Y. Liu, D.-Y. Chen, G.-H. Lee, S.-M. Peng, S.-T. Liu, *Organometallics* 15 (1996) 1055.
- [300] F.E. Hahn, M. Tamm, L. Imhof, T. Lügger, *J. Organomet. Chem.* 526 (1996) 149.
- [301] M. Weidenbruch, A. Stilter, K. Peters, H.G. von Schnering, *Z. Anorg. Allg. Chem.* 622 (1996) 534.
- [302] K. Bieger, G. Bouhadir, R. Réau, F. Dahan, G. Bertrand, *J. Am. Chem. Soc.* 118 (1996) 1038.
- [303] S. Cao, Y. Shi, J. Hollmann, R. van Eldik, E.M. Eyring, *J. Chem. Soc., Dalton Trans.* (1996) 1629.
- [304] S. Ernst, C. Vogler, A. Klein, W. Kaim, S. Zalis, *Inorg. Chem.* 35 (1996) 1295.
- [305] M.N. Ackermann, W.G. Fairbrother, N.S. Amin, C.J. Deodene, C.M. Lamborg, P.T. Martin, *J. Organomet. Chem.* 523 (1996) 145.
- [306] J. Granifo, M.E. Vargas, E.S. Dodsworth, D.H. Farrar, S.S. Fielder, A.P.B. Lever, *J. Chem. Soc., Dalton Trans.* (1996) 4369.
- [307] E.C. Alyea, V.K. Jain, *Polyhedron* 15 (1996) 1723.
- [308] I.T. Macleod, E.R.T. Tiekink, C.G. Young, *J. Organomet. Chem.* 506 (1996) 301.
- [309] V. Patinec, I. Gardinier, J.-J. Yaouanc, J.-C. Clément, H. Handel, H. des Abbayes, *Inorg. Chim. Acta* 244 (1996) 105.
- [310] E.C. Alyea, S.Q. Song, *Comm. Inorg. Chem.* A18 (1996) 189; *Chem. Abstr.* 125 (1996) 124286s.
- [311] C. Kaya, *Spectrochim. Acta A* 52 (1996) 615.
- [312] S. Song, E.C. Alyea, *Can. J. Chem.* 74 (1996) 2304.
- [313] K. Eichele, R.E. Wasylshen, J.M. Kessler, L. Solujic, J.H. Nelson, *Inorg. Chem.* 35 (1996) 3904.
- [314] J.A.S. Howell, P.C. Yates, N.F. Ashford, D.T. Dixon, R. Warren, *J. Chem. Soc., Dalton Trans.* (1996) 3959.
- [315] S. Dapprich, G. Frenking, *Organometallics* 15 (1996) 4547.
- [316] J. Li, T. Ziegler, *Organometallics* 15 (1996) 3844.
- [317] D.-L. An, K. Toyota, M. Yasunami, M. Yoshifuji, *J. Organomet. Chem.* 508 (1996) 7.
- [318] K. Maitra, W.L. Wilson, M.M. Jemin, C. Yeung, W.S. Rader, K.D. Redwine, D.P. Striplin, V.J. Catalano, J.H. Nelson, *Synth. React. Inorg. Met.-Org. Chem.* 26 (1996) 967; *Chem. Abstr.* 125 1996 156960y.
- [319] L. Weber, O. Sommer, H.-G. Stämmler, B. Neumann, *Z. Anorg. Allg. Chem.* 622 (1996) 543.
- [320] C. Müller, R. Bartsch, A. Fischer, P.G. Jones, R. Schmutzler, *J. Organomet. Chem.* 512 (1996) 141.
- [321] O. bin Shawkataly, T. Saminathan, K. Muniswaran, H.-K. Fun, K. Sivakumar, *Acta Crystallogr. C* 52 (1996) 1352.
- [322] G.M. Gray, F.P. Fish, C.H. Duffey, *Inorg. Chim. Acta* 246 (1996) 229; correction 254 (1997) 201.
- [323] M. Ahmad, S.D. Perera, B.L. Shaw, M. Thornton-Pett, *Inorg. Chim. Acta* 245 (1996) 59.

- [324] E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna, E. Olmos, *J. Chem. Soc., Dalton Trans.* (1996) 3603.
- [325] S.M. Young, V. Carperos, A.D. Norman, *Inorg. Chem.* 35 (1996) 2000.
- [326] S.J. Chadwell, S.J. Coles, P.G. Edwards, M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.* (1996) 1105; correction 3163.
- [327] S. Grundei, H. Höth, R.T. Paine, *Chem. Ber.* 129 (1996) 1233.
- [328] A.A. Karasik, S.V. Bobrov, G.N. Nikonov, I.A. Litvinov, A.S. Dokuchaev, *Koord. Khim.* 22 (1996) 38; *Russ. J. Coord. Chem.* 22 (1996) 35; *Chem. Abstr.* 124 (1996) 192380x.
- [329] E.C. Alyea, G. Ferguson, S. Kannan, *Acta Crystallogr. C* 52 (1996) 765.
- [330] N.R. Champness, A.M. Hopkins, G. Reid, *Acta Crystallogr. C* 52 (1996) 797.
- [331] E.C. Alyea, G. Ferguson, S.Q. Song, *Acta Crystallogr. C* 52 (1996) 66.
- [332] G. Hogarth, T. Norman, *Polyhedron* 15 (1996) 2859.
- [333] G. Hogarth, J.Y. Pang, *J. Organomet. Chem.* 515 (1996) 193.
- [334] G. Hogarth, T. Norman, *J. Chem. Soc., Dalton Trans.* (1996) 1077.
- [335] G. Hogarth, T. Norman, *Inorg. Chim. Acta* 248 (1996) 167.
- [336] D. Rodewald, D. Rehder, *J. Chem. Soc., Chem. Commun.* (1996) 1603.
- [337] M.P. Gamasa, J. Gimeno, L. Zhang, M. Lanfranchi, A. Tiripicchio, *J. Organomet. Chem.* 514 (1996) 287.
- [338] F. Hilgers, W. Bruns, I. Fiedler, W. Kaim, *J. Organomet. Chem.* 511 (1996) 273.
- [339] M. Iglesias, A. Santos, *Inorg. Chim. Acta* 248 (1996) 67.
- [340] Y. Yamaguchi, H. Nakazawa, T. Itoh, K. Miyoshi, *Bull. Chem. Soc. Jpn.* 69 (1996) 983.
- [341] H. Nakazawa, Y. Yamaguchi, K. Miyoshi, A. Nagasawa, *Organometallics* 15 (1996) 2517.
- [342] Y. Yamaguchi, H. Nakazawa, M. Kishishita, K. Miyoshi, *Organometallics* 15 (1996) 4383.
- [343] H. Nakazawa, Y. Yamaguchi, K. Miyoshi, *Phosphorus, Sulfur, Silicon Relat. Elem.* 109/110 (1996) 129.
- [344] D.C.R. Hockless, Y.B. Kang, M.A. McDonald, M. Pabel, A.C. Willis, S.B. Wild, *Organometallics* 15 (1996) 1301.
- [345] D. Walter, G. Huttner, R. Kern, *Z. Naturforsch.* 51b (1996) 922.
- [346] S.J. Coles, P.G. Edwards, J.S. Fleming, M.B. Hursthouse, S.S. Liyanage, *J. Chem. Soc., Chem. Commun.* (1996) 293.
- [347] P.G. Edwards, J.S. Fleming, S.S. Liyanage, *Inorg. Chem.* 35 (1996) 4563.
- [348] P.G. Edwards, J.S. Fleming, S.S. Liyanage, S.J. Coles, M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.* (1996) 1801.
- [349] P. Stössel, H.A. Mayer, C. Maichle-Mossmeyer, R. Fawzi, M. Steimann, *Inorg. Chem.* 35 (1996) 5860.
- [350] M. Drieß, H. Pritzkow, M. Reigys, *Chem. Ber.* 129 (1996) 247.
- [351] S. Charles, J.C. Fettingier, B.W. Eichhorn, *Inorg. Chem.* 35 (1996) 1540.
- [352] M.-F. Fan, G. Jia, Z. Lin, *J. Am. Chem. Soc.* 118 (1996) 9915.
- [353] D. Wang, R.J. Angelici, *J. Am. Chem. Soc.* 118 (1996) 935.
- [354] G. Nakamura, Y. Harada, Y. Mizobe, M. Hidai, *Bull. Chem. Soc. Jpn.* 69 (1996) 3305.
- [355] A.F. Chiffey, J. Evans, W. Levason, M. Webster, *Organometallics* 15 (1996) 1280.
- [356] D.J. Darensbourg, K.K. Klausmeyer, J.H. Reibenspies, *Inorg. Chem.* 35 (1996) 1529.
- [357] N. Kuhn, R. Fawzi, T. Kratz, M. Steimann, G. Henkel, *Phosphorus, Sulfur, Silicon Relat. Elem.* 108 (1996) 107; *Chem. Abstr.* 125 (1996) 156988p.
- [358] A. Galindo, C. Mealli, *Inorg. Chem.* 35 (1996) 2406.
- [359] B. Zhuang, G. Pan, L. Huang, *Polyhedron* 15 (1996) 3019.
- [360] S. Poder-Guillou, P. Schollhammer, F.Y. Pétillon, J. Talarmin, S.E. Girdwood, K.W. Muir, *J. Organomet. Chem.* 506 (1996) 321.
- [361] A.L. Sargent, E.P. Titus, C.G. Riordan, A.L. Rheingold, P. Ge, *Inorg. Chem.* 35 (1996) 7095.
- [362] Z.-Z. Zhang, H. Cheng, S.-M. Kuang, Y.-Q. Zhou, Z.-X. Liu, J.-K. Zhang, H.-G. Wang, *J. Organomet. Chem.* 516 (1996) 1.
- [363] S.-M. Kuang, H. Cheng, L.-J. Sun, Z.Z. Zhang, Z.-Y. Zhou, B.-M. Wu, T.C.W. Mak, *Polyhedron* 15 (1996) 3417.
- [364] I. Ara, E. Delgado, J. Forniés, E. Hernández, E. Lalinde, N. Mansilla, M.T. Moreno, *J. Chem. Soc., Dalton Trans.* (1996) 3201.

- [365] A.J. Deeming, S. Doherty, *Polyhedron* 15 (1996) 1175.
- [366] S.D. Orth, M.R. Terry, K.A. Abboud, B. Dodson, L. McElwee-White, *Inorg. Chem.* 35 (1996) 916.
- [367] W. Weng, A.M. Arif, R.D. Ernst, *J. Cluster Sci.* 7 (1996) 629; *Chem. Abstr.* 126 (1997) 126101x.
- [368] J.W. Freeman, A.M. Arif, R.D. Ernst, *Inorg. Chim. Acta* 250 (1996) 15.
- [369] V. Trapp, P. Christensen, A. Hamnett, *J. Chem. Soc., Faraday Trans.* 92 (1996) 4311.
- [370] G. Hsu, S.R. Wilson, J.R. Shapley, *Inorg. Chem.* 35 (1996) 923.
- [371] J.T. Lin, C.C. Yu, C.H. Lo, S.Y. Wang, T.Y.R. Tsai, M.M. Chen, Y.S. Wen, K.J. Lin, *Organometallics* 15 (1996) 2132.
- [372] P. Mathur, P. Sekar, C.V.V. Satyanarayana, M.F. Mahon, *J. Chem. Soc., Dalton Trans.* (1996) 2173.
- [373] P. Mathur, R. Trivedi, P. Sekar, D. Chakrabarty, M.M. Hossain, V.G. Puranik, *J. Cluster Sci.* 7 (1996) 191; *Chem. Abstr.* 125 (1996) 103468n.
- [374] P. Mathur, P. Sekar, *J. Chem. Soc., Chem. Commun.* (1996) 727.
- [375] G. Friedrich, O.J. Scherer, G. Wolmershäuser, *Z. Anorg. Allg. Chem.* 622 (1996) 1478.
- [376] C.L. Hill, *J. Mol. Catal.* 114 (1996) 1.
- [377] B. Kraut, Z. Szilak, J. Szoke, A. Horvath, *Magy. Kem. Foly.* 102 (1996) 301; *Chem. Abstr.* 125 (1996) 288448x.
- [378] M. Hilbers, M. Meiwald, R. Mattes, *Z. Naturforsch.* 51b (1996) 57; *Chem. Abstr.* 124 (1996) 248753r.
- [379] X.-M. Lu, H.J. Zhu, S.-C. Liu, *Gaodeng Xuexiao Huaxue Xuebao* 17 (1996) 183; *Chem. Abstr.* 124 (1996) 276785w.
- [380] Y. Imada, T. Shido, R. Ohnishi, K. Isobe, M. Ichikawa, *Catal. Lett.* 38 (1996) 101; *Chem. Abstr.* 124 (1996) 299936k.
- [381] M. Ichikawa, W. Pan, Y. Imada, M. Yamaguchi, K. Isobe, T. Shido, *J. Mol. Catal. A* 107 (1996) 23.
- [382] Y.-D. Chang, J.A. Zubieta, *Inorg. Chim. Acta* 245 (1996) 177.
- [383] M. Inoue, T. Yamase, *Bull. Chem. Soc. Jpn.* 69 (1996) 2863.
- [384] S.-G. Roh, A. Proust, F. Robert, P. Gouzerh, *J. Cluster Sci.* 7 (1996) 593; S.-G. Roh, A. Proust, F. Robert, P. Gouzerh, *Chem. Abstr.* 126 (1997) 126100w.
- [385] A. Proust, O. Horner, P. Villanneau, P. Gouzerh, *New J. Chem.* 20 (1996) 643.
- [386] S.-G. Roh, S.O. Oh, *J. Korean Chem. Soc.* 40 (1996) 28; *Chem. Abstr.* 124 (1996) 248668s.
- [387] X.-X. Xu, X.-Z. You, X. Wang, *Acta Chem. Scand.* 50 (1996) 1.
- [388] H.-W. Hou, X.-Q. Xin, K.-B. Yu, Z.-M. Wang, S.-X. Liu, J.-L. Huang, *Chin. J. Chem.* 14 (1996) 123; *Chem. Abstr.* 125 (1996) 47578j.
- [389] X. Lu, Y. Zhao, E. Qu, L. Xiao, S. Liu, X. Jin, *Jiegou Huaxue* 15 (1996) 293; *Chem. Abstr.* 125 (1996) 236782g.
- [390] X.-M. Lu, S.-C. Liu, X.-L. Jin, *Gaodeng Xuexiao Huaxue Xuebao* 17 (1996) 1173; *Chem. Abstr.* 125 (1996) 264221s.
- [391] W. Clegg, M.R.J. Elsegood, R.J. Errington, J. Havelock, *J. Chem. Soc., Dalton Trans.* (1996) 681.
- [392] J.-Y. Niu, X.-Z. You, H.-K. Fun, Z.-Y. Zhou, B.-C. Yip, *Polyhedron* 15 (1996) 1003.
- [393] D.I. Kondarides, K. Tomishige, Y. Nagasawa, U. Lee, T. Iwasawa, *J. Mol. Catal. A* 111 (1996) 145.
- [394] A.L. Nolan, R.C. Burns, G.A. Lawrance, *J. Chem. Soc., Dalton Trans.* (1996) 2629.
- [395] M. McCann, A.J. Beaumont, *J. Mol. Catal. A* 108 (1996) 23.
- [396] H.-K. Fun, B.-C. Yip, J.-Y. Niu, X.-Z. You, *Acta Crystallogr. C52* (1996) 506.
- [397] W.T.A. Harrison, L.L. Dussack, A.J. Jacobson, *Acta Crystallogr. C52* (1996) 1075.
- [398] T. Yamase, M. Sugeta, E. Ishikawa, *Acta Crystallogr. C52* (1996) 1869.
- [399] P.G. Roy, R. Jaiswal, P.K. Sinha, *J. Ind. Chem. Soc.* 73 (1996) 409; *Chem. Abstr.* 125 (1996) 236775g.
- [400] A. Proust, S. Tautier, V. Artero, F. Robert, R. Thouvenot, P. Gouzerh, *J. Chem. Soc., Chem. Commun.* (1996) 2195.
- [401] J. Evans, M. Pillinger, J.M. Rummey, *J. Chem. Soc., Dalton Trans.* (1996) 2951.
- [402] Z. Chen, Xiangtan Kuangye Xueyuan Xuebao 11 (1996) 59; *Chem. Abstr.* 125 (1996) 156996q.
- [403] D.-G. Lyxell, D. Boström, M. Hashimoto, L. Pettersson, *Acta Chem. Scand.* 50 (1996) 985.
- [404] M.A. Parent, J.B. Moffat, *Langmuir* 12 (1996) 3733.

- [405] W. Xie, X. Ye, X. Yang, Y. Wu, *Wuji Huaxue Xuebao* 12 (1996) 299; *Chem. Abstr.* 126 (1997) 191423t.
- [406] R. Bayer, C. Marchal, F.X. Liu, A. Tézé, G. Hervé, *J. Mol. Catal. A* 110 (1996) 65.
- [407] R. Bayer, C. Marchal-Roch, F.X. Liu, A. Tézé, G. Hervé, *J. Mol. Catal. A* 114 (1996) 277.
- [408] E. Wang, Y. Zhou, Z. Wang, L. Zhang, *Trans. Met. Chem.* 21 (1996) 447; *Chem. Abstr.* 125 (1996) 346085q.
- [409] M. Zhang, R. Cui, Y. Nie, R. Liu, C. Xie, *Yingyong Huaxue* 13 (1996) 99; *Chem. Abstr.* 125 (1996) 211055j.
- [410] M. Ai, *J. Mol. Catal. A* 114 (1996) 3.
- [411] M. Shimizu, H. Orita, K. Suzuki, T. Hayakawa, S. Hamakawa, K. Takehira, *J. Mol. Catal. A* 114 (1996) 217.
- [412] B. Török, I. Bucsí, T. Beregszászi, I. Kapocsi, A. Molnar, *J. Mol. Catal. A* 107 (1996) 305.
- [413] N. Mizuno, D.-J. Suh, W. Han, T. Kudo, *J. Mol. Catal. A* 114 (1996) 309.
- [414] G. Busca, F. Cavani, E. Etienne, E. Finocchio, A. Galli, G. Sella, F. Trifiro, *J. Mol. Catal. A* 114 (1996) 343.
- [415] R.I. Maksimovskaya, V.M. Bondareva, G.S. Litvak, *Zh. Neorg. Khim.* 41 (1996) 1173; *Chem. Abstr.* 125 (1996) 315305g.
- [416] C. Rocchiccioli-Deltcheff, A. Aouissi, M.M. Bettahar, S. Launay, M. Fournier, *J. Catal.* 164 (1996) 16.
- [417] M.A. Castillo, P.G. Vázquez, M.N. Blanco, C.V. Cáceres, *J. Chem. Soc., Faraday Trans.* 92 (1996) 3239.
- [418] C. Rocchiccioli-Deltcheff, A. Aouissi, S. Launay, M. Fournier, *J. Mol. Catal. A* 114 (1996) 331.
- [419] S. Li, J.S. Lee, *J. Catal.* 162 (1996) 76; *Chem. Abstr.* 125 (1996) 291439a.
- [420] E. Stochmal-Pomarzanska, M. Hasik, W. Turek, A. Pron, *J. Mol. Catal. A* 114 (1996) 267.
- [421] B. Wang, S. Dong, *Electrochim. Acta* 41 (1996) 895; *Chem. Abstr.* 124 (1996) 273003d.
- [422] C. Rong, F.C. Anson, *Inorg. Chim. Acta* 242 (1996) 11.
- [423] T. Hori, S. Himeno, O. Tamada, *J. Chem. Soc., Dalton Trans.* (1996) 2083.
- [424] W. Huang, H. Lin, G. Xi, *Hecheng Huaxue* 4 (1996) 69; *Chem. Abstr.* 125 (1996) 211180w.
- [425] Q. Xu, H. Zhang, L. Yang, H. Wang, *Yunnan Daxue Xuebao, Ziran Kexueban* 18 (1996) 289; *Chem. Abstr.* 126 (1997) 112370x.
- [426] C.L. Hill, R.D. Gall, *J. Mol. Catal. A* 114 (1996) 103.
- [427] R.D. Gall, C.L. Hill, J.E. Walker, *Chem. Mater.* 8 (1996) 2523.
- [428] J.H. Grate, *J. Mol. Catal. A* 114 (1996) 93.
- [429] T. Yokota, S. Fujibayashi, Y. Nishiyama, S. Sakaguchi, Y. Ishii, *J. Mol. Catal. A* 114 (1996) 113.
- [430] H. Grennberg, K. Bergstad, J.E. Bäckvall, *J. Mol. Catal. A* 113 (1996) 355.
- [431] K.I. Matveev, V.F. Odyakov, E.G. Zhizhina, *J. Mol. Catal. A* 114 (1996) 151.
- [432] K.I. Matveev, E.G. Zhizhina, V.F. Odyakov, N.S. Kotsarenko, V.P. Shmachkova, *React. Kinet. Catal. Lett.* 57 (1996) 182.
- [433] S. Fujibayashi, K. Nakayama, M. Hamamoto, S. Sakaguchi, Y. Nishiyama, Y. Ishii, *J. Mol. Catal. A* 110 (1996) 105.
- [434] R.J.J. Jansen, H.M. van Veldhuizen, H. van Bekkum, *J. Mol. Catal. A* 107 (1996) 241.
- [435] I.V. Kozhevnikov, A. Sinnema, H. van Bekkum, *J. Chem. Res. (S)* (1996) 238.
- [436] C.L. Hill, H. Zeng, X. Zhang, *J. Mol. Catal. A* 113 (1996) 185.
- [437] A.W. Stobbe-Kreemers, M. van der Zon, M. Makkee, J.J.F. Scholten, *J. Mol. Catal. A* 107 (1996) 247.
- [438] S. Wang, L. Sun, B. Zeng, X. Zhou, *Wuhan Daxue Xuebao, Ziran Kexueban* 42 (1997) 419; *Chem. Abstr.* 126 (1997) 244027a.
- [439] J.-Y. Niu, X.-Z. You, T.C.W. Mak, Z.-Y. Zhou, *Polyhedron* 15 (1996) 519.
- [440] J.-Y. Niu, J.-P. Wang, X.-Z. You, T.C.W. Mak, X.-Y. Zhou, *Polyhedron* 15 (1996) 3963.
- [441] J.-Y. Niu, X.-Z. You, J.-P. Wang, *Trans. Met. Chem.* 21 (1996) 38; *Chem. Abstr.* 124 (1996) 305580h.
- [442] E. Cadot, M. Fournier, A. Tézé, G. Hervé, *Inorg. Chim. Acta* 252 (1996) 282.
- [443] E. Cadot, V. Béreau, F. Sécheresse, *Inorg. Chim. Acta* 252 (1996) 101.
- [444] E. Cadot, V. Béreau, B. Marg, S. Halut, F. Sécheresse, *Inorg. Chim. Acta* 252 (1996) 3099.

- [445] X.M. Zhang, L. Cheng, X.D. Xi, B.F. Liu, S.J. Dong, *Chin. Chem. Lett.* 7 (1996) 81; *Chem. Abstr.* 124 (1996) 214410m.
- [446] L. Cheng, X. Zhang, X. Xi, B. Liu, S. Dong, *J. Electroanal. Chem.* 407 (1996) 97; *Chem. Abstr.* 125 (1996) 70103j.
- [447] B. Ly, Y. Shan, Y. Wu, Y. Ying, Y. Lin, S. Bai, *Jiegou Huaxue* 15 (1996) 301; *Chem. Abstr.* 125 (1996) 211163t.
- [448] P. Huang, R. Zhao, H. Zhou, Y. Shan, *Zhongguo Xitu Xuebao* 14 (1996) 83; *Chem. Abstr.* 125 (1996) 211182y.
- [449] M. Cindric, N. Strukan, Z. Veksli, B. Kamenar, *Polyhedron* 15 (1996) 2121.
- [450] Q. Chen, C.L. Hill, *Inorg. Chem.* 35 (1996) 2403.
- [451] A. Müller, E. Krickemeyer, S. Dillinger, J. Meyer, H. Bögge, A. Stammeler, *Angew. Chem., Int. Ed. Engl.* 35 (1996) 171.
- [452] M.I. Khan, Q. Chen, J. Salta, C.J. O'Connor, J. Zubietta, *Inorg. Chem.* 35 (1996) 1880.
- [453] J. Gong, L.Y. Qu, *Chin. Chem. Lett.* 7 (1996) 199; *Chem. Abstr.* 124 (1996) 330703h.
- [454] J. Yu, Y. Liu, Y. Yang, T. Wu, H. Zhang, J. Sun, *Jilin Daxue Ziran Kexue Xuebao* (1996) 89; *Chem. Abstr.* 125 (1996) 74660m.
- [455] D. Gatteschi, R. Sessoli, W. Plass, A. Müller, E. Krickemeyer, J. Meyer, D. Sölter, P. Adler, *Inorg. Chem.* 35 (1996) 1926.
- [456] A. Müller, J. Meyer, E. Krickemeyer, E. Diemann, *Angew. Chem., Int. Ed. Engl.* 35 (1996) 1206.
- [457] Z. Lin, I.D. Williams, *Polyhedron* 15 (1996) 3277.
- [458] J.R. Schoonover, T.C. Zietlow, D.L. Clark, J.A. Heppert, M.H. Chisholm, H.B. Gray, A.P. Sattelberger, W.H. Woodruff, *Inorg. Chem.* 35 (1996) 6606.
- [459] D. Bublitz, W. Preetz, *Z. Anorg. Allg. Chem.* 622 (1996) 1107.
- [460] L.M. Robinson, D.F. Shriver, *J. Coord. Chem.* 37 (1996) 119; *Chem. Abstr.* 125 (1996) 47463t.
- [461] J.A. Jackson, M.D. Newsham, C. Worshau, D.G. Nocera, *Chem. Mater.* 8 (1996) 558.
- [462] A. Peppenhorst, H.-L. Keller, *Z. Anorg. Allg. Chem.* 622 (1996) 663.
- [463] T.A. Budzichowski, M.H. Chisholm, K. Folting, W.E. Streib, M. Scheer, *Inorg. Chem.* 35 (1996) 3659.
- [464] V.G. Kessler, N.Y. Turova, A.N. Panov, A.I. Yanovsky, A.P. Pisarevsky, Y.T. Struchkov, *Polyhedron* 15 (1996) 335.
- [465] L. Xu, X. Li, J. Huang, *Inorg. Chem.* 35 (1996) 5097.
- [466] L. Huang, X. Li, H. Jinshin, C. Wendan, H. Xiaoyin, H. Xin, *Polyhedron* 15 (1996) 2003.
- [467] L. Xu, Z. Li, H. Liu, J. Huang, *Trans. Met. Chem.* 21 (1996) 498; *Chem. Abstr.* 126 (1997) 112349x.
- [468] H. Liu, L. Xu, J. Huang, W. Chen, Q. Zhang, *Acta Crystallogr. C52* (1996) 69.
- [469] L. Xu, Z. Li, H. Liu, J. Huang, *J. Coord. Chem.* 40 (1996) 133; *Chem. Abstr.* 126 (1997) 258037r.
- [470] H. Zhuang, D. Wu, J. Huang, J. Huang, *Jiegou Huaxue* 15 (1996) 257; *Chem. Abstr.* 125 (1996) 211162s.
- [471] L. Huo, N. Chen, J. Huang, *Jiegou Huaxue* 15 (1996) 187; *Chem. Abstr.* 125 (1996) 70124s.
- [472] B. Kamenar, B. Korpar-Colig, M. Penavic, *Croat. Chem. Acta* 69 (1996) 1377; *Chem. Abstr.* 126 (1997) 180364y.
- [473] Y. Mizobe, M. Hosomizu, Y. Kubota, M. Hidai, *J. Organomet. Chem.* 507 (1996) 179.
- [474] J. Lang, K. Tatsumi, H. Kawaguchi, J. Lu, P. Ge, W. Ji, S. Shi, *Inorg. Chem.* 35 (1996) 7924.
- [475] S.-Y. Niu, B. Yang, K. Luo, W.-L. Wang, Z.-G. Zhang, L. Shi, *Gaodeng Xuexiao Huaxue Xuebao* 17 (1996) 14; *Chem. Abstr.* 124 (1996) 218571n.
- [476] Q. Wang, X. Wu, Q. Huang, T. Sheng, *Acta Crystallogr. C52* (1996) 2738.
- [477] R.E. Cramer, K. Yamada, H. Kawaguchi, K. Tatsumi, *Inorg. Chem.* 35 (1996) 1743.
- [478] M.N. Sokolov, S.S. Yarovoi, V.P. Fedin, V.E. Fedorov, *Zh. Neorg. Khim.* 41 (1996) 1862; *Chem. Abstr.* 126 (1997) 139080q.
- [479] S.-F. Lu, J.-Q. Huang, Q.-J. Wu, X.-Y. Huang, *Jiegou Huaxue* 15 (1996) 415; *Chem. Abstr.* 126 (1997) 69305r.
- [480] Y.-G. Yao, L. Wu, Y.-B. Zhu, S.-F. Lu, *Jiegou Huaxue* 15 (1996) 117; *Chem. Abstr.* 124 (1996) 330731r.
- [481] J. Mizutani, S. Yamada, H. Imoto, T. Saito, *Inorg. Chem.* 35 (1996) 244.

- [482] K. Tsuge, S. Mita, H. Fujita, H. Imoto, T. Saito, *J. Cluster Sci.* 7 (1996) 407; *Chem. Abstr.* 125 (1996) 346014r.
- [483] F.A. Cotton, L.M. Daniels, M. Shang, R. Llusar, W. Schwotzer, *Acta Crystallogr. C* 52 (1996) 835.
- [484] L.-H. Huo, N.S. Chen, J.-L. Huang, *Jiegou Huaxue* 15 (1996) 150; *Chem. Abstr.* 124 (1996) 273020g.
- [485] J. Lang, X. Xin, *Huaxue Xuebao* 54 (1996) 461; *Chem. Abstr.* 125 (1996) 103431v.
- [486] Z. Lin, X. Huang, H. Chen, L. Chi, *Jiegou Huaxue* 15 (1996) 333; *Chem. Abstr.* 125 (1996) 211167x.
- [487] D. Long, S. Shi, X. Xin, B. Luo, L. Chen, X. Huang, B. Kang, *J. Chem. Soc., Dalton Trans.* (1996) 2617.
- [488] Y.-B. Cai, X.-T. Wu, L. Dai, J.-X. Lu, *Jiegou Huaxue* 15 (1996) 52; *Chem. Abstr.* 124 (1996) 218632h.
- [489] S. Shi, Z. Lin, Y. Mo, X.Q. Xin, *J. Phys. Chem.* 100 (1996) 10696.
- [490] P.E. Hoggard, H.-W. Hou, X.-Q. Xin, S. Shi, *Chem. Mater.* 8 (1996) 2218.
- [491] W. Ji, P. Ge, W. Xie, S.H. Tang, S. Shi, *J. Luminesc.* 66/67 (1995) 115.
- [492] D. Wu, M. Hong, R. Cao, H. Liu, *Inorg. Chem.* 35 (1996) 1080.
- [493] H. Hou, D. Long, X. Xin, X. Huang, B. Kang, P. Ge, W. Ji, S. Shi, *Inorg. Chem.* 35 (1996) 5363.
- [494] Q. Huang, X. Wu, Q. Wang, T. Sheng, J. Lu, *Inorg. Chem.* 35 (1996) 893.
- [495] Q. Huang, X. Wu, T. Sheng, Q. Wang, *Polyhedron* 15 (1996) 3405.
- [496] W. Ji, W. Xie, S.H. Tang, S. Shi, *Mater. Chem. Phys.* 43 (1996) 45.
- [497] G.R. Helz, C.V. Miller, J.M. Charnock, J.F.W. Mosselmans, R.A.D. Patrick, C.D. Garner, D.J. Vaughan, *Geochim. Cosmochim. Acta* 60 (1996) 3631.
- [498] J.-Q. Xu, X.-G. Xiang, H. Cai, N.-H. Hu, C.-P. Wei, G.-Y. Yang, T.-G. Wang, *J. Chem. Soc., Chem. Commun.* (1996) 757.
- [499] K.D. Demadis, S.M. Malinak, D. Coucouvanis, *Inorg. Chem.* 35 (1996) 4038.
- [500] D. Coucouvanis, K.D. Demadis, S.M. Malinak, P.E. Mosier, M.A. Tyson, L.J. Laughlin, *J. Mol. Catal. A* 107 (1996) 123.
- [501] Q.-T. Liu, Y.-H. Deng, C.-N. Cheng, D.-Z. Liao, J.-Z. Cui, *Jiegou Huaxue* 15 (1996) 408; *Chem. Abstr.* 126 (1997) 25667f.
- [502] K. Hegetschweiler, M. Wörle, M.D. Meienberger, R. Nesper, H.W. Schmalle, R.D. Hancock, *Inorg. Chim. Acta* 250 (1996) 35.
- [503] W. McFarlane, M. Nasreddin, D.M. Sayersell, Z.-S. Jia, W. Clegg, M.R.J. Elsegood, K.S. Murray, B. Moubarak, A.G. Sykes, *J. Chem. Soc., Dalton Trans.* (1996) 363.
- [504] J.E. Varey, G.J. Lamprecht, V.P. Fedin, A. Holder, W. Clegg, M.R.J. Elsegood, A.G. Sykes, *Inorg. Chem.* 35 (1996) 5525.
- [505] V.P. Fedin, M.N. Sokolov, A.G. Sykes, *J. Chem. Soc., Dalton Trans.* (1996) 4089.
- [506] D.M. Sayersell, A.G. Sykes, *Inorg. Chem.* 35 (1996) 5536.
- [507] J.C. Varey, A.G. Sykes, *Polyhedron* 15 (1996) 1887.
- [508] D.M. Sayersell, Z.-X. Huang, A.G. Sykes, *J. Chem. Soc., Dalton Trans.* (1996) 2623.
- [509] M. Brorson, C.J.H. Jacobsen, H.K.M. Helgesen, I. Schmidt, *Inorg. Chem.* 35 (1996) 4808; correction 36 (1997) 264.
- [510] I. Schmidt, J. Hyldtoft, J. Hjortkjær, C.J.H. Jacobsen, *Acta Chem. Scand.* 50 (1996) 871.
- [511] T. Shibahara, G. Sakane, M. Maeyama, H. Kobashi, T. Yamamoto, T. Watase, *Inorg. Chim. Acta* 251 (1996) 207.
- [512] D.M. Sayersell, C.D. Borman, C.-H. Kwak, A.G. Sykes, *Inorg. Chem.* 35 (1996) 173.
- [513] D.M. Sayersell, G.J. Lamprecht, J. Darkwa, A.G. Sykes, *Inorg. Chem.* 35 (1996) 5531.
- [514] T. Tatsumi, M. Taniguchi, S. Yasuda, Y. Ishii, T. Murata, M. Hidai, *Appl. Catal. A* 139 (1996) L5.
- [515] T. Wakabayashi, Y. Ishii, K. Ishikawa, M. Hidai, *Angew. Chem., Int. Ed. Engl.* 35 (1996) 2123.