ELSEVIER

Coordination Chemistry Reviews
164 (1997) 289–344

COORDINATION CHEMISTRY REVIEWS

Molybdenum 1995

Michael J. Morris *

University of Sheffield, Dept. of Chemistry, Sheffield S3 7HF, U.K.

Contents

---

* Corresponding author. E-mail: m.morris@sheffield.ac.uk

PII S0010-8545(97)00033-7

1. Introduction

This review surveys the coordination chemistry of molybdenum reported in 1995, and follows the same format as those which covered 1992, 1993 and 1994 [1–3]. The references have been located by a search of volumes 122, 123 and 124 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 1994 have also been included. The review is restricted to coordination complexes, including carbonyls but excluding organometallic compounds and solid-state chemistry. Synthetic models of Mo centres and clusters in biological systems are covered, but biochemical studies of the enzymes themselves are not. However one particularly notable achievement in this context was the first crystal structure determination of an oxomolybdenum enzyme, specifically the aldehyde oxidoreductase from *Desulfovibrio gigas*, which confirmed the presence of a pterin ligand coordinated through a dithiolene unit [4].

A large review on confacial bioctahedral complexes of molybdenum and tungsten has been published [5]. Review articles have also appeared dealing with recent advances in the chemistry of dinitrogen complexes, in particular the $[Mo(N_2)_2L_4]$ type [6], and the synthesis and reactivity of diazoalkane complexes [7]. Some relevant material can also be found in reviews dealing with the mechanistic and kinetic aspects of metal-dioxygen chemistry [8], with recent developments in early transition metal porphyrin chemistry [9], and with complexes of selenolate and tellurolate ligands [10], of pyridonate ligands [11], of phosphorus hydrazides [12], and of CO_2, CS_2 and COS [13]. An article proposing a new classification system for covalent transition metal compounds is illustrated with examples largely drawn from its author's own extensive work on molybdenum chemistry [14]. The coordination chemistry of V and Mo, especially with ligands of biological relevance such as imidazoles, has been reviewed [15].

The book entitled "Early Transition Metal Clusters with π-Donor Ligands", edited by M.H. Chisholm [16], contains chapters on Mo oxide systems [16a], chalcogenide clusters [16b], alkoxide clusters of Mo and W [16c], and oxo clusters incorporating either phosphate or phosphonate units [16d,16e]. A related review has covered V and Mo oxo clusters incorporating oxygen donor ligands [17], and the catalytic activity of anionic metal oxo clusters has also been surveyed [18]. Chisholm has also reviewed the chemistry of polynuclear metal alkoxides with hydride ligands [19] and co-edited a *Polyhedron* 'Symposium in Print' on alkoxide chemistry which contained a small amount of molybdenum chemistry [20].

The abstracts of the 7th International Conference on Bioinorganic Chemistry, held in Lubeck in September 1995, were published in a special issue of *J. Inorg. Biochem.*; this contained one lecture [21] and a number of abstracts [22] on molybdenum chemistry. A symposium on bioinorganic chemistry contained contributions on molybdenum-sulfur chemistry [23] and molybdenum-copper antagonism [24]. Reviews of the synthesis of the FeMo cofactor of nitrogenase [25] and the organometallic chemistry of nitrogenase [26] have also appeared, as well as one dealing with molybdenum-sulfur chemistry from the perspective of dinitrogen reduction

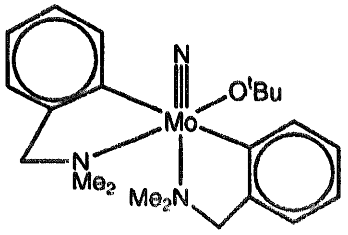
[27]. A review of the deoxygenation of sulfoxides such as dmso also contained some Mo chemistry [28].

An annual review of the coordination chemistry of Cr, Mo and W during 1994 has been published [29], as has a volume of the Gmelin handbook covering compounds of Mo with Se, Te and Po [30].

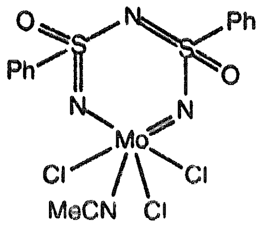
2. Molybdenum(VI)

2.1. *Complexes with nitrogen donor ligands*

Alkylation of the nitrido complex [Mo(N)(O^{t}Bu)$_3$] with mesityl Grignard, MesMgBr, produced [Mo(N)Mes$_3$]; in contrast to the previously reported [Mo(N)(CH$_2^t$Bu)$_3$] which was presumed to be polymeric, the mesityl analogue is monomeric, displaying a pyramidal geometry with a Mo≡N bond length of 1.649(4) Å. The related [Mo(N)(C$_6$H$_4$CH$_2$NMe$_2$)$_2$(O^{t}Bu)] (**1**), which is distorted octahedral, was obtained in a similar fashion [31]. The cyclic complex (**2**) resulted from the reaction of PhS(=O)N(SiMe$_3$)$_2$ with [Mo(=NCl)Cl$_4$] in MeCN [32].



(**1**)

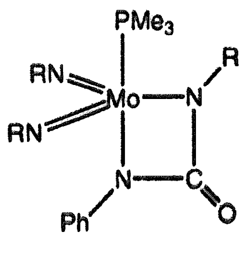


(**2**)

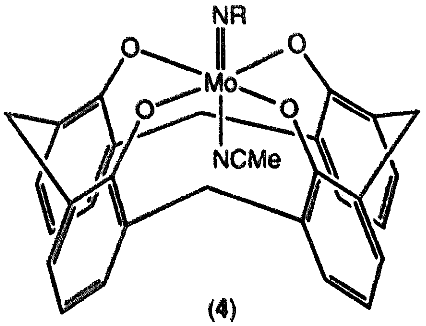
The readily available complexes [Mo(NR)$_2$Cl$_2$(dme)] continue to provide a convenient entry into Mo(VI) imido chemistry. The reaction of [Mo(NR)$_2$Cl$_2$(dme)] (R=2,6-C$_6$H$_3^i$Pr$_2$, ^{t}Bu, or adamantyl) with two equivalents of EtMgBr or PrMgBr in the presence of PMe$_3$ gave [Mo(NR)$_2$(PMe$_3$)$_2$(η-CH$_2$=CHR)]; the alkene ligand can be exchanged for an alkyne [33]. When R=2,6-C$_6$H$_3^i$Pr$_2$, the propene complex loses the alkene ligand spontaneously at room temperature to afford four-coordinate [Mo(NR)$_2$(PMe$_3$)$_2$], which is also accessible by reduction of the starting material with Mg. In the case of R=^{t}Bu, however, such a reduction produced [{Mo(N^{t}Bu)(PMe$_3$)(μ-N^{t}Bu)}$_2$] [34].

Attempts to prepare a complex of the [Mo(NR)$_2$Cl$_2$(dme)] type from the new amine (F$_3$C)$_2$MeCNH$_2$ met with failure, though [MoO(NR)Cl$_2$(py)$_2$] could be made and converted into the mixed imido complex [Mo(NR)(NAr)Cl$_2$(py)$_2$] (Ar=2,6-C$_6$H$_3^i$Pr$_2$) by treatment with ArNH$_2$ [35]. The heterodinuclear complexes [L^{1}L^{2}Rh(η-C$_5$H$_4$CH$_2$C$_5$H$_4$)Mo(NR)$_2$Cl] (L^1=L^2=CO or L^1=P^{i}Pr$_3$, L^2=η-C$_2$Ph$_2$; R=^{t}Bu or Mes) result from the reaction of [Mo(NR)$_2$Cl$_2$(dme)] with the Li or Tl salt of the rhodium-containing cyclopentadiene [36]. The complex $[Mo(N^tBu)_2Cl_2]$ and its Cr analogue have been used as Lewis acid catalysts in the ring-opening of epoxides such as styrene oxide by Me_3SiN_3 [37].

A careful study of the reaction of $[Mo(NR)_2Cl_2(thf)_2]$ ($R=2,6\text{-}C_6H_3{}^iPr_2$) with two equivalents of LiNHR in thf has revealed that the primary kinetic product is the tris-imido anion $[Li(thf)_4][MoCl(NR)_3]$, which, under most conditions, reacts further with the RNH_2 by-product to give the isolated thermodynamic product, $[Mo(NR)_2(NHR)_2]$. The anion was also found to react with MeLi to give $[MoMe(NR)_3]^-$, with cyclopentadiene to give $[CpMo(NR)_2(NHR)]$, and with PMe_3 to give neutral $[Mo(NR)_3(PMe_3)]$ which in turn produced the trigonal bipyramidal cycloaddition product (**3**) on treatment with PhNCO [38,39].



(**3**)



(**4**)

The reaction of $[Mo(NR)_2(O^tBu)_2]$ ($R=2,6\text{-}C_6H_3{}^iPr_2$) with calix-4-arene ($H_4L^1$) in MeCN gave the novel complex $[Mo(NR)(NCMe)(L^1)]$ (**4**) with loss of 2 ^tBuOH and RNH_2; the imido ligand and a coordinated acetonitrile occupy *trans* positions in an octahedral structure, with the four calixarene oxygen atoms in the equatorial plane. In a similar way, reaction with calix-8-arene (H_8L^2) gave $[\{Mo(NR)(NCMe)\}_2(L^2)]$ [40].

The complex $[\{(HBpz_3)Mo(O)(NR)\}_2(\mu\text{-}O)]$ ($R=2,6\text{-}C_6H_3{}^iPr_2$) has been structurally characterized. Its mode of formation involves reaction of the alkylidene complex $[Mo(=CHCMe_2Ph)(NR)(OTf)_2(dme)]$ with $KHBpz_3$, followed by hydrolysis on wet alumina to give $[\{(HBpz_3)Mo(O)(NR)(CH_2CMe_2Ph)\}]$; crystallization of this complex for structure determination also gave a single crystal of the oxo dimer [41]. The synthesis of a range of compounds of the general type $[(HBpz^*_3)MoO_2X]$ where X=Cl, Br, NCS, OMe, OEt, OPh, S^iPr, SCH_2Ph, and SPh, has been described; similar compounds were prepared with the tris(3-isopropylpyrazolyl)borate ligand and with the tris(3,5-dimethyl-1,2,4-triazolyl)borate ligand, and one example with each tridentate ligand was structurally characterized. By tuning the properties of the complex, reduction to a Mo(V) anion, $[(HBpz^*_3)MoO_2X]^-$, can be facilitated, protonation of which occurs at one of the oxo ligands to yield $[(HBpz^*_3)Mo(O)(OH)X]$ [42].

2.2. Complexes with oxygen donor ligands

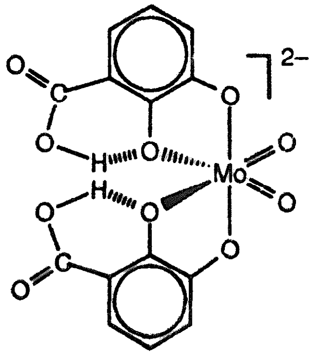
The influence of scalar relativistic effects on ^{17}O NMR chemical shifts in a range of metal tetraoxides, $[MO_4]^{n-}$, including $[MoO_4]^{2-}$, has been probed by ab initio calculations [43]. Molecular mechanics calculations have been employed to predict the geometries of a range of dioxo and di-imido complexes of Cr, Mo, Re and Os with d^0, d^1 and d^2 electron counts [44]. The X-ray structure of molybdate as its protonated tren salt, $[N(CH_2CH_2NH_3)_3]_4[MoO_4]_6.6H_2O$, has been determined and shows a strong hydrogen bonded network linking anions and cations [45]. The effect of resorcinol and pyrogallol on the electrochemical reduction of sulfuric acid solutions of Mo(VI), ultimately to Mo(III), has been investigated [46].

Complex formation between molybdate and mandelate, $PhCH(OH)COO^-$, has been studied in aqueous solution over the pH range 1.5–7.5 by potentiometric, spectrophotometric and enthalpimetric titration; the results indicate the presence of one major species, identified as $[MoO_2(man)_2]^{2-}$, and several minor ones [47]. A similar study of the interaction of molybdate and benzilic acid, $Ph_2C(OH)CO_2H$, over the pH range 2–7 showed the formation of two complexes, one of which was proposed to be a dinuclear 2:2 species; the other was isolated and identified crystallographically as $[NH_4]_2[MoO_2(O_2CCPh_2O)_2] \cdot 2H_2O$ [48]. Complex formation between molybdate and citrate has been studied over the pH range 1.0–9.0, and revealed a more complicated system involving a series of complexes [49]. A 1:1 species was postulated in a spectrophotometric study of complex formation between molybdate and aspartate [50]. The reducing ability of a range of sugars and glycols towards Mo(VI) in aqueous acid has been investigated [51].

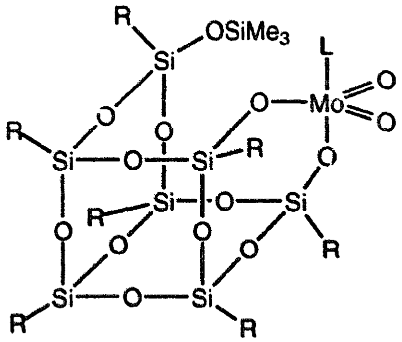
Complexes of the type $[MoO_2L_2]^{2-}$ where $H_2L=2,3$- or 3,4-dihydroxybenzoic acid have been prepared from molybdate and the free acid; the ligand is coordinated as a catecholate, as shown in (**5**) [52]. Complexes containing the protected sugar diacetone glucose (1,2,5,6-diisopropylidene glucose, HL) of the type $[MoOL_4]$ and $[MoO_2L_2]$ can be made from LiL and $[MoOCl_4]$ or $[MoO_2Cl_2]$. The X-ray structure of $[MoO_2L_2]$ shows that the ligands are didentate and utilize one of the ketal groups for coordination; addition of Lewis bases to these complexes gave $[MoOL_4(py)]$ and $[MoO_2L_2(phen)]$ respectively [53]. The incompletely condensed silsesquioxanes $R_7Si_7O_9(OSiMe_3)(OH)_2$ ($R = Cy$, c-C_5H_9), after deprotonation with thallium ethoxide, react with $[MoO_2Cl_2]$ to afford the complexes $[(R_7Si_7O_9(OSiMe_3)MoO_4]$, which form monoadducts (**6**) with Lewis bases such as py or Ph_3PO [54]. Anodic oxidation of rhenium metal in a methanolic solution of $[MoO(OMe)_4]$ in the presence of LiCl electrolyte, followed by hexane extraction, gave the mixed-metal alkoxide $[ReMoO_2(OMe)_7]$, which consists of two $M(O)(OMe)_5$ octahedra sharing a face; the metal sites are disordered in the crystal structure [55]. The hindered rotation of the oximate ligand in the complexes $[MoOF_4(ON{=}CMeR)]^-$, where R = Me or Et, has been studied by multinuclear NMR spectroscopic methods [56].

The chemistry and application of molybdenum peroxo complexes continue to attract attention. The reaction of $Na_2MoO_4.2H_2O$ with H_2O_2 has been studied by ^{95}Mo NMR spectroscopy in D_2O solution, allowing the identification of mono-, di-, tri- and tetra-peroxo complexes; for comparison the spectrum of tetraperoxomolybdate, $Na_2[Mo(O_2)_4]$, was also recorded. The triperoxo species $[MoO(O_2)_3]^{2-}$ was suggested as the source of the singlet oxygen which is generated quantitatively during the reaction [57].

The kinetics of the oxidation of *S*-phenylmercaptoacetic acid by perborate,



(5)



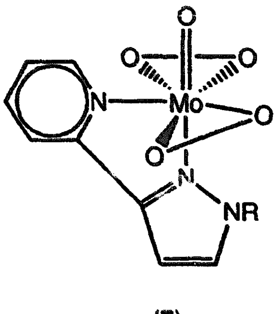
(6)

catalysed by Mo(VI), suggest a dimeric peroxo complex to be the active species [58]. The Mo(VI)-catalysed perborate oxidation of iodide has also been studied [59], and the effects of temperature and pressure on the Mo(VI)-catalysed clock reaction of iodide, bromate and ascorbic acid have been examined [60]. The bromination of phenols and other arenes with a system of KBr in H_2O_2 is catalysed by Mo(VI) species; $[Mo_2O_3(O_2)_4]^{2-}$, which was synthesized independently, was proposed to be the most likely active ingredient [61]. A related study compared the performance of sodium tungstate, ammonium molybdate and ammonium vanadate in a similar reaction [62]. The oxidation of NO in aqueous solution by complexes of the type $K_2[MoO(O_2)_2(L)]$ where L is a dicarboxylate such as glycerate, malate or citrate, has been investigated [63].

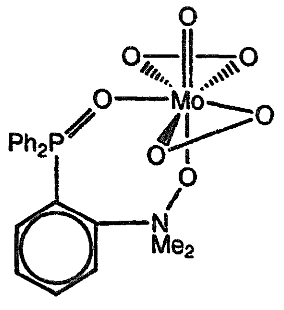
The reaction of $[MoO_2(Mes)_2]$ with $[Pt(O_2)(PPh_3)_2]$ causes transfer of the peroxo ligand to Mo and formation of a species formulated as $[PPh_4]_2[Mo_2O_6(O_2)]$, which epoxidizes TCNE at a rate approximately 10^4 times greater than conventional $[MoO(O_2)_2(hmpa)]$ [64]. The reaction of $[MoO_2(Mes)_2]$ with isonitriles RNC ($R = {}^tBu$, Cy, $PhCH_2$) produced three compounds; two of these were organic, $Mes_2C{=}NR$ and MesCONHR, but the third was the unusual Mo(V) dimer $[\{MoO(Mes)(\eta^2\text{-}CMes{=}NR)\}_2(\mu\text{-}O)]$, the first oxo-iminoacyl complex [65]. The new Mo(VI) alkyls $[MoO_2R_2(bpy)]$ where $R = CH_2CH_2Ph$ or $CH_2C_6H_4$-4-Me have also been reported [66].

Molybdenum peroxo complexes with substituted 3-pyrazolylpyridine ligands such as (7) have been prepared. In some cases, alkene functionalities were incorporated ($R = CH_2CH{=}CH_2$ or $CH_2CH_2CH{=}CH_2$); an X-ray structure determination of the first of these showed that the pyridine ligand was in the equatorial plane and the pyrazole axial, though a second isomer (presumably with the coordination interchanged) was present in solution [67]. In another study, the complex with $R = C_{18}H_{37}$ was prepared for increased solubility and used to epoxidize alkenes in hydrocarbon solution [68]. Oxidation of 2-diphenylphosphinoyl-*N*,*N*-dimethylaniline with H_2O_2 in the presence of $[MoO(O_2)_2(H_2O)_x]$ occurred with coordination of the resulting *N*-oxide ligand to give (8) [69]. The complex $[MoO(O_2)_2(L)(H_2O)]$ where L = urea has also been prepared, whereas *N*-acetyl-*N*-methyl urea acted as a didentate ligand in $[MoO(O_2)_2(L)]$ [70]. The monoperoxo species

$[MoO(O_2)L_2(L')]$ where HL = phthalimide or succinimide and L' = bpy or phen have also been reported [71].

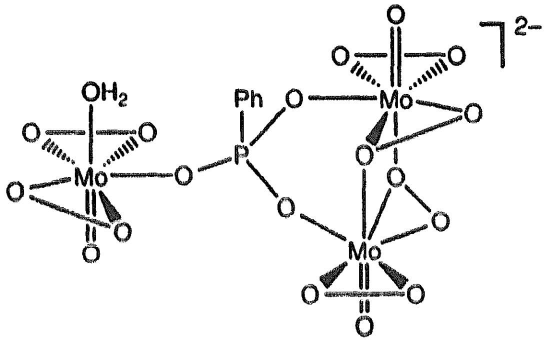


(7)



(8)

The catalytic oxidation of amines to amine oxides using H_2O_2 and a catalyst of either $[XO_4\{MO(O_2)_2\}_4]^{3-}$ (X = P, As; M = Mo, W) or $[M_2O_3(O_2)_4]^{2-}$ has been explored [72]. The same group have reported the synthesis of $[NMe_4]_2[(RPO_3)\{MoO(O_2)_2\}_2\{MoO(O_2)_2(H_2O)\}]$ (R = Ph, Me, Et, Bu, ^tBu) from $MoO_3 \cdot H_2O$, H_2O_2, $RPO(OH)_2$ and NMe_4Cl in a water-ethanol solvent mixture. The structure of the complex with R = Ph, determined crystallographically and depicted as (**9**), reveals the presence of two η^2, η^1-bridging peroxy groups [73].

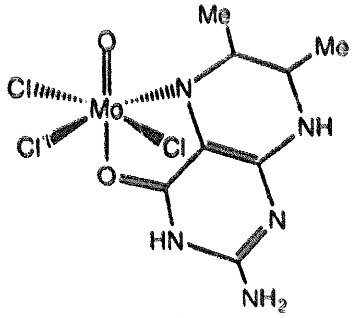


(9)

Three different types of calculation have been employed in a theoretical study of model oxygen atom transfer reactions from hypothetical species such as $H_4Mo{=}O$, $H_2Mo{=}O$ and $MoO_2(NH_3)_2(SH)_2$ to phosphines [74]. The reaction of $[PPh_4]_2[MoO_2(NCS)_4]$ with 4,4'-$^tBu_2$bpy afforded neutral $[MoO_2(NCS)_2(^tBu_2bpy)]$, which proved to have exceptional O-atom transfer properties: not only will it oxidize phosphines efficiently, but will also oxidize arylalkanes, for example tetralin to tetralone, either thermally or photochemically. The related complex $[MoO_2Br_2(^tBu_2bpy)]$ also proved effective [75].

The catalytic reduction of nitrobenzene to aniline by PhSH in the presence of Amberlite resin as a proton source has been achieved with a system consisting of the thiobenzilate complex $[MoO_2(O_2CCPh_2S)_2]^{2-}$ intercalated into a Zn(II)–Al(III) layered double hydroxide in order to stop conproportionation of the Mo(VI)–Mo(IV) catalyst system to inactive Mo(V) species. The reaction is presumed to proceed by reduction to the Mo(IV) species $[MoO_2(O_2CCPh_2S)_2]^{2-}$ with concomitant formation of PhSSPh, followed by oxygen atom transfer from $PhNO_2$ to the Mo(IV) centre to give PhNO, which is then reduced to aniline via PhNHOH [76]. In a similar way, intercalation allows catalytic oxidation of thiols to disulfides by O_2, whereas this reaction only occurs stoichiometrically in free solution [77]. The electrochemical reduction of nitrite to ammonium ions in the presence of $[MoO_2(O_2CCPh_2S)_2]^{2-}$ has been observed both when the complex is immobilized on a membrane and in solution [78]. A theoretical study of the complex $[MoO_2(O_2CCH_2S)_2]^{2-}$ and the related Mo(V) species $[MoO(O_2CCH_2S)_2]^-$ has led to geometry optimization and comparison with the published crystal structure of the thiobenzilate [79]. The crystal structure of $[NHEt_3]_2[MoO_2(O_2CC_6H_4S)_2]$, formed from $[MoO_2(acac)_2]$ and 2-mercaptobenzoic acid, has been determined [80], as has that of the analogous hydrazide species $[NHEt_3]_2[MoO(NNPh_2)(O_2CC_6H_4S)_2]$ made from $[MoO(NNPh_2)(acac)_2]$ [81].

Two groups have synthesized complexes of dihydropterin ligands by reacting precursors such as $[MoO_2Cl_2]$ and $[MoO_2(acac)_2]$ with tetrahydropterin hydrochloride. A typical example of a $[MoOCl_3(pterin)]$ complex is shown as (**10**), and it provides a functional as well as structural model for the dmso reductase enzyme in that it can reduce dmso to dimethyl sulfide. The dinuclear species $[Mo_2O_4Cl_2(pterin)_2]\cdot 4dmf$ was also prepared and structurally characterized; in methanol it dissociates into mononuclear units. Because of the quinonoid nature of the ligand, the exact oxidation state of the Mo atom is hard to define; however Hückel molecular orbital calculations suggest an oxidation state of between 5 and 6 for the metal, indicating that a Mo(VI)-H_4L description is perhaps more valid than the Mo(IV)-H_2L picture previously favoured. This in turn implies that the synthetic reaction does not involve a redox process [82,83].



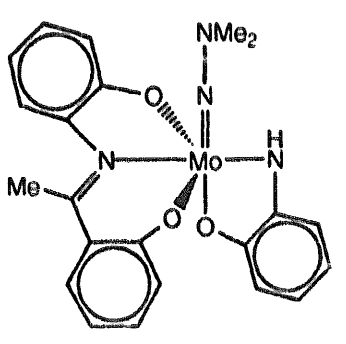
(**10**)

The electrochemistry of $[MoO_2Cl_2]$ at a Pt electrode has been studied, and displays a one-electron reduction to a radical anion which reacts with further Mo(VI) complex to give a mixed Mo(VI)–Mo(V) species, which itself can be either oxidized or reduced. Some evidence of partial dissociation to $[MoO_2]^{2+}$, $[MoO_2Cl_4]^{2-}$ and $[MoO_2Cl_3]^-$ ions was observed too [84]. The synthesis of $[MoO_2Cl_2(dmso)_2]$ and its oxygen atom transfer reaction with PPh_3 has been developed as a small-scale teaching experiment [85]. The complex $[MoO_2Cl_2L_2]$ where L = bis(1-phenyltetrazolin-5-yl) disulfide has been reported [86].

Complexes of the type [$MoO_2Cl_2(L)$] where L is a β-ketophosphonate derived from camphor have been prepared and tested as catalysts for alkene epoxidation with ^tBuOOH. Although very fast initial rates are observed (400 turnovers per minute), these slow as the ligand is replaced by diols from the reaction mixture. The fast phase can be extended by the presence of molecular sieves, and this allowed the epoxidation of styrene with 98% conversion and 94% selectivity [87]. Molybdate units have also been anchored to polymer supports through Schiff's base linkages and used as alkene epoxidation catalysts [88,89]. Attachment of Mo(VI) species to polystyrene resins functionalized with imidazole or pyridine units led to catalysts which were particularly active for cyclohexene epoxidation with ^tBuOOH and did not require pre-treatment with the oxidant [90]. The same species immobilized on polybenzimidazole resins also gave good activity, and the catalysts could be recycled with no loss of metal content, though with some loss of activity [91].

The preparation of the useful starting material [$MoO_2(acac)_2$] has been adapted as a microscale laboratory experiment [92]. Numerous complexes of the MoO_2^{2+} unit containing Schiff's base ligands have been prepared, mostly from [$MoO_2(acac)_2$]. For uninegative ligands (from HL), they usually take the form [MoO_2L_2] or [$Mo_2O_5L_2$], and for dianionic ones (from H_2L) they tend to be [$MoO_2L(S)$] where S = solvent. Tetradentate ligands H_4L form dinuclear complexes. Further details of some of the compounds prepared are given in Table 1.

Full details have appeared of the complex [$MoO_2(L)(MeOH)$], where H_2L is the Schiff's base derived from 5-substituted salicylaldehydes and the amines $H_2NCR(CH_2OH)_2$ (R = Me, Et). One of these reacted with cupric acetate in MeOH/MeCN to give a complex formulated as [$Cu_2Mo_2O_4(L)_2(OMe)_2$], which on heating in MeCN with bpy produced [$CuMo_3O_8(L)_2(bpy)_2$] containing a $Mo_3O_8^{2-}$ unit bound to a $Cu(bpy)_2^{2+}$ fragment [104]. The Schiff's base complexes [$MoO_2(OC_6H_4N{=}CRC_6H_4O)(hmpa)$] (R = H, Me, Ph) have been treated with substituted hydrazines. When R = Me, reaction with Me_2NNH_2 unexpectedly produced [$Mo(NNMe_2)(OC_6H_4N{=}CMeC_6H_4O)(OC_6H_4NH)$] (11) which presumably arose through degradation of the ligand; by using a mixture of the hydrazine and 2-aminophenol, analogous complexes could be prepared for a range of hydrazines [105].



(11)

Complexes of the type [$MoO_2(L)$] have also been made from H_2L = 1-(2-hydroxyphenylazo)-2-hydroxynapthalene; they coordinate Lewis bases

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

Carbonyl compound	Amine	Complex type	Reference
Salicylaldehyde	2-aminothiophenol	$[MoO_2(L)(dmso)]$	[93]
Salicylaldehyde	*p*-anisidine *p*-toluidine *m*-phenetidine *o, m, p*-phenylene diamine	$[MoO_2L_2][MoO_2(H_2L)]$ or $[Mo_2O_4(L)(OMe)_2]$	[94]
Salicylaldehyde Benzoylacetone	Benzoylhydrazide Thiobenzoylhydrazide 2-aminophenol Benzoylhydrazide	$[MoO_2(L)(MeOH)]$ $[MoO_2(L)(O{=}PPh_3)]$	[95]
Salicylaldehyde	Isonicotinic hydrazide	$[MoO_2(L)(MeOH)]$	[96]
Benzoylacetone	Naphthoylhydrazide	$[MoO_2(L)(MeOH)]$ $[MoO_2(L)(dmso)]$ $[MoO_2(L)(py)]$ etc.	[97]
2-acetylthiophene 2-acetylpyridine 2-formylthiophene 2-formylpyridine	Semicarbazide Thiosemicarbazide 2-aminothiophenol	$[MoO_2(L)]$	[98–100]
4-COR-3-Me-1-Ph-5-pyrazolin-5-one (R = Me, Et, Ph)	4-aminoantipyrine	$[MoO_2L_2]$	[101]
Methylenebis(salicylaldehyde) Dithiobis(salicylaldehyde)	Benzoylhydrazide *p*-nitrobenzoylhydrazide	$[\{MoO_2\}_2L]_n$ $[\{MoO_2(py)\}_2L]$ $[\{MoO_2(HIm)\}_2L]$	[102]
Methylenebis(salicylaldehyde) Dithiobis(salicylaldehyde)	*S*-methyldithiocarbazate *S*-benzyldithiocarbazate	$[\{MoO_2\}_2L]_n$	[103]

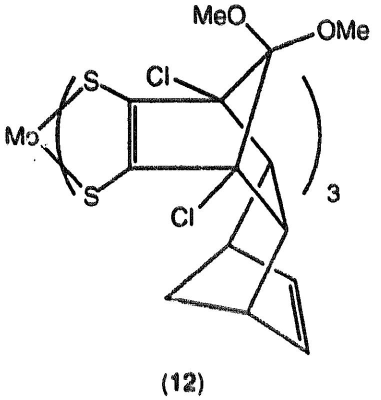
such as dmso, dmf, hmpa or 4-picoline [106]. The complex $[MoO_2L_2]$ where HL = benzoyl *m*-nitroacetanilide has also been reported [107]. Whereas the macrocycle tmtaa (H_2tmtaa = 5,7,12,14-tetramethyldibenzo-1,4,8,11-tetraazacyclotetradecine) reacted with $[Mo(CO)_4(pip)_2]$ to give the known $[Mo(CO)_4(H_2L)]$, which contains a rearranged didentate ligand, the related 6,13-di-*p*-tolyltetraazaannulene reacted to give $[MoO_2(L)]$ after oxidation during crystallization [108].

2.3. *Complexes with sulfur donor ligands*

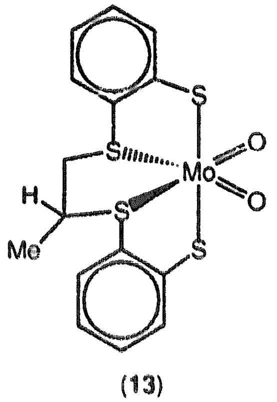
The use of $[PhCH_2NEt_3]_2[MoS_4]$ as a reagent in organic chemistry is a growing area. The reductive dimerization of RSCN in the presence of $[MoS_4]^{2-}$ affords RSSR in around 90% yield [109]. Deoxygenation of nitrones and *N*-oxides to the corresponding imines or amines also occurred in good yield, whereas sulfoxides and azoxybenzenes were unaffected [110]. The conversion of chloroiminium salts, obtained from the reaction of amides or lactams with oxaloyl chloride or $POCl_3$, into the corresponding thioamides and thiolactams has also been described [111].

The preparation of nickel salts with tetrathiomolybdate anions has been reported, including [Ni(en)$_3$][MoS$_4$], [Ni(dien)$_2$][MoS$_4$], and [Ni(phen)$_2$][MoS$_4$] [112]. The thermal decomposition of [NH$_4$]$_2$[MoS$_4$], as well as [NH$_4$]$_2$[Mo$_2$(S$_2$)$_6$] and [NH$_4$]$_2$[Mo$_3$S$_{13}$], has been studied by thermogravimetry; in the first two cases, the ultimate product is MoS$_3$ [113]. A method for the determination of Mo in aqueous solutions of [MoS$_4$]$^{2-}$ by atomic absorption spectroscopy has been developed [114]. The deposition of [MoS$_4$]$^{2-}$ onto the Cu$_2$O layer present on a copper surface has been shown to lead to the formation of films which contain Mo–S–Cu bonds, as demonstrated by a variety of techniques including FTIR, XPS and AES [115], [116].

Degradation of unsymmetrical 1,3-dithiol-2-ones with NaOEt followed by coordination to Mo with Na$_2$MoO$_4$.2H$_2$O afforded the tris-dithiolene species [Mo(SCR^1=CR^{2}S)$_3$] (R^1=H, R^2=Ph, *p*-tol, *p*-C$_6$H$_4$OMe; R^1=Ph, R^2=Ph, *p*-C$_6$H$_4$OMe); the products undergo two quasi-reversible electrochemical reductions [117]. New dithiolene ligands have also been made from the Diels–Alder adduct of 2,3-bis(benzylthio)-1,4-dichloro-5,5-dimethoxycyclopentadiene with norbornadiene, and complexed to Mo(VI) as (**12**) [118]. The new tripodal ligand 1,3,5-C$_6$H$_3$-{NHCOC$_6$H$_3$(SH)$_2$}$_3$ has been prepared; it reacts with [MoO$_2$(acac)$_2$] to afford the encapsulated tris-dithiolene complex [MoL] [119].



(**12**)



(**13**)

The resonance Raman spectra of [PPh$_4$]$_2$[MoO$_2$(SC$_6$H$_4$)$_2$], its SC$_6$H$_3$MeS analogue, and [PPh$_4$]$_2$[MoO$_2$(mnt)$_2$]·2MeOH [mnt = S$_2$C$_2$(CN)$_2^{2-}$] have been recorded; two bands are observed for symmetric and asymmetric stretching of the MoO$_2$ unit, at 885–858 cm^{-1} and 851–835 cm^{-1} respectively; some vibronic coupling with an excited state was observed in the symmetric portion. The corresponding Mo(IV) complexes [MoO(SC$_6$H$_4$S)$_2$]$^{2-}$ and [MoO(mnt)$_2$]$^{2-}$ were also studied [120]. Sellmann has reported the preparation of substituted S4 ligands by the template alkylation of [Ni(SC$_6$H$_4$S)$_2$]$^{2-}$ with BrCHRCH$_2$Br; the ligand with R=Me was complexed to [MoO$_2$(acac)$_2$] to yield [MoO$_2$(MeS4)] (**13**) [121].

The ^{95}Mo NMR chemical shifts of [MoO$_2$(S$_2$CNR$_2$)$_2$] (R=Me, Et, ^{i}Pr, ^{i}Bu, Ph, CH$_2$Ph) vary between 151 and 216 ppm, and show a good correlation with the rate of oxygen atom transfer to PPh$_3$ [122]. The convenient preparation of [MoO$_2$(dtc)$_2$] (dtc=S$_2$CNEt$_2$), and from it [MoO(dtc)$_2$], [Mo$_2$O$_3$(dtc)$_4$], [MoOCl$_2$(dtc)$_2$] and [MoO(S$_2$)(dtc)$_2$], has been adapted as an undergraduate teaching experiment [123]. The reactions of chlorosilanes with a variety of dioxo molybdenum complexes have been explored. With Me$_3$SiCl,

$[MoO_2(dtc)_2]$ (dtc$=S_2CNEt_2$) afforded $[MoOCl_2(dtc)_2]$ and $O(SiMe_3)_2$, but with $^tBuSiMe_2Cl$ the reaction was slower, enabling the isolation of a new species, $[(dtc)_2MoO(Cl)(\mu\text{-}O)MoO(Cl)(dtc)_2]$ [124].

3. Molybdenum(V)

3.1. Complexes with halide and cyanide ligands

A procedure for the solid state synthesis of MoS_2 from $MoCl_5$ and Na_2S has been published [125] and the metathesis reaction between $MoCl_5$ and hydrazine in MeCN or thf solution has been explored as a possible route to the nitride Mo_2N. The same paper also contained details of the interaction of $MoCl_5$ with these solvents [126]. The formation of complexes on dissolution of $MoCl_5$ or $[MoOCl_4]$ in dmf has been studied by ESR and IR spectroscopic methods [127]. The polymerization of thioalkynes $PhSC\equiv CR$ (R = alkyl) by a catalyst system of $MoCl_5$ and Ph_3SiH has been reported [128], and the reductive cyclization of 2-nitrobenzaldehyde or 2-nitrophenyl ketones with formamide to give quinazaline derivatives has been achieved with $MoCl_5$ and $[PdCl_2(PPh_3)_2]$ under an atmosphere of CO [129].

The compound $[Cl_2(O)Mo(\mu\text{-}OEt)_2(\mu\text{-}EtOH)Mo(O)Cl_2]$, formed from $MoCl_5$ and EtOH in chloroform, reacted with SbF_3 to give a low yield of $[Mo_8O_8Cl_6(\mu_3\text{-}O)_4(OH)_2(\mu\text{-}OH)_4(\mu\text{-}OEt)_4(EtOH)_4]$, which contains two layers of Mo_4 units in a structure reminiscent of that of rutile-like MoO_2 [130]. The reaction of $MoCl_5$ with two equivalents of phenols ArOH ($Ar = C_6H_4\text{-}4\text{-}R$ where R = ^tBu or OMe, and $C_6H_2\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}OMe$) in CCl_4 affords dimeric complexes $[\{MoCl_3(OAr)_2\}_2]$ [131].

The salts $[Mg(thf)_6][MoOCl_5]$ and $[Mg_2(\mu\text{-}Cl)_3(thf)_6][MoOCl_4(thf)]$ have been studied electrochemically [132]. Salts of $[MoOCl_5]^{2-}$ have also been prepared with diprotonated 15-crown-5 and Kryptofix-22 as counterions [133]. The reaction of MoO_3 with 2-(2-pyridyl)benzothiazole and HBr afforded initially $[H_2L][MoOBr_5]$, which was then converted into $[MoOBr_3(L)]$, $[Mo_2O_3Br_4(L)_2]$, and $[Mo_2O_4Br_2(L)_2]$ [134].

The reaction of elemental selenium with $[MoOCl_4]$ in a sealed tube at 190°C gave crystals of $[Se_4\{MoOCl_4\}_2]$ which consists of planar Se_4^{2+} cations and dimeric $[\{Mo_2OCl_3(\mu\text{-}Cl)\}_2]^{2-}$ anions [135]. The crystal structure of $[PPN][MoOCl_4]$ has been determined at low temperature [136] and the salt [BEDT-TTF]$[MoOCl_4(H_2O)]$ has also been structurally characterized, showing chains of hydrogen-bonded anions between ribbons of edge-linked TTF molecules [137].

Attempts to prepare $[MoBr_2(CO)_2(PCy_3)_2]$ led instead to the isolation of $[HPCy_3][MoOBr_4(L)]$ where $L = O{=}PCy_3$ or H_2O; the phosphine oxide complex was absorbed into sodium montmorillonite with elimination of NaBr, leading to a new material with expanded layers. The Mo(VI) complex $[MoO_2Br_2(O{=}PCy_3)_2]$ was also obtained and crystallographically characterized [138]. Air oxidation of $[PPh_4]_3[Mo_3I_{12}]$ afforded $[PPh_4][MoOI_4]$, the first time that a base-free version of this complex had been obtained and structurally characterized, thus completing the series of $[MoOX_4]^-$ compounds [139]. Oxidation of the alkylidyne complex $[LMo(\equiv Ctol)(CO)_2]$, where L is the tridentate Kläui ligand $[CpCo\{P(O)(O^iPr)_2\}_3]^-$, with elemental dibromine produced the Mo(V) species $[LMoBr_4]$ [140].

The kinetics of the oxidation of $[RuO_4]^{2-}$ by $[Mo(CN)_8]^{3-}$ were examined as part of a study to find the self-exchange rate for the $[RuO_4]^{2-}/[RuO_4]^-$ couple [141]. A stopped-flow kinetic study of the oxidation of the Re(IV) dimer $[(ox)_2Re(\mu\text{-}O)_2Re(ox)_2]^{4-}$ to Re(VII) species by a variety of reagents, including $[Mo(CN)_8]^{3-}$, has also been reported [142].

3.2. Complexes with nitrogen donor ligands

The nitrido porphyrin complex [Mo(N)(TPP)] underwent alkylation with MeI to afford the imido derivative $[Mo(=NMe)(TPP)(H_2O)][I_3]$ [143]. It also forms adducts with BF_3 and with $M(CO)_5$ fragments (M = Mo, W), and reacts with sulfur to give the thionitrosyl complex [(TPP)Mo(NS)]. Under more forcing conditions it will also form an adduct with Lewis bases such as PBu_3 [144]. Efficient, irreversible oxygen atom transfer occurred between $[(TPP)MoO(\mu\text{-}O)MoO(TPP)]$ and [Cr(TPP)] to afford [MoO(TPP)] and [CrO(TPP)], or if excess chromium porphyrin is present, $[(TPP)Cr(\mu\text{-}O)Cr(TPP)]$ [145]. The electron spin lattice relaxation rates of [MoO(X)(TTP)] (X = Cl, OH, OEt) have been measured at variable temperatures in a study of the temperature and orientation dependence of the ESR spectrum [146]. The complex [MoO(Cl)(por)] where H_2por is tetrakis(4-dodecylphenyl)porphyrin, has been prepared and its liquid crystal properties investigated [147]. The kinetics of the reduction of [MoO(Cl)(TPP)] to [MoO(TPP)] by superoxide have been investigated in dmso and a CH_2Cl_2/dmso mixture, with a series of intermediates being postulated [148], [149], and the kinetics of the reduction and demetalation of [MoO(OH)(por)], where H_2por = tetrakis(*p*-sulfonatophenyl)porphyrin, by ascorbic acid have also been studied [150].

A number of papers deal with complexes of the $HBpz_3^*$ (i.e. Tp*) ligand, denoted for this paragraph by L. The preparation of $[LMoOX_2]$ (X = F, Cl, Br) by treatment of $[LMoO(OMe)_2]$ with HX has been described, together with their electrochemical and redox properties [151]. Refluxing the complex $[LMoO(OCH_2CH_2O)]$ in toluene with various catechols led to complexes [LMoO(cat)], which were characterized by their ESR spectra and electrochemical properties (all show a quasi-reversible one-electron reduction). The HOMO in these complexes is the metal d_{xy} orbital which does not interact to any great extent with the catecholate ligand; consequently the ESR spectra are hardly affected by substituents on the catecholate ligand, whereas the redox potential is affected [152]. Further details have appeared of the complexes $[LMoO\{cat\text{-}PFe(B)_2\}]Cl$ (B = HIm, *N*-MeIm, dmap) in which the catecholate ligand is one substituent of a tetratolyl porphyrin bound to an iron centre. The interaction between the two paramagnetic centres was studied, as was the hindered rotation of one of the axial ligands on iron caused by the presence of the Mo substituent [153].

The interaction between the Mo(V) centre and a phosphorus nucleus has been studied by ESR spectroscopy in the diphenylphosphate-substituted complex $[LMoO\{O_2C_6H_3\text{-3-OPO(OPh)}_2\}]$ and its 4-isomer, and is detectable up to distances of 7–8 Å [154].

A range of related complexes have been prepared for the analogous uncharged ligand $CHpz^*_3$. Treatment of $MoCl_5$ with the ligand in thf gave $[(CHpz^*_3)MoOCl_2][Cl]$, which on standing converted into $[(CHpz^*_3)MoO(\mu\text{-}O)_2MoOCl_2]$. Compounds of the type $[(CHpz^*_3)Mo(cat)]^+$ and $[(CHpz^*_3)Mo(SCH_2CH_2S)]^+$ were also produced [155].

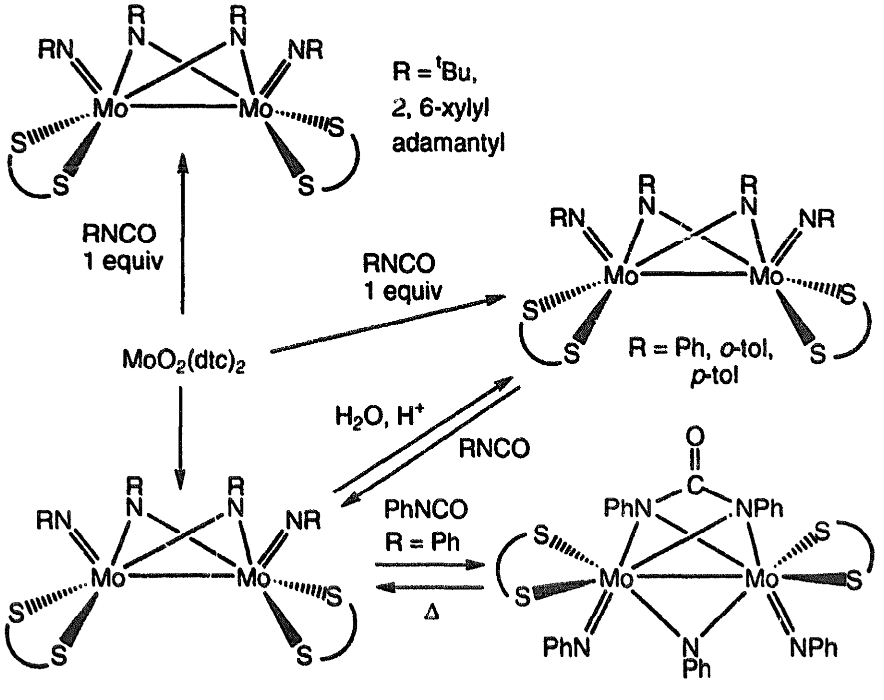
3.3. *Complexes with oxygen or sulfur donor ligands*

A review of the synthesis, structure and stereochemistry of dinuclear Mo(V) and W(V) complexes of the type $[M_2O_2(\mu\text{-}E)(\mu\text{-}E')(L)]^n$ where E, E′=O or S, and L= edta or pdta (n=2−) or *N,N,N′,N′*-tetrakis(2-pyridylmethyl) ethylene diamine (n= 2+) has been published [156]. The latter, and its propylene diamine analogue, have been made by treating $[MoOCl_5]^{2-}$ with L and were crystallized either as $[MoOCl_4]^-$ or perchlorate salts respectively [157]. The crystal structure of $Na_2[Mo_2O_4(edta)]\cdot 4H_2O$ has been determined [158], and this compound has been identified as the product of photolysis of solutions of molybdate and H_4edta [159].

The species $[N_2H_5]_2[Mo_2O_4(OH)_4(H_2O)_2]$, made by reducing molybdate with hydrazine hydrate, has been used as the starting material for the preparation of dinuclear complexes with carboxylate ligands such as oxalate [160]. Similarly, complexes of the type $[Mo_2O_4(H_2O)_2(L)]$ were produced by the reaction of dicarboxylate ligands $H_2L=RCH(SCH_2CO_2H)_2$ where R=Pr, Ph, C_5H_{11} etc. with $[Mo_2O_4(H_2O)_6]^{2+}$ [161]. This same aqua complex catalyses the oxidation of bromide by chlorate; a kinetic study proposed a rate-determining step involving an intermediate such as $[Mo_2O_4(H_2O)(Br)(OH)]$ [162]. Extraction of $[Mo_2O_4]^{2+}$ with 2-methyl-5-octyloxymethyl-8-quinolinol (HL) occurs as a complex $[Mo_2O_4L_2]$ [163].

Tridentate Schiff's base ligand derived from salicylaldehyde and 2-aminophenol (H_2L, and various substituted analogues) have been incorporated into Mo(V) complexes both as mononuclear systems of the type $[MoOCl_2(L)]^-$ [164] and dinuclear ones of the type $[Mo_2OL_4]$ and $[Mo_2O_3L_2(H_2O)_2]$; similar compounds were prepared from the condensation product of salicylaldehyde with 2-aminopyridine [165]. Complexes $[MoO(NCS)_2(L)]^-$ (from H_2L) and $[MoOCl_2L]$ (from HL) were also prepared from the related Schiff's base ligands *S*-alkyl-3-(2-hydroxyphenyl)methylenedithiocarbazate and *S*-alkyl-3-(2-pyridyl)methylenedithiocarbazaterespectively [166,167]. Air oxidation of $[MoCl_2(CO)_3(PPh_2C_{10}H_{15}NH)]$ afforded the Mo(V) complex $[\{MoOCl_2(O{=}PPh_2C_{10}H_{15}NH)\}_2(\mu\text{-}O)]$ which was structurally characterized; the ligand is derived from camphor [168].

Heating $[MoO_2(dtc)_2]$ ($dtc=S_2CNEt_2$) or $[Mo_2O_3(\mu\text{-}E)(dtc)_2]$ (E=O, S) with isocyanates RNCO gave a range of complexes depending on the identity of R and the reagent ratio; a summary of the transformations is shown in Scheme 1 [169]. In the case of R=*o*-tol, the tetraimido complex $[Mo_2(NR)_4(dtc)_2]$ was formed, which in solution exists as a mixture of rotamers due to hindered rotation around the *N*-aryl bond [170].



Scheme 1.

The dinuclear imido complex $[Mo_2(NAr)_2\{S_2P(OEt)_2\}_2(\mu\text{-}S)_2(\mu\text{-}O_2CMe)]^-$ ($R = 2,6\text{-}C_6H_3Me_2$) reacts with halogens to give complexes with bridging halosulfide ligands, either μ-SX or $\mu\text{-}SX_3$, which are polymeric in the solid state (through charge transfer interactions with neighbouring μ-S) but which depolymerize in solution. Photolysis of the $\mu\text{-}SI_3$ complex results in the formation of disulfide bridges between the dinuclear units [171]. The same starting complex reacts with NO^+ (or NOCl, NO_2^- or organic nitrites) at the bridging sulfido ligand to give products with a μ-SNO group. These in turn are very reactive and undergo nitrosyl migration processes, leading to oxo-for-imido exchange and ultimately decomposition [172].

The mononuclear Mo(V) species $[NEt_4][MoO\{SC_6H_3(SiPh_3)S\}_2]$ has been prepared from the bulky dithiolate ligand 3-triphenylsilylbenzenedithiol; it can be oxidized to the dinuclear Mo(VI) compound $[\{MoO_2(SC_6H_3(SiPh_3)S)\}_2(\mu\text{-}O)]^{2-}$ [173]. The complex $[Mo(SC_6H_4O)_3]^-$, derived from *o*-hydroxythiophenol, has been prepared, as well as adducts with molybdenum carbonyl fragments such as $[Mo_2(CO)_3(SC_6H_4O)_3]^{2-}$ and $[Mo_3(CO)_7(SC_6H_4O)_3]^{2-}$ [174]. The dinuclear species $[Mo_2O_3(\mu\text{-}S)L_2]^{2-}$ where H_2L = 2-mercaptobenzoic acid has also been synthesized [175].

The reaction of $[Mo(dtc)_4]$ (dtc = S_2CNMe_2 or S_2CNEt_2) with TCNQ gave charge transfer complexes, firstly $[Mo(dtc)_4][TCNQ]$ and then $[Mo(dtc)_4][TCNQ]_2$. A similar complex was obtained from TCNE in an inert atmosphere, but in air $[Mo(dtc)_4][(NC)_2C\text{–}C(CN)\text{–}C(CN)_2]$ was produced [176]. The IR and Raman spectra of the TCNQ adducts have been recorded in order to probe the charge state of the TCNQ [177]. The UV-visible spectra of $[Mo_2S_4(dtp)_4]$ and the cluster $[Mo_3S_4(dtp)_4]\cdot py$ $[dtp = S_2P(OEt)_2]$ have been recorded [178]. *Ab initio* calculations have also been carried out on the dinuclear species [179].

The kinetics of the oxygen atom transfer reaction between $[Mo_2O_3I_2(dtc)_2(thf)_2]$ with pyridine-*N*-oxide, giving $[MoO_2(I)(dtc)]$, have been studied. Evidence of a dinuclear complex with the pyridine oxide which breaks down into mononuclear units was found, and results with substituted pyridines suggested that the strength of the N–O bond may determine the rate [180].

4. Molybdenum(IV)

4.1. *Complexes with halide and cyanide ligands*

The thioether complexes $[MCl_4(SEt_2)_2]$ (M = Mo, W) have been synthesized; their X-ray structures both confirmed *trans* geometries [181].

A ^{17}O NMR spectroscopic study has compared the rate of oxygen exchange reactions in $[MO_2(CN)_4]^{4-}$ (M = Mo, W) and $[MO_2(CN)_4]^{3-}$ (M = Tc, Re). The molybdenum complex is two orders of magnitude more reactive than the tungsten one. The rate law is a two-term expression involving both mono- and diprotonated species [182]. The reaction of $[MoO(H_2O)(CN)_4]^{4-}$ (or its W analogue) with 2-acetylpyridine in the presence of $MeNH_2$ or $BuNH_2$ afforded $[MoO(CN)_3(L_2)]^-$ where L_2 is the Schiff base condensation product of the acetylpyridine with the amine [183]. A similar reaction in the presence of en gave $[MoO(CN)_2(L_4)]\cdot H_2O$ containing a tetradentate Schiff base ligand; the X-ray structure showed a pentagonal bipyramidal coordination in which the two cyanide ligands occupy the axial sites [184,185]. Further investigations of the photochemistry of $[Mo(CN)_8]^{4-}$ in acid media containing bpy or phen (L) have ruled out the formation of $[Mo(CN)_6(L)]^{2-}$; instead $[MoO(CN)_3(L)]^-$ is formed, and a new product, $[MoO(CN)_2(L)_2]$, has been detected [186]. The photoproducts of $[Mo(CN)_8]^{4-}$ with 1,2,3-benzotriazole have been isolated as 8-hydroxyquinoline adducts [187]. Coordination polymers $[M(CN)_8(SnMe_3)_4]$ (M = Mo, W) have been obtained from $[M(CN)_8]^{4-}$ and Me_3SnCl. Both were structurally characterized, revealing that the coordination geometry around the metal has changed from dodecahedral to square antiprismatic [188].

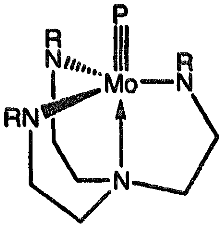
4.2. *Complexes with nitrogen and phosphorus donor ligands*

The complex $[(TTP)Mo(=S)]$ has been prepared by reaction of $[(TTP)Mo(\eta\text{-}C_2Ph_2)]$ with elemental sulfur or $[Cp_2TiS_5]$, or by treatment of $[(TTP)MoCl_2]$ with Li_2S. The selenium analogue could also be obtained by using $[(TTP)Sn(=Se)]$ as a selenium transfer reagent. Both the sulfide and selenide are reduced to $[(TTP)(Mo(PPh_3)_2]$ by PPh_3 [189].

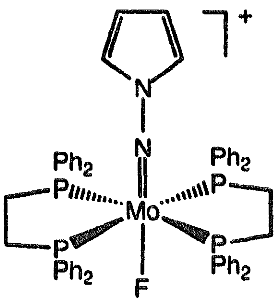
The reaction of $[MoCl_3(thf)_3]$ with the lithiated triamide $N(CH_2CH_2NRLi)_3$

($R = SiMe_3$, SiMe$_2^t$Bu) afforded [MoCl{N($CH_2CH_2NR)_3$}] instead of the expected Mo(III) species [190]. The same compound ($R = SiMe_3$) has been prepared by Schrock, who also studied its alkylation with cyclopentyl lithium; the initial alkyl complex decomposed by β-elimination on heating to give [MoH{N($CH_2CH_2NR)_3$}] [191]. The reaction of [MoCl{N($CH_2CH_2NR)_3$}] ($R = SiMe_3$) with one equivalent of LiPHPh results in a simple substitution reaction to give [Mo(PHPh){N($CH_2CH_2NR)_3$}]; however if two equivalents were used, the terminal phosphide complex [Mo(≡P){N($CH_2CH_2NR)_3$}] (**14**) was obtained [192]. As noted in an accompanying commentary, this complex and the related one prepared by Cummins are the first examples of such compounds [193].

The thermal reaction of [$MoCl_3$(thf)$_3$] with phenylformamidine (HL) and PPh_4Cl in dichlorobenzene led to the isolation of crystals of [PPh_4][Mo_2(L)$_2$(μ-NPh)Cl_5]·$2CH_2Cl_2$ in which the bridging imido ligand presumably arises through cleavage of a formamidine unit [194].



(14)



(15)

Protonation of the nitrido complex *trans*-[Mo(≡N)(N_3)(dppe)$_2$] with HOTf produced [Mo(NH_2)(OH)(dppe)$_2$][OTf]$_2$, representing the first example of the conversion of a nitride to an amide in such complexes. The X-ray structure shows the triflate anions hydrogen bonded to the amide and hydroxy groups. Stirring the product in MeOH released ammonia and formed [MoO(OMe)(dppe)$_2$][OTf], also structurally characterized [195]. Treatment of [MoF(NNH_2)(dppe)$_2$]$^+$ with 2,5-dimethoxy-thf afforded the pyrrollylimido complex *trans*-[MoF(NNCH=CHCH=CH)(dppe)$_2$]$^+$ (**15**), which on reduction with $LiAlH_4$ produced free pyrrole and aminopyrrole, together with [MoH_4(dppe)$_2$] [196]. Alkylation of *trans*-[MoCl(N)(dppe)$_2$] to afford *trans*-[MoCl(=NR)(dppe)$_2$]$^+$ has been extended to a range of functionalized R groups (R = Me, Et, ^{i}Pr, $CH_2CH=CH_2$, CH_2CO_2Me, etc.). The cationic products undergo deprotonation at the carbon attached to nitrogen, and can then be further alkylated to complete homologation of the chain (e.g. Me to Et to ^{i}Pr). The crystal structure of [MoCl(N=$CHCO_2Me$)(dppe)$_2$] was determined. Electroreduction in the presence of H^+ releases amines such as methyl glycinate [197].

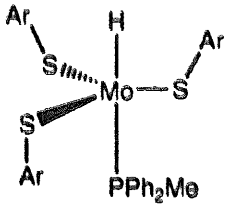
The crystal structure of [MoH_4(dppe)$_2$]·thf has been determined, confirming the dodecahedral coordination geometry [198]. A low temperature IR and UV spectroscopic study of the interaction of this compound with acids such as PhOH,

$(CF_3)_2CHOH$ and CF_3CO_2H has implicated a hydrogen-bonded adduct as the first stage in the protonation reaction [199].

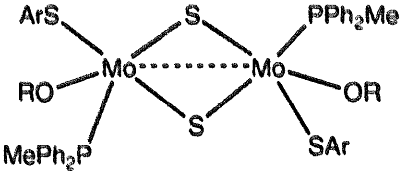
4.3. Complexes with oxygen or sulfur donor ligands

The reaction of $[MoCl_4(MeCN)_2]$ with $R_2C(CH_2SCH_2CMe_2CH_2OLi)_2$ (Li_2L; R = H, Me) gave dithioether-alkoxide complexes $[MoCl_2(L)]$. Recrystallization of the compound with R = H from thf yielded crystals of $[MoCl_2(L)MoOCl_2(thf)]$ in which a second Mo(IV) unit has coordinated to the two alkoxide oxygen atoms [200].

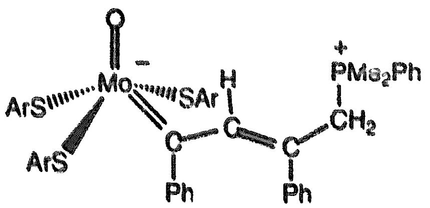
Treatment of $[MoH_4L_4]$ (L = PPh_2Me or PPh_2Et) with HSAr (Ar = C_6H_2-2,4,6-R_3 where R = Me, ^iPr) gave $[MoH(SAr)_3(L)]$ (**16**), which form adducts with various pyridines of the type $[MoH(SAr)_3(L)(py)]$, and react with pyridine-2-thiol to give seven-coordinate pentagonal bipyramidal $[MoH(SAr)(NC_5H_4S)_2(L)]$. The square pyramidal $[MoO(SAr)_4]^-$ was accessible by reaction of $[MoH(SAr)_3(L)]$ with $LiBHEt_3$ in MeOH [201]. The reaction of $[MoH(SAr)_3(L)]$ with ROH (R = Me, Et) in thf caused elimination of ArH (or ArD in the case of $[MoD(SAr)_3(L)]$) and formation of $[\{Mo(SAr)(OR)(L)\}_2(\mu\text{-}S)_2]$ (**17**) [202]. Carbonylation of $[MoH(SAr)_3(PPh_2Me)]$ gave *mer*-$[Mo(CO)_3(SAr)_2(PPh_2Me)]$ and $[Mo(CO)_2(SAr)_2(PPh_2Me)_2]$; the first of these has a distorted octahedral structure whereas the latter is presumed to be trigonal prismatic. The distortions in complexes of this type were analysed in terms of θ, the angle between the two sets of *fac*-ligands, ranging from 0° for trigonal prism to 60° for octahedral [203]. The reaction of $[MoH(SAr)_3(PMe_2Ph)_2]$ with PhC≡CH in thf, followed by addition of methanol gave the zwitterionic alkylidene complex $[MoO(SAr)_3(=CPhCH=CPhCH_2PMe_2Ph)]$ (**18**) [204].



(**16**)



(**17**)



(**18**)

5. Molybdenum(III)

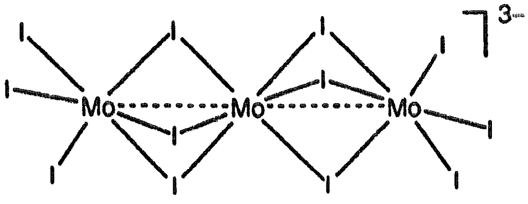
5.1. Complexes with halide and phosphine or carbonyl ligands

A solid state metathesis reaction between $MoCl_3$ and NaN_3 which proceeds with a thermal flash to give a mixture of Mo metal and the nitride Mo_2N has been described [205]. The chemistry of $[MoCl_3(L)]$, where $L = PhP(CH_2CH_2PPh_2)_2$, has been explored; it serves as a useful starting point for the synthesis of compounds such as $[Mo(\eta\text{-arene})(L)]$, $[CpMoH(L)]$, and *fac*-$[Mo(N_2)(PMe_3)_2(L)]$ [206]. Similar chemistry has been developed from $[MoBr_3(L)]$ where $L = N(CH_2CH_2PPh_2)_3$ [207]. The complexes $[MoCl_3(PPh_3)_2(MeCN)]$ and $[MoCl_3(L_2)(MeCN)]$ where $L_2 = o\text{-}C_6H_4(NH_2)_2$ have been prepared from $MoCl_3$ in MeCN; addition of $AgClO_4$ leads to halide abstraction and the formation of cationic species [208]. The complexes $[LMoX_3]$ where $L = CHpz_3^*$ were made by oxidizing $[LMo(CO)_3]$ with $SOCl_2$, Br_2 or I_2 [155].

The synthesis of the Mo(III) complexes $[MoCl_4(L)_2]^-$ where $L = PPh_2Me$, $PPhEt_2$, and PEt_3, has been reported. This paper also contained the crystal structures of $[HPMe_2Ph]_2[MoCl_5(PMe_2Ph)]$, $[MoCl_3(MeCN)(PPh_2Et)_2]$, and the Mo(IV) complex $[PMe_2PhCl]_2[MoCl_6]$ [209]. Addition of PEt_3 to $[MoCl_4(thf)_2]^-$ also produced $[PPh_4][Mo_2Cl_8(PEt_3)] \cdot 2CH_2Cl_2$, which has a face-sharing bioctahedral structure with an Mo–Mo bond of 2.767(2) Å [210].

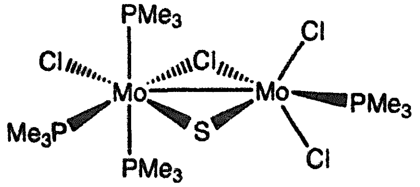
The reaction of $[pyH]_3[MoCl_6]$ with py afforded $[MoCl_5(py)]^{2-}$ which was structurally characterized as its $NMe_2H_2^+$ and NMe_4^+ salts. Further reaction gave *cis*- or *trans*-$[MoCl_4(py)_2]^-$ and *mer*-$[MoCl_3(py)_3]$ [211]. The crystal structure of $[PPh_4][MoBr_4(py)_2]$ has been determined and shows a slightly distorted octahedron with the two py ligands in a *cis* arrangement [212].

The reaction of *trans*-$[MoI_4(thf)_2]^-$ with dppe afforded the *cis* isomer of $[MoI_4(dppe)]^-$, which could also be prepared in one step from $[MoI_3(thf)_3]$, iodide and dppe. The X-ray structure of the product was determined as its $[Na(thf)_3]^+$ salt and contained an octahedrally coordinated sodium ion with three iodides bridging between Na and Mo [213]. Spontaneous loss of thf from $[MoX_4(thf)_2]^-$ (X = Br, I) in non-coordinating solvents led to the formation of $[Mo_3X_{12}]^{3-}$; the structure of $[PPh_4]_3[Mo_3I_{12}]$ (**19**) showed a linear arrangement with three face-sharing octahedra [214].



(**19**)

The reversible dissociation of a phosphine ligand from $[Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5]$ produced $[Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_4]$ (**20**) which has an unprecedented edge-sharing structure rather than the face-sharing bioctahedral arrangement usually found for Mo_2L_9 compounds. Coordination of other ligands to the product is possible, giving $[Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_4(L)]$ (L = CO, MeCN) while addition of Cl^- afforded $[NMe_4][Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_4(PMe_3)_4]$; alkyne complexes $[Mo_2(\mu\text{-}S)(\mu\text{-}alkyne)Cl_4(PMe_3)_4]$ were also prepared [215].



(20)

5.2. *Complexes with oxygen and nitrogen donor ligands*

The Mo–D_2O bonding in the $[Mo(D_2O)_6]^{3+}$ ion has been examined by a polarized neutron diffraction study of $[CsMo(SO_4)_2]\cdot 12D_2O$, which enables the electron distribution to be probed accurately. Approximately 90% of the spin density is contained in the Mo t_{2g} orbital set, but there is also evidence for some π-interaction between metal and ligand [216].

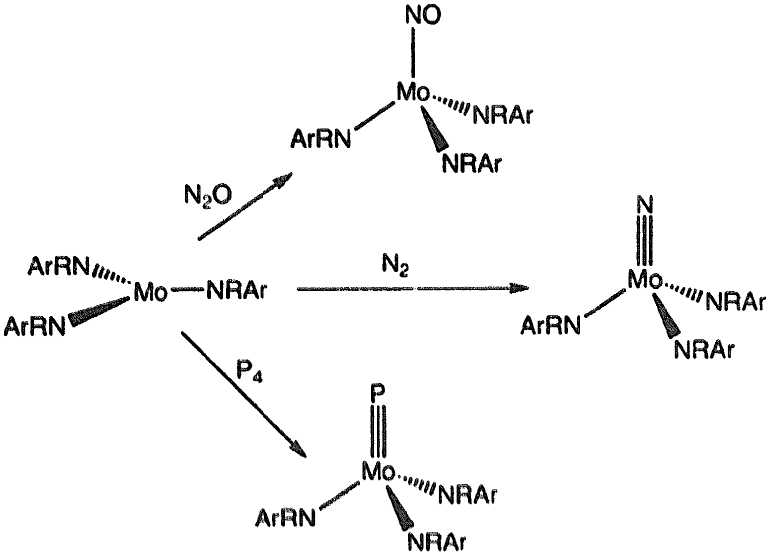
The reaction of $[Mo_2(H)Cl_8]^{3-}$ with carboxylic acids in aqueous solution gave a purple intermediate which decomposed to $[Mo_2(O_2CR)_4]$. In the case of glycine (glyH), this intermediate was isolated and characterized as $[Mo_2(H)(OH)(gly)_2Cl_4]$, in which the two Mo(III) centres are joined by a rather short bond of 2.353(5) Å and bridged by the hydride, the OH group, and the two carboxylic acids [217]. Interaction of $[Mo_2Cl_6(thf)_3]$ with sodium benzoate and PEt_3 in thf gave three compounds: $[Mo_2(O_2CPh)_6(PEt_3)_2]$, $[Mo_2(O_2CPh)_4]$, and $[Mo_4O_6(O_2CPh)_6(PEt_3)_2]$. The first of these contains bridging didentate, bridging monodentate and terminal benzoate ligand [218].

Treatment of $[M_2(OR)_6]$ (M = Mo, W) with KOR in the presence of 18-crown-6 (18C6) led to the formation of $[K(18C6)][M_2(OR)_7]$; the structure of $[Mo_2(OCH_2^tBu)_7]^-$ showed one bridging alkoxide and a Mo–Mo bond of 2.218(1) Å. For this R group, the compounds $K_2[M_2(OR)_8]$ could also be isolated; in this case the alkoxides are all terminal and the Mo_2 unit sits in a cube of oxygens, with a K^+ ion coordinated to the four alkoxides at each end of the structure. Oxidation with PPh_3Br_2 gave insoluble $[M_2(OR)_8]$ which would dissolve on addition of pyridine [219].

Reaction of $[Mo_2(NMe_2)_6]$ with the protected sugar diacetone glucose (1,2:5,6-diisopropylidene glucose, HL) gave $[Mo_2L_6]$ which has a Mo–Mo bond length of 2.218(2) Å [220]. A thermogravimetric study of the decomposition of $[Mo_2(OR)_6]$ showed that in the main the compounds sublimed, but Mo_2C was formed when R = Cy and also from the related $[Mo_2(CH_2Ph)_2(O^iPr)_4]$ [221].

Some of the most exciting developments this year (Scheme 2) have occurred in the area of Mo(III) amide chemistry exploited by Cummins, and concern the reactivity of complexes $[Mo(NRAr)_3]$ where $R = C(CD_3)_2Me$ and

Ar = 3,5-$C_6H_3Me_2$, prepared by the reaction of [$MoCl_3(thf)_3$] with LiNRAr(OEt_2). The complex reacts with N_2O by cleavage of the N–N bond and formation of [Mo(NO)$(NRAr)_3$] and [Mo(N)$(NRAr)_3$]; the latter product could also be made from $MesN_3$ or NO [222]. Most impressively, the complex reacts with dinitrogen itself with cleavage of the N≡N bond to afford again [Mo(N)$(NRAr)_3$], presumably via an intermediate dinuclear complex with a bridging N_2 ligand [223]. According to a quantum chemical calculation study, this reaction should be even more effective for the W(III) analogue [224]. The tris(amide) complex also reacts with P_4 to give the terminal phosphide complex [Mo(P)$(NRAr)_3$]; the X-ray structure showed that the product is monomeric with an Mo≡P bond length of 2.119(4) Å [225]. Together with the closely related accompanying compound described by Schrock it represents the first example of such species [192,193].



Scheme 2.

Salts formulated as K[Mo$(py)_6$][Fe$(NCS)_6$] and K[Mo$(L_2)_3$][Fe$(NCS)_6$] (L_2 = bpy, phen) have been described [226].

6. Molybdenum(II)

6.1. Complexes with halide and phosphine or carbonyl ligands

Quadruply-bonded complexes of the type [$Mo_2X_4L_4$] have remained an active area of research. A systematic molecular modelling study of quadruply-bonded dimolybdenum complexes has been carried out in order to probe the relationship between bond lengths, force constants and bond orders. All the structural details independent of the Mo–Mo bond were modelled with a transferable force field, allowing a simulation of the inherent properties of the bond in terms of a characteristic length, 2.02 Å, and a characteristic force constant of 4.07 mdyne $Å^{-1}$ [227].

In an attempt to resolve the crystallographic disorder in $[Mo_2Cl_8]^{4-}$, its structure was determined as the $[H_3N(CH_2)_3NH_3)]^{2+}$ and $[H_3N(CH_2)_4NH_3)]^{2+}$ salts, and the previously studied $[H_3NCH_2CH_2NH_3]^{2+}$ and K^+ salts were redetermined. The K^+ salt has a 9:1 disorder of the metal units in two perpendicular directions, whereas for the diaminopropane salt this was nearly 1:1 [228]. The complex $[Mo_2Cl_4(dppm)_2]$ undergoes photochemical reactions with disulfides such as S_2Ph_2 to afford Mo(III) products, $[Mo_2Cl_4(\mu\text{-}Cl)(\mu\text{-}SPh)(dppm)_2]$. The wavelength dependence of the reaction indicates that an excited state higher in energy than the $\delta\delta^*$ is involved [229]. The electronic and circular dichroism spectra of $[Mo_2Cl_4(R,R\text{-}dach)_2]$ where the ligand is (−)-*trans*-1,2-diaminocyclohexane, have been recorded and correlated with those of the corresponding phosphine complex; the signs of the bands at 546 and 461 nm are consistent with the helicity rules for this type of compound [230].

An improved preparation of $[MoBr_2(CO)_3(PPh_3)_2]$ and its decarbonylation to $[MoBr_2(CO)_2(PPh_3)_2]$ have been developed: bromination of $[Mo(CO)_6]$ at −70°C is followed by warming to −40°C, addition of the phosphine, isolation of the tricarbonyl, and then decarbonylation in refluxing xylene under partial vacuum [138]. Air oxidation of the dicarbonyl yielded $[MoO_2Br_2(O{=}PPh_3)_2]$ in a process which probably involves dissociation of the PPh_3, oxidation and recoordination [231]. Reaction of the dicarbonyl with AgOTf affords $[Mo(CO)_2(PPh_3)_2(OTf)_2]$, which can be used as a synthon for the $[Mo(CO)_2(PPh_3)_2]^{2+}$ unit. Thus, reaction with MeCN gave $[Mo(CO)_2(PPh_3)_2(MeCN)_2]^{2+}$, with H_2O gave $[Mo_2(\mu\text{-}OH)_3(CO)_4(PPh_3)_4]^+$, and with alkynes ($C_2Me_2$, PhC_2Me) gave $[Mo(CO)\text{-}(alkyne)(PPh_3)_2(OTf)_2]$. A different product, $[Mo(CO)(\eta\text{-}C_2Me_2)_2(PPh_3)_2(OTf)]^+$, was obtained from a direct reaction of $[MoBr_2(CO)_3(PPh_3)_2]$ with AgOTf and alkyne [232].

Nitrile exchange in $[MoI_2(CO)_3(MeCN)_2]$ with PhCN gave $[MoI_2(CO)_3(PhCN)_2]$ which reacted with one equivalent of L ($L{=}PPh_3$, $AsPh_3$, $SbPh_3$) to give $[MoI_2(CO)_3(PhCN)(L)]$ [233]. The reaction of $[MoI_2(CO)_3(MeCN)(PPh_3)]$ with potassium pyridine-2-thiolate afforded $[MoI(CO)_3(PPh_3)(pyS)]$ in which the ligand is didentate [234] whereas reaction of $[MoI_2(CO)_3(MeCN)_2]$ with pySH (or pyrimidine-2-thiol) gave $[MoI_2(CO)_3(pySH)_2]$ [235]. Oxidation of $[Mo(CO)_4(nbd)]$ with iodine gave polymeric $[MoI_2(CO)_2(nbd)]_n$, which in acetonitrile formed monomeric $[MoI_2(CO)_2(nbd)(MeCN)]$ and on reaction with bpy or 4,4′-di^{t}Bu-bpy produced $[MoI_2(CO)(nbd)(bpy)]$. The analogous bromide complexes were also made [236].

The cationic phosphenium complexes $[Mo(CO)_3(L_2)\{P(NMeCH_2CH_2NMe)\}]^+$ ($L_2{=}$bpy, phen) react with ligands L′ [$L'{=}PPh_3$, $P(NMeCH_2CH_2NMe)OMe$] to afford an equilibrium mixture of *cis*- and *trans*-$[Mo(CO)_2(L_2)\text{-}(L')\{P(NMeCH_2CH_2NMe)\}]^+$; the X-ray structures of two examples which each contain one phosphite and one phosphenium ligand were determined [237].

The complex $[MoCl_2(PMe_3)_2]$ was isolated from the reaction of $[(\eta\text{-}C_5Me_4Et)MoCl_2PMe_3)_2]$ with Li_2PMes; the dinuclear complex

$[\mathrm{Mo_2(\mu\text{-}PPh_2)_2(PPh_2)_2(PMe_3)_2}]$ was made by treatment of $[\mathrm{MoCl_2(PMe_3)_4}]$ with $\mathrm{KPPh_2}$ [238].

6.2. *Complexes with nitrogen donor ligands*

The oxidation potentials of the diarylformamidinate complexes $[\mathrm{Mo_2(ArNCHNAr)_4}]$, which are a direct measure of the HOMO δ-orbital energy, correlate with the Hammett constants of Ar for a range of aryl groups, showing that one can tune the redox properties by altering the ancillary ligands. However the UV–VIS spectra of all the compounds are virtually identical, showing that the HOMO-LUMO energy gap remains the same [239]. Oxidation of $[\mathrm{Mo_2(ArNCHNH)_4}]$ with $\mathrm{PhICl_2}$ gave $[\mathrm{Mo_2(ArNCHNH)_4Cl_3}]$ in which two formamidinate ligands are bridging didentate, one bridging monodentate and one terminal chelating [194].

Further developments in the extensive chemistry of the tris(3,5-dimethylpyrazolyl)borate complex $[\mathrm{(HBpz^*_3)Mo(NO)X_2}]$ ($\mathrm{X = Cl, Br, I}$) have been reported [240], [241]. This redox-active 16-electron compound reacts with alcohols and amines with elimination of HX and formation of $[\mathrm{(HBpz^*_3)Mo(NO)(X)(OR)}]$ or $[\mathrm{(HBpz^*_3)Mo(NO)(X)(NHR)}]$, or the corresponding disubstituted species, but also reacts with neutral donors such as pyridines to give 17-electron compounds $[\mathrm{(HBpz^*_3)Mo(NO)(X)(L)}]$. Complexes of the type $[\mathrm{(HBpz^*_3)Mo(NO)(I)(L)}]$ where $\mathrm{L = py}$, 4-phenylpyridine, isoquinoline) and $[\mathrm{(HBpz^*_3)Mo(NO)(L)_2}][\mathrm{X}]$ ($\mathrm{X = I, I_3}$ or $\mathrm{BPh_4}$) have been made. Some show invariant magnetic behaviour consistent with one unpaired electron, but others only fall to the spin only moment at low temperature. The cationic species can be reduced to 18-electron species at potentials 400 mV more anodic than the neutral complexes [242].

Several papers explore the interaction between two Mo centres linked by various spacer groups. Electrochemical reduction of $[\{\mathrm{(HBpz^*_3)Mo(NO)(X)}\}_2(\mu\text{-}1,n\text{-}\mathrm{HNC_6H_4NH})]$ ($n = 2,3,4$; $\mathrm{X = Cl, Br, I}$) gave the corresponding mixed-valence anion; in the case of the 1,2- and 1,4- diamidobenzene bridge, this state is delocalized on the ESR timescale whereas for the 1,3-isomer it is valence trapped [243]. New polypyridine ligands with alkenyl (or ethynyl) spacer groups such as $1,3,5\text{-}\mathrm{C_6H_3(CH{=}CH\text{-}4\text{-}pyridyl)_3}$ and $1,2,4,5\text{-}\mathrm{C_6H_2(CH{=}CH\text{-}4\text{-}pyridyl)_4}$ have been synthesized, and then $\mathrm{(HBpz^*_3)Mo(NO)(X)}$ units attached to each pyridyl group. The electrochemical communication between the metal centres (measured by the difference in reduction potentials between them) depends on the substitution pattern, and ESR spectra show that all the systems are delocalized on the ESR timescale [244].

Functionalization of porphyrin ligands with the $\mathrm{(HBpz^*_3)Mo(NO)(X)}$ group has been achieved, for example from the *o*-, *m*- and *p*- isomers of $5\text{-}\mathrm{C_6H_4OH}\text{-}10,15,20\text{-}\mathrm{Ph_3}$ porphyrin; the porphyrin ligand could then be complexed to Zn, Ni and Pt centres. The tetrasubstituted species tetra-$[\mathrm{Mo\text{-}OC_6H_4}]$ porphyrin was also prepared [245]. New ferrocenyl ligands such as $\mathrm{NC_5H_4CH{=}CRFc}$ ($\mathrm{R = H, Me, Ph}$), $\mathrm{NC_5H_4CH{=}CHC_6H_4Fc}$, $\mathrm{NC_5H_4CH{=}NC_6H_4Fc}$ etc. have been prepared and complexed to the $\mathrm{(HBpz^*_3)Mo(NO)(X)}$ unit. Coordination of the Mo causes a shift in the ferrocene redox potential by about 40 mV in a positive direction. The complex of the ligand $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_4CMe{=}CHC_5H_4N})_2]$ shows some interaction between the two Mo centres in its ESR spectrum [246]. Redox active metallomacrocycles of the form $[\{(\mathrm{HBpz}_3^*)\mathrm{Mo(NO)}(\mu\text{-L})\}_2]$ have been prepared by the action of the diols $\mathrm{H_2L}$ ($\mathrm{H_2L{=}HOC_6H_4CH_2C_6H_4OH}$, $\mathrm{HOCH_2C_6H_4CH_2OH}$ or 2,7-$\mathrm{HOC_{10}H_6OH}$) on $[(\mathrm{HBpz}_3^*)\mathrm{Mo(NO)(I)_2}]$ [247].

Compounds of the type $[(\mathrm{HBpz}_3^*)\mathrm{Mo(NO)(X)(EC_6H_4CH{=}CHC_6H_4\text{-}4\text{-}R)}]$ where E=O or NH and R=Fc, OMe or $\mathrm{NMe_2}$) and some analogous ones with dimethoxyphenyl groups have been investigated by the Kurtz powder test as possible non-linear optical materials. Only the ferrocenyl complex was active, but this may be a structural effect as the crystal structure of one example showed that even though it crystallized in a non-centrosymmetric space group (a requirement for activity), pairs of molecules were aligned in a pseudo-centrosymmetric way [248]. The compounds $[(\mathrm{HBpz}_3^*)\mathrm{Mo(NO)(Cl)(NC_5H_4CH{=}CHC_6H_4\text{-}4\text{-}OR)}]$ ($\mathrm{R{=}C_nH_{2n+1}}$ where n=6, 8, or 12) have been tested for liquid crystal properties, but no mesophases were observed [249].

The reaction of $[(\mathrm{HBpz}_3^*)\mathrm{Mo(NO)(I)_2}]$ with β-diketones such as acacH gave complexes of the type $[(\mathrm{HBpz}_3^*)\mathrm{Mo(NO)(acac)}][\mathrm{I_3}]$. These could be reduced to neutral species with cobaltocene, and the crystal structure of $[(\mathrm{HBpz}_3^*)\mathrm{Mo(NO)(acac)}]$ was carried out [250]. The complexes $[(\mathrm{HBpz}_3^*)\mathrm{Mo(NO)(L_2)}]$ where $\mathrm{L_2{=}S(CH_2)_nS}$ (n=5,6) or $\mathrm{S(CH_2)_2CONH(CH_2)_2S}$ have been prepared in order to judge the effect of N–H···S hydrogen bonding on the redox potentials of thiolate complexes; that of the amide ligand is markedly different, attributed to this reason [251].

Complexes $[(\mathrm{HBimpz_3})\mathrm{Mo(NO)(I)(OR)}]$ (R=^{i}Pr, ^{t}Bu, $\mathrm{CH_2SiMe_3}$, *p*-tol) and $[(\mathrm{HBimpz_3})\mathrm{Mo(NO)(I)(NHR)}]$ (R=Ph, *p*-tol) have been prepared containing the 3-^{i}Pr-5-Me-pz group. Some exist as a mixture of isomers which rearrange on heating in a boratropic shift to a single isomer; this appears to be sterically driven as it depends on the size of R. Structure determinations suggest that the bulky ^{i}Pr group prefers the 3-position [252].

Proton transfer from $[(\mathrm{HBpz}_3^*)\mathrm{Mo(CO)_3H}]$ or $[\mathrm{CpMo(CO)_3H}]$ has been used to quench the excited state of *trans*-$[\mathrm{ReO_2(py)_4}]^+$ [253]. The reaction of $[(\mathrm{HBpz_3})\mathrm{Mo(CO)_3}]^-$ with $\mathrm{RN_2^+}$ afforded $[(\mathrm{HBpz_3})\mathrm{Mo(CO)_2(N_2R)}]$ when R=substituted aryl, but if the HBpz_3^* analogue was used the acyl species $[(\mathrm{HBpz}_3^*)\mathrm{Mo(CO)_2(COR)}]$ was isolated. By increasing the steric bulk of the R group or the $\mathrm{HBpz_3}$ ligand still further, simple substitution was re-established, allowing the crystal structure of $[(\mathrm{HBpz}_3^*)\mathrm{Mo(CO)_2(N_2C_6H_3\text{-}2,6\text{-}Me_2)}]$ to be determined [254].

6.3. *Complexes with oxygen donor ligands*

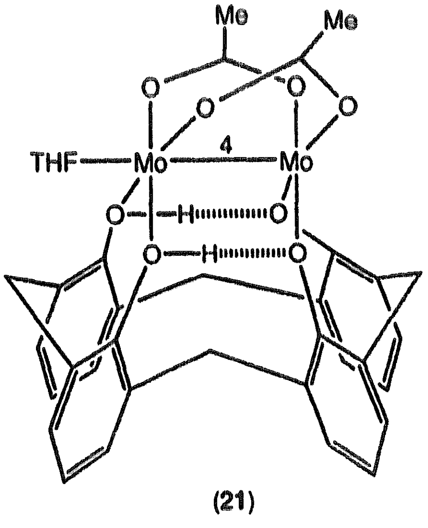
The variable photon energy PES of $[\mathrm{Mo_2(O_2CCF_3)_4}]$ has been recorded and shows a strong enhancement of the metal based δ and $\sigma+\pi$ ionizations; their similar size suggests a similar amount of d-orbital character for the associated MO's [255].

The synthesis of $[\mathrm{Mo_2(O_2CCHF_2)_4}]$ has been described together with a study of its adduct formation in acetone and py solutions and with PBu_3; with increasing donor ability the presence of axial, mono-equatorial and di-equatorial adducts becomes evident [256]. Adducts of $[Mo_2(O_2CR)_4]$ (R = Me, ${}^tBu$, CF_3) with TCNE have been made in which the TCNE is σ-bonded to the metal; the magnetic properties were studied [257]. Linear chain complexes $[Mo_2(OAc)_4(L)]_n$ where L = pyrazine, 4,4′-di-${}^tBu$-bpy and dabco (1,4-diazabicyclo[2,2,2]octane) have been prepared with Mo–Mo distances of 2.093(1), 2.103(1) and 2.095(1) Å, respectively. The coordination of the nitrogen ligands is fairly weak [258]. An adduct of $[Mo_2(O_2CCHF_2)_4]$ with 2,6-di-${}^tBu$-p-benzoquinone has been described; the Mo–Mo distance is 2.117 Å. The ${}^tBu$ groups are to stop the formation of a chain structure, which happened in the case of the 2,6-dimethyl analogue; the chain consists of alternating dimers in which the metals are bonded to the hindered or unhindered end of the quinone, with Mo–Mo distances of 2.108(1) and 2.111(1) Å, respectively [259].

The adducts $[Mo_2(OAc)_4X_2]^{2-}$ and $[Mo_2(OAc)_2X_4]^{2-}$ (X = Br, I) have been isolated as their pyH^+, $pipH^+$ or morpholinium salts; the coordination of the axial ligands is again weak. The tetrahalide adducts showed some of the shortest Mo-Mo quadruple bonds yet observed, in the range 2.078–2.086 Å [260,261].

An exchange reaction between $[Mo_2(O_2CH)_4]$ and $[Mo_2(O_2CCHF_2)_4]$ in acetone resulted in the formation of mixed ligand species in approximately statistical amounts [262]. The thermolysis of $[Mo_2\{O_2CCCo_3(CO)_9\}_4]$ has been studied in order to form solids which are catalytically active [263].

The reaction of $[Mo_2(O_2CR)_2(NCMe)_6][BF_4]_2$ (R = Me, CF_3) with calix-4-arene or p-${}^tBu$-calix-4-arene (H_4L) (previously deprotonated by two equivalents of KH to K_2H_2L) gave $[Mo_2(\mu\text{-}O_2CR)_2(\mu\text{-}H_2L)]$ (**21**). The ${}^tBu$-substituted complex with R = Me was crystallographically characterized with an Mo–Mo bond of 2.1263(6) Å, two bridging acetates, and the bridging calixarene. The two protonated oxygens of the macrocycle are attached to the same Mo, and take part in hydrogen-bonding with the other two; one Mo atom also bears a thf ligand [264,265].

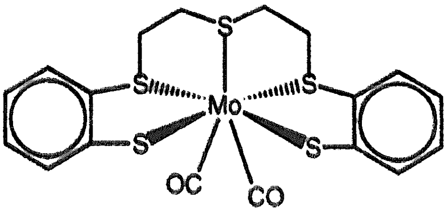


(**21**)

The reaction of $[Mo_2(OAc)_2(MeCN)_6][BF_4]_2$ with RNC (R = Mes or 2,6-$C_6H_3Me_2$) gave $[Mo_2(\mu\text{-}O)(CNR)_{10}][BF_4]_2$ as well as the mononuclear Mo(IV) species $[MoO(F)(CNR)_4][BF_4]$. The dinuclear complex has an unusual eclipsed structure with an unsupported Mo–O–Mo bridge [266].

6.4. Complexes with sulfur donor ligands

The complex $[Mo(CO)_2(PCy_3)(S4)]$ (S4 = $-SC_6H_4SCH_2CH_2SC_6H_4S-$) and its analogue with the 3,5-$^tBu_2$-substituted S4 ligand have been prepared. Heating these caused the dismantling of the S4 ligand to yield $[Mo(CO)(PCy_3)(SC_6H_4S)_2]$. Optimization of the conditions allowed the synthesis of bulk quantities of $[Mo(CO)_2(SC_6H_2^tBu_2S)_2]$ [267]. The related ligands S5, NS4 and OS4, $-SC_6H_4SCH_2CH_2ECH_2CH_2SC_6H_4S-$ where E = S, NH or O, have been described. Reaction with $[Mo(CO)_4Cl_2]$ gave $[Mo(CO)_2(ES4)]$ (**22**), which has a seven-coordinate capped trigonal prismatic geometry. Oxidation of this gave $[MoO(ES4)]$ which in turn reacted with PMe_3 to give initially $[MoO(ES4)(PMe_3)]$ and then, when ES4 = S5, breakdown of the ligand to form $[Mo(PMe_3)_2(SC_6H_4S)_2]$. Reaction of $[Mo(CO)_2(S5)]$ with NO^+ gave either $[Mo(NO)(S5)]^+$ or $[Mo(NO)_2(S5)]$ [268].



(22)

7. Molybdenum(I)

Oxidation of $[NEt_4]_2[Mo_2(\mu\text{-}SPh)_2(CO)_8]$ with iodine under CO gave neutral $[Mo_2(\mu\text{-}SPh)_2(CO)_8]$ which has a Mo–Mo bond [269].

8. Molybdenum(0)

8.1. Complexes with carbonyl ligands

Density functional calculations have been carried out on a number of metal carbonyls in order to compute the M–CO dissociation energy; values of 193.1, 165.9 and 182.7 kJ mol^{-1} were obtained for Cr, Mo and W hexacarbonyls. The carbonyl association energy for the formation of the $M(CO)_7$ fragment was also calculated, with the results of 196.5, 168.9 and 149.6 kJ mol^{-1} respectively implying that substitution reactions can occur by an associative as well as dissociative mechanism [270]. Double charge transfer spectroscopy has been used to determine the double ionization energy of $[Mo(CO)_6]$ to a triplet-state dication; the values for Cr, Mo and W were similar [271]. The Mo, K and L edge EXAFS spectra of $[Mo(CO)_6]$ and MoF_6 have been recorded in the gas phase [272].

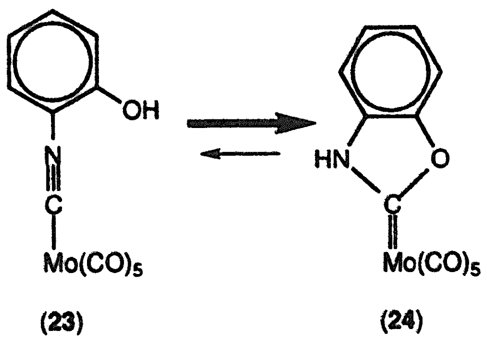
An IR and UV-spectroscopic study of the adsorption of $[Mo(CO)_6]$ on partially dehydroxylated alumina has shown adsorption at two types of Lewis acidic sites followed by loss of CO, initially to $Mo(CO)_5$ groups and then to $Mo(CO)_3$. On hydroxylated alumina adsorption occurs at surface OH sites [273]. A temperature programmed decomposition study of $[Mo(CO)_6]$ on a variety of solid supports showed that the activation energy for CO loss was less than in the gas phase, and was less on very basic supports such as ZnO or MgO [274]. The location of $[Mo(CO)_6]$ adsorbed in faujasite zeolites has been probed by DRIFTS and Raman scattering, backed up by Monte Carlo simulations; evidence for different sites of adsorption in aluminium-containing zeolites was obtained [275]. The activity of highly dispersed Pd–Mo catalysts prepared either from a mixed-metal cluster or from $[PdCl_2(PhCN)_2]$ and $[Mo(CO)_6]$ has been compared [276].

Carbonyl ligands in $[Mo(CO)_6]$ can be labilized by treatment with amines and H_2O_2, which form hydroxylamines in situ; from a reaction with NH_2OH itself, the resulting $[Mo(CO)_5(NH_3)]$ was isolated [277]. Treatment of $[Mo(CO)_6]$ with $Te(O)Ar_2$ ($Ar = p\text{-}C_6H_4OMe$) gave $[Mo(CO)_5(TeAr_2)]$; the tellurium reagent acts as an oxygen transfer reagent as well as a ligand [278]. The photochemistry of $[Mo(CO)_6]$ in alkane solution has been studied by actinometry and photoacoustic calorimetry. The displacement of heptane from the solvent complex with pip enabled the Mo-heptane and Mo-pip bond energies to be estimated as 71 and 142 kJ mol^{-1} at the most [279]. Photolysis of $[Mo(CO)_6]$ in alkyne-doped CH_4 matrices produced $[Mo(CO)_5(alkyne)]$ and a species tentatively identified as a disubstituted complex [280].

The allylic substitution of allyl acetates with MeOH is catalysed by a new Mo(II) species formed in situ by reaction of $[Mo(CO)_6]$ with $[PhCH_2NEt_3][Cl]$ and then three equivalents of AgOTf; a possible formulation is $[Mo(CO)_5(OTf)][OTf]$ [281]. The retention of stereochemistry in Mo-catalysed allylic substitution reactions has also been studied [282]. Generation of cyclic stannyl vinyl ethers from alkynols in the presence of $[Mo(CO)_5(NEt_3)]$ probably involves carbene complex intermediates [283]. Metathesis of hydroxyphenylalkynes such as $HOC_6H_4C{\equiv}CMe$ occurs readily with catalytic amounts of $[Mo(CO)_6]$ [284]; cross-metathesis reactions can also be achieved as long as a phenolic compound is present [285]. No interaction was observed between trialkyl aluminium reagents and $[Mo(CO)_6]$ [286].

The reaction of $[M_2(CO)_{10}]^{2-}$ (M = Cr, Mo, W) with Ph_2BiCl produced the three isostructural complexes $[Ph_2Bi\{M(CO)_5\}_2]^-$ [287].

Desilylation of $[M(CO)_5\{o\text{-}CNC_6H_4OSiMe_3)]$ (M = Cr, Mo, W) afforded the corresponding $[M(CO)_5\{o\text{-}CNC_6H_4OH)]$ (**23**), which was found to be in equilibrium with the carbene complex $[M(CO)_5({=}CNHC_6H_4O)]$ (**24**) [288]. A spectroelectrochemical study of the redox chemistry of $[Mo(CO)_{6-n}(CNR)_n]$ (n = 1–6; $R = 2,6\text{-}C_6H_3Me_2$) has shown that as n increases, the oxidation potential decreases. For n = 5 and 6 stable monocations are formed, *fac*-$[Mo(CO)_3(CNR)_3]$ and *cis*-$[Mo(CO)_2(CNR)_4]$ isomerize on oxidation, and when n = 1 or 2 the cations decompose with release of free RNC [289]. Carbene complexes $[Mo(CO)_4(L)_2]$ and



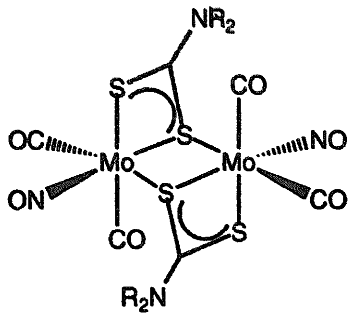
(23) **(24)**

fac-[Mo(CO)$_3$(L)$_3$] have been prepared where L = the stable imidazole carbene (=CNMeCH=CHNMe) [290]. The double bond of this carbene ligand in [Mo(CO)$_5$(L)] can be subjected to reaction with OsO$_4$ and forms a stable complex [291]. Irradiation of [Mo(CO)$_6$] with PhSiH$_2$(C$_6$H$_4$CH$_2$NMe$_2$) produced the intramolecularly-stabilized silylene complex [Mo(CO)$_5${=SiPh(C$_6$H$_4$CH$_2$NMe$_2$)}] [292].

The reaction of [M(CO)$_6$] (M = Cr, Mo, W) with [PPN][NO$_2$] in the presence of Me$_3$NO gave [PPN][M(CO)$_5$(NO$_2$)] in which the nitrite is bound through N [293]. The π-bonding in [Mo(CO)$_5$(quinuclidine)] and its tungsten analogue has been studied by measuring the ^{13}C and ^{17}O NMR spectroscopic spin lattice relaxation times, and from these the values of the ^{17}O quadrupolar coupling constants and CO π^* orbital populations. The CO strengthening induced by the presence of the amine is strongly *trans*-directed [294]. The influence of solvent on the absorption spectra of [Mo(CO)$_4$(bpy)] in which the bpy ligand bears a range of substituents has been studied, but cannot be correlated with solvent polarity, presumably because of structural distortions induced by the substituents [295].

Reaction of [Mo(CO)$_4$(L$_2$)] (L$_2$ = CH$_2$pz$_2$ or CH$_2$pz$_2^*$) with NO$^+$ in MeOH afforded [Mo(CO)$_2$(NO)(MeOH)(L$_2$)]$^+$. The reactivity of the CH$_2$pz$_2^*$ complexes was studied: the MeOH can be replaced by a range of nucleophiles (X$^-$, N$_3^-$, SCN$^-$, OAc$^-$, CN$^-$, py) while with phosphines, [Mo(CO)(NO)(PR$_3$)$_2$(L$_2$)]$^+$ (R = Ph, Me, OMe) was formed and with didentate ligands (L$_2'$) such as bpy, phen or dppm, [Mo(CO)(NO)(L$_2$)(L$_2'$)]$^+$ resulted. Reaction with Nadtc (dtc = S$_2$CNMe$_2$, S$_2$CNEt$_2$) gave [{Mo(CO)$_2$(NO)(dtc)}$_2$] (**25**) with displacement of L$_2$ [296]. The synthesis of [Mo(CO)(NO)(dtc)(PR$_3$)$_2$] (same R) and [Mo(CO)$_2$(NO)(dtc)(X)]$^-$ (X = Cl, Br, NCS, N$_3$) has also been reported [297]. The reaction of [Mo(CO)$_4$(pip)$_2$] with BuLi and CS$_2$ affords [Mo(CO)$_4$(S$_2$CNC$_5$H$_{10}$)]$^-$ in high yield by insertion of CS$_2$ into the Mo–N bond [298].

The reaction of [M(CO)$_6$] (M = Cr, Mo, W) with bis(2-pyridyl)amine afforded [M(CO)$_4$(L)] in which the ligand is didentate [299]. The ligand 4,4′,4″-tri-^{t}Bu-terpy reacted with [Mo(CO)$_4$(nbd)] to give [Mo(CO)$_4$(L)] which shows a typical on-off terpy fluxionality. Oxidation with I$_2$ or SnBr$_4$ caused ligand breakdown to complexes of 4,4′-di^{t}Bu-bpy [300]. The ligand 3,5,6-tris-(2-pyridyl)-1,2,4-triazine forms a complex [Mo(CO)$_4$L] which can then use its



(25)

remaining coordination sites to bond to $[M(hfacac)_2]$ fragments (M = Mn, Fe, Co, Ni, Cu, Zn) [301].

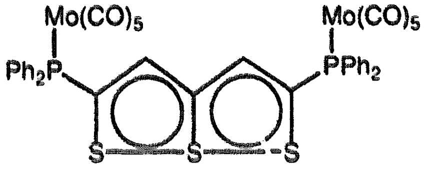
The functionalized imines $R^1R^2C{=}NCH_2CH_2N{=}CR^1R^2$ (R^1 = Me, R^2 = Ph) have been made into complexes $[Mo(CO)_4(L)]$. Because of the restricted rotation about the double bonds, several isomers are possible; in some cases, heating caused isomerization [302]. The amine portion of the oxalamidine complexes $[Mo(CO)_4\{ArN{=}C(NHAr)C(NHAr){=}NAr\}]$ (Ar = Ph, *p*-tol) can coordinate to other metal fragments as a didentate dianionic ligand by reaction with Cl_2ML_n (ML_n = $TiCp_2$, $SnMe_2$, $SiMe_2$). Deprotonation enabled crystallization of the sodium salt of the monoanion as $[Na_2(thf)_8][Mo(CO)_4\{ArN{=}C(NAr)C(NHAr){=}NAr\}]_2$ [303]. A similar ligand prepared from 2-pyridylmethylamine and $ArN{=}C(Cl)C(Cl){=}NAr$ has also been complexed to the $Mo(CO)_4$ fragment and deprotonated with $NaN(SiMe_3)_2$ [304].

The complexes *trans, mer*-$[Mo(CO)_3(PR_3)_2(\mu\text{-}L)Mo(PR_3)_2(CO)_3]$ (R = ^{i}Pr, Cy) where L = 4,4′-bpy, pyrazine, or 3,6-bis(4-pyridyl)tetrazine have been prepared and their spectroscopic and electrochemical properties studied. They undergo oxidation to mixed valence monocations which are completely delocalized, and also reduction to radical anions which lose one phosphine ligand. Mononuclear analogues $[Mo(CO)_3(PR_3)_2(L)]$ where L = thf or H_2 were studied for comparison [305]. Similar dinuclear species $[Mo(CO)_3(PBu_3)_2(\mu\text{-}L)Mo(PBu_3)_2(CO)_3]$ where L = 2,2′-bipyrimidine or 2,5-bis(2-pyridyl)pyrazine have also been made; the combination of two electron rich metal centres and a π-accepting ligand means that the HOMO-LUMO energy gap is small, leading to a difference of around 1 V between their reversible oxidation and reduction processes. In the case of the bipyrimidine complex these processes occur at the metal, but reduction of the pyrazine complex leads to occupation of the ligand π* orbitals [306].

Substituted hexahydrotriazines, $(RNCH_2)_3$, can be complexed to the $Mo(CO)_3$ fragment and oxidized under carefully controlled conditions to $[LMoO_3]$ [307]. Complexation reactions of linear tri- and tetramines with $[M(CO)_6]$ (M = Cr, Mo, W) can give rise to a variety of species such as $[M(CO)_4L]$, $[\{M(CO)_4\}_2L]$ and $[M(CO)_3L]$ depending both on M and the chain length of the ligand. Having a longer spacer group in the middle of the chain, such as in $H_2N(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$ encouraged the formation of dinuclear species

[308]. In a similar way, complexation reactions of various tetraazamacrocycles with $[M(CO)_6]$ gave $[M(CO)_4L]$, $[M(CO)_3L]$ or $[M(CO)_2L]$ depending on ring size. Increasing the length of the spacer groups between the nitrogen donors from 2 methylene groups to 3 or 4 encouraged the formation of the tetracarbonyl species [309]. Selective functionalization of one nitrogen atom of cyclen (1,4,7,10-tetraazacyclododecane) and cyclam (1,4,8,11-tetraazacyclotetradecane) can be achieved via their $M(CO)_3$ complexes in two ways: reaction with an enolizable aldehyde to produce an enamine which is then reduced with $NaBH_4$, or reaction with an acyl chloride followed by reduction with $BH_3 \cdot SMe_2$ [310].

To investigate the π-acceptor behaviour of halophosphine ligands, the X-ray structures of $[M(CO)_5(PX_3)]$ (M = Cr, Mo; X = Cl, Br) and $[Mo(CO)_5(PMe_3)]$ were analysed. Although the study supports the presence of a π-backbonding component, no convincing evidence was obtained for the involvement in it of P–X σ^* orbitals [311]. On the other hand, a ^{95}Mo, ^{31}P and ^{13}C NMR spectroscopic study of compounds of the type $[Mo(CO)_{6-n}(L)_n]$ (n = 1–3) where $L = PPh_{3-m}Cl_m$ (m = 0–3) concluded that PCl_3, although previously considered a good π-acceptor, is actually a poor one; it appears that a weak σ-donor can still form a short M–L bond without a strong π-bonding component [312].



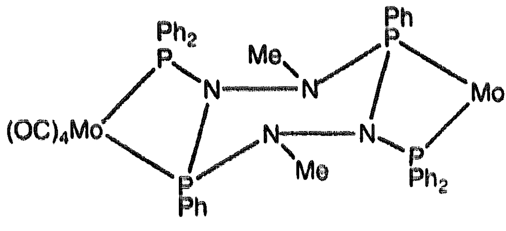
(26)

The first metal complex of a trithiapentalene fragment, (**26**), has been prepared by cyclization of $[Mo(CO)_5\{PPh_2C(=S)SCH_2C\equiv CH\}]$ in the presence of NEt_3. If a primary amine such as $EtNH_2$ or $PhCH_2NH_2$ was used, $[Mo(CO)_5\{PPh_2C(=S)NHR\}]$ was formed instead [313]. The ligand *o*-$H_2PC_6H_4CH_2EH$ (E = O, NPh) forms simple adducts $[Mo(CO)_5(L)]$ bound through the phosphine, whereas *o*-$C_6H_4(PH_2)_2$ forms both a bis-adduct and a chelate $[Mo(CO)_4(L)]$ [314]. Deprotonation of $^tBu_2Si(OH)_2$ and reaction with PPh_2Cl gave the diphosphinite ligand $^tBu_2Si(OPPh_2)_2$ which was made into a chelate complex $[Mo(CO)_4(L)]$ [315]. The crystal structure of $[Mo(CO)_4(naphos)]$, where naphos = the chiral phosphine 2,2′-bis(diphenylphosphinomethyl)-1,1′-binaphthyl, has been determined; molecular mechanics calculations show a good agreement with the observed structure [316].

The complexation reaction of $HgCl_2$ with the polyether macrocycle complexes *cis*-$[Mo\{PPh_2(CH_2CH_2O)_nCH_2CH_2PPh_2\}]$ depends on the ring size; if n = 5 a complex is formed, but if n = 4 the ring is not large enough and instead the Hg^{2+} catalyses the isomerization of the complex from *cis* to *trans* [317]. The assembly and X-ray structure of $[Mo(CO)_4\{Ph_2P(CH_2)_8PPh_2\}_2Mo(CO)_4]$, which contains a 22-membered ring, has been described. The related phosphine $Ph_2P(CH_2)_6PPh_2$ formed a simple mononuclear chelate [318].

The reaction of [Mo(CO)$_4$(nbd)] with (R$_2$NPO)$_3$ (R = ^{i}Pr, Cy) gave initially [Mo(CO)$_4${(R$_2$NPO)$_3$}] which transformed into the known tetraphosphoxane cage species [(OC)$_4$Mo{P(NR$_2$)O}$_4$Mo(CO)$_4$]. The heteronuclear species [(OC)$_4$Mo{P(NR$_2$)O}$_4$ML$_n$] where ML$_n$ = NiBr$_2$ or Fe(CO)$_3$, were also described [319].

The synthesis of a range of pyrrollyl phosphines and their complexes, including [Mo(CO)$_4$(L)] where L = (C$_4$H$_4$N)$_2$PCH$_2$CH$_2$P(NC$_4$H$_4$)$_2$, has been described. The ligands are poor σ-donors but reasonable π-acceptors [320]. Coordination of the phosphite hydrazide (RO)$_2$PNMeNMeP(OR)$_2$ to the Mo(CO)$_4$ fragment occurred as a simple 5-membered ring chelate [321]. Treatment of the cyclic phosphorus hydrazide [{PhPNHNMe}$_2$] with PPh$_2$Cl and base led to [{PhPN(PPh$_2$)NMe}$_2$], which was complexed to two metal tetracarbonyl units to form the bis-chelate complex [{PhPN(PPh$_2$)NMe}$_2${Mo(CO)$_4$}$_2$] (**27**) [322]. The complex [Mo(CO)$_4${P(OR)(NPh)$_2$P(OR)}$_2$] R = *p*-tol, CH$_2$CF$_3$) can use the two pendant aminophosphites as ligands towards other metal-ligand fragments to give [Mo(CO)$_4${μ-P(OR)(NPh)$_2$P(OR)}$_2$ML$_n$] (ML$_n$ = Mo(CO)$_4$, PdCl$_2$, PtCl$_2$). In a similar way, two equivalents of *cis*-[Mo(CO)$_4$(L){P(OR)(NPh)$_2$P(OR)}] where L = pip or P(OMe)$_3$ reacted to give [Mo(CO)$_4$(L){P(OR)(NPh)$_2$P(OR)}]$_2$ML$_n$ [323]. The reaction of *fac*-[Mo(CO)$_3$(MeCN)(L$_2$)] where L$_2$ = Ph$_2$PN^{i}PrPPhpz* bonded as a *P,P*-chelate, with didentate ligands such as HN(PPh$_2$)$_2$, dppm or dppe gave monodentate complexes which can be used to construct heterodinuclear complexes. Oxidation of the η^1-dppm complex occurred at the pendant arm to give the monoxide, which was structurally characterized [324].



(27)

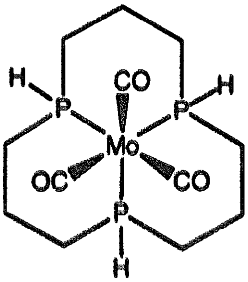
The reaction of [Mo(CO)$_4$(nbd)] with PPh(CH$_2$CH$_2$PPh$_2$)$_2$ followed by addition of [Mo(CO)$_6$] and Me$_3$NO gave [Mo(CO)$_4$(μ-L)Mo(CO)$_5$] in which the phosphine is didentate at one metal and monodentate at the other. The related isomeric species [Mo(CO)$_3$(μ-L')Mo(CO)$_5$] and [Mo(CO)$_4$(μ-L')Mo(CO)$_4$], in which L' is P(CH$_2$CH$_2$PPh$_2$)$_3$ and is either tridentate/monodentate or didentate at both metal centres, has also been made, as have various heterometallic examples [325], [326]. A Mo(CO)$_5$ fragment has also been coordinated to the pendant phosphine of [CpRu(Cl){(PPh$_2$)$_2$CHCH$_2$PPh$_2$}] [327]. Deprotonation of [Mo(CO)$_4$(dppm)] and reaction with RHgCl (R = Me, Et, Ph, Fc) gave [Mo(CO)$_4${(PPh$_2$)$_2$CHHgR}] [328].

Free radical cyclization of the allylphosphine complex *fac*-[Mo(CO)$_3${PH$_2$-(CH$_2$CH=CH$_2$)}$_3$] gave [Mo(CO)$_3$(PHCH$_2$CH$_2$CH$_2$)$_3$] (**28**). The P-H units of the macrocycle can then be functionalized by deprotonation with BuLi and alkylation, or by addition to allyl amine [329]. Addition of halogens to

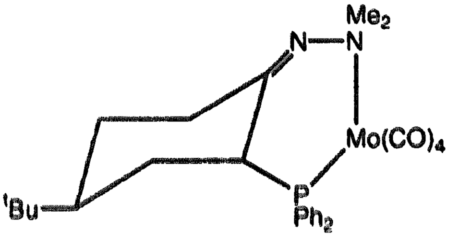
$[Mo(CO)_3\{(PRCH_2CH_2CH_2)_3\}]$ ($R = H$, ^iPr, CH_2SiMe_3) affords initially $[Mo(CO)_3(X)\{(PRCH_2CH_2CH_2)_3\}]^+$ and then $[Mo(CO)_2X_2\{(PRCH_2CH_2CH_2)_3\}]$ [330].

An electrochemical study of the photolysis of *fac*-$[Mo(CO)_3\{PPh(CH_2CH_2PPh_2)_2\}]$, which results in isomerization to the *mer* isomer, was unable to detect any intermediates involving loss of phosphine or CO [331]. The new tripodal phosphine ligands 1,3,5-tris(cyano)- and 1,3,5-tris(methoxycarbonyl)-1,3,5-tris(diphenylphosphino)cyclohexane have been prepared and incorporated into complexes *fac*-$[Mo(CO)_3(L)]$ [332,333]. The crystal structure of *fac*-$[Mo(CO)_3\{P(OPh)_3\}_3]$ has been determined [334].

The kinetics of the intramolecular substitution reaction of $[Mo(CO)_2(\eta^1\text{-}L)(PPh_3)_2(SO_2)]$ to afford $[Mo(CO)_2(\eta^2\text{-}L)(PPh_3)(SO_2)]$ (L = dmpe or dppe) have been studied in thf solution. The activation parameters indicate an associative mechanism; it was proposed that SO_2 may be able to change its coordination mode from η^2 to η^1 to allow this to happen. The substitution of SO_2 in $[Mo(CO)_3(\eta^2\text{-}L)(SO_2)]$ by phosphines can take place by dissociative or associative pathways. The crystal structure of $[Mo(CO)_2(dmpe)(PPh_3)(SO_2)]$ was determined [335,336].



(28)



(29)

The redox chemistry of $[MH(CO)_2(L_2)_2][OTf]$ (M = Cr, Mo, W; L_2 = dppm, dppe) has been investigated. There is a relationship between the potentials of the protonated species and the starting neutral carbonyl species. Oxidation gives a dication which can lose H^+ to give *trans*-$[M(CO)_2(L_2)_2]^+$, which itself can then be oxidized to a dication. Reduction of $[MH(CO)_2(L_2)_2]^+$ gave *cis*-$[M(CO)_2(L_2)_2]$ [337]. The reaction of $[Mo(CO)(L_2)_2]$ ($L_2 = R_2PCH_2CH_2PR_2$; R = Ph, ^iBu) with SiH_4 gave the first transition metal complex of silane itself, $[Mo(CO)(\eta^2\text{-}H\text{–}SiH_3)(L_2)_2]$. Where R = Et, this compound is in equilibrium with the oxidative addition product $[MoH(SiH_3)(CO)(L_2)_2]$ [338].

The phosphinimine ligand $Ph_3P{=}N(CH_2)_3PPh_2$ reacts with $[Mo(CO)_5Br]^-$ to afford $[Mo(CO)_4(L)]$ in which it acts as a simple *P,N*-chelate, but with $[Mo(CO)_6]$ it undergoes an unusual reaction to give the isocyanide complex $[Mo(CO)_5\{CN(CH_2)_3PPh_2\}]$ [339]. Coordination of the ligand $^tBuN{=}S{=}NP(^iPr)_2$ to $[M(CO)_5(thf)]$ (M = Cr, Mo, W) occurs initially through P to give $[Mo(CO)_5(L)]$, which on standing in sunlight decarbonylates to the five-membered *P,N*-chelate complex $[Mo(CO)_4(L)]$ [340]. Lithiation of

4-^{t}Bu-cyclohexanone dimethylhydrazone at the 2-position and reaction with PPh_2Cl gave a ligand which formed $[Mo(CO)_4(L)]$ (**29**) [341]. A *P,N*-chelate complex $[Mo(CO)_4(L)]$ was also made from an oxazaphosphorinane ligand with a pendant tmeda moiety [342]. The X-ray crystal structure of $[Mo(CO)_4\{PPh(CH_2CH_2CH_2NH_2)_2\}]$ has been determined, confirming that it is a tetracarbonyl and not as previously thought a tricarbonyl [343]. Functionalization of $[Mo(CO)_3\{Ph_2PCH_2C(^tBu){=}NN{=}C(^tBu)CH_2PPh_2\}]$ with BuLi and MeI occurred by deprotonation and alkylation at the methylene group [344]. Complexation of the thioether azine phosphine $Ph_2PCH_2C(^tBu){=}NN{=}CMeCH_2Stol$ to $[Mo(CO)_4(nbd)]$ gave the *P,N*-chelate $[Mo(CO)_4(L)]$, whereas with $[Mo(CO)_3(cht)]$ the *P,N,S*-bonded species $[Mo(CO)_3(L)]$ was formed [345].

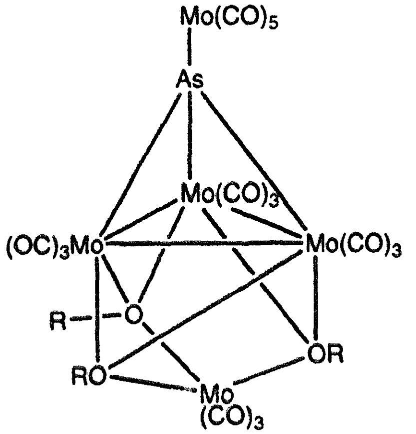
Comparison of the rates of free ligand release by solvolysis of $[Mo(CO)_3L]$ in dmso showed that the complex where L = [9]ane-S3 is approximately 4×10^5 slower than for where L is the linear thioether 2,5,8-trithianonane [346]. The reaction of $[Mo(CO)_5(thf)]$ with $2,6\text{-}NC_5H_3(CH_2SR)_2$ (R = Me, *p*-tol) gave $[Mo(CO)_4(L)]$ in which three fluxional processes operate: inversion at the coordinated sulfur, coordination switching between the two sulfur atoms, and a combined switch and inversion; activation energies for all three were determined [347].

The reaction of $[M(CO)_5(thf)]$ (M = Cr, Mo, W) with $[Cp_2M'(H)(PPh_2)]$ (M′ = Mo, W) gave $[Cp_2M'(H)(\mu\text{-}PPh_2)M(CO)_5]$ and metal-metal bonded $[Cp_2M'(\mu\text{-}H)(\mu\text{-}PPh_2)M(CO)_4]$; the latter could also be made from $[M(CO)_4(nbd)]$ in the same way [348]. A number of similar heterodinuclear complexes have been made by a similar approach, including $[Cp_2Nb(CO)(\mu\text{-}SEt)Mo(CO)_5]$ [349], $[Cp_2Ta(CO)(\mu\text{-}PMe_2)Mo(CO)_5]$ [350], $[(\eta\text{-}C_5H_4{}^tBu)_2Ta(H)(\mu\text{-}S)Mo(CO)_5]$ [351] and $[Cp_2Zr\{\mu\text{-}P(SiMe_3)_2\}_2Mo(CO)_4]$ [352]. The reaction of $[Cp^*Ti(NMe_2)_3]$ with $[M(CO)_6]$ (M = Cr, Mo, W) afforded firstly the carbene complex $[Cp^*Ti(NMe_2)_2\{OC(NMe_2){=}M(CO)_5]$ and then $[Cp^*Ti(\mu\text{-}NMe_2)_2(\mu\text{-}CONMe_2)M(CO)_3]$ on heating [353]. An adduct of $[Mo(CO)_6]$ with $[Nb_2Cl_8(dppe)_4]$ has also been reported [354].

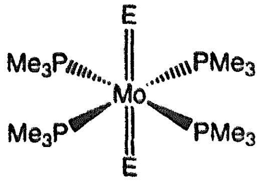
The reaction of $[M(CO)_3(L_2)(\eta^1\text{-}dppm)]$ (M = Mo, W; L_2 = bpy, phen) with $[\{RhCl(diene)\}_2]$ gave $[(OC)_2(L_2)M(\mu\text{-}CO)(\mu\text{-}dppm)RhCl(diene)]$ [355]. The complexes $[(dppe)Rh(\mu\text{-}CO)_2M(CO)_3]$ (M = Cr, Mo, W) have also been prepared and tested for catalytic activity [356]. Reduction of $[(OC)_3Mn(\mu\text{-}Br)(\mu\text{-}S_2PR_3)Mo(CO)_3]$ (R = Cy, ^{i}Pr), treatment with Ph_3SnCl and with a didentate phosphine such as dppm or tedip gave $[(OC)_2Mn(\mu\text{-}L_2)(\mu\text{-}S_2CPR_3)Mo(CO)(SnPh_3)]$ in which the coordination mode of the S_2CPR_3 ligand has been reversed [357]. Deprotonation of $[ReH_7(PPh_3)_2]$ and reaction with $[Mo(CO)_3(diglyme)]$ afforded $[(Ph_3P)_2ReH_6Mo(CO)_3]^-$. The related Cr and W complexes were also made, and three bridging hydrides are postulated on the basis of structural and NMR spectroscopic evidence [358].

Heating a mixture of $[Fe_3(CO)_{12}]$, $[Mo(CO)_6]$ and Na_2Te_2 with PPh_4Br in a sealed tube gave $[Fe_2(CO)_6(\mu\text{-}Te)\{\mu\text{-}TeTeMo(CO)_5\}]^{2-}$ which consists of a $Mo(CO)_5$ fragment coordinated to the known $[Fe_2(CO)_6(\mu\text{-}Te)(\mu\text{-}Te_2)]^{2-}$ ion [359]. Heating $[Mo(CO)_6]$ with $NaAsO_2$ in MeOH or EtOH gave

$[NEt_4]_2[(OC)_5MoAsMo_3(CO)_9(\mu_3\text{-}OR)_3Mo(CO)_3]$ (**30**) which contains a Mo_3As tetrahedron. The cluster has 50 electrons against an expected value of 48; calculations show that the extra lone pair is located in the Mo_3 triangle [360].



(30)



(31)

8.2. Complexes with nitrogen and phosphorus donor ligands

Reduction of $MoCl_5$ with Na/K alloy in neat PMe_3 solvent gave $[Mo(PMe_3)_6]$, which is in equilibrium with $[MoH(CH_2PMe_2)(PMe_3)_4]$ and free phosphine. Reaction of these complexes with H_2S, H_2Se or elemental Se, or Te and PMe_3 gave *trans*-$[Mo(E)_2(PMe_3)_4]$ (**31**; E = S, Se, Te) which were all structurally characterized. The Mo=E bond length increases down the group from 2.253(1) to 2.381(1) to 2.597(1) Å [361]. The reaction of $[MH_2(PMe_3)_5]$ (M = Mo, W) with elemental tellurium afforded $[MH_2(\eta\text{-}Te_2)(PMe_3)_4]$; both compounds are isostructural. Decomposition with loss of H_2 gave $[Mo(Te)_2(PMe_3)_4]$ among other products, showing oxidative cleavage of the ditelluride ligand [362].

The reduction of $[MoCl_3(PEt_3)_3]$ with Na/Hg under 2–3 atm of N_2 gave the μ-N_2 complex $[\{Mo(N_2)_2(PEt_3)_3\}_2(\mu\text{-}N_2)]$. This reacts with 3 equivalents of PMe_3 to give *trans*-$[Mo(N_2)_2(PMe_3)_3(PEt_3)]$, with 4 equivalents to give *trans*-$[Mo(N_2)_2(PMe_3)_4]$, and with a larger excess to give $[Mo(N_2)(PMe_3)_5]$ which was structurally characterized. The complexes $[Mo(N_2)(PMe_3)\{N(CH_2CH_2PMe_2)_3\}]$ and $[Mo(N_2)(PMe_3)_3(L_2)]$ where L_2 = dmpm, dmpe or depe were also prepared [363].

The reaction of *trans*-$[Mo(N_2)_2(depe)_2]$ with ethyl acetate is now known to give $[\{Mo(CO)(depe)_2\}_2(\mu\text{-}N_2)]$, as shown by an X-ray structure and not, as previously thought, $[Mo(CO)(depe)_2]$. However heating in refluxing xylene expels N_2 and produces the monocarbonyl. In contrast the analogous compound with the $^tBu_2PCH_2CH_2P^tBu_2$ ligand does form the monocarbonyl directly on treatment with EtOAc [364]. The reaction of *trans*-$[Mo(N_2)_2(L_2)_2]$ (L_2 = dppe, depe) with $HC(=S)NMe_2$ gave $[MoH\{\eta^2\text{-}C(=S)NMe_2\}(L_2)_2]$, which in turn rearranges to the hydrosulfide-carbyne complex $[Mo(SH)(\equiv CNMe_2)(L_2)_2]$, probably by way of a

Fischer thiocarbene [365]. The photoelectron spectra of *trans*-$[Mo(N_2)_2(dppe)_2]$ and $[MoBr(NNH_2)(dppe)_2][Br]$ have been recorded [366].

The complex *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ has been labelled with $^{15}N_2$. Subsequent reaction with unlabelled $NOBF_4$ or NO_2BF_4 gave $^{15}N^{14}NO$, ^{15}NO and $^{14}N^{15}N$, probably via a protonated species, as the same products were obtained from $[Mo(N_2H_2)(Cl)_2(PMe_2Ph)_3]$ [367].

Protonation of *trans*-$[Mo(CNMe)_2(dppe)_2]$ with HBF_4, HPF_6, or HCl gave *trans*-$[MoX(\eta^2\text{-}MeNHC{\equiv}CNHMe)(dppe)_2]^+$ (X = F, Cl) through coupling of the two isonitrile ligands to form an alkyne. The diprotonated species, *trans*-$[Mo(CNHMe)_2(dppe)_2]^{2+}$, was isolated. A detailed examination of the mechanism showed that the monoprotonated species $[Mo(CNHMe)(CNMe)(dppe)_2]^+$ underwent a rate-limiting migration to $[MoH(CNMe)_2(dppe)_2]^+$ [368,369].

The reactivity of $[Mo(NO)_2Cl_2]$ towards ligands such as PPh_3, $O{=}PPh_3$ and $Me_3SiN{=}PPh_3$ has been explored. Crystal structure determinations of the products $[\{MoCl_2(NO)_2(O{=}PEt_3)\}_2]$, $[MoCl_3(NO)(O{=}PPh_3)_2]\cdot[MoCl_4(O{=}PPh_3)]$, $[MoCl_2(NO)(PPh_3)_2(MeCN)]$ and $[MoCl_4(NPPh_3)(O{=}PPh_3)]$ were carried out [370]. The complexes $[MoCl_2(NO)_2(L)_2]$ where L = py, $NC_5H_4\text{-}4\text{-}NMe_2$ or isoquinoline) have been prepared and treated with L and $AgClO_4$ to afford cationic species $[Mo(NO)_2L_4]^{2+}$ [371].

9. Molybdenum clusters

9.1. *Polyoxomolybdates*

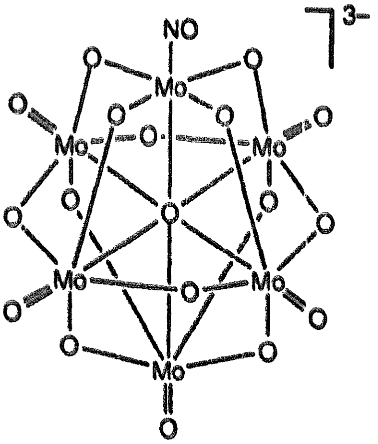
The following brief discussion is arranged in order of increasing nuclearity, dealing first with homonuclear species and then with heteropolymolybdates. As well as those mentioned in the Introduction, two review articles have appeared on polyoxometalate chemistry [372,373].

The reaction of ammonium molybdate with *R*- or *S*-malic acid (H_3mal) gave $[NH_4]_4[Mo_4O_{11}(mal)_2]$ which contains two Mo_2O_5 units linked by a further oxygen [374]. The complex $[NBu_4]_2[Mo_4O_{10}(OC_{10}H_6O)_2(OMe)_2]$, containing a 2,3-dihydroxynaphthalene ligand, has been characterized [375]. The synthesis of $[Mo_4O_{12}\{RC(NH_2)NO\}_2]^{2-}$ (R = ^iPr, Pr, CH_2SMe) by treatment of precursors with substituted acetamidoximes has been reported, together with the crystal structure of the R = ^iPr derivative [376]. The related species $[Mo_5O_{12}(NO)_2\{RC(NH_2)NHO\}_2\{RC(NH)NO\}_2]$ have also been made, containing two $Mo_2O_5^{2+}$ units and a central $Mo(NO)_2$ fragment [377].

Full details of the self-assembly of pentamolybdodiphosphonate cages in the complexes $[C(NH_2)_3][Mo_5(PR)_2O_{21}]$ where $R = CH_2NH^+(CH_2CH_2)_2E$ (E = O, S, CH_2), have appeared. There are short C–H···O contacts between the aminomethyl moiety and the cage, presenting a possible model for the interaction of organic substrates with polyoxometalate catalysts [378]. Monitoring the assembly reaction between RPO_3H and $[MoO_4]^{2-}$ by ^{31}P NMR spectroscopy reveals the presence of several intermediates, some of which interconvert [379]. The synthesis and structure of $K_3Na[Se_2Mo_5O_{21}]\cdot 2H_2O$ have been reported [380].

The $[CpFe(\eta\text{-}C_5H_4CH_2NMe_3)]^+$ salt of the $[Mo_6O_{19}]^{2-}$ ion has been crystallized. The X-ray structure shows some interaction between the Cp ligand and the surface of the polyoxoanion. Laser flash photolysis produced transient dications and trianions by charge transfer from the Fe^{2+} centre [381]. Salts with hemicyanine dyes such as $Me_2NC_6H_4CH{=}CHC_5H_4NMe^+$ as the counterion have also been prepared [382], and the anion has also been crystallized as a sodium salt in the presence of dibenzo-18-crown-6 [383]. A single crystal of $[NBu_4]_2[Mo_6O_{19}]$, in combination with $EtAlCl_2$, catalysed the ring-opening polymerization of norbornene. Improved yields of soluble polymers are obtained in the presence of a chain transfer reagent such as 1-hexene [384]. Reduction of $[Mo_6O_{19}]^{2-}$ to the trianion and its UV–VIS spectrum have been reported [385].

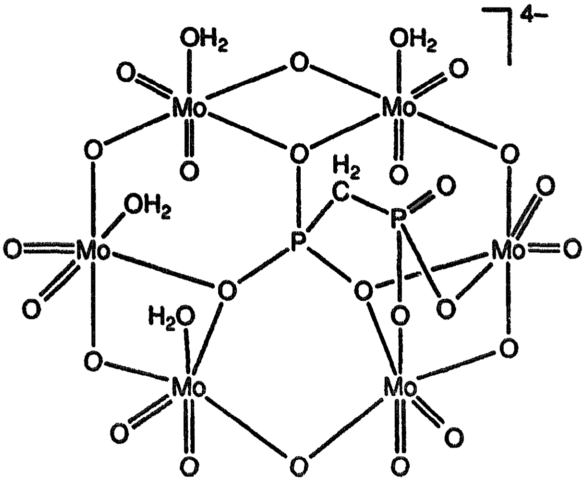
Progress has continued to be made in the functionalization of $[Mo_6O_{19}]^{2-}$ with imido groups. Using FcNCO, a ferrocenylimido unit can be incorporated to give $[Mo_6O_{18}(NFc)]^{2-}$; the electronic spectrum showed a new charge transfer band from Fe^{2+} to the cluster [386]. Reaction of $[Mo_6O_{19}]^{2-}$ with *p*-phenylene diamine gave $[Mo_6O_{17}(NC_6H_4NH_2)_2]^{2-}$ in which the two imido groups occupy *trans* positions in the cluster, raising the possibility that clusters could be linked together in a chain this way [387]. On the same theme, reaction with 0.5 equivalents of difunctional isocyanates such as $1,4\text{-}C_6H_4(NCO)_2$ gave clusters linked by the spacer group, for example $[O_{18}Mo_6(NC_6H_4N)Mo_6O_{18}]^{4-}$ [388].



(32)

The synthesis and structure of the mixed-metal ions $[Mo_5WO_{19}]^{2-}$ and $[Mo_{4.5}W_{1.5}O_{19}]^{2-}$ has been reported [389], [390]. The mixed anions $[V_2Mo_nW_{4-n}O_{19}]^{4-}$ (n=0–4) have been generated in solution and identified through ^{51}V NMR spectroscopy; the two V atoms are situated next to each other [391]. The complexes $[NBu_4]_3[M_5O_{18}M'(NO)]$ (32) where M, M'=Mo, W have been made in all combinations from $[Mo(NO)\{MeC(NH_2)NO\}(acac)_2]$ or $[W(NO)Cl_3(MeCN)_2]$ in combination with $[Mo_2O_7]^{2-}$ or $[WO_4]^{2-}$. They contain five M(VI) centres and one M'(II) [392]. Two salts which contain the cyclic

$[Mo_6O_{12}(OH)_3(O_3PPh)_4]^{5-}$ anion have been prepared by hydrothermal synthesis and structurally characterized; their relationship to $[Mo_2O_4Cl_3(H_2O)_3]^-$ was discussed [393]. The synthesis of the diphosphate complexes $[(O_3PXPO_3)Mo_6O_{18}(H_2O)_4]^{4-}$ (X=O, CH_2) and the crystal structure of the methylene compound (**33**) have been reported [394].



(**33**)

The crystal structure of $Cs_6[Mo_7O_{24}]\cdot 7H_2O$ has been determined [395]. A catalyst for alkane dehydrogenation has been prepared from the $[PtMo_6O_{24}]^{8-}$ anion [396]. The reaction of $[NHEt_3]_4[Mo_8O_{26}]$ with $MgCl_2$ or $CaCl_2$ gave $[NHEt_3]_2[Mg(H_2O)_6][Mo_8O_{26}]$ and $[NHEt_3]_3[(H_3O)Mo_8O_{26}]$, which were both structurally characterized [397]. A solution of the initial $[NHEt_3]^+$ salt in water and 2-butanol remained colourless when irradiated with UV light, whereas the Mg^{2+} salt and a related Na^+ salt went blue and released H_2 gas and 2-butanone quantitatively over a period of 24 h [398]. Acidification of sodium molybdate in the presence of lysine (lysH) produced $Na_2[Mo_8O_{26}(lysH_2)_2]$ in which the amino acids are coordinated through their carboxyl groups [399]. The crystal structure of $[Sm_2(H_2O)_{12}][Mo_8O_{27}]\cdot 6H_2O$ which consists of chains of $[Mo_8O_{27}]^{6-}$ clusters supported by hydrated Sm^{3+} cations, has been determined [400].

The electrochemistry of $K_{10}H_3[Dy\{SiMo_{11}O_{39}\}_2]$ and its incorporation into polypyrrole films have been investigated [401]. The basicity of the Co(II) centre in complexes such as $[Co\{PMo_2W_9O_{39}\}(H_2O)]^{5-}$ and $[Co\{SiMo_2W_9O_{39}\}(H_2O)]^{6-}$ has been studied [402].

Kinetic studies on the oxygen atom transfer reaction between α-$[PMo_{12}O_{40}]^{3-}$ or A-β-$[PMo_3W_9O_{40}]^{3-}$ and PPh_3 have shown that it is first order in both reagents. The activation parameters are similar for both anions, but the homometallic system has a higher rate constant [403]. The reaction of $[K(18C6)][PPN]_2[PMo_{12}O_{40}]$ (18C6=18-crown-6) with PPh_3 in MeCN gave $[K(18C6)]_2[PPN]_2$-$[HPMo_{12}O_{40}]\cdot 8MeCN$, containing a 2-electron reduced anion [404]. Salts of α-Keggin anions have been prepared with BEDT-TTF as cation [405]. A compound formulated as $[NH_4]_3[H_4PMo_{12}O_{40}]$ has been described [406].

The formation of $[H_4SiMo_{12}O_{40}]$ on silica-supported Mo oxide catalysts has been studied; Raman spectra show that during catalysis of methanol oxidation, it decomposes to MoO_3 [407]. The thermal stability of P- and Si-containing Keggin ions has been studied experimentally [408,409], while other articles deal with their stability from a theoretical viewpoint [410,411] or in terms of pH [412], and with their isomerization [413]. Thin polypyrrole films have been grown from solutions of phosphomolybdic acid [414].

The synthesis and catalytic properties of the $[PVMo_{11}O_{40}]^{4-}$ ion have been studied [415]. New ways of making $[H_{3+n}PMo_{12-n}V_nO_{40}]$ where n = 1-6, from H_3PO_4, MoO_3 and $[H_6V_{10}O_{28}]$ have been developed [416]. Three new compounds containing the $[PVMo_{11}O_{40}]^{6-}$, $[PV_2Mo_{10}O_{40}]^{7-}$ and $[PV_3Mo_9O_{40}]^{8-}$ anions have been isolated [417]. A new mixed valence species, $K_6[PMo_3W_9O_{40}]$, has been made [418], while electrochemical reduction led to the isolation of the $[SiVMo_2W_9O_{40}]^{6-}$ ion, which has a slightly distorted Keggin structure [419]. The electrochemical two step reduction of heteropolymolybdates has been studied in different solvents [420].

The compound $[Hmorph]_6[(V^{IV}, V^{V}, Mo_{10})VO_{40}]$ has been isolated from the reaction of MoO_3, NH_4VO_3 and morpholine. It consists of an α-Keggin structure with a VO_4 tetrahedron at the centre of twelve MO_6 octahedra, with the V^{4+}, V^{5+} and Mo sites randomly distributed. The ESR spectrum proves the existence of V^{4+} sites [421].

The $[H_6(P_2O_7)Mo_{15}O_{48}]^{4-}$ anion has been generated in solution from $[(P_2O_7)Mo_{18}O_{54}]^{4-}$ and isolated as the NPr_4^+ salt [422]. The crystal structure of the $[Mo_{16}V_{14}O_{84}]^{14-}$ anion, obtained by a hydrothermal synthesis, revealed that it consists of two $Mo_8V_7O_{42}$ subunits linked through two VO bonds; each half of the molecule is structurally similar to $[V_{15}O_{42}]^{9-}$ [423].

A flow channel electrochemical study of the photochemical properties of $[S_2Mo_{18}O_{62}]^{4-}$ showed that it is a powerful oxidant, being reduced by electron donors such as thf or toluene to the analogous 5− and 6− anions, but not further. The cluster is potentially a valuable photo-oxidant [424]. This same anion reacts with PPh_3 in MeCN to give the 4-electron-reduced species $[NBu_4]_5[H_3S_2Mo_{18}O_{62}]$ with the α-Dawson structure; the metal-metal distances become slightly elongated on reduction [404]. A four electron reduction wave was observed in the electrochemistry of $[(P_2O_7)Mo_{18}O_{54}]^{4-}$ [425]. Four new compounds of formula α-$[P_2W_{15}Mo_2NbO_{62}]^{7-}$ have been isolated [426]. The fused Keggin anion $K_8[P_2W_{18}Mo_2Co_2(H_2O)_2O_{68}][MoO_6]\cdot 15H_2O$ has been studied electrochemically [427].

The influence of the cation lattice in giant clusters has been explored by determining the crystal structure of $[NH_4]_{15}[Mo_{57}Fe_6(NO)_6O_{174}(OH)_3(H_2O)_{24}]\cdot 73H_2O$ and comparing it with the previously described $Na_3[NH_4]_{12}$ salt [428]. The synthesis and crystal structure of $Na_3H_3[H_8Mo_{57}Fe_6O_{185}(NO)_6(H_2O)_{16}(MoO)_2]\cdot 81H_2O$ has been reported; it consists of three Mo_{17} units associated with six FeO_6 octahedra and two Mo_2O_9 groups [429].

From a mixture of Na_2MoO_4, NH_4VO_3, $NH_2OH.HCl$, HCl and H_2O, the giant anion $[Mo_{154}(NO)_{14}O_{420}(OH)_{28}(H_2O)_{70}]^{(25\pm 5)-}$ was isolated. It is a cyclic structure consisting of 140 MoO_6 octahedra and 14 pentagonal bipyramidal $Mo(NO)O_6$ units. The NH_4^+ counterions are disordered, thus making it impossible to ascertain the overall charge on the cluster [430].

9.2. *Halide clusters*

The reaction of $[Mo_2(MeCN)_8]^{4+}$ with iodide gave the known butterfly cluster $[Mo_4I_{11}]^{2-}$ which was crystallographically characterized as its PPh_4^+ salt [431].

Calculations on six compounds of the type $[Mo_6Cl_8L_6]^n$ have been carried out in order to gauge the consequences of changing L from Cl^- to PH_3 or bpy; a significant effect on the electronic structure and optical properties is observed. The computations also predict a closed shell ground state and dipole forbidden LUMO to HOMO transition when L = halide, thought, to cause the long lived excited states of these clusters [432]. The nature of the interaction of $[Mo_6Cl_{14}]^{2-}$ and $[Mo_6Cl_8(OTf)_6]^{2-}$ with silica gel in organic solvents has been studied; both are adsorbed, but not from all solvents. In polar solvents such as MeOH the triflate groups are replaced to give $[Mo_6Cl_8(solvent)_6]^{2+}$ which interacts with the surface. The absorption and emission spectra of the adsorbed clusters are identical to those in solution [433].

The preparation of *cis*-$[Mo_6Cl_8(Cl)_4(PEt_3)_2]\cdot 2thf$ from *trans*-$[Mo_6Cl_8(Cl)_4(PR_3)_2]$ (R = pentyl) has been developed. Unusually for such species, adjacent Mo atoms bear the phosphine ligands [434]. The X-ray structure of $[Mo_6Cl_7(Te)Cl_6]^{3-}$, in which one of the inner cube of chloride ligands has been replaced by Te, has been determined [435]. The synthesis of two isomers of the double substitution product $[Mo_6Cl_6(Se)_2(Cl)_6]^{n-}$ where n = 3 and 4 has been described; the crystal structure of one isomer was determined in each oxidation state [436].

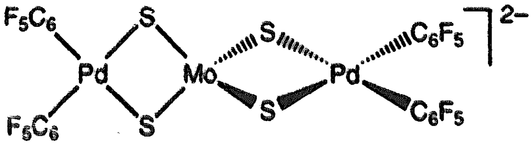
Treatment of $[NBu_4]_2[Mo_6Cl_8(OTf)_6]$ with KSH followed by $SbCl_5$ in MeCN produced $[Mo_6Cl_8(MeCN)_6][SbCl_6]_4$ by replacement of the triflate ligands [437]. A method for dispersing the Mo clusters in an organic polymer has been developed involving free radical polymerization of $[Mo_6Cl_8(L)_6][OTf]_4$ where L = *N*-vinylimidazole [438].

Calculated electronic spectra and XPS data for $[Mo_6E_8(PH_3)_6]$ (X = S, Se) were found to give good agreement with those observed experimentally for the PEt_3 derivative [439]. The thermal degradation of $[Mo_6S_8(L)_6]$ where L = propylamine, pyrrollidine or piperidine, has been investigated in an attempt to form Chevrel phases [440].

9.3. *Other clusters, including cubanes*

Heating $[M(CO)_6]$ (M = Mo, W) with Na_2S_2 in MeOH afforded the di- and trinuclear species $[(OC)_4MS_2MS_2]^{2-}$ and $[(OC)_4MS_2MS_2M(CO)_4]^{2-}$, which contain M(VI) and M(0) centres adjacent to each other [441]. The self assembly of $[Cl_2FeS_2MoS_2FeCl_2]^{2-}$ from $[MoS_4]^{2-}$ and $FeCl_2$ in dmf has been studied in the presence of dppm and dppe by UV–VIS spectroscopy; dppe inhibits the formation of the trinuclear species [442]. Aerial oxidation of the product reforms $[MoOS_3]^{2-}$

and $[MoS_4]^{2-}$ in a 1.5:1 ratio [443]. An article about multicentre bonding and quasi-aromaticity in various clusters including $[NEt_4][Cl_2FeS_2MoS_2Cu(PPh_3)_2]$ has appeared [444]. Treatment of $[NH_4]_2[MS_4]$ (M = Mo, W) with $[NBu_4]_2[\{M'R_2(\mu\text{-}OH)\}_2]$ (M′ = Pd, Pt; R = C_6F_5, C_6Cl_5) afforded $[NBu_4]_2[R_2M'S_2MS_2M'R_2]$ (e.g. 34). The X-ray structure of the PdW complex showed tetrahedral coordination at M and square planar at M′, with a metal–metal distance possibly indicative of some degree of bonding interaction [445]. A similar trinuclear species, $[Cp^*_2SmS_2MoS_2SmCp^*_2]^-$, containing an Mo(V) centre, was formed from the reaction of $[PPh_4]_2[MoS_4]$ with $[Cp^*_2Sm(thf)_2]$ [446]. The reaction of $[PPh_4]_2[MoSe_4]$ with two equivalents of AuCN in MeCN produced $[PPh_4]_2[(NC)AuSe_2MoSe_2Au(CN)]$, whereas in the presence of PMe_2Ph the monoanion $[PPh_4][(PhMe_2P)AuSe_2MoSe_2]$ was formed. Use of only one equivalent of gold reagent led to $[PPh_4]_2[(NC)AuSe_2MoSe_2]$ [447].



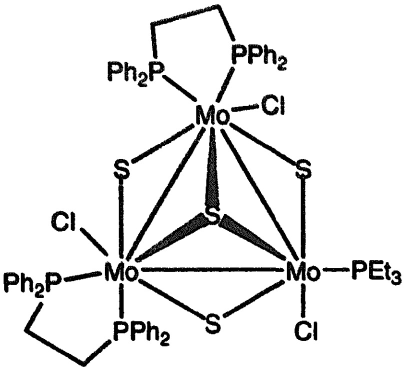
(34)

The reaction of $[Mo_3S_4(dtp)_4(H_2O)]$ where dtp = $[S_2P(OEt)_2]^-$ with $p\text{-}MeC_6H_4SO_3H$ in the presence of $CdCl_2$ and PPh_3 led to the new species $[Mo_3S_4(\mu\text{-}O_3SC_6H_4Me)(dtp)_3(EtOH)]$; an X-ray structure determination showed infinite chains of clusters linked by S···S contacts [448]. The electrochemical reduction of $[Mo_3S_4(CN)_9]^{5-}$ in one electron steps, resulting ultimately in expansion to $[Mo_4S_4(CN)_{12}]^{8-}$, has been reported [449].

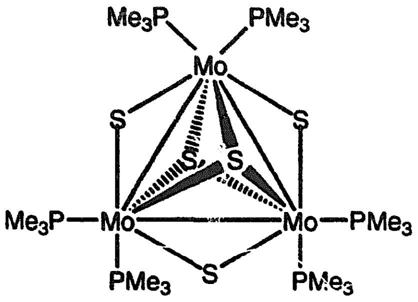
The X-ray structure of $[Mo_3S_7(dtc)_3Cl]$ (dtc = $S_2CNC_4H_8$) has been determined [450]. The reaction of $[Mo_3S_7Cl_4]$ with PEt_3 gave a compound formulated as $[Mo_3S_4Cl_4(PEt_3)_x(thf)_{5-x}]$, which was reduced with Mg and treated with dppe to give ultimately $[Mo_3S_4Cl_3(dppe)_2(PEt_3)]$ (35) which was structurally characterized; two molybdenums bear dppe ligands and the third the PEt_3 [451]. A series of lanthanide complexes $[M(dmso)_m(H_2O)_n]^{3+}$ (M = Pr, m = 6, n = 2; M = Tm, m = 6, n = 1; M = Eu, m = 7, n = 1) have been isolated using $[Mo_3S_7Br_7]^{3-}$ as counterion [452].

The first compound with a $Mo_3Te_7^{4+}$ core, $Cs_3[Mo_3(\mu_3\text{-}Te)(\mu\text{-}Te_2)_3(CN)_6(I)]$, has been prepared by the solid state reaction of Mo, Te and I at 380°C followed by reaction with aqueous CN^-. Three different crystalline forms were isolated [453]. A similar reaction using a different ratio of elements gave $[Mo_3(\mu_3\text{-}Te)(\mu\text{-}Te_2)_3(TeI_3)][I]$ in which each Mo bears a TeI_3 unit bound in an unusual didentate fashion through the Te and one of the iodides. Treatment with KCN gave $[Mo_3Te_7(CN)_6]^{2-}$ again [454].

The reaction of $[NH_4]_2[Mo_3S_{13}]$ with a large excess of PMe_3 afforded $[Mo_3(\mu_3\text{-}S)_2(\mu\text{-}S)_3(PMe_3)_6]$ (36) with an average Mo oxidation state of 3.33. The X-ray structure showed an equilateral triangle of Mo atoms with a bond length of 2.714(1) Å; calculations comparing this compound to $[Mo_3(\mu_3\text{-}S)_2Cl_9]^{3-}$, which has



(35)



(36)

an isosceles metal triangle, show this is caused by a reversal of HOMO and LUMO [455]. The XPS spectra obtained during sulfidation of MoO_3-silica catalysts have been compared to those of clusters such as $[Mo_3S_{13}]^{2-}$, thus showing the presence of S_2^{2-} ligands [456]. The hydrothermal synthesis of $[NH_4]_2[Mo_3S_{11.72}Se_{1.28}]$, which crystallizes in a layer structure with neutral Se_{12} molecules, from $Na_2S_3Se_3$ and $[MoS_4]^{2-}$ has been reported [457]. Hydrothermal treatment of MoO_3, Na_2Se_2 and NMe_4Cl (1:3:2 ratio) at 135°C for 3 days gave $[NMe_4]_2[Mo_3Se_{13}]$. The compound $K_6[Mo_6Se_{27}]\cdot 6H_2O$ was also prepared and contains two Mo_3Se_{13} clusters with Se^{2-} sandwiched between them [458].

A review of the synthesis of clusters starting from $[Mo_3S_4(dtp)_4(H_2O)]$ has appeared [459]. The incomplete cubanes $[Mo_3O_nS_{4-n}(dtp)_4(L)]$ where dtp = $S_2P(OEt)_2^-$ (n = 0-3, L = H_2O, MeCN, py) have been synthesized by addition of dtpH to $[Mo_3O_nS_{4-n}(H_2O)_9]^{4+}$. The crystal structures of $[Mo_3OS_3(dtp)_4(MeCN)]$ and of its reaction product with acetic anhydride, EtOH and py, $[MoOS_3(OAc)(dtp)_2(py)(OEt)]$, were determined. The ^{31}P NMR spectra of these clusters proved useful for assigning structures and studying interconversions [460,461].

The complex $[Mo_4S_4(dtp)_6]$ reacted with NaO_2CPh by replacement of the two bridging dtp ligands, yielding $[Mo_4S_4(\mu\text{-}O_2CPh)_2(dtp)_4]$ [462]. The reaction of $[W_2S_4(dtp)_4]$ with $[Mo(CO)_6]$ in $AcOH/Ac_2O$ gave the mixed cubane $[Mo_2W_2S_4(OAc)_2(dtp)_3(dtpH)]$; a statistical disorder of the four metals was observed in the X-ray structure [463]. A straightforward route for the construction of tetranuclear clusters from $Mo(CO)_6$ involves firstly reaction with $R_2P(S)S{-}SP(S)R_2$ (R = Et, Pr) to give $[Mo_2S_4(dtp)_2]$. Addition of $[W(CO)_3(MeCN)_3]$ and more disulfide gave the incomplete cubane $[Mo_2WS_4(dtp)_4]$; the remaining vertex can then be inserted with CuI [464].

Starting from $[Mo_3S_4(dtp)(H_2O)]$, the complexes $[Mo_3CuS_4(I)(\mu\text{-dtc})(dtc)_3(py)]$ (dtc = S_2CNEt_2) and $[Mo_3CuO_{0.75}S_{0.25}S_3(I)(O)_2(dtc)_3(py)]$ (dtc = $S_2CCC_4H_8$) were prepared by ligand substitution and reaction with CuI [465]. Clusters containing Mo or W, Cu and dtc ligands have been reviewed [466]. The reaction between $[MoO_nS_{4-n}]^{2-}$ and CuCl in the presence of Nadtc has been monitored by ^{95}Mo NMR spectroscopy [467].

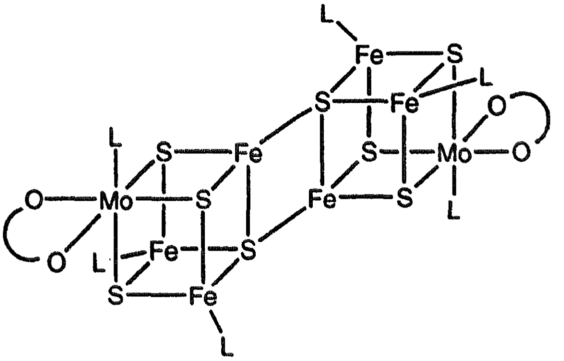
A number of papers have appeared on the use of $[MoS_4]^{2-}$ and $[MoSe_4]^{2-}$ in reactions with coinage metal compounds to form cubane clusters, especially in the solid state; two review articles deal with synthetic methods [468] and reactivity, in which the reactions undergone by these clusters were classified into five basic types [469]. The solid phase synthesis of the butterfly cluster $[MoOS_3Cu_2(PPh_3)_3]$ and a related tungsten species have been reported. These clusters show interesting self-focusing non-linear optical properties [470,471]. The related complex $[MoOS_3Cu_2(py)_2(PPh_3)_2]$ has also been prepared [472]. A solid state reaction between $[NH_4]_2[MoO_2S_2]$, CuBr and NEt_4Br led to $[NEt_3]_3[MoOS_3Cu_3Br_4]$ [473]. Similar reactions led to $[NBu_4]_2[MoOS_3Cu_3(SCN)_3]$ and $[NBu_4]_2[MoOS_3Cu_3(Br)Cl_2]$. In contrast to the butterfly clusters above, these three compounds have a nest-shaped structure and display interesting self-defocusing non-linear optical properties [474–476]. Reaction of the last cluster with py led to $[MoOS_3Cu_3(py)_5Br]$ [477]. The compounds $[MS_4Cu_3(AsPh_3)_3(I)]$ ($M = Mo$, W) have been made by low temperature solid state reactions [478]. The synthesis and crystal structure of $[MoS_4Cu_2Ag(PPh_3)_3Br]\cdot H_2O$ has been reported; it is the first example to contain both Cu and Ag [479]. The clusters $[NBu_4]_3[MoS_4Ag_3(Br)X_3]$ ($X = Cl$, I), which display optical limiting properties, have also been made [480].

The reaction of $[NH_4]_2[MS_4]$ ($M = Mo$, W) with AgBr and CuBr in 4-methylpyridine gave $[MS_4Cu_4(Mepy)_8][M_6O_{19}]$; the X-ray structure of the W complex showed that four edges of the WS_4 tetrahedron bear CuL_2 units [481]. A solid state reaction between $[NH_4]_2[MoOS_3]$, Cu_2S and NBu_4Br gave the giant cube $[NBu_4]_4[Mo_8Cu_{12}O_8S_{24}]$, which has Mo atoms at each corner and Cu atoms in the middle of each edge. The compound displays a large third-order non-linear molecular susceptibility [482]. The non-linear optical properties of the hexagonal prismatic cluster $[Mo_2S_8Ag_4(PPh_3)_4]$ have also been studied; it displays a large optical limiting response in MeCN or acetone solution [483].

A short account of some approaches to polynuclear assemblies of biological interest, including the $[MoFe_4S_6(PEt_3)_4Cl]$ cluster, has appeared [484]. The improved synthesis of some iron sulfido clusters has led to an improved route to the known cluster $[MoOFe_5S_6(CO)_{12}]^{2-}$ involving treatment of $[Fe_2S_2(CO)_6]$ with $LiBHEt_3$ to give a mixture of $[Fe_2S_2(CO)_6]^{2-}$ and $[Fe_4S_4(CO)_{12}]^{2-}$, then addition of $[MoOCl_3(thf)_2]$; the overall yield is over 50% [485].

Coucouvanis and co-workers have continued to examine the chemistry of $MoFe_3$ cubanes and double cubanes, often with the cluster $[MoFe_3S_4Cl_3(OC_6Cl_4O)(MeCN)]^{2-}$ serving as starting material. This compound has been found to reduce acetylene to ethylene and a small amount of ethane. Replacement of the labile MeCN with a more strongly bound ligand retards the reaction, implying bonding of the alkyne at the Mo, though the iron sites will catalyse the reaction but at a much slower rate. Monitoring the ESR spectra of the solution confirms that the integrity of the cluster is maintained [486].

Reaction of $[MoFe_3S_4Cl_3(OC_6Cl_4O)(MeCN)]^{2-}$ with oxalic acid gave the double cubane $[\{MoFe_3S_4Cl_4\}_2(\mu\text{-ox})]^{4-}$ whereas with oxalate $[MoFe_3S_4Cl_4(ox)]^{3-}$ was formed. One of the chloride ligands in the latter can be replaced by CN^- [487]. Treatment of the starting cluster with $HSCHRCO_2H$ gave double cubanes $[NEt_4]_4[\{MoFe_3S_4Cl_3(\mu\text{-}SCHRCOO)\}_2)]$, which show no ESR signal and catalyse hydrazine reduction. With thioglycollic acid, the single cubane $[MoFe_3S_4Cl_3(O_2CCH_2SCH_2CO_2)]^{2-}$ was formed in which the ligand acts as a tridentate chelate [488]. The reaction of $[MoFe_3S_4Cl_3(OC_6Cl_4O)(MeCN)]^{2-}$ with PEt_3 in the presence of $NaBPh_4$ or $NaPF_6$ gave edge-linked double cubanes $[\{MoFe_3S_4(PEt_3)_3(OC_6Cl_4O)\}_2]^{4+}$ (37) [489].



(37)

The functionalized macrocycle 1,4,7-tris(4-mercaptobenzoyl)-1,4,7-triazacyclononane (H_3L) coordinates as a tridentate thiolate ligand to the iron centres of $[MoFe_3S_4(SEt)_4(dmpe)]^-$ and $[MoFe_3S_4Cl_3(OC_6Cl_4O)(MeCN)]^{2-}$ to give respectively $[MoFe_3S_4(L)(SEt)(dmpe)]^-$ and $[MoFe_3S_4(L)(OC_6Cl_4O)(MeCN)]^{2-}$ [490]. The iron centres in $[Mo(CO)_3Fe_3S_4(SEt)_3]^{3-}$ can be spanned by another tridentate thiolate, 1,3,5-tris{(4,6-dimethyl-3-mercaptophenyl)thio}-2,4,6-tris(*p*-tolylthio)benzene [491].

Condensation of $[Mo_3O_4(H_2O)_9]^{4+}$ led to the Mo_{12} cluster $[\{Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(\mu\text{-}OH)_2(H_2O)_5\}_4][OTs]_8$, which consists of four incomplete cubane units bridged by OH groups; there are four distinct types of Mo–O distance [492]. Further developments in the chemistry of the incomplete cubane $[Mo_3S_4(H_2O)_9]^{4+}$ have been summarized in two articles [493,494]. Approximately 15 other metals have now been incorporated into this cluster. Its reaction with Fe gave $[FeMo_3S_4(H_2O)_{10}]^{4+}$ which was structurally characterized, as was the ammonia analogue $[FeMo_3S_4(H_2O)(NH_3)_9]^{4+}$. Both compounds show three successive electrochemical reductions, and the suggested oxidation states are $Mo^{IV}Mo_2^{III}Fe^{II}$ [495]. The reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with metallic lead in 2M HCl forms a useful route to the Mo(III) species $[Mo_4S_4(H_2O)_{12}]^{4+}$ in 80% yield [496].

The $[Mo_3S_4(H_2O)_9]^{4+}$ cluster and the cubanes $[MMo_3S_4(H_2O)_9(Cl)]^{3+}$ (M = Ni, Pd) have been incorporated into NaY zeolite, creating catalysts which are highly selective for the formation of C_2 species from CO/H_2 mixtures. Adding Ni^{2+} to the adsorbed incomplete cubane did not give the same activity, implying that the cubanes are adsorbed intact [497]. The complex $[PdMo_3S_4(tacn)_3Cl][PF_6]_3$ is a highly efficient and selective catalyst for the addition of carboxylic acids to activated alkynes, giving *trans*-products [498].

References

[1] M.J. Morris, Coord. Chem. Rev. 138 (1995) 121.
[2] M.J. Morris, Coord. Chem. Rev., 146 Part 1 (1995) 43.
[3] M.J. Morris, Coord. Chem. Rev. 152 (1996) 309.
[4] M.J. Romao, M. Archer, I. Moura, J.J.G. Moura, J. LeGall, R. Engh, M. Schneider, P. Hof, R. Huber, Science 270 (1995) 1170.
[5] H.B. Kraatz, P.M. Boorman, Coord. Chem. Rev. 143 (1995) 35.
[6] M. Hidai, Y. Mizobe, Chem. Rev. 95 (1995) 1115.
[7] Y. Mizobe, Y. Ishii, M. Hidai, Coord. Chem. Rev. 139 (1995) 281.
[8] A. Bakac, Prog. Inorg. Chem. 43 (1995) 267.
[9] H. Brand, J. Arnold, Coord. Chem. Rev. 140 (1995) 137.
[10] J. Arnold, Prog. Inorg. Chem. 43 (1995) 353.
[11] J.M. Rawson, R.E.P. Winpenny, Coord. Chem. Rev. 139 (1995) 313.
[12] K.V. Katti, V.S. Reddy, P.R. Singh, Chem. Soc. Rev. 24 (1995) 97.
[13] K.K. Pandey, Coord. Chem. Rev. 140 (1995) 37.
[14] M.L.H. Green, J. Organomet. Chem. 500 (1995) 127.
[15] K.C. Dash, J. Ind. Chem. Soc., 72 (1995) 359; Chem. Abstr., 123 (1995) 216692h.
[16] M.H. Chisholm, Ed. Early Transition Metal Clusters with π-Donor Ligands, VCH, New York, 1995: (a) R.E. McCarley, p. 27; (b) T. Saito, p. 63; (c) M.H. Chisholm, p. 165; (d) R.C. Haushalter, L.M. Meyer, J. Zubieta, p. 127; (e) M.I. Khan, J. Zubieta, p. 247.
[17] M.I. Khan, J.A. Zubieta, Prog. Inorg. Chem. 43 (1995) 1.
[18] C.L. Hill, C.M. Prosser-McCartha, Coord. Chem. Rev. 143 (1995) 407.
[19] M.H. Chisholm, Chem. Soc. Rev. 24 (1995) 79.
[20] M.H. Chisholm, I.P. Rothwell, Eds. Polyhedron, 14 (1995) No. 22.
[21] C.G. Young, A.G. Wedd, J. Inorg. Biochem. 59 (1995) 84.
[22] J. Inorg. Biochem., 59 (1995) 723.
[23] D. Coucouvanis, NATO ASI Ser., Ser C, 459 (1995) 247; Chem. Abstr., 123 (1995) 191852v.
[24] D.P. Kessissoglou, NATO ASI Ser., Ser C, 459 (1995) 385; Chem. Abstr., 123 (1995) 245069r.
[25] A. Müller, E. Krahn, Angew. Chem. Int. Ed. Engl. 34 (1995) 1071.
[26] G.J. Leigh, C.N. McMahon, J. Organomet. Chem. 500 (1995) 219.
[27] D. Sellmann, Curr. Plant Sci. Biotechnol. Agric., 27 (1995) 123; Chem. Abstr., 124 (1996) 358947q.
[28] V.Y. Kukushkin, Coord. Chem. Rev. 139 (1995) 375.
[29] H. Sloan, Ann. Rep. Prog. Chem., Sect A, 91 (1994) 177; Chem. Abstr., 124 (1996) 104430k.
[30] Gmelin Handbook of Inorganic, Organometallic Chemistry, 8th Ed., Mo: Supplement volume B, part 9, Springer-Verlag, Berlin, 1994.
[31] K.G. Caulton, M.H. Chisholm, S. Doherty, K. Folting, Organometallics 14 (1995) 2585.
[32] T. Lübben, M. Witt, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, Inorg. Chem. 34 (1995) 4275.
[33] P.W. Dyer, V.C. Gibson, J.A.K. Howard, B. Whittle, C. Wilson, Polyhedron 14 (1995) 103.
[34] P.W. Dyer, V.C. Gibson, W. Clegg, J. Chem. Soc., Dalton Trans., (1995) 3313.
[35] M. Buchmeiser, R.R. Schrock, Inorg. Chem. 34 (1995) 3553.
[36] B. Stempfle, S. Schmidt, J. Sundermeyer, H. Werner, Chem. Ber. 128 (1995) 877.
[37] W.-H. Leung, E.K.F. Chow, M.-C. Wu, P.W.Y. Kum, L.-L. Yeung, Tetrahedron Lett. 36 (1995) 107.
[38] D.L. Morrison, D.E. Wigley, J. Chem. Soc., Chem. Commun., (1995) 79.
[39] D.L. Morrison, D.E. Wigley, Inorg. Chem. 34 (1995) 2610.
[40] V.C. Gibson, C. Redshaw, W. Clegg, M.R.J. Elsegood, J. Chem. Soc., Chem. Commun., (1995) 2371.
[41] W.M. Vaughan, K.A. Abboud, J.M. Boncella, J. Organomet. Chem. 485 (1995) 37.
[42] Z. Xiao, M.A. Bruck, C. Doyle, J.H. Enemark, C. Grittini, R.W. Gable, A.G. Wedd, C.G. Young, Inorg. Chem., 34 (1995) 5950; correction: 35 (1996) 5752.
[43] M. Kaupp, V.G. Malkin, O.L. Malkina, D.R. Salahub, J. Am. Chem. Soc., 117 (1995) 1851; correction: p. 8492.

[44] B. Blaive, G. Legsai, R. Lai, J. Mol. Struct., 354 (1995) 245; Chem. Abstr., 123 (1995) 209340p.

[45] E.C. Alyea, G. Ferguson, Z. Xu, Acta Crystallogr., Sect. C 51 (1995) 353.

[46] A.M.A. Ibrahim, M.S. Ismail, Indian J. Chem., Sect. A, 34 (1995) 540; Chem. Abstr., 123 (1995) 95973q.

[47] J.J. Cruywagen, E.A. Rohwer, J. Chem. Soc., Dalton Trans., (1995) 3433.

[48] A. Cervilla, E. Llopis, A. Ribera, A. Domenech, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans., (1995) 3891.

[49] J.J. Cruywagen, E.A. Rohwer, G.F.S. Wessels, Polyhedron 14 (1995) 3481.

[50] F. Gharib, K. Zare, S.A. Khorrami, A. Behju, J. Chem. Eng. Data 40 (1995) 1214.

[51] R.P. Bandwar, C.P. Rao, Carbohydrate Res. 277 (1995) 197.

[52] W.P. Griffith, H.I.S. Nogueira, B.C. Parkin, R.N. Sheppard, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans., (1995) 1775.

[53] U. Piarulli, D.N. Williams, C. Floriani, G. Gervasio, D. Viterbo, J. Chem. Soc., Dalton Trans., (1995) 3329.

[54] F.J. Feher, K. Rahimian, T.A. Budzichowski, J.W. Ziller, Organometallics 14 (1995) 3920.

[55] V.G. Kessler, G.A. Seisenbaeva, A.V. Shevelkov, G.V. Khvorykh, J. Chem. Soc., Chem. Commun., (1995) 1779.

[56] S.G. Sakharov, N.A. Ovchinnikova, Y.A. Buslaev, Zh. Neorg. Khim., 40 (1995) 1984; Chem. Abstr., 124 (1996) 212977c.

[57] V. Nardello, J. Marko, G. Vermeersch, J.M. Aubry, Inorg. Chem. 34 (1995) 4950.

[58] C. Karunakaran, K. Gnanasekaran, R. Alamelu, Afinidad 52 (1995) 245.

[59] C. Karunakaran, B. Muthukumaran, Transition Metal Chem. 20 (1995) 460.

[60] I. Fabian, R. van Eldik, Int. J. Chem. Kinet. 27 (1995) 491.

[61] M. Bhattercharjee, J. Mukherjee, J. Chem. Res. (S), (1995) 238.

[62] J.R. Hanson, A. Opakunle, P. Petit, J. Chem. Res. (S), (1995) 457.

[63] J.O. Dzięgielewski, R. Hassa, Pol. J. Chem., 69 (1995) 185; Chem. Abstr., 123 (1995) 209864n.

[64] H. Arzoumanian, J. Sanchez, G. Strukul, R. Zennaro, Bull. Soc. Chim. Fr. 132 (1995) 1119.

[65] R. Lai, O. Desbois, F. Zamkotsian, R. Faure, J. Feneau-Dupont, J.-P. Declerq, Organometallics 14 (1995) 2145.

[66] H. Teruel, N. Romero, I. Henriquez, Transition Metal Chem., 20 (1995) 426; Chem. Abstr., 124 (1996) 87270p.

[67] W.R. Thiel, T. Priermeier, Angew. Chem. Int. Ed. Engl. 34 (1995) 1737.

[68] W.R. Thiel, M. Angstl, N. Hansen, J. Mol. Catal. 103A (1995) 5.

[69] W.R. Thiel, T. Priermeier, T. Bog, J. Chem. Soc., Chem. Commun., (1995) 1871.

[70] A.P. Timosheva, E.K. Kazakova, S.G. Vul'fson, N.D. Chichirova, Y.I. Sal'nikov, Zh. Obshch. Khim., 64 (1994) 1945; Chem. Abstr., 123 (1995) 73255e.

[71] M.S. Islam, M.M. Uddin, Bangladesh J. Sci. Ind. Res., 30 (1995) 55; Chem. Abstr., 123 (1995) 245138n.

[72] A.J. Bailey, W.P. Griffith, B.C. Parkin, J. Chem. Soc., Dalton Trans., (1995) 1833.

[73] W.P. Griffith, B.C. Parkin, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans., (1995) 3131.

[74] M.A. Pietsch, M. Couty, M.B. Hall, J. Phys. Chem. 99 (1995) 16315.

[75] H. Arzoumanian, G. Agrifoglio, H. Krentzian, M. Capparelli, J. Chem. Soc., Chem. Commun., (1995) 655.

[76] A. Cervilla, A. Corma, V. Fornés, E. Llopis, F. Pérez, F. Rey, A. Ribera, J. Am. Chem. Soc. 117 (1995) 6781.

[77] A. Corma, V. Fornes, F. Rey, A. Cervilla, E. Llopis, A. Ribera, J. Catal., 152 (1995) 237; Chem. Abstr., 123 (1995) 143149z.

[78] F. Vicente, J.J. Garcia-Jareno, R. Tamarit, A. Cervilla, A. Domenech, Electrochim. Acta, 40 (1995) 1121; Chem. Abstr., 123 (1995) 95923y.

[79] L.R. Domingo, M.T. Picher, V. Sanz, P. Palanca, Theochem (J. Mol. Struct.) 339 (1995) 201.

[80] J. Li-Kao, O. González, R.F. Baggio, M.T. Garland, D. Carrillo, Acta Crystallogr., Sect. C 51 (1995) 575.

[81] J. Li-Kao, O. González, R. Mariezcurrena, R. Baggio, M.T. Garland, D. Carrillo, Acta Crystallogr., Sect. C 51 (1995) 2486.

[82] B. Fischer, H. Schmalle, E. Dubler, A. Schäfer, M. Viscontini, Inorg. Chem. 34 (1995) 5726.

[83] S.J. Nieter Burgmayer, M.R. Arkin, L. Bostick, S. Dempster, K.M. Everett, H.L. Layton, K.E. Paul, C. Rogge, A.L. Rheingold, J. Am. Chem. Soc. 117 (1995) 5812.

[84] F.W. Nyasulu, J.M. Mayer, J. Electroanal. Chem., 392 (1995) 35; Chem. Abstr., 123 (1995) 211193m.

[85] F.J. Arnaiz, R. Aguado, J. Chem. Educ. 72 (1995) A196.

[86] R.N. Pandey, R. Kumari, N. Kumar, Asian J. Chem., 7 (1995) 285; Chem. Abstr., 122 (1995) 305224d.

[87] R. Clarke, M. Gahagan, R.K. Mackie, D.F. Foster, D.J. Cole-Hamilton, M. Nicol, A.W. Mountford, J. Chem. Soc., Dalton Trans., (1995) 1221.

[88] A. Corma, M. Iglesias, J.R. Obispo, F. Sanchez, Proc. 1st Europ. Symp. Chiral React. Heterog. Catal., (1994) 179; Chem. Abstr., 124 (1995) 353692t.

[89] E. Tempestri, P. Ferruti, E. Ranucci, A. Boyaca, G. Airoldi, React. Functional Polym. 26 (1995) 67.

[90] M.M. Miller, D.C. Sherrington, J. Catal. 152 (1995) 368.

[91] M.M. Miller, D.C. Sherrington, J. Catal. 152 (1995) 377.

[92] F.J. Arnaiz, J. Chem. Educ. 72 (1995) A7.

[93] R. Hahn, W.A. Herrmann, G.R.J. Artus, M. Kleine, Polyhedron 14 (1995) 2953.

[94] N.S. Rao, D.D. Mishra, R.C. Maurya, N.N. Rao, Synth. React. Inorg. Met.-Org. Chem., 25 (1995) 437; Chem. Abstr., 122 (1995) 305166m.

[95] W. Banße, E. Ludwig, U. Schilde, E. Uhlemann, F. Weller, A. Lehmann, Z. Anorg. Allg. Chem. 621 (1995) 1275.

[96] M.R. Maurya, J. Chem. Res. (S), (1995) 248.

[97] V.M. Leovac, I. Ivanovic, K.,elkovic, S. Mitrovski, J. Serb. Chem. Soc., 60 (1995) 1; Chem. Abstr., 122 (1995) 203795y.

[98] S.C.S. Jadon, N. Gupta, C. Saxena, R.V. Singh, Bol. Soc. Chil. Quim., 40 (1995) 189; Chem. Abstr., 123 (1995) 159211z.

[99] S.C.S. Jadon, N. Gupta, R.V. Singh, Indian J. Chem., Sect. A, 34 (1995) 733; Chem. Abstr., 123 (1995) 216702m.

[100] S.C.S. Jadon, N. Fahmi, R.V. Singh, Synth. React. Inorg. Met.-Org. Chem., 25 (1995) 1345; Chem. Abstr., 123 (1995) 274352h.

[101] N.S. Rao, D.D. Mishra, R.C. Maurya, N.N. Rao, Bull. Chem. Soc. Jpn. 68 (1995) 1589.

[102] M.R. Maurya, D.C. Antony, S. Gopinathan, C. Gopinathan, K.V. Mohanan, Indian J. Chem., Sect. A, 34 (1995) 360; Chem. Abstr., 122 (1995) 329129c.

[103] M.R. Maurya, D.C. Antony, S. Gopinathan, C. Gopinathan, Bull. Chem. Soc. Jpn. 68 (1995) 554.

[104] A.N. Papadopoulos, C.P. Raptopoulou, A. Terzis, A.G. Hatzidimitriou, A. Gourdon, D.P. Kessissoglou, J. Chem. Soc., Dalton Trans., (1995) 2591.

[105] M. Retboll, E.R. Moller, R.G. Hazell, K.A. Jorgensen, Acta. Chem. Scand. 49 (1995) 278.

[106] S. Mitra, H. Biswas, P. Bandyopadhyay, Polyhedron 14 (1995) 1581.

[107] T. Pal, A. Pal, N.R. Jana, J. Ind. Chem. Soc., 71 (1994) 725; Chem. Abstr., 123 (1995) 24561t.

[108] D.L. Davies, A.J. Grist, Inorg. Chim. Acta 236 (1995) 39.

[109] K.R. Prabhu, A.R. Ramesha, S. Chandrasekaran, J. Org. Chem. 60 (1995) 7142.

[110] P. Ilankumaran, S. Chandrasekaran, Tetrahedron Lett. 36 (1995) 4881.

[111] P. Ilankumaran, A.R. Ramesha, S. Chandrasekaran, Tetrahedron Lett. 36 (1995) 8311.

[112] F. Brezina, P. Kopel, Z. Sindelar, R. Pastorek, Transition Metal Chem., 20 (1995) 56; Chem. Abstr., 122 (1995) 254613v.

[113] J.L. Brito, M. Ilija, P. Hernandez, Thermochim. Acta, 256 (1995) 325; Chem. Abstr., 123 (1995) 131187x.

[114] A. Voulgaropoulos, A. Ayiannidis, J. Stratis, G. Zachariadis, S. Giroussi, Fresenius J. Anal. Chem. 351 (1995) 139.

[115] X.R. Ye, H.W. Hou, X.Q. Xin, C.F. Hammer, Appl. Surf. Sci., 89 (1995) 151; Chem. Abstr., 123 (1995) 267363j.

[116] X.R. Ye, X.Q. Xin, Huaxue Xuebao, 53 (1995) 462; Chem. Abstr., 123 (1995) 238618r.

[117] P. Falaras, C.A. Mitsopoulou, D. Argyropoulos, E. Lyris, N. Psaroudakis, E. Vrachnou, D. Katakis, Inorg. Chem. 34 (1995) 4536.

[118] Z.-Q. Tian, J.P. Donahue, R.H. Holm, Inorg. Chem. 34 (1995) 5567.
[119] F.E. Hahn, W.W. Seidel, Angew. Chem. Int. Ed. Engl. 34 (1995) 2700.
[120] H. Oku, N. Ueyama, A. Nakamura, Inorg. Chem. 34 (1995) 3667.
[121] D. Sellmann, P. Bail, F. Knoch, M. Moll, Chem. Ber. 128 (1995) 653.
[122] K. Unoura, R. Kikuchi, A. Nagasawa, Y. Kato, Y. Fukuda, Inorg. Chim. Acta 228 (1995) 89.
[123] C.G. Young, J. Chem. Educ. 72 (1995) 751.
[124] H. Arzoumanian, H. Krentzien, C. Corao, R. Lopez, G. Agrifoglio, Polyhedron 14 (1995) 2887.
[125] P.R. Bonneau, J.B. Wiley, R.B. Kaner, Inorg. Synth. 30 (1995) 33.
[126] M.A. Sriram, P.N. Kumta, E.I. Ko, Chem. Mater. 7 (1995) 859.
[127] N.F. Drobot, N.A. Ovchinnikova, V.V. Otdel'nov, V.A. Krenev, Zh. Neorg. Khim., 40 (1995) 266; Chem. Abstr., 123 (1995) 24607n.
[128] T. Watase, H. Tachimori, T. Masuda, Bull. Chem. Soc. Jpn. 68 (1995) 393.
[129] M. Akazome, J. Yamamoto, T. Kondo, Y. Watanabe, J. Organomet. Chem. 494 (1995) 229.
[130] A.J. Blake, A.J. Downs, C. Limberg, S. Parsons, J. Chem. Soc., Dalton Trans., (1995) 3263.
[131] N. Sharma, R. Sharma, S.S. Bhatt, S.C. Chaudhry, Indian J. Chem., Sect. A, 34 (1995) 313; Chem. Abstr., 122 (1995) 254700w.
[132] L.M.D. Ribeiro, M.A.N.D.A. Lemos, A.J.L. Pombeiro, P. Sobota, Russian J. Electrochem. 31 (1995) 1009.
[133] M. Mitewa, P. Bontchev, T. Mantarova, God. Sofii, Univ. "Sv. Kliment. Okhridski", Khim. Fak., 81 (1994) 167; Chem. Abstr., 123 (1995) 216784q.
[134] S.S. Mandal, P.C. Ghorai, S. Ray, H.K. Saha, J. Ind. Chem. Soc., 72 (1995) 807; Chem. Abstr., 124 (1996) 104605w.
[135] J. Beck, Z. Anorg. Allg. Chem. 621 (1995) 131.
[136] A.J. Blake, S. Parsons, A.J. Downs, C. Limberg, Acta Crystallogr., Sect. C 51 (1995) 571.
[137] C.J. Kepert, M.R. Truter, M. Kurmoo, P. Day, Synth. Met., 70 (1995) 781; Chem. Abstr., 123 (1995) 216721s.
[138] J.R. Backhouse, H.M. Lowe, E. Sinn, S. Suzuki, S. Woodward, J. Chem. Soc., Dalton Trans., (1995) 1489.
[139] J.C. Gordon, S.P. Mattamana, R. Poli, P.E. Fanwick, Polyhedron 14 (1995) 1339.
[140] W. Kläui, T. Hardt, H.-J. Schulte, H. Hamers, J. Organomet. Chem. 498 (1995) 63.
[141] T.-C. Lau, S.L.L. Kong, J. Chem. Soc., Dalton Trans., (1995) 2221.
[142] J.W. Atkinson, M.-C. Hong, D.A. House, P. Kyritsis, Y.-J. Li, M. Nasreldin, A.G. Sykes, J. Chem. Soc., Dalton Trans., (1995) 3317.
[143] J.C. Kim, ReesW.S., Jr., V.L. Goedken, Inorg. Chem. 34 (1995) 2483.
[144] J.C. Kim, B.M. Lee, J.I. Shin, Polyhedron 14 (1995) 2145.
[145] S. Yamashita, T. Imamura, Y. Sasaki, Chem. Lett., (1995) 417.
[146] R. Husted, J.L. Du, G.R. Eaton, S.S. Eaton, Magn. Reson. Chem. 33 (1995) 566.
[147] A. Nagata, Y. Shimizu, H. Nagamoto, M. Miya, Inorg. Chim. Acta 238 (1995) 169.
[148] X. Cui, W. Huang, H. Yang, P. Gao, D. Han, Beijing Daxue Xuebao, Ziran Kexueban, 31 (1995) 666; Chem. Abstr., 124 (1996) 271642n.
[149] X. Cui, W. Huang, H. Yang, P. Gao, D. Han, Beijing Daxue Xuebao, Ziran Kexueban, 31 (1995) 675; Chem. Abstr., 124 (1996) 271643p.
[150] R. Luo, J. Ren, Z. Qin, J. Wuhan Univ. Technol., Mater. Sci. Ed., 9 (1994) 33; Chem. Abstr., 123 (1995) 267589n.
[151] N.S. Nipales, T.D. Westmoreland, Inorg. Chem. 34 (1995) 3374.
[152] P. Basu, M.A. Bruck, Z. Li, I.K. Dhawan, J.H. Enemark, Inorg. Chem. 34 (1995) 405.
[153] P. Basu, N.V. Shokhirev, J.H. Enemark, F.A. Walker, J. Am. Chem. Soc. 117 (1995) 9042.
[154] V.V. Kurshev, L. Kevan, P. Basu, J.H. Enemark, J. Phys. Chem. 99 (1995) 11288.
[155] I.K. Dhawan, M.A. Bruck, B. Schilling, C. Grittini, J.H. Enemark, Inorg. Chem. 34 (1995) 3801.
[156] K. Saito, Y. Sasaki, R Hazama, J. Cluster Sci., 6 (1995) 549; Chem. Abstr., 124 (1996) 104423k.
[157] R. Hazama, K. Umakoshi, A. Ichimura, S. Ikari, Y. Sasaki, T. Ito, Bull. Chem. Soc. Jpn. 68 (1995) 456.
[158] K. Mukherjee, P. Roychowdhury, K. Roy, D. Mukherjee, M. Kusunoki, Acta Crystallogr., Sect. C 51 (1995) 32.

[159] A.L. Poznyak. L.V. Stopolyanskaya, Zh. Neorg. Khim., 40 (1995) 787; Chem. Abstr., 123 (1995) 301195t.

[160] O.V. Klimov, M.A. Fedotov, D.I. Kochubei, S.P. Degtyarev, A.N. Startsev, Koord Khim., 21 (1995) 709; Russian J. Coord. Chem., 21 (1995) 678; Chem. Abstr., 123 (1995) 328419f.

[161] K.-M. Doh, I.-C. Kim, B.-Y. Choi, J. Korean Chem. Soc., 39 (1995) 198; Chem. Abstr., 123 (1995) 73324b.

[162] L.S. Villata, D.O. Mártire, A.L. Capparelli, J. Mol. Catal. 99 (1995) 143.

[163] Y. Feng, H. Imura, K. Ohashi, Bull. Chem. Soc. Jpn. 68 (1995) 604.

[164] J.S. Kim, H.J. Kim, B.K. Koo, Bull. Korean Chem. Soc., 16 (1995) 26; Chem. Abstr., 122 (1995) 203771n.

[165] Y.-K. Choi, M.-S. Song, C.-P. Rim, K.H. Chjo, J. Korean Chem. Soc., 39 (1995) 47; Chem. Abstr., 122 (1995) 176976z

[166] H.J. Kim, B.K. Koo, J. Korean Chem. Soc., 39 (1995) 434; Chem. Abstr., 123 (1995) 159279c.

[167] S. Bhattacharjee. R. Bhattacharyya, Proc. Indian Acad. Sci., Chem. Sci., 107 (1995) 343; Chem. Abstr., 124 (1996) 192335m.

[168] S.D. Perera, B.L. Shaw, M. Thornton-Pett, Inorg. Chim. Acta 234 (1995) 185.

[169] T.A. Coffey, G.D. Forster, G. Hogarth, J. Chem. Soc., Dalton Trans., (1995) 2337.

[170] G.D. Forster, G. Hogarth, Polyhedron 14 (1995) 1401.

[171] J.Q. Lee, M.L. Sampson, J.F. Richardson, M.E. Noble, Inorg. Chem. 34 (1995) 5055.

[172] E.K. Haub, A.C. Lizano, M.E. Noble, Inorg. Chem. 34 (1995) 1440.

[173] H. Oku, N. Ueyama, A. Nakamura, Chem. Lett., (1995) 621.

[174] B.-T. Zhuang, L.-R. Huang, A.-J. Lan, L.-J. He, B.-H. Pan, P.-H. Yu, Jiegou Huaxue, 14 (1995) 161; Chem. Abstr., 123 (1995) 131167r.

[175] S. Mitra, P. Bandyopadhyay, Indian. J. Chem., 34A (1995) 493; Chem. Abstr., 123 (1995) 73332c.

[176] M. Decoster, F. Conan, J.E. Guerchais, Y. Le Mest, J. Sala-Pala, J.C. Jeffery, E. Faulques, A. Leblanc, P. Molinie, Polyhedron 14 (1995) 1741.

[177] E. Faulques, A. Leblanc, P. Molinie, M. Decoster, F. Conan, J.E. Guerchais, J. Sala-Pala, Spectrochim. Acta, 51A (1995) 805; Chem. Abstr., 123 (1995) 73334e

[178] C. Wen-Dan, G. Guo-Cong, H. Jin-Shin, L. Jia-Xi, Polyhedron 14 (1995) 3649.

[179] R.Z. Chen, J. Li, C.-W. Liu, X.-H. Cai, L.-P. Meng, S.-J. Zheng, Huaxue Xuebao, 53 (1995) 695; Chem. Abstr., 123 (1995) 209208b.

[180] D.M. Baird, C. Aburri, L.S. Barron, S.A. Rodriguez, Inorg. Chim. Acta 237 (1995) 117.

[181] P. Dierkes, G. Frenzen, S. Wocadlo, W. Massa, S. Berger, J. Pebler, K. Dehnicke, Z. Naturforsch. 50B (1995) 159.

[182] A. Roodt, J.G. Leipoldt, L. Helm, A. Abou-Hamdan, A.E. Merbach, Inorg. Chem. 34 (1995) 560.

[183] B. Burda, J. Burgess, S.A. Parsons, A. Samotus, J. Szklarzewicz, Transition Metal Chem., 20 (1995) 291; Chem. Abstr., 123 (1995) 159270t.

[184] J. Szklarzewicz, A. Samotus, J. Burgess, J. Fawcett, D.R. Russell, J. Chem. Soc., Dalton Trans., (1995) 3057.

[185] A. Samotus, B. Burda, J. Burgess, B. Sieklucka, J. Szklarzewicz, Proc. 15th Conf. Coord. Chem., (1995) 221; Chem. Abstr., 124 (1996) 133961q.

[186] J. Szklarzewicz, A. Samotus, Transition Metal Chem. 20 (1995) 174.

[187] S.I. Ali, A.M.A. Ansari, N.K.S. Pundhir, Indian J. Chem., Sect. A, 34 (1995) 423; Chem. Abstr., 123 (1995) 186884c.

[188] J. Lu, W.T.A. Harrison, A.J. Jacobson, Angew. Chem. Int. Ed. Engl. 34 (1995) 2557.

[189] L.M. Berreau, YoungV.G., Jr., L.K. Woo, Inorg. Chem. 34 (1995) 3485.

[190] Z. Duan, J.G. Verkade, Inorg. Chem. 34 (1995) 1576.

[191] R.R. Schrock, K.-Y. Shih, D.A. Dobbs, W.M. Davis, J. Am. Chem. Soc. 117 (1995) 6609.

[192] N.C. Zanetti, R.R. Schrock, W.M. Davis, Angew. Chem. Int. Ed. Engl. 34 (1995) 2044.

[193] M. Scheer, Angew. Chem. Int. Ed. Engl. 34 (1995) 1997.

[194] F.A. Cotton, D.J. Maloney, J.R. Su, Inorg. Chim. Acta 236 (1995) 21.

[195] T. Adachi, D.L. Hughes, S.K. Ibrahim, S. Okamoto, C.J. Pickett, N. Yabanouchi, T. Yoshida, J. Chem. Soc., Chem. Commun., (1995) 1081.

[196] H. Seino, Y. Ishii, T. Sasagawa, M. Hidai, J. Am. Chem. Soc. 117 (1995) 12181.

[197] S.A. Fairhurst, D.L. Hughes, S.K. Ibrahim, M.-L. Abasq, J. Talarmin, M.A. Queiros, A. Fonseca, C.J. Pickett, J. Chem. Soc., Dalton Trans., (1995) 1973.

[198] A.J.L. Pombeiro, A. Hills, D.L. Hughes, R.L. Richards, Acta Crystallogr., Sect. C 51 (1995) 23.

[199] E.S. Shubina, A.N. Krylov, N.V. Belkova, L.M. Epstein, A.P. Borisov, V.D. Mahaev, J. Organomet. Chem. 493 (1995) 275.

[200] M. Chaussade, M.C. Durrant, D.L. Hughes, A. Loose, R.L. Richards, Bull. Soc., Chim. Fr. 132 (1995) 265.

[201] D.L. Hughes, N.J. Lazarowych, M.J. Maguire, R.H. Morris, R.L. Richards, J. Chem. Soc., Dalton Trans., (1995) 5.

[202] T.E. Burrow, D.L. Hughes, A.J. Lough, M.J. Maguire, R.H. Morris, R.L. Richards, J. Chem. Soc., Dalton Trans., (1995) 2583.

[203] T.E. Burrow, D.L. Hughes, A.J. Lough, M.J. Maguire, R.H. Morris, R.L. Richards, J. Chem. Soc., Dalton Trans., (1995) 1315.

[204] D.L. Hughes, K. Marjani, R.L. Richards, J. Organomet. Chem. 505 (1995) 127.

[205] A.L. Hector, I.P. Parkin, Polyhedron 14 (1995) 93.

[206] T.A. George, H.H. Hammond, J. Organomet. Chem. 503 (1995) C1.

[207] T.A. George, D.J. Rose, Y. Chang, Q. Chen, J. Zubieta, Inorg. Chem. 34 (1995) 1295.

[208] S.-O. Oh, E.Y. Lyou, J. Korean Chem. Soc., 39 (1995) 530; Chem. Abstr., 123 (1995) 186850p.

[209] F.A. Cotton, K. Vidyasagar, Polyhedron 14 (1995) 3077.

[210] K. Vidyasagar, Inorg. Chim. Acta 229 (1995) 473.

[211] J.V. Brencic, I. Leban, B. Modec, O. Carugo, Inorg. Chim. Acta 229 (1995) 421.

[212] J.V. Brencic, B. Modec, Z. Yao, Acta Crystallogr., Sect. C 51 (1995) 197.

[213] S.P. Mattamana, R. Poli, Inorg. Chim. Acta 229 (1995) 55.

[214] J.C. Fettinger, S.P. Mattamana, C.J. O'Connor, R. Poli, G. Salem, J. Chem. Soc., Chem. Commun., (1995) 1265.

[215] K.A. Hall, J.M. Mayer, Inorg. Chem. 34 (1995) 1145.

[216] S.P. Best, B.N. Figgis, J.B. Forsyth, P.A. Reynolds, P.L.W. Tregenna-Piggott, Inorg. Chem. 34 (1995) 4605.

[217] M. Ardon, A. Bino, Inorg. Chim. Acta 229 (1995) 417.

[218] F.A. Cotton, J. Su, J. Cluster Sci., 6 (1995) 39; Chem. Abstr., 123 (1995) 73263f.

[219] T.A. Budzichowski, M.H. Chisholm, K. Folting, J.C. Huffman, W.E. Streib, J. Am. Chem. Soc. 117 (1995) 7428.

[220] U. Piarulli, D.N. Williams, C. Floriani, G. Gervasio, D. Viterbo, J. Organomet. Chem. 503 (1995) 185.

[221] D.V. Baxter, M.H. Chisholm, V.F. DiStasi, S.T. Haubrich, Chem. Mater. 7 (1995) 84.

[222] C.E. Laplaza, A.L. Odom, W.M. Davis, C.C. Cummins, J.D. Protasiewicz, J. Am. Chem. Soc. 117 (1995) 4999.

[223] C.E. Laplaza, C.C. Cummins, Science 268 (1995) 861.

[224] Q. Cui, D.G. Musaev, M. Svensson, S. Sieber, K. Morokuma, J. Am. Chem. Soc. 117 (1995) 12366.

[225] C.E. Laplaza, W.M. Davis, C.C. Cummins, Angew. Chem. Int. Ed. Engl. 34 (1995) 2042.

[226] S.B. Sharma, I.N. Tewari, J. Indian Chem. Soc., 72 (1995) 443; Chem. Abstr., 123 (1995) 216876w.

[227] J.C.A. Boeyens, F.M.M. O'Neill, Inorg. Chem. 34 (1995) 1988.

[228] F.A. Cotton, J.H. Matonic, D.D. Silva, Inorg. Chim. Acta 234 (1995) 115.

[229] T.-L.C. Hu, S.A. Helvoigt, C.M. Partigianoni, C. Turró, D.G. Nocera, Inorg. Chem. 34 (1995) 6186.

[230] M. Gerards, Inorg. Chim. Acta 229 (1995) 101.

[231] H.-S. Park, H.-K. Yu, J.-H. Jung, Y.-W. Kim, S.W. Lee, Bull. Korean Chem. Soc., 16 (1995) 193; Chem. Abstr., 122 (1995) 229377p.

[232] P. Rosendorfer, W. Beck, Chem. Ber. 128 (1995) 729.

[233] P.K. Baker, M.E. Harman, M.B. Hursthouse, A.I. Karaulov, A.J. Lavery, K.M. Abdul Malik, D.J. Muldoon, A. Shawcross, J. Organomet. Chem. 494 (1995) 205.

[234] P.K. Baker, M.E. Harman, S. Hughes, M.B. Hursthouse, K.M. Abdul Malik, J. Organomet. Chem. 498 (1995) 257.

[235] P.K. Baker, S. Hughes, J. Coord. Chem., 35 (1995) 1; Chem. Abstr., 123 (1995) 305105m.

[236] T. Daniel, H. Nagao, K. Tanaka, A. Nakamura, Chem. Ber. 128 (1995) 1007.

[237] H. Nakazawa, Y. Yamaguchi, T. Mizuta, K. Miyoshi, Organometallics 14 (1995) 4173.

[238] K. Fromm, M. Plaikner, E. Hey-Hawkins, Z. Naturforsch., 50B (1995) 894; Chem. Abstr., 123 (1995) 199042b.

[239] C. Lin, J.D. Protasiewicz, E.T. Smith, T. Ren, J. Chem. Soc., Chem. Commun., (1995) 2257.

[240] M.D. Ward, Chem. Soc. Rev. 24 (1995) 121.

[241] A. Wlodarczyk, S.S. Kurek, Wybrane Pr. Zakresu Inz. Chem. Procesowej, 2 (1995) 53; Chem. Abstr., 124 (1996) 74595y.

[242] F.S. McQuillan, T.L. Green, T.A. Hamor, C.J. Jones, J.P. Maher, J.A. McCleverty, J. Chem. Soc., Dalton Trans., (1995) 3243.

[243] A. Wlodarczyk, J.P. Maher, J.A. McCleverty, M.D. Ward, J. Chem. Soc., Chem. Commun., (1995) 2397.

[244] A.J. Amoroso, A.M.W. Cargill-Thompson, J.P. Maher, J.A. McCleverty, M.D. Ward, Inorg. Chem. 34 (1995) 4828.

[245] N.M. Rowley, S.S. Kurek, J.-D. Foulon, T.A. Hamor, C.J. Jones, J.A. McCleverty, S.M. Hubig, E.J.L. McInnes, N.N. Payne, L.J. Yellowlees, Inorg. Chem. 34 (1995) 4414.

[246] N.M. Bhadbhade, A. Das, J.C. Jeffery, J.A. McCleverty, J.A. Navas Badiola, M.D. Ward, J. Chem. Soc., Dalton Trans., (1995) 2769.

[247] F.S. McQuillan, C.J. Jones, J.A. McCleverty, Polyhedron 14 (1995) 3157.

[248] B.J. Coe, T.A. Hamor, C.J. Jones, J.A. McCleverty, D. Bloor, G.H. Cross, T.L. Axon, J. Chem. Soc., Dalton Trans., (1995) 673.

[249] J.A. Thomas, C.J. Jones, J.A. McCleverty, D.W. Bruce, M.G. Hutchings, Polyhedron 14 (1995) 2499.

[250] A. Wlodarczyk, A. Wlodarczyk, J.C. Jeffery, J.A. McCleverty, M.D. Ward, Transition Metal Chem., 20 (1995) 559; Chem. Abstr., 124 (1996) 163208s.

[251] J. Huang, R.L. Ostrander, A.L. Rheingold, M.A. Walters, Inorg. Chem. 34 (1995) 1090.

[252] M. Cano, J.V. Heras, A. Monge, E. Pinilla, E. Santamaria, H.A. Hinton, C.J. Jones, J.A. McCleverty, J. Chem. Soc., Dalton Trans., (1995) 2281.

[253] W. Liu, H.H. Thorp, J. Am. Chem. Soc. 117 (1995) 9822.

[254] F.J. Lalor, T.J. Desmond, G.M. Cotter, C.M. Shanahan, G. Ferguson, M. Parvez, B. Ruhl, J. Chem. Soc., Dalton Trans., (1995) 1709.

[255] J. Brennan, G. Cooper, J.C. Green, M.P. Payne, C.M. Redfern, J. Electron Spectrosc. Relat. Phenom. 73 (1995) 157.

[256] T.R. Webb, J.D. Pollard, G.W. Goodloe, M.L. McKee, Inorg. Chim. Acta 229 (1995) 127.

[257] K.R. Dunbar, X. Ouyang, Mol. Cryst. Liq. Cryst. Sci. Technol., 273A (1995) 459; Chem. Abstr., 124 (1996) 133893u.

[258] M. Handa, M. Mikuriya, T. Kotera, K. Yamada, T. Nakao, H. Matsumoto, K. Kasuga, Bull. Chem. Soc. Jpn. 68 (1995) 2567.

[259] M. Handa, H. Matsumoto, T. Namura, T. Nagaoka, K. Kasuga, M. Mikuriya, T. Kotera, R. Nukada, Chem. Lett., (1995) 903.

[260] P. Segedin, Acta Chim. Slov., 42 (1995) 349; Chem. Abstr., 124 (1996) 163146v.

[261] I. Leban, P. Segedin, Proc. 15th Conf. Coord. Chem., (1995) 133; Chem. Abstr., 124 (1996) 192271n.

[262] H. Chen, F.A. Cotton, Polyhedron 14 (1995) 2221.

[263] M.A. Ba-ares, L. Dauphin, X. Lei, W. Cen, M. Shang, E.E. Wolf, T.P. Fehlner, Chem. Mater. 7 (1995) 553.

[264] J.A. Acho, S.J. Lippard, Inorg. Chim. Acta 229 (1995) 5.

[265] J.A. Acho, T. Ren, J.W. Yun, S.J. Lippard, Inorg. Chem. 34 (1995) 5226.

[266] T. Igoshi, T. Tanase, Y. Yamamoto, J. Organomet. Chem. 494 (1995) 37.

[267] D. Sellmann, H.-J. Kremitzl, F. Knoch, M. Moll, Z. Naturfirsch. 50B (1995) 1601.

[268] D. Sellmann, B. Hadawi, F. Knoch, M. Moll, Inorg. Chem. 34 (1995) 5963.

[269] B.T. Zhuang, L.-R. Huang, L.-J. He, Jiegou Huaxue, 14 (1995) 359; Chem. Abstr., 123 (1995) 357548c.

[270] J. Li, G. Schreckenbach, T. Ziegler, J. Am. Chem. Soc. 117 (1995) 486.

[271] F.M. Harris, P.J. Jackson, J.A. Rowntree, S.R.,rews, D.E. Parry, J. Mass Spectrom., 30 (1995) 601; Chem. Abstr., 122 (1995) 325506a.

[272] F. Guillot, D. Dezarnaud-Dandine, M. Tronc, A. Lisini, P. Dedeva, G. Fronzoni, Chem. Phys., 191 (1995) 289; Chem. Abstr., 122 (1995) 118067t.

[273] K.P. Reddy, T.L. Brown, J. Am. Chem. Soc. 117 (1995) 2845.

[274] H.-G. Ang, K.-S. Chan, G.-K. Chuah, S. Jaenicke, S.-K. Neo, J. Chem. Soc., Dalton Trans., (1995) 3753.

[275] C. Brémard, G. Ginestet, J. Laureyns, M. Le Maire, J. Am. Chem. Soc. 117 (1995) 9274.

[276] S. Kawi, O. Alexaev, M. Shelef, B.C. Gates, J. Phys. Chem. 99 (1995) 6926.

[277] V.A. Maksakov, V.A. Ershova, J. Organomet. Chem. 485 (1995) 69.

[278] Y. Gao, X. Yang, Q. Shi, Inorg. Chim. Acta 240 (1995) 661.

[279] G.-L. Leu, T.J. Burkey, J. Coord. Chem., 34 (1995) 87; Chem. Abstr., 123 (1995) 322455t.

[280] T. Szymanska-Buzar, A.J. Downs, T.M. Greene, A.S. Marshall, J. Organomet. Chem. 495 (1995) 149.

[281] H. Dvorákova, D. Dvorák, J. Srogl, P. Kocovsky, Tetrahedron Lett. 36 (1995) 6351.

[282] D. Dvorak, I. Stary, P. Kocovsky, J. Am. Chem. Soc. 117 (1995) 6130.

[283] F.E. McDonald, C.C. Schultz, A.K. Chatterjee, Organometallics 14 (1995) 3628.

[284] N. Kaneta, T. Hirai, M. Mori, Chem. Lett., (1995) 627.

[285] N. Kaneta, K. Hikichi, S. Asaka, M. Uemura, M. Mori, Chem. Lett., (1995) 1055.

[286] S. Pasynkiewicz, J. Jackowski, Appl. Organomet. Chem. 9 (1995) 335.

[287] R.E. Bachman, K.H. Whitmire, Inorg. Chem. 34 (1995) 1542.

[288] F.E. Hahn, M. Tamm, Organometallics 14 (1995) 2597.

[289] L.J. Lyons, S.L. Pitz, D.C. Boyd, Inorg. Chem. 34 (1995) 316.

[290] K. Öfele, W.A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, T. Priermeier, P. Kiprof, J. Organomet. Chem. 498 (1995) 1.

[291] W.A. Herrmann, P.W. Roesky, M. Elison, G. Artus, K. Öfele, Organometallics 14 (1995) 1085.

[292] B.P.S. Chauhan, R.J.P. Corriu, G.F. Lanneau, C. Priou, N. Auner, H. Handwerker, E. Herdtweck, Organometallics 14 (1995) 1657.

[293] A. Sieker, A.J. Blake, S. Parsons, B.F.G. Johnson, J. Chem. Soc., Dalton Trans., (1995) 1391.

[294] K.S. Wang, D. Wang, K. Yang, M.G. Richmond, M. Schwartz, Inorg. Chem. 34 (1995) 3241.

[295] P.N.W. Baxter, J.A. Connor, J. Organomet. Chem. 486 (1995) 115.

[296] K.-B. Shiu, S.-T. Lin, D.-W. Fung, T.-J. Chan, S.-M. Peng, M.-C. Cheng, J.L. Chou, Inorg. Chem. 34 (1995) 854.

[297] K.-B. Shiu, S.-T. Lin, S.-M. Peng, M.-C. Cheng, Inorg. Chim. Acta 229 (1995) 153.

[298] K.-H. Yih, S.-C. Chen, Y.-C. Lin, G.-H. Lee, Y. Wang, J. Organomet. Chem. 494 (1995) 149.

[299] K. Kundu, P. Sultana, M.S.T.S. Akhter, J. Bangladesh Chem. Soc., 8 (1995) 75; Chem. Abstr., 124 (1996) 218599c.

[300] T. Daniel, N. Suzuki, K. Tanaka, A. Nakamura, J. Organomet. Chem. 505 (1995) 109.

[301] J. Granifo, Polyhedron 14 (1995) 1593.

[302] M.A. Pal-Sandoval, M.E. Domínguez-Durán, C. Pazos-Mayen, A. Ariza-Castolo, M. de J. Rosales-Hoz, R. Contreras, J. Organomet. Chem., 492 (1995) 1; correction: 503 (1995) C40.

[303] P. Fehling, M. Döring, F. Knoch, R. Beckert, H. Görls, Chem. Ber. 128 (1995) 405.

[304] R. Beckert, M. Döring, H. Görls, F. Knoch, E. Uhlig, J. Wuckelt, J. Prakt. Chem./Chem. Ztg., 337 (1995) 38; Chem. Abstr., 122 (1995) 280568d.

[305] W. Bruns, W. Kaim, E. Waldhör, M. Krejcik, Inorg. Chem. 34 (1995) 663.

[306] W. Kaim, W. Bruns, S. Kohlmann, M. Krejcik, Inorg. Chim. Acta 229 (1995) 143.

[307] H. Schumann, Z. Naturforsch. 50B (1995) 1038.

[308] N. Le Bris, J.-J. Yaouanc, J.-C. Clément, H. Handel, H. des Abbayes, J. Organomet. Chem. 487 (1995) 131.

[309] V. Patinec, J.-J. Yaouanc, J.-C. Clément, H. Handel, H. des Abbayes, M.M. Kubicki, J. Organomet. Chem. 494 (1995) 215.

[310] V. Patinec, J.-J. Yaouanc, J.-C. Clément, H. Handel, H. des Abbayes, Tetrahedron Lett. 36 (1995) 79.

[311] M.S. Davies, M.J. Aroney, I.E. Buys, T.W. Hambley, J.L. Calvert, Inorg. Chem. 34 (1995) 330.

[312] E.C. Alyea, S. Song, Inorg. Chem. 34 (1995) 3864.

[313] K.-H. Yih, Y.-C. Lin, G.-H. Lee, Y. Wang, J. Chem. Soc., Chem. Commun., (1995) 223.

[314] J. Kalbitz, E. Leißring, H. Schmidt, Z. Anorg. Allg. Chem. 621 (1995) 1605.

[315] H. Voelker, S. Freitag, U. Pieper, H.W. Roesky, Z. Anorg. Allg. Chem. 621 (1995) 694.

[316] W.A. Herrmann, R. Schmid, C.W. Kohlpaintner, T. Priermeier, Organometallics 14 (1995) 1961.

[317] G.M. Gray, C.H. Duffey, Organometallics 14 (1995) 245.

[318] C.H. Ueng, T.T. Luo, Inorg. Chim. Acta 237 (1995) 199.

[319] X. Sun, E.H. Wong, M.M. Turnbull, A.L. Rheingold, B.E. Waltermire, R.L. Ostrander, Organometallics 14 (1995) 83.

[320] K.G. Moloy, J.L. Petersen, J. Am. Chem. Soc. 117 (1995) 7696.

[321] V.S. Reddy, K.V. Katti, C L. Barnes, Inorg. Chem. 34 (1995) 5483.

[322] V.S. Reddy, K.V. Katti, C.L. Barnes, Inorg. Chem. 34 (1995) 1273.

[323] V.S. Reddy, S.S. Krishnamurthy, M. Nethaji, J. Chem. Soc., Dalton Trans., (1995) 1933.

[324] R.P.K. Babu, S.S. Krishnamurthy, M. Nethaji, Organometallics 14 (1995) 2047.

[325] D.N. Horng, C.H. Ueng, J. Organomet. Chem. 505 (1995) 53.

[326] D.N. Horng, C.H. Ueng, Inorg. Chim. Acta 232 (1995) 175.

[327] N. Nawar, A.K. Smith, J. Organomet. Chem. 493 (1995) 239.

[328] A.T. Hutton, F.P. Wewers, J. Organomet. Chem. 492 (1995) C14.

[329] S.J. Coles, P.G. Edwards, J.S. Fleming, M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1995) 1139.

[330] S.J. Coles, P.G. Edwards, J.S. Fleming, M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1995) 4091.

[331] R.G. Compton, J.C. Eklund, A. Hallik, S. Kumbhat, A.M. Bond, R. Colton, J. Chem. Soc. Perkin II, (1995) 1327.

[332] H.A. Mayer, P. Stößel, R. Fawzi, M. Steimann, Chem. Ber. 128 (1995) 719.

[333] H.A. Mayer, P. Stößel, R. Fawzi, M. Steimann, J. Organomet. Chem. 492 (1995) C1.

[334] E.C. Alyea, G. Ferguson, S.Q. Song, Acta Crystallogr., Sect. C 51 (1995) 2238.

[335] J.K. Shen, F. Basolo, G.J. Kubas, J. Organomet. Chem. 488 (1995) C1.

[336] J.K. Shen, G.J. Kubas, A.L. Rheingold, Inorg. Chim. Acta 240 (1995) 99.

[337] F. Marken, A.M. Bond, R. Colton, Inorg. Chem. 34 (1995) 1705.

[338] X.-L. Luo, G.J. Kubas, C.J. Burns, J.C. Bryan, C.J. Unkefer, J. Am. Chem. Soc. 117 (1995) 1159.

[339] C.-Y. Liu, D.-Y. Chen, M.-C. Cheng, S.-M. Peng, S.-T. Liu, Organometallics 14 (1995) 1983.

[340] M. Herberhold, C. Köhler, W. Milius, B. Wrackmeyer, Inorg. Chim. Acta 231 (1995) 249.

[341] S.D. Perera, B.L. Shaw, M. Thornton-Pett, Inorg. Chim. Acta 236 (1995) 7.

[342] A. Fischer, I. Neda, P.G. Jones, R. Schmutzler, Z. Anorg. Allg. Chem. 621 (1995) 105.

[343] M.B. Hursthouse, K.M. Abdul Malik, M.A. Beckett, Acta Crystallogr., Sect. C 51 (1995) 2480.

[344] U.U. Ike, S.D. Perera, B.L. Shaw, M. Thornton-Pett, J. Chem. Soc., Dalton Trans., (1995) 2057.

[345] S.D. Perera, M. Shamsuddin, B.L. Shaw, Can. J. Chem. 73 (1995) 1010.

[346] M.C. Durrant, B. Gördt, C. Hauser, T. Krawinkel, R.L. Richards, Transition Metal Chem., 20 (1995) 583; Chem. Abstr., 124 (1996) 157160d.

[347] E.W. Abel, E.S. Blackwall, M.L. Creber, P.J. Heard, K.G. Orrell, J. Organomet. Chem. 490 (1995) 83.

[348] C. Barré, P. Boudot, M.M. Kubicki, C. Moise, Inorg. Chem. 34 (1995) 284.

[349] M.M. Kubicki, P. Oudet, C. Martin, C. Barré, J. Chem. Soc., Dalton Trans., (1995) 3699.

[350] G. Boni, P. Sauvageot, E. Marpeaux, C. Moise, Organometallics 14 (1995) 5652.

[351] H. Brunner, S. Challet, M.M. Kubicki, J.C. Leblanc, C. Moise, F. Volpato, J. Wachter, Organometallics 14 (1995) 3623.

[352] F. Lindenberg, T. Gelbrich, E. Hey-Hawkins, Z. Anorg. Allg. Chem. 621 (1995) 771.

[353] M. Galakhov, A. Martin, M. Mena, F. Palacios, C. Yélamos, P.R. Raithby, Organometallics 14 (1995) 131.

[354] S. Sharma, S. Gupta, O.P. Vermani, A.K. Narula, Indian J. Chem., Sect. A, 34 (1995) 883; Chem. Abstr., 123 (1995) 357536x.

[355] M. Cano, P. Ovejero, J.V. Heras, J. Organomet. Chem. 486 (1995) 63.

[356] C.P. Shao, J.Y. Wang, X.Z. Yang, H.F. Guo, Chin. Chem. Lett., 6 (1995) 519; Chem. Abstr., 123 (1995) 153676h; Fenzi Cuihua, 9 (1995) 353; Chem. Abstr., 124 (1996) 67833w.

[357] E.M. Lopez, D. Miguel, J.A. Pérez-Martínez, V. Riera, S. Garcia-Granda, J. Organomet. Chem. 492 (1995) 23.

[358] J.W. Freeman, A.M. Arif, R.D. Ernst, Inorg. Chem. Acta 240 (1995) 33.

[359] B.K. Das, M.G. Kanatzidis, Inorg. Chem. 34 (1995) 5721.

[360] J.W. van Hal, K.H. Whitmire, B. Zouchoune, J.-F. Halet, J.Y. Saillard, Inorg. Chem. 34 (1995) 5455.

[361] V.J. Murphy, G. Parkin, J. Am. Chem. Soc. 117 (1995) 3522.

[362] V.J. Murphy, D. Rabinovich, S. Halkyard, G. Parkin, J. Chem. Soc., Chem. Commun., (1995) 1099.

[363] A. Galindo, E. Gutiérrez, A. Monge, M. Paneque, A. Pastor, P.J. Pérez, R.D. Rogers, E. Carmona, J. Chem. Soc., Dalton Trans., (1995) 3801.

[364] X.-L. Luo, G.J. Kubas, C.J. Burns, R.J. Butcher, J.C. Bryan, Inorg. Chem. 34 (1995) 6538.

[365] X.-L. Luo, G.J. Kubas, C.J. Burns, R.J. Butcher, Organometallics 14 (1995) 3370.

[366] T.A. George, M.E. Kwarcinski, J. Coord. Chem., 35 (1995) 349; Chem. Abstr., 123 (1995) 305103j.

[367] V.S. Lenenko, P. Kranke, M. Wahren, V.B. Shur, M.E. Vol'pin, Russian Chem. Bull., 44 (1995) 1293; Izv. Akad. Nauk., Ser. Khim., (1995) 1340; Chem. Abstr., 124 (1996) 16282h.

[368] Y. Wang, J.J.R. Frausto da Silva, A.J.L. Pombeiro, M.A. Pellinghelli, A. Tiripicchio, R.A. Henderson, R.L. Richards, J. Chem. Soc., Dalton Trans., (1995) 1183.

[369] R.A. Henderson, A.J.L. Pombeiro, R.L. Richards, J.J.R. Frausto da Silva, Y. Wang, J. Chem. Soc., Dalton Trans., (1995) 1193.

[370] G. Philipp, S. Wocadlo, W. Massa, K. Dehnicke, D. Fenske, C. Maichle-Mossmer, E. Niquet, J. Strähle, Z. Naturforsch., 50B, (1995) 1; Chem. Abstr., 122 (1995) 150162f.

[371] K.-M. Doh, I.-C. Kim, B.-Y. Choi, J. Korean Chem. Soc., 39 (1995) 191; Chem. Abstr., 123 (1995) 73324b.

[372] G.M. Maksimov, Russian Chem. Rev., 64 (1995) 445; Usp. Khim., 64 (1995) 480.

[373] E. Coronado, C.J. Gomez-Garcia, Comments Inorg. Chem., 17 (1995) 255; Chem. Abstr., 124 (1996) 20192w.

[374] Z.-H. Zhou, W.-B. Yan, H.-L. Wan, K.-R. Tsai, Jiegou Huaxue, 14 (1995) 255; Chem. Abstr., 123 (1995) 186805c.

[375] X.-M. Lu, H.J. Zhu, N. Yang, S.-C. Liu, X.-L. Jin, Jiegou Huaxue, 14 (1995) 135; Chem. Abstr., 123 (1995) 73303u.

[376] S.-G. Roh, S.O. Oh, J. Korean Chem. Soc., 39 (1995) 552; Chem. Abstr., 123 (1995) 186851q.

[377] S.-G. Roh, S.O. Oh, J. Korean Chem. Soc., 39 (1995) 393; Chem. Abstr., 123 (1995) 101294n.

[378] M.P. Lowe, J.C. Lockhart, G.A. Forsyth, W. Clegg, K.A. Fraser, J. Chem Soc., Dalton Trans., (1995) 145.

[379] M.P. Lowe, J.C. Lockhart, J. Chem. Soc., Dalton Trans., (1995) 3511.

[380] G.-Q. Huang, S.-W. Zhang, M.-C. Shao, Gaodeng Xuexiao Huaxue Xuebao, 16 (1995) 670; Chem. Abstr., 123 (1995) 101094x.

[381] P.L. Veya, J.K. Kochi, J. Organomet. Chem. 488 (1995) C4.

[382] X.-X. Xu, X.-Z. You, X.-Y. Huang, Polyhedron 14 (1995) 1815.

[383] Y.-Z. Zhou, S.-J. Tu, X.-L. Jin, S.-C. Liu, Jiegou Huaxue, 14 (1995) 139; Chem. Abstr., 123 (1995) 73304v.

[384] M. McCann, D. McDonnell, B.L. Goodall, J. Mol. Catal. 96 (1995) 31.

[385] H.R. Sun, G.Y. Yang, J.N. Xu, J.Q. Xu, Chin. Chem. Lett., 6 (1995) 1059; Chem. Abstr., 124 (1996) 129720t.

[386] J.L. Stark, V.G. Young, Jr., E.A. Maatta, Angew. Chem. Int. Ed. Engl. 34 (1995) 2547.

[387] W. Clegg, R.J. Errington, K.A. Fraser, S.A. Holmes, A. Schäfer, J. Chem. Soc., Chem. Commun., (1995) 455.

[388] J.L. Stark, A.L. Rheingold, E.A. Maatta, J. Chem. Soc., Chem. Commun., (1995) 1165.

[389] X.-M. Lu, G.X. Liu, S.J. Tu, S.C. Liu, Jiegou Huaxue, 14 (1995) 157; Chem. Abstr., 123 (1995) 46701r.

[390] H. Liu, L. Xu, X.-Y. Huang, W.-D. Chen, J.-S. Huang, Jiegou Huaxue, 14 (1995) 78; Chem. Abstr., 122 (1995) 203863u.

[391] J.J. Hastings, O.W. Howarth, J. Chem. Soc., Dalton Trans., (1995) 2891.

[392] A. Proust, R. Thouvenot, S.-G. Roh, J.-K. Yoo, P. Gouzerh, Inorg. Chem. 34 (1995) 4106.

[393] M.I. Khan, Q. Chen, J. Zubieta, Inorg. Chim. Acta 235 (1995) 135.

[394] U. Kortz, M.T. Pope, Inorg. Chem. 34 (1995) 2160.

[395] U. Kortz, M.T. Pope, Acta Crystallogr., Sect. C 51 (1995) 1717.

[396] D.I. Kondarides, K. Tomishige, Y. Nagasawa, Y. Iwasara, Stud. Surf. Sci. Catal., 91 (1995) 141; Chem. Abstr., 123 (1995) 267539w.

[397] M. McCann, K. Maddock, C. Cardin, M. Convery, G. Ferguson, Polyhedron 14 (1995) 3655.

[398] M. McCann, K. Maddock, Polyhedron 14 (1995) 2919.

[399] M. Inoue, T. Yamase, Bull. Chem. Soc. Jpn. 68 (1995) 3055.

[400] T. Yamase, T. Ozeki, I. Kawashima, Acta Crystallogr., Sect. C 51 (1995) 545.

[401] M. Liu, S. Dong, Electrochim. Acta, 40 (1995) 197; Chem. Abstr., 122 (1995) 225105a.

[402] D. Itul, G. Marcu, Rev. Chem., 46 (1995) 902; Chem. Abstr., 124 (1996) 104564g.

[403] I. Kawafune, G. Matsubayashi, Bull. Chem. Soc. Jpn. 68 (1995) 838.

[404] R. Neier, C. Trojanowski, R. Mattes, J. Chem. Soc., Dalton Trans., (1995) 2521.

[405] C. Bellitto, M. Bonamico, V. Fares, F. Federici, M. Kurmoo, P. Day, Chem. Mater. 7 (1995) 1475.

[406] E. Zang, S. Liang, Yingyong Huaxue, 12 (1995) 107; Chem. Abstr., 123 (1995) 186860s.

[407] M.A. Banares, H.C. Hu, I.E. Wachs, J. Catal. 155 (1995) 249.

[408] E. Wang, J. Niu, L. Xu, D. Zhou, Wuji Huaxue Xuebao, 10 (1994) 352; Chem. Abstr., 123 (1995) 73412d.

[409] Z.-P. Wang, J.-Y. Niu, L. Xu, J. Peng, E.-B. Wang, Huaxue Xuebao, 53 (1995) 757; Chem. Abstr., 123 (1995) 357582j.

[410] S.H. Wang, S.A. Jansen, D.J. Singh, J. Catal. 154 (1995) 137.

[411] S.H. Wang, S.A. Jansen, D.J. Singh, Mater. Res. Soc. Symp. Proc., 368 (1995) 229; Chem. Abstr., 123 (1995) 153681f.

[412] A. Jürgensen, J.B. Moffat, Catal. Lett., 34 (1995) 237; Chem. Abstr., 123 (1995) 357486f.

[413] Z.-P. Wang, L. Xu, E.-H. Shen, E.-B. Wang, Chem. Res. Chin. Univ., 11 (1995) 98; Chem. Abstr., 124 (1996) 44058h.

[414] M.S. Freund, C. Karp, N.S. Lewis, Inorg. Chim. Acta 240 (1995) 447.

[415] C. Rabia, M.M. Bettahar, S. Launay, G. Herve, M. Fournier, J. Chim. Phys.-Chim. Biol., 92 (1995) 1442; Chem. Abstr., 123 (1995) 186840k.

[416] V.F. Odyakov, E.G. Zhizhina, R.I. Maksimovskaya, K.I. Matveev, Kinet. Catal., 36 (1995) 733; Chem. Abstr., 124 (1996) 74691b.

[417] W. [illegible]iang, H. Lin, G. Xi, Wuji Huaxue Xuebao, 11 (1995) 331; Chem. Abstr., 124 (1996) 120362b.

[418] A. Leclaire, M.M. Borel, J. Chardon, B. Raveau, Mater. Res. Bull., 30 (1995) 1075; Chem. Abstr., 123 (1995) 186839s.

[419] Z. Wang, Q. Ren, L. Xi, E. Shen, E. Wang, Wuji Huaxue Xuebao, 11 (1995) 63; Chem. Abstr., 122 (1995) 305174n.

[420] K. Maeda, H. Katano, T. Osakai, S. Himeno, A. Saito, J. Electroanal. Chem., 389 (1995) 167; Chem. Abstr., 123 (1995) 95999e.

[421] M. Cindric, B. Kamenar, N. Strukan, Z. Veksli, Polyhedron 14 (1995) 1045.

[422] S. Himeno, T. Kubo, A. Saito, T. Hori, Inorg. Chim. Acta 236 (1995) 167.

[423] Y. Zhang, R.C. Haushalter, A. Clearfield, J. Chem. Soc., Chem. Commun., (1995) 1149.

[424] A.M. Bond, D.M. Way, A.G. Wedd, R.G. Compton, J. Booth, J.C. Eklund, Inorg. Chem. 34 (1995) 3378.

[425] S. Himeno, A. Saito, J. Electroanal. Chem., 391 (1995) 207; Chem. Abstr., 123 (1995) 95957n.

[426] L.-Y. Qu, J. Gong, J. Peng, S.-R. Sun, J.G. Zhang, Gaodeng Xuexiao Huaxue Xuebao, 16 (1995) 5; Chem. Abstr., 122 (1995) 280588k.

[427] H.B. Zhang, X.Y. Qi, J.W. Zheng, S.J. Li, Chem. J. Chin. Univ. 16 (1995) 124.

[428] A. Müller, H. Bögge, E. Krickemeyer, S. Dillinger, Bull. Pol. Acad. Sci. Chem., 42 (1994) 291; Chem. Abstr., 123 (1995) 46661e.

[429] G.Q. Huang, S.W. Zhang, M.C. Shao, Chin. Sci. Bull., 40 (1995) 1438; Chem. Abstr., 124 (1996) 218483k.

[430] A. Müller, E. Krickemeyer, J. Meyer, H. Bögge, F. Peters, W. Plass, E. Diemann, S. Dillinger, F. Nonnenbruch, M. Randerath, C. Menke, Angew. Chem. Int. Ed. Engl. 34 (1995) 2122.

[431] J.C. Gordon, R. Poli, Acta Crystallogr., Sect. C 51 (1995) 14.

[432] L.M. Robinson, R.L. Bain, D.F. Shriver, D.E. Ellis, Inorg. Chem. 34 (1995) 5588.

[433] L.M. Robinson, H. Lu, J.T. Hupp, D.F. Shriver, Chem. Mater. 7 (1995) 43.

[434] G.M. Ehrlich, H. Deng, L.I. Hill, M.L. Steigerwald, P.J. Squattrito, F.J. DiSalvo, Inorg. Chem. 34 (1995) 2480.

[435] M. Ebihara, T. Imai, T. Kawamura, Acta Crystallogr., Sect. C 51 (1995) 1743.

[436] M. Ebihara, K. Toriumi, Y. Sasaki, K. Saito, Gazz. Chim. Ital., 125 (1995) 87; Chem. Abstr., 122 (1995) 305232e.

[437] G.M. Ehrlich, C.J. Warren, R.C. Haushalter, F.J. DiSalvo, Inorg. Chem. 34 (1995) 4284.

[438] J.H. Golden, H.B. Deng, F.J. DiSalvo, J.M.J. Frechet, P.M. Thompson, Science 268 (1995) 1463.

[439] H. Imoto, T. Saito, H. Adachi, Inorg. Chem. 34 (1995) 2415.

[440] S.J. Hilsenbeck, R.E. McCarley, A.I. Goldman, Chem. Mater. 7 (1995) 499.

[441] S.P. Huang, M.G. Kanatzidis, Inorg. Chim. Acta 230 (1995) 9.

[442] A. Liu, Y. Yuan, H. Zhang, M. Zhou, R. Yang, H. Wan, K. Tsai, Xiamen Daxue Xuebao, Ziran Kexueban, 33 (1994) 809; Chem. Abstr., 123 (1995) 101216p.

[443] J.-W. Huang, H.T. Zhang, R. Yang, M.-Y. Zhou, H.-L. Wan, Q.R. Cai, Chem. J. Chin. Univ. (Gaodeng Xuexiao Huaxue Xuebao), 16 (1995) 632; Chem. Abstr., 123 (1995) 106405j.

[444] Z. Chen, J. Cluster Sci., 6 (1995) 357; Chem. Abstr., 123 (1995) 238024u.

[445] J. Ruiz, V. Rodriguez, G. López, P.A. Chaloner, P.B. Hitchcock, J. Organomet. Chem. 493 (1995) 77.

[446] W.J. Evans, M.A. Ansari, J.W. Ziller, S.I. Khan, Organometallics 14 (1995) 3.

[447] R.J. Salm, A. Misetic, J.A. Ibers, Inorg. Chim. Acta 240 (1995) 239.

[448] S.-F. Lu, J.-Q. Huang, X.-Y. Huang, Q.J. Wu, Jiegou Huaxue, 14 (1995) 482; Chem. Abstr., 124 (1996) 20321n.

[449] S. Sarkar, R. Sah, P.K. Chaudhury, R. Maiti, S.K. Das, Proc. Indian Acad. Sci., Chem. Sci., 107 (1995) 355; Chem. Abstr., 124 (1996) 192405j.

[450] M. Wang, G. Guo, Xiamen Daxue Xuebao, Ziran Kexueban, 34 (1995) 475; Chem. Abstr., 124 (1996) 20281z.

[451] J. Mizutani, H. Imoto, T. Saito, J. Cluster Sci., 6 (1995) 523; Chem. Abstr., 124 (1996) 133845e.

[452] V.E. Fedorov, O.A. Geras'ko, Y.V. Mironov, K. Hegetschweiler, R. Stoop, J. Gallus, F. Gramlich, Zh. Strukt. Khim., 36 (1995) 1046; Chem. Abstr., 124 (1996) 305474b.

[453] V.P. Fedin, H. Imoto, T. Saito, W. McFarlane, A.G. Sykes, Inorg. Chem. 34 (1995) 5097.

[454] V.P. Fedin, H. Imoto, T. Saito, J. Chem. Soc., Chem. Commun., (1995) 1559.

[455] K. Tsuge, H. Imoto, T. Saito, Inorg. Chem. 34 (1995) 3404.

[456] J.C. Muijsers, T. Weber, R.M. van Hardeveld, H.W. Zandbergen, J.W. Niemantsverdriet, J. Catal., 157 (1995) 698; Chem. Abstr., 124 (1996) 61002e.

[457] R.A. Stevens, C.C. Raymond, P.K. Dorhout, Angew. Chem. Int. Ed. Engl. 34 (1995) 2509.

[458] J.-H. Liao, J. Li, M.G. Kanatzidis, Inorg. Chem. 34 (1995) 2658.

[459] J.-Q. Huang, J.-L. Huang, S.-F. Lu, H.-H. Zhuang, X.-T. Lin, D.M. Wu, R.-M. Yu, H.B. Chen, Q.H. Chen, Jiegou Huaxue, 14 (1995) 180; Chem. Abstr., 123 (1995) 46577e.

[460] Y. Yao, H. Akashi, G. Sakane, T. Shibahara, H. Ohtaki, Inorg. Chem. 34 (1995) 42.

[461] Y. Yao, H. Akashi, T. Shibahara, Shizen Kagaku Kenkyusho Kenkyu Hokoku, Okayama Rika Daigaku, 20 (1994) 117; Chem. Abstr., 123 (1995) 305026m.

[462] H.-H. Zhuang, D.-M. Wu, J.-Q. Huang, J.-L. Huang, Jiegou Huaxue, 14 (1995) 245; Chem. Abstr., 123 (1995) 131140b.

[463] Q.-H. Chen, S.-F. Lu, Y.H. Huang, X.-Y. Huang, J.-Q. Huang, Jiegou Huaxue, 14 (1995) 97; Chem. Abstr., 123 (1995) 46699w.

[464] H. Diller, H. Keck, H. Wunderlich, W. Kuchen, J. Organomet. Chem. 489 (1995) 123.

[465] S.F. Fu, H.B. Chen, J.-Q. Huang, Q.J. Wu, Q.L. Sun, J. Li, J.X. Lu, Inorg. Chim. Acta 232 (1995) 43.

[466] R. Cao, X.J. Lei, M.-C. Hong, X.-L. Xie, B.-S. Kang, F.-L. Jiang, Q.-T. Liu, H.-Q. Liu, Jiegou Huaxue, 14 (1995) 33; Chem. Abstr., 122 (1995) 229121a.

[467] R. Cao, D. Wu, X. Xie, M. Hong, F. Jiang, H. Liu, Bopuxue Zazhi, 12 (1995) 13; Chem. Abstr., 122 (1995) 305129b.

[468] Q.-T. Liu, Y. Yang, X.-J. Lei, Y.-H. Deng, C.-N. Chen, B.-S. Kang, Jiegou Huaxue, 14 (1995) 436; Chem. Abstr., 123 (1995) 357431j.
[469] H.-W. Hou, X.-Q. Xin, Jiegou Huaxue, 14 (1995) 405; Chem. Abstr., 123 (1995) 357430h.
[470] S. Shi, H.W. Hou, X.Q. Xin, J. Phys. Chem. 99 (1995) 4050.
[471] S. Shi, X.Q. Xin, Mater. Res. Soc. Symp. Proc., 374 (1994) 151; Chem. Abstr., 124 (1996) 133880n.
[472] H.W. Hou, X.Q. Xin, X.X. Huang, J.H. Cai, B.S. Kang, Chin. Chem. Lett., 6 (1995) 91; Chem. Abstr., 122 (1995) 254626b.
[473] S. Shi, Z. Chen, H. Hou, X. Xin, K. Yu, Chem. Mater. 7 (1995) 1519.
[474] H. Hou, X. Ye, X. Xin, J. Liu, M. Chen, S. Shi, Chem. Mater. 7 (1995) 472.
[475] S. Shi, X.Q. Xin, W. Ji, W. Xie, Mater. Res. Soc. Symp. Proc., 374 (1994) 311; Chem. Abstr., 124 (1996) 133881p.
[476] S. Shi, W. Ji, W. Xie, T.C. Chong, H.C. Zeng J.P. Lang, X.Q. Xin, Mater. Chem. Phys., 39 (1995) 298; Chem. Abstr., 122 (1995) 251397s.
[477] H. Hou, X. Xin, S. Lu, X. Huang, Q. Wu, J. Coord. Chem., 35 (1995) 299; Chem. Abstr., 123 (1995) 305099n.
[478] H. Hou, Y. Liu, X. Xin, Q. Wu, S. Lu, Synth React. Inorg. Met.-Org. Chem., 25 (1995) 1417; Chem. Abstr., 123 (1995) 357521p.
[479] D.L. Long, X.Q. Xin, X.Y. Huang, J.H. Cai, B.S. Kang, Chin. Chem. Lett., 6 (1995) 263; Chem. Abstr., 122 (1995) 280602k.
[480] S. Shi, W. Ji, X.Q. Xin, Mater. Res. Soc. Symp. Proc., 374 (1994) 363; Chem. Abstr., 124 (1996) 133882q.
[481] M.T. Pope, J.-P. Lang, X.-Q. Xin, K.-B. Yu, Chin. J. Chem., 13 (1995) 40; Chem. Abstr., 122 (1995) 229226p.
[482] S. Shi, W. Ji, X.Q. Xin, J. Phys. Chem. 99 (1995) 894.
[483] W. Ji, S. Shi, H.J. Du, P. Ge, S.H. Tang, X.Q. Xin, J. Phys. Chem. 99 (1995) 17297.
[484] R.H. Holm, Pure Appl. Chem. 67 (1995) 217.
[485] D.E. Barber, M. Sabat, E. Sinn, B.A. Averill, Organometallics 14 (1995) 3229.
[486] L.J. Laughlin, D. Coucouvanis, J. Am. Chem. Soc. 117 (1995) 3118.
[487] K.D. Demadis, D. Coucouvanis, Inorg. Chem. 34 (1995) 436.
[488] K.D. Demadis, D. Coucouvanis, Inorg. Chem. 34 (1995) 3658.
[489] K.D. Demadis, C.F. Campana, D. Coucouvanis, J. Am. Chem. Soc. 117 (1995) 7832.
[490] J.E. Barclay, D.J. Evans, G. Garcia, M.D. Santana, M.C. Torralba, J.M. Yago, J. Chem. Soc., Dalton Trans., (1995) 1965.
[491] J. Zhou, R.H. Holm, J. Am. Chem. Soc. 117 (1995) 11353.
[492] T. Shibahara, M. Sasaki, G. Sakane, Inorg. Chim. Acta 237 (1995) 1.
[493] C.D. Borman, V.P. Fedin, M.-C. Hong, G.J. Lamprecht, C.-H. Kwak, C.A. Routledge, D.M. Saysell, A.G. Sykes, Pure Appl. Chem. 67 (1995) 305.
[494] D.M. Saysell, A.G. Sykes, J. Cluster Sci., 6 (1995) 449; Chem. Abstr., 124 (1996) 104421h.
[495] T. Shibahara, G. Sakane, Y. Naruse, K. Taya, H. Akashi, A. Ichimura, H. Adachi, Bull. Chem. Soc. Jpn. 68 (1995) 2769.
[496] M. Brorson, J. Hyldtoft, C.J.H. Jacobsen, K.G. Olesen, Inorg. Chim. Acta 232 (1995) 171.
[497] M. Taniguchi, Y. Ishii, T. Murata, T. Tatsumi, M. Hidai, J. Chem. Soc., Chem. Commun., (1995) 2533.
[498] T. Wakabayashi, Y. Ishii, T. Murata, Y. Mizobe, M. Hidai, Tetrahedron Lett. 36 (1995) 5585.