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REVIEWS

7. Rhenium 1993

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CONTENTS

INTRODUCTION

This review delineates the advances in rhenium chemistry as reported in the literature for 1993. As in previous reviews [1], the emphasis is mainly on coordination compounds and the format is similar, with some references to organometallic compounds which may be pertinent. It is based

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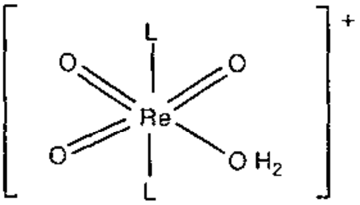
on a search of volumes 118, 119 and 120 of *Chemical Abstracts*. In addition, major inorganic chemistry journals have been searched separately for the calendar year 1993.

7.1 RHENIUM(VII)

7.1.1 Complexes with oxygen donor ligands

Complexes of Re(VII)oxide with *N*-alkylphenothiazines have been synthesised and characterised [2]. The molecular formulae of the new ionic complexes are $[ReO(PTZ)_2(H_2O)][ReO_4]$, PTZ = chlorpromazine, promethazine and ethopropazine. A tentative general structure (**1**), has been proposed for the complex cations.

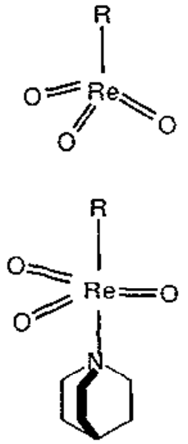


L = PTZ

(1)

Alkylrhenium oxides of formulae $RReO_3$ and $RReO_3 \cdot L$, L = quinuclidine (**2**) have been obtained from the reaction in equation (1) [3].

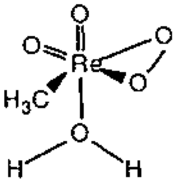
$$2Re_2O_7 \xrightarrow[40^\circ C,\ THF]{ZnR_2} 2RReO_3 + Zn(ReO_4)_2(THF)_2 \qquad (1)$$



	R		R
1	CH_3	6	$CH_3(CH_2)_6$
2	CH_3CH_2	7	$(CH_3)_2CH[CH_2]_2$
3	$(CH_3)_2CHCH_2$	8	$CH_3CH_2CH(CH_3)CH_2$
4	$CH_3[CH_2]_2$	9	$CH_3[CH_2]_3CH(CH_2CH_3)CH_2$
5	$CH_3[CH_2]_4$	10	CH_2CH_2CH

(2)

The active species of the catalytic system $[CH_3ReO_3]/H_2O_2$ has been elucidated [4]. The first isolated peroxo-metal complex (**3**) has been obtained which contains a metal alkyl group that is stable to hydrolysis and peroxide. Addition of a small amount diglyme to *n*-pentane/diethyl ether solutions of the former gives (4) as thermally stable orange-yellow crystals of the 1:1 diglyme adduct. A single crystal X-ray structure has been obtained.



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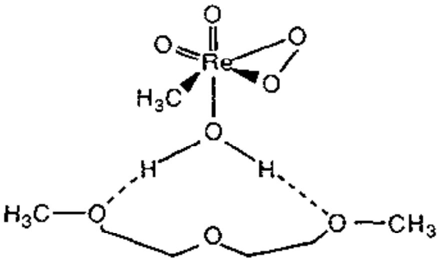

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7.1.2 *Complexes with nitrogen donor ligands*

The synthesis of new mixed-alkyl rhenium(VII) organoimido complexes and a new facile route to $Me_3SiORe(N^tBu)_3$ have been documented [5]. Alkylation of $MeRe(NR')_2Cl_2py$ with MeMgCl, Et_2Zn and ^iPrMgCl yielded the d^0 trialkyl diimido complexes of the formula $MeR_2Re(NR')_2$, R = Me, Et, ^iPr; R' = 2,6 dimethylphenyl. The ethyl and isopropyl derivatives decompose within a few hours. In a similar manner the alkylation of the new tert-butyl imido derivative $MeRe(N^tBu)_2Cl_2$ gave trialkyl complexes of formula $MeR_2Re(N^tBu)_2$, R = Me, Et and ^iPr which are thermo-labile. The gas-phase decomposition of these complexes was studied.

A study of outer-sphere complexes of Re(VII) with acridine and rhodamine dyes has been conducted [6]. The complexes were characterized by EPR and electronic absorption spectroscopy.

7.2 *RHENIUM(VI)*

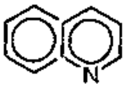
The synthesis and crystal structure of $[ReNCl(NPPh_2C_6H_4)]_2 \cdot [Ph_3PNH_2]Cl \cdot [CH_3CN]$ has been obtained [7]. The rhenium atoms are μ_2-bridged via the N-atoms of the phosphoraneiminato ligands and are six-coordinate.

7.3 *RHENIUM(V)*

7.3.1 *Complexes with hydride ligands*

The reactions of the polyhydride complex $ReH_7(PPh_3)_2$ with quinoline, qn, (5), 2-hydroxyquinoline Hhq, (6) and 2-mercaptoquinoline, (7), Hmq, have been studied [8]. The species $ReH_5(PPh_3)_2(qn)$, $ReH_4(hq)(PPh_3)_2$, and $ReH_4(mq)(PPh_3)_2$ were obtained from the thermal reaction of the title complex with qn, Hhq and Hmq when refluxing thf or EtOH was used as the reaction solvent whereas paramagnetic chlororhenium(III) species $ReCl_3(qn)_2(PPh_3)$, $ReCl_2(hq)(PPh_3)_2$ and $ReCl_2(mq)(PPh_3)_2$ were formed in refluxing 1,2-dichloroethane solutions.

These complexes have been characterized by NMR spectroscopy, cyclic voltammetry and X-ray crystallography.



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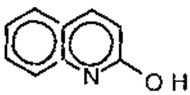

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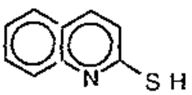

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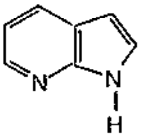
7.3.2 *Complexes with oxygen donor ligands*

Neutral and ionic rhenium(V) and technetium(V) complexes of the form [$MOXL_2$] and [$MOX_3(ma)$]$^-$ where M = Tc, X = Cl or M = Re, X = Br and L is a didentate (*O,O'*) monobasic ligand, 2-methyl-3-oxy-4-pyronate (maltolato, ma$^-$) or 1,2-dimethyl-3-oxy-4-pyridinonate (dpp$^-$) were synthesised and characterised [9]. These complexes have been studied by IR, ^{1}H NMR, mass spectroscopy and X-ray crystallography. For [$ReOBr(ma)_2$] solution ^{1}H NMR and crystallography indicate *cis*-geometry in which the Re atom is in the centre of a highly distorted octahedron of *cis*-(bromo, oxo) donors and ketonic oxygen and hydroxy oxygen donors of the two mutually orthogonal maltolato ligands.

Neutral oxometal(V) complexes of the type [$MOL_2(OR)$], M = Tc or Re; R = alcoholate, glycolate or acetate have been synthesised by treating (*o*-aminophenyl)diphenylphosphine with [$ReOCl_4$]$^-$ in basic media and a strictly controlled metal/ligand stoichiometric ratio (1/2 for Re, 1/3 for Tc) [10]. The compounds are referred to as equatorial because the coordination of both didentate L$^-$ chelates occurs symmetrically in the equatorial plane orthogonal to the M=O moiety with a mutual *cis*-phosphorus configuration. The site *trans* to the oxo group is always occupied by an oxygen-containing monodentate ligand. Elemental analyses, FAB mass, IR, electronic, ^{1}H and ^{31}P NMR spectroscopy and X-ray data are reported.

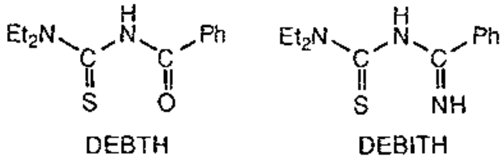
The preparation and structure of oxo-rhenium(V) complexes containing the ligand 7-azaindole (**8**), Haza, has been described [11]. The complexes may have potential utility as precursors to metal-metal bonded rhenium(III) dimers of the "paddle-wheel" type. The reaction of $ReOCl_3(PPh_3)_2$ and Haza yielded $Re_2O_3Cl_4(Haza)_4$, the oxo-ethoxo monomers $ReO(OEt)Cl_2(Haza)_2$ and $ReO(OEt)Cl_2(Haza)(PPh_3)$ and the dioxo [$ReO_2(Haza)_4$]Cl salt. The iodide salt was prepared from $ReO_2I(PPh_3)_2$. X-ray diffraction on $ReO(OEt)Cl_2(Haza)_2$ shows it consists of individual molecules of the *trans-trans* type in which the azaindole is *N* bonded. Crystals of [$ReO_2(Haza)_4$]Cl contain well separated Cl$^-$ anions and *trans*-dioxo cations. The *N*-bonded azaindole ligands are held parallel to the O=Re=O axis by intramolecular N–H.....O hydrogen bonds.



(8)

The structure of *trans*-dibromo(ethoxo)oxobis(triphenylphosphine)rhenium(V) $[ReBr_2O(OC_2H_5)\{P(C_6H_5)_3\}_2]$, has been determined [12]. The crystal contains molecules which are roughly octahedral. The linear O-Re-O unit lies on a twofold axis and the ethyl group of the ethoxo ligand is disordered over two orientations. The Re-O(oxo) distance is 1.678(6) Å and the Re-O(ethoxo) distance of 1.894(6) Å is suggestive of partial multiple bond character.

The preparation of Re(V) oxo and imido complexes employing the ligands *N,N*-diethyl-*N'*-benzoylthiourea (DEBTH) and *N,N'*-diethyl-*N'*-benzoyliminothiourea (DEBITH), (**9**), has been documented [13]. The neutral complexes $[ReOCl(DEBT)_2]$ and $[ReOCl(DEBIT)_2]$ were obtained. The X-ray crystal structure for the former shows that the complex possesses a pseudo-octahedral geometry with the oxo and chloride ligands in a *cis* position. When reacted with $ArNH_2$ imido complexes $[ReCl(NAr)DEBT)_2]$ were obtained in good yield. Reaction with PPh_3 gave rise to an Re(III) complex $[ReDEBT)_2(PPh_3)_2]^+$. The spectroscopic and electrochemical properties of these complexes are discussed. The X-ray crystal structure for the former shows that the complex possesses a pseudo-octahedral geometry with the oxo and chloride ligands in a *cis* position. When reacted with $ArNH_2$ imido complexes $[ReCl(NAr)DEBT)_2]$ were obtained in good yield. Reaction with PPh_3 gave rise to an Re(III) complex $[ReDEBT)_2(PPh_3)_2]^+$. The spectroscopic and electrochemical properties of these complexes are discussed.



(9)

7.3.3 Complexes with oxygen and sulfur donor ligands

The reaction of $ReCl_5$ with $Na_2[C_3S_5]$, $C_3S_5^{2-}$ = 4,5-dimercapto-1,3-dithiole-2-thionate(2–) in ethanol in the presence of $[PPh_4]Br$ yielded $[PPh_4][ReO(C_3S_5)_2]$ [14]. An X-ray crystal structure has been obtained and shows the rhenium atom to possess a square-pyramidal geometry. The reaction of $ReCl_5$ with $[N^nBu_4]_2[Zn(C_3S_5)_2]$ in acetonitrile gave the salt $[N^nBu_4][Re(C_3S_5)_3]$. These complexes have been studied by CV, electronic absorption spectroscopy, IR, ESR and X-ray PES.

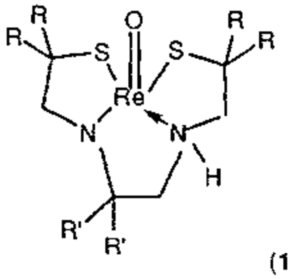
7.3.4 Complexes with oxygen and nitrogen donor ligands

The synthesis and characterization of Re(V) complexes with cyclam and cyclam derivatives has been achieved [15]. They were synthesised by ligand exchange reactions of the macrocycles with a variety of starting compounds including $ReOCl_3(PPh_3)_2$ and $ReO_2(en)_2Cl$. Those synthesised include $[ReO_2(cyclam)]^+$, $[ReO(OH)(cyclam)]^{2+}$, $ReO_2(H_{-1}O_1cyclam)$, $ReO(OH)H_{-1}O_1cyclam)$, and $ReO(H_{-2}O_2cyclam)Cl$.

The synthesis and characterization of neutral $M^{V}O$ (M = Tc, Re) amine-thiol complexes has been reported [16]. The rhenium analogues were prepared by ligand exchange reactions with bis(amino thio)-phenylpiperidine BAT-PPP. They were characterized by NMR spectroscopy and X-ray crystallography.

A series of isoelectronic Re(V)-cyclam complexes with oxo, dioxo and phenylimido moieties has been prepared [17]. In particular, *trans*-$[ReO_2(cyclam)]ReO_4 \cdot {}^1/_2H_2O$, *trans*-$[ReO(OEt)(cyclam)](ClO_4)_2$ and *trans*-$[Re(NPh)(OH)(cyclam)(ClO_4)_2$, were prepared and structurally characterized. The rhenium-oxo bond distances in *trans*-$[ReO_2(cyclam)]^+$, and *trans*-$[ReO(OEt)(cyclam)]^{2+}$ are 1.775(9) and 1.643(9) Å respectively. UV-Visible spectroscopy has been conducted and *trans*-$[ReO_2(cyclam)]^+$ shows two ligand field transitions in its spectrum at 423 and 530 nm whereas for *trans*-$[ReO(OEt)(cyclam)]^{2+}$ the corresponding ligand field bands are red-shifted to 481 and 625 nm respectively. The *trans*-$[Re(NPh)(OH)(cyclam)(ClO_4)_2$ complex is intriguing in that it is stable in aqueous medium and the Re-NPh distance is 1.731(9)Å is consistent with a metal-imido formulation. These complexes were further characterized electrochemically.

Rhenium diamino dithiolate complexes which have potential in tumour-targeting therapy have been synthesised [18]. The complexes ReO(tedadt), ReO(tedmdadt) and ReO(hmdadt), (**10**) were prepared by $SnCl_2 \cdot 2H_2O$ reduction of NH_4ReO_4 in the presence of dadt ligands under strong acidic conditions. A single crystal of ReO(tedadt) was obtained and subjected to X-ray crystallography, the complex is a centrosymmetric hydrogen-bonded dimer and constitutes the first time that hydrogen bonding has been observed in rhenium diamino dithiolate complexes. One amine is deprotonated whereas the other couples to rhenium by means of its lone pair.

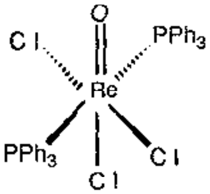


(10)

	R	R'
tedadt	Et	H
tedmdadt	Et	Me
hmdadt	Me	Me

7.3.5 *Complexes with oxygen and phosphorus donor ligands*

The stereoisomerism of $ReOCl_3(PPh_3)_2$ has been reinvestigated [19]. Of the three "isomers" previously reported in the literature, this work shows that two are polymorphs of the *mer*-trichloro-*trans*-bis(phosphine) molecule (**11**). X-ray crystallography of crystals of the bright green polymorph show the same monomeric molecule, but with a differing conformation of the PPh_3 ligands and a different packing pattern. Attempts to prepare the third "isomer" were unsuccessful. Results from IR and ^{31}P NMR spectroscopies are reported.



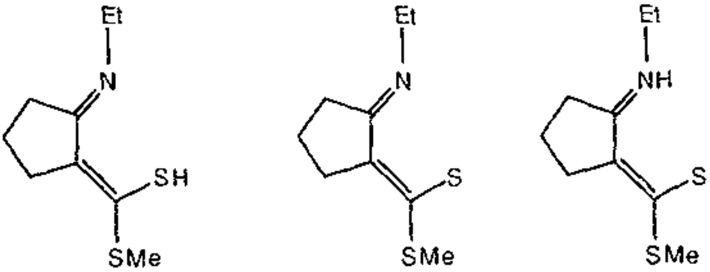
(11)

7.3.6 Complexes with oxygen, sulfur and nitrogen donor ligands

The preparation of technetium and rhenium complexes of the *S,N,N,O*-ligand mercaptoacetyl diglycine and the X-ray structure of the Tc complex has been reported [20]. The preparation was achieved by reacting either technetium(V) or rhenium(V) gluconate in aqueous solution with mercaptoacetyl diglycine.

7.3.7 Complexes with oxygen, sulfur and phosphorus donor ligands

Monodentate coordination of a potentially didentate *N,S*-donor ligand has been demonstrated recently [21]. Specifically, the reaction of the ligand methyl 2-(*N*-ethylamino)-1-cyclopentene-dithiocarboxylate, HL, which exists in three tautomeric forms (**12**), with *trans*-$ReOCl_3(PPh_3)_2$ has led to the complex $ReOCl_3(PPh_3)(HL)$ in which coordination of HL occurs through the neutral thiocarbonyl sulfur atom only. An X-ray crystal structure has been obtained and shows the rhenium atom to be in a distorted octahedral environment with an Re-S distance of 2.369(2)Å.



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7.3.8 Complexes with nitrogen donor ligands

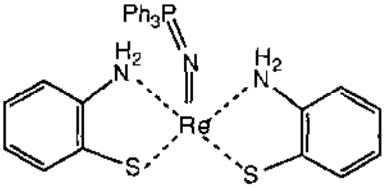
The first example of increased basicity of a nitrido complex in its thermally equilibrated excited state compared to its ground state has been reported [22]. The photoprotonation of the ground and excited states of *trans*-$[NRe(R_2PCH_2CH_2PR_2)Cl]^+$, R = Me, has been observed in HCl solution. An imido complex *trans*-$[HNRe(R_2PCH_2CH_2PR_2)Cl]^{2+}$ was obtained. The increase in basicity which has been rationalized by a simple orbital diagram is due to an increase in electron density at the nitride nitrogen in the excited state.

The reactivity of various rhenium(V) complexes containing different cores with bis(diphenylphosphino)methane has been studied [23]. In particular, the reactivity of $[ReOCl_3(PPh_3)_2]$, $[AsPh_4][ReOCl_4]$, $[Re(NCH_3)Cl_3(PPh_3)_2]$ and $[ReNCl_2(PPh_3)_2]$ has been documented and a complete crystallographic study was undertaken.

The electrochemistry of arylimido rhenium(V) dithiocarbamate complexes $[\{Re(NR)(S_2CNR'_2)_2\}_2O]$ where R = phenyl, *p*-tolyl, *p*-chlorophenyl and *p*-methoxyphenyl in dmf was explored [24]. These complexes were found to undergo a quasi-reversible one-electron reduction followed by cleavage of the μ-oxo bond (Re-O-Re) concomitant with the release of one dithiocarbamate ligand from the complex. The redox potential for the couple and stability of the redox products was found to be dependent on R and R'.

7.3.9 Complexes with nitrogen and sulfur donor ligands

A neutral, diamagnetic phosphorane thioiminato complex, $Re(NPPh_3)$(2-aminothiphenolato)$_2$ has been obtained from the ligand exchange reaction between $ReNCl_3(PPh_3)_2$ and 2-aminothiophenol [25]. X-Ray crystallography shows the complex to be square planar (**13**). Since nucleophilic attack by a free triphenylphosphine ligand onto a nitrido group is unusual, a second complex ReO(2-aminthiophenolato)$_2$, in which one amino group is deprotonated, was synthesised and its reactivity towards nucleophilic attack by triphenylphosphine investigated. No reactivity was apparent.



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7.3.10 Complexes with nitrogen and phosphorus donor ligands

Nitrido rhenium and technetium complexes with chelating phosphines have been synthesised and their reactivity and crystal structures studied [26]. The complexes of general formula $[MNCl_2L]$ L = bis(diphenylphosphinoethyl)propylamine, 1,8-bis(diphenylphosphino)-3,6-dioxaoctane, and 1,1,1-tris(diphenylphosphinomethyl)ethane were obtained. Reaction of these complexes with an excess of potassium *O*-ethyl dithiocarbonate yielded $[MN(S_2CO)L]$ as neutral compounds while reaction with $K(S_2CNEt_2)$ gave cationic and neutral complexes $[MN(S_2CNEt_2)L]^+$ and $[MN(S_2CNEt_2)_2]$.

Treatment of $[Re^VNCl_2(PPh_3)_2]$ with LiR afforded the complexes $[Re^VNR_2(PPh_3)_2]$, R = Me, CC^{t}Bu, Ph or C_6H_4Me-*p* [27]. These complexes have been characterised by spectroscopy and electrochemistry. An X-ray crystal structure for the methylrhenium analogue has been determined and shows an Re-N distance of 1.641Å.

7.4 RHENIUM(IV)

7.4.1 Complexes with halide ligands

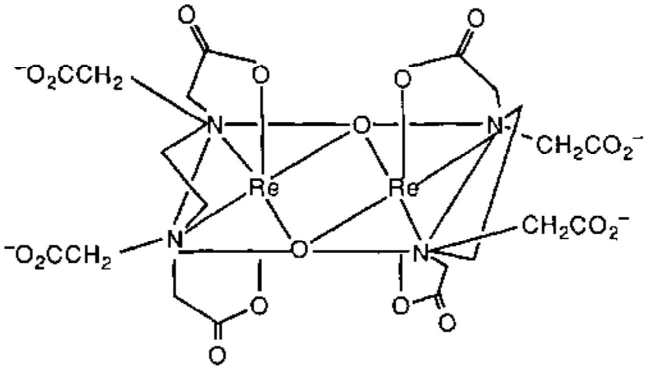
The complete structural determination of bis(tetramethylammonium)hexachlororhenate(IV), $[N(CH_3)_2]_2[ReCl_6]$, has been described [28]. The Cl atoms occupy octahedral positions around the central Re atom and the Re-Cl distance is 2.360(2)Å.

7.4.2 Complexes with oxygen donor ligands

The synthesis, properties and crystal structures of $Re_2Cl_4(C_5H_7O)_2(C_5H_8O_2)_2$ and $Re_2Br_4(C_5H_7O)_2(C_5H_8O_2)_2$ has been achieved [29]. An X-ray crystal structure on the former shows it to consist of neutral dimeric molecules with an Re-Re quadruple bond of 2.236(1) Å, two equatorial acac groups are incorporated to become chelate rings. In addition, two neutral acac molecules occupy axial positions each being coordinated by one oxygen atom to a rhenium centre.

7.4.3 Complexes with oxygen and nitrogen donor ligands

The preparation, structure and reactivity of a dinuclear di-μ-oxo-bis[(ethylenediamine-*N,N,N',N''*,-tetraacetato rhenate(IV) complex has been described [30]. The *meso* ΔΛ–form of the complex $Ba_2[Re_2(\mu\text{-}O)_2(edta)_2]\cdot 4.5H_2O$, **(14)**, has been characterized by X-ray crystallography. The Re atoms possess distorted octahedral symmetry and each tetradentate $edta^{4-}$ ligand has two uncoordinated $\text{-}CH_2CO_2^-$ groups. The Re_2O_2 and has an Re-Re distance of 2.362Å. Evidence from ^1H and ^{13}C NMR spectroscopy of the uncrystallised sodium salt in aqueous solution points to the existence of the *meso* ΔΛ as well as racemic ΔΔ– and ΛΛ–forms. Cyclic voltammetric and kinetic studies have been carried out and results are reported.



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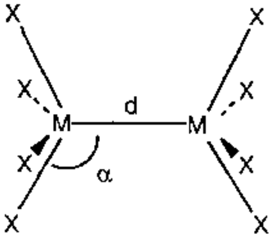
7.5 RHENIUM(III)

7.5.1 Complexes with halide ligands

Several edge sharing bioctahedral dirhenium and dimolybdenum compounds with polydentate phosphines have been synthesised [31]. The compounds 1,2,7,8-Re_2Cl_6(*meso*-tetraphos-1) and 1,2,7,8-Re_2Cl_6(*meso*-tetraphos-1)·$(CH_3CH_2)_2O$ (where tetraphos-1 = $Ph_2PCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2$) represent new isomeric forms of the $M_2(\mu\text{-}Y)_2X_4P_4$ core. The metal-metal distance in both these compounds is 2.625(1) Å

Pyramidality angles and metal-metal bond distances in more than 350 dinuclear complexes including those of Re(III) have been analysed to elucidate if a correlation exists [32]. A clear correlation was found to exist between the average pyramidality angle (M-M-X, α) and the metal-metal bond distance (**15**). The presence of axial ligands favours elongation of the metal-metal bond but this effect is also attenuated by changes in the pyramidality angle. Electronic structure calculations were carried out using EH, HF-SCF and multiconfiguration CASSCF levels and show good agreement with experimental trends.



(15)

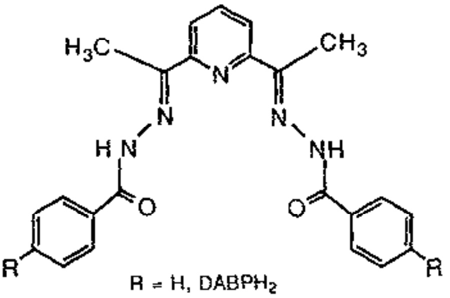
A chloroacid of rhenium(III), $H_3O[Re_3Cl_{10}(H_2O)_2]\cdot 5H_2O$ has been obtained at room temperature from a saturated solution of $ReCl_3\cdot 2H_2O$ with an excess of NaCl in concentrated HCl [33]. X-ray crystallography has been carried out and reveals isolated cluster anions which are enclosed by a cage of water molecules. The building units are connected through a strong hydrogen bonding system.

The crystal structure of $(NMe_4)_2[Re_3Br_{11}(H_2O)][Re_3Br_9(H_2O)_3](H_2O)_2$ has been determined from four-circle diffractometer data recently [34]. Two differing cluster units are apparent, isolated anionic $[Re_3Br_{11}(H_2O)]^-$ units and neutral cluster units that are connected through crystal water molecules to chains of ${}^1_\infty\{[Re_3Br_9(H_2O)_3](H_2O)_2\}$.

A new trimeric complex $(Me_2NH_2)_3[Re_3Br_{10}(HCOO)]Br$ containing the trinuclear anion $[Re_3Br_{10}(HCOO)]^{2-}$ has been obtained [35]. Two terminal bromine atoms have been substituted by a bridging formate group in this anion.

7.5.2 Complexes with oxygen and nitrogen donor ligands

The synthesis and characterization of some novel pentagonal bipyramidal 2,6-diacetylpyridine bis(benzoylhydrazone) ($DAPBH_2$) complexes has been achieved [36]. The reaction of $[ReCl_3(MeCN)(PPh_3)_2]$ with $DAPBH_2$ and $DAP\text{-}Me\text{-}BH_2$, (**16**), yielded the seven-coordinate complexes $[ReCl(L)PPh_3]$ containing the doubly deprotonated ligands $DAPB^{2-}$ and $DAP\text{-}Me\text{-}B^{2-}$. The $DAPB^{2-}$ derivative has been studied by X-ray crystallography and shows the DAPB ligand coordinates in a pentadentate manner in the equatorial plane of the complex.



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7.5.3 Complexes with sulfur donor ligands

The reaction of *trans*-$[ReOCl_3(PPh)_2]$ with excess arenethiol and 1,2-bis(dimethylphosphino)ethane, DMPE, generated *cis* and *trans* -$[Re(SC_6H_4X\text{-}p)_2(DMPE)_2]PF_6$, X = H, Me or Cl [37]. The complexes have been characterized by FAB mass spectrometry, UV-VIS spectroscopy, cyclic voltammetry and elemental analyses. X-ray crystallographic characterisation of the *cis* isomer showed the Re-S(av.) bond to be 2.293(4)Å.

7.5.4 Complexes with nitrogen donor ligands

A low-temperature voltammetric study of $(Bu_4N)_2[Re_2(NCS)_8]$ has been carried out in ^nPrCN at 290K [38]. Results show two reversible one-electron reductions at –0.20 ($8e^- \rightarrow 9e^-$) and –0.90V ($9e^- \rightarrow 10e^-$) and a reversible oxidation at 1.10V ($8e^- \rightarrow 7e^-$). At 215K the reduction at -0.90V becomes sluggish, i.e. quasi-reversible with $E_{P,C} - E_{P,A} = 0.27V$. In ^nPrCN, at 1.40V, a further oxidation ($7e^- \rightarrow 6e^-$) has been observed for the first time.

The reactions of the *N,O*-chelated complexes $[ReCl_2(N_2COC_6H_4\text{-}4\text{-}R)(PPh_3)_2]$, R = H, Me, NO_2) with *N,N* and certain *N*-substituted hydrazines gave the ammine complexes $[ReCl_2(NH_3)(NNCOC_6H_4\text{-}4\text{-}R)(PPh_3)_2]$, (R = H, Me, NO_2) [39]. The mechanism is thought to involve intermolecular homolytic cleavage of the N-N bond.

7.5.5 Clusters

The synthesis of a homoleptic rhenium(III) isopropoxide cluster and its participation in an alkoxide β-hydrogen elimination equilibrium has been described [40]. The cluster $Re_3(\mu\text{-}O\text{-}{}^iPr)_3(O\text{-}{}^iPr)_6$ was synthesized by the reaction of dry $Re_6(\mu\text{-}Cl_3)Cl_6(thf)_3$ with NaO^iPr. Chemical and spectroscopic studies including direct NMR spectroscopic observation indicate that the cluster is in equilibrium with acetone and $Re_3(\mu\text{-}O\text{-}{}^iPr)_3(H)(O\text{-}{}^iPr)_5$ via reversible isopropoxide β-hydrogen elimination. Solid-state thermal decomposition of $Re_3(\mu\text{-}O\text{-}{}^iPr)_3(O\text{-}{}^iPr)_6$ resulted in $Re_3(\mu\text{-}O\text{-}{}^iPr)_3(H)(O\text{-}{}^iPr)_5$ and the monopyridine adduct, $Re_3(\mu\text{-}O\text{-}{}^iPr)_3(H)(O\text{-}{}^iPr)_5(py)$ was isolated by trapping the hydride cluster from the equilibrium reaction mixture. The presence of destabilizing steric interactions in the parent alkoxide clusters has been proposed as a necessary condition for the alkoxide β-hydrogen elimination process.

Explorations in sulfido-chlorine Re_6 cluster systems have been conducted [41]. In particular, soluble salts of alkali metal cations were sought. The solid state synthesis, solution chemistry and redox properties are reported for the series of salts $Rb_n[Re_6(S_{4+n}Cl_{10-n}]$, ($n$ = 1-3). X-ray analysis reveals that the cluster core contracts upon addition of sulfur atoms but not necessarily in a regular fashion. This discontinuity was reflected in the redox data obtained.

7.6 RHENIUM(II)

7.6.1 Complexes with halide ligands

The isolation and structural characterization of mixed-carbonyl-bis(dimethylphosphino)methane complexes of dirhenium(II) has been reported [42]. The reaction of the complex $Re_2Cl_4(\mu\text{-}dppm)_3$ with CO and xylNC in deoxygenated acetone in the presence of $TlPF_6$ produced the salts $[Re_2Cl_3L(\mu\text{-}dppm)_3]PF_6$, L = CO, xylNC and is the first example in which one of the equatorial ligands has been displaced by a π-acceptor ligand L. X-Ray crystallography for the carbonyl derivative shows a very short Re-Re bond 2.3565(7)Å. Dicarbonyl complexes were produced by the reaction of $Re_2(\mu\text{-}O_4CCH_3X_2(\mu\text{-}dppm)_3]PF_6$, X = Cl, Br with CO in deoxygenated acetone/HPF_6(aq) mixtures. Of note in these structures is the fact that the bridging dmpm ligands are now in a chelating mode and two halide ligands are bridging the metal centres. The X-ray crystal structure for $[Re_2(\mu\text{-}Cl)_2(\mu\text{-}dppm)(CO)_2(\mu\text{-}dppm)_2](H_2PO_4)_2$ shows an Re-Re distance of 2.918(2) Å consistent with the presence of an Re-Re single bond.

The reaction of the dirhenium complexes $Re_2X_4(\mu\text{-}dppm)_2$, X = Cl, Br with O_2 has been described [43,44]. Interestingly these reactions proceed with the retention of the $Re_2X_4(\mu\text{-}dppm)_2$ unit generating the compounds $Re_2(\mu\text{-}O)(\mu\text{-}X)(O)X_3(\mu\text{-}dppm)_2$ and $Re_2(\mu\text{-}O)(O)_2X_4(\mu\text{-}dppm)_2$ in which the four and six electron oxidations of the dirhenium unit has occurred. X-ray crystallography for the former compounds indicates edge-sharing bioctahedral structures, and in the case of $Re_2(\mu\text{-}O)(\mu\text{-}X)(O)Cl_3(\mu\text{-}dppm)_2\cdot(CH_3)_2CO$ shows a very long Re-Re distance of 3.363(2)Å, the structure was also found to be disordered involving a terminal oxo ligand and the *syn* terminal chloro ligand. These compounds have been derivatised with isocyanide ligands and results are reported. For the latter complexes, a centrosymmetric corner-sharing bioctahedral structure has been observed.

The reactions of quadruply bonded dirhenium(III) complexes of the type *cis*-$Re_2(O_2CCH_3)_2X_4L_2$, (X = Cl or Br; L = H_2O or py) has resulted in a new route to novel dirhenium(II) cations $[Re_2(\mu\text{-}X)_3(\text{triphos})_2]^+$, (X = Cl or Br) [45]. The dirhenium cation has been characterised by X-ray crystallography and is a confacial bioctahedral species with a surprisingly long Re-Re distance (3.199(1)Å, implying the absence of a metal-metal bond while the Re-Cl bonds average 2.455Å. The complexes have been further studied by NMR and ESR spectroscopic, and cyclic voltammetric measurements.

The synthesis and crystal structure of $K_2[Re_6Br_{14}]\cdot2.5H_2O$ has been described [46]. The main structural unit comprises a hexanuclear complex $[Re_6Br_{14}]^{2-}$ with three multiple Re-Re bonds of 2.26(Å)

7.6.2 *Complexes with nitrogen donor ligands*

Several mononuclear octahedral Re(II) and Re(III) species containing only amine and halide ligands have been reported [47]. The reduction of $[ReO_2(en)_2]^+$, $[ReO_2(NH_3)_2]^+$, $[ReO_2(ampy)_2]^+$ in HCl(aq) gave $[ReCl_2(en)_2]^+$, $[ReCl_2(NH_3)_4]^+$, and $[ReCl_2(ampy)_2]^+$ respectively. When chloride substitution in *trans*-$[ReCl_2(en)_2]$ was carried out using pyridine, isonicotinamide, 4-picoline, 4-(dimethylamino)-pyridine and *n*-propylamine it was accompanied by isomerization to a *cis* geometry. X-ray crystallography has been conducted for $[ReCl_2(en)_2]^+$, $[ReCl_2(ampy)_2]^+$ and $[ReCl(\text{picoline})(en)_2](PF_6)_2$. The $[ReCl(en)_2]^{2+}$ shows a preference for σ and π donors in contrast to the corresponding Re(II) fragment which shows a relative affinity for pyridine π acids. Various equilibrium constants have been determined.

7.7 *RHENIUM(I)*

7.7.1 *Complexes with hydride ligands*

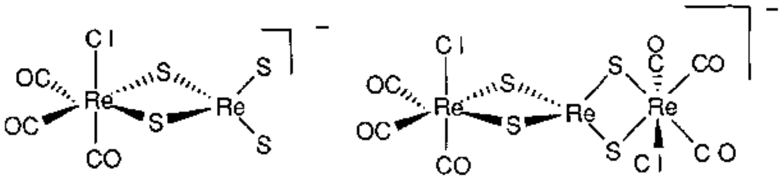
Studies on the ^1H selective and non-selective relaxation times as a function of temperature in rhenium and manganese hydride complexes have been carried out [48]. The complexes $ReH(CO)_n(PMe_3)_{5-n}$, n = 1, 2, 3, and $ReH_2(CO)(NO)(PR_3)_2$ were prepared. As a result of these measurements, the contribution of the M-H dipole-dipole interaction to the relaxation time of the H ligands was isolated and the M-H bond distances were calculated using the model of an isotropic motion.

7.7.2 *Complexes with oxygen and phosphorus donor ligands*

The synthesis of octahedral rhenium(I) complexes containing the Re(NO)[*trans*-$[P(O\text{-}^iPr)_3]_2$ fragment has been described [49]. The complex $[(MeC_6H_4)OSO_2]Re(CO)(NO)$[*trans*-$[P(O\text{-}^iPr)_3]_2]$ has been obtained, it has a *cis* arrangement of $O_2SO(C_6H_4Me)$ groups and Re-O distances are 2.097(5) and 2.114(4) Å while Re-P distances were found to be 2.431(3)Å and 2.439(3)Å.

7.7.3 *Complexes with sulfur donor ligands*

Di and trinuclear sulfide-bridged complexes with rhenium in very different oxidation states have been obtained and the d^0/d^1 transition studied [50]. In particular the dinuclear complex $[Cl(CO)_3Re(\mu\text{-}S)_2ReS_2]^-$ and the trinuclear complex $[Cl(CO)_3Re(\mu\text{-}S)_2Re(\mu\text{-}S)_2Re(CO)_3Cl]^-$ (**17**), were synthesised and characterised by spectroelectrochemistry . Both complexes were found to undergo reduction to a dianion but UV-VIS and IR spectroelectrochemistry showed that the less symmetrical complex slowly decomposes after the first one-electron reduction. The second reduction steps were found to be irreversible for both complexes.



(**17**)

7.7.4 *Complexes with nitrogen donor ligands*

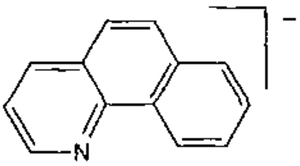
The photophysics of a series of monometallic Re(I) tricarbonyl complexes containing various methyl- and phenyl-substituted phenanthroline ligands has been explored [51]. These complexes were found to be highly emissive at room temperature in solution or at 77K in a glass. The room temperature data are consistent with emission from a ^{3}MLCT state while low temperature measurements indicate the presence of two unequilibrated emitting states, a ^{3}MLCT and a ^{3}LC one. Time-resolved spectroscopy indicates that the latter is a longer-lived state and yields a structured spectrum similar to that of the uncoordinated ligand L.

The complex *fac*-$ClRe(CO)_3(4,7\text{-}Ph_2phen)$, ($4,7\text{-}Ph_2phen$ = 4,7-diphenyl-1,10-phenanthroline) has been used as a spectroscopic probe of the environmental changes occurring during polymerization of photosensitive thin films [52]. UV-Curable trimethylolpropane triacrylate/poly(methyl methacrylate) (TMPTA/PMMA) and bisphenolA-novalac/diglycidyl ether of bisphenol-A epoxy resins have been studied using the title complex since it exhibits readily detectable luminescence upon incorporation into UV-curable coatings. The luminescence characteristics from these thin films is attributed to a lowest energy triplet-centred MLCT excited state arising from the complex. When these acrylate and epoxy resins are exposed to UV light polymerization is accompanied by a change in emission properties which is attributed to a luminescence rigidochromic effect.

The FAB spectrometry of a series of cyano-bridged Re(I)-Ru(II) polypyridine compounds has been described [53]. In particular, the complexes of general formula $[Re(CO)_3(phen)(CN)\text{-}[Ru(bpy)_2(CN)]^{(n+1)+}$, n = 0-2 have been studied. The production of singly, doubly and triply charged ions was observed in a 3-nitrobenzyl alcohol matrix and their unimolecular decomposition processes has been studied by mass-analysed kinetic energy spectra. The decomposition pathways involve losses of CO and bpy neutral ligands, oxidative addition of coordinated bpy with the expulsion of HX (X = CN^-, PF_6^-) and the cleavage of the CN-Ru bond.

The reaction of [ReX(CO)$_5$], X = Cl, Br or I with terpy, solution NMR studies of the dynamic stereochemistry of the resultant *fac*-[ReX(CO)$_3$(terpy)] complexes, the conversion of *fac*-[ReBr(CO)$_3$(terpy)] to *cis*-[ReX(CO)$_2$(terpy)] and the crystal structure of the [ReBr(CO)$_3$(terpy)] have been reported [54]. In solution these carbonyl complexes were found to be fluxional with the terpyridine oscillating between equivalent didentate bonding modes. At low temperatures rotation of the uncoordinated py ring was restricted and in CD_2Cl_2 solution two preferred rotamers were found to exist. The Re-N bonds in [ReBr(CO)$_3$(terpy)] were found to be 2.143(10) and 2.209(10) Å.

The luminescence characterizations of cyclometallated Re(I) carbonyl complexes has been described [55]. The complexes Re(CO)$_4$(bzq) and Re(CO)$_3$(bzq)(PPh$_3$), bzq = benzo[*h*]quinolin-10-yl anion (**18**) were studied. No emission could be seen from either complex in air-saturated solutions at room temperature but strong emissions were observed in deoxygenated solutions. The luminescence spectra of these complexes were assigned to ligand-centred excited states of the metallated bzq ligand.

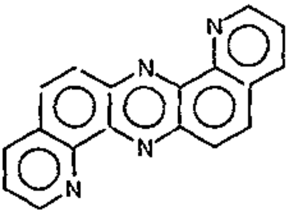


(18)

The successful synthesis of several new [ReL(CO)$_3$(py)]$^+$, L = 2,9-Ph$_2$phen, 2,5,9-Ph$_3$phen, 2,4,7,9-Ph$_4$phen, and 2,9-Me$_2$-4,7-Ph$_2$phen with demonstrated excellent luminescent properties and potential utility as sensors has been reported [56]. All complexes showed MLCT transitions in the 360 - 450 nm region and LL transitions at higher energies. Phenyl substituted ligands yielded more intense absorptions and extended them to lower energies than did unsubstituted or methyl-substituted phenyls. The effect was greatest for the 2,4,7,9-Ph$_4$phen followed by the 2,9-Me$_2$-4,7-Ph$_2$phen.

Time-resolved resonance Raman spectroscopy has been used to study intramolecular transfer in a series of chromophore quencher complexes based on MLCT excited states [57]. In this study the complexes *fac*-[Re^I(bpy)(CO)$_3$(py-PTZ)]$^+$, [(MQ$^+$)(CO)$_3$Re^I(μ-bbpe)Re^I(CO)$_3$(py-PTZ)]$^{3+}$, and *fac*-[Re^I(bpy)(CO)$_3$(MQ$^+$)]$^{2+}$, py-PTZ = 10-(4-picolyl)phenothiazine, MQ$^+$ = *N*-methyl-4,4'-bipyridinium cation, bbpe = *trans*-1,2-bis(4-(4'-methyl)-2,2'-bipyridyl)ethene were studied and the data obtained supplemented those of transient absorption results and allowed for the structure of short-lived intermediates to be inferred.

The synthesis and characterization of the mono and dimetallic [Re(CO)$_3$Cl]$_{1,2}$(dpop) complexes containing the bis-didentate ligand dipyrido(2,3-*a*;2',3'-*h*)phenazine, dpop, (**19**) has been described [58]. Electronic spectroscopy revealed solvato-chromatic MLCT absorptions in the visible spectrum which are red shifted from other tricarbonylrhenium(I) complexes having similar ligands. Electrochemical results indicated dpop centred reversible reductions in these complexes occur at less negative potentials than those seen for similar pyridyl ligands in other tricarbonylrhenium(I) complexes.



(19)

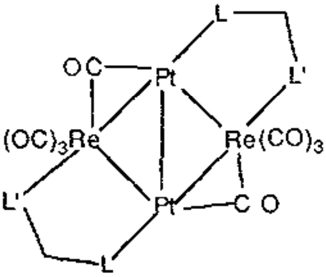
The transient infrared technique has been used in a novel application to elucidate intramolecular energy transfer in the ligand-bridged complex cation $[(phen)(CO)_3Re^I(NC)Ru^{II}(CN)(bpy)_2]^+$ [59]. This technique has demonstrated utility in the elucidation of oxidation states and mechanisms involving photochemical intermediates through the direct observation of ligand vibrations.

The first electrocatalytic reduction of CO_2 by $[Re(bpy)(CO)_3Br]$ and $[Re(terpy)(CO)_3Br]$ in an aqueous medium has been achieved [60]. Incorporation of the rhenium complexes into a coated Nafion membrane thereby providing a hydrophobic environment around the catalysts has facilitated the electroreduction of CO_2 resulting in the production of formic acid and carbon monoxide. The selectivity for HCO_2H and CO was found to depend strongly on the applied potentials. Hydrogen was also detected as a byproduct.

Time-resolved infrared spectroscopy has been carried out on the complex $[ReCl(CO)_3(bpy)]$ [61]. Results indicate that the ν(CO) bands shift up in frequency in the MLCT excited state. The excited state is quenched by triethanolamine or triethylamine producing $[ReCl(CO)_3(bpy)]^-$ which displays a lowering in frequency of the ν(CO) bands.

7.7.5 *Clusters*

A new cluster $[Pt_2Re_2(\mu\text{–}CO)_2(CO)_6(\mu\text{–}dppm)_2]$ **(20)** with a planar metal core which is noteworthy in that it represents the first example of a *triangulo*-Re_2Pt_n cluster in which rhenium -



LL' = dppm

(20)

rhenium bonding occurs [62]. An X-ray crystal structure for the molecule shows it to possess a crystallographically imposed centre of inversion, the Re-Re distance is 3.094(1)Å and the Pt-Pt distance is 2.982(1).

REFERENCES

1. J. C. Vites and M. M. Lynam, *Coord. Chem. Rev.*, 131 (1994) 127.
2. N. M. Made Gowda, H. P. Phyu and B. E. Ackerson, *Transition Metal Chem. (London)*, 18 (1993) 64.
3. W. A. Herrmann, F. E. Kühn, C. C. Romão, H. T. Huy, M. Wang, R. W. Fischer, P. Kiprof and W. Scherer, *Chem. Ber.*, 126 (1993) 45.
4. W. A. Herrmann, R. W. Fisher, W. Scherer and M. U. Rauch, *Angew. Chem. Int. Ed. Eng.*, 32 (1993) 1157.
5. J. Takacs and W. A. Herrmann, *Polyhedron*, 12 (1993) 2371.
6. L. A. Grigoryan, S. Musa, K. G. Gazaryan and Sh. A. Markaryan, *Russ. J. Inorg. Chem.*, 38 (1993) 1590
7. D. Nubhar, F. Weller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 619 (1993) 1121.
8. M. Leeaphon, K. Rohl, R. J. Thomas, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 32 (1993) 5562.
9. H. Luo, S. J. Rettig and C. Orvig, *Inorg. Chem.*, 32 (1993) 4491.
10. F. Refosco, F. Tisato, G. Bandoli, C. Bolzati, A. Dolmella, A. Moresco and M. Nicolini, *J. Chem. Soc., Dalton Trans.*, (1993) 605.
11. A-M Lebuis and A. L. Beauchamp, *Can. J. Chem.*, 71 (1993) 2060.
12. A-M Lebuis, C. Roux and A. L. Beauchamp, *Acta Crystallogr., Sect. C*, 49 (1993) 33.
13. J. R. Dilworth, J. S. Lewis, J. R. Miller and Y. Zheng, *Polyhedron*, 12 (1993) 221.
14. G-E Matsubayashi, T. Maikawa and M. Nakano, *J. Chem. Soc., Dalton Trans.*, (1993) 2995.
15. B. Winckler Tsang, J. Reibenspies and A. E. Martell, *Inorg. Chem.*, 32 (1993) 988.
16. L. C. Francesconi, G. Graczyk, S. Wehrli, S. N. Shaikh, D. McClinton, S. Liu, J. Zubieta and H. F. Kung, *Inorg. Chem.*, 32 (1993) 3114.
17. Y-P Wang, C-M Che, K-Y Wong and S-M Peng, *Inorg. Chem.*, 32 (1993) 5827.
18. T. W. Jackson, M. Kojima and R. M. Lambrecht, *Aust. J, Chem.*, 46 (1993) 1093.
19. A-M Lebuis and A. L. Beauchamp, *Can. J. Chem.*, 71 (1993) 441.
20. B. Johannsen, B. Noll, P. Leibnitz, G. Reck, S. Noll and H. Spies, *Inorg. Chim. Acta*, 210 (1993) 209.
21. G. Bandoli, J. G. H. du Preez, T. I. A. Gerber and H. G. Kemp., *Inorg. Chem.*, 32 (1993) 3964.
22. W. J. Vining, G. A. Neyhart, S. Nielsen and B. P. Sullivan, *Inorg. Chem.*, 32 (1993) 4214.
23. R. Rossi, A. Marchi, L. Marvelli, L. Magon, M. Peruzzini, U. Casellato and R. Graziani, *Inorg. Chim. Acta*, 204 (1993) 63.
24. K. Nwe Soe, A. Ichimura and T. Kitagawa, *Inorg. Chim. Acta*, 207 (1993) 21.
25. B. Winkler Tsang, J. Reibenspiues and A. E. Martell, *Inorg. Chim. Acta*, 211 (1993) 23.
26. A. Marchi, L. Marvelli, R. Rossi, L. Magon, L. Uccelli, V. Bertolasi, V. Ferretti and F. Zanobino, *J. Chem. Soc., Dalton Trans.*, (1993) 1281.
27. V. W-W Yam, K-K Tam and T-F Lai, *J. Chem. Soc., Dalton Trans.*, (1993) 651.
28. R. Loris, D. Maes, J. Lisgarten, M. Bettinelli and C. Flint, *Acta Crystallogr., Sect. C*, 49 (1993) 231.
29. N. S. Osmanov, M. D. Surazhskaya, T. A. Abbasova, T. B. Larina, A. S. Kotel'nikova and P. A. Koz'min, *Russ. J. Inorg. Chem.*, 38 (1993) 941.
30. S. Ikari, T. Ito, W. McFarlane, M. Nasreldin, B-L Ooi,Y. Sasaki and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, (1993) 2621.
31. F. A. Cotton, B. Hong, M. Shang and G. S. Stanley, *Inorg. Chem.*, 32 (1993) 3620.
32 F. Mota, J. J. Novoa, J. Losada, S. Alvarez, R. Hoffmann and J. Silvestre, *J. Am. Chem. Soc.*, 115 (1993) 6216.
33. A. Moller and G. Meyer, *Z. Anorg. Allg. Chem.*, 619 (1993) 695.
34. A. Moller and G. Meyer, *Z. Anorg. Allg. Chem.*, 619 (1993) 1655.
35. P. A. Koz'min, M. D. Surazhskaya, T. B. Larina, N. S. Osmanov, A. G. Matyushkov and A. S. Kotel'nikova, *Russ. J. Inorg. Chem.*, 38 (1993) 419.
36. A. S. M. Al-Shihri, J. R. Dilworth, S. D. Howe, J. Silver, R. M. Thompson, J. Davies and D. C. Povey, *Polyhedron*, 12 (1993) 2297.
37. L Chang and E. Deutsch, *Transition Metal Chem. (London)*, 18 (1993) 335.

38. G. A. Heath and R. G. Raptis, *J. Am. Chem. Soc.*, 115 (1993) 3768.
39. J. R. Dilworth, P. Jobanputra, J. R. Miller and S. J. Parrott, *Polyhedron*, 12 (1993) 513.
40. D. M. Hoffman, D. Lappas and D. A. Wierda, *J. Am. Chem. Soc.*, 115 (1993) 10538.
41. J-C Gabriel, K. Boubekeur and P. Batail, *Inorg. Chem.*, 32 (1993) 2894.
42. I. Ara, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 32 (1993) 2958.
43. S. L. Bartley, K. R. Dunbar, K-Y Shih, P. E. Fanwick and R. A. Walton, *J. Chem. Soc., Chem. Commun.*, (1993) 98.
44. S. L. Bartley, K. R. Dunbar, K-Y Shih, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 32 (1993) 1341.
45. M. T. Costello, P. W. Schrier, P. E. Fanwick and R. A. Walton, *Inorg. Chim. Acta*, 212(1993) 157.
46. P. A. Koz'min, N. S. Osmanov, M. D. Surazhskaya, T. A. Abbasova, T. B. Larina, I. B. Tagiev and A. S. Kotel'nikova, *Russ. J. Inorg. Chem.*, 38 (1993) 421.
47. S. D.Orth, J. Barrera, M. Sabat and W. D. Harman, *Inorg. Chem.*, 32 (1993) 594.
48. D. G. Gusev, D. Nietlispach, A. B. Vymentis, V. I. Bakhmutov and H. Berke, *Inorg. Chem.*, 32 (1993) 3270.
49. I. L. Eremenko, V. I. Bakhmutov, F. Ott and H. Berke, *Russ. J. Inorg. Chem.*, 38 (1993) 1541.
50. R. Schafer, W. Kaim and J. Fiedler, *Inorg. Chem.*, 32 (1993) 3199.
51. L. Wallace and D. P. Rillema, *Inorg. Chem.*, 32 (1993) 3836.
52. T. G. Kotch, A. J. Lees, S. J. Fuerniss, K. I. Papathomas and R. W. Snyder, *Inorg. Chem.*, 32 (1993) 2570.
53. R. Argazzi, C. A. Bignozzi, O. Bortolini and P. Traldi, *Inorg. Chem.*, 32 (1993) 1222.
54. E. W. Abel, V. S. Dimitrov, N. J. Long, K. G. Orrell, A. G. Osborne, H. M. Pain, V. Sik, M. B. Hursthouse and M. A. Mazid, *J. Chem. Soc., Dalton Trans.*, (1993) 597.
55. P. Spellane, R. J. Watts and A. Vogler, *Inorg. Chem.*, 32 (1993) 5633.
56. A. P. Zipp, L. Sacksteder, J. Streich, A. Cook, J. N. Demas and B. A. DeGraff, *Inorg. Chem.*, 32 (1993) 5629.
57. J. R. Schoonover, G. F. Strouse, P. Chen, W. D. Bates and T. J. Meyer, *Inorg. Chem.*, 32 (1993) 2618.
58. R. R. Reuminski and D. Lehmpuhl, *Inorg. Chim. Acta*, 204 (1993) 45.
59. J. R. Schoonover, K. C. Gordon, R. Argazzi, W. H. Woodruff, K. A. Peterson, C. A. Bignozzi, R. B. Dyer and T. J. Meyer, *J. Am. Chem. Soc.*, 115 (1993) 10996.
60. T. Yoshida, K. Tsutsumida, S. Teratani, K. Yasufuku and M. Kaneko, *J. Chem. Soc., Chem. Commun.*, (1993) 631.
61. M. W. George, F. P. A. Johnson, J. R. Westwell, P. M. Hodges and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, (1993) 2977.
62. J. Xiao, J. J. Vittal and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, (1993) 167.