Coordination Chemistry Reviews, 73 (1986) 1—57
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

3 RHENIUM

JANET E. TURP AND NEIL TURP

CONTENTS

0010-8545/86/$19.95 © 1986 Elsevier Science Publishers B.V.

Introduction

The period of this review covers those publications in volumes 96 and 97 of Chemical Abstracts. Thus, although the majority of papers covered were published in 1982, many from 1981 are also included. The major journals are covered up to the end of 1982.

The review concentrates upon the coordination chemistry of rhenium. No attempt has been made to cover work of an essentially organometallic, catalytic or kinetic nature.

Three publications of general interest to rhenium chemists have been published this year: the first is a review with 38 references on the chemistry of carbonyl fluoro complexes including rhenium [1]. Another review with 38 references on the oxygen compounds of rhenium and rare earth elements, including rare earth rhenates(VII) and rhenium rare earth double oxides has been published [2], along with a review of the luminescence properties of complexes of rhenium(III), with, *inter alia*, 64 references [3].

3.1 Rhenium(VII)

3.1.1 Oxides and Hydroxides

The $[ReO_4]^-$ ion is found to lose its tetrahedral symmetry when isolated in CsCl-structured alkali metal halides. Infrared and Raman spectra indicate at least two types of stable orientation for the $[ReO_4]^-$ within this structure, resulting in systems which have different symmetries, probably C_{2v} and C_{3v}. These are thought to be energetically similar to one another and significantly lower in energy than any other possible orientation [4]. The effect of uniform compression on the spectral characteristics of praesodymium rhenate tetrahydrate, $Pr[ReO_4]_3.4H_2O$, was investigated [5]. The chemical shifts ΔE of the X-ray L_{III} absorption discontinuities of rhenium in some of its binary and ternary compounds, including $[Re_2O_7]$, $K[ReO_4]$ and $Na[ReO_4]$, were studied using a bent crystal X-ray spectrograph. The values of ΔE were governed by the effective charge (q) on the absorbing ions, which were calculated using the theory of J.-P. Suchet. The $\Delta E/q$ plot was used to determine the charges on the rhenium ions in $K[ReO_4]$ and $Na[ReO_4]$ [6]. $[Ni(NH_3)_4][ReO_4]_2$ and $[Ni(py)_4][ReO_4]_2$ were prepared by reacting $Ni[ReO_4]_2$ with aqueous ammonia or pyridine. Heating them to 150 $^{\circ}$C gave $[Ni(NH_3)_2(ReO_4)_2]$ and $[Ni(py)_2(ReO_4)_2]$. The kinetics of the thermal decomposition of the diammine complex was studied. IR and Raman spectroscopy, electron and X-ray powder diffraction, and magnetic susceptibility studies suggest that these are tetragonal compounds of nickel(II) containing coordinated rhenate(VII) [7]. The salts $[Zn(NH_3)_4][ReO_4]_2$ and $[Cd(NH_3)_4][ReO_4]_2$ were prepared from $M[ReO_4]_2$ (M = Cd, Zn) and aqueous ammonia solution. $[Zn(py)_4][ReO_4]_2$ and $[Cd(py)_4][ReO_4]_2$ were obtained by reacting $M[NO_3]_2$ with aqueous pyridine solution followed by the addition of $H[ReO_4]$. Pyrolysis of these complexes gave $[Zn(NH_3)_2(ReO_4)_2]$, $[Cd(NH_3)_2(ReO_4)_2]$, $[Zn(py)_2(ReO_4)_2]$ and $[Cd(py)_2(ReO_4)_2]$. IR and Raman spectroscopy and X-ray powder diffraction studies showed that the $[ReO_4]^-$ is coordinated to the metal centre in all cases except that of the tetraammines [8].

The extraction of $H[ReO_4]$ was studied at pH 1–10 and 0.001–0.2 M concentrations of organic oxide (trioctylarsine oxide or trioctylamine oxide) in benzene solution. The extraction isotherms indicated formation of mono- and di-solvates. The IR spectra were given for the extractants $[R_3EOH][ReO_4]$ and $[(R_3EO)_2H][ReO_4]$ (E = As or N) which do not contain water [9].

The light yellow oxide $Ba_3ReSb\ O_9$ crystallises with a tetragonal unit cell. The structure consists of three perovskite units piled up in the c direction. The cationic vacancies are partially ordered [10]. The complex salt $Hg_5Re_2O_{10}$, which crystallises in a monoclinic space group, $P2_1/b$, is composed of $\{(Hg_2)_4O_4\}$ rings, formed by Hg_2^{2+} pairs joined together by oxygen atoms. These rings are bridged by Hg^{2+} ions and form a two dimensional network in which the $[ReO_4]^-$ tetrahedra are located. The cohesion of this structure is assured by electrostatic bonds between $\{[(Hg_2)_4O_4Hg_2]^{4+}\}_n$ macrocations and

$[ReO_4]^-$ anions [11]. Phase equilibria in the rhenium(VII) oxide–selenium(IV) oxide system were determined. This system is of a simple eutectic type. The distribution coefficient of SeO_2 between Re_2O_7 melt and crystal is 0.044. The liquid-vapour equilibrium curves show negative deviation from ideality [12].

Electrical conductivity and pH measurements at 20 °C and solubility measurements at 25 °C were made for the NaOH/Na$[ReO_4]$, KOH/K$[ReO_4]$ and $[NH_4]OH/[NH_4][ReO_4]$ aqueous systems. The results were interpreted in terms of equilibria between $[ReO_4]^-$ hydrated and condensed species [13]. A spectrophotometric study was made of saturated Na$[ReO_4]$ solutions in concentrated hydrochloric acid at 360–700 nm. Dilution of these solutions with 18 *M* sulfuric acid changes the colour to bright yellow. Dehydration of H$[ReO_4]$ was studied as a function of temperature; evaporation gave a mixture of pale yellow and dark green crystals [14]. The problem of the dehydration of rhenic(VII) acid was also investigated: during the dehydration of H$[ReO_4]$, $Re_2O_5(OH)_4$ appears as the first dehydration product which undergoes intramolecular reduction in the solid phase to a rhenium(IV) species $ReO(OH)_2$, which was identified by spectrophotometry [15].

A spectrophotometric study was made of the Re(VII)/H_2SO_4/$[SCN]^-$ system: some reduction to ReO_2 and $ReO(OH)_2$ was observed. At pH 0.8, the solution is colourless, while addition of H_2SO_4 causes it to change to a yellow and then to a yellow/brown solution and finally a yellow/brown precipitate appears. Hydroxo–oxo and thiocyanato complexes of rhenium(VII) are proposed along with condensation and hydration products [16].

The preparation of $[ReOBr_4]$ has been reported [17]: $[NH_4][ReO_4]$ is dissolved in 98% H_2SO_4 and a 20–50 fold excess of NaBr added. The solution turns green/blue and HBr and Br_2 are evolved to give a dark blue/black solid, which is extracted with toluene; the extracts when dried give $[ReOBr_4]$. Visible, mass and Raman spectral properties were reported. A similar reaction does not yield $[ReOCl_4]$ [17]. A new, high yield synthetic route to $[Re_2Cl_8]^{2-}$

has been developed. This involves the reaction of $[(C_4H_9)_4N][ReO_4]$ with [PhCOCl] at about 209 °C (the boiling point of [PhCOCl] at slightly greater than atmospheric pressure), and then subsequent addition of a HCl(g) saturated solution of $[(C_4H_9)_4N]Br$ followed by a further period under reflux to yield the observed product in high purity. Similar reactions with $K[ReO_4]$ gave poorer yields [18].

3.1.2 Oxohalides

The molecular structure of $[ReOF_5]$ in the gas phase was determined by electron diffraction. The molecule has C_{4v} symmetry. The Re–O and Re–F distances are 0.1642(40) nm and 0.1810(7) nm respectively. The corresponding mean vibrational amplitudes are 0.065(55) and 0.040(18) and the O–Re–F angle is 93.1(2)° [19].

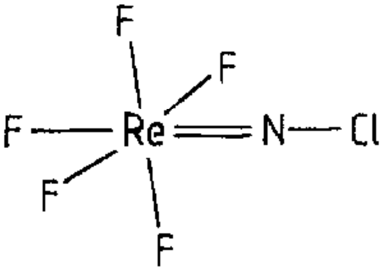
By using a rigid-rotor harmonic oscillator approximation, the standard thermodynamic functions were calculated for gaseous $[ReO_2F_3]$ and $[ReO_2F_2]$ at 298.15 - 6000 K [20].

3.1.3 Sulfides

$[NH_4][ReO_4]$ reacts with $Na_2[S_2O_3]$ in hydrochloric acid solution over a wide range of component ratios to precipitate elemental rhenium and a new rhenium sulfide [21]. The degree of precipitation of the rhenium sulfide increases with increasing concentration of $Na_2[S_2O_3]$ in the original aqueous solution containing rhenium(VII) and sulfuric acid. The dependence of the degree of precipitation of Re_2S_7 on sulfuric acid concentration was also studied. A comparison of these results with those for solutions containing hydrochloric acid indicates that the nature of the acid affects the decomposition of the thiosulfate ion with the formation of elemental sulfur. The decomposition of thiosulfate is more rapid in hydrochloric acid than in sulfuric acid [22].

3.1.4 Halides and Halocomplexes

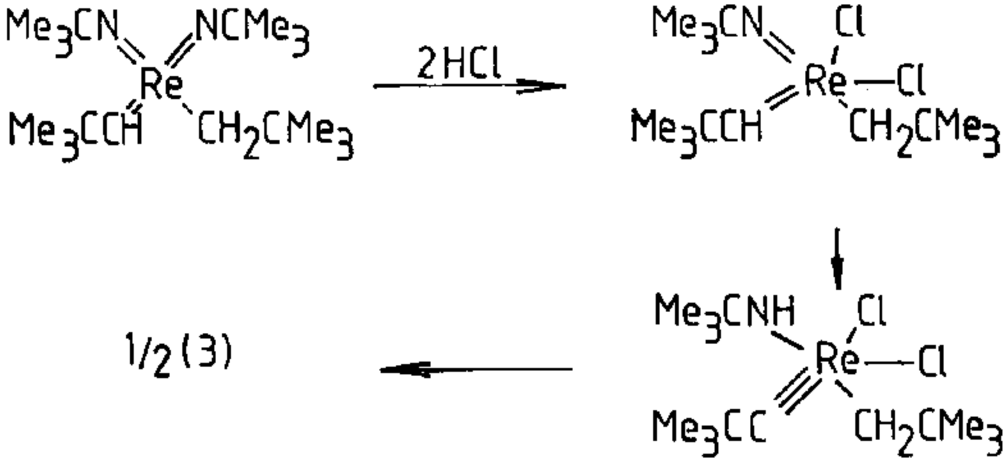
Pseudopotential SCF-MO calculations have been carried out on [IF_7] with good agreement with experimental data for the structure. Vibrational assignments and intermolecular force calculations were also carried out, and it was suggested that a similar assignment to that of [IF_7] would be appropriate for [ReF_7] [23]. Azidotrimethylsilane, [Me_3SiN_3], reacted with [ReF_6] at $-50^{\circ}C$ in 1,1,2-trichlorotrifluoroethane to give an orange solid, which on warming liberated N_2 to give [$ReNF_4$] (ν(Re≡N) 1110 cm^{-1}) and a black residue. Subsequent reaction with [ClF_3] yielded the nitrenes [ReF_5NF] (1) and [ReF_5NCl] (**2**). The crystal structure of purple [ReF_5NCl] shows the ReNCl and *trans* F all to be in a crystallographic mirror plane. The *trans* Re-F bond length indicates that the NCl group has a small *trans*-influence; the Re=N bond is quite long (0.1684 nm). The crystal structure of [ReF_5NF] was also determined and was shown to be very similar to [ReF_5NCl], although NF exerts an even smaller *trans*-influence [24].



(**2**)

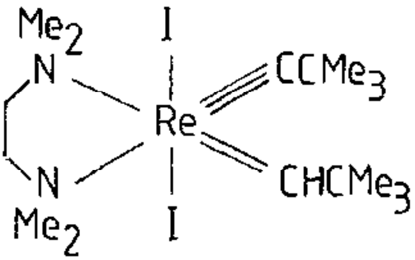
ReF_5S was prepared, along with fluorosulfides of lower oxidation states, by the reaction of [ReF_7] with [Sb_2S_3] or [B_2S_3], and is a moisture sensitive maroon solid. Mass spectrometry and X-ray powder diffraction confirm that the product does not contain ReF_5 and IR spectral data show the presence of terminal and bridging Re-F bonds, and of the terminal Re=S bond [25].

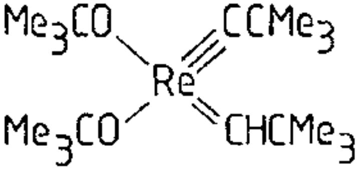
Addition of four equivalents of hydrogen chloride gas in dichloromethane solution to $[Re(NCMe_3)_3(OSiMe_3)]$ gave one equivalent of $[N(CMe_3)H_3]Cl$ and orange $[Re(NCMe_3)_2Cl_3]$, proposed as a trigonal bipyramidal species with equatorial imido ligands. Trialkyl compounds can be made in high yield from this chloroimido complex by using the appropriate alkylating agent. However, all attempts to prepare $[Re(NCMe_3)_2(CH_2CMe_3)_3]$ have failed, and instead a monomeric alkylidene complex $[Re(NCMe_3)_2(=CHCMe_3)(CH_2CMe_3)]$ is formed. This complex reacts with three equivalents of 2,4-dimethylpyridinium chloride in dichloromethane solution to give the dimeric complex $[\{Re(CCMe_3)(CHCMe_3)(L)Cl_2\}_2]$ (3), ($L = N(CMe_3)H_2$), possibly by the mechanism shown in Scheme 1:



Scheme 1: Possible Mechanism of Formation of $[\{Re(CCMe_3)(CHCMe_3)(L)Cl_2\}_2]$

Two other $=CHCMe_3$ complexes, shown below, have also been prepared and characterised by ^1H and ^{13}C NMR spectroscopy [26].





3.1.5 Hydrides

Reductive elimination of hydrogen gas from the polyhydride complexes [$ReH_7(PR_3)_2$] (PR_3 = PPh_3 or PPh_2Et) in the presence of an excess of isocyanide and potassium hexafluorophosphate yielded the rhenium(I) complexes [$Re(CNR)_4(PR_3)_2$][PF_6] [27,28]. Treatment of pentane with heptahydridobis(triarylphosphine)rhenium(VII) and 3,3-dimethylbutene gave trihydrido(*trans*-penta-1,3-diene)bis(triarylphosphine)rhenium(III), which is then converted to pent-1-ene by trimethylphosphite with high selectivity [29]. Cycloalkanes C_nH_{2n} (n = 6–8) are dehydrogenated at $\leq$80 °C to the corresponding cycloalkene by [$(Ar_3P)_2ReH_7$] in the presence of 3,3-dimethylbutene *via* the coordinated metal cycloalkene, which dissociates from the metal before further dehydrogenation can occur [30]. Furthermore, the complex [$(Ph_3P)_2ReH_7$] reacts with 3,3-dimethylbutene and benzene to give the dihydrocyclohexadienyl compound [$(Ph_3P)_2(\eta^5\text{-}C_6H_7)ReH_2$], whose X-ray crystal structure was reported [31].

3.2 RHENIUM(VI)

The pressure dependence of the β and γ_1 de Haas-van Alphen (dHvA) frequencies of ReO_3 for the (011) direction show a non-linear change with pressure in the region of 0 – 3 kbar. This behaviour is electronic in origin, either from a change in bandwidth or an electronic redistribution in the band structure, and is precursory to the transition between 3 and 5 kbar observed in all the dHvA frequencies [32]. Chemical shifts in the X-ray L_{III} absorption discontinuities of rhenium in ReO_3 were studied using a bent crystal X-ray spectrograph. The ΔE values are governed by the effective charge (q) of the absorbing ions which was calculated using the theory of J.-P. Suchet [6].

The standard thermodynamic functions were calculated for gaseous [ReO_2F_2] using a rigid rotor harmonic oscillator approximation [20]. According to EPR spectrometric data, $ReCl_5$ is oxidised in concentrated sulfuric acid solutions to [$ReOCl_5$]$^-$, which is very stable in this medium [33]. The extraction of [$ReOBr_4$] from concentrated sulfuric acid was studied at 20 °C. The best extractants were found to be non-polar aliphatic hydrocarbons, and the extraction behaviour was discussed in terms of the optimum electronic structure of the extracted compound [34]. The addition of a 20 – 50 fold excess of sodium bromide to [NH_4][ReO_4], dissolved in 98% sulfuric acid yields a solution which turns green/blue. HBr and Br_2 are evolved to leave a blue/black solid which can be extracted into toluene to give [$ReOBr_4$]: visible, Raman and mass spectral characterisation were reported [17]. A similar reaction does not yield [$ReOCl_4$] [17].

Azidotrimethylsilane, [Me_3SiN_3], reacts with [ReF_6] at –50 °C in 1,1,2-trichlorotrifluoroethane to give an orange solid which, on warming, liberates nitrogen gas to yield [$ReNF_4$], (ν(Re≡N) 1110 cm^{-1}), and a black residue. Subsequent reaction with [ClF_3] yields the nitrenes [ReF_5NF] and [ReF_5NCl], described earlier (Section 3.1.4) [24]. ReF_4S was prepared by reaction of [ReF_6] with antimony(III) sulfide or boron(III) sulfide:

$$3ReF_6 + Sb_2S_3 \rightarrow 3ReF_4S + 2SbF_3$$

$$3ReF_6 + B_2S_3 \rightarrow 3ReF_4S + 2BF_3$$

Characterisation was achieved by X-ray powder diffraction, IR and mass spectrometry. The structure is thought to be similar to that of ReF_4O, with a fluorine-bridged chain [25].

3.3 RHENIUM(V)

3.3.1 Oxides

The crystal structure of $LiReO_3$, obtained by lithium insertion into ReO_3, was determined by neutron diffraction powder profile analysis and refined by the Ritveld method. The ReO_3 host lattice, made exclusively of corner-shared octahedra, was altered significantly on lithium insertion without breaking bonds. The original 12-coordinate perovskite-like cavity was changed into two octahedral sites, which may be occupied by lithium ions [35,36].

A study of heteropolyanions in the P(V)–Re(V)–Mo(VI) system was carried out by the trichromatic method. At pH 2–3.6, a 1:1:11 P:Re:Mo complex is formed with stability constant $\log \beta = 8.1 \pm 0.1$ (20 $^\circ$C, ionic strength 0.02). The rhenium replaces a molybdenum atom in a (MoO_6) octahedron of the molybdophophoric acid. Formation of the highly coloured complex can serve as the basis for a method of determining phosphorus or rhenium in complex mixtures [37].

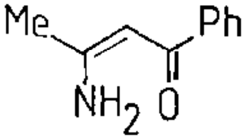
3.3.2 Halides, Oxohalides and Pseudohalides

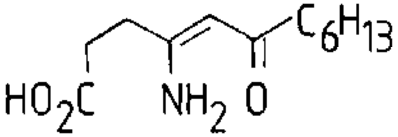
According to EPR spectral data, in concentrated sulfuric acid solutions, $ReCl_5$ is oxidised to $[ReOCl_5]^-$ (which is very stable in this medium) [33]. The chemical shifts of the X-ray L_{III} absorption discontinuities of $ReCl_5$ have been studied, and the ionic radius of pentavalent rhenium was determined [6].

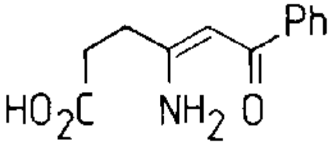
The complex *trans*-$[ReOCl_3(PPhEt_2)_2]$ crystallises with a monoclinic space group $P2_1/c$. The atomic parameters and bond lengths are presented and compared to those of other rhenium complexes. The structure is monomeric with the rhenium atom octahedrally coordinated [38].

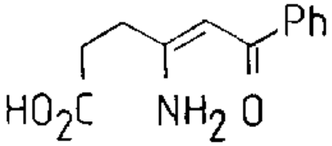
Reduction of $ReCl_5$, $[ReOCl_3(py)_2]$ or $[ReCl_5(py)]$ with trimethylphosphite yields a variety of products depending on reaction conditions. Products isolated include $[Re_2\{P(OMe)_3\}_{10}]$, $[HRe\{P(OMe)_3\}_5]$, $[Re\{P(OMe)_3\}_5\{P(O)(OMe)_2\}]$, $[H_3Re\{P(OMe)_3\}_4]$ and $[HRe\{P(OMe)_3\}_3\{(MeO)_2POP(OMe)_2\}]$ [39].

The reactions of *trans*-$[ReOCl_3(PPh_3)_2]$ with vinyl amides such as $[RCOCH=C(R')NH_2]$ (where R = Ph or C_6H_{13}, R' = $CH_2CH_2CO_2H$; or R = Ph, R' = Me or $CH_2CH_2CO_2Me$):

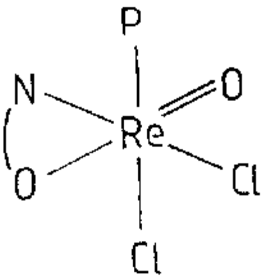




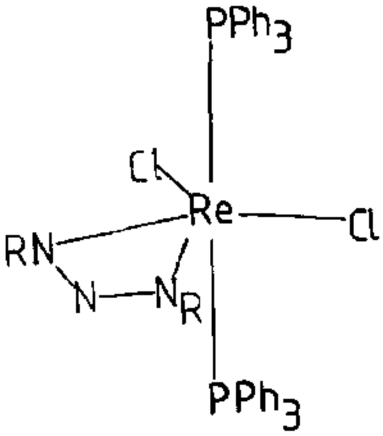




in dry thf or benzene, give complexes of the type $[ReOCl_2\{RC(O)=CH(R')=NH\}(PPh_3)]$. The ligands behave like chelating agents and bind to the metal ion through *N* and *O*; the coordination geometry was deduced from IR and ^1H NMR spectroscopy, which leads to the proposed structure below [40]:

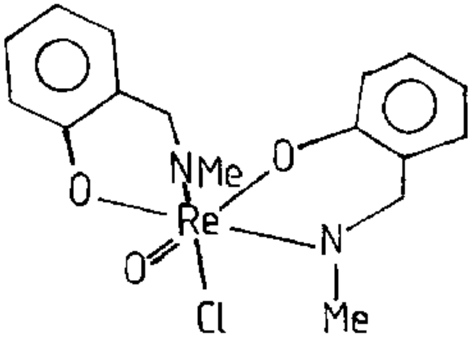


The complex $[PPh_4][ReOCl_3(sal)]$ was synthesised from $[PPh_4]_2[ReCl_6]$ and salicylaldehyde; characterisation was by analytical, IR spectral and magnetic susceptibility methods [41]. Reaction of *trans*-$[ReOCl_3(PPh_3)_2]$ and triphenylphosphine with a boiling thf solution of Li[RN–N=NR] (R = 4-MeC_6H_4, Ph, 4-ClC_6H_4 or 4-FC_6H_4), generated *in situ* by the action of butyl lithium on [RNH–N=NR], gives the reduced rhenium(III) complexes $[ReCl_2(RN{-}N{=}NR)(PPh_3)_2]$ in 60–70 % yield as green air-stable solids. The reducing agent is believed to be the triphenylphosphine. The crystal structure of the derivative with R = 4-MeC_6H_4 was determined [42].



Some isomers of $[ReOX_2(PPh_3)L]$ (X = Cl or Br; L = *N*-methyl salicylideneiminate, *N*-phenyl salicylideneiminate, 1/2 *N,N'*-ethylenebis(salicylideneiminate) or 8-hydroxyquinolinate) were synthesised and characterised. Two different mechanisms for reactions of the *trans*-$[ReOX_3(PPh_3)_2]$ complexes with the Schiff bases are supported by the qualitative studies on such parameters as the Schiff base ligand form, concentration of free triphenylphosphine, reaction temperature and solvent [43]. The complexes $[ReOX_2(PPh_3)L]$ (L and X as above) react with dimethylphenylphosphine to give the simple displacement products $[ReOX_2(PPhMe_2)L]$, which then reduce to give the rhenium(III) complexes $[ReX_2L(PPhMe_2)_2]$ [44]. The crystal structure of *trans*-dibromooxo(*N*-phenyl salicylideneiminato)(triphenylphosphine)rhenium(V) has been determined and shows the complex to crystallise with a monoclinic space group $P2_1/a$. Coordination around the rhenium atom is approximately octahedral and the two oxygen and two bromine atoms are *trans* to each other. The deformation from octahedral is due to repulsions exerted by the oxo group on the *cis* ligands, and the conformation was discussed in terms of non-bonded intramolecular potential energy [45].

The crystal structure has also been reported [46a] for chlorobis(*N*-methylsalicylideneiminato)oxorhenium(V):



having a monoclinic *I2/c* space group. Coordination around the rhenium metal is approximately octahedral with the two bidentate ligands mutually orthogonal and the oxygen of one of them *trans* to the multiply bonded oxo group. The reasons for this arrangement were discussed in terms of the *trans*-influence of the Re=O bond. It is thought that there is a *trans* weakening caused by the Re=O bond which becomes more noticeable according to the *trans* ligand in the order $RO^- < Cl^- < Br^- < R_3N$. There is a slight distortion in the coordination around the rhenium and it is suggested that this is due to steric effects within the crystal and not to crystal packing forces as proposed by Bright and Ibers [46b].

The metal and ligand binding energies have been measured for the low-spin rhenium complexes $[ReCl_3(PPhMe_2)_3]$, $[Re(N_2Ph)Cl_2(PPhMe_2)_2(NH_3)]$ and $[ReOCl_3(PPh_3)_2]$ and, to a first approximation, the observed bond energies can be reproduced from a single set of ligand group shifts referred to the bare metal atom. The metal bond energy increases 1 eV per unit increase in the formal oxidation state of the metal [47].

The behaviour of $ReCl_5$ was studied in the solvents pyridine, nitromethane, tetrachloromethane, trichloromethane, dichloromethane, benzene, toluene, dichloroethane, carbon disulfide, pentane, hexane and cyclohexane, which the authors refer to as oxidation resistant (*sic*). The crystalline products, violet $[ReCl_4(MeNO_2)]$ and yellow-brown $[ReCl_4.(py)_2]$, were separated from nitromethane and pyridine solutions, respectively. Coloured solutions in CS_2 and benzene or toluene did not give any solvent complexes [48]. Trichloroethanenitrile reacts with rhenium(V) chloride to give $[ReCl_5(NCCl_3)_2]$. However, when $ReCl_5$ reacts with Me_3CCN, reduction occurs with the formation of $[ReCl_4(NCCMe_3)_2]$, isolated in two isomeric forms [49]. Reaction of ReF_5 with antimony(III) sulfide yields the fluorosulfide ReF_3S as a yellow solid which is very moisture sensitive [25]:

$$3ReF_5 + Sb_2S_3 \rightarrow 3ReF_3S + 2SbF_3$$

The thermolysis of several transition metal cyano complexes, including $K_3[Re(CN)_8].H_2O$ and $K_3[Re(CN)_6].H_2O$ has been studied. The decomposition of the rhenium(V) complex begins 80-180 °C lower than that of the rhenium(III) complex [74].

3.3.3 Hydrides

Reductive elimination of hydrogen gas from $[ReH_5(PR_3)L]$ (L = PPh_3, $PPhEt_2$, pyridine, piperidine or cyclohexylamine) in the presence of isocyanides affords the rhenium(I) complexes $[Re(CNR)_4(PR_3)L]^+$ [27,28]. Photogeneration of $[ReD_5(PMe_2Ph)_2]$ (by 366 nm irradiation of $[ReD_5(PMe_2Ph)_3]$) in benzene solution in the presence of naphthalene leads to the deuteration of the naphthalene, with preference for the H/D exchange at the four β-carbons of naphthalene. Photolysis of $[ReH_5(PMe_2Ph)_3]$ and 1-hexene in perdeuterocyclohexane or hexafluorobenzene under one atmosphere of hydrogen gas leads to complete hydrogenation of the alkene in three hours. With internal alkenes, (*e.g.* cyclopentene), a stable hydrido alkene complex such as $[ReH_3(PMe_2Ph)_3(\text{cyclopentene})]$ is formed, with no hydrogenated alkene produced. The X-ray crystal structure of the cyclopentene adduct has been determined. Photolysis of this adduct in benzene gives both hydrogenation and dehydrogenation of the ring to give cyclopentane, $[(cp)ReH_2(PMe_2Ph)_2]$ and $[(cp)ReH_4(PMe_2Ph)]$. This last complex can also be isolated in 20% yield after the photolysis of $[ReH_5(PMe_2Ph)_3]$ and cyclopentadiene in hexane. Reaction of $[ReH_5(PMe_2Ph)_2]$ and $[Me_3CCH{=}CH_2]$ in benzene under nitrogen gas gives $[(C_6H_6)Re(PMe_2Ph)_2(CH_2CH_2CMe_3)]$ and the dinitrogen complex *fac*-$[(PMe_2Ph)_3Re(PMe_2C_6H_4)(N_2)]$ whose crystal structure was also reported [50].

3.4 RHENIUM(IV)

3.4.1 Oxides, Sulfides, Selenides and Tellurides

The crystal structure of Li_2ReO_3, obtained by lithium insertion into ReO_3, was determined by neutron diffraction powder profile analysis, and refined by the Ritveld method. The ReO_3 host lattice, made exclusively of corner sharing octahedra, was altered significantly on lithium insertion without breaking bonds. The original 12-coordinate perovskite-like cavity was changed to two 6-coordinate octahedral sites, which are occupied by lithium ions [35,36]. During dehydration of rhenic(VII) acid, the first dehydration products are rhenium(VII) oxo and hydroxo species, $H[ReO_4]$ and $Re_2O_5(OH)_4$, which undergo solid phase intramolecular reduction to a rhenium(IV) species $ReO(OH)_2$, which was identified by spectrometric methods [15]. A spectrometric study of the $Re(VII)/H_2[SO_4]/[SCN]^-$ system was carried out, and some reduction to ReO_2 and $ReO(OH)_2$ was observed [16].

The chemical shifts (ΔE) of the X-ray L_{III} absorption discontinuities of rhenium in ReO_2, ReS_2, $ReSe_2$ and $ReTe_2$ were studied using a bent crystal X-ray spectrograph [6]. The free energy changes and pressure equilibrium constants were calculated for ReS_2 reduction by hydrogen gas at 298 – 1300 K. Reduction begins at 937 K, and the activation energy is $125 kJmol^{-1}$ [51]. The dependence of the dissociation pressure P of $ReS_{2\pm x}$ on its composition was studied [52].

The complexes $K_2[Re_2O(SO_4)_2(L)_2(OH)_2]$ (HL = 2- or 4-pyridinecarboxylic acid) were prepared by treating $K_2H_2[Re_2O(L)_2(SO_4)_4]$ with potassium hydroxide. The compounds $[Re_2O(SO_4)_2(Q)_2(OH)_2]$ (Q = nicotinamide or isonicotinamide) were prepared similarly. IR spectra were used to elucidate the structures. The rate of base hydrolysis of the anion $[Re_2O(SO_4)_2(L)_2]^{4-}$ was found to be independent of the concentration of the complex but is significantly affected by the nature of the ligand L [53].

3.4.2 Halides and Halocomplexes

The structure of $ReCl_4$ was studied [54] by X-ray diffraction and IR spectroscopy. The crystal has a monoclinic unit cell, with space group *C2/m*. The new compound $ReCl_{2.58\pm0.03}$ was isolated [54].

Measurements of the temperature dependence of the intensities of the halogen nuclear quadrupole resonances in $K_2[ReCl_6]$ in the cubic phase are reported. The results provide indirect evidence for the formation of dynamic clusters of the low symmetry phase as a precursor to the occurence of rotative type phase transition to tetragonal structures in these crystals. It was thought that the occurence of these precursor crystals is almost certainly a general phenomenon associated with all structural phase transitions in antifluorite crystals [55].

The EPR spectra of rhenium(IV) in single crystals of $[NH_4]_2[PtCl_6]$ at frequencies near 10 GHz have been reported. The results were interpreted in terms of two types of centre, one with octahedral symmetry and the other with axial distortion along the *c* trigonal axis. It is suggested that this distortion could be due to variations in the orientations of the $[NH_4]^+$ ions [56]. High resolution IR luminescence spectra of $[ReCl_6]^{2-}$ in $K_2[PtCl_6]$ and of $[ReBr_6]^{2-}$ in $Cs_2[ZrBr_6]$ have been measured between 10000 cm^{-1} and 3000 cm^{-1} at liquid helium temperatures. Comparison with the luminescence spectra in the visible region has enabled nine luminescence transitions to be observed in the bromide and five transitions in the chloride. These correspond to every transition between states separated by more than six quanta of the ν_3 vibrational mode of the ions. Most of the transitions show extensive vibrational structure, but the relative intensities of the magnetic dipole origins and the three vibronic origins vary greatly from transition to transition. The mechanisms of the various radiative and non-radiative processes were also discussed [57].

The low temperature (0–30 K) antiferromagnetic susceptibilities of $K_2[ReCl_6]$ and $K_2[ReBr_6]$ have been explained using correlated effective field theory and by considering the XY symmetry of the exchange Hamiltonian. The theory gives a good account of the observed magnetic susceptibilities of these compounds and the sublattice magnetism of $K_2[ReCl_6]$ [58]. The general quadratic valence force field has been applied to some octahedral hexahalide ions, *viz.* $[ReCl_6]^{2-}$ and $[ReBr_6]^{2-}$ using molecular kinetics constants and Wilson's F.G. matrix method. The kinetic constants, the seven independent potential constants, the vibrational mean amplitude, the Coriolis coupling constant and rotational distortion constants at 298.46 K were reported. The ionic character of the bonds was also briefly discussed [59]. The electrolysis of a molten mixture of NaCl(41–42%), KCl(45–46%) and $K_2[ReCl_6]$(12–13%) at 780–900°C with an airtight seal under an atmosphere of argon deposits a film of rhenium metal [60].

When $ReCl_5$ is allowed to react with Me_3CCN, reduction occurs with the formation of the complex $[ReCl_4(NCCMe_3)_2]$, isolated in two isomeric forms. This is in contrast to the reaction with trichloroethanenitrile which forms a simple rhenium(V) adduct $[ReCl_5(Cl_3CCN)_2]$ [49]. The behaviour of $ReCl_5$ in the solvents nitromethane and pyridine, which the authors report to be oxidation resistant, has been studied. The violet $[ReCl_4(MeNO_2)]$ and yellow-brown $[ReCl_4(py)_2]$ were separated as crystals from nitromethane and pyridine solutions, respectively [48].

$[PPh_4][ReOCl_3(sal)]$ was synthesised from the rhenium(IV) complex $[PPh_4]_2[ReCl_6]$ and salicylaldehyde. Characterisation was by the standard techniques of analysis, magnetic and conductivity measurements and IR spectroscopy [41].

When $[HPEtPh_2]_2[ReCl_6]$ was heated in argon at 180 °C, the complex $[Re(PEtPh_2)_2Cl_4]$ was formed. Further heating in air yielded $[Re(OPEtPh_2)_2Cl_4]$ which can be further oxidised to $[Re\{OP(OEt)Ph_2\}Cl_4]$. The oxidation products were identified by IR spectroscopy [61].

The crystal structure has been determined of *trans*-trichlorobis- (diethylphenylphosphino)hydroxorhenium(IV). The crystal has a monoclinic unit cell, with space group $P2_1/a$. Structural data are given and agree with IR spectral data in indicating that the violet compound corresponds to the formula $[Re(OH)Cl_3(PEtPh_2)_2]$ [62].

3.4.3 Hydrides

Dark red $[Re_2H_8(PPh_3)_4]$ was shown to undergo a reversible one-electron oxidation to give the blue monocation $[Re_2H_8(PPh_4)_4]^+$ ($E_{1/2}$ = −0.24 V vs SCE by CV). The X-band EPR spectrum of a dichloromethane glass containing the monocation is in accord with the HOMO being a delocalised metal-based orbital [28].

$[Re_2H_4(PMe_2Ph)_4\{P(OCH_2)_3CEt\}_2]$ (4) and its conjugate acid (5) have been prepared. $[Re_2H_8L_4]$ (L = PMe_2Ph) reacts with two equivalents of $P(OCH_2)_3CEt$ (L') in benzene to give $[Re_2H_4L_4L'_2]$ [63].

3.4.4 Phosphates

The rhenium(IV) phosphate ReP_2O_7 has been synthesised and shown to be isomorphous with ZrP_2O_7 [64].

3.5 RHENIUM(III)

3.5.1 Halides

The chemical shifts of the X-ray L_{III} absorption discontinuities of rhenium in $ReCl_3$ was studied using a bent crystal X-ray spectrograph. The shifts were governed by the effective charge on the absorbing ions [6]. The ^{35}Cl NQR frequencies, ν, were determined for rhenium(III) chloride at various temperatures, T:

	ν/MHz		
T/°C	27	-78	-196
	21.772±0.003	21.843±0.003	21.921±0.003
	16.475±0.003	16.481±0.003	16.494±0.003
	15.040±0.003	15.058±0.003	15.074±0.003

Three resonance frequencies were observed and were attributed to three chemically different chlorine atoms in the crystal. By analogy with NQR spectroscopic results for dimeric Group 13 metal halides, the high frequency line was assigned to the terminal chlorine, and the others to the two types of bridging chlorine. Since the asymmetric bridging chlorine forms a weakly bridging bond with rhenium in the neighbouring trimer, this chlorine atom was thought to have some terminal character and hence the middle frequency line was assigned to the asymmetric bridge, and the lower line to the symmetrically bridging chlorine [65]. Argon ion bombardment of ReX_3 (X = Cl, Br or I) in a photoelectron spectrometer yielded the lower valency rhenium halides ($ReCl_2$, ReCl, *etc.*). The presence of these new compounds was established on the basis of the destabilisation of the Re($^4f_{5/2,7/2}$) spin-orbit component binding energies and the relative decrease of the halogen spectral line intensities. A linear correlation between the Re(4f) binding energies for each series of rhenium halides and the oxidation number was observed [66].

The electronic structure of the quadruply metal-metal bonded $[Re_2Cl_8]^{2-}$ species has been studied using *ab initio* wave functions and relativistic effective core potentials. The weak coupling between the metal orbitals of the δ-bond, in particular, necessitates a multiconfigurational description in terms of MO's, and a valence bond interpretation can often yield insights into the nature of the states [67]. A new high yield synthetic route to $[Re_2Cl_8]^{2-}$ has been developed. The reaction involves heating tetrabutylammonium rhenate(VII) with benzoyl chloride at about 209 °C, and then subsequent addition of a HCl(g)-saturated solution of tetrabutylammonium bromide followed by further heating at reflux. This yields the desired product in high purity. Similar reactions with the potassium salt gave poorer yields [18].

When $[Re_2Br_4(O_2CMe)_2.L_2]$ (L = dimethylethanamide) in trichloromethane solution was heated to reflux, protonation and dimerisation of the ligand occurred, forming ultimately $[L_2H]_2[Re_2Br_8]$. The crystal structure of this complex showed the unit cell to be triclinic [68,69].

3.5.2 Halo and Pseudohalo Complexes

The new rhenium(III) complexes $[ReCl_2(RN{-}N{-}NR)(PPh_3)_2]$ (R = 4-MeC_6H_4, Ph, 4-ClC_6H_4 or 4-FC_6H_4) were obtained, in 60-70% yield, by adding *trans*-$[ReOCl_3(PPh_3)_2]$ and PPh_3 to a boiling thf solution of Li[RN-N=NR], generated *in situ* by the action of butyllithium on RNH-N=NR. The triphenylphosphine is thought to act as a reducing agent. The complexes are all green air-stable solids, which were characterised by IR spectroscopy, with ν(RNNNR) between 1250 and 1200 cm^{-1}, and ν(ReCl) between 310 and 294 cm^{-1}. The crystal structure of the 4-tolyl derivative was determined. The unit cell has a monoclinic space group, $P2_1/c$. The rhenium atom is in a distorted octahedral environment, with two axial phosphine groups, two *cis*-chlorine atoms and the chelate ligand forming a four-membered ring with the metal [42].

Dimethylphenylphosphine acts as a coordinating, reducing agent in its reaction with $[ReOX_2L(PPh_3)]$ (X = Cl or Br; L = *N*-methylsalicylideneiminate, *N*-phenylsalicylideneiminate, 1/2 *N,N'*-ethylenebis(salicylideneiminate) or 8-hydroxyquinolinate), initially forming the rhenium(V) adduct $[ReOX_2L(PMe_2Ph)]$ which is then reduced to the rhenium(III) complex $[ReX_2L(PMe_2Ph)_2]$ [44]. When *cis*–diaquatetrabromodi-μ-trimethylethanoatodirhenium was heated in an inert *atmosphere at 240-250 °C*, *trans*–tetrabromodi-μ-trimethylethanoatodirhenium (6) was obtained in 90% yield. (6) reacts with Me_3CCOOH to give $[Re_2Br_2(\mu\text{-}OOCCMe_3)_4]$. The crystal structure of (6) has shown the unit cell to be triclinic, with space group *P*1, and the rhenium–rhenium quadruple bond is 0.221 nm long [70].

The metal and ligand core binding energies of low–spin rhenium complexes, including $[ReCl_3(PMe_2Ph)_3]$, have been measured. The observed metal binding energies can be reproduced from a single set of ligand group shifts referred to the bare metal atom. The metal binding energy increases 1eV per unit increase in the formal oxidation state of the metal. Metal binding energy shifts are negative for σ–donors and positive for π–acceptors. The reference state is taken as the bare unligated low–spin rhenium(0) atom, and has a value 4.0eV greater than that of the bulk metal [47].

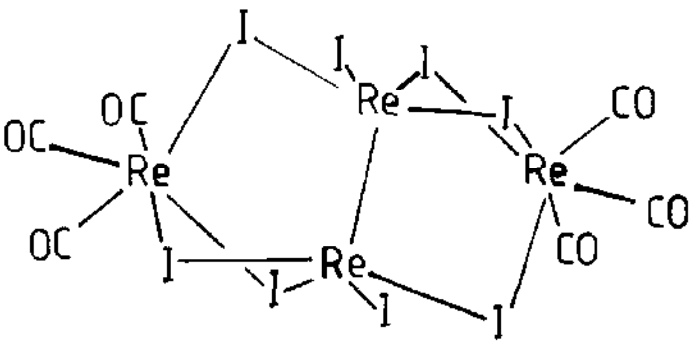
Cocondensation of rhenium atoms generated from a positive hearth electron gas furnace with 1,2–dibromoethane, followed by extraction with thf, gave $[Re_3Br_9(thf)_3]$ in 90% yield. Further reaction with trimethylphosphine forms the reduced rhenium(II) dimer $[(Me_3P)_2Br_2Re{\equiv}ReBr_2(PMe_3)_2]$ in 65% yield [71]. A new synthetic route is reported for the preparation of rhenium(I) isonitrile complexes. Treatment of the dinuclear quadruply metal–metal bonded complexes $[Re_2(OOCR)_4Cl_2]$ (R = Me or Ph) with alkyl isonitriles (R'NC; R' = CMe_3 or cyclohexyl) gives solutions from which salts of the $[Re(CNR')_6]^+$ cation can be isolated in good yield. This cation is inert to further substitution by monodentate phosphines. The halide-rich salts $[Bu_4N]_2[Re_2X_8]$ (X = Cl or Br) react with Me_3CNC to give the seven–coordinate rhenium(III) species $[Re(CNCMe_3)_5X_2]^+$, isolated as their hexafluorophosphate salts. The mixed rhenium(III) complexes $[Re(CNCMe_3)_4L'_2Cl_2]^+$ (L' = $PEtPh_2$ or 1/2 [dppe]) are likewise prepared by the isonitrile cleavage of the quadruply metal–metal bonded $[Re_2Cl_6(PEtPh_2)_2]$ or $[Re_2Cl_6(dppe)]$, respectively. Spectral and electrochemical data were reported [27].

The reaction of photogenerated $[ReCl(dppe)_2]$, from $[ReCl(N_2)(dppe)_2]$, with methanol gives decarbonylation under mild conditions to yield $[ReCl(CO)(dppe)_2]$ and the rhenium(III) species $[ReClH_2(dppe)_2]$. $[ReH_3(dppe)_2]$ may also be formed in small yield. The reaction with the tetrakis(phenyldimethylphosphine) analogue also gave carbonyl and hydrido products, but the reaction is not as clean as with the chelating phosphine, and at least four different hydrides can be identified [72].

A paper has been published, enlarging on a communication discussed in last year's review [73a; ref 57], concerning the preparation and crystal structure of $[Re_3I_6(CO)_6]$. This paper also reports the formation of $[ReI_3(CO)_3]$ and $[Re_4I_8(CO)_6]$ by the room temperature oxidation of $[Re_2I_2(CO)_6(thf)_2]$ in heptane (at reflux, the trimer is formed). $[ReI_3(CO)_3]$ was initially formed as a deep blue compound:

$$[Re_2I_2(CO)_6(thf)_2] + 2I_2 - 2[ReI_3(CO)_3] + 2thf$$

Magnetic susceptibility and IR spectral characterisation (ν(CO) 2012, 1982 cm^{-1}) indicate a *fac*-stereochemistry. This dimeric rhenium(III) complex is converted to the tetramer $[Re_4I_8(CO)_6]$ on standing in heptane at room temperature. An X-ray crystallographic analysis of the tetramer showed that the crystal has a monoclinic unit cell, with space group *C2/c*.



It belongs to the family of $[Re_2X_8]^{2-}$ complexes, with bridging iodine to two terminal $\{Re(CO)_3\}$ groups. The complex is a mixed valence rhenium(I)/rhenium(III) species, the two central rhenium(III) atoms being triply bonded (r(Re≡Re) 0.2279 nm), and having a distorted square pyramidal coordination. $[ReI_3(CO)_3]$ rearranges in thf solution to form the triiodo complex $[Re(I_3)(CO)_3(thf)]$ containing the $[I_3]^-$ ion [73].

Thermolysis of several transition metal cyano complexes including $K_3[Re(CN)_8].H_2O$ and $K_3[Re(CN)_6]$ was studied. The decomposition of the higher valent state complex begins 80 °C lower than that of the lower valent state. The thermal stability increases $Os^{2+} < Re^{3+} < Mo^{2+} < Ru^{2+} < V^{2+} < Fe^{2+}$ [74].

3.5.3 Sulfides

$Ba_2[Re_6S_{11}]$ and $Sr_2[Re_6S_{11}]$ were prepared by the reaction of $M[CO_3]$ (M = Ba or Sr) with rhenium metal at 1350 °C and 1450 °C respectively, in a stream of H_2S. X-ray studies on the barium salt show a framework of $\{Re_6S_8\}$ clusters linked in three dimensions with bridging sulfur. The barium ions are inserted in holes in this framework. The barium compound is diamagnetic [75].

3.5.4 Hydrides

The reaction of photogenerated $[ReCl(dppe)_2]$ with methanol results in decarbonylation under mild conditions to yield $[ReCl(CO)(dppe)_2]$ and the rhenium(III) hydride $[ReClH_2(dppe)_2]$. $[ReH_3(dppe)_2]$ is sometimes also formed. The tetrakis(phenyldimethylphosphine) analogue also yields carbonyl and hydride complexes, but the reaction is not as clean and at least four different hydrides can be identified [72].

Reduction of the complexes $ReCl_5$, $[ReOCl_3(py)_2]$ and $\{ReCl_5(py)\}$ with trimethylphosphite yielded a variety of products as a sensitive function of experimental conditions. Products formed in the reactions include a number of rhenium(0) and rhenium(I) phosphito complexes (*vide infra*) and the rhenium(III) hydride $[ReH_3\{P(OMe)_3\}_4]$. Photoactivation of another product, $[Re_2\{P(OMe)_3\}_{10}]$, in the presence of hydrogen gas also yielded this rhenium(III) hydride [39].

Reaction of $[Re_2H_8(PPhMe_2)_4]$ with two equivalents of $P(OCH_2)_3CEt$ (L') in benzene gave the rhenium(II) hydride $[Re_2H_4L_4L'_2]$ ($L = PPhMe_2$). Reaction of this hydrido complex with excess $H[BF_4].Et_2O$ in benzene at room temperature yielded $[Re_2H_5L_4L'_2][BF_4]$ as a red oil. The crystal structure has been determined, and protonation does not change the formal Re–Re bond order, nor lengthen it to any chemical significance (see Section 3.7). It is also evident that five hydride bridges are not formed in the ground state of this d^4–d^4 dimer. ^1H and ^{31}P NMR spectra have been recorded and studied [63].

Photolysis of $[ReH_5(PPhMe_2)_3]$ and 1-hexene in perdeuterocyclohexane or hexafluorobenzene under 1 atm of hydrogen gas led to complete hydrogenation of the alkene, but with internal alkenes, such as cyclopentene, a stable rhenium(III) hydrido-alkene complex was formed. The X-ray crystal structure of $[ReH_3(PPhMe_2)_3(cyclopentene)]$ is presented. Photolysis of this cyclopentene complex in benzene gave both hydrogenated and dehydrogenated products, *viz.* cyclopentane, $[(cp)ReH_2(PPhMe_2)_2]$ and $[(cp)ReH_4(PPhMe_2)]$ [50]. Treatment of pentane with heptahydridobis(triarylphosphine)rhenium(VII) and 3,3-dimethylbutene yielded trihydro(*trans*-penta-1,3-diene)bis(triarylphosphine)rhenium(III). Trimethylphosphite converts this with high selectivity into pent-1-ene [29]. Heptahydridobis(triphenylphosphine)rhenium(VII) reacts with 3,3-dimethylbutene and benzene to give the dihydridocyclohexadienyl compound, $[(PPh_3)_2(\eta^5\text{-}C_6H_7)ReH_2]$: its X-ray crystal structure was reported [31].

3.6 RHENIUM(II)

Cocondensation of rhenium atoms with 1,2-dibromoethane followed by extraction with thf gave $[Re_3Br_9(thf)_3]$; further reaction with trimethylphosphine in thf at 40 °C led to the dimer $[(Me_3P)_2Br_2Re{\equiv}ReBr_2(PMe_3)_2]$ in 65% yield, reported as being a much better synthetic route than earlier methods. The cocondensation of rhenium atoms with excess oxalyl chloride gave the well known complex $[\{Re(CO)_4Cl\}_2]$ in 40% yield [71]. Argon ion bombardment of some rhenium(III) halides, *viz.* chloride, bromide and iodide, in a photoelectron spectrometer yielded lower valency rhenium halides ($ReCl_2$, ReCl, *etc.*). The presence of these new compounds was established on the basis of the destabilisation of the $Re(4f_{5/2,7/2})$ spin-orbit components of the binding energies and the relative decrease of the halogen spectral line intensities. A linear correlation between the Re(4f) binding energies for each series of rhenium halides and the oxidation number was observed [66].

The cation $[Re(CNR)_4(PR_3)_2]^+$ has been prepared, amongst other methods (see Sections 3.1.5 and 3.5.2), by the reductive cleavage of the triply-bonded complex $[Re_2Cl_4(PR_3)_4]$ by RNC ligands [27].

The complex previously reported as $[ReCl_2(NO)(PPh_3)]$ has been reformulated as the methoxide complex $[ReCl_2(OMe)(NO)(PPh_3)_2]$, on the basis of IR spectral data, and by comparison with the ethoxide analogue. Reformulation also enables the observed paramagnetic moment of 1.7 μ_B to be rationalised. This is now presented as a pseudooctahedral compound of rhenium(II) with a linear NO^+ group. This has led to the suggestion that previously reported reactions of this compound proceed *via* substitution. $[ReCl_2(OMe)(NO)(PPh_3)_2]$ reacts with $Na[BH_4]$ and PPh_3 in ethanolic solution to give improved yields of $[ReH_2(NO)(PPh_3)]$ [76].

The rhenium(II) hydride $[Re_2H_4L_4L'_2]$ ($L = PMe_2Ph$, $L' = P(OCH_2)_3CEt$) and its conjugate acid have been prepared. $[Re_2H_8L_4]$ reacts with two equivalents of phosphite L' in benzene to give $[Re_2H_4L_4L'_2]$, whose X-ray crystal structure has revealed an unusual asymmetric feature of the molecule: the two rhenium atoms have different coordination numbers (six and seven) and different formal oxidation numbers (1.5 and 2.5). The intermetallic distance {r(Re-Re)

0.2597(1) nm) is very close to that found in the triply bonded [$Re_2H_6L_5$] (r(Re≡Re) 0.2589(1) nm). Protonation of the complex with tetrafluoroboric acid yields [$Re_2H_5L_4L'_2$][BF_4] as a red oil. The X-ray crystal structure, determined at -160 °C, shows a symmetric molecule, and this is the first structural determination of a multimetal conjugate acid/base pair where the proton is added to and removed from a terminal site. The protonated acid form shows no significant lengthening of the Re-Re bond. ^1H and ^{31}P NMR spectra of the complexes were recorded and studied [63].

3.7 LOW OXIDATION STATES OF RHENIUM

3.7.1 Rhenium(I) and Rhenium(0)

Argon ion bombardment of the rhenium(III) halides ReX_3 (X = Cl, Br or I) in a photoelectron spectrometer yielded lower valence halides, including rhenium(I). The presence of these new compounds was established on the basis of the destabilisation of the Re($4f_{5/2,7/2}$) spin-orbit components of the binding energies and the relative decrease of the halogen spectral line intensities. A linear correlation between the Re(4f) binding energies for each series of rhenium halides and the oxidation number was observed [66].

Treatment of [$Re(O_2CR)_4Cl_2$] (R = Me or Ph) with alkyl isocyanides R'NC (R' = CMe_3 or cyclohexyl) gave solutions from which salts of the [$Re(CNR')_6$]$^+$ cation were isolated in good yield. This cation itself is inert to substitution by the monodentate tertiary phosphines, but routes to species of the type [$Re(CNR')_4(PR_3)_2$]$^+$ are afforded by the reductive cleavage of the rhenium(II) dimers [$Re_2Cl_4(PR_3)_4$] by R'NC ligands, or by reductive elimination of hydrogen gas from the polyhydride complexes [$ReH_7(PR_3)_2$] and [$ReH_5(PR_3)_2L$] (L = PPh_3 or cyclohexylamine) in the presence of an excess of isocyanide. Spectroscopic and electrochemical properties were also reported [27]. Shake-up satellite structure associated with the nitrogen and carbon binding energies in the X-ray photoelectron spectra of [$Re(CNCMe_3)_6$][PF_6] (and other similar alkyl and aryl isocyanide complexes of chromium, molybdenum and tungsten) was studied. It was concluded that these satellites most probably arise from $M(d)\rightarrow\pi^*(CNR)$ and $M(d)\rightarrow\pi^*(CNAr)$ excitations accompanying the primary photoemission process [77]. The isocyanide complexes *trans*-$[ReCl(CNR)(dppe)_2]$ (R = Me, CMe_3, 4-tolyl, 2-tolyl, 4-chlorophenyl, 4-methoxyphenyl or 2,6-dichlorophenyl) have been prepared by isocyanide displacement of dinitrogen from *trans*-$[ReCl(N_2)(dppe)_2]$, and their ^1H and ^{31}P NMR spectra reported. The redox properties were investigated using cyclic voltammetry and it was found that the oxidation potentials of the complexes became more positive in the order R = CMe_3 < Me < 4-MeOPh < 4-MePh < 2-MePh < 4-ClPh < 2,6-Cl_2Ph and it broadly reflects the increasing electron withdrawing effect of the R group. These were correlated with a ligand parameter P_C (which is a measure of the net σ and π acceptor/donor properties of a particular ligand), and this data was interpreted as showing bent coordination of the isocyanide [78].

The low frequency vibrational (IR and Raman) spectra of the complex $[ReCl(N_2)(PMe_2Ph)_4]$ were measured and partially interpreted. Vibrational spectral lines were identified as belonging to the valence vibration of the Re–N bond and deformation of the {ReNN} fragment [79]. The reaction of photogenerated $[ReCl(dppe)_2]$ derived from the dinitrogen adduct $[ReCl(N_2)(dppe)_2]$, with methanol resulted in decarbonylation under mild conditions to yield $[ReCl(CO)(dppe)_2]$ and $[ReClH_2(dppe)_2]$; $[ReH_3(dppe)_2]$ is sometimes also formed. The similar reaction of the complex $[ReCl(N_2)(PMe_2Ph)_4]$ also forms carbonyl and hydride complexes, but this reaction is not as well defined as with the chelating phosphine, and gives at least four different metal hydrides [72].

The metal and ligand core binding energies of low spin rhenium complexes have been measured, including $[ReCl_2(N_2Ph)(PMe_2Ph)_2(NH_3)]$, a formally rhenium(I) complex (see also Section 3.5.2) [47].

Together with other reductions of organic compounds, it is reported that

$[ReH_5(PPhMe_2)_2]$ reacts with $Me_3CCH{=}CH_2$ in benzene under nitrogen gas to yield $[(C_6H_6)Re(PPhMe_2)_2(CH_2CH_2CMe_3)]$ and *fac*-$[(PPhMe_2)_3Re(PMe_2C_6H_4)(N_2)]$, whose crystal structure was also reported [50].

Reduction of $ReCl_5$, $[ReOCl_3(py)_2]$ and $[ReCl_5(py)]$ with trimethyl phosphite yielded a variety of products including $[Re_2\{P(OMe)_3\}_{10}]$ (7), $[HRe\{P(OMe)_3\}_5]$, $[Re\{P(OMe)_3\}_5\{P(O)(OMe)_2\}]$, $[H_3Re\{P(OMe)_3\}_4]$ and $[HRe\{P(OMe)_3\}_3\{(MeO)_2POP(OMe)_2\}]$. Complex (7) reacts readily with protic acids to give a series of cationic and hydridic products. It also undergoes substitution reactions through photodissociation of the phosphite, and through photoactivation of (7) in the presence of dihydrogen, the three hydride complexes mentioned above were prepared [39].

3.7.2 Carbonyl complexes

Mingos postulates that the successful synthesis of high-nuclearity clusters requires due consideration not only of the relevant electronic factors but also of the steric requirements of the ligands on the periphary of the molecule, and has quantified this function using cone angles found in clusters. This model suggests that $[Re_4(CO)_{12}]$ is unsaturated as is substantiated by the existence of $[Re_4H_4(CO)_{12}]$ and $[Re_4H_6(CO)_{12}]^{2-}$ [81].

A multiphoton ionisation (MPI) time-of-flight mass spectrum of $[Re_2(CO)_{10}]$ was recorded and it showed peaks due to $\{Re_2\}^+$ and $\{Re\}^+$. A similar MPI mass spectrum of a 1:10 mixture of $[Re_2(CO)_{10}]$ with $[Mn_2(CO)_{10}]$ showed peaks due to the reaction of $\{Mn\}^+$ with $[Re_2(CO)_{10}]$ such as $\{MnRe_2(CO)_8\}^+$ and $\{MnRe_2(CO)_{10}\}^+$ [82].

The $[Re(CO)_5]^{\cdot}$ radical was generated in the pulse radiolysis of a variety of organorhenium complexes in ethanolic solution as well as in the flash photolysis of $[Re_2(CO)_{10}]$ in 2,2,4-trimethylpentane solution. The radical absorbs radiation in the visible region in ethanol (λ_{max} 535 nm, ϵ 1000 ±100 $M^{-1}cm^{-1}$). Absolute rate constants were determined for the reactions of the solvated electron in ethanol with $[Re(CO)_5Br]$ (k = 6.7 x 10^9 $M^{-1}s^{-1}$), $[Re(CO)_5(SO_2CH_3)]$ (k = 6.6 x 10^9 $M^{-1}s^{-1}$) and $[Re_2(CO)_{10}]$ (k = 7.8 x 10^9 $M^{-1}s^{-1}$). The rate of chloride abstraction from CCl_4 in ethanol by $[Re(CO)_5]^{\cdot}$ was measured (k = 3.9 x 10^7 $M^{-1}s^{-1}$) and is sixty-five times greater than that of $[Mn(CO)_5]^{\cdot}$ [83].

Single crystal IR reflectance and transmittance spectra have been obtained for $[Re(CO)_5Br]$ and $[Re_2(CO)_{10}]$ and their manganese analogues. Together with some additional Raman spectral data for the bromides, these data have led to revised assignments of IR and Raman spectral bands for all four materials which show a good degree of internal consistency. This report is the first detailed investigation of their IR spectra, and almost all the predicted lattice modes were found as well as the internal modes [84]. Further experiments have been conducted [85a] on the substitution reactions of $[Re_2(CO)_{10}]$ and $[MnRe(CO)_{10}]$ to investigate more thoroughly the homolytic cleavage of the metal-metal bond as the first step in the substitution mechanism as suggested by Poe [85b]. The results of these new crossover experiments support initial dissociation of CO in substitution reactions of $[Re_2(CO)_{10}]$ and $[MnRe(CO)_{10}]$ on the absence of significant concentrations of metal intermediates. It was not excluded that metal-metal bond cleavage may become important at temperatures greater than 140 °C [85a].

Quaternary ammonium tetrahydroborates (used directly or generated in phase transfer reactions) have proved highly effective reagents for preparing metal carbonyl anions from the metal carbonyl $[Re_2(CO)_{10}]$. Reaction with tetraethylammonium tetrahydroborate in ethanenitrile appears to give $[Et_4N][HRe_2(CO)_9]$, and if reduction is carried out in dichloromethane solution, $[Re_2(CO)_9Cl]^-$ is obtained in high yield [86].

The photochemical reaction of $[Re_2(CO)_{10}]$ with water was studied in various solvents using radiation of varying wavelength. The initial reaction led to substitution of a water molecule for a carbonyl ligand on irradiation at 313 nm, by homolytic fission of the metal-metal bond followed by thermal substitution and reformation of the Re–Re bond. Irradiation at 366 nm led to the formation of the hydrido and hydroxo species $[HRe(CO)_5]$ and $[Re_4(CO)_{12}(OH)_4]$ for which a mechanism was proposed [87,88].

Reaction of $[Re_2(CO)_{10}]$ with CF_3SO_3H has been studied with regard to the production of methane from carbon monoxide, but it was shown that no detectable quantities of methane were produced [89].

3.7.3 Carbonyl Halo Complexes

Exposure of dilute solutions of $[Re(CO)_5Br]$ and $[Re(CO)_5I]$ in methyltetrahydrofuran to ^{60}Co γ-rays at 77 K gave electron-addition products characterised by large hyperfine couplings to the halogen and metal nuclei. Orbital populations for the extra electron estimated therefrom showed trends characteristic of antibonding electrons and in all cases the extra electron appears to be accomodated in the metal–halogen σ^* orbital comprising primarily (d_z2–p_z) orbitals. The parallel components were easy to assign while the perpendicular components were more difficult [90]. The reduction of $[Re_2(CO)_{10}]$ with quaternary ammonium tetrahydroborates has proved very effective for preparing carbonyl anions; if the reduction is carried out in dichloromethane solution, the chloroanion $[Re_2(CO)_9Cl]^-$ is obtained in high yield [86]. Cocondensation of rhenium atoms, generated from a positive hearth electron gas furnace, with excess oxalyl chloride yielded the well-known complex $[\{Re(CO)_4Cl\}_2]$ in 40% yield [71].

In thf solution, $[ReI_3(CO)_3]$ rearranges to give the rhenium(I) complex containing the $[I_3]^-$ anion, $[Re(I_3)(CO)_3(thf)]$ [73].

The preparations of rhenium carbonyl complexes with glycylglycine as a mono- and bidentate ligand have been reported. Reaction of $[Re(CO)_5Br]$ with glycylglycine (HL) in a 1:2 molar ratio in dioxane (Q) solution yielded the complex *fac*-$[Re(CO)_3Br(HL)(Q)]$ in which the amino acid is monodentate and bonded through the amino-*N* atom, as postulated on the basis of IR and ^1H NMR spectral data, and the presence of one titratable proton. When an equimolar ratio of reactants is used, the amino acid is reported to deprotonate and act as a bidentate ligand. Furthermore, reaction between the rhenium carbonyl bromide and potassium glycylglycinate in dioxane gave a product which analysed as $C_{11}H_{15}N_2O_8Re$, and on the basis of ^1H NMR and IR spectra and pH measurements was also postulated to contain a bidentate deprotonated amino acid ligand. Addition of ethanolic potassium hydroxide to a solution of the first complex also produced this adduct [91,92].

The resonance Raman spectra of $[Re(CO)_3ClL]$ {L = 1,2-bis(arylimino)ethane or 1,2-bis(isopropylimino)ethane}, obtained by the excitation into the lowest energy band (MLCT), has been reported, and compared to those of $[M(CO)_4L]$ (M = Mo or W) and $[Ru(CO)_3L]$. The observed bands were assigned. It was found that an increase of π-backbonding from the metal to the di-imine ligand appears to be accompanied by a decrease in the resonance Raman effect for the symmetrical stretching modes of the ligand with respect to the symmetrical M-L stretching modes. At the same time an increase in the resonance Raman effect is observed for vibrations of the aryl rings which are virtually inactive in the Raman spectra of free ligands. This was interpreted in terms of a distortion of the aryl rings in the MLCT excited state [93].

The effects of pressure and freezing on the radiative and non-radiative rates from the excited states of $[Re(CO)_3Cl(4,7\text{-}Ph_2phen)]$ and $[Re(CO)_3Cl(phen)]$ were investigated in a variety of solvents with varying polarity. The radiative rates depend on the low frequency dielectric constant (ϵ) of the solvent. A clear demonstration of this dependence is exhibited at the phase transition of the solvent. In polar solvents k_r and ϵ drop continuously, whilst in non-polar solvents k_r and ϵ show no substantial change. The non-radiative rates in the liquid and solid phases depend primarily on the energy gap between the emitting and ground states. The blue shift in energy, shown in all solvents on freezing, causes a drop in k_{nr}. At the phase transition, both the blue shift in peak energy and narrowing in the ground state potential well affect k_{nr} [94].

Reaction of photogenerated $[ReCl(dppe)_2]$ (from $[ReCl(N_2)(dppe)_2]$) with methanol resulted in decarbonylation under mild conditions to yield $[ReCl(CO)(dppe)_2]$ (and $[ReClH_2(dppe)_2]$). The related reaction using $[ReCl(N_2)(PPhMe_2)_4]$ also gave carbonyl and hydride complexes, but the reaction was not as well defined as with the chelating phosphine [72].

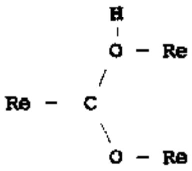
$[ReBr(CO)_5]$ has been used as a reagent for the preparation of the following complexes: $[(CO)_4BrRe\{P(CMe_3)_2(SiMe_3)\}]$, $[(CO)_4BrRe\{P(CMe_3)(EMe_3)_2\}]$, $[(CO)_4BrRe\{P(EMe_3)_3\}]$ (E = Si, Ge or Sn) and the dimeric rhenium(I) species $[\{(CO)_4Re\}_2(\mu\text{-}PR_2)_2]$ (PR_2 is $P(CMe_3)_2$, $P(CMe_3)(SiMe_3)$ or $P(GeMe_3)_2$) [95]. Ligand substitution of $[\{BrRe(CO)_4\}_2]$ with $Ph_2P(CH_2)_nCl$ gave $[(CO)_4BrRe\{PPh_2(CH_2)_nCl\}]$. The crystal structure of the complex for $n = 2$ was determined [96]. Complexes of the type $[ReX(CO)_3L]$ (X = Cl, Br or I; L = $MeE(CH_2)_nEMe$, $n = 2$ or 3, or MeECH=CHEMe; E = S or Se) have also been prepared, and the energy barriers associated with the pyramidal inversions at the individual chalcogen atoms were calculated using total band shape dynamic NMR effects. These barriers were found to be lower than those for selenoxides and sulfoxides, which was attributed to $(p\text{-}d)\pi$ bonding between the ligand and metal in the transition state. Comparisons were made with similar platinum complexes. The crystal structure of $[ReL(CO)_3\{MeSe(CH_2)_2SeMe\}]$ was determined and showed a distorted octahedral environment around the rhenium atom with the iodide being *cis* to both the selenium atoms of the chelate ring. The two methyl groups on the selenium atoms were positioned away from the bulky iodide ligand [97].

When carbon disulfide is allowed to react with the compound $Ph_3PCR'R''$, the initially formed zwitterion $Ph_3P^+CR'R''CS_2^-$ is stable if R' and R" are alkyl groups. If R' = H, the molecule can further react to form the salt $[Ph_3PCH_2R''][Ph_3P{=}CR''CS_2]$. The reactions of $Ph_3P^+CR'R''CS_2^-$ have been investigated: when R' = R" = Me, reaction with $[BrRe(CO)_5]$, or even better with $[\{BrRe(CO)_4\}_2]$ under strict exclusion of light yields *fac*-[$(CO)_3ReBr(S_2CCMe_2PPh_3)$], whose crystal structure has been determined. In the case when R' = Me and R" = H, reaction with bromopentacarbonylrhenium(I) yielded the expected *cis*-tetracarbonyl compounds, which were detected by IR spectroscopy but could not be isolated. Irradiation of the compounds resulted in cleavage of the P–CR_2 bond [98]. Reaction of $Ph_3P^+CMe_2CS_2^-$ in boiling thf with [$BrRe(CO)_5$] under the action of light led to the formation of an orange solution in which no new metal carbonyl complex could be detected [99].

The reaction between [$BrRe(CO)_5$] and the CS_2 adduct of dicarbonyl(cyclopentadienyl)iron(II) produced, in good yield, [$(cp)(CO)_2Fe(CS_2)Re(CO)_4$] in which the {$CS_2$} group acted as a bridge between the two metal atoms: {FeC(=S)SRe}. Depending on the reaction conditions, both the S_2–chelated complex [$(cp)(CO)_2FeC(=S)SRe(CO)_4$] and the unidentate complex [$(cp)(CO)_2FeC(=S)SRe(CO)_5$] were obtained. Alkylation of the {FeC(=S)SRe} unit in this unidentate complex with methyl trifluoromethane sulfonate yielded [$(cp)(CO)_2FeC(SMe)SRe(CO)_5$]$^+$ (only the second metallodithiocarbenemetal complex to be reported), which reacted with methylamine to produce [$Re(CO)_4(NH_2Me)(CONHMe)$]. Characterisation was by ^1H NMR and IR spectroscopy. The chelated derivatives reacted with PPh_3 to give the adduct with the phosphine bound to rhenium with loss of CO [100].

3.7.4 *Carbonyl Hydroxo, Hydrido and CO_2 Complexes*

Reaction of [$(CO)_5ReFBF_3$] with aqueous alkali yielded "$Re(CO)_5(OH)$", a solution of which in propanone gave crystals of [$\{(CO)_5Re(CO_2)Re(CO)_4\}_2$]. IR and mass spectral data were recorded, and X-ray crystallographic analysis showed a tetranuclear framework with CO_2 bridges, every atom of the two CO_2 ligands being bound to a rhenium atom. [$Re_3(CO)_4(COOH)$], with the following structural element



has been isolated. Other reactions of $[(CO)_5ReFBF_3]$ with methanoate, oxalate, nitrate and nitrite were also reported [101].

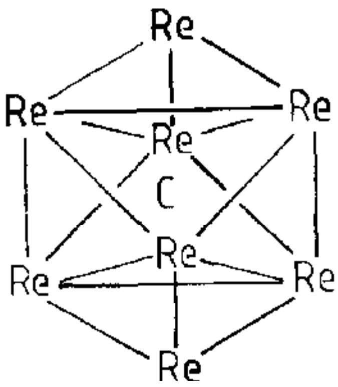
$[\{Re(CO)_3OH\}_4].2C_6H_6$ crystallises in a cubic space group *Pn3m*. The structure consists of discrete tetramers of four rhenium and four oxygen atoms occupying the corners of a distorted cube. There are two benzene rings per formula unit in the lattice. The compound is probably the first characterised example of a benzene ring using both faces as acceptors for OH-π hydrogen bonding [102].

The photochemical reaction of $[Re_2(CO)_{10}]$ with water in thf and other solvents was studied using radiation of varying wavelengths. The initial reaction led to $[Re_2(CO)_9(OH_2)]$ formed upon irradiation at 313 nm, by homolysis of the Re-Re bond followed by thermal substitution of the $[Re(CO)_5]$ radical by water, and then reformation of the Re-Re bond to give the monosubstituted product. This decomposed under 366 nm irradiation to form $[HRe(CO)_5]$ and $[Re_4(CO)_{12}(OH)_4]$. The decomposition pathway was thought to involve $[Re_2(CO)_8(OH)_2]$ as an unstable intermediate, which decomposed *via* initial loss of water and oxidative addition of an O–H bond to form $[HRe_2(CO)_8(OH)]$, which then itself decomposed to give the observed products [88].

The reaction of tetraethylammonium tetrahydroborate with $[Re_2(CO)_{10}]$ in ethanenitrile yields the product $[Et_4N][HRe_2(CO)_9]$, while analogous chloro-derivatives can be prepared in dichloromethane [86].

Reactions of $[Re_2(CO)_{10}]$ and $[H_3Re_3(CO)_{12}]$ with CF_3SO_3H have been investigated with respect to the production of methane from carbon monoxide, and it has been shown that no detectable quantity of methane was produced. Larger rhenium clusters were not studied [89].

The complex $[Re_7C(CO)_{21}]^{3-}$ was isolated from the pyrolysis of $[Et_4N][ReH_2(CO)_4]$ in tetradecane as a red crystalline solid, and the crystal structure of the tetraphenylphosphonium salt was determined. ^1H NMR and IR spectra were also reported. The molecule in the solid state consists of a monocapped octahedron of rhenium atoms (r(Re-Re)$_{av}$ 0.2992 nm). The anion is the first reported example of a carbido species in a carbonyl cluster not belonging to Group 8. The carbido atom lies at the centre of the octahedron (r(Re-C) 0.211-0.215 nm). All carbonyl molecules are terminally bonded. The carbido carbon is reported to have a fundamental role in stabilising the complex [103]. Similarly, the carbido species $[Re_8C(CO)_{24}]^{2-}$ was isolated from the same reaction mixture as the $\{Re_7\}$ species reported above. The crystal structure of the tetraethylammonium salt of this anion showed an octahedron of rhenium atoms capped on two opposite triangular faces by the remaining rhenium atoms, resulting in a rhombohedron of idealised D_{3h} symmetry.



This is the first reported *trans*-bicapped octahedron of metal atoms. Some reported bond lengths are:

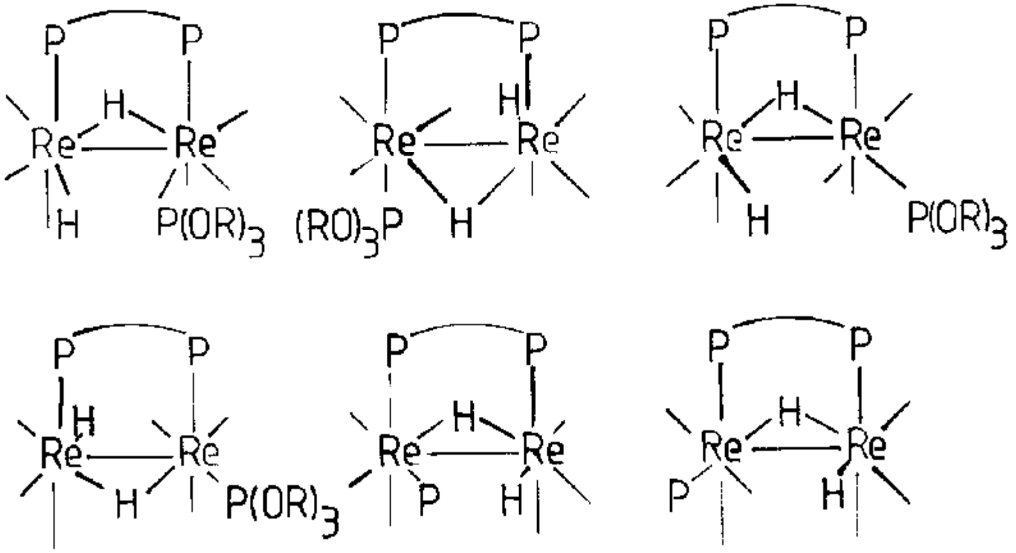
Re-Re(octahedron) 0.2993 nm

Re–Re(capping)	0.2985 nm
Re–C	0.2110(1)–0.2119(1) nm; mean 0.2116 nm

^{13}C NMR spectral studies indicate that the structure in solution is the same as that in the solid [104].

The reactions of $[Re_3H_3(CO)_{12}]$ with bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe) and $[(EtO)_2POP(OEt)_2]$ (tedip) were investigated. With dppm in octane, the previously known $[Re_2(CO)_8(dppm)]$ (8) was formed in 5% yield, together with the novel complexes $[Re_2H_2(CO)_6(dppm)]$ (9) (25% yield), $[Re_3H_3(CO)_{10}(dppm)]$ (10) (12% yield) and $[Re_3H_3(CO)_8(dppm)_2]$ (11) (30% yield) [105]. The reactions with tedip proceeded similarly, forming products (12), (13) and (14), analogous to (9), (10) and (11), along with an isomer of (13), $[Re_3H_3(CO)_{10}(tedip)]$ (15), in which the diphosphine ligand chelates to a single rhenium atom in an axial–equatorial configuration. Protonation of (14) gave $[Re_3H_4(CO)_8(tedip)_2]^+$ (16). The protonation was reversible, and the structure was studied by NMR spectral techniques in solution (as the solid could not be isolated). The crystal structures of (9) and (14) were reported. (9) has a unit cell of space group *Pbca* and (7) $P2_1/c$. In molecule (9), the dppm and two hydrogens bridge the formal Re–Re double bond. The Re–Re bond length is 0.2893(2) nm, which is considerably shorter than in systems with unbridged Re–Re single bonds or with hydride-bridged single bonds. In molecule (14), the $\{Re_3(\mu\text{-}H)_3\}$ core of $[Re_3H_3(CO)_{12}]$ is preserved with four axial sites occupied by the two tedip ligands, which bridge two edges of the $\{Re_3\}$ triangle. The Re–Re bonds bridged by tedip are contracted relative to the hydride-bridged edge (0.3261(5) *vs.* 0.3308(2) nm), and this was attributed to the bite angle of the phosphine ligand. Hydride positions were confirmed by combined X-ray/neutron studies. The reaction between $[Re_3H_3(CO)_{12}]$ and dppe gave *fac*–$[ReH(CO)_3(dppe)]$ in 48% yield as the major product. The minor product was formulated as $[Re_2H(CO)_7(Ph_2PCH_2CH_2PPhC_6H_4)]$ (17), as assigned by NMR, IR and mass spectrometry, but this was not confirmed [105].

Complexes (9) and (12) above, $[Re_2H_2(CO)_6(L{-}L)]$ (L-L = dppm or tedip), react with trimethylphosphite to yield 1:1 adducts which exist in solution in two isomeric forms, both containing a terminal hydride and a bridging hydride ligand. These were investigated by ^{1}H NMR spectroscopy, and there are three pairs of possible optical isomers:



If the first two are present, then simple bridge/terminal hydrogen-atom exchange converts these into their respective optical isomers, which is consistent with the observed spectra. The alternative is that two of the three pairs of isomers are present, and that these interconvert rapidly on the NMR timescale by reversible phosphite dissociation at high temperature. It has not been possible to distinguish between these alternatives. Both the trimethylphosphite adducts react with isocyanides RNC (R = CMe_3, Bu, 4-$MeOC_6H_4$ or 4-$MeC_6H_4SO_2CH_2$) to give the complexes $[Re_2H(CO)_6(L{-}L)(\mu\text{-}HCNR)]$ containing an NC-bonded formimidoyl ligand. With ethanenitrile, the major product is $[Re_2H(CO)_6(L{-}L)(\mu\text{-}NCHMe)]$ containing an *N*-bonded ethylidenimino group. For the dppm complex, an X-ray diffraction study showed a rhenium-rhenium single bond {r(Re-Re) 0.3035(3) nm}. The NCHMe ligand bridges symmetrically the Re-Re bond, which is also believed to be bridged by hydride. Both (9) and (13) form an unstable adduct with CO, but do not react with ethyne, ethene or

[MeOOCC≡CCOOMe] [106].

Reaction of the 4-fluorobenzene diazonium ion with [(cp)Re(CO)$_2$H$_2$] in methanol/propanone solution at room temperature yielded [(cp)Re(CO)$_2$(N$_2$C$_6$H$_4$-4-F)][PF$_6$] and no insertion intermediates could be detected [107].

3.7.5 *Carbonyl Complexes with Other Ligands*

The synthesis of the ureadiido compounds A[Re(CO)$_n$L] (A = Li or K; n = 5 or 4; H$_2$L = OC(NHR)$_2$), in which the ureadiide ions act as a monodentate or bidentate ligand respectively, have been described. Coordination of the ureadiide ligand is *via N*, or *N* and *O* atoms. The force constants of the CO stretching vibrations were calculated and the σ-donor and π-acceptor properties of the ureadiide ligands discussed [108].

The EPR spectra of the controversial binuclear Group 15 organometal-substituted rhenium radicals were studied. The stable quinone-rhenium carbonyl radical complex [(dtbq)Re(CO)$_4$] (dtbq = 3,5-ditertbutylquinone) was prepared in solution and then allowed to exchange its labile carbonyl ligands with Group 15 ligands. Complexes studied include [(dtbq)Re(CO)$_3$L] (where L is PPh$_3$, P(4-MeC$_6$H$_4$)$_3$,PBu$_3$, P(OPh)$_3$, dppm, dppe, dppp, dppb, SbPh$_3$, NH$_3$, AsPh$_3$, hmpa, Ph$_2$PCH$_2$CH$_2$AsPh$_2$ or P(C$_6$H$_4$NMe$_2$)$_3$), and [(dtbq)Re(CO)$_2$(P(OMe)$_3$)$_2$]. The EPR spectra of complexes formed by substitution with bulky phosphines, such as triphenylphosphine, show that there is significant redistribution of spin density. It is suggested that the exchange site is in an equatorial position. With P(OR)$_3$ complexes, there is disubstitution and it is suggested that both phosphite ligands replace the two equatorial carbonyl groups. It was found that the order of the rate of ligand exchange reactions in the [(dtbq)Re(CO)$_4$] radical with Group 15 ligands is N ~ P > As > Sb [109].

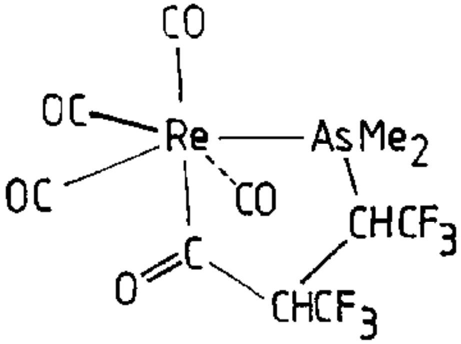
Reaction of the 4-fluorobenzene diazonium ion with $[(cp)Re(CO)_2H_2]$ in a methanol/propanone solution at room temperature yielded $[(cp)Re(CO)_2(N_2C_6H_4{-}4{-}F)][PF_6]$ and no insertion intermediates could be detected [107]. The aryldiazenido complexes $[(\eta^5{-}C_5H_5)Re(CO)_2(N_2R)][BF_4]$ (where R is 4-Me, 4-MeO, 2-MeO, 4-NEt_2 or 2-CF_3 substituted phenyl, or 2,6- or 3,5-xylyl) have been synthesised from the reaction of the appropriate arenediazonium tetrafluoroborate with $[(cp)Re(CO)_2(thf)]$. They react with $Na[BH_4]$ under dinitrogen to yield the corresponding aryldiazene complexes $[(cp)Re(CO)_2(NHNR)]$ ($\delta\{NH\}\sim15$ ppm) and with methyl lithium under dinitrogen to give the hydrazido(2−) derivatives $[(cp)Re(CO)_2\{NN(Me)R\}]$. The crystal structure of $[(cp)Re(CO)_2\{NN(Me)4{-}C_6H_4OMe\}]$ shows it to contain a bent metal hydrazido(2−) skeleton [110]. The rhenium atom lies in an irregular tetrahedral environment provided by two carbonyls, the cyclopentadienyl ring and the hydrazido nitrogen. The hydrazido ligand is coordinated in an end-on fashion with a distinctly bent Re–N(1)–N(2) geometry (138.1°). The hydrazido(2−) complex can be protonated at N(1) to give the hydrazido(1−) complex [110].

Trans-bis(triphenylphosphine)dicarbonyl(1,3-di-{4-tolyl}-triazenido)-rhenium(I) crystallised in the triclinic space group *P*I. The coordination around the rhenium atom is approximately octahedral, with the triazenido ligand coordinated to the metal in a bidentate mode with a bite angle N(1)–Re–N(3) of 105.1°. The bond distances Re–N(1) and Re–N(3) are 0.221(1) nm and 0.218(1) nm and the N(1)–N(2) and N(2)–N(3) bond lengths are 0.133(1) nm and 0.131(1) nm respectively. The entire rhenium–triazenido system is essentially planar, indicative of π delocalisation over the whole system [111].

The photoinduced homolytic fission of $[Re_2(CO)_8(PPh_3)_2]$ was found to be photosensitised by 2,3-butanedione, which is excited to its triplet state by visible radiation, but this was not observed for $[Re_2(CO)_{10}]$. It is postulated that the triplet energy is transferred as such to the dinuclear carbonyls

[112].

The bis(tertiary)arsine *cis*-[$Me_2AsC(CF_3)=C(CF_3)AsMe_2$] reacted, photolytically, with [$Re_2(CO)_{10}$]in degassed benzene to give, after chromatography, a solid - $C_{11}H_6AsF_6O_5Re$, which crystallised in space group PI. The coordination around the rhenium is close to octahedral, and a {Me_2As} group has been cleaved from the ligand. The {$Re(CO)_4$} unit is coordinated to the remaining arsenic and to a carbonyl which has inserted between the rhenium and the olefinic carbon to give a five-membered ring. The Re-As distance (0.250 nm) is shorter than found previously ($r_{av.}$ 0.257 nm) and this is thought to be due to some double bond character in the Re-As bond caused by dπ-pπ back donation from the rhenium atom [113].

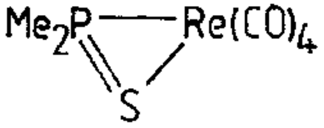


Carbonyl hydrogensulfido metal complexes were prepared by the reaction of [$\{(CO)_n(R_3P)_mRe(SSnMe_3)\}_p$] ($n = 4$, $m = 0$,
$p = 2$; $n = 3$, $m = 2$, $p = 1$; $n = 2$, $m = 3$, $p = 1$; R = Me) with hydrogen chloride, to yield complexes of the form [$\{(CO)_n(R_3P)_mRe(SH)\}_p$]$_2$. [$(CO)_2\{P(OMe)_3\}_3Re(SH)$] was also prepared. Reactions of these SH complexes with main group element halides were investigated. In some cases (*e.g.* MeI, S_2Cl_2 or $HgCl_2$), the SH ligand was replaced by the halogen. Reactions with Me_3SnCl in the presence of triethylamine gave back the starting stannyl

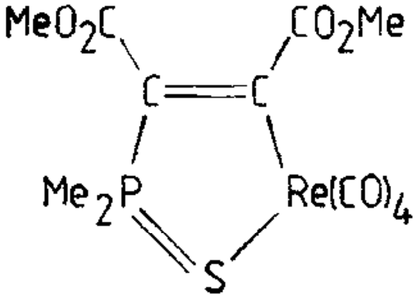
complex. With Me_2AsCl and CH_3COCl, the novel compounds $[(Me_3P)_2(CO)_3Re(SAsMe_2)]$ and $[(Me_3P)_2(CO)_3Re(SCOCH_3)]$, respectively, were obtained. Reaction of $[(Me_3P)_3(CO)_2Re(SH)]$ with $[W(CO)_5(thf)]$ gave $[(Me_3P)_3(CO)_2Re(SH)W(CO)_5]$ [114].

When $[(Me_3P)_2(CO)_3Re(SSiMe_3)]$ was treated with the compounds: Me_2AsCl, Me_2PCl, Me_2PSCl, S_2Cl_2, Me_2SnCl_2, $MeAsCl_2$ or CH_3COCl, the following new complexes were formed: $[(Me_3P)_2(CO)_3Re(SAsMe_2)]$ (**18**), $[(Me_3P)_2(CO)_3Re(SPMe_2)]$ (**19**), $[(Me_3P)_2(CO)_3Re(SCOCH_3)]$ (**20**), $[\{(Me_3P)_2(CO)_3Re{-}S\}_2X]$ (**21**) (X = S_2, $SnMe_2$ or AsMe). Complexes (**18**) and (**19**) reacted with elemental sulfur, selenium and $[Fe_2(CO)_9]$ to give complexes (**22**) - (**26**): $[(Me_3P)_2(CO)_3Re(SAsMe_2{=}S)]$ (**22**), $[(Me_3P)_2(CO)_3Re(SAsMe_2{=}Se)]$ (**23**), $[(Me_3P)_2(CO)_3Re(SPMe_2{=}Se)]$ (**24**), $[(Me_3P)_2(CO)_3Re(SAsMe_2)Fe(CO)_4]$ (**25**) and $[(Me_3P)_2(CO)_3Re(SPMe_2)Fe(CO)_4]$ (**26**). Other similar reactions with more stable carbonyl metal fragments gave dinuclear complexes (*e.g.* with $[Mn(CO)_2(cp)]$, $[(Me_3P)_2(CO)_3Re(SAsMe_2)Mn(CO)_2(cp)]$ is formed), and on further reaction the trinuclear species produced. These reactions demonstrate the synthetic potential of reactive sulfur ligands [115].

Cyclisation of the thiaphospharheniocycle (**27**) with $MeO_2CC{\equiv}CCO_2Me$ gave (**28**) [116].

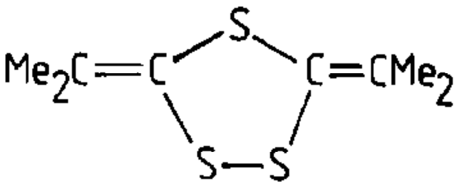


(27)



(28)

$[Ph_3P^+CMe_2CS_2^-]$ (29) was prepared by the addition of Ph_3PCMe_2 to carbon disulfide. Reaction of compound (**29**) with $[BrRe(CO)_5]$ gave (**30**):

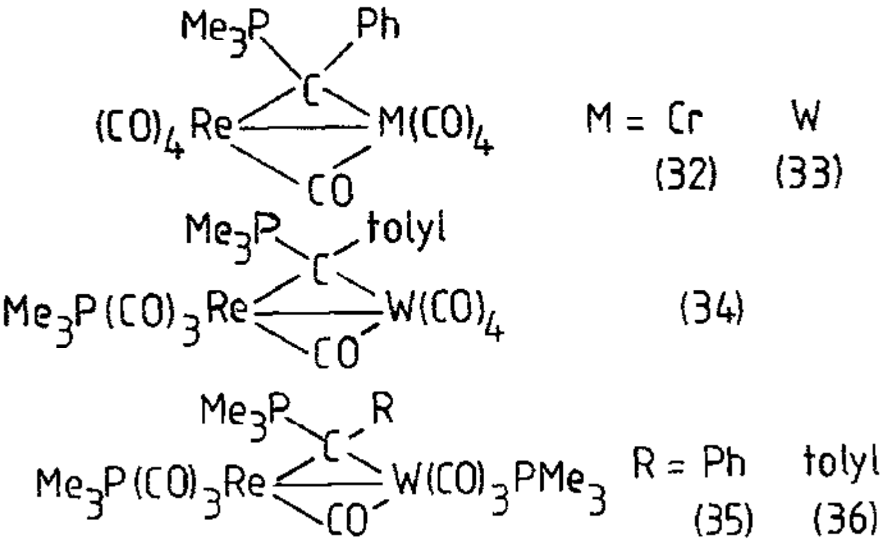


fac-$[(CO)_3ReX(S_2CCMe_2PPh_3)]$ (X = Cl or Br) were prepared from the compound (**29**) and $[\{XRe(CO)_4\}_2]$, and the structure of the product was determined crystallographically [117]. The complexes (**31**) (R = Me, Et or Ph) were prepared by treating $Ph_2P(S)CSNHR$ with $[ClRe(CO)_5]$. $Ph_2P(O)CSNHR$ and $[ClRe(CO)_5]$ gave the dimeric complex $[\{(CO)_3Re\{SC(=NR)P(O)Ph_2\}\}_2]$. Heating complex (**31**) to reflux in hexane gave the dimeric complex $[\{(CO)_3Re\{SC(=NR)P(S)Ph_2\}\}_2]$ [118].

3.7.6 Metallo Carbonyl Complexes

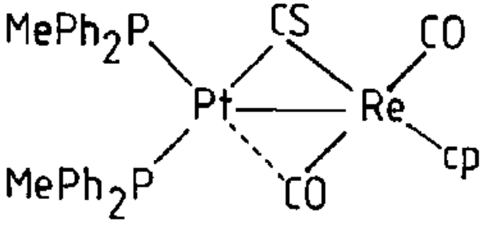
Trans-Pentacarbonylrhenio tetracarbonyl carbyne complexes of chromium and tungsten, $[\{(OC)_5Re\}M(\equiv CR)(CO)_4]$ (R = Ph or 4-MeC_6H_4), react with trimethylphosphine to give binuclear transition metal ylid complexes (**32**) and (**33**) which have one bridging ylid as well as a bridging carbonyl ligand and a metal-metal σ-bond. An excess of trimethylphosphine leads to the substitution of one, or at higher temperature, two terminal carbonyl ligands, to give (**34**), or (**35**) or (**36**) respectively. The reaction conditions, the results of spectroscopic measurements and the crystal structure of (**34**) are reported

[119].



(32–36)

It has also been reported that $[Cl(CO)_4OsOs(CO)_4Os(CO)_4SnCl_3]$ reacts with nucleophilic reagents to give $[Cl(CO)_4OsOs(CO)_4Os(CO)_4SnCl_2Re(CO)_5]$, which contains a {Os–Sn–Re} linkage: the product was characterised by IR spectroscopy [120]. $[M(CO)_5SnCl_2]$.thf (M = Cr or W) reacts with $Na[Re(CO)_5]$ in thf solution to yield $[M(CO)_5Sn\{Re(CO)_5\}_2]$, and the product was characterised by IR spectroscopy [121]. Addition of $[M(CO)_2(CS)(cp)]$ (M = Mn or Re) to $[Pt(C_2H_4)(PR_3)_2]$ (PR_3 = PMe_2Ph) in light petrol at 0 °C gives $[MPt(\mu\text{-}CS)(CO)_2(PR_3)_2(cp)]$. Variable temperature NMR studies show that the compound undergoes dynamic behaviour in solution – at room temperature only one ^{31}P resonance is seen, whereas at –60 °C two resonances can be seen corresponding to PR_3 groups *transoid* and *cisoid* to the metal-metal bond. By analogy with the manganese compound, for which a crystal structure has been determined, it was proposed that the structure of the rhenium complex was:



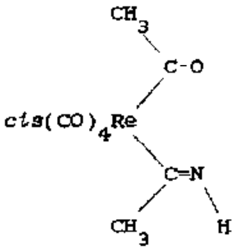
and that the dynamic behaviour was due to CO or PR_3 site exchange - a mechanism for both was suggested [122].

$[BrHgRe(CO)_5]$ reacts with $[PtL_3]$ (L = PPh_3) in benzene to give $[BrL_2PtHgRe(CO)_5]$ [123]. $[(CO)_5ReSmCl_3]$, containing a Re-Sm σ-bond, was prepared by the reaction of $Na[Re(CO)_5]$ with $SmCl_3$ in thf solution [124].

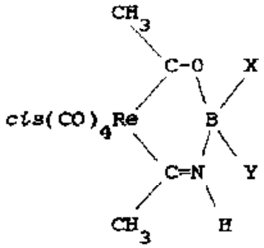
3.7.7 Organometallic Complexes

When $[(\eta^5-C_5Me_5)Re(CO)_3]$ was irradiated with UV light, two dinuclear rhenium compounds were formed: yellow $[(\eta^5-C_5Me_5)_2Re_2(CO)_5]$ and orange-red $[(\eta^5-C_5Me_5)_2Re_2(CO)_3]$. The crystal structure of the latter complex was studied and revealed a highly symmetrical D_{3h} molecule, with a very short rhenium-rhenium triple bond {r(Re≡Re) 0.2411 nm}. IR and NMR spectra were reported [125].

Several rhena-β-ketoimine derivatives of biologically important primary amines containing a 2-ethylamino group, including 2-chloroethylamine (a DNA alkylating agent), cystamine (an heparin antagonist), histamine (a potent vasodilator), tryptamine and *O*-methylserotonin (two indole alkaloids) and *O*,*O*-dimethyldopamine (an adrenogenic drug), have been prepared. These have different distribution and transport properties to the free amines and may act as latent or prodrug forms of the biologically active amines. The complexes were characterised by ^1H NMR spectroscopy [126]. Rhena-β-diketoneimines (formed from the reaction of the rhena-β-diketone and ammonia or a primary amine) have also been found to react with sodium hydride to give, e.g. the anion:



and this will complex with boron halides to give complexes of the form



where X = Y = Cl, Br or I, or X = Cl, Y=Ph. The products were characterised by ^1H NMR and IR spectroscopy [127].

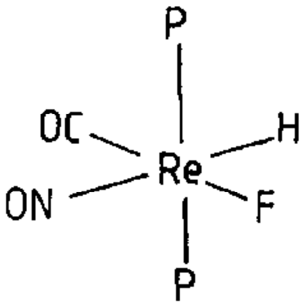
$[Re(CO)_5(CH_2Cl)]$ has been prepared by the reaction of $Na[Re(CO)_5]$ with $ClCH_2OCH_3$ [128]. Low temperature synthesis of the kinetically unstable formyls $[Re(CO)_4(CHO)(PPh_3)]$ and $[(cp)Re(NO)(CO)(CHO)]$ by reaction of $Li[BHEt_3]$ with the corresponding metal carbonyl cations have been discussed. These complexes were also synthesised by hydride transfer from the stable neutral formyl – $[(cp)Re(CO)(PPh_3)(CHO)]$ – to the appropriate metal carbonyl cation precursor (*e.g.* transformylation). The decomposition of $[(Re(CO)_4(CHO)(PPh_3)]$ is very complex and sometimes involves the solvent dichloromethane [131].

3.7.8 Formyl and Carbonyl/Nitrosyl Compounds

Metal formyl anions were produced by the reaction of hydroborates with metal carbonyls. Reaction of $[(cp)Re(CO)_2(NO)]^+$ with $[HB(OR)_3]^-$ produced the formyl complex, $[(cp)Re(NO)(CO)(CHO)]$ which underwent disproportionation to give the metalloester $[(cp)(CO)(NO)ReCO_2CH_2Re(CO)(NO)(cp)]$. Indirect hydrolysis of this metalloester produced $[(cp)Re(CO)(NO)(CH_2OH)]$, the first authentic hydroxymethyl metal compound. Reduction of $[(cp)Re(NO)(CO)_2]^+$ with $[H_2AlEt_2]^-$ provided a more convenient synthesis of $[(cp)Re(NO)(CO)(CH_2OH)]$. This complex does not react with CO below 90 °C, the temperature at which the hydroxymethyl group loses water to form an ether linked dimer: $[\{(cp)Re(CO)(NO)CH_2\}_2O]$. At room temperature, $[(cp)Re(NO)(CO)(CH_3)]$ reacts with two equivalents of trimethylphosphine to produce $[(\eta^1\text{-}C_5H_5)Re(NO)(CO)(PMe_3)_2(CH_3)]$ [129]. Reduction of $[(cp)Re(NO)(CO)_2][BF_4]$ (**37**) by $Na[BH_4]$ in thf or thf/water mixtures affords the formyl $[(cp)Re(NO)(CO)(CHO)]$ (**38**), hydroxymethyl $[(cp)Re(NO)(CO)(CH_2OH)]$ (**39**) and methyl $[(cp)Re(NO)(CO)(CH_3)]$ (**40**) derivatives in high yields, depending on the stoicheiometry of the reaction. One equivalent of $Na[BH_4]$ with (**37**) in water gave (**38**) in 62% yield, as orange crystals with low thermal stability. Two equivalents gave (**39**), while one equivalent of $Na[BH_4]$ under anhydrous conditions gave (**40**) as red air-stable crystals. Individual reduction steps between (**37**) and (**40**) were investigated: reduction of (**38**) to (**40**) and (**39**) to (**40**) by $Na[BH_4]$ in thf demonstrates the activation of formyl and hydroxymethyl functional groups in these complexes. The pentamethylcyclopentadienyl analogues were also prepared: $[(C_5Me_5)Re(NO)(CHO)]$ has greater stability than (**37**) [130].

Low temperature syntheses of the kinetically unstable formyls $[(cp)Re(NO)(CO)(CHO)]$ (**41**) and $[(PPh_3)Re(CO)_4(CHO)]$ (**42**) by the reaction of $Li[BHEt_3]$ with the corresponding metal carbonyl cations were discussed. These complexes were also synthesised by hydride transfer from the stable neutral formyl $[(cp)Re(NO)(PPh_3)(CHO)]$ to the appropriate metal carbonyl cation precursor (transformylation). This latter method avoids the formation of BEt_3 as a side product. (**41**), in dilute solution, decarbonylates to detectable metal hydrides upon warming, while the decomposition of the other formyl complex is more complex [131]. [(cp)ReH(NO)(CO)] reacts with tropylium tetrafluoroborate to give the yellow air-stable salt $[(cp)Re(NO)(CO)(1,2\text{-}\eta^2\text{-}C_7H_8)][BF_4]$, which can then be deprotonated by triethylamine to give $[(cp)Re(NO)(CO)(\eta^1\text{-}C_7H_7)]$ as dark red air-stable crystals: ^{1}H NMR and IR spectra were recorded [132]. Thermally stable $[(cp)Re(NO)(CHO)(PPh_3)]$ has also been synthesised. At 50–105 °C in appropriate solvents, it decomposes to rhenium hydrides, and it can be reduced to $[(cp)Re(NO)(PPh_3)(CH_3)]$ by $[H_3B.thf]$. With CH_3SO_3F or CF_3CO_2H, facile ligand disproportionation occurs and $[(cp)Re(NO)(CO)(PPh_3)]^+$ salts are formed. Other reactions of these compounds have been investigated and characterised by NMR spectroscopy [133].

$[ReH_2(NO)(PPh_3)_3]$ reacts with $H[BF_4]$ in the presence of CO to give the novel fluoro cation $[ReF(NO)(CO)(PPh_3)_3]^+$, which reacts with some coordinating anions to give the neutral $[ReXF(NO)(CO)(PPh_3)_2]$ (X = H, OMe or F). $[ReHF(NO)(CO)(PPh_3)_2]$ is unusual in that its stereochemistry can be unambiguously determined by a combination of IR and ^{1}H NMR spectroscopy:



The structure of a crystal of $[ReF(NO)(CO)(PPh_3)_3][BF_4]$ (grown from a dichloromethane/cyclohexane solution) has been determined. The monoclinic unit cell has solvent molecules disordered about a centre of symmetry. The structure of the cation is that of a distorted octahedron with a *meridional* arrangement of phosphine ligands, and the fluoride *trans* to the nitrosyl group [76].

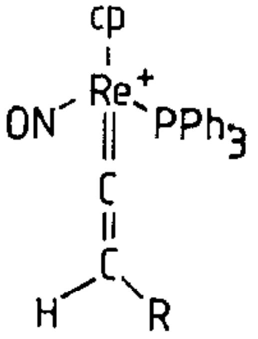
3.7.9 Nitrosyl Compounds

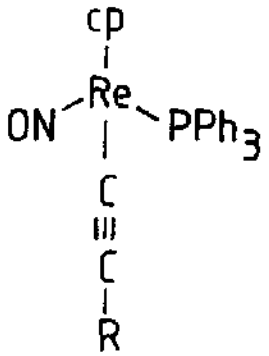
The thermally stable nitrosyl formyl complex $[(cp)Re(NO)(PPh_3)(CHO)]$ has been synthesised. At 50-105 °C in appropriate solvents, it decomposes to rhenium hydrides, and can be reduced by $[H_3B.thf]$ to $[(cp)Re(NO)(PPh_3)(CH_3)]$. In trifluoroethanoic acid or methylfluorosulfate, facile formyl ligand disproportionation occurs and $[(cp)Re(NO)(PPh_3)(CO)]^+$ salts are formed. Other reactions were investigated and studied spectroscopically [133].

The methylidene complex $[(cp)Re(NO)(PPh_3)(CH_2)][PF_6]$ yields kinetically stable sulfenium salts when treated with MeSMe, $MeSCH_2Ph$ or $[(cp)Re(NO)(PPh_3)(CH_2SMe)]$. The binuclear adduct formed in the latter case $[\{(cp)Re(NO)(PPh_3)CH_2\}_2SMe]^+$ is more stable than the others, but undergoes hydride transfer disproportionation to $[(cp)Re(NO)(PPh_3)(=CHSMe)][PF_6]$ and $[(cp)Re(NO)(PPh_3)(CH_3)]$ when heated [134]. $[(cp)Re(NO)(PPh_3)(CH_2Ph)]$ reacts with $[Ph_3C][PF_6]$ at -78 °C to give the benzylidene *sc*-$[(cp)Re(NO)(PPh_3)(=CHPh)][PF_6]$ (**43**) by stereospecific α-hydrogen abstraction; this isomerises on warming to a new geometric isomer *ac*-$[(cp)Re(NO)(PPh_3)(=CHPh)][PF_6]$ (**44**). At room temperature, the (**44**)/(**43**) equilibrium is >99:1, but irradiation between -78 and -20 °C establishes a 55:45 photostationary state. Structures of the two isomers were confirmed by X-ray crystallography, and they were the subject of extended Huckel MO calculations. Nucleophiles react stereospecifically with (**44**) and stereoselectively with (**43**) (~92-95:8-5), with the minor component being produced from the reaction with (**44**). Full details of all reactions and NMR spectra of the products were reported, and an analysis of the thermodynamics and stereospecificity of the reactions given [135]. It was reported above that

$[(cp)Re(NO)(PPh_3)(=CHPh)][PF_6]$ exists as a 99:1 mixture of anticlinal and synclinal Re=C bond geometric isomers at room temperature, and isomerises under irradiation at low temperatures in CD_2Cl_2, CD_3CN or $(CD_3)_2CO$ to a 55(3):45(3) photostationary state. The propylidene analogue $[(cp)Re(NO)(PPh_3)(=CHEt)][PF_6]$ exists as a 95(1):5(1) mixture of anticlinal and synclinal isomers at room temperature, and similarly isomerises to a 59(2):41(2) photostationary state. Absorption spectra of both anticlinal isomers, and an unsuccessful attempt to photosensitise the benzylidene isomerisation were also reported [136].

Chiral rhenium vinylidene and acetylide complexes have been synthesised:

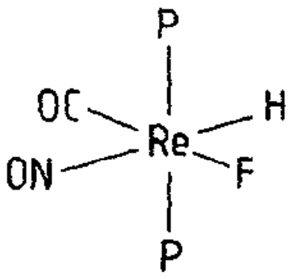




Geometric isomers of the vinylidene complexes occur corresponding to the different orientations of H and R. These two isomers could be thermally and photochemically interconverted and the thermodynamic parameters of the conversion were calculated. Stereospecific reactions of the acetylide complexes were found with methylfluorosulfate which entailed transfer of the metal chirality through a C≡C triple bond of formal cylindrical symmetry and a possible explanation for this asymmetric induction is suggested [137].

The complex previously formulated as rhenium(I) $[ReCl_2(NO)(PPh_3)]$ has been reformulated as the methoxide complex $[ReCl_2(NO)(OMe)(PPh_3)_2]$, on the basis of IR spectral data and by comparison with the ethoxide analogue.

Reformulation has enabled the observed paramagnetic moment to be rationalised, and has led to the suggestion that previously reported reactions proceed *via* substitution. Reduction of the methoxide complex with sodium tetrahydroborate and triphenylphosphine in ethanol gave improved yields of $[ReH_2(NO)(PPh_3)_3]$. This then reacts with HCl in an ethanolic suspension to form the air sensitive complex $[ReCl_2(NO)(PPh_3)_2]$, which further reacts with CO or CNR to give $[ReCl_2(CO)(NO)(PPh_3)_2]$ and $[ReCl_2(CNR)_2(NO)(PPh_3)_2]$ (R = 4-MeC_6H_4) respectively. $[ReH_2(NO)(PPh_3)_3]$ reacts with $H[BF_4]$ in the presence of CO to give the novel fluoro cation $[ReF(CO)(NO)(PPh_3)_3]^+$ which reacts with some coordinating anions to give neutral $[ReXF(CO)(NO)(PPh_3)_2]$ (X = H, OMe or F). $[ReHF(CO)(NO)(PPh_3)_2]$ is unusual in that its stereochemistry can be determined absolutely by a combination of IR and ^1H NMR spectroscopic techniques:



The crystal structure of solvated $[ReF(CO)(NO)(PPh_3)_3][BF_4]$, recrystallised from a dichloromethane/cyclohexane solvent mixture has been determined and shows the unit cell to be monoclinic, with solvent molecules disordered about a centre of symmetry. The structure of the cation is that of a distorted octahedron with a *meridional* array of phosphine ligands and fluoride {r(Re-F): 0.1973 nm} *trans* to the linear NO group. All bond lengths are as expected [76].

The reaction was reported between $ReCl_5$ and Cl_3CNO_2 to give $ReCl_3(NO)_2$ containing chloro bridges. This complex reacts with an excess of boiling ethanenitrile to give $[ReCl_3(NO)_2(MeCN)]$ (**45**). (**45**) and tetraphenylarsonium chloride react to form the salt $[Ph_4As][ReCl_4(NO)_2]$ (**46**). The crystal structure of (**45**) shows it to have a monoclinic space group $P2_1/n$. In the *pseudo*-octahedral environment of the rhenium, the three chlorides are in a *facial* arrangement. (**46**) has a tetragonal space group $P4/n$. The NO groups have *cis* stereochemistry. All complexes were characterised by IR spectroscopy [138].

3.8 MISCELLANEOUS BINARY AND TERNARY COMPOUNDS

The chemical shifts of the X-ray L_{III} absorption discontinuities of rhenium in some of its binary and ternary compounds were studied and compared to that of the pure metal, using a bent crystal X-ray spectrograph. The shifts ΔE were governed by the effective charge on the absorbing ions which was calculated using the theory of J.-P. Suchet [6].

Re_2P_5 was prepared by the reaction of the elemental components in a tin flux. The crystal is triclinic (space group $P1$). The metal atoms are all approximately octahedrally coordinated, with the octahedra distorted to allow metal-metal bonding along common edges {r(Re–Re) 0.265–0.296 nm}, thus forming planar (Re_4) clusters. The phosphorus atoms are all tetrahedrally coordinated. The formal oxidation numbers are: Re +3,+4; P 0,–1,–2,–3. The compound is diamagnetic and semiconducting [139].

The crystal structure of $La_2Re_3B_7$ shows it to be orthorhombic, space group *Pcca*, with the boron atoms forming a zig-zag chain structure [140]. The crystallisation of intermetallic compounds in the Re–Ge systems was investigated at high pressure and temperature. A new phase Re_4Ge_7 was found which is a Nowotny chimney ladder structure, having the Tc_4Si_7-type structure and a tetragonal unit cell which contains four molecular units [141].

3.9 MISCELLANEOUS

There has been a charge overlap study of multiple metal-metal bonding and conjugation in linear chains of transition metal atoms including rhenium and technetium [142].

The intramolecular effects of metal coordination (for example, rhenium pyridylketones) on the photochemistry of ketones has been investigated [143].

References

1 S.N. Misra, *J. Sci. Ind. Res.*, 40 (1981) 709
2 M.B. Varfolomeev and V.V. Ilyukhin, *Koord. Khim.*, 8 (1982) 579
3 Y. Yamoto, *Bunko Kenkyu*, 31 (1982) 2; *Chem. Abstr.*, 97 (1982) 153151
4 M.R. Mohammed and W.F. Sherman, *J. Phys. C*, 14 (1981) 4121
5 V.A. Voloshin, M.G. Krimnus and A.M. Prudnikov, *Optich. Issled. Poluprovodn., Sverdlovsk*, (1980) 45; *Chem. Abstr.*, 96 (1982) 60280
6 A.V. Barhate, V.B. Sapre and C.Mande, *J. Phys. Chem.*, 43 (1982) 761
7 M.C. Chakravorti, M.B. Sarkar and P.K. Bharadwaj, *Trans. Met. Chem., (Weinheim Ger.)*, 6 (1981) 211
8 M.C. Chakravorti and M.B. Sarkar, *Trans. Met. Chem., (Weinheim Ger.)*, 7 (1982) 19
9 A.M. Rosen, A.S. Skotnikov and E.G. Teterin, *Zh. Neorg. Khim.*, 27 (1982) 739; *Chem. Abstr.*, 96 (1982) 206282
10 S. Kemmler-Sack and U. Treiber, *Z. Anorg. Allgem. Chem.*, 484 (1982) 173
11 J-P. Picard, G. Baud, J-P. Besse, R. Chevalier and M. Gasperin, *Acta Cryst.*, B38 (1982) 2242
12 L.A. Nisel'son, T.D. Sokolova, V.A. Popov and A.D. Miklyaev, *Zh. Neorg. Khim.*, 27 (1982) 1335; *Chem. Abstr.*, 96 (1982) 224078
13 G.S. Sinyakova, *Deposited Doc.*, (1980) VINITI 4533; *Chem. Abstr.*, 96 (1982) 58714
14 G.S. Sinyakova and A. Deme, *Deposited Doc.*, (1980) VINITI 4534; *Chem. Abstr.*, 96 (1982) 78923
15 G.S. Sinyakova and A. Deme, *Deposited Doc.*, (1981) VINITI 272; *Chem. Abstr.*, 96 (1982) 27740
16 G.S. Sinyakova and A. Deme, *Deposited Doc.*, (1980) VINITI 4532; *Chem. Abstr.*, 96 (1982) 58715
17 L.V. Borisova, B.J. Brisdon and D.A. Edwards, *Inorg. Chim. Acta*, 54 (1981) L233
18 T.J. Barder and R.A. Walton, *Inorg. Chem.*, 21 (1982) 2510

19 V.V. Ugarov, V.B. Sokolov and N.G. Rambidi, *Zh. Strukt. Khim.*, 22 (1981) 182; *Chem. Abstr.*, 97 (1982) 110573

20 B.S. Averbukh, A.S. Dudin, S.L. Kuznetsov and Yu.Ya. Kharitonov, *Zh. Neorg. Khim.*, 27 (1982) 35; *Chem. Abstr.*, 96 (1982) 150085

21 L.B. Koval, V.G. Sadykov, I.S. Chaus, I.A. Sheka and A.P. Starchenko, *Ukr. Khim. Zh.*, 48 (1982) 18; *Chem. Abstr.*, 96 (1982) 114840

22 V.G. Sadykov, L.B. Koval, I.S. Chaus and A.P. Starchenko, *Ukr. Khim. Zh.*, 48 (1982) 139; *Chem. Abstr.*, 96 (1982) 154418

23 L.S. Bartell, M.J. Rothman and A. Gavezzotti, *J. Chem. Phys.*, 76 (1982) 4136

24 J. Fawcett, R.D. Peacock and D.R. Russell, *J. Chem. Soc., Chem. Commun.*, (1982) 958

25 J.H. Holloway, D.C. Puddick, G.M. Staunton and D. Brown, *Inorg. Chim. Acta*, 64 (1982) L209

26 D.S. Edwards and R.R. Schrock, *J. Amer. Chem. Soc.*, 104 (1982) 6806

27 J.D. Allison, T.E. Wood, R.E. Wild and R.A. Walton, *Inorg. Chem.*, 21 (1982) 3540

28 J.D. Allison, C.J. Cameron, R.E. Wild and R.A. Walton, *J. Organomet. Chem.*, 218 (1981) C62

29 D. Baudry, M. Ephritikhine, H. Felkin and J. Zakrzewski, *J. Chem. Soc., Chem. Commun.*, (1982) 1235

30 D. Baudry, M. Ephritikhine and H. Felkin, *J. Chem. Soc., Chem. Commun.*, (1982) 606

31 D. Baudry, M. Ephritikhine, H. Felkin, Y. Jeannin and F. Robert, *J. Organomet. Chem.*, 220 (1981) C7

32 F.S. Razavi and W.R. Datars, *Phys. Rev. B*, 25 (1982) 4263

33 G.M. Larin, R.A. Bukharizode, A.M. Bol'shakov and P.M. Solozhenkin, *Izv. Akad. Nauk. SSSR, Neorg. Mater.*, 18 (1982) 695; *Chem. Abstr.*, 96 (1982) 209850

34 E.I. Plastinina, L.V. Borisova and O.M. Petrukhin, *Zh. Neorg. Khim.*, 27 (1982) 457; *Chem. Abstr.*, 96 (1982) 111070

35 R.J. Cava, A. Santoro, D.W. Murphy, S. Zahurak and R.S. Roth, *J. Solid State Chem.*, 42 (1982) 251

36 A. Santoro, R.J. Cava, D.W. Murphy and R.S. Roth, *A.I.P. Conf. Procl.*, (1982) 162

37 I.P. Alimarin, E.M. Basova and E.N. Semenovskaya, *Koord. Khim.*, 8 (1982) 319; *Chem. Abstr.*, 96 (1982) 150026

38 R.S. Sergienko and M.A. Porai-Koshits, *Koord. Khim.*, 8 (1982) 251; *Chem. Abstr.*, 96 (1982) 133597

39 H.W. Choi and E.L. Muetterties, *J. Amer. Chem. Soc.*, 104 (1982) 153

40 A. Duatti, S. Benetti, R. Rossi and L. Magon, *Trans. Met. Chem., (Weinheim, Ger.)*, 6 (1981) 380

41 U. Mazzi, E. Roncari and G. Bandoli, *Trans. Met. Chem., (Weinheim,* Ger.), 7 (1982) 163

42 R. Rossi, A. Duatti, L. Magon, U. Castellato, R. Graziani and L. Toniolo, *J. Chem. Soc., Dalton Trans.*, (1982) 1949

43 *E. Roncari, U. Mazzi, R. Rossi, A. Duatti and L. Magon, Trans. Met. Chem., (Weinheim, Ger.)*, 6 (1981) 169

44 A. Duatti, R. Rossi, A. Marchi, L. Magon, E. Roncari and U. Mazzi, *Trans. Met. Chem., (Weinheim, Ger.)*, 6 (1981) 360

45 V. Bertolasi, M. Sacerdoti, G. Gilli and U. Mazzi, *Acta Cryst., Sect. B*, B38 (1982) 426

46a G. Gilli, M. Sacerdoti, V. Bertolasi and R. Rossi, *Acta Cryst., Sect. B*, B38 (1982) 100

46b D. Bright and J.A. Ibers, *Inorg. Chem.*, 8 (1969) 709

47 R.D. Feltham and P. Brant, *J. Amer. Chem. Soc.*, 104 (1982) 641

48 N.V. Ul'ko and A.G. Kolchinskii, *Visn. Kiiv. Univ., (Ser.): Khim.*, 22 (1981) 12; *Chem. Abstr.*, 97 (1982) 61827

49 N.V. Ul'ko and G.Z. Goloverda, *Zh. Neorg. Khim.*, 27 (1982) 2132; *Chem. Abstr.*, 97 (1982) 137695

50 M.A. Green, J.C. Huffman, K.G. Caulton, W.K. Bybak and J.J. Ziolkowski, *J. Organomet. Chem.*, 218 (1981) C39

51 G.N. Zviadadze, K.E. Akopyan, T.B. Gol'shtein and I.S. Turganev, *Izv. Akad. Nauk, Arm. SSR, Nauki Zemle*, 34 (1981) 60; *Chem. Abstr.*, 96 (1982) 169503

52 L.E. Ugryumova, R.A. Isakova and V.A. Snurnikova, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 18 (1982) 969; *Chem. Abstr.*, 97 (1982) 98756

53 S.M. Basitova, L.S. Yusupova and L.G. Pasechnikova, *Koord. Khim.*, 7 (1981) 1203; *Chem. Abstr.*, 95 (1981) 196530

54 E.A. Pisarev, D.V. Drobot and I.V. Makarchuk, *Zh. Neorg. Khim.*, 27 (1982) 19; *Chem. Abstr.*, 96 (1982) 95387

55 R.L. Armstrong, M. D'Iorio and M.E. Ramio, *Can. J. Phys.*, 60 (1982) 397

56 R.F. Bufaical and E.A. Harris, *Solid State Commun.*, 39 (1981) 1143

57 C.D. Flint and A.G. Paulusz, *Mol. Phys.*, 43 (1981) 321

58 I. Chatterjee and V.P. Desai, *Phys. Rev.*, *B*, 24 (1981) 5132

59 J. Moham and A. Mukurthan, *Ind. J. Phys.*, *(Part B)*, 56B (1982) 91

60 V.I. Ermakov, V.I. Neustroev and O.N. Vinogrado-Zhabrov, *Tsvetn. Met.*, (1982) 69; *Chem. Abstr.*, 96 (1982) 151339

61 K.V. Kotegov, Z.A. Lovchikova and V.I. Lobadyuk, *Zh. Neorg. Khim.*, 26 (1981) 3286; *Chem. Abstr.*, 96 (1982) 62126

62 M. Sacerdoti, V. Bertolasi, G. Gilli and A. Duatti, *Acta Cryst.*, *Sect. B*, B38 (1982) 96

63 M.A. Green, J.C. Huffman and K.J. Caulton, *J. Amer. Chem. Soc.*, 104 (1982) 2319

64 E. Banks and R. Jacks, *Mater. Res. Bull.*, 17 (1982) 1053

65 Y. Kume and D. Nakamura, *Bull. Chem. Soc. Jpn.*, 55 (1982) 309

66 A. Kafrib, R.M. Yousef and N.J. Fitzpatrick, *Inorg. Chem.*, 21 (1982) 1523

67 P.J. Hay, *J. Amer. Chem. Soc.*, 104 (1982) 7007

68 P.A. Koz'min, M.D. Surazhskaya, T.B. Larina, A.V. Shtemenko and A.S. Kotel'nikova, *Koord. Khim.*, 7 (1981) 1271; *Chem. Abstr.*, 95 (1981) 196533

69 P.A. Kozmin, M.D. Surazhskaya and T.B. Larina, *Koord. Khim.*, 8 (1982) 709; *Chem. Abstr.*, 97 (1982) 136870

70 A.V. Shtemenko, A.S. Kotel'nikova, P.A. Koz'min, M.D. Surazhskaya and T.B. Larina, *Koord. Khim.*, 7 (1981) 1750; *Chem. Abstr.*, 96 (1982) 27704

71 P.R. Brown, F.G.N. Cloke, M.L.H. Green and R.C. Tovey, *J. Chem. Soc.*, *Chem. Commun.*, (1982) 519

72 M.G. Bradly and B.R. Hofmann Jr., *J. Chem. Soc.*, *Chem. Commun.*, (1982) 1180

73a J.E. Turp, *Coord. Chem. Rev.*, 52 (1983) 249

73b F. Calderazzo, F. Marchetti, R. Poli, D. Vitali and P.F. Zanazzi, *J. Chem. Soc.*, *Dalton Trans.*, (1982) 1665

74 A.N. Sergeeva, L.I. Pavlenko, V.V. Dovgei, D.I. Zubritskaya and Zh.I. Tkachenko, *Koord. Khim.*, 7 (1981) 1450; *Chem. Abstr.*, 96 (1982) 14610

75 W. Bronger and H.J. Miessen, *J. Less Common Met.*, 83 (1982) 29

76 T.S. Cameron, K.R. Gundy and K.N. Roberts, *Inorg. Chem.*, 21 (1982) 4149

77 W.S. Mialki and R.A. Walton, *Inorg. Chem.*, 21 (1982) 2791

78 A.J.L. Pombeiro, C.J. Pickett and R.L. Richards, *J. Organomet. Chem.*, 224 (1982) 285

79 L.M. Kachapina, G.A. Kichigina, V.D. Makhaev and A.P. Borisov, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, (1981) 2185; *Chem. Abstr.*, 96 (1982) 13233

81 D.M.P. Mingos, *Inorg. Chem.*, 21 (1982) 464

82 D.A. Lichtin, R.B. Bernstein and V. Vaida, *J. Amer. Chem. Soc.*, 104 (1982) 1830

83 W.K. Meckstroth, R.T. Walters, W.C. Waltz, A. Wojcicki and L.M. Dorfman, *J. Amer. Chem. Soc.*, 104 (1982) 1842

84 D.M. Adams and I.D. Taylor, *J. Chem. Soc.*, *Faraday Trans. 2*, 78 (1982) 1065

85a S.P. Schmidt, W.C. Trogler and F. Basolo, *Inorg. Chem.*, 21 (1982) 1698

85b A. Poe, *Inorg. Chem.*, 20 (1981) 4029, 4032

86 D.H. Gibson, F.U. Ahmed and K.R. Phillips, *J. Organomet. Chem.*, 218

(1981) 325

87 D.R. Gard, *Diss. Abstr. Int. B*, 42 (1981) 623; *Chem. Abstr.*, 95 (1981) 17838

88 D.R. Gard and T.L. Brown, *J. Amer. Chem. Soc.*, 104 (1982) 6340

89 M.A. Drezdzon, K.H. Whitmire, A.A. Bhattacharyya, Wen-Liang Hsu, C.C. Nagel, S.G. Shore and D.F. Shriver, *J. Amer. Chem. Soc.*, 104 (1982) 5630

90 M.C.R. Symons, S.W. Bratt and J.L. Wyatt, *J. Chem. Soc., Dalton Trans.*, (1982) 991

91 A.A. Ioganson, Yu.G. Kovalev and E.D. Korniets, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1982) 1647; *Chem. Abstr.*, 97 (1982) 137669

92 A.A. Johansson, Yu.G. Kovalyov and E.D. Korniyets, *Inorg. Chim. Acta*, 65 (1982) L31

93 R.W. Balk, D.J. Stufkens and A. Oskam, *J. Chem. Soc., Dalton Trans*, (1982) 275

94 O.A. Salman and H.G. Drickamer, *J. Chem. Phys.*, 77 (1982) 337

95 H. Schumann and H. Neumann, *Z. Naturforsch., B; Anorg. Chem., Org. Chem.*, 36B (1981) 708

96 E. Lindner, G. Funk and S. Hoehne, *Chem. Ber.*, 114 (1981) 2465

97 E.W. Abel, S.K. Bhargava, M.M. Bhatti, K. Kite, M. Mazid, K.G. Orrell, V. Sik, B.L. Williams, M.B. Hursthouse and K.M. Abdul-Malik, *J. Chem. Soc., Dalton Trans.*, (1982) 2065

98 U. Kunze, R. Merkel and W.Winter, *Angew. Chem.*, 94 (1982) 300; *Angew. Chem., Int. Ed.*, 21 (1982) 290

99 U. Kunze, R. Merkel and W. Winter, *Angew. Chem.*, 94 (1982) 301; *Angew. Chem., Int. Ed.*, 21 (1982) 291

100 L. Busetto, A. Palazzi and M. Monari, *J. Chem. Soc., Dalton Trans.*, (1982) 1631

101 W. Beck, K. Raab, U. Nagel and M. Steimann, *Angew. Chem.*, 94 (1982) 556; *Angew. Chem., Int. Ed.*, 21 (1982) 526

102 B. Nuber, F. Oberdorfer and M.L. Ziegler, *Acta Cryst.*, 37B (1981) 2062

103 G. Ciani, G. D'Alfonso, M. Freni, P. Romiti and A. Sironi, *J. Chem. Soc., Chem. Commun.*, (1982) 339

104 G. Ciani, G. D'Alfonso, M. Freni, P. Romiti and A. Sironi, *J. Chem. Soc., Chem. Commun.*, (1982) 705

105 D.W. Prest, M.J. Mays, P.R. Raithby and A.G. Orpen, *J. Chem. Soc., Dalton Trans.*, (1982) 737

106 D.W. Prest, M.J. Mays and P.R. Raithby, *J. Chem. Soc., Dalton Trans.*, (1982) 2021

107 F.W.B. Einstein, T. Jones, A.J.C. Hanlan and D. Sutton, *Inorg Chem.*, 21 (1982) 2585

108 W. Dannecker and H.W. Muller, *Z. Naturforsch.*, 37b (1982) 318

109 K.A.M. Creber and J.K.S. Wan, *Chem. Phys. Letts.*, 81 (1981) 453

110 C.F. Barrientos-Penna, F.W.B. Einstein, T. Jones and D. Sutton, *Inorg. Chem.*, 21 (1982) 2578

111 R. Graziani, L. Toniolo, U. Casellato, R. Rossi and L. Magon, *Inorg Chim. Acta*, 52 (1981) 119

112 A. Fox, A. Poe and R. Ruminski, *J. Amer. Chem. Soc.*, 104 (1982) 7327

113 R.J. Barton, S. Hu, L.M. Mihichuk and B.E. Robertson, *Inorg. Chem.*, 21 (1982) 3731

114 R. Kury and H. Vahrenkamp, *J. Chem. Res. (S)*, (1982) 30

115 R. Kury and H. Vahrenkamp, *J. Chem. Res. (S)*, (1982) 31

116 E. Lindner, A. Ray and S. Hohne, *Angew. Chem.*, 93 (1981) 821

117 U. Kunze and R. Merkel, *J. Organomet. Chem.*, 219 (1981) 69

118 U. Kunze and A. Antoniadis, *Z. Naturforsch. B; Anorg. Chem., Org. Chem.*, 36B (1981) 1117

119 W. Uedelhoven, D. Neugebauer and F.R. Kreissl, *J. Organomet. Chem.*, 217 (1981) 183

120 S.P. Gubin, O.M. Chentsova, G.V. Burmakina and A.A. Ioganson, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 12 (1981) 2790; *Chem. Abstr.*, 97 (1982)

119463

121 G.I. Magomedov, L.V. Morozova and G.V. Druzhkova, *Zh. Obshch. Khim.*, 51 (1981) 2384; *Chem. Abstr.*, 96 (1982) 27695

122 J.C. Jeffry, H. Razay and F.G. Stone, *J. Chem. Soc., Dalton Trans.*, (1982) 1733

123 V.I. Sokolov, A.A. Musaev, V.V. Bashilov and O.A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1981) 2409; *Chem. Abstr.*, 96 (1982) 14584

124 I.P. Beletskaya, G.Z. Suleimanov, L.F. Rybakova and O.P. Syutkina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1981) 1925; *Chem. Abstr.*, 95 (1981) 196526

125 J.K. Hoyano and W.A.G. Graham, *J. Chem. Soc., Chem. Commun.*, (1982) 27

126 C.M. Lukehart and M. Raja, *Inorg. Chem.*, 21 (1982) 1278

127 C.M. Lukehart and M. Raja, *Inorg. Chem.*, 21 (1982) 2100

128 C. Botha, J.R. Moss and S. Pelling, *J. Organomet. Chem.*, 220 (1981) C21

129 C.P. Casey, M.A. Andrews, D.R. McAlister, W.D. Jones and S.G. Harsy, *J. Mol. Catal.*, 13 (1981) 43

130 J.R. Sweet and W.A.G. Graham, *J. Amer. Chem. Soc.*, 104 (1982) 2811

131 W. Tam, G-Y. Lin and J.A. Gladysz, *Organometallics*, 1 (1982) 525

132 J.R. Sweet and W.A.G. Graham, *J. Organomet. Chem.*, 217 (1981) C37

133 W.A. Tam, G-Y. Lin, W-K. Wong, W.A. Kiel, V.W. Wong and J.A. Gladysz, *J. Amer. Chem. Soc.*, 104 (1982) 141

134 F.B. McCormick and J.A. Gladysz, *J. Organomet. Chem.*, 218 (1981) C57

135 W.A. Kiel, G-Y. Lin, A.G. Constable, F.B. McCormick, C.E. Strouse, O. Eisenstein and J.A. Gladysz, *J. Amer. Chem. Soc.*, 104 (1982) 4865

136 F.B. McCormick, W.A. Kiel and J.A. Gladysz, *Organometallics*, 1 (1982) 405

137 A. Wong and J.A. Gladysz, *J. Amer. Chem. Soc.*, 104 (1982) 4948

138 N. Mronga, U. Muller and K. Dehnicke, *Z. Anorg. Allgem. Chem.*, 482 (1981) 95

139 R. Ruhl and W. Jeitschko, *Inorg. Chem.*, 21 (1982) 1886

140 Yu.B. Kuzma, S.I. Mikhalenkon, B.Ya. Kotur and Ya.P. Yarmolyuk, *Dopov. Akad. Nauk Ukr. RSR, Ser. B: Geol., Khim. Biol. Nauki*, (1982) 24; *Chem. Abstr.*, 97 (1982) 172756

141 V.I. Larchev and S.V. Popova, *J. Less Common Met.*, 84 (1982) 87

142 Y-N. Chiu and F.E. Wang, *Inorg Chem.*, 21 (1982) 4264

143 R. Bartoszek, *Diss. Abstr. Int. B*, 43 (1982) 425; *Chem. Abstr.*, 97 (1982) 172368