

7. RHENIUM

JANET E. TURP

CONTENTS

Introduction	249
7.1 Rhenium(VII)	250
7.2 Rhenium(VI)	251
7.2.1 Halides and oxohalides	252
7.2.2 Oxides	253
7.2.3 Complexes with nitrogen donor ligands	253
7.3 Rhenium(V)	253
7.3.1 Halides, pseudohalides and oxohalides	254
7.3.2 Oxides	254
7.3.3 Sulphides and complexes with sulphur donor atoms	255
7.3.4 Complexes with group VB donor ligands	256
7.4 Rhenium(IV)	256
7.4.1 Halides and oxohalides	258
7.4.2 Oxides	258
7.4.3 Complexes with other donor ligands	259
7.5 Rhenium(III)	259
7.5.1 Halides	259
7.5.2 Oxides and complexes with oxygen donor ligands	260
7.5.3 Complexes with selenium donor ligands	261
7.5.4 Complexes with group VB donor ligands	261
7.5.5 Complexes with group IVB donor ligands	262
7.6 Rhenium(II)	262
7.7 Rhenium(I)	262
7.7.1 Non-carbonyl containing complexes	264
7.7.2 Halides Group	266
7.7.3 Complexes with Group VIB donor ligands	268
7.7.5 Complexes with Group IVB donor ligands	271
7.8 Rhenium(O)	272
7.9 Complexes containing rhenium-cobalt and rhenium-platinum bonds	273
7.10 Metal clusters	275
7.11 Nitrosyl complexes	277
References	279

INTRODUCTION

The period of this review coincides with the coverage of volumes 94 and 95 of Chemical Abstracts, so although the majority of the papers reviewed were published in 1981 some from 1980 are also included. The major journals are covered until the end of 1981. The review covers the coordination chemistry of rhenium although no attempt has been made to include work of a purely organometallic or catalytic nature.

A review has been published this year containing one hundred and fifty-two references on the fluorides, oxofluorides, fluoro and oxofluoro complexes of rhenium [1].

7.1 RHENIUM(VII)

The reduction of $[\text{ReO}_4]^-$ in mildly acidic solution is made easier by the addition of oxalate or citrate ions through the formation of 1:1 complexes which expand the rhenium coordination sphere to six [2]. The optimum coordinations for the extraction of Re(VII), as $[\text{ReO}_4]^-$, from sulphuric acid solutions by petroleum sulfoxides in benzene have been established [3].

XPS and thermogravimetric analysis were used to study $[\text{NH}_4][\text{ReO}_4]$ (with up to 14% w/w of rhenium) supported on TiO_2 . With low rhenium content, the rhenium is atomically dispersed as a perrhenate-like surface compound which forms the dispersed metal on heating to 500 °C in dihydrogen. With medium rhenium concentrations, as well as the perrhenate surface compound, small crystallites of $[\text{NH}_4][\text{ReO}_4]$ are present which form ReO_2 (which is incorporated into the host) on reduction. With large rhenium concentrations, large crystallites of $[\text{NH}_4][\text{ReO}_4]$ are formed which reduce in the manner expected of the compound [4].

The polarised IR spectra of $\text{K}[\text{ReO}_4]$ single crystals were investigated in the ranges 600 - 900 cm^{-1} and 170 - 625 K. The temperature dependence of the damping constant of the high frequency phonons is mainly explained by the anharmonic mechanism of double quantum phonon scattering of high frequency phonons involving those of low frequency [5].

Single crystals of KCl , KBr , KI and RbI doped with up to 0.1% $[\text{ReO}_4]^-$ have been grown and studied by IR and Raman spectroscopy. The spectra were interpreted as showing, contrary to an earlier paper [6], that the $[\text{ReO}_4]^-$ ion isolated in sodium chloride structured alkali halides retains full T_d symmetry [7]. However, when isolated in alkali halides with the caesium chloride structure, the $[\text{ReO}_4]^-$ ion is found to lose its T_d symmetry [8]. It has previously been observed that with small T_d ions it is common that if they retain their full symmetry with respect to one type of supporting alkali halide lattice, then they fail to retain it when isolated in the other [*e.g.* 9].

$\text{Ba}_2\text{NaReO}_6$ has been prepared hydrothermally at 350 °C and 1500 bars from $\text{Ba}[\text{ReO}_4]_2$ and $\text{Ba}[\text{OH}]_2$ in aqueous 15 M NaOH and the crystallographic parameters of the cubic crystal found [10]. The crystal structure of the compound with the empirical formula $\text{Ba}_5\text{Re}_3\text{O}_{17}$ was found to be similar to those of $\text{Ba}_5[\text{ReO}_5] \text{X}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$ or I) and refinements indicated that the formula should be written as $\text{Ba}_5(\text{ReO}_5)_3\text{O}_2$: the presence of the $[\text{O}_2]^-$ anion was confirmed by Raman spectroscopy [11]. Monoclinic Y_3ReO_8 , β phase, was synthesised at 40 K bar and 900 °C. The crystal structure can be visualised as a fluorite

superstructure, the large difference between the radii of the Re^{7+} and Y^{3+} being favourable to cation ordering. Heating at 500°C and atmospheric pressure leads to the disordered fluorite structure of the α phase [12]. The phases Bi_3ReO_8 and $\text{Bi}(\text{ReO}_4)_3$ have been prepared by X-ray emission in an analytical electron microscope. It was found that the Bi-Re-O system has several features in common with the rare earth-Re-oxide systems [13].

7.2 RHENIUM(VI)

7.2.1 Halides and oxohalides

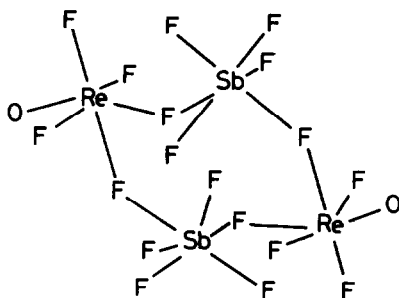
Redox reactions of $[\text{ReF}_6]$ with a selected series of reductants have been studied and compared with $[\text{OsF}_6]$ and $[\text{IrF}_6]$. It was shown that oxidant strength increases progressively from ReF_6 to IrF_6 . ReF_6 is not a strong enough oxidant to oxidise AsF_3 , SF_4 or SeF_4 , but was found to oxidise PF_3 to PF_5 itself being reduced to rhenium(V) [14].

The photoelectron spectrum of ReF_6 was studied and compared with other, closed shell spectra. The experimental ionisation potentials were compared with those calculated by Ellis and Rosen for the series $[\text{MF}_6]$ ($M = \text{W}, \text{Re}, \text{Os}, \text{Ir}$ or Pt) [15]. The published optical, electronic and p.e. spectra of MoF_6 , WF_6 and ReF_6 were reanalysed, with the aid of recent numerical calculations, to determine the electron orbital symmetry orderings of MoF_6 and WF_6 and these then used to analyse the partial spectrum of ReF_6 . The $e_g + t_{2g}$ transition was estimated at 5.5 eV [16].

Analysis of the photoelectron spectrum of $[\text{ReOF}_4]$ led to the conclusion that the representation of the Re-O bond as being a dioxide bond is not consistent with the measured orbital energies [17]. High purity $[\text{ReOF}_4]$ has been prepared in quantitative yield by the reduction of $[\text{ReOF}_5]$ in anhydrous HF in the presence of silicon. The structure of gaseous $[\text{ReOF}_4]$ was determined by electron diffraction and it was found that the increase in number of 5d electrons compared with $[\text{WOF}_4]$, does not affect the C_{4v} symmetry of the molecule [18]. Blue $\text{ReOF}_4 \cdot \text{SbF}_5$ was prepared by the dissolution of ReOF_4 in a twelve fold excess of SbF_5 . Single crystal studies showed the complex to consist of dimers of the adduct linked through fluorine bridges into distorted eight-membered rings (1). The ionicity value for the complex is low, showing that considerable ionic contribution is not necessary for a stable adduct [19].

The optimum conditions for the existence of rhenium(VI) complexes in $\text{HCl-H}_4\text{P}_2\text{O}_7$ solutions were determined and the equilibrium constant for the reaction:





(1)

was found to be *ca.* $6 \times 10^{-2} \text{ l mol}^{-1}$ [20].

7.2.2 Oxides

A self-consistent Madelung potential (SCMP), calculated from the exterior ionic charge, which is consistent with the charge on the inner cluster ion, was combined with the DV- $X\alpha$ cluster method for partial ionic solids and applied to the $\{\text{ReO}_6\}^{6-}$ cluster in ReO_3 crystals. Agreement of the valence electronic structure and XPES with APW band calculations is improved by using the SCMP, instead of the MP, with formal ionic charge [21]. The surface electronic structure of ReO_3 has also been studied by the DV- $X\alpha$ cluster method. The electronic state of the defect level induced by the surface oxygen is discussed in relation to catalytic activity [22]. Comparison of the UV-PES and XPES measurements on ReO_3 showed oxygen 2p derived non-bonding levels and Re 5d-0 2p bonding levels, confirming covalency effects in ReO_3 . An SCF- $X\alpha$ -SW calculation on a $\{\text{ReO}_6\}^{6-}$ cluster has also been presented and compared with experiment [23]. XPES was used to observe the Re 4f electrons during the reduction of ReO_3 and the oxidation of rhenium metal. On the basis of SCF- $X\alpha$ calculations for double O_h models for different rhenium oxides, the formation of multiple M-M bonds in clusters of edge sharing octahedra and the presence of an apparent +5 oxidation state in ReO_3 were inferred [24].

The ReO_3 Fermi surface above the pressure induced "compressibility collapse" transition was derived from simple cubic band structure by assuming T_h^5 ($Im3$) symmetry for the distorted phase. A new set of closely spaced de Haas-van Alphen frequencies were observed which were thought consistent with this model [25]. These measurements were combined with NMR results to determine the temperature-pressure phase diagram delineating the "compressibility collapse" transition between 1 and 300 K. There is a change in the amplitude of the NMR signal of

the ^{187}Re nucleus due to the onset of a first order quadrupolar effect [26].

7.2.3 Complexes with nitrogen donor ligands

The crystal structure and IR spectrum of $[\text{AsPh}_4][\text{ReNCl}_4]$, prepared by the addition of $[\text{ReNCl}_4]$ to $[\text{AsPh}_4]\text{Cl}$ in POCl_3 , both show the nearly ideal C_{4v} symmetry of the $[\text{ReNCl}_4]^-$ ion. The $\text{Re}=\text{N}$ bond length (1.169(10) Å) is shorter than that in $[\text{ReN}(\text{NCS})_5]^-$ and the $\text{Re}-\text{Cl}$ distance (2.322(2) Å) is one of the first to be reported for a rhenium(VI) complex [27].

ReNCl_3 reacted with bipy to give $[\text{ReNCl}_3(\text{bipy})]$ whereas the analogous reaction with pyridine gave $[\text{ReNCl}_3(\text{py})_3]$. The reaction of $[\text{AsPh}_4][\text{ReNCl}_4]$ with pyridine gave $[\text{AsPh}_4][\text{ReNCl}_4(\text{py})]$. $[\text{ReNCl}_3(\text{PPh}_3)_2]$, formed by the reaction of ReNCl_3 with PPh_3 will react with $[\text{AsPh}_4]\text{Cl}$ to give $[\text{AsPh}_4][\text{ReNCl}_4(\text{PPh}_3)_2]$ which can also be obtained from the reaction of $[\text{AsPh}_4][\text{ReNCl}_4]$ and PPh_3 [28]. Reaction of $[\text{AsPh}_4]\text{Cl}$ with the POCl_3 solvates $(\text{Cl}_3\text{PO})\text{Cl}_4\text{Re}=\text{N}-\text{R}$ ($\text{R} = \text{OCl}_3$ or C_2Cl_5) yields the corresponding chloride salt, *viz.* $[\text{AsPh}_4][\text{Cl}_5\text{Re}=\text{N}-\text{R}]$. The d^1 system causes a Jahn-Teller stabilisation of the $\text{Re}=\text{N}$ triple bond which can be observed in the IR spectrum [29].

7.3 RHENIUM(V)

7.3.1 Halides, pseudohalides and oxohalides

The optimum conditions for the preparation of graphite intercalation compounds, maximising the amount of intercalated chloride, were found to correspond to $\text{C}_{12}\text{ReCl}_{4.5}$. The structure is considered to consist of two $\{\text{ReCl}_6\}$ octahedra sharing an edge to give an $\{\text{Re}_2\text{Cl}_{10}\}$ unit. These bi-octahedra are then linked by a shared chlorine atom to form infinite chains of $\{\text{Re}_2\text{Cl}_9\}$ units ordered with respect to the adjacent carbon layers in such a way that a layer sequence of the type $\text{C}-\text{Cl}-\text{Re}-\text{Cl}-\text{Re}-\text{Cl}-\text{C}$ results [30].

The $\text{ReCl}_5/\text{MeCN}$ system was studied over a wide range of composition and temperature. The red and green forms observed have the same composition (*i.e.* $\text{ReCl}_5 \cdot 2\text{MeCN}$) but different molar absorptivities. Conversion of the red *cis*- $[\text{ReCl}_4(\text{MeCN})_2]\text{Cl}$ to the green *trans*-isomer (which is favoured at low temperatures) is thought to occur *via* the square pyramidal complex, $[\text{ReCl}_4(\text{MeCN})_2]\text{Cl}$ [31].

The reaction of H_2ReOCl_5 with thiourea in aqueous HCl gave $[\text{ReO}(\text{tu})_4]\text{Cl}_3 \cdot [\text{tuH}]\text{Cl}$. $[\text{Re}_2\text{OQ}_4]\text{Cl}_8$ ($\text{Q} = 1\text{-phenylthiosemicarbazide}$) was prepared by the reaction of $\text{K}[\text{ReO}_4]$ with Q in hydrochloric acid solution [32]. The optimum region for the existence of rhenium(V) complexes in $\text{HCl}-\text{H}_4\text{P}_2\text{O}_7$ solution

was determined. The dimerisation constant for $[\text{Re}_2\text{OCl}_{10}]^{2-}$ was determined as 130 l mol^{-1} [20].

The electronic energy levels of $[\text{Re}_2\text{O}_3(\text{CN})_8]^{4-}$ were calculated using the self consistent and charge configuration molecular orbital method [33].

The IR spectra of a single crystal of $\text{K}_3[\text{ReO}_2(\text{CN})_4]$ were recorded using polarised radiation. The dichroic behaviour of the bonds was discussed on the basis of molecular geometry and the orientated molecular mode. Experimentally obtained dichroic ratios were used to obtain a full set of vibrational frequencies which were combined with Raman data to assign the fundamental lattice and internal vibrations [34].

$[\text{AsPh}_4]_2[\text{ReO}(\text{NCS})_5]$ has been prepared by three different methods: firstly from $\text{Na}[\text{ReO}_4]$ and $[\text{NH}_4][\text{SCN}]$ in acidic solution, with SnCl_2 as the reducing agent, secondly from $[\text{AsPh}_4][\text{ReOBr}_4(\text{CH}_3\text{CN})]$ and $[\text{NH}_4][\text{SCN}]$ and thirdly from $\text{K}_2[\text{ReOCl}_5]$, suspended in CH_3CN , and $[\text{NH}_4][\text{SCN}]$. Precipitation in all cases was effected with $[\text{AsPh}_4]\text{Cl}$. $[\text{ReO}(\text{NCS})_5]^{2-}$ reacted with SnCl_2 and $[\text{NCS}]^-$ to give $[\text{Re}(\text{NCS})_6]^{2-}$ in solution, but the solid could not be isolated [39].

7.3.2 Oxides

A review has been published, of the electronic structure and symmetry of rhenium(V) oxo compounds containing $[\text{ReO}]^{3+}$ and $[\text{ReO}_2]^+$ groups on the basis of IR, UV- visible and X-ray spectroscopic data [35].

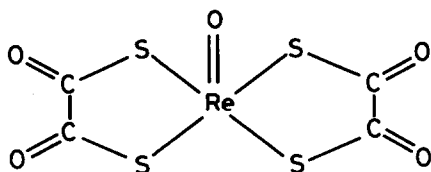
The mixed oxidation state phases, $\text{Bi}_3\text{Re}_3\text{O}_{11}$ and BiRe_2O_6 {Re(V)/Re(IV)} have been prepared by X-ray emission in an analytical electron microscope; their cubic space groups were determined [13].

Positive Knight shifts of approximately 500 ppm were observed in the proton NMR spectrum of $\text{H}_{0.39}\text{ReO}_3$ at low temperatures. Band structure calculations on perovskite HReO_3 show that the hydride derived 1s layer is partially populated. These data were interpreted as suggesting that the hydrogen is not completely protic in H_xReO_3 [36].

7.3.3 Sulphides and complexes with sulphur donor ligands

The polymeric complexes ReSCl_3 and ReS_2Cl_3 were formed by the reaction of ReCl_5 with S_2Cl_2 at 140°C and 300°C , respectively. In ReS_2Cl_3 the Re atoms are bridged by S-S moieties. Heating ReS_2Cl_3 to 250°C causes decomposition to $\text{Re}_2\text{S}_3\text{Cl}_4$, S_2Cl_2 and Cl_2 [37].

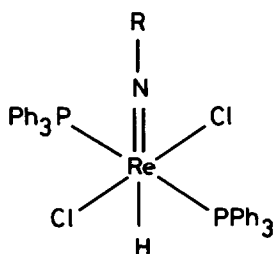
The structure of $\text{Cs}[\text{ReO}(\text{dtox})_2]$ (2) (dtox = 1,2 dithiooxalate) has been determined from X-ray data. The rhenium is five-coordinate and 0.752 \AA above the basal plane formed by the four sulphur atoms [38].



(2)

7.3.4. Complexes with Group VB donor ligands.

By reaction of $[\text{ReCl}_3(\text{NR})(\text{PPh}_3)_2]$ ((3) ; $\text{R} = 4\text{-C}_6\text{H}_4\text{Me}$) or (4 ; $\text{R} = 4\text{-C}_6\text{H}_4\text{OMe}$) with ZnO in CHMe_2OH , the arylimido complexes $[\text{ReCl}_2\text{H}(\text{NR})(\text{PPh}_3)_2]$, (5) or (6), were obtained, respectively. (5) can also be obtained by using $\text{Na}[\text{OCHMe}_2]$ instead of



(5; $\text{R} = 4\text{-C}_6\text{H}_4\text{Me}$)

(6; $\text{R} = 4\text{-C}_6\text{H}_4\text{OMe}$)

ZnO . Treating (3) with ZnO in EtOH gives $[\text{ReClH}(\text{OEt})(\text{NR})(\text{PPh}_3)_2]$ (7 ; $\text{R} = 4\text{-C}_6\text{H}_4\text{Me}$), *via* the intermediate formation of (5). When the reaction was carried out in $\text{C}_2\text{D}_5\text{OD}$ the product was $[\text{ReClD}(\text{OC}_2\text{D}_5)(\text{NR})(\text{PPh}_3)_2]$. The reaction of (7) with HCl or KCl gave (5). The reaction of (5) with Cl_2 gave (3) [40.41].

$[\text{ReN}(\text{S}_2\text{CNR}_2)_2(\text{PMe}_2\text{Ph})_n]$ ($\text{R} = \text{Me}$ or Et ; $n = 0$ or 1), prepared by treating $[\text{ReCl}_2\text{N}(\text{PMe}_2\text{Ph})_3]$ with the appropriate dialkylthiocarbamate, reacts with $\text{R}'\text{X}$ ($\text{R}' = \text{PhCO}$, PhSO_2 , $2,4(\text{NO}_2)_2\text{C}_6\text{H}_3$ or $2,4\text{-}(\text{NO}_2)_2\text{C}_6\text{H}_3\text{S}$, $\text{X} = \text{Cl}$; $\text{R}' = \text{Me}$, $\text{X} = \text{I}$), $[\text{R}'_3\text{O}][\text{BF}_4]$ ($\text{R}' = \text{Me}$ or Et) or $[\text{Ph}_3\text{C}][\text{BF}_4]$ to give the imido complexes $[\text{Re}(\text{NR}')(\text{S}_2\text{CNR}_2)_2(\text{PMe}_2\text{Ph})_n]$ [42].

The reactions of *trans* - $[\text{ReOX}_3(\text{PPh}_3)_2]$ with LH ($\text{L} = 2\text{-HOC}_6\text{H}_4\text{CH:NR}$, $\text{R} = \text{Me}$ or Ph), $(\text{LH})_2\text{en}$ ($\text{R} = \text{H}$) and $[\text{8-O-quin}]^-$ are reported to give *cis* and *trans*- $[\text{ReOX}_2(\text{L})(\text{PPh}_3)]$, $[\text{Re}_2\text{O}_2\text{X}_4(\text{L}_2\text{en})(\text{PPh}_3)_2]$ and $[\text{ReOX}_2(\text{8-O-quin})(\text{PPh}_3)]$; other products

were $[\text{ReOX}(\text{L})_2]$ and $[\text{ReOX}(8\text{-O-quin})_2]$, ($\text{X} = \text{Cl}$ or Br) [43,44].

Two published papers have investigated the 336 nm irradiation of $[\text{ReH}_5\text{L}_3]$ ($\text{L} = \text{PMe}_2\text{Ph}$, PMePh_2 or PPh_3) [45,46]. Both groups of workers have obtained the same results, as shown later. However where as one emphasises the mechanistic results [43], the other emphasises the new compounds produced [46]. It was found that this irradiation leads to efficient loss of phosphine in the primary photochemical reaction. Under a dihydrogen atmosphere the pentahydrides oxidatively add H_2 to give $[\text{ReH}_7\text{L}_2]$ complexes [45,46].

7.4 RHENIUM (IV)

A review has been published, containing sixty-nine references to the structure and magnetism of rhenium(IV) complexes [47].

7.4.1 Halides and oxohalides

Five electronic transitions have been observed, by absorption spectroscopy at liquid helium temperatures, for the $[\text{ReF}_6]^{2-}$ ion in a single $\text{Cs}_2[\text{ReF}_6]$ crystal and also in a $\text{Cs}_2[\text{GeF}_6]$ host lattice. The observed transitions can be assigned, with a crystal field model, to give B, C, Dq and λ_{so} values for $[\text{ReF}_6]^{2-}$. Raman and luminescence results were reported and a detailed phonon structure assigned [48].

The enthalpies of solution of $[\text{ReF}_6]^{2-}$ salts, obtained by direct calorimetric measurements, have been reported. The enthalpy of hydrolysis of $\text{K}_2[\text{ReF}_6]$ in chlorine water was measured and an estimate of $-2558 \text{ kJ mol}^{-1}$ made for the ΔH_f of $\text{K}_2[\text{ReF}_6]$ using ancilliary thermochemical data. The ion hydration enthalpy of $[\text{ReF}_6]^{2-}$ has been estimated at -960 kJ mol^{-1} by the direct minimisation method [49].

The near IR intraconfigurational t_{2g}^3 absorption and MCD spectra of Re(IV) in $\text{Cs}_2[\text{ZrBr}_6]$ and $\text{Cs}_2[\text{ZrCl}_6]$ at liquid helium temperatures have been measured and assigned. The resulting energy levels are discussed in terms of a ligand field model [50]. By the use of the $[\text{NH}_3\text{D}]^+$ probe ion, the IR spectra of $[\text{NH}_4]_2[\text{ReCl}_6]$ were studied between 10 and 293 K with no structural transitions observed above 10 K [51]. Raman and far IR mode frequency shifts have been seen under hydrostatic conditions for $\text{A}_2[\text{ReCl}_6]$ ($\text{A} = \text{Cs}$, Rb or K). The effect is discussed and the shift of $\tilde{\nu}_1$ with temperature for $\text{K}_2[\text{ReCl}_6]$ analysed into explicit and implicit anharmonic contributions [52]. New room temperature measurements of the chlorine spin-lattice and spin-spin relaxation times in $\text{K}_2[\text{ReCl}_6]$ give hyperfine parameters parallel and perpendicular to the Re-Cl bond which are in acceptable agreement with more accurate spectroscopic values obtained from NMR

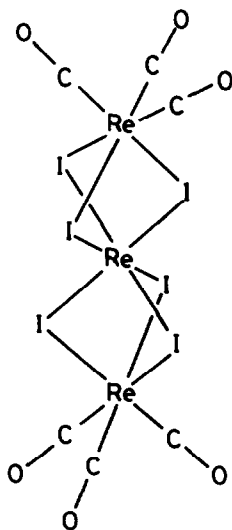
measurements [53].

Low temperature magnetic investigations have shown $[\text{C}_2\text{H}_6\text{NH}_3]_2[\text{ReBr}_6]$ to be paramagnetic with a transition temperature of 9.7 K. The superexchange interactions among the paramagnetic Re^{4+} centres are thought to proceed *via* the bromide ions [54].

The aquapentachlororhenate(IV) ion has been prepared by the addition of hydrochloric acid to a mixture of $[\text{NH}_4][\text{ReO}_4]$ and $(\text{NH}_2)_2\text{CS}$ to give $[(\text{NH}_3)_2\text{CSSC}(\text{NH}_3)_2][\text{ReCl}_5(\text{H}_2\text{O})]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$. The crystal structure shows that the H_2O , Re and one Cl lie on the mirror plane [55].

The electronic energy levels of the $[\text{Re}_2\text{OCl}_{10}]^{4-}$ ion were calculated using the self consistent and charge configuration molecular orbital method [33]. Resonance Raman studies on this ion and $[\text{Re}_2\text{OCl}_{10}]^{3-}$ show one or more progressions in which the $\nu_1(a_{1g})$ symmetric Re-O-Re stretching mode is the dominant progression forming mode. Excitation profile measurements on the a_{1g} Raman bands were seen to indicate that the resonant electronic transition is anaxially polarised $\pi^* \leftarrow \pi$ transition of the Re-O-Re π system. Force constant calculations suggest Re-O-Re double bond character [56].

$[\text{Re}_3\text{I}_6(\text{CO})_6]$ (8) has been prepared by refluxing $[\text{Re}_2\text{I}_2(\text{CO})_8]$ in heptane for several days with an equivalent amount of I_2 . The black crystals were shown by X-ray diffraction to contain a trinuclear, iodide bridged S_6 complex with Re



(8)

on the three-fold axis of symmetry. The oxidation state of the terminal rhenium is +1 and that of the central rhenium is +4 [57].

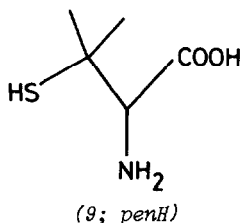
7.4.2 Oxides

Experimental values of ΔG_f° for ReO_2 between 850 and 1125 K have been measured and the literature values reviewed. The best values of the thermodynamic parameters for ReO_2 are suggested [58].

TiO_2 containing a few percent of rhenium was prepared by impregnation of TiO_2 with $[\text{NH}_4][\text{ReO}_4]$, subsequent reduction in dihydrogen at 773 K, and then a further heating at 1273 K under dihydrogen. Thermogravimetric measurements and X-ray diffraction show that the rhenium is present on the surface as rhenium metal and rhenium(VII), and in solid solution as rhenium(IV) [59,60].

7.4.3 Complexes with other donor ligands

The reaction of $\text{K}_2[\text{ReCl}_6]$ with cysteine (Hcys) in aqueous solution gave olive-green crystals of $\text{H}_2[\text{Re}_2\text{O}_3(\text{cys})_4]$ which were characterised by Raman, IR and electronic spectroscopy and magnetic susceptibility measurements. It contains one bridging and two terminal oxygens with the cysteine ligand being coordinated *via* both S and N [61]. A penicillamine (9) complex of rhenium, with the ligand



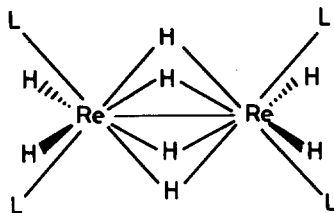
also coordinated *via* S and N, has been prepared and is formulated as $\text{H}_2[\text{Re}_2\text{O}_3(\text{pen})_4]$, with a single oxygen bridge [62].

A complex formulated as $\text{Re}(\text{tu})_4\text{Cl}_4 \cdot \text{SnCl}_2$ was prepared by adding hydrochloric acid and thiourea to $[\text{NH}_4][\text{ReO}_4]$, followed by addition of SnCl_2 . $\text{Re}(\text{NCS})_4 \cdot 2\text{H}_2\text{O}$ was prepared by an analogous route. $\text{ReL}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (HL = 2-furil dioxime) was prepared by the reaction of $\text{K}[\text{ReO}_4]$ with HL in the presence of SnCl_2 in aqueous hydrochloric acid [32]. A solution of $[\text{Re}(\text{NCS})_6]^{2-}$ was prepared by the reaction of $[\text{ReO}(\text{NCS})_5]^{2-}$ with $[\text{NCS}]^-$ in the presence of SnCl_2 , but the solid could not be isolated [39].

A mixture of $[\text{Re}(\text{OPEt}_{2-n}(\text{OEt})_n\text{Ph})_2\text{Cl}_4]$ ($n = 0, 1$ or 2) was obtained by the oxidation of PEt_2Ph , occurring during the heating of $[\text{HPEt}_2\text{Ph}]_2[\text{ReCl}_6]$ and $[\text{Re}(\text{PEt}_2\text{Ph})_2\text{Cl}_4]$ in air. The solid state thermal reactions of the two initial

compounds were studied by IR and thermogravimetry [63].

$[\text{Re}_2\text{H}_8\text{L}_4]$ (10; L = PMe_2Ph , PMePh_2 , PEt_2Ph or PPh_3) was formed by the



(10)

photolysis, under a dihydrogen purge, of $[\text{H}_7\text{ReL}_2]$ [45,46]. The crystal structure of (10; L = PEt_2Ph) has been determined and shows four bridging and four terminal hydrides with $r(\text{ReRe}) = 2.350(4)$ Å [45].

7.5 RHENIUM(III)

7.5.1 Halides

F.A. Cotton has written an article about coordination complexes with metal-metal bonds, *e.g.* $[\text{Re}_2\text{Cl}_8]^{2-}$, which considers the reconciliation of theory and experiment [64]. The chemistry of $[\text{Re}_2\text{Cl}_8]^{2-}$ ($\delta\delta^*$ singlet) was investigated. The complex ion was found to function as a strong oxidant, as well as a moderately good reductant in non-aqueous solution: for example tetracyanoethene (tcne) will oxidatively quench the $[\text{Re}_2\text{Cl}_8]^{2-}$ * luminescence to give $[\text{Re}_2\text{Cl}_8]^-$ and $[\text{tcne}]^-$ as a transient [65].

$[\text{Re}_4\text{I}_8(\text{CO})_6]$ was prepared by the reaction of $[\text{Re}_2\text{I}_2(\text{CO})_6(\text{thf})_2]$ with I_2 in heptane and consists of a central $\{\text{Re}_2^{\text{III}}\text{I}_8\}$ unit with iodide bridges to two $\{\text{Re}(\text{CO})_3\}$ groups [57].

7.5.2 Oxides and complexes with oxygen donor ligands

$[\text{Re}_2\text{X}_4(\text{O}_2\text{CR})_2\text{L}_2]$ (X = Cl or Br; R = Me, Et, Pr, Bu, CHMe_2 , CMe_3 or Ph; L = H_2O , dmf, Me_2SO , dma, Ph_3PO or py) and $[\text{Re}_2\text{X}_2(\text{O}_2\text{CR})_4]$ were obtained by the reduction of $\text{K}[\text{ReO}_4]$ in an $\text{HX}-\text{RCO}_2\text{H}$ mixture in the presence and absence of L, respectively. $[\text{Re}_2\text{I}_2(\text{O}_2\text{CMe})_4]$ was also prepared. In the dichloride complex the carboxylate ligands bridge the Re-Re bond and are *cis* with respect to this bond [66]. Similar complexes (*e.g.* $[\text{Re}_2\text{Cl}_4(\text{O}_2\text{CMe})_2\text{L}_2]$ (L = dmf, dma, Me_2SO , py or Ph_3PO)) were prepared from $[\text{Re}_2\text{Cl}_4(\text{O}_2\text{CMe})_2(\text{H}_2\text{O})_2]$ in $\text{Me}_2\text{CO}/\text{MeCOOH}$ by treatment

with the appropriate ligand, L. The donor ligands, L, are in the axial positions, but substitution of the H₂O in [Re₂Cl₄(O₂CMe)₂(H₂O)₂] by L led to only slight changes in the IR and electronic spectra [67]. Thermal treatment of *cis*-[Re₂X₄(O₂CMe)₂(H₂O)₂] (X = Cl or Br) gives *trans*-[Re₂X₄(O₂CMe)₂] [66,68]. The thermal loss of the axial ligands in [Re₂Cl₄(O₂CMe)₂L₂] (L = Me₂SO, H₂O, dmf or dma) was found to occur in two stages and did not seem to be related to the donor capacity of L [69]. Dissolution of *trans*-[Re₂X₄(O₂CMe)₂] (X = Cl or Br) in HOAc gave [Re₂Cl₃(O₂CMe)₃], or [Re₂Br₂(O₂CMe)₄] with [Re₂Br₃(O₂CMe)₃] acting as an intermediate. Dissolution of *trans*-[Re₂Br₄(O₂CMe)₂] in HCl₃ containing a stoichiometric amount of MeCOOH gave [Re₂Br₃(O₂CMe)₃] [68]. [Re₂(O₂CMe)₄Cl₂] was cleaved by an excess of Me₃CNC in methanol to give [Re(CNCMe₃)₆]Cl [70].

³⁵Cl and ⁸¹Br NQR spectroscopy was used to study the binuclear rhenium(III) compounds; [Re₂X₄(O₂CMe)₂L₂] (L = H₂O, dmf or Me₂SO, X = Cl or Br; L = dma, X = Br; L = Ph₃PO or py, X = Cl). [Re₂X₄(O₂CMe)₂].2L (L = dmf or Me₂SO, X = Cl), *trans*-[Re₂X₄(O₂CMe)₂] (X = Cl or Br), [Re₂Br₂(O₂CMe)₄] and A₂[Re₂X₈] (A = K, [NH₄] or [PyH], X = Cl; A = K, X = Br). Their structures and chemical bonding were considered [71]. The most prevalent compound in the mixed halo species *cis*-[Re₂(O₂CMe)₂Cl_xBr_yL₂] (L = dmf or dma, x + y = 4) is that in which x = y = 2, with the like halo groups *trans* [72]. The crystal structures of [Re₂(O₂CMe)₄Cl₂]{r(ReRe) = 2.2240 Å} [73], [Re₂(O₂CMe)₂Br₄]{r(ReRe) = 2.216(3) Å} [74] and [Re₂(O₂CMe)₂Cl₂{HC(O)NPh₂}₂] [75] have been determined.

The *trans* influence of the Re-Re quadruple bond has been investigated by XPES, examining the axial ligands. The bonding energies of acid ligands in axial positions is much lower than for *cis*-equatorial ligands showing a noticeable *trans* effect of the Re-Re bond [76]. [NH₄]₂[Re₂(SO₄)₄·2H₂O] was prepared by dissolving [NH₄]₂[Re₂Cl₆(HCOO)₂] in sulphuric acid under argon. The crystal structure shows a Re-Re quadruple bond length of 2.217 Å, with the sulphato groups bridging the rhenium atoms [77]. The reaction of K₂[ReCl₆] with homocysteine (HL') in aqueous solution gave a black amorphous precipitate of [Re₂L'₄Cl₂]. The chloride ligands are thought probably to be bridging with L' coordinated *via* the carboxy oxygen, but not the nitrogen atom: coordination of the sulphur is uncertain [61].

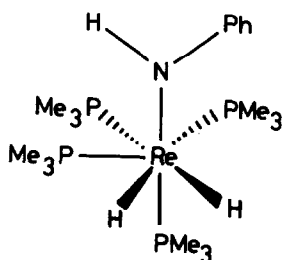
7.5.3 Complexes with selenium donor ligands

[Re(CO)(Se₂CNR₂)₃] (R = Et or R₂ = Morpholyl) was prepared by the irradiation of [Re₂(CO)₁₀] mixed with [Se₂CNR₂]⁻ in thf to give [Re(CO)₄L], which was then heated under reflux for a week in the presence of [Se₂CNR₂]⁻. [Re(CO)Se₂CNR₂]₃ is thought to be seven-coordinate [78].

7.5.4 Complexes with Group VB donor Ligands

The existence of $[\text{Re}(\text{NCS})_6]^{3-}$ has been postulated on the basis of CV data in the reduction of $[\text{Re}(\text{CNS})_6]^{2-}$ in non-aqueous solvents, and has now been prepared by adding a 1:4 mixture of thf:MeOH to $[\text{Bu}_4\text{N}]_2[\text{Re}(\text{NCS})_6]$ followed by addition of $\text{N}_2\text{H}_4 \cdot 2\text{H}_2\text{O}$ to give a pale yellow solution. Precipitation using $[\text{NBu}_4][\text{ClO}_4]$ gave pale yellow, air-sensitive crystals of $[\text{NBu}_4]_3[\text{Re}(\text{NCS})_6]$. $E_{1/2}$ for $[\text{Re}(\text{NCS})_6]^{3-}/[\text{Re}(\text{NCS})_6]^{2-}$ was found to be -0.11 V v.s. SCE [79]

The reduction of $[\text{Re}(\text{NPh})\text{Cl}_3(\text{PMe}_3)_2]$ in thf containing excess PMe_3 by sodium amalgam under dihydrogen, gives (11), which was characterised by ^1H and ^{31}P NMR spectroscopy [80].



UV irradiation of a benzene solution of $[\text{ReH}_3(\text{dppe})_2]$ gives a gold coloured solution of $[\text{ReH}(\text{dppe})_2]$ and dihydrogen [81,82]. The photolysis of $[\text{H}_7\text{ReL}_2]$ ($\text{L} = \text{PMe}_2\text{Ph}$, PMePh_2 or PPh_3) under a dihydrogen purge gave the dimer $[\text{Re}_2\text{H}_6\text{L}_5]$ as one of the products. This dimer can also be obtained by photolysis of degassed $[\text{Re}_2\text{H}_5\text{L}_2]$ together with $[\text{ReH}_3\text{L}_4]$ [45, 46]. NMR results suggest that $[\text{Re}_2\text{H}_6\text{L}_5]$ has the structure $[\text{L}_3\text{HRe}(\mu\text{-H})_3\text{ReH}_2\text{L}_2]$. It was also found that $[\text{Re}_2\text{H}_6\text{L}_5]$ activated arene C-H bonds [45].

7.5.5 Complexes with group IVB donor ligands

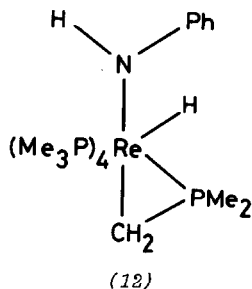
A series of compounds of general formula $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{X})\text{Y}]$, where X or Y, or both, may be silyl, germyl or stannyl derivatives, has been prepared. The reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3]$ with GeHCl_3 or Ph_3SnH gave *trans*- $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{X}_2]$ ($\text{X} = \text{GeCl}_3$ or SnPh_3) [83]. The reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3]$ with Cl_2 or I_2 gave $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3\text{Cl}]^+$ or *cis*- and *trans*- $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{I}_2]$, respectively [84].

7.6 RHENIUM(II)

The arc emission spectrum of ReO has been photographed in the region 590–860 nm and three bands of single electronic transition were rotationally analysed. The analysis of lines due to ^{185}ReO and ^{187}ReO in the spectrum leads to the vibrational assignment of these bands [85].

A series of tetracarbonyl and tricarbonyl complexes of rhenium with phosphine chelate ligands LH or L^- ($\text{LH} = [\text{HXC}(\text{Y})\text{PPh}_2]$; X, Y = NR, O or S) were prepared by reaction of the metal carbonyl with the free ligands or their silyl analogues. The silyl methods gave *cis*- $[(\text{CO})_4\text{ReL}]$ and on careful addition of water, *fac*- $[(\text{CO})_3\text{Re}(\text{X})(\text{L})]$ (X = Cl or Br) [86].

The reduction of $[\text{Re}(\text{NPh})\text{Cl}_3(\text{PMe}_3)_2]$ in thf containing an excess of PMe_3 , by sodium amalgam under argon, gave the phenyl amido complex (12) [80].



7.7 RHENIUM(I)

Most of the rhenium(I) chemistry this year has concerned carbonyl containing complexes and these have been classified according to the other ligands present. Non-carbonyl complexes have been grouped separately.

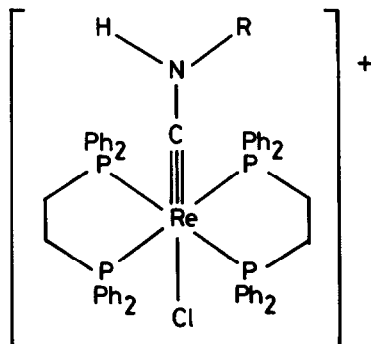
7.7.1 Non-carbonyl containing complexes

XPES spectra have been recorded for $[\text{ReCl}(\text{N}_2)\text{L}_n]$ ($\text{L} = \frac{1}{2}[\text{dppe}]$, PMe_2Ph or PMePh_2) and, considered with their IR spectra, it was found that the variation of q_{N1} and q_{N2} within each N_2 group is very small, so that the position of the most negative nitrogen could not be derived [87].

Some electron poor Re(I) dinitrogen complexes have been synthesised by treating $[\text{ReCl}_2(\text{N}_2\text{COPh})(\text{PPh}_3)_2]$ with carbon monoxide or organophosphites in two-stage reactions. The complexes were $[\text{ReN}_2\text{XL}_2]^{n+}$ (X = Cl, L = dppe or $[(\text{MeO})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OMe})_2]$ -dmope, $n = 0$; X = NCPH or NCMc, L = dppe, $n = 1$), $[\text{Re}(\text{CO})(\text{N}_2)\{\text{P}(\text{OMe})_3\}_{3-n}(\text{PPh}_2)_n]$ ($n = 0$ or 2), $[\text{ReCl}(\text{CO})_2(\text{N}_2)(\text{PPh}_3)_2]$ and

$[\text{ReCl}(\text{N}_2)\{\text{P}(\text{OMe})_3\}_4]$. The $E_{1/2}$ values were measured, and found to vary linearly with $\nu(\text{N}_2)$. The complexes were treated with LiR and the nature of the products was found to vary with R . Thus, $[\text{ReCl}(\text{CO})_2(\text{N}_2)(\text{PPh}_3)_2]$ gives $[\text{ReCl}\{\text{C}(\text{OH})\text{Me}\}(\text{CO})(\text{N}_2)(\text{PPh}_3)_2]$ with LiMe/H^+ but $[\text{ReCl}(\text{CO})_2(\text{PPh}_3)_2]$ with LiPh/H^+ : attack on the N_2 group by LiR was not observed [88]. The ^{15}N NMR chemical shift was determined for $[\text{Re}(\text{PPhMe}_2)_4(\text{N}_2)\text{Cl}]$ and compared with those for other complexes: it was concluded that the interpretation of ^{15}N NMR spectra cannot unambiguously be linked with electron density [89].

Trans- $[\text{ReCl}(\text{CNR})(\text{dppe})_2]$ ($\text{R} = \text{Me}$ or OMe_3) has been prepared by heating $[\text{ReCl}(\text{N}_2)(\text{dppe})_2]$ with an excess of isocyanide under reflux and irradiation from a tungsten lamp. The ^1H and ^{31}P NMR spectra were recorded. The isocyanide nitrogen can be protonated by reaction with $[\text{Et}_2\text{OH}][\text{BF}_4]$ to give the carbyne complex *trans*- $[\text{ReCl}(\text{CHNR})(\text{dppe})_2][\text{BF}_4]$ (13). The crystal structure for (13; $\text{R} = \text{Me}$) has been obtained and shows $r(\text{ReC}) = 1.803 \text{ \AA}$. [90].

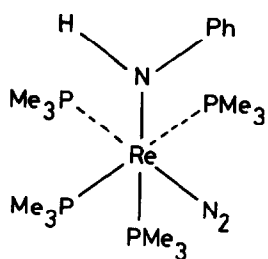


(13)

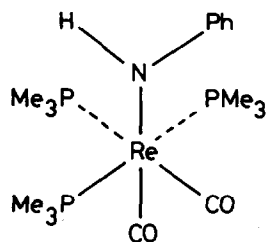
The reduction of $[\text{Re}(\text{NPh})\text{Cl}_3(\text{PMe}_3)_2]$ in *thf* containing an excess of PMe_3 by sodium amalgam gives a new series of phenylamido containing complexes (14-17). Under dinitrogen (14) is obtained, and is converted to (15) by the addition of carbon monoxide. When the reduction is performed under carbon monoxide the product is (16), and under butadiene (17) is produced [80].

Treatment of $[\text{Re}_2(\text{O}_2\text{CMe})_4\text{Cl}_2]$ with Me_3CNC cleaves the $\text{Re}-\text{Re}$ quadruple bond to give $[\text{Re}(\text{CNCMe}_3)_6]\text{Cl}$ [70].

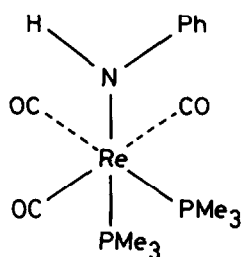
$[\text{ReH}(\text{dppe})_2]$ is produced by 336 nm irradiation of a degassed benzene solution of $[\text{ReH}_3(\text{dppe})_2]$. If the reaction is carried out in the presence of reactive gases, the substituted products $[\text{ReH}(\text{N}_2)(\text{dppe})_2]$, $[\text{ReH}(\text{CO})(\text{dppe})_2]$ and $[\text{ReH}(\text{C}_2\text{H}_4)(\text{dppe})_2]$ were obtained [82]. Under CO_2 , the orange methanoate complex $[\text{Re}(\text{O}_2\text{CH})(\text{dppe})_2]$ is obtained by reversible insertion into the $\text{Re}-\text{H}$ bond of $[\text{ReH}(\text{dppe})_2]$ [81,82].



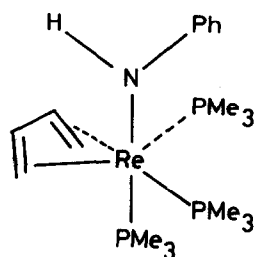
(14)



(15)



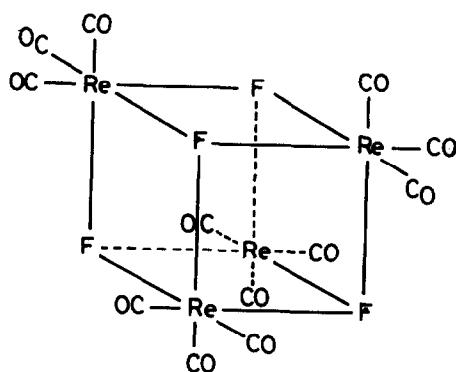
(16)



(17)

7.7.2 Halides

$[\text{Re}(\text{CO})_3\text{F}]_4 \cdot 4\text{H}_2\text{O}$ (18) was prepared from $[\text{Re}(\text{CO})_3\text{Br}]$ by bromide extraction



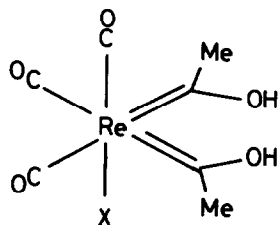
(18)

with AgF in fluorobenzene. Each of the fluorine atoms is involved in a μ_3 -type bridge with rhenium at an average bonding distance of 2.200(5) Å. The clusters are held together by hydrogen bonding between the fluorides and water [91].

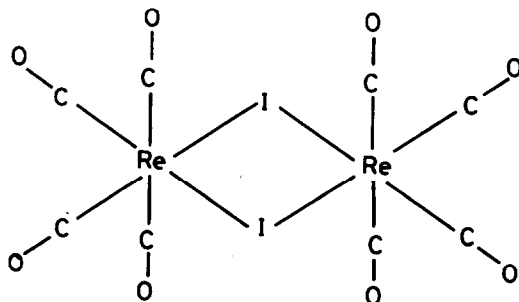
The photochemistry of $[\text{Re}(\text{CO})_5\text{Br}]$ was investigated at low temperature to see if Re-Br photolysis did occur as previously reported [92]. It was found that on irradiation in 2-Methf, spectral changes occurred that were consistent with the formation of $[\text{Re}(\text{CO})_4(\text{Methf})\text{Br}]$, which is in agreement with the general observation that monomeric carbonyl complexes usually undergo M-CO cleavage as the primary photoprocess [93].

$[\text{Re}(\text{CO})_5\text{X}]$ (X = Cl or Br) have been studied by X-ray powder diffractometry and found to be orthorhombic [94]. $[\text{Re}(\text{CO})_5\text{X}]$ (X = Cl, Br or I) have been studied using $^{35,37}\text{Cl}$, $^{79,81}\text{Br}$, ^{127}I and ^{185}Re NQR spectroscopy at 77 and 293 K. A linear correlation was observed between the number of unbalanced p-electrons and the electronegativity of the halogen [95]. $[\text{Re}_3\text{I}_6(\text{CO})_6]$, (8), prepared from $[\text{Re}_2\text{I}_2(\text{CO})_8]$ and iodine consists of a trinuclear iodide bridged S_6 complex with the rhenium on the three fold axis of symmetry. The oxidation state of the terminal rhenium is +1 and that of the central rhenium +4 (see Section 7.4.1) [57].

When $[\text{Re}(\text{CO})_5\text{X}]$ (X = Cl, Br or I) is treated with methyl lithium in thf at -78°C the corresponding diacetylhalorhenate (I) di-anion is obtained, which on protonation with HX gives the *fac*- $[(\text{OC})_3\text{XRe}\{\text{C}(\text{Me})\text{OH}\}_2]$ complex (19). The iodobis-carbenoid complex, (19; X = I) decomposes in solution with the elimination of ethanal and the formation of $[\{\text{Re}(\text{CO})_4\text{I}\}_2]$ (20) [96].



(19)



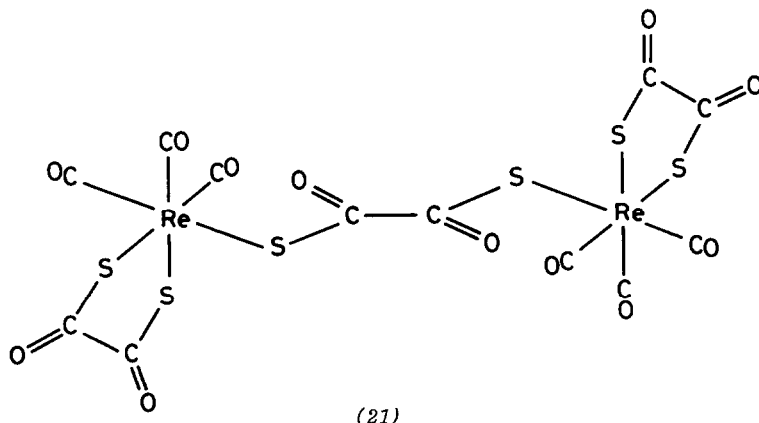
(20)

7.7.3 Complexes with Group VIB donor ligands

The reaction of $[\text{Re}(\text{CO})_5(\text{SO}_2)][\text{A}_5\text{F}_6]$ or $\text{Re}(\text{CO})_5\text{F}\cdot\text{AsF}_5$ with oxygen σ -donors L (L = H_2O , MeOH or Me_2CO) gives complexes of the type $[\text{Re}(\text{CO})_5\text{L}]^+$ in quantitative yield [97]. The mixed metal compounds *cis*- $[\{(\text{CO})_4\text{Re}(\text{CH}_3\text{CO})_2\}_n\text{M}]$ (M = Fe or Cr, $n = 3$; M = Cu, $n = 2$) and the corresponding acac complexes were studied by CV in dichloromethane. It was found that the reduction potential for the heteronuclear complexes was more positive than for the non-metallo ligands *e.g.* the reduction potential for the rhenia-acetylacetonate iron complex, $[\{(\text{CO})_4\text{Re}(\text{CH}_3\text{CO})_2\}_3\text{Fe}]$, is 0.63V more positive than that of $[\text{Fe}(\text{acac})_3]$. This was thought to reflect the higher electronegativity of the rhenia-acetylacetonate ligands [98].

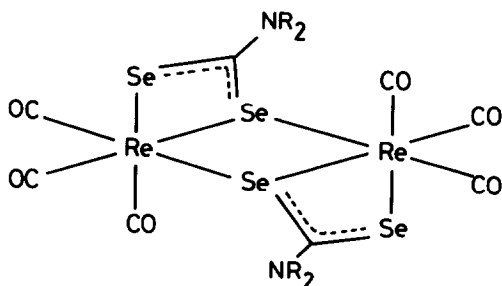
Carbamoyl derivatives such as $[(\text{CO})_4\text{Re}(\text{CONHMe})(\text{NH}_2\text{Me})]$ react with various thiocyanates (RNCS) to give dithiocarbamate complexes of the type $[(\text{CO})_4\text{Re}(\text{S}_2\text{CNHR})]$ or $[(\text{CO})_3\text{Re}(\text{CNMe})(\text{S}_2\text{CHNR})]$. The presence of the CNMe group bound to the metal indicates that in these reactions the source of the isocyanide is the carbamoyl group rather than the iso-thiocyanate reagent [99,100]. Chemical evidence has been presented which suggested that the reaction of CS_2 or COS with carbamoyl derivatives of transition metals occurs *via* electrophilic attack of the N atom of the carbamoyl group and the CS_2 route to dithiocarbamates was assessed [100].

$\text{Cs}_4[\text{Re}_2(\text{CO})_6(\text{dtox})_3]$ is formed by the reaction of $\text{CS}_2[\text{dtox}]$ with $[\text{Re}(\text{CO})_5\text{Br}]$. The dimeric complex ion contains one ligand in a transplanar conformation connecting the two rhenium atoms, each bearing one chelating *dtox* ligand (21) [38].



A series of tetracarbonyl complexes with phosphine chelate ligands $[\text{HXC}(\text{Y})\text{PPh}_2]$ (LH; X, Y = NR, O or S) was prepared by reaction of the metal carbonyl with the free ligands or their silyl analogues. The thiomethanamido ligands in complexes such as *cis*- $[(\text{CO})_4\text{Re}\{(\text{S})\text{C}(\text{NH})\text{PPh}_2\}]$ were shown by crystallographic studies to coordinate *via* phosphorus and sulphur [86].

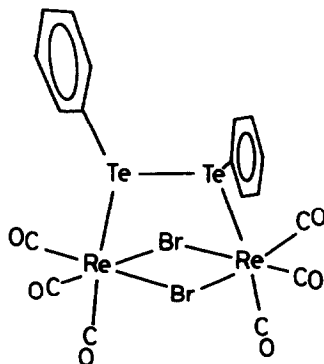
Irradiation of a mixture of $[\text{Re}_2(\text{CO})_{10}]$ and L-L (a 1:1 mixture of $[\text{R}_2\text{NC}(\text{Se})\text{Se}(\text{Se})\text{CNR}_2]$ and $[\text{R}_2\text{NC}(\text{Se})\text{Se}_3(\text{Se})\text{CNR}_2]$ {R = Et or R = morpholyl}) in thf under dinitrogen yields $[\text{Re}(\text{CO})_4\{\text{SeC}(\text{Se})\text{NR}_2\}]$. Heating this complex at reflux for 2 h yields $[\text{Re}_2(\text{CO})_8\{\text{SeC}(\text{Se})\text{NR}_2\}_2]$ (22; R = Et) [78]. The photochemical reaction which produced these diselenocarbamate complexes have been extensively studied and



(22)

an $\text{S}_{\text{N}}1$ type reaction mechanism is proposed involving homolytic M-M fission as the rate determining step [101].

The dimeric complexes $[\text{Re}_2\text{X}_2(\text{CO})_6\{\text{E}_2\text{Ph}_2\}]$ (X = Br, E = Te; X = I, E = Se, S or Te) were prepared either by the reaction of $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{thf})_2]$ with TePh_2 in methylbenzene at reflux. The X-ray structure of $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{Te}_2\text{Ph}_2)]$ (23) shows two *pseudooctahedral* rhenium(I) centres joined by Br^- and Te_2Ph_2 bridges { $r(\text{ReBr}) = 2.64(6) \text{ \AA}$, $r(\text{TeBr}) = 3.674 \text{ \AA}$ (non-bonded) and $r(\text{ReRe}) = 3.945(2) \text{ \AA}$ (non-bonded)} [102].



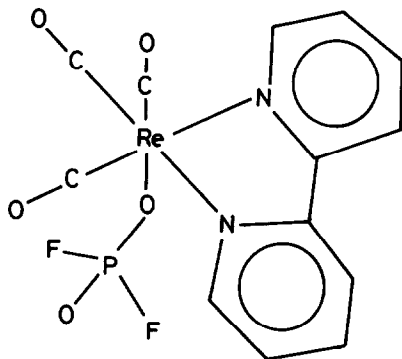
(23)

7.7.4 Complexes with group VB donor ligands

$[\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{ArNXNAr})]$ ($X = \text{N}$ or CH , $\text{Ar} = 3\text{-CH}_3\text{-C}_6\text{H}_4$, C_6H_5 , or $3\text{-Cl-C}_6\text{H}_4$) were obtained in good yield by adding $[\text{Re}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}]$ to a solution of $\text{Li}[\text{ArNXNAr}]$ in boiling thf. The yellow-orange complexes were characterised by NMR, UV and IR spectroscopy and it was thought that the triazenido-ligands were chelating [103,104].

The crystal structure of *fac*- $[\text{ReBr}(\text{CO})_3\{\text{Me}(\text{H})\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}\}]$ prepared by heating $[\text{Re}_2\text{Br}_2(\text{CO})_8]$ and the diamine together in trichloromethane, showed that the rhenium has a distorted octahedral environment with the diamine ligand forming a chelate ring [106]. The resonance Raman spectra of a series of *fac*- $[\text{Re}(\text{CO})_3\text{L}(\text{X})]$ ($\text{L} = \text{alkyl}$ or $\text{aryl N,N}'\text{-disubstituted ethane-1,2-dimine}$ or $2\text{-(N-mono substituted-iminomethyl) pyridine}$, $\text{X} = \text{Cl}$ or Br) complexes obtained by excitation within the lowest absorption band were reported and the effect of L and X discussed [106].

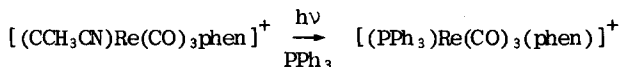
$[\text{Re}(\text{CO})_3(\text{bipy})\text{Br}]$ was prepared by heating a mixture of $[\text{ReBr}(\text{CO})_5]$ and bipy at reflux. Bromide abstraction in the presence of $\text{Ag}[\text{ClO}_4]$ or $\text{Ag}[\text{PF}_6]$ led to the formation of $[\text{Re}(\text{CO})_3(\text{bipy})(\text{ClO}_4)]$ or $[\text{Re}(\text{CO})_3(\text{bipy})(\text{PO}_2\text{F}_2)]$ respectively. The crystal structure of the $[\text{PO}_2\text{F}_2]^-$ complex (24) shows a *fac*-structure, with the $[\text{PO}_2\text{F}_2]^-$ being coordinated *via* a single oxygen atom [107]. A new chemiluminescent reaction involving a rhenium coordination complex has been observed. The reaction



(24)

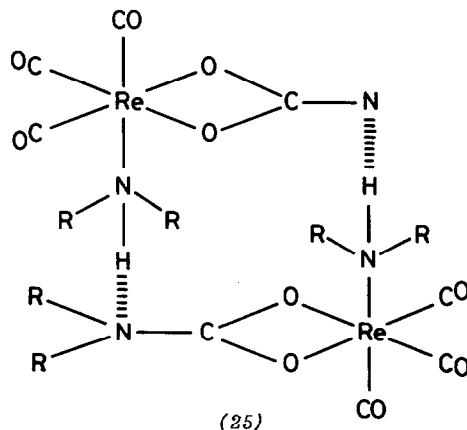
of $[(\text{OC})_5\text{ReRe}(\text{OC})_3(\text{phen})]$ with dichlorine gives $[\text{Re}(\text{CO})_3\text{Cl}]$, $[\text{Re}(\text{CO})_3(\text{phen})\text{Cl}]$ and luminescence. The chemiluminescence was tentatively assigned to $[\text{Re}(\text{CO})_3(\text{phen})\text{Cl}]$ which is known to show photoexcited emission [108]. Chemiluminescence was also observed in the catalytic decomposition of organic peroxides by $[\text{Re}(\text{CO})_3(\text{phen})\text{Cl}]$. This was interpreted as suggesting that the catalysis occurred according to the

Shurtester mechanism, involving initial oxidation of the rhenium complex [109]. A new mechanism for photosubstitution, in inert complexes, with a quantum yield greater than one has been proposed. In the reaction:

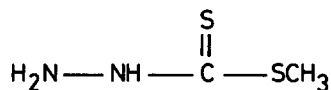


irradiation of the Re→phen MLCT transition does not give an excited state leading to quantum efficient substitution (*e.g.* on irradiation of $[(\text{CH}_3\text{CN})\text{Re}(\text{CO})_3\text{phen}]^+$ in CH_3CN containing 2*M* pyridine, there is no substitution reaction observed). However, irradiation of the complex in CH_3CN containing 0.2 *M* PPh and 0.1 *M* $[\text{Bu}_4\text{N}][\text{PF}_6]$ gives clean quantum efficient substitution. The 0.2 *M* PPh₃ is thought to quench all the excited rhenium complexes (by electron transfer from triphenyl phosphine to the excited rhenium complex) and hence substitution must occur after quenching *i.e.* at the nineteen electron stage [110].

The crystal and molecular structures of $[\text{ReBr}(\text{CO})_3(\text{NHR}_2)_2]$ (R = Me or Et) have been studied by X-ray diffraction. The molecular structure shows a *fac*-arrangement around a six-coordinate rhenium with the *cis*-ligands interacting appreciably. $[\text{ReBr}(\text{CO})_3(\text{NHET}_2)_2]$ reacts with dry carbon dioxide in methylbenzene in the presence of $[\text{HNET}_2]$ to give $[\text{Re}(\text{CO})_3(\text{O}_2\text{CNET}_2)(\text{NHET}_2)]$. This carbamate complex shows some association and is believed to exist as an H-bonded dimer (25) [111]. The reaction of $[(\text{MeCN})_2\text{Re}(\text{CO})_3\text{Br}]$ with $[\text{NO}_2][\text{BF}_4]$ gives $[(\text{MeCN})_3\text{Re}(\text{CO})_3][\text{BF}_4]$



as one of the products (see also Section 7.12). Complexes of the type $[\text{RRe}(\text{CO})_3]$ (R = η^5 -fluorenyl) can be prepared by reaction $[(\text{MeCN})_2\text{Re}(\text{CO})_3\text{Br}]$ with $\text{K}[\text{R}]$ [112]. The carbonyl complexes $[\text{Re}(\text{CO})_3(\text{NH}_2\text{NHCS}_2\text{CH}_3)_2]\text{Br}$ and $[\text{Re}(\text{CO})_3(\text{NH}_2\text{NHCS}_2\text{CG}_3)\text{Br}]$ were prepared by the reaction of $[\text{Re}(\text{CO})_3\text{Br}]$ with an *S*-methylthiocarbamate (26) in acidic or neutral conditions. In alkaline solutions complexes such as $[\text{Re}_2(\text{CO})_6(\text{NH}_2\text{NCS}_2\text{CH}_3)_2]$ with the deprotonated ligand

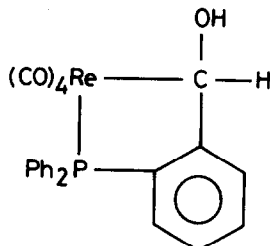


(26)

are obtained [113].

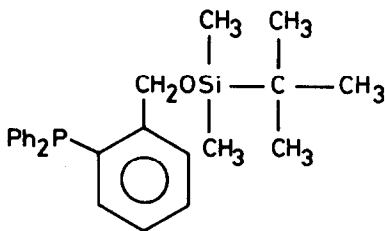
$[\text{Re}(\text{CO})_3\text{L}_2]_n$ (HL = glycine, dl-leucine, dl- β -phenyl- α -alanine, dl- β -phenyl- β -alanine, dl- β -2-thienyl- α -alanine or dl- β -2-thientyl- β -alanine) prepared by the reaction of $[\text{Re}(\text{CO})_5\text{Br}]$ with KL and KBr, react with neutral ligands in dioxane to give $[\text{Re}(\text{CO})_3\text{L}(\text{py})_2]$ and $[\text{Re}(\text{CO})_2\text{LQ}_2]$ {Q = PPh_3 or $\text{P}(\text{OMe})_3$ } [114]. $[\text{IRe}(\text{CO})_4\text{Br}]$ (L = *N*-diphenylphosphine-2,5-dimethylpyrrole) was prepared by mixing L with $[\text{Re}(\text{CO})_5\text{Br}]$ in benzene at 80 °C. The IR spectrum indicated that the product has a *cis*-octahedral structure analogous to $[(\text{Ph}_3\text{P})\text{Re}(\text{CO})_4\text{Br}]$ [115]. The reaction of $[(\text{PPh}_3)\text{Re}(\text{CO})_4\text{Br}]$ with LiMe proceeds *via* an intermediate to finally give $[(\text{Ph}_3\text{P})(\text{CO})_4\text{Re}(\text{CH}_3)]$. The intermediate was characterised by NMR and IR spectroscopy as having the structure *fac*- $[(\text{CO})_3\text{Re}(\text{COCH}_3)(\text{PPh}_3)\text{Br}]^-\text{Li}^+$ *i.e.* the substitution reaction occurred by initial $[\text{Me}]^-$ attack on coordinated CO [116].

Two synthetic routes have been used to prepare (27). The first involved

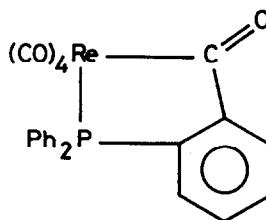


(27)

the reaction of $[(\text{CO})_5\text{Re}(\text{CH}_2\text{C}_6\text{H}_5)]$ with (28) in octane under reflux followed by reaction of the silylated product with $[\text{Et}_4\text{N}]\text{F}$ to give (27). The second method involved the partial reduction of (29) by $\text{BH}_3\cdot\text{thf}$ and is the first example of



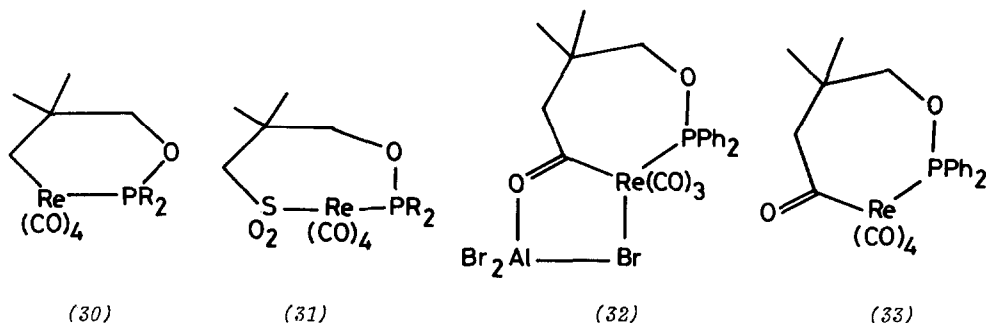
(28)



(29)

the partial reduction of an acyl ligand by BH_3 . The products were characterised by NMR and other spectroscopic techniques [117].

The reaction of $[(\text{OC})_8(\text{R}_2\text{PO})_2\text{Re}_2]$ ($\text{R} = \text{Ph}$ or Me) with $[\text{Me}_2\text{C}(\text{CH}_2\text{O}_3\text{SCF}_3)_2]$ gives the six-membered rhenacycloalkane (30). This will insert sulphur dioxide to give the ring expanded product (31) [118-120]. The crystal structure of (30; $\text{R} = \text{Me}$) has been determined [118]. The seven membered analogues of (30), viz. $[(\text{OC})_4\text{RePR}_2\text{O}(\text{CH}_2)_3\text{CH}_2]$, are thermally unstable and cleave at the $\alpha\text{-C-C}$ bond [119]. Reaction of (30; $\text{R} = \text{Pr}$) with AlBr_3 gives (32) and is the first example of insertion of CO into a Re-C σ -bond. Addition of CO to (32), followed by hydrolysis, gives (33) [120].



The IR and NMR spectra of $[\text{Re}(\text{CO})_6]\text{Cl} \cdot \text{HCl}$ and $[\text{Re}(\text{CO})_6\text{PPh}_3][\text{PF}_6]$ were discussed in terms of σ and π interaction of the metal ligand system. These were compared with the ^{51}V NMR data of the analogous carbonyl vanadates. The ^{185}Re and ^{187}Re NMR spectra of $[\text{Re}(\text{CO})_6]\text{Cl} \cdot \text{HCl}$ were obtained and showed $\sigma(\text{Re})$ 3400 ppm (relative to $\text{Na}[\text{ReO}_4]/\text{H}_2\text{O}$ in CH_2Cl_2) [121].

7.7.5 Complexes with Group IVB donor ligands

$\text{Na}[\text{Re}(\text{CO})_5]$ has been prepared by the reaction of $[\text{Re}_2(\text{CO})_{10}]$ with sodium amalgam in thf. This reacted with SnCl_2 in thf to give $[\{\text{Re}(\text{CO})_5\}_2\text{Sn}]$ and $[\{\text{Re}(\text{CO})_5\}_4\text{Sn}]$. $[\{\text{Re}(\text{CO})_5\}_2\text{Sn}]$ reacted with MeI to give $[\{\text{Re}(\text{CO})_5\}_2\text{Sn}(\text{Me})\text{I}]$. The complexes were characterised by IR and mass spectrometry and were shown to contain Re-Sn bonds [130]. The reaction of $\text{Na}[\text{Re}(\text{CO})_5]$ with $\text{Cl}(\text{CH}_2)_2\text{Me}_2\text{SiC}\equiv\text{CCH}_2\text{Cl}$ has also been investigated [131]. The series of complexes $[(\text{R}_3\text{E})\text{Re}(\text{CO})_3\text{L}]$ ($\text{R} = \text{Ph}$ or Me , $\text{E} = \text{Ge}$ or Sn , $\text{L} = \text{bipy}$, phen or biquinoline) were prepared by the reaction, under argon, of $[\text{ClRe}(\text{CO})_3\text{L}]$ with sodium amalgam followed by the addition of R_3ECl . The lowest lying excited state in these complexes is due to charge transfer $\{(\text{E}-\text{Re})\sigma_p \rightarrow \pi^*\text{L}\}$ and several of the complexes ($\text{R} = \text{Ph}$, $\text{E} = \text{Ge}$ or Sn , $\text{L} = \text{bipy}$ or phen) exhibited optical emission from this state at 298 K with lifetimes of the order of 10^{-6} s. The CV of these complexes in $\text{MeCN}/0.1 \text{ M}$

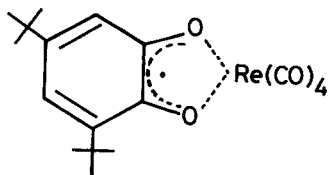
$[n\text{-Bu}_4\text{N}][\text{ClO}_4]$ typically shows one electron reversible reduction in the -1.1 to 1.7V (VS SCE) range associated with the population of the lowest π^* orbital principally located on L [132].

7.8 RHENIUM(O)

$[\text{Re}_2\{\text{P}(\text{OMe}_3)\}_{10}]$ has been prepared by the treatment of either $[\text{ReCl}_4\text{py}]$ or $[\text{Re}(\text{O})\text{Cl}_3(\text{py})_2]$ with the K-KI reagent in cyclohexane followed by the addition of $\text{P}(\text{MeO})_3$. The product was characterised by ^1H and ^{31}P NMR and mass spectrometry. $[\text{HRe}\{\text{P}(\text{OMe}_3)\}_5]$ was also obtained from this reaction [122]. The IR and NMR spectra of $[\text{Re}_2(\text{CO})_8(\text{PPh}_2)_2]$ was discussed in context of the σ - and π -interaction of the metal-ligand system and compared with the spectra of the analogous carbonyl vanadates [121].

Accurate room temperature X-ray diffraction studies of $[\text{Re}_2(\text{CO})_{10}]$ have been reported and show a Re-Re bond length of 3.0413(11) Å and Re-C bond lengths of 1.811(3) Å (axial) and 1.865 Å (equatorial). The difference in lengths of the axial and equatorial bonds is explained as being the result of competition for the $d\pi$ electron density between mutually *trans* pairs of equatorial carbonyl ligands [123].

When a hexane solution of $[\text{Re}_2(\text{CO})_{10}]$ was subject to flash photolysis under an atmosphere of carbon monoxide, the near UV absorbance due to the dinuclear species returned to the original value according to a bimolecular rate law. In degassed solutions, more complex behaviour was observed suggesting the formation of $[\text{Re}_2(\text{CO})_8]$ and $[\text{Re}_2(\text{CO})_9]$ as intermediates [124]. Generation of $[\text{Re}(\text{CO})_5]^+$ radicals in degassed cyclohexane in the presence of CCl_4 and PPh_3 gave $[\text{ClRe}(\text{CO})_5]$ and $[\text{ClRe}(\text{CO})_4(\text{PPh}_3)]$. Analysis of the product ratios led to the conclusion that substitution was first order in $[\text{PPh}_3]$ and associative and also closely proportional to $[\text{CCl}_4]$ at constant $[\text{PPh}_3]$, showing the second order nature of the reaction [125]. HPLC-EPR has been used to separate and characterise the rhenium carbonyl-3,5-di-*tert*-butyl-1,2-quinone complex (34) formed by the 310 nm irradiation



(34)

of $[\text{Re}_2(\text{CO})_{10}]$ in the presence of the quinone in benzene to give a red solution of the complex [126,127]. Optically active diop was then added to this red solution to give a blue solution which was separated by EPR-HPLC. The product was characterised as a quinone-Re-carbonyl-(+) or (-) diop radical, with the diop being monodentate in this example [127].

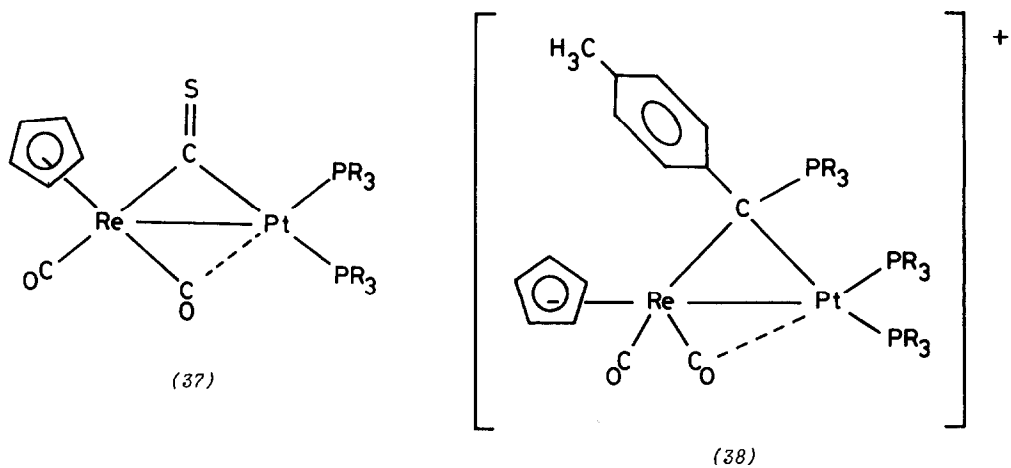
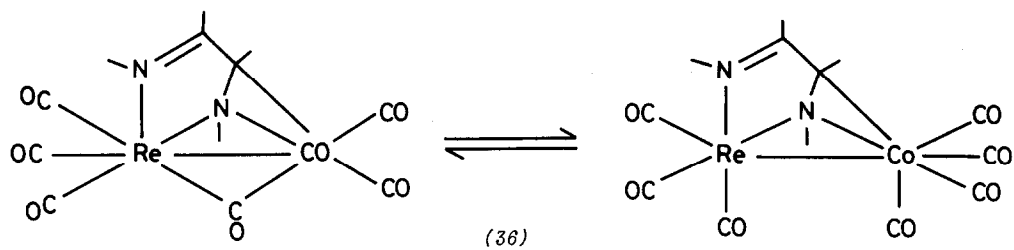
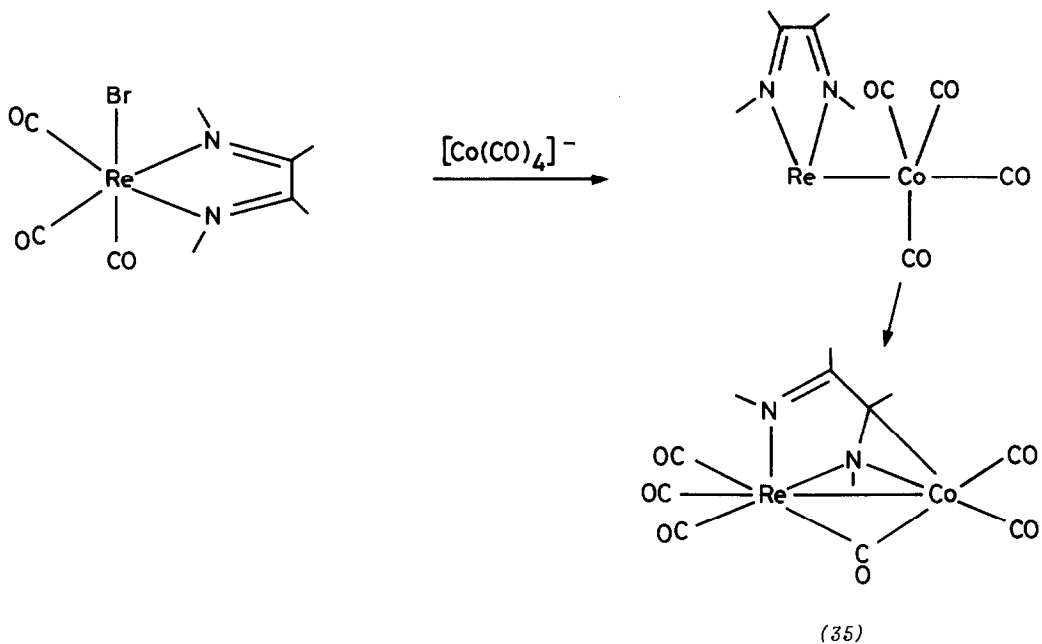
The mixed metal carbonyls $[\text{MnRe}(\text{CO})_{10}]$ and $[\text{TcRe}(\text{CO})_{10}]$ have been synthesised. The manganese-rhenium complex was produced by the reduction of $[\text{Mn}_2(\text{CO})_{10}]$ to $[\text{Mn}(\text{CO})_5]^-$ followed by the dropwise addition of $[\text{Re}(\text{CO})_5\text{Br}]$ in thf. The technetium-rhenium complex was produced in a similar way, but involves the reduction of $[\text{Tc}_2(\text{CO})_{10}]$ as the initial step. This synthesis follows the general procedure of using the weakest nucleophile with the corresponding bromide [128]. The experimental and literature values for the thermodynamic parameters of formation, phase transitions and dissociation for these mixed metal carbonyls have been discussed. Sets of the best values are proposed and M-M bond energies were determined [129].

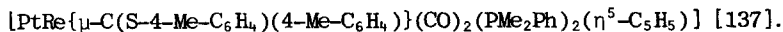
7.9 COMPLEXES CONTAINING RHENIUM-COBALT AND RHENIUM-PLATINUM BONDS

The IR spectrum, and its complete assignment on the basis of the free rotational model, of $[\text{ReCo}(\text{CO})_9]$ has been reported. The force attraction constants have been calculated and it was shown that K_{eq} and K_{ax} values of the rhenium species are less than those of the analogous technetium compound. There is considerable polarisation of the Re-Co bond in the sense $[(\text{CO})_5\text{Re}^{\delta+} - \text{Co}^{\delta-}(\text{CO})_4]$ [133]. $[\text{ReCo}(\text{CO})_6(\text{dab})]$ (35) (dab = diazabutadiene) was prepared by heating $[\text{Re}(\text{CO})_3\text{Br}(\text{dab})]$ under reflux with an excess of $[\text{Co}(\text{CO})_4]^-$ in thf [134]. The ^{13}C NMR spectrum showed characteristic features related to the bonding mode of the dab ligand to the binuclear Re-Co fragment. In $[\text{ReCo}(\text{CO})_6(\text{dab})]$ there is a semibridging carbonyl group and there is rapid interchange of this carbonyl with the terminal carbonyl groups on cobalt (36). The electronic balance is maintained by an internal compensation within the dab ligand [135].

The yellow complex $[\text{RePt}(\mu\text{-CS})(\text{CO})_2(\text{PPhMe}_2)_2(\eta^5\text{-C}_5\text{H}_5)]$ (37) has been prepared by the addition of one equivalent of $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPhMe}_2)_2]$ to $[\text{Re}(\text{CO})_2(\text{CS})(\eta^5\text{-C}_5\text{H}_5)]$ in light petroleum. The NMR spectra show that the CO and CS ligands undergo bridge-terminal site exchange at room temperature, but this ceases at -60°C [136].

$[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_2\text{Re}\{\mu\text{-C}(\text{PR}_3)(4\text{-Me-C}_6\text{H}_4)\}\text{Pt}(\text{PR}_3)_2][\text{BF}_4]$ (38; $\text{PR}_3 = \text{PMe}_3$ or PPhMe_2) were prepared by the reaction of the appropriate tertiary phosphine with $[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_2\text{Re}\{\mu\text{-C}(4\text{-Me-C}_6\text{H}_4)\}\text{Pt}(\text{PR}_3)_2][\text{BF}_4]$ in light petroleum. The structure of the product was confirmed by ^{31}P and ^1H NMR spectroscopy. (38) will undergo ligand exchange with $\text{Na}[S\text{-}4\text{-Me-C}_6\text{H}_4]$ to give

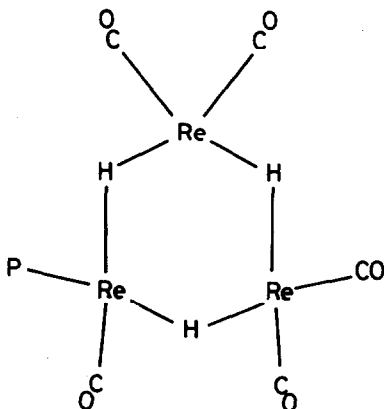




7.10 METAL CLUSTERS

He-I and He-II gas phase PE spectra have been reported for $[\text{H}_3\text{Re}_3(\text{CO})_{12}]$ and $[\text{H}_4\text{Re}_4(\text{CO})_{12}]$. The spectra were assigned with the use of fragment MO analyses of the electronic structures. The bridging hydrogen bonds are discussed in terms of being two electron polycentre bonds, and the multicentre orbitals were shown to possess a high degree of electron localisation at the hydrogen atoms. The hydrogen atoms in these clusters were thought to provide some of the necessary electrons for cluster bonding and stabilisation of the cluster molecular orbitals [138]. The excited state decay properties of $[\text{H}_4\text{Re}_4(\text{CO})_{12}]$ and $[\text{Bu}_4\text{N}]_2[\text{H}_6\text{Re}_4(\text{CO})_{12}]$ have been compared to those of their deuterated analogues. The effect of replacing ^1H by ^2H in both cases is to lower the rate constant for non-radiative decay with no effect on the radiative rate constant. The quantum yields and omission lifetimes are increased by the change [139].

The molecular structure of *eq*- $[\text{H}_3\text{Re}_3(\text{CO})_{11}(\text{PPh}_3)]$ (39) has been obtained

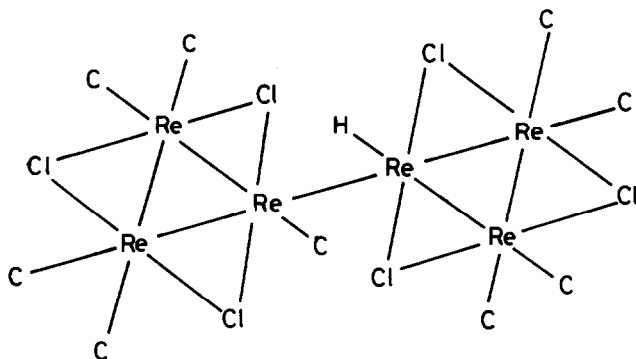


(39; the $\{\text{Re}_3\text{H}_3\}$ core in the equatorial plane)

using single crystal X-ray and neutron diffraction. The molecule has edge-bridging hydrogen atoms, with approximate D_{3h} symmetry for the $\{\text{Re}_3\text{H}_3\}$ core. One striking feature of the equatorial PPh_3 ligand is that the Re-H bond *trans* to it is markedly shorter than the other Re-H distances (1.78(1) Å vs. 1.82–1.83 Å). This may be related to the poor π acceptor properties of PPh_3 compared with CO [140].

The synthesis and characterisation of a series of polynuclear alkyl compounds derived from $[\text{Re}_3\text{Cl}_3(\text{CH}_2\text{SiMe}_3)_6]$ (40) has been reported by Wilkinson and coworkers [141]. The hydrogenation of (40) in thf led to the formation of $[(\text{Me}_3\text{SiCH}_2)_5(\mu\text{-Cl})_3\text{Re}_3\text{-Re}_3(\mu\text{-Cl})_3\text{H}(\text{CH}_2\text{SiMe}_3)_4]$ (41) with the two triangular $\{\text{Re}_3\}$

units being linked by a single Re-Re bond $\{r(\text{ReRe}) = 2.993 \text{ \AA}\}$. In benzene,



(41; the $\{\text{Re}_6(\mu\text{-Cl})_6\text{HC}_9\}$ core)

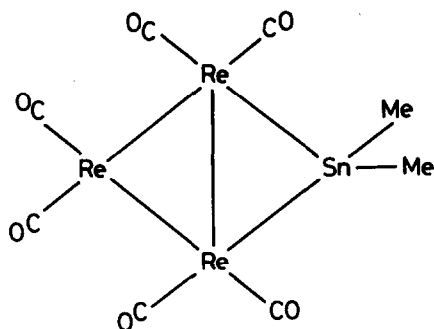
however, $[\text{Re}_6(\mu\text{-Cl})_6\text{H}_6(\text{CH}_2\text{SiMe}_3)_6]$ is the major product, with the two $\{\text{Re}_3\text{Cl}_3\}$ units linked by alkyl bridges and containing terminal hydrogens.

$[\text{Re}_3(\mu\text{-Cl})_3\text{ClH}(\text{CH}_2\text{SiMe}_3)_5(\text{PPh}_3)]$ is produced by the hydrogenation of $[\text{Re}_3(\mu\text{-Cl})_3\text{Cl}(\text{CH}_2\text{SiMe}_3)_5]$ in the presence of PPh_3 . The crystal structure shows the phosphine to be only weakly bound. The interaction of dihydrogen with $[\text{Re}_3(\mu\text{-Cl})_3(\text{CH}_2\text{SiMe}_3)_6\text{L}_3]$ ($\text{L} = \text{CO}$, PPh_3 , py or H_2O) will give reductive cleavage ($\text{L} = \text{CO}$ or PPh_3) to give the Re^{II} dimers $[\text{Re}_2\text{Cl}_2(\text{CH}_2\text{SiMe}_3)_2\text{L}_2]$. However when $\text{L} = \text{py}$, a complex, $[\text{Re}_3(\mu\text{-Cl})_3(\text{CH}_2\text{SiMe}_3)_3(\text{py})_3]$, where the $\{\text{Re}_3\}$ unit is retained, is produced. This contains paramagnetic $\text{Re}(\text{II})$ and the EPR spectrum was discussed. With $\text{L} = \text{H}_2\text{O}$, a polynuclear cluster $[\{\text{Re}_3(\mu\text{-Cl})_3(\text{CH}_2\text{SiMe}_3)_3(\text{OH}_2)_3\}_6]$ is produced [141].

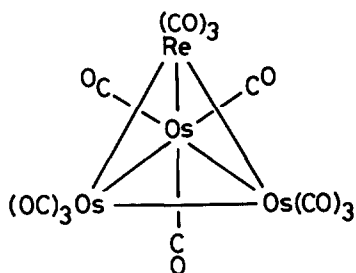
The tertiary sulphides $\text{Na}_2\text{Re}_3\text{S}_6$ and $\text{K}_2\text{Re}_3\text{S}_6$ have been synthesised by the reduction of alkali carbonates with rhenium, at 800°C in a stream of hydrogen sulphide. The X-ray diffraction study showed the key structural units to be, hitherto unknown $\{\text{Re}_6\text{S}_8\}$ clusters. These clusters are linked in a 3-D array [142].

$[\text{Re}_3(\mu\text{-H})(\mu\text{-SnMe}_2)(\text{CO})_{12}]$ (42) was prepared by the treatment of $[\text{Ph}_4\text{As}]_2[\text{Re}_3(\mu\text{-H})(\text{CO})_{12}] \cdot \frac{1}{2}\text{C}_4\text{H}_8\text{O}$ with $(\text{CH}_3)_2\text{SnCl}_2$ or $(\text{CH}_3)_3\text{SnCl}$. The crystal and molecular structure of this yellow-orange compound has been determined, and showed the SnMe_2 to be assymmetrically bridging one edge of the $\{\text{Re}_3\}$ triangle, with the hydrogen probably bridging one of the other sides. The bond lengths show the assymetry of the Sn-Re bridge, *viz.* $r(\text{SnRe}) = 2.87, 2.60 \text{ \AA}$ [143].

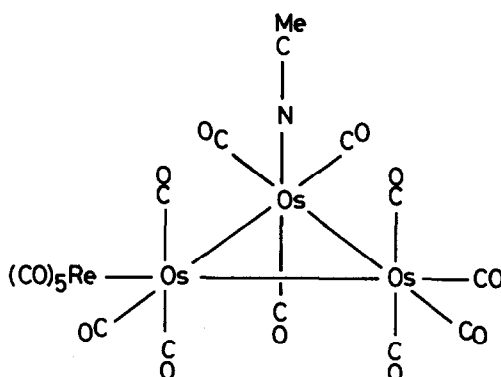
A metal hydride coupling reaction, where $[\text{HRe}(\text{CO})_5]$ acts as a two-electron donor to $[\text{Os}(\text{CO})_{12-x}\text{L}_x]$ ($\text{L} = \text{CH}_3\text{CN}$ or C_6H_{14} ; $x = 1$ or 2) will give, after oxidative addition, $[\text{HReOs}_3(\text{CO})_{16}]$ and $[\text{H}_2\text{Re}_2\text{Os}_5(\text{CO})_{20}]$ [144]. The latter complex will react, on heating with ethanenitrile to give $[(\mu\text{-H})\text{Os}_3\text{Re}(\text{CO})_{15}(\text{NCCH}_3)]$ (43) which was shown by X-ray diffraction, to contain a triangular core of osmium atoms with the rhenium bound to one of the osmium equatorial sites [145,146]. Heating



(42)



(43)



(44)

on MeCN solution of (43) under dihydrogen with an excess of trimethylamine *N*-oxide dihydrate closes the structure to give the Re capping the triangular $\{\text{Os}_3\}$ face (44) [144,145].

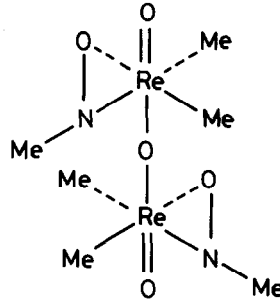
7.11 NITROSYL COMPLEXES

$[(\text{MeCN})_2(\text{Re}(\text{CO})_3\text{Br})]$ will react with $[\text{NO}_2][\text{BF}_4]$ to give the nitrosyl compound $[(\text{MeCN})_2\text{Re}(\text{CO})_2(\text{NO})\text{Br}][\text{BF}_4]$ as one of the products [112].

$[(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})(\text{NO})\text{PPh}_3][\text{BF}_4]$ was obtained by the nitrosation of $[(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})\text{PPh}_3]$ with $[\text{NO}_2][\text{BF}_4]$. $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{NO})][\text{BF}_4]$ has been found to react with KI or I_2 to give the new π -complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})(\text{NO})\text{I}]$ [147].

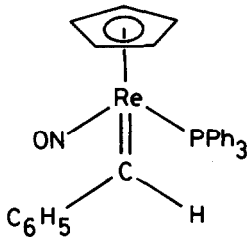
$[\text{ReMe}_6]$ reacts with NO at -78°C in light petroleum to give $[\text{ReMe}_6(\text{NO})]$ as orange red needles. The IR spectrum suggests a non-rigid seven-coordinate structure. In diethyl ether $[\text{Re}(\text{Me})_6(\text{NO})]$ remains in solution and on warming

under NO gives *cis*-[ReO₂Me₃]. Li [ReMe₆] reacts with NO at -78 °C to give a diamagnetic complex of stoichiometry [Re₂O₃Me₄(ONMe)₂]. The ¹H NMR spectrum is consistent with the structure (45) [148].

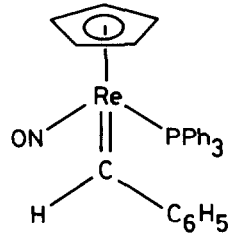


(45)

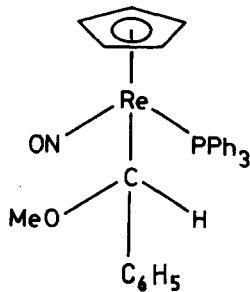
Addition of methoxide to either isomer (46) or (47) of [(η⁵-C₅H₅)Re(NO)(PPh₃)(CHC₆H₅)] [PF₆]⁻ gives [(η⁵-C₅H₅)Re(NO)(PPh₃){CH(OCH₃)C₆H₅}] (48) and (49), in which a new chiral centre has been generated stereospecifically



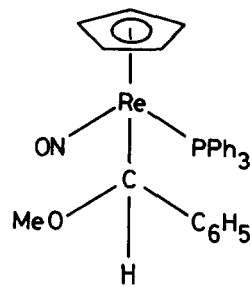
(46)



(47)



(48)



(49)

Reaction of (48) and (49) with $[\text{Ph}_3\text{C}][\text{PF}_6]$ results in the chemo-specific abstraction of a methoxy group and the stereospecific regeneration of (46) and (47) [149].

$[\text{Re}(\text{NO})\text{I}_5]$ has been prepared by dissolving $[\text{Re}(\text{NO})(\text{OH})_3]$ in HI and adding $\text{Cs}_2[\text{CO}_3]$. However the dissolution of $[\text{Re}(\text{NO})(\text{OH})_3]$ in a minimum amount of HI followed by removal of all HI and I_2 gives $[\text{Re}(\text{H}_2\text{O})(\text{OH})(\text{NO})\text{I}_2]$. Other nitrosyl complexes, *i.e.* $[\text{Re}(\text{NO})\text{I}_3\text{L}]$ and $[\text{Re}(\text{NO})\text{IL}_2](\text{PtCl}_6)$ (L = phen or bipy), have been prepared [150].

REFERENCES

1. E.G. Rakov, A.S. Dudin and A.A. Opalouskii, *Usp. Khim.*, **49** (1980) 1945 [*Chem. Abst.* **94** (1981) 201913].
2. J.J. Vajo, D.A. Aikens, L. Ashley, D.E. Peolttl, R.A. Bailey, H.M. Clark and S.C. Bince, *Inorg. Chem.*, **20** (1981) 3328.
3. I.U. Numanov, R.G. Akhmadieva and N.A. Yusupova, *Dokl. Akad. Nauk Tadzh SSR*, **23** (1980) 582 [*Chem. Abst.* **94** (1981) 109976].
4. A. Cimino, B.A. de Angelis, D. Gazzoli and M. Valigi, *Z. Anorg. Allg. Chem.*, **471** (1980) 208.
5. T.G. Shevchenko, *Phy. Stat. Sol. (b)* **103** (1981) 391.
6. V.M. Zaporozhets and V.A. Pasechnyi, *Ukr. Fiz. USSR*, **24** (1979) 875.
7. M.R. Mohammad and W.F. Sherman, *J. Phys. C: Solid State Phys.*, **14** (1981) 283.
8. M.R. Mohammad and W.F. Sherman, *J. Phys. C: Solid State Phys.*, **14** (1981) 4121.
9. J.C. Decius and D. Murhammer, *Spectrochim Acta.*, **36A** (1980) 965.
10. J.-P. Piccard, M. Aneas, G. Baud, J.-P. Besse and R. Chevalier, *J. Less-Common Met.*, **79** (1981) 165.
11. J.-P. Besse, G. Baud, R. Chevalier and I. Zarembowitch, *Mat. Res. Bull.*, **15** (1980) 1255.
12. G. Baud, J.-P. Besse, R. Chevalier and M. Gasperin, *J. Solid State Chem.*, **38** (1981) 186.
13. A.K. Cheetham and A.R. Rae-Smith, *Mat. Res. Bull.*, **16** (1981) 7.
14. R.C. Burns and T.A. O'Donnell, *J. Inorg. Nucl. Chem.*, **42** (1980) 1285.
15. V.I. Vouna, A.S. Dudin, S.N. Lopatin and E.G. Rakov, *Koord. Khim.*, **6** (1980) 1580, [*Chem. Abs.* **93** (1980) 212852].
16. R. Mcdiarmid, *Chem. Phys. Letts.*, **76**, (1980) 300.
17. V.I. Vouna, A.S. Dudin, A.M. Kleshchevnikov, S.M. Lopatin and E.G. Rakov, *Koord. Khim.*, **7** (1981) 574 [*Chem. Abst.* **94** (1981) 200362].
18. I.S. Alekseiuchuk, U.V. Ugarov, N.G. Rambidi, V.A. Legasov and V.B. Sokolov, *Dokl. Akad. Nuak SSSR*, **257** (1981) 625 [*Chem. Abst.*, **94** (1981) 201932].
19. J. Fawcett, J.H. Holloway and D.R. Russell, *J. Chem. Soc. Dalton Trans.*, (1981) 1212.
20. I.I. Antipova-Karataeva, L.V. Bonsova, O.D. Prasolova and A.N. Ermakov, *Zh. Neorg. Khim.*, **26** (1981) 956, [*Chem. Abst.* **94** (1981) 198452].
21. M. Tsukada, *J. Phys. Soc. Japan*, **49** (1980) 1183.
22. M. Tsukada, N. Tsuda and F. Minami, *J. Phys. Soc. Japan*, **49** (1980) 1115.
23. A. Fumimori, F. Minami, T. Akahne and N. Tauda, *J. Phys. Soc. Japan*, **49** (1980) 1820.
24. E. Brockawik, J. Haber and L. Ungier, *J. Phys. Chem. Solids*, **42** (1981) 20.
25. J.E. Schirber and L.F. Mattheis, *Phys. Rev. B.* **24** (1981) 693.
26. J.E. Schirber, L.J. Azevedo, A. Narath and B. Morosin, *Mater. Sci. Eng.*, **49** (1981) 7.

27. W. Liese, K. Dehnicke, R.D. Rogers, R. Shakir and J.C. Atwood, *J. Chem. Soc., Dalton Trans.*, (1981) 1061.
28. K. Dennicke, H. Prinz, W. Kafitz and R. Kujaneck, *Liebigs Ann. Chem.*, (1981) 20.
29. K. Dennicke and U. Weiher, *Z. Anorg. Allg. Chem.*, 469 (1980) 45.
30. K. Steinwede and K. Stumpp, *Z. Inorg. Allg. Chem.*, 469 (1980) 101.
31. A.G. Kolchinskii and N.V. Ul'Ko, *Ukr. Khim. Zh.*, 47 (1981) 159 [*Chem. Abst.* 94 (1981) 145983].
32. E.I. Plastinina, L.V. Borisova and V.A. Sipachev, *Zh. Neorg. Khim.*, 126 (1981) 1785. [*Chem. Abstr.* 95 (1981) 107698].
33. I. Sztterenber, L. Natkaniec and B. Jezowska-Trzebiatowska, *Proc. Conf. Coord. Chem.*, 8th (1980) 405.
34. J. Hanuza, B. Jezowska-Trzebiatowska and A. Müller, *J. Molec. Struct.*, 69 (1980) 17.
35. M. Baluka, *Probl. Metody, Chem. Koor.* (1981) 177, Ed. J. Kalecinski and T. Mikulski [*Chem. Abst.* 95 (1981) 158813].
36. A. Fujimori, H. Nozaki, N. Kimizuka, N. Tsuda, K. Tahara and H. Nagasawa, *Phys. Lett.*, 80A (1980) 188.
37. N.V. Ul'Ko and V.L. Kolesnichenko, *Zh. Neorg. Khim.*, 25 (1980) 2565 [*Chem. Abst.* 93 (1980) 196876].
38. R. Mattes and H. Weber, *Z. Anorg. Allg. Chem.*, 474 (1981) 216.
39. A. Davison, A.C. Jones, L. Müller, R. Tatz and H.S. Trop, *Inorg. Chem.*, 20 (1981) 1160.
40. G. La Monica, S. Cenini and F. Porta, *Inorg. Chim. Acta*, 48 (1981) 91.
41. A. La Monica and S. Cenini, *Cong. Naz. Chem. Inorg.* [Atti] 13th (1980) 117.
42. M.W. Bishop, J. Chatt, J.R. Dilworth, P. Dahlstrom, J. Hyde and J. Zubieta, *J. Organomet. Chem.*, 213 (1981) 109.
43. U. Mazzi, E. Ronacri and R. Rossi, *Trans. Met. Chem.* (Weinheim, Ger.) 5 (1980) 289.
44. R. Rossi, U. Mazzi, E. Roncari, A. Duatti and L. Magon, *Congr. Naz. Chim., Inorg.*, 12th (1979) 108.
45. M.A. Green, J.C. Huffman and K.A. Caulton, *J. Am. Chem. Soc.*, 103 (1981) 695.
46. D.A. Roberts and G.L. Geoffroy, *J. Organomet. Chem.*, 214 (1981) 221.
47. J. Mrozinski, *Probl. Metody Chem. Koor.* (1981) 215, Ed. by J. Kalecinski and T. Mikulski, [*Chem. Abst.* 95 (1981) 160995].
48. J. Lomenzo, H. Patterson, S. Strobridge and H. Engstrom, *Mol. Phys.* 40 (1980) 1401.
49. M.J. Blandauer, J. Burgess, S.J. Hamshere, R.D. Peacock, J.H. Rogers and H.D.B. Jenkins, *J. Chem. Soc., Dalton Trans.* (1981) 726.
50. B.A. Kozikowski and T.A. Keiderling, *Chem. Phys.* 53 (1980) 323.
51. O. Knop, I.A. Oxton, W.J. Westerhaus and M. Falk, *J. Chem. Soc., Faraday Trans. 2*, 77 (1981) 811.
52. D.M. Adams, R.W. Berg and A.D. Williams, *J. Chem. Phys.*, 74 (1981) 2800.
53. M. D'Iorio and R.L. Armstrong, *Can. J. Phys.*, 58 (1980) 1483.
54. J. Mrozinski, *Proc. Conf. Coord. Chem.* 8th (1980) 293.
55. T. Lis, *Acta Cryst. B36* (1980) 2782.
56. J.R. Campbell and R.J.H. Clark, *J. Chem. Soc. Faraday Trans. II*, 76 (1980) 1103.
57. F. Calderazzo, F. Marchetti, R. Poli, D. Vitaci and P.F. Zanazzi, *J. Chem. Soc.; Chem. Commun.* (1981) 893.
58. T.N. Rezukhina and T.I. Gorshkova, *Zh. Fiz. Khim.*, 54 (1980) 2688 [*Chem. Abst.* 93 (1980) 246533].
59. M. Valigi, D. Cordischi, D. Gazzoli, C.P. Keijzers and A.A.K. Klaassen, *J. Chem. Soc., Faraday Trans. I*, 77 (1981) 1871.
60. M. Valigi and D. Gazzoli, *Congr. Naz. Chim. Inorg.* [Atti] 13th (1980) 267.
61. A. Arkowska and W. Wojciechowski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 27 (1979) 963 [*Chem. Abst.* 94 (1981) 184705].
62. A. Arkowska and W. Wojciechowski, *Polish J. Chem.*, 54 (1980) 1847.

63. K.V. Kotegov, Z.A. Lovchikova and G.B. Avetikyan, *Zh. Neorg. Khim.*, 26 (1981) 2167 [*Chem. Abst.* 95 (1981) 161258].
64. F.A. Cotton, *Pure Appl. Chem.*, 52 (1980) 2331.
65. D.G. Nocera and H.B. Gray, *J. Am. Chem. Soc.*, 103 (1981) 7349.
66. A. Shtemenko and A.S. Kotel'nikova, *Izv. Akad. Nauk SSSR, Ser. Khim.* 11 (1980) 2630. [*Chem. Abst.* 94 (1981) 131406].
67. T.V. Misialova, A.S. Kotel'nikova, I.F. Golovaneva, O.N. Eustaf'eva and U.G. Lebedev, *Zh. Neorg. Khim.* 26 (1981) 634 [*Chem. Abst.* 94 (1981) 184762].
68. A.V. Shtmento, Sh. A. Bagirov, A.S. Kotel'nikova, U.G. Lebedev, O.I. Kazymov and A.I. Alieva, *Zh. Neorg. Khim.* 26 (1981) 111. [*Chem. Abst.* 94 (1981) 131439].
69. A.S. Kotel'nikova, A.S. Mosko, T.V. Misailova, I.V. Miroshnichenko and Sh. A. Bagirov, *Zh. Neorg. Khim.* 25 (1980) 3014. [*Chem. Abst.* 94 (1981) 095089].
70. G.S. Girdami and R.A. Andersen, *Inorg. Chem.*, 20 (1981) 2040.
71. A.I. Kuzmin, A.V. Shtemenko and A.S. Kotel'nikova, *Zh. Neorg. Khim.*, 25 (1980) 3024 [*Chem. Abst.* 94 (1981) 182962].
72. P.A. Kozmin, M.D. Surazhskaya, T.B. Larina, A.V. Shtemenko, A.S. Kotel'nikova and I.F. Golovanova, *Koord-Khim.*, 7 (1981) 792 [*Chem. Abstr.* 95 (1981) 125305].
73. P.A. Kozmin, M.D. Surazhskaya, T.B. Larina, A.S. Kotel'nikova and T.V. Misailova, *Koord. Khim.* 6 (1980) 1256 [*Chem. Abst.* 93 (1980) 213705].
74. P.A. Kozmin, M.D. Surazhskaya and T.B. Larina, *Zh. Neorg. Khim.* 26 (1981) 107 [*Chem. Abst.* 94 (1981) 148633].
75. P.A. Kozmin, M.D. Surazhskaya and T.B. Larina, *Koord. Khim.*, 6 (1980) 1259 [*Chem. Abstr.* 93 (1980) 213706].
76. V.I. Nefedov, Ya. V. Salyn, A.V. Shtemenko, A.S. Kotel'nikova, *Inorg. Chim. Acta*, 45 (1980) L49.
77. P.A. Kozmin, T.B. Larina, M.D. Surazhskaya, A.S. Kotel'nikova and N.S. Osmanov, *Koord. Khim.* 6 (1980) 1264. [*Chem. Abst.* 93 (1980) 196863].
78. P. Deplano and E.F. Trogu, *J. Inorg. Nucl. Chem.*, 43 (1981) 711.
79. H.S. Trop, A. Davison and A.G. Jones, *Inorg. Chem. Acta*, 54 (1981) L61.
80. K.W. Chiu, W-K. Wong and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, (1981) 451.
81. D.R. Roberts, G.L. Geoffroy and M.G. Bradley, *J. Organomet. Chem.*, 198 (1980) C75.
82. M.G. Bradley, D.A. Roberts and G.L. Geoffroy, *J. Am. Chem. Soc.*, 103 (1981) 379.
83. D.F. Dong, I.K. Hoyano and W.A.G. Graham, *Can. J. Chem.*, 59 (1981) 1455.
84. N.E. Kolobova, Z.P. Valueva and E.I. Kazimirschuk, *Izv. Akad. Nauk. SSSR. Ser. Khim.*, 12 (1981) 408. [*Chem. Abst.* 95 (1981) 62345].
85. W.J. Balfour and F.B. Orth, *J. Molec. Spectroscopy.*, 84 (1980) 424.
86. U. Kunze, A. Antoniadis and M. Moll, *J. Organomet. Chem.*, 215 (1981) 187.
87. A. Malek, B. Folkesson and R. Larsson, *Acta Chemica. Scand.*, A34 (1980) 483.
88. G.J. Leigh, R.H. Morris, C.J. Pickett, D.R. Stanely and J. Chatt, *J. Chem. Soc., Dalton Trans.*, (1981) 800.
89. A.L. Biyamfel'd, V.S. Lenenko, B. Lorenz, G. Moebius, M. Wahren, V.B. Shur and M.E. Vol'pin, *Dokl. Akad. Nauk. SSSR.*, 251 (1980) 6111 [*Chem. Abst.*, 93 (1980) 185249].
90. A.J.L. Pombeiro, M.F.N.N. Carvalko, P.B. Hitchcock and R.L. Richards, *J. Chem. Soc., Dalton. Trans.*, (1981) 1629.
91. E. Horn and M.R. Snow, *Aust. J. Chem.*, 34 (1981) 737.
92. D.M. Allen, A. Cox, T.J. Kemp and U. Sultana, *Inorg. Chem. Acta.*, 21 (1977) 191.
93. D.R. Tyler and D.P. Petrylak, *Inorg. Chim. Acta.*, 53 (1981) L185.
94. A.A. Kruglov, L.L. Zaitseva and A.S. Kotel'nikova, *Zh. Neorg. Khim.*, 26 (1981) 960. [*Chem. Abstr.*, 94 (1981) 183873].

95. A.I. Kuzmin, A.V. Shetemenko and A.S. Kotel'nikova, *Zh. Neorg. Khim.*, 26 (1981) 843. [*Chem. Abstr.*, 94 (1981) 165177].
96. K.P. Darst, P.G. Lenhert, C.M. Lukehart and L.T. Warfield, *J. Organomet. Chem.*, 195 (1980) 317.
97. M. Oltmanns and R. Mews, *Z. Naturforsch., Teille B*, 36 (1980) 1324.
98. B.D. Beaver, L.C. Hall, C.M. Lukehart and L.D. Preston, *Inorg. Chem. Acta.*, 47 (1981) 25.
99. L. Busetto and A. Palazzi, *Cong. Naz. Chim. Inorg.* [Atti]. 13th (1980) 122.
100. L. Busetto and A. Palazzi, *Cong. Naz. Chim. Inorg.*, [Atti], 12th (1979) 60.
101. R. Deplano and E.F. Trogu, *J. Inorg. Nucl. Chem.*, 42 (1981) 1213.
102. F. Calderazzo, D. Vitali, R. Poli, J.L. Atwood, R.D. Rogers, J.M. Cummings and I. Berhal, *J. Chem. Soc., Dalton. Trans.*, (1981) 1005.
103. R. Rossi, A. Duatti, L. Magon and L. Toniolo, *Inorg. Chim. Acta.*, 48 (1981) 243.
104. R. Rossi, A. Duatti, L. Magon, L. Toniolo, *Cong. Naz. Chim. Inorg.*, [Atti] 13th (1980) 53.
105. E.W. Abel, M.M. Bhatti, M.B. Hursthouse, K.M.A. Malik and M.A. Mazid, *J. Organomet. Chem.*, 197 (1980) 345.
106. R.W. Balk, D.J. Stufkens and A. Oskam, *J. Chem. Soc., Dalton, Trans.*, (1981) 1124.
107. E. Horn and M.R. Snow, *Aust. J. Chem.*, 33 (1980) 2369.
108. A. Vogler, L. El-Sayed, R.G. Jones, J. Namnath and A.W. Adamson, *Inorg. Chem. Acta.*, 53 (1981) L35.
109. A. Vogler and H. Kukely, *Agnew Chem.*, 93 (1981) 470.
110. D.P. Summers, J.C. Luong and M.S. Wrighton, *J. Am. Chem. Soc.*, 103 (1981) 5238.
111. F. Calderazzo, D. Vitali, I.P. Mavani, F. Marchetti, I. Bernal, J.D. Korp, J.L. Atwood, R.D. Rogers and M.S. Dalton, *J. Chem. Soc., Dalton Trans.*, (1981) 2523.
112. N.E. Kolobova, I.A. Lobanova and V.I. Zdanovich, *Izv. Nauk, SSSR, Ser. Khim.*, 7 (1980) 1651. [*Chem. Abst.* 93 (1980) 239580].
113. H. Weber and R. Mattes, *Chem. Ber.*, 113 (1980) 2833.
114. A.A. Loganso and V.V. Derunov, *Koord. Khim.*, 6 (1980) 1704 [*Chem. Abst.* 94 (1981) 57286].
115. L.K. Peterson, I.W. Johnson, J.K. Hoyano, S. Au-Yeung and B. Gour, *J. Inorg. Nucl. Chem.*, 33 (1981) 935.
116. D.W. Parker, M. Marsi and J.A. Gladysz, *J. Organomet. Chem.*, 194 (1980) C1.
117. G.D. Vaughn and J.A. Gladysz, *J. Am. Chem. Soc.*, 103 (1981) 5608.
118. E. Lindner and G. Von Au, *Z. Naturforsch. Teille B*, 35 (1980) 1104.
119. E. Lindner and G. Von Au, *J. Organomet. Chem.*, 202 (1980) 163.
120. E. Lindner and G. Von Au, *Angew. Chem.*, 92 (1980) 843.
121. A. Kececl and D. Rehder, *Z. Naturforsch. Teille B*, 36 (1981) 20.
122. H.W. Choi and E.L. Muetterties, *Bull. Soc. Chim. Belg.*, 89 (1980) 809.
123. M.R. Churchill, K.M. Amoh and H.J. Wasserman, *Inorg. Chem.*, 20 (1981) 1609.
124. R.W. Wegman, R.J. Olsen, D.R. Gard, L.R. Faulkner and T.L. Brown, *J. Am. Chem. Soc.*, 103 (1981) 6089.
125. A. Fox, J. Malito and A. Poe, *J. Chem. Soc. Chem. Commun.*, (1981) 1052.
126. K.A.M. Creber and J.K.S. Wan, *J. Am. Chem. Soc.*, 103 (1981) 2101.
127. T-I Ho, K.A.M. Creber and J.K.S. Wan, *J. Am. Chem. Soc.*, 103 (1981) 6524.
128. G.D. Michels and H.J. Sveck, *Inorg. Chem.* 20 (1981) 3445.
129. A.K. Baev, *Zh. Fiz. Khim.*, 54 (1980) 2169. [*Chem. Abst.*, 93 (1980) 193064].
130. G.K. Magomedov and L.V. Morozova, *Koord. Khim.*, 7 (1981) 381 [*Chem. Abst.*, 94 (1981) 184766].

131. Sh. O. Guseinov, S.F. Karaev and Sh. V. Garaeva, *Azerb. Khim. Zh.*, 5 (1979) 98 [*Chem. Abst.*, 93 (1980) 204734].
132. J.C. Luong, R.A. Faltynek and M.S. Wrighton, *J. Am. Chem. Soc.*, 102 (1980) 7892.
133. G. Sbrignadello, *Inorg. Chim. Acta*, 48 (1981) 237.
134. L.H. Staal, J. Keijsper, G. Van Kotan, K. Vrieze, J.A. Cras and W.P. Bosman, *Inorg. Chem.* 20 (1981) 555.
135. L.H. Staal, J. Keijsper, C.H. Polm and K. Vrieze, *J. Organomet. Chem.*, 204 (1981) 101.
136. J.C. Jeffery, H. Razay and F.G.A. Stone, *J. Chem. Soc., Chem. Commun.*, (1981) 243.
137. J.C. Jeffery, R. Navarno, H. Razay and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1981) 2471.
138. J.C. Green, D.M.P. Mingos and E.A. Seddon, *Inorg. Chem.*, 20 (1981) 2595.
139. J.L. Graff and M.S. Wrighton, *J. Am. Chem. Soc.*, 103 (1981) 2225.
140. G-Y Wei, L. Garlaschelli, R. Bau and T.F. Koetzle, *J. Organomet. Chem.*, 213 (1981) 63.
141. K. Mertis, P.G. Edwards, G. Wilkinson, K.M.A.M. Malik and M.B. Hursthouse, *J. Chem. Soc. Dalton Trans.*, (1981) 705.
142. W. Bronger and M. Spangenberg, *J. Less Common Mets.*, 76 (1980) 73.
143. B.T. Huie, S.W. Kirtley, C.B. Knobler and H-D. Kaesz, *J. Organomet. Chem.*, 213 (1981) 45.
144. G.A. Pearson, *Diss. Abstr. Int. B.*, 41 (1981) 4113.
145. M.R. Churchill, F.J. Hollander, R.A. Lashewycz, G.A. Pearson and J.R. Shapley, *J. Am. Chem. Soc.*, 103 (1981) 2430.
146. M.R. Churchill and F.J. Hollander, *Inorg. Chem.*, 20 (1981) 4124.
147. N.E. Kolobova, I.A. Lobonova, V.I. Zdanovich and P.V. Petrovskii, *Izv. Akad. Nauk. SSSR., Ser. Khim.*, (1981) 935. [*Chem. Abst.*, 95 (1981) 115712].
148. A.R. Middleton and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, (1981) 1898.
149. A.G. Constable and J.A. Gladysz, *J. Organomet. Chem.*, 202 (1980) C21.
150. T.K. Jana, S. Kakshit, P. Bandyopadhyaj and B.K. Sen, *Z. Anorg. Allg. Chem.*, 477 (1981) 229.