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4 RHENIUM

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INTRODUCTION

The period of this review covers those publications in volumes 98 and 99 of Chemical Abstracts. Thus, although the majority of papers covered were

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published in 1983, many from 1982 are also included. The major journals are covered up to the end of 1983.

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.

Six articles of general interest to rhenium chemists have been published this year: the first is a review with 143 references on the coordination chemistry of rhenium and technetium [1]. Another review with 308 references considers the chemistry of the elements of groups 4, 5, 6 and 7, including rhenium [2], while an encyclopaedia entry discusses the physical and chemical properties of rhenium and some of its compounds, with 15 references [3]. A dissertation on the chemistry of octahedral rhenium clusters has also been published [4].

The photochemical activation of monomeric rhenium polyhydride complexes for synthesis and catalysis [5], and the effect of pressure on the luminescence of 3-hydroxyflavone, indole and rhenium complexes [6] were studied.

4.1 RHENIUM(VII)

4.1.1 Oxides and Hydroxides

The structure of Re_2O_7 on alumina at loadings of 5% and 17.5% closely resembled that of crystalline Re_2O_7 [7]. The nature and existence of the interaction between a magnesium oxide support and dispersed rhenium(VII) oxide has been studied by XPES, X-ray diffraction and thermogravimetric analysis, and the effect on XPES peak intensities of several parameters such as surface area, degree of hydration and chemical composition examined. It was concluded that a surface rhenate(VII)-like complex was formed which was not mobile under thermal variations [8].

The results of EPR spectroscopic studies at 4.2 K on irradiated KBr crystals doped with $[ReO_4]^-$ indicated the formation of $[ReO_4]^{2-}$ subjected to an intramolecular Jahn-Teller distortion. Uniaxial stress experiments showed that the rhenate(VI) ion was reoriented locally, and a model based on the approach of O'Brien was proposed to explain the results [9].

The temperature dependence of the spin-lattice and spin-spin relaxation rates of the quadrupolar nucleus in $[ReO_4]^-$ was studied, and it was shown that, for rhenium, the lifetime of the excited state is greater than the correlation time of orientational motion [10]. The matrix IR and Raman spectra of vaporized potassium and caesium rhenate(VII) showed spectra characteristic of the molecular species $MReO_4$ with C_{2v} symmetry. Additional ^{18}O enrichment experiments provided unequivocal assignments for the Re-O vibrational modes, and it was also shown that the bond dipole model led to a useful simulation of relative bond intensities [11].

Extraction compositions and constants were calculated from partition data between aqueous solutions and 0.5 *M* solutions of phosphoryl compounds in tetrachloromethane, by assuming a hydrate-solvate mechanism. Hydrate solvates were formed by tbp (tributylphosphate) and diisopentyl methyl phosphonate, and unhydrated solvates by octyl dioctylphosphinate and trioctylphosphine oxide. The extraction constants increased as the number of extractant molecules in the solvate increase, from $HClO_4$ to $HReO_4$, and in the series from tbp to trioctylphosphine oxide [12].

Distribution constants, extraction constants and slopes of extraction curves of ion-associated complexes of rhenate(VII) with monotetrazolium salts (dimethylthiazolium bromide and iodonitrotetrazolium chloride) and ditetrazolium salts (neotetrazolium chloride and Nitro Blue tetrazolium chloride) were determined spectrophotometrically by estimating the distribution coefficients. These constants characterised the extraction equilibria between the two liquid phases. Association constants were thus calculated [13,14].

The IR and Raman spectra of the crystalline $Ba_{10}(ReO_5)_6(NO_3)_2$ apatite were reported and the vibrational properties of the nitrate ion discussed in depth [15]. The crystal structure of $Ba_5(ReO_5)_3(NO_3)$ was also determined, and reported as being similar to the halide analogues [16].

Reaction of Re_2O_7 with 1,4-dioxane yielded $[Re_2O_6(OH)_2].3C_4H_8O_2$. The unit cell was triclinic and contained dimeric, centrosymmetric $\{Re_2O_6(\mu\text{-}OH)_2\}$ units linked by coordinated 1,4-dioxane, as shown in Fig.1 [17].

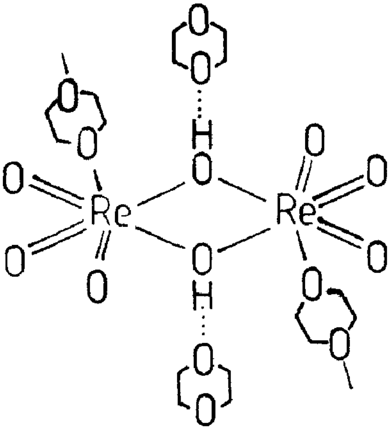


Fig.1: $[Re_2O_6(OH)_2].3C_4H_8O_2$

During an investigation by mass spectrometry into the chlorination of metal oxides, the presence of ReO_3Cl was identified from the appearance of its mass spectrum. Traces of $HReO_4$ were also noted, and when using brominated compounds, ReO_3Br was detected. A mechanism involving reactions with the rhenium filament in the spectrometer was discussed [18].

The rhenium(V) complexes $[ReO_2(py)_4]X$ (X = Cl or ClO_4) were prepared by the reduction of potassium rhenate(VII) by iodide, and subsequent reaction with pyridine in water. The products were fully characterised [19]. Reduction of rhenate(VII) with hydroxylamine in the presence of thiocyanate yielded the complex $[Re(NO)(NCS)_3(H_2O)]^-$ or its derivatives $[Re(NO)(NCS)_2(LL)(H_2O)]$ (LL = 2,2'-bipyridine or 1,10-phenanthroline). Full details of the preparation and characterisation were quoted [20].

4.1.2 Oxohalides

The thermal stability of $CsCl.Cs[ReO_2Cl_4]$ was studied by tensimetry. The decomposition products were identified as CsCl and [ReO_2Cl_3]. Equations were derived, and entropy and enthalpy values calculated [21]. Reaction of caesium rhenate(VII) with caesium chloride in concentrated hydrochloric acid gave crystals of $Cs_2[ReO_3Cl_3]$ which were studied by single crystal X-ray diffraction. The unit cell contained discrete $[ReO_3Cl_3]^{2-}$ anions, which have approximately C_{3v} symmetry. The structure was briefly discussed [22].

4.1.3 Sulfides

Rate constants and activation energies were determined for ReS_2 and Re_2S_7 dissolution in aqueous sodium hydroxide, taking into account differences in surface area. The dissolution mechanisms in the presence of dioxygen involved dioxygen adsorption and subsequent reaction with hydroxide ions to give $\{Re_2O_7(OH)\}^+$ or $\{ReO_2(OH)\}^+$ species along with $[S_2O_2]^{2-}$ (which was oxidised to $[SO_4]^{2-}$). The free energies of formation of ReS_2 and Re_2S_7 correlated with the free energies of dissolution in sodium hydroxide solution [23].

4.1.4 Hydrides

Reaction of $[ReCl_3(NPh)(PMe_3)_2]$ with $Li[AlH_4]$ followed by methanolysis yielded $[ReH_6(NHPh)(PMe_3)_2]$, a nine-coordinate rhenium(VII) hydrido complex. The ^{31}P and ^{1}H NMR spectra and IR spectrum were reported [24].

$[ReH_7(PPh_3)_2]$ reacted with cyclic and acyclic dienes to yield crystalline, air stable rhenium(III) complexes $[ReH_3(PPh_3)_2(\eta^4\text{-diene})]$. NMR spectral studies indicated the majority to be fluxional at room temperature, with a pentagonal bipyramidal structure having apical phosphine groups at low temperature [25].

It was reported that reaction of $[ReH_7(PPh_3)_2]$ with furan in the presence of 3,3-dimethylhex-1-ene yielded a complex of the 4-oxobut-2-enyl ligand, whose structure is shown in Fig.2:

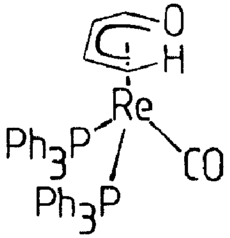


Fig.2: $[Re(PPh_3)_2(CO)(C_4H_5O)]$.

In the reaction, one furan molecule was converted to propene and carbon monoxide, while a second was reduced to the 4-oxobut-2-enyl ligand. The crystal structure was determined, and presented together with IR and NMR spectral data [26]. Reaction between $[ReH_7(PPh_3)_2]$ and the allyl halides C_3H_5X (X = Cl, Br or I) yields the rhenium(IV) complex $[Ph_3PC_3H_5]_2[ReX_6]$, with some propene and dihydrogen. The heptahydrido complex also reacts with 2-chloro-2-methylpropane, tetrachloromethane, trichloromethane, dichloromethane and chlorobenzene to produce *trans*-$[ReCl_4(PPh_3)_2]$. These and other reactions were discussed [27].

4.2 RHENIUM(VI)

An EPR spectral study of $[ReO_4]^{2-}$ in crystalline KCl has shown that a strong, essentially intramolecular, Jahn-Teller effect has occurred. Experiments on uniaxial stress and static electric fields were also carried out [28]. Irradiation at 4.2 K of crystals of KBr doped with rhenate(VII) resulted in the formation of rhenate(VI) ions subjected to a similar Jahn-Teller distortion. A model was proposed to explain the distortions [9].

FANO-type resonances in the 5d conduction band intensity spectra have been observed at ${}^5P_{1/2}$ and ${}^5P_{3/2}$ photoabsorption thresholds for ReO_3. The complex structure of the photoelectron core level 4f spectra for ReO_3 was discussed on the basis of these results [29]. The charge densities in ReO_3 were investigated by X-ray structural analysis. Anisotropic charge distributions around the rhenium atom were attributed to π-bonding between Re(5d) and O(2p) electrons. The results were discussed in detail [30].

The complex anion $[Re_2O_3Cl_8]^{2-}$ was prepared as the tetraphenylarsonium and 2,3,5-triphenyltetrazolium salts. The magnetic, conduction, IR and electronic spectral properties were noted and reported. On the basis of IR spectral data, the authors have assigned a *cis,cis-* configuration to the $\{Re_2O_3\}$ core of the anion, as shown in Fig.3 [31].

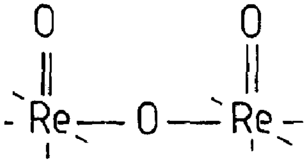


Fig.3: $\{Re_2O_3\}$ core.

The synthesis of the rhenium(V) complex $A_2[ReO(NCS)_4(SCN)]$ (A = $AsPh_4$, PPh_4 or NEt_4) was reported, from $M[ReOCl_5]$ (prepared from $K[ReO_4]$ and ACl) in dichloromethane, and K[SCN] in ethanoic acid [32].

Ultrasonic attenuation in $[ReF_6]$ has been measured at 293K, and a single relaxation process was observed and attributed to the total vibrational energy of the relaxing molecule. The isothermal relaxation time was measured, and the vibrational relaxation time for this and other hexafluorides, which were studied closely, followed the Lambert-Salter correlation [33].

The force constants and Coriolis coupling constants have been evaluated for the octahedral compounds [ReCl$_6$] and [ReBr$_6$] over a range of temperatures up to 1000 K [33a].

It was reported that reaction of rhenium(VI) fluoride with tetramethoxysilane gave [Re(OMe)$_6$] in 80% yield. ^{1}H NMR and IR spectral data were presented [34]. Reaction of rhenium(VI) fluoride with elemental sulfur at 300 °C in stainless steel reactors gave the compound [ReF$_4$S]. The X-ray crystal structure was determined and shown to contain six {ReSF$_5$} octahedra in a *cis*-linked configuration (see Fig.4), with Re-F-Re bridges and terminal Re=S groups [35].

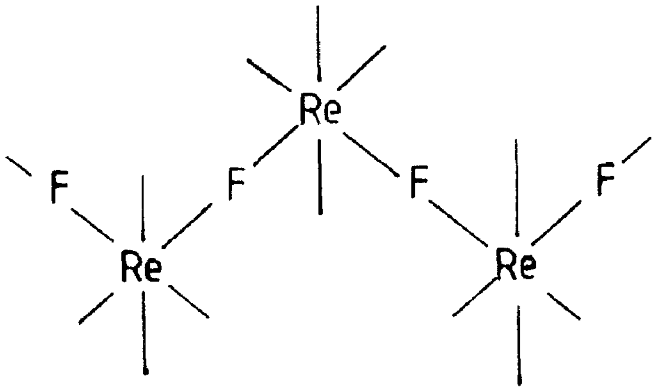


Fig.4: [ReF$_4$S]

The salt [AsPh$_4$][Br$_4$ReN-BBr$_3$] was obtained from [AsPh$_4$][Cl$_4$ReN] and an excess of [BBr$_3$], forming dark violet, moisture sensitive crystals. Thermal cleavage at 210 °C *in vacuo* yielded [AsPh$_4$][Br$_4$ReN]. IR spectra indicated that both anions contain {Re N} groups (1170 and 1099 cm^{-1}, respectively). The crystal structure of [AsPh$_4$][Br$_4$ReN] was determined. The anion [ReNBr$_4$]$^-$ had C_{4v} symmetry and the Re-N bond length was seen to be 0.162nm, corresponding to a triple bond [36].

4.3 RHENIUM(V)

4.3.1 *Oxo and Oxohalo Complexes*

The emission spectroscopic properties of *trans*-$[ReO_2L_4]^n$ (L = CN^-, *n*=-3; L = py, *n*=+1; L = 1/2en, *n*=+1) have been reported, and the spectroscopic data were discussed [37]. The preparations of $[ReO_2(py)_4]X$ (X = Cl or $[ClO_4]$) from potassium rhenate(VII) were reported. Reaction of the rhenate(VII) with potassium iodide in boiling concentrated hydrochloric acid produced $K_2[ReCl_6]$, which was heated with pyridine in water from which the chloride salt $[ReO_2py_4]Cl.2H_2O$ crystallized. Addition of a concentrated solution of sodium chlorate(VII) to a concentrated solution of the chloride yielded the chlorate(VII) salt as a precipitate [19].

The synthesis of $A_2[ReO(NCS)_4(SCN)]$ (A = $AsPh_4$, PPh_4 or NEt_4) was reported from the rhenium(VI) complex $A[ReOCl_5]$ (prepared from $K[ReO_4]$ and ACl) in dichloromethane, and K[SCN] in ethanoic acid. Analytical and magnetic data, molar conductances, electronic and IR spectra were discussed, and supported the formulation $A_2[ReO(NCS)_4(SCN)]$, with one *S*-bonded and four *N*-bonded thiocyanate ligands [32].

Reaction of $[ReOCl_3(PPh_3)_2]$ with an excess of an arylthiolate anion, $[ArS]^-$, followed by addition of tetraphenylphosphonium bromide yielded the salts $[PPh_4][ReO(SAr)_4]$. IR and ^1H NMR spectral data were mentioned, together with some electrochemical measurements. In boiling ethanenitrile, these complexes reacted with an excess of triphenylphosphine to yield the rhenium(III) complexes $[Re(SAr)_3(NCMe)(PPh_3)]$, which could also be prepared from the reaction of the arylthiolate anions with the trichloro derivative. The nitrido complex $[ReNCl_2(PPh_3)_2]$ reacted with an excess of phenylthiolate anion in boiling ethanenitrile to give a solution which, after aerial oxidation, yielded $[Re(NPPh_3)(SPh)_4]$ in 20% yield. The X-ray crystal structure of the complex was determined, and used to help assignment of the IR spectrum: the complex contained the $[Ph_3PN]^{2-}$ ligand [38].

A study of the secondary ion mass spectrometry (SIMS) spectra of rhenium complexes, including [$ReOCl_3(PPh_3)_2$], has shown that it is not possible to differentiate between triphenylphosphine ligands and the corresponding phosphonium ions in these complexes, while it is possible with trialkylphosphines and their phosphonium ions [39].

The structures of [$ReOX_3L_n$] (X = Br or Cl; L = $PPhEt_2$, $OPPhEt_2$, dppe, dmf, OEt or PPh_3) were investigated by X-ray diffraction: the structures of the *cis*- and *trans*- isomers of [$ReOCl_3(PPhEt_2)_2$] were both determined [40]. The rhenium(V) complexes M_2[$ReOCl_5$] (M = K, Rb or Cs) and Cs_2[$ReOBr_5$] were prepared, and the unit cell parameters of the bromide evaluated: the nature of the potassium salt was discussed with reference to its thermal stability [41].

The IR and Raman spectra of solid $K_3[ReO_2(CN)_4]$, $K_3[ReO_2(^{13}CN)_4]$ (99% ^{13}C enriched) and $K_3[Re^{18}O^{16}O(CN)_4]$ (20% ^{18}O enriched) were measured and assignments made for the vibrational frequencies of the D_{4h} ion. Force constants and potential energy distributions were calculated and the results discussed in detail [42].

4.3.2 *Halo Complexes*

The crystal structure of dichlorotris(dimethylphenylphosphino)-nitridorhenium(V) has been determined by single crystal X-ray diffraction. The molecule has distorted octahedral coordination, and the Re-N bond length is 0.1660(8)nm. The structure was discussed with reference to similar rhenium complexes [43].

The sodium amalgam reduction of rhenium(V) chloride in the presence of 1,10-phenanthroline or 2,2′-bipyridine yielded a mixture of products, in contrast to the reduction of the rhenium(IV) complex [$ReCl_4(thf)_2$] [44].

The reaction of rhenium(V) chloride in $POCl_3$ solution with [$(NSCl)_3$] yielded chloronitrenes: a rhenium(IV) complex [$(Cl_3PO)ReCl_4(NSCl)$], (*1*), and a rhenium(III) complex [$(Cl_3PO)ReCl_3(NSCl)_2$], (*2*). Reaction of tetraphenylarsonium chloride with (*1*) gave the rhenium(VI) complex $[AsPh_4][ReNCl_4]$, while reaction with (*2*) gave $[AsPh_4][ReCl_4(NSCl)_2]$, whose crystal structure was determined [45,46]

The reaction of trimethylphosphine with $[Re(NPh)Cl_3(PPh_3)_2]$ yielded $[Re(NPh)Cl_3(PPh_3)(PMe_3)]$. Reduction with sodium amalgam led to a range of rhenium(I) and rhenium(III) products dependent on the atmosphere of the reaction (Ar, N_2, CO, butadiene or H_2); IR and NMR spectral data were presented [47]. The reaction of $[ReCl_3(NPh)(PMe_3)_2]$ with lithium tetrahydroaluminate(III), followed by methanolysis, gave a nine-coordinate rhenium(VII) hydrido complex $[ReH_6(NHPh)(PMe_3)_2]$. The IR and NMR spectra were reported [24].

4.3.3 *Sulfido Complexes*

The five-coordinate anion $[ReS(SCH_2CH_2S)_2]^-$ was prepared from the reaction of potassium hexachlororhenate(IV) with an excess of 1,2-ethanedithiol. Addition of tetraalkylammonium or tetraphenylphosphonium salts produced crystals, and the tetramethylammonium salt was studied by X-ray crystallography. IR spectral and CV data were also presented. The thio anion was also prepared from $[ReCl_4(PPh_3)_2]$ or $[ReCl_2N(PPh_3)_2]$ with 1,2-ethanedithiol. The reaction between $[ReOCl_3(PPh_3)_2]$ and an excess of dithiolate anion produced the analogous oxo complex $[ReO(SCH_2CH_2S)_2]^-$ in 80-90% yield [48]. Potassium hexachlororhenate(IV) was allowed to react with $[MeC(CH_2SH)_3]$ to give, after addition of tetraphenylphosphonium bromide, the complex $[PPh_4][Re\{(SCH_2)_3CMe\}_2]$. Its crystal structure showed that the molecule was almost trigonal prismatic, with a twist angle of only 6°. The interligand sulfur-sulfur distance of 0.283 nm indicated significant sulfur-sulfur interaction, contributing to the stabilisation of the trigonal prismatic geometry. NMR spectral and CV data were quoted [49].

The new rhenium nitrene complexes $[Re(NR)(S_2CNR'_2)_3]$ and $[Re(OR'')(NR)(S_2CNR'_2)_2]$ (R = Me, Ph or $4\text{-}MeC_6H_4$; R′ = Me or Et; R″ = Me or Et) have been prepared from $[ReCl(NR)(S_2CNR'_2)_2]$ with $Tl[S_2CNR'_2]$, $Me_3SiSC(S)NR'_2$ or $Na[OR'']$. IR and NMR spectra suggested that the tris(dithiocarbamato) complexes had *cis*-six-coordinate geometry, with one monodentate dithiocarbamate ligand, and that the two *trans*-isomers of the alkoxy complex were present in solution. A detailed discussion of the complexes was presented. Brown crystals of $[Re(OEt)(4\text{-}MeC_6H_4N)(S_2CNMe_2)_2]$ were grown, and the structure determined at -175°C by X-ray diffraction (Fig.5). The complex was seen to be monomeric, six-coordinate, and to possess a distorted *trans* octahedral geometry. The nitrene ligand was very bent (Re-N-C = 155.5(5)°) with an abnormally long Re-N bond (0.1745(5) nm). The ethoxy group was also bent (Re-O-C = 131.7(4)°) [50].

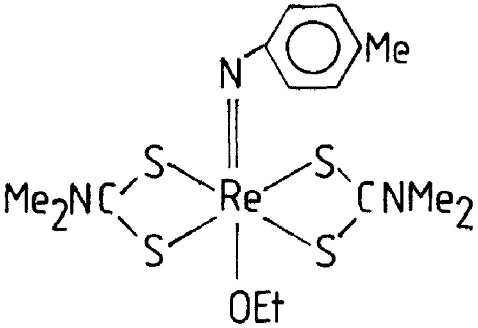


Fig.5: $[Re(OEt)(4\text{-}MeC_6H_4N)(S_2CNMe_2)_2]$.

4.3.4 Complexes of Group 15 Donor Ligands

Dimethylmagnesium reacted with phenylimidotrichlorobis(trimethylphosphine)rhenium(V) to yield the trimethyl compound $[Re(NPh)Me_3(PMe_3)_2]$, and the mono- and di-methylated intermediates have been isolated [51]. The trimethyl complex reacted with tetrafluoroboric acid to yield $[Re(NHPh)Me_2F(PMe_3)_2][BF_4]$, with ethanoic acid to give

$[Re(NPh)Me(O_2CMe)_2(PMe_3)_2]$, and with $[Ph_3C][BF_4]$ to give $[Re(NPh)Me_2(PMe_3)_2][BF_4]$. Reaction of $[Re(NPh)Cl_3(PR_3)_4]$ with bis(trimethylsilylmethyl)magnesium and trimethylphosphine gave $[(Me_3SiCH_2)_3(O)Re(\mu\text{-}O)Re(PMe_3)_4Re(O)_2(CH_2SiMe_3)]$ whose structure was determined, as shown in Fig.6:

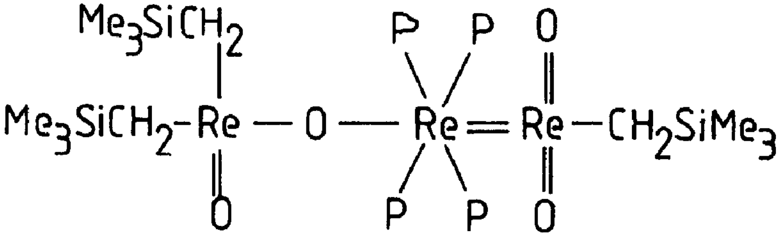


Fig.6: $[(Me_3SiCH_2)_3(O)Re(\mu\text{-}O)Re(PMe_3)_4Re(O)_2(CH_2SiMe_3)]$.

The molecule contained three rhenium atoms, the central atom with four phosphine ligands bonded to a second rhenium atom by a metal-metal bond, and to a third rhenium atom by an asymmetric oxygen bridge [51].

4.3.5 Hydrides

A study of the secondary ion mass spectra of $[ReH_5(PPh_3)_3]$, $[ReH_5(PPh_3)_2(py)]$ and $[ReH_5(PPh_3)_2(PPhEt_2)]$, together with those of other rhenium(V), -(IV) and -(III) complexes, demonstrated that it was possible to differentiate between trialkylphosphine ligands and phosphonium ions in these complexes, while the triphenyl derivatives did not show such a distinction [39].

Reaction between allyl chloride and $[ReH_5(PPh_3)_2(L)]$ ($L = C_6H_{11}NH_2$ or

$C_5H_{10}NH$) gave the rhenium(IV) species $[Ph_3PC_3H_5]_2[ReCl_6]$. It was also reported that treatment of the rhenium(IV) hydride $[Re_2H_8(PPh_3)_4]$ with hydrogen chloride gas in methanol yielded crystals of the mixed salt $[Ph_3PH]_2[Re_2Cl_8].5[Ph_3PH][ReCl_5(PPh_3)]$ [27].

Activation of the rhenium(V) hydride $[ReH_5(PPh_3)_2(L)]$ (L = monodentate ligand), and a rhenium(IV) hydride, has been achieved by protonation using tetrafluoroboric acid, the formation of solvent complexes, and their oxidation to reactive paramagnetic cations; this procedure has produced a range of novel species. Reaction of tetrafluoroboric acid in ethanenitrile with $[ReH_5(PPh_3)_2(py)]$ gave yellow crystals of $[ReH(NCMe)_3(PPh_3)_2(py)][BF_4]_2$, while similar reactions gave $[ReH(NCMe)_3(PPh_3)_2(cychNH_2)][BF_4]_2$ and $[ReH(NCMe)_4(PPh_3)_2][BF_4]_2$. Other novel species that were generated included $[Re_2H_7(PPh_3)_4L]^+$ and $[Re_2H_5(PPh_3)_4(CNCMe_3)_2]^+$, together with their 17-electron congeners. The CV's of many of these complexes were described [52].

Addition of $[Cu(NCMe)_4][PF_6]$ to a cooled solution of $[ReH_5(PMePh_2)_3]$, followed by warming to room temperature, yielded the colourless complex $[\{ReH_5(PMePh_2)_3\}_2Cu][PF_6]$, whose crystal structure was determined (see Fig.7). The copper(I) centre was coordinated octahedrally to six hydride ligands; the rhenium was eight coordinate.

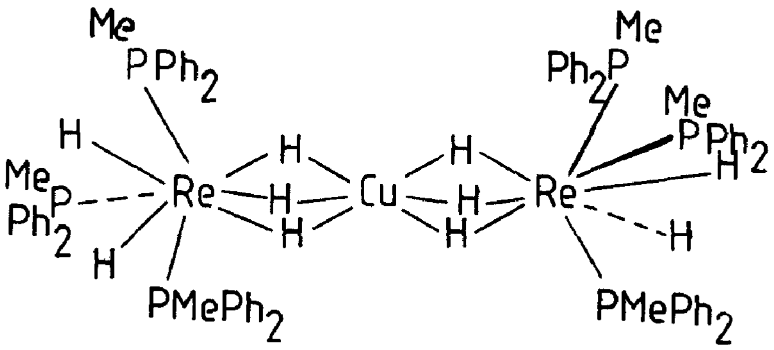


Fig.7: $[\{ReH_5(PMePh_2)_3\}_2Cu][PF_6]$.

In solution, the cation $[\{ReH_5(PMe_2Ph)_3\}_2Cu]^+$, which was similarly prepared, was shown by low temperature ^1H NMR spectroscopy to be consistent with an analogous structure. The reaction of the copper salt with rhenium(IV) hydrides was also studied [53].

4.4 RHENIUM(IV)

The structures of $[ReOX_2L_n]$ (X = Br or Cl; L = $PPhEt_2$, $OPPhEt_2$, dppe, dmf, OEt or PPh_3; *n* = 1 or 2) were studied by X-ray diffraction, and the results discussed with reference to the analogous rhenium(V) complexes [40].

Earlier EPR spectroscopic measurements on rhenium(IV) in $[NH_4]_2[PtCl_6]$ have indicated the presence of non-octahedral centres. An estimation of the degree of distortion of the $\{ReCl_6\}$ complex (required to account for these observations) was made [54]. A theoretical analysis of the spectra of rhenium(IV) $(5d^3)$ in $K_2[PtCl_6]$ was performed by the means of the ligand field method. Also, in the chosen scheme of octahedral symmetry, the energy curves in terms of crystal field and spin-orbit parameters were calculated. The results were in accord with those obtained by the strong field treatment, but some spectral terms which were previously inadequately assigned were corrected [55]. The theoretically calculated vibrational spectra of ammonium derivative salts of $[PtCl_6]^{2-}$ were used for assigning the frequencies in the vibrational spectra of the analogous $[ReCl_6]^{2-}$ salts; the results were discussed [56]. The low temperature tunnelling splittings of reorienting ammonium ions in tetrahedral surroundings have been measured in $[NH_4]_2[ReCl_6]$ with neutron inelastic scattering techniques. The tunnelling splittings in this and other ammonium hexachloro complexes was related to lattice dimensions [57].

The low temperature single crystal absorption spectra of $[ReX_6]^{2-}$ (X = F, Cl or Br) in different $[SnX_6]^{2-}$ host lattices of trigonal symmetry were recorded using polarized light, and band assignments made. Ligand field calculations were performed and indicated that the $[ReX_6]^{2-}$ ions were present as trigonally compressed or expanded species [58].

Reaction of $K_2[ReCl_6]$ with an excess of $MeC(CH_2SH)_3$ yielded a rhenium(V) complex, which was isolated as the tetraphenylphosphonium salt $[Ph_4P][Re\{(SCH_2)_3CMe\}_2]$. The crystal structure was determined and the nature of the trigonal prismatic geometry discussed [49]. The five-coordinate rhenium(V) anion $[ReS(SCH_2CH_2S)_2]^-$ was also prepared from potassium hexachlororhenate(IV) with an excess of 1,2-ethanedithiol, and the tetramethylammonium salt was studied by X-ray crystallography. The thio anion was also prepared from $[ReCl_4(PPh_3)_2]$ with ethanedithiol [48].

Sodium amalgam reduction of $[ReCl_4(thf)_2]$ in the presence of 2,2′-bipyridine or 1,10-phenanthroline gave the complexes $[Re(bipy)_3]$ or $[Re(phen)_3]$ in high yield. Analytical and magnetic moment data were presented [44]. $ReCl_5$ reacted in $POCl_3$ solution with $[(NSCl)_3]$ to form the chloronitrenes $[(Cl_3PO)ReCl_4(NSCl)]$ {(*1*), a rhenium(IV) complex}, and $[(Cl_3PO)ReCl_3(NSCl)_2]$ {(*2*), a rhenium(III) complex}. Complex (*1*) reacted with tetraphenylarsonium chloride in dichloromethane solution to yield the rhenium(VI) species $[Ph_4As][ReNCl_4]$, while under the same conditions complex (*2*) produced a rhenium(III) adduct $[Ph_4As][ReCl_4(NSCl)_2]$, whose crystal structure was determined [45].

The cathodic and anodic behaviour of the rhenium(IV) complex

$[ReCl_4(PMe_2Ph)_2]$ was studied in ethanenitrile at platinum and mercury electrodes. The reduction and oxidation products were identified, and aspects of the mechanisms involved were studied. New rhenium(III) and rhenium(IV) species were detected [59].

Reaction between $[ReH_7(PPh_3)_2]$ and the allyl halides C_3H_5X (X = Cl, Br or I) yielded rhenium(IV) complexes $[Ph_3PC_3H_5]_2[ReX_6]$ with some propene and hydrogen gas; allyl thiocyanate reacted similarly. The hydrides $[ReH_5(PPh_3)_2L]$ (L = cychNH$_2$ or piperidine) were also converted to triphenylallylphosphonium hexachlororhenate(IV) by allyl chloride. However, with $[Re_2H_8(PPh_3)_4]$, the core was preserved with allyl chloride and bromide yielding $[Ph_3PC_3H_5]_2[Re_2X_8]$, while allyl iodide cleaved the metal-metal bond to give the hexaiodorhenate(IV) complex. The rhenium(VII) hydride, $[ReH_7(PPh_3)_2]$, also was shown to react with chlorinated compounds such as the chloromethanes, 2-chloro-2-methylpropane and chlorobenzene, to produce *trans*-$[ReCl_4(PPh_3)_2]$ [27].

The reduction of $[ReCl_4(thf)_2]$ with sodium amalgam in the presence of an excess of trimethylphosphine yielded $[ReCl(PMe_3)_5]$ and $[ReH(PMe_3)_5]$. The hydride reacted slowly with hydrogen gas to form $[ReH_3(PMe_3)_4]$. The reactions of some of these species were reported. Further, reduction of $[ReCl_4(thf)_2]$ with sodium amalgam in the presence of diethylphenylphosphine gave the complex $[ReCl(N_2)(PPhEt_2)_4]$, whose crystal structure was determined and reported [60].

The reaction of $[Cu(MeCN)_4][PF_6]$ with $[Re_2H_8(PMe_2Ph)_4]$ was studied, and an X-ray diffraction study of the crystalline product, $[Re_4Cu_2H_{16}(PMe_2Ph)_8][PF_6]_2$ (see Fig.8), showed that the molecule contained two copper cations and two rhenium dimers [53].

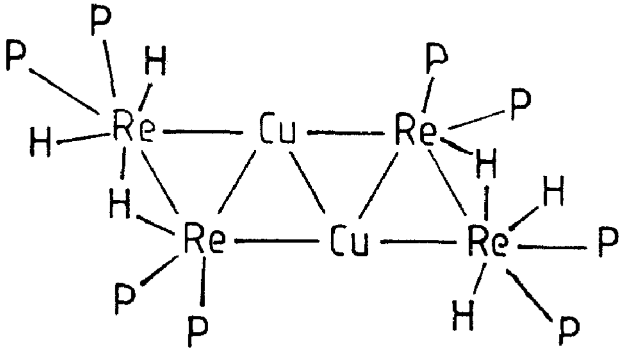


Fig.8: $[Re_4Cu_2H_{16}(PMe_2Ph)_8][PF_6]_2$.

Activation of the rhenium(IV) hydride $[Re_2H_8(PPh_3)_4]$ has been achieved through protonation, the formation of solvento-complexes and oxidation to reactive paramagnetic cations. The cations $[Re_2H_7(PPh_3)_4L]^+$ and $[Re_2H_5(PPh_3)_4(CNCMe_3)_2]^+$ were amongst the novel species generated, together with their "17 electron" congeners. The cyclic voltammogramss of many of these complexes were described [52]. A study of the SIMS spectra of complexes of rhenium, including $[Re_2H_8(PPh_3)_4]$, has shown that, although trialkylphosphine ligands may be differentiated from the respective phosphonium ions, this distinction does not exist for triphenylphosphine complexes [39].

Rate constants and activation energies were determined for ReS_2 dissolution in sodium hydroxide solution. The mechanism in the presence of dioxygen involved dioxygen adsorption and subsequent reaction with hydroxide ions to give $\{ReO_2(OH)\}^+$ along with $[S_2O_3]^{2-}$. The free energy of formation of ReS_2 correlated with the free energy of dissolution [23].

4.5 RHENIUM(III)

The cathodic and anodic behaviour of $[ReCl_3(PMe_2Ph)_3]$ were studied at platinum and mercury electrodes in ethanenitrile. The reduction and oxidation products were identified, and both thermodynamic and kinetic aspects of the mechanisms were studied. New rhenium derivatives, such as $[ReCl_3(PMe_2Ph)_3]^+$ and $[ReCl_3(PMe_2Ph)_2(NCMe)]^+$, were prepared, and their redox chemistry was discussed [59].

A study of the SIMS spectra of complexes of rhenium including $[ReCl_3(PMe_2Ph)_3]$ and $[Re_2Cl_6(PR_3)_2]$ (R = Et or Ph) showed that trialkylphosphine ligands and the respective phosphonium ions could be identified and distinguished, but this was not possible for the triphenyl derivatives [39].

Rhenium(V) chloride reacted in $POCl_3$ solution with $(NSCl)_3$ to form the chloronitrenes $[(Cl_3PO)ReCl_4(NSCl)]$ {(*1*), a rhenium(IV) derivative}, and $[(Cl_3PO)ReCl_3(NSCl)_2]$ {(*2*), a rhenium(III) derivative}. While reaction of (*1*) with tetraphenylarsonium chloride yielded a rhenium(VI) complex, with (*2*) under the same conditions $[Ph_4As][ReCl_4(NSCl)_2].CH_2Cl_2$, (*3*), was formed. IR spectra of all compounds were recorded and assigned, and the X-ray crystal structure of (*3*) was determined.

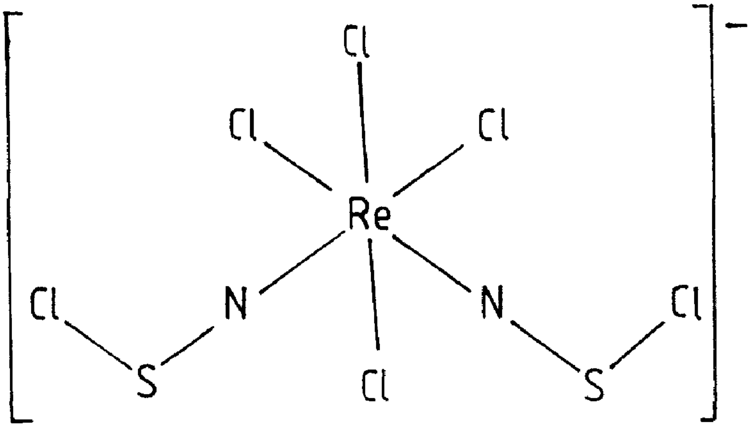


Fig.9: (3).

The two NSCl ligands adopted a *cis* configuration, with nearly linear Re=N=S groups. Reaction of (3) with $GaCl_3$ in dichloromethane generated $[ReCl_3(NSCl)_2]$ [45,46].

The rhenium(III) complex $[ReCl_3(MeCN)(PPh_3)_2]$ was shown to react with arylthiolate anions, $[ArS]^-$, to yield $[Re(SAr)_3(MeCN)(PPh_3)]$. The crystal structure of the phenylthiolate complex was determined. The ethanenitrile ligand was noted as being in a molecular cavity, which was used to explain the ready substitution of this ligand by CO, while molecules which bind "side-on" (such as ethyne) cannot react in this manner. The complex was also prepared by the reduction of $[ReO(SAr)_4]^-$ by triphenylphosphine in boiling ethanenitrile [38].

The electronic spectrum and structure of $[Re_2Cl_8]^{2-}$ have been reinvestigated, and a new SCF-X_α-SW calculation has given results in essential agreement with the earlier reports. However, the inclusion of various corrections has caused notable shifts that are important in analysing the spectrum. The polarised single-crystal spectrum has been remeasured, and the new results have revealed several minor and one major flaw in the earlier work. Revised assignments of the weak, forbidden bands lying between the δ-δ^* transition and the strong near UV absorptions have been made [61].

When allyl chloride or bromide was allowed to react with the rhenium(IV) hydride $[Re_2H_8(PPh_3)_4]$, the core of the molecule was preserved yielding $[Ph_3PC_3H_5]_2[Re_2X_8]$ (X = Cl or Br). However, when allyl iodide was used, the quadruple bond was cleaved and the phosphonium salt of hexaiodorhenate(IV) was formed. Treatment of the rhenium(IV) hydride with hydrogen chloride gas in methanol gave crystals of $[Ph_3PH]_2[Re_2Cl_8].5[Ph_3PH][ReCl_5(PPh_3)]$, a mixed salt whose reactions and properties were discussed [27].

Reaction of $[Bu_4N]_2[Re_2Cl_8]$ with an excess of dppp in boiling ethanenitrile gave $[(dppp)ReCl_2\ ReCl_2(dppp)]$ as a green crystalline solid, whose crystal structure was determined [62]. $[Re(CO)_5Cl]$ was prepared from $[Bu_4N]_2[Re_2Cl_8]$ with carbon monoxide in ethanenitrile, and the crystal structure of the carbonyl determined [63].

The reduction with sodium amalgam of $[Re(NPh)Cl_3(PPh_3)_n(PMe_3)_m]$ (n=0, m=2; n=1, m=1) led to products whose nature depended on the atmosphere of the reaction vessel: the rhenium(III) products included $[ReH(NHPh)(\eta^1\text{-}CH_2PMe_2)(PMe_3)_4]$, $[ReH_2(NHPh)(PMe_3)_4]$ and $[Re(NHPh)Cl_2(PMe_3)_3]$. IR and NMR spectral data were presented [47].

Reduction of $[ReCl_4(thf)_2]$ with sodium amalgam in the presence of trimethylphosphine gave the rhenium(I) hydride $[ReH(PMe_3)_5]$, which slowly reacted with hydrogen gas to form $[ReH_3(PMe_3)_4]$, and the rhenium(I) chloride $[ReCl(PMe_3)_5]$, which reacted with $H[BF_4]$ or $[Ph_3C][BF_4]$ to yield $[ReHCl(PMe_3)_5][BF_4]$. It was also reported that $[Re(NHPh)(N_2)(PMe_3)_4]$ reacted with iodine to yield $[Re(NHPh)I(PMe_3)_4]I$ [60].

Activation of rhenium polyhydrides such as $[ReH_5(PPh_3)_2L]$ (where L is a monodentate ligand) and $[Re_2H_8(PPh_3)_4]$ has been achieved through protonation, the formation of solvento-complexes and their oxidation to reactive paramagnetic cations, and has led to a wide range of novel species. Addition of $H[BF_4]$ to a slurry of $[ReH_5(PPh_3)_2(py)]$ in ethanenitrile gave a yellow solution from which was isolated $[ReH(NCMe)_3(PPh_3)_2(py)][BF_4]_2$. Similar reactions produced $[ReH(NCMe)_3(PPh_3)_2(cychNH_2)][BF_4]_2$ and $[ReH(NCMe)_4(PPh_3)_2][BF_4]_2$. Many other novel complexes were generated, and the cyclic voltammorams of these were described in detail [52].

$[(PPh_3)_2ReH_7]$ reacted with cyclic and acyclic dienes to yield crystalline, air-stable rhenium(III) complexes $[(PPh_3)_2(\eta^4\text{-diene})ReH_3]$. NMR spectral studies indicated the majority to be fluxional at room temperature, with a pentagonal bipyramidal structure having apical phosphine groups at low temperature. The complex $[(PPh_3)_2(\eta^4\text{-cyclopentadiene})ReH_3]$ lost hydrogen to form $[(PPh_3)_2Re(cp)H_2]$, while other complexes were more thermally stable to such reactions: the cyclohexa-1,3-diene complex lost hydrogen at >100°C to yield initially the (cyclohexadienyl)dihydridorhenium(III) complex and then the (η^6-benzene)hydridorhenium(I) complex. Protonation of the trihydrido complexes with trifluoroethanoic acid gave saturated hydrocarbons and/or alkenes [25].

4.6 RHENIUM(II)

The emission spectrum of ReO in the range 375-870 nm has been studied, and the rotational constants calculated [64].

Reaction between $[Bu_4N]_2[Re_2Cl_8]$ and an excess of dppp in boiling ethanenitrile gave $[(dppp)ReCl_2\ ReCl_2(dppp)]$ as a green crystalline solid. The molecule has virtual C_{2h} symmetry. When compared to $[Re_2X_4(PR_3)_4]$, the metal-ligand distances {r(Re-Re):0.2266nm, r(Re-Cl):0.2392nm, r(Re-P):0.2401nm} showed the existence of a structural *trans* effect in the $\{ReCl_2P_2\}$ unit [62].

4.7 LOW OXIDATION STATES OF RHENIUM AND CARBONYL COMPLEXES

4.7.1 Rhenium(I) and Rhenium(0)

The sodium amalgam reduction of rhenium(V) chloride in the presence of 1,10-phenanthroline or 2,2′-bipyridine yielded a mixture of products, but when $[ReCl_4(thf)_2]$ was similarly reduced, the complexes $[Re(bipy)_3]$ and $[Re(phen)_3]$ were formed in high yield. Analytical and magnetic moment data were presented

[44]. A dissertation has been published on excited state decay processes in rhenium(I) polypyridine complexes [65].

The complexes *mer*-$[ReCl(N_2)(CNMe)\{P(OMe)_3\}_3]$, (4), and $[ReCl(N_2)(CNMe)(PPh_3)\{P(OEt)_3\}_2]$, (5), were prepared by the reaction of MeNC with $[ReCl_2(NNCOPh)L_3]$ (L_3 = $\{P(OMe)_3\}_3$ or $(PPh_3).\{P(OEt)_3\}_2$). Reaction of $[ReCl_2(NNCOPh)(PPh_3)_2]$ with trimethylphosphite yielded *mer*-$[ReCl(N_2)(PPh_3)\{P(OMe)_3\}_3]$. The structure of complex (4) was authenticated by X-ray crystallography [66].

Resonance Raman spectra were recorded for the rhenium(I) complexes $[Cl(PPhMe_2)_4Re(N_2)A]$ (A = $\{TiCl_4(thf)\}$, $\{MoCl_4(OMe)\}$ or $\{CrCl_3(thf)_2\}$). The observed lines were associated with the $\{ReN_2M\}$ group, and the results were discussed in great detail [67]. The electronic and vibrational spectra of the complex $[\{Cl(PMe_2Ph)_4Re(N_2)\}_2MoCl_4]$ have also been studied in detail. The Raman spectra were recorded with a variety of exciting lines, and were found to be enhanced in the vicinity of the intense absorption bands in the visible region, in particular for the bands at 1818, 689 and 290 cm^{-1}, attributed to the $\nu_1(a_{1g})$ $\{\nu(NN)\}$; $\nu_2(a_{1g})$ $\{\nu(MN)\}$ and $\nu_5(a_{1g})$ $\{\nu(ReCl)\}$ fundamentals. Raman band excitation profiles for many a_{1g} bands, and approximate force-constant calculations, have been coordinated with a proposed molecular orbital scheme for the linear skeleton. The resonant electronic bands were assigned to transitions of the linear chain [68].

The reaction of $[Re(NPh)Cl_3(PPh_3)_2]$ with trimethylphosphine yielded two rhenium(V) complexes which, when reduced with sodium amalgam, led to rhenium(III) and rhenium(I) products whose formulation depended on the atmosphere of the reaction (argon, dinitrogen, carbon monoxide, butadiene or dihydrogen). Rhenium(I) products included $[Re(NHPh)(N_2)(PMe_3)_4]$, $[Re(NHPh)(CO)_2(PMe_3)_3]$, $[Re(NHPh)(CO)_3(PMe_3)_2]$ and $[Re(NHPh)(\eta^4\text{-}C_4H_6)(PMe_3)_3]$. Crystal structures were presented for the first and last of these complexes. IR and NMR data were also quoted [47].

The reduction of $[ReCl_4(thf)_2]$ with sodium amalgam in the presence of trimethylphosphine yielded [ReH(PMe$_3$)$_5$] and [ReCl(PMe$_3$)$_5$]. The hydride reacted slowly with dihydrogen to form the rhenium(III) complex [ReH$_3$(PMe$_3$)$_4$], while the chloride reacted with tetrafluoroboric acid or trityl tetrafluoroborate to form [ReHCl(PMe$_3$)$_5$][BF$_4$]. In methanol, the chloride reacted with dinitrogen, forming [Re(N$_2$)(PMe$_3$)$_5$]Cl.MeOH, while in the absence of dinitrogen, a white crystalline solid is formed reported to be [Re(PMe$_3$)$_5$]Cl. Methylation of the chloride with methyllithium yielded [ReMe(PMe$_3$)$_5$], the reaction with carbon monoxide produced [ReCl(CO)$_2$(PMe$_3$)$_3$] and the reaction with phenylethyne at 110°C yielded a dimeric complex of the ligand, shown in Fig.10:

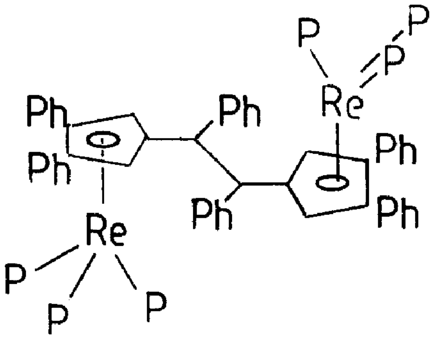


Fig.10: [({Re(PMe$_3$)$_3$(η^5C$_5$H$_2$Ph$_2$)}$_2$CHPh)$_2$].

The crystal structure of the [{(Re(PMe$_3$)$_3$$\eta^5$-C$_5H_2Ph_2$)CHPh}$_2$] was reported. Reduction of [ReCl$_4$(thf)$_2$] by sodium amalgam in the presence of diethylphenylphosphine gave the complex [ReCl(N$_2$)(PPhEt$_2$)$_4$] (whose crystal structure was reported), along with a trace of the hydride analogue. [Re(NHPh)(N$_2$)(PMe$_3$)$_4$] was also reported to react with tetrafluoroboric acid to give [Re(N$_2$)(PMe$_3$)$_5$]$^+$. Reaction with carbon dioxide produced [Re(NHPh)(η^2-CO$_2$)(PMe$_3$)$_3$], which was characterised by IR and NMR spectral techniques. The synthesis of [Re(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)], and its reactions with dihydrogen and methyl iodide, were also reported [60].

4.7.2 Carbonyl Complexes

The IR spectra of [$Re_2(CO)_{10}$] were measured in the carbonyl stretching region in the gas phase and seventy-four solvents. Comparisons with similar studies for [$Mn_2(CO)_{10}$] indicated that in the rhenium complex, there is a stronger metal-metal bond and greater double-bond character in the axial carbonyl groups [69]. Raman spectra of polycrystalline samples of [$Re_2(CO)_{10}$], [$Mn_2(CO)_{10}$] and various mixtures thereof, were recorded at 123-296 K in the range 10-170 cm^{-1} [70].

It was reported that [$MnRe(CO)_{10}$] underwent two first-order phase transitions under hydrostatic pressures, at ca7 and ca13 kbar. These transitions were followed by Raman spectroscopy and interpreted in terms of a change of molecular geometry from staggered to eclipsed, and back to staggered [71].

The reaction of dirhenium decacarbonyl with dimanganese decacarbonyl at 170-190 °C in decalin was studied. Two mechanisms were identified with the major pathway involving prior aggregation to $Mn_2Re_2(CO)_{20}$, which then underwent stepwise loss of CO to $Mn_2Re_2(CO)_{20-n}$ clusters (n = 1-4). These clusters were *quasi*-tetrahedral, with one Mn-Mn and one Re-Re bond, n Mn-Re bonds and (4-n) Mn(μCO)Re bonds. CO insertion or M-M bond redistribution led to $Mn_2Re_2(CO)_{20}$ containing two Mn-Re bonds, and fragmentation produced [$MnRe(CO)_{10}$]. Thermodynamic data were presented [72]. The mechanisms of the substitution reactions of [$Re_2(CO)_{10}$] were examined, using ^{185}Re and ^{187}Re isotopes in combination with crossover experiments to probe for fragmentation in thermal and photochemical substitution reactions. ^{13}CO-^{12}CO interchange was studied, as well as the thermal reaction of dirhenium decacarbonyl with triphenylphosphine under a pressure of CO. No crossover was detectable for [$Re_2(CO)_{10}$] or [$Re_2(CO)_8(PPh_3)_2$], indicating that substitution proceeded without fragmentation of the dirhenium core. In the absence of a CO atmosphere, ^{185}Re/^{187}Re interchange was almost complete at 150 °C within fourteen to sixteen half-lives. Photochemical reactions led to complete crossover with short reaction times. The mechanisms of thermal and photochemical substitution were discussed [73]. Unlike the dimanganese analogue, dirhenium and manganeserhenium decacarbonyl did not undergo appreciable ligand substitution under ultrasonic irradiation. However, rapid sonochemical halogenation did occur, with halocarbon solvents generating halogen atoms, which could be trapped by $[Re_2(CO)_{10}]$, and organic radicals, which have been characterised as dimers [74].

The state of rhenium was studied in catalysts prepared by the deposition of $[Re_2(CO)_{10}]$ on γ-Al_2O_3 which involved a reaction of Lewis acid centres and hydroxyl groups on the support. The low oxidation state rhenium ions formed on the catalyst surface due to thermal degradation. On subsequent adsorption of dioxygen at room temperature, a significant concentration became reduced to superoxide. At 570 K the adsorption led to oxidation of the rhenium to rhenium(VII), which resisted reduction with dihydrogen to metallic rhenium at 770 K [75].

4.7.3 Carbonyl Halo Complexes

The X-ray crystal structure of $[Re(CO)_5Cl]$, prepared from the reaction of $[NBu_4]_2[Re_2Cl_8]$ with CO in ethanenitrile, was determined. The molecule has approximately C_{4v} symmetry, with a strictly linear Cl-Re-C-O chain. The equatorial carbonyl ligands were bent away from the axial carbonyl by about 1°. The axial Re-CO bond length (0.1912 nm) was significantly shorter than the equatorial bond lengths (0.2005 - 0.2031nm) [63].

The AC electrolysis of the complex $[Re(trans\text{-}sp)_2(CO)_3Cl]$ (sp = 4-styrylpyridine) in ethanenitrile in an undivided electrochemical cell converted *trans*-sp into *cis*-sp in the coordinated state. It was suggested that the reaction proceeds *via* an electrochemically excited state of the complex, generated by a cation-anion annihilation process [76].

Raman spectral data were reported for *fac*-$[ReX(CO)_3(bipy)]$ (X = Cl or

Br) in their lowest electronic excited state, and the spectra compared to those for $[Ru(bipy)_3]^{2+}$ [77].

Efficient photogeneration of CO occurred on visible light irradiation of carbon dioxide solutions in triethanolamine-dmf containing $[ReX(bipy)(CO)_3]$ (X = Cl or Br). The mechanism was thought to proceed *via* an excited rhenium(I) species, and to also involve carbon dioxide coordinated to the metal, with possible loss of halide affording the free coordination site [78].

It was reported that treatment of $[ReBr(CO)_5]$ with $Ag[CH(SO_2F)_2]$ gave $[Re(CO)_5\{CH(SO_2F)_2\}]$ [79]. Heating $[ReBr(CO)_5]$ with 1,3,5-trimethylbenzene in boiling nonane for three hours gave, in 80% yield, $[(Me_3C_6H_3)Re(CO)_3]^+[Re_2(CO)_6Br_3]^-$. In the absence of 1,3,5-trimethylbenzene, heating $[ReBr(CO)_5]$ in boiling nonane for five hours under argon yielded $[Re_6(CO)_{14}Br]$ [80].

The novel ligand tri-CN (1,3,5-tris-{2-cyanophenyl}benzene) has been synthesised and used to prepare [Re(CO)$_3$(tri-CN)Br], where the ligand acts in a bidentate mode, and [Re(CO)$_3$(tri-CN)][PF$_6$], where it acts in a tridentate mode. Synthetic and spectral data were reported [81]. The synthesis and structure were reported for *fac*-[Re(CO)$_3$Br(bpnp)] (bpnp = 2,7-bis{2'-pyridyl}-1,8-naphthyridine), along with electrochemical, IR and electronic spectral data. The crystal structure (see Fig.11) was discussed, noting the bidentate nature of the bpnp ligand [82].

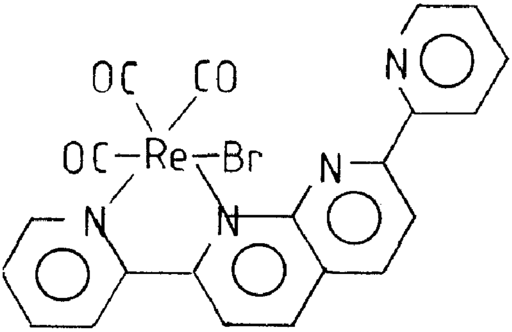


Fig.11: *fac*-[Re(CO)$_3$Br(bpnp)].

The crystal structure of the rhenium(I) complex [Re(CO)$_3$Br(S$_2$CCMe$_2$PPh$_3$)], as shown in Fig.12, has been determined at −110 °C. The complex decomposed at room temperature, with loss of triphenylphosphine [83].

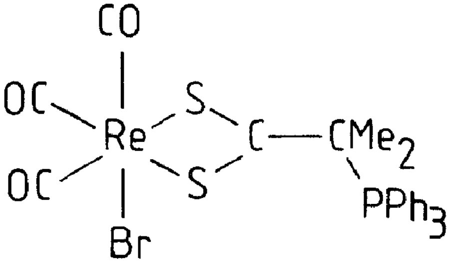


Fig.12: [Re(CO)$_3$Br(S$_2$CCMe$_2$PPh$_3$)].

The reactions of the unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ with iodine in various solvents has been investigated. While in donor solvents such as ethanol, the only product was the anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}I)(CO)_{10}]^-$, in dichloromethane and similar solvents the reaction yielded hydrogen gas and mixtures of products dependent on the quantity of iodine used. The process implied stepwise degradation with substitution of bridging hydride groups by bridging iodide groups, leading eventually to $[Re_2(\mu-I)_3(CO)_6]^-$ and $[Re_2(\mu-I)_2(CO)_8]$. The intermediate products have been identified, and all species were characterized by spectroscopic methods. The crystal structures of $[Re_3(\mu-H)_2(\mu-I)_2(CO)_{10}]^-$, (6), and $[Re_2(\mu-H)(\mu-I)(CO)_6]^-$, (7), have been determined. In (6), there was an open trimetallic array, with the terminal rhenium atoms bridged by iodine, while in (7), the molecule had idealised C_{2v} symmetry, and the rhenium atoms displayed almost octahedral coordination. The Re-Re distance of 0.2954nm indicated a metal-metal bond, unknown in other $Re(\mu-X)_3Re$ systems. An Re-Re bond was also postulated for $[Re_2(\mu-H)(\mu-I)(CO)_8]$ [84].

4.7.4 *Carbonyl Complexes containing Hydrido Ligands*

The complex $[Re(cp)(CO)_2H_2]$ was prepard from the photolytic reaction of $[Re(CO)_3(cp)]$ with diethylsilane, followed by treatment with silica gel in trichloromethane. The compound was characterized by spectroscopic techniques. Deprotonation with ethanolic potassium hydroxide yielded $[Re(cp)(CO)_2]^{2-}$, isolated as its tetraethylammonium salt. The dihydride was used to prepare $[Re(cp)(CO)_2(SnCl_3)H]$, $[Re(cp)(CO)_2(SnMe_3)_2]$, $[Re(cp)(CO)_2Me_2]$ and $[Re(cp)(CO)_2(1,2-\eta^2-C_7H_8)]$. IR spectroscopy was used to study the stereochemistry of these complexes. The dianion was also allowed to react with ethanoyl chloride to yield $[Re(cp)(CO)_2(\eta^2$-ethenyl ethanoate$)]$. A mechanistic sequence was suggested for this latter reaction [85]. It was reported that reaction of $[Re(cp)(CO)_2H_2]$ with potassium hydroxide or ethoxide in ethanol gave the anion $[Re(cp)(CO)_2H]^-$ as the potassium salt. Spectral and analytical data were presented. The anion reacted with iodomethane to form $[Re(cp)(CO)_2(H)Me]$. Reaction of the dihydride with 1,4-diiodobutane in thf solution in the presence of 1,8-diazabicyclo-[5,4,0]-undec-7-ene yielded the metallocycle (8), shown in Fig.13:

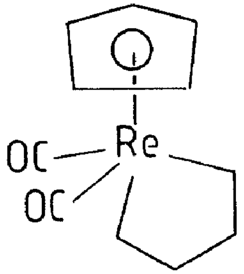


Fig.13: (*8*).

as yellow air-stable crystals; IR, NMR, mass spectral, and analytical data were presented. Thermolysis of the rhenacyclopentane gave methylcyclopropane in 40% yield. A mechanism to account for this was discussed [86].

The X-ray crystal structure of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}NC_5H_4)]$, (*9*), has been determined. The molecule contains a hydride-bridged rhenium-rhenium single-bond, and a bridging orthometallated pyridyl group. Reaction of this complex with trimethylamine *N*-oxide yielded $[Re_2(CO)_7(\mu\text{-}H)(\mu\text{-}NC_5H_4)(NMe_3)]$, (*10*), which reacted with an excess of trimethylamine *N*-oxide to produce $[Re_2(CO)_7(\mu\text{-}H)(\mu\text{-}NC_5H_4)(ONMe_3)]$, (*11*), the crystal structure of which was shown to be analogous to that of (*9*) with the amine oxide bonded to the same rhenium atom as the pyridyl-*N*. The reactions of (*9*) with ligands under various conditions have been studied, and the spectral data quoted and discussed for all complexes prepared [87].

The complex $[Re_3(\mu\text{-}H)_3(CO)_8\{(EtO)_2POP(OEt)_2\}_2]$ has been studied by X-ray crystallography and neutron diffraction, and the structure (see Fig.14) was discussed. The molecule has C_2 symmetry, with a $\{Re_3\}$ triangle bridged in the same plane on all sides by hydride ligands. The chelating phosphines bridge two of the Re-Re bonds, on opposite sides of the plane of the rhenium atoms, while the carbonyl ligands are all bonded terminally to the rhenium atoms [88].

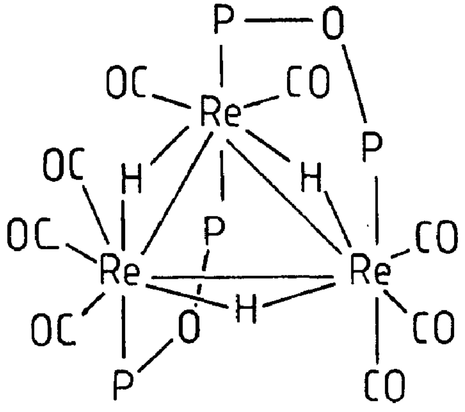


Fig.14: $[Re_3(\mu\text{-}H)_3(CO)_8\{(EtO)_2POP(OEt)_2\}_2]$.

It was reported that $[ReH_7(PPh_3)_2]$ reacted with furan in the presence of 3,3-dimethylhex-1-ene, to form a complex of the 4-oxobut-2-enyl ligand, whose structure was shown earlier, in Fig.2. In the reaction, one furan molecule was converted to propene and carbon monoxide, while a second furan molecule was reduced to the 4-oxobut-2-enyl ligand. The X-ray crystal structure was determined, and presented together with IR and NMR spectral data; a reaction mechanism was proposed [26].

4.7.5 Carbonyl Complexes with Other Ligands

The photochemically induced reactions of dirhenium decacarbonyl in thf solution with nitrogen oxide, cyclooctatetraene and 1,3-butadiene were studied. Reaction with NO yielded $[Re_3(CO)_{15}(OH)]$ and $[Re_3(CO)_{14}(NO_2)]$, and crystal structures were determined for these compounds. UV irradiation of mixtures of the carbonyl with cyclooctatetraene or 1,3-butadiene yielded the 2,5-dihydrofuran-dirhenium octacarbonyl complex. Cyclooctatetraene was cleaved in the reaction forming two 1,3-butadiene fragments. The known butadiene-bridged dimer $[Re(CO)_4(C_4H_6)Re(CO)_4]$ was obtained [89].

The influence of paramagnetic ligands on the mobility of carbonyl groups was studied by the kinetics of ligand substitution in (1,2-quinone)tetracarbonylrhenium [90]. Electronic absorption spectra were studied for a series of rhenium and manganese 1,2-semiquinone complexes and compared to the spectra of the ligand anion radical. The high degree of similarity between the two spectra was interpreted in terms of highly polar metal-oxygen bonds. The bonding of the second oxygen atom to the metal resulted in a substantial hypsochromic shift due to exchange interactions between the orbitals of the metal and ligand. The results were consistent with the EPR spectra of the complexes [91].

The first full optical characterisation of the tetracarbonyl(3,5-$(CMe_3)_2$-1,2-quinone)rhenium radical, $[Re(CO)_4(dtbq)]^{\cdot}$, was reported. The fluorescence lifetime and quantum yield in solution were determined [92]. Organorhenium radical complexes have been studied by CIDEP and EPR-HPLC techniques. The spin-trapping of rhenium carbonyl fragments by 1,2-quinones, 1,2-diketones and some nitrogen donor ligands was reported, together with HPLC and EPR spectral data. It was also possible to prepare optically active organorhenium radical adducts, such as $[(dtbq)Re(CO)_3\{(+)\text{-diop}\}]$ and $[(dtbq)Re(CO)_3\{(-)\text{-diop}\}]$ [93].

The complexes $[Re_2(CO)_{10-n}(RCN)_n]$ (R = Me, Et, Pr or $CHMe_2$) were prepared *via* (triethylamine *N*-oxide)-assisted reaction of dirhenium decacarbonyl with the cyanoalkane. The complexes were characterised by IR and NMR spectroscopy and mass spectrometry. The cyanoalkane ligands preferentially occupied equatorial sites, although some minor axial substitution occurred with the bulkier ligands. The ligands were not displaced by nucleophiles under mild conditions [94].

The reactions of *eq*-$[Re_2(CO)_9L]$ and of 1,2-*eq*,*eq*-$[Re_2(CO)_8L_2]$ under sunlamp irradiation have been studied. 1,2-*eq*,*eq*-$[Re_2(CO)_8(NCMe)_2]$ was observed as the primary product from the continuous photolysis of *eq*-$[Re_2(CO)_9(NCMe)]$. Traces of water in the solvent led to some formation of $[Re_4(CO)_{12}(OH)_4]$. Photolysis of the pyridine complexes yielded dirhenium decacarbonyl, $[Re(CO)_3(py)_3]^+$, $[HRe_4(CO)_{16}]^-$ and $[Re_2(\mu\text{-}H)(CO)_7(\mu\text{-}NC_5H_4)]$. Photolysis of the amine derivatives yielded the decacarbonyl and 1,1-$[Re_2(CO)_8(RNH_2)_2]$. Mechanisms for these reactions were proposed, involving initial metal-metal bond cleavage followed by ligand dissociation [95].

The complexes $[(bipy)Re(CO)_3L]^{2+}$ have been prepared and a report was made on the appearance of a low energy vibrational progression in the emission spectrum, the appearance of a short-lived MLCT fluorescence emission and an intramolecular electron-transfer quenching mechanism [96].

The crystal structure of *trans*-bis(triphenylphosphine)-dicarbonyl(1,3-diphenylformamidino)rhenium(I) has been determined. The rhenium atom had approximate octahedral coordination, and the formamidino ligand was coordinated through both nitrogen atoms [97].

The complexes $[Re(CO)_2L(PR_3)_2]$ (L = *N*-methylsalicylideneiminate, *N*-phenylsalicylideneiminate, 1/2 *N,N'*-ethylenebis{salicylideneiminate} or 8-hydroxyquinolinate; PR_3 = PPh_3 or PMe_2Ph) were prepared from the $[ReCl(CO)_3(PR_3)_2]$ complexes, and characterised by IR and NMR spectroscopy. The products were reported to have *cis* carbonyls and *trans* phosphine groups on the basis of the spectral evidence. A mechanism was postulated [98].

It was shown that there is a direct relationship between $\ln(k_{nr})$ (k_{nr} is the nonradiative decay rate constant) and E_{em} (the emission energy) for MLCT excited states in the series *fac*-$[Re(bipy)(CO)_3L][PF_6]$ (L = PMe_3, CO, MeCN, 4-Etpy, py, *N*-Meimid, 4-NH_2py or 4-(NMe_2)py) [99]. The heats of formation of the adducts formed between $[Re(cp)(CO)_3]$ and $AlBr_3$ or $GaCl_3$ have been measured [100].

The reaction of $[(CO)_5Re(NSF)][AsF_6]$ with dimethyl(trimethylsilyl)amine yielded the thiazylamide complex $[(CO)_5Re(NSNMe_2)][AsF_6]$, whose crystal structure was determined (Fig.15):

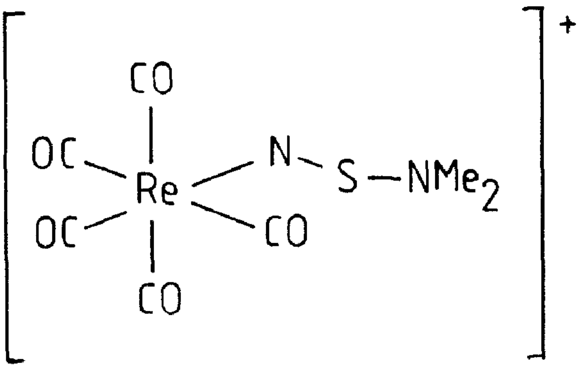


Fig.15: $[(CO)_5Re(NSNMe_2)][AsF_6]$.

The Re-N-S angle of 130 ° was considerably smaller than found in other thiazyl derivatives. The reaction of methylbis(trimethylsilyl)amine with $[(CO)_5Re(NSF)][AsF_6]$ yielded the bridged dimeric complex $[(CO)_5Re(NSN\{Me\}SN)Re(CO)_5][AsF_6]_2$ [101].

The preparation was reported of the thionylimide complex $[Re(CO)_5(HNSO)][AsF_6]$ by two different routes: reaction of the SO_2 adduct $[Re(CO)_5(SO_2)]^+$ with an excess of preformed HNSO yielded the product quantitatively. The NSF adduct $[Re(CO)_5(NSF)]^+$ was hydrolysed in SO_2 solution with Me_3SnOH, and removal of the insoluble trimethyltin fluoride yielded the thionylimide adduct. Elemental analysis, IR and Raman spectral data were quoted [102]. It was reported that reaction of $[Re(CO)_5(NSF)][AsF_6]$ with fluoro Lewis acids, such as AsF_5, yielded the $[Re(CO)_5(NS)]^{2+}$ cation. Its preparation from bromopentacarbonylrhenium(I) and $[NS][SbF_6]$ was also noted. IR spectral data were quoted [103].

The complexes $[Re(CO)_4\{R'NC(R)NR'\}]$, (*12*); (R = Me or Ph, R' = Ph or Me-4-C_6H_4) containing bidentate *N,N'*-chelated amidino groups, have been prepared by four reactions:

(a) $[\{Re(CO)_4X\}_2]$ with R'N(Li)C(R)NR',

(b) $[Re(CO)_4\{R'NC(R)NHR'\}X]$ with butyllithium,

(c) $[Re_2(CO)_{10}]$ with R'NHC(R)NR' or

(d) decarbonylation of $[Re(CO)_4\{OCN(R')C(R)NR'\}]$.

Triphenylphosphine displaced CO from (*12*) to form $[Re(CO)_3L\{R'NC(R)NR'\}]$, (*13*); ($L = PPh_3$), which was also formed from $[Re(CO)_4LBr]$ ($L = PPh_3$ or $AsPh_3$) and the amidine. When a trisubstituted amidine $R'NC(R)N(Me)R'$ was used, the reaction stopped at $[Re(CO)_3(PPh_3)\{R'NC(R)N(Me)R'\}Br]$. Treatment of (*13*) with aqueous hydrobromic acid yielded $[Re(CO)_3(PPh_3)\{R'NC(R)NHR'\}Br]$. $[Re(CO)_5X]$ (X = Cl or Br) or $[\{Re(CO)_4Br\}_2]$ reacted with amidines to form orthometallated species which contained a six-membered orthometallated ring. Benzamidines also produced an orthometallated complex in which the R-substituent was involved in a five-membered ring. Intermediate complexes $[Re(CO)_3\{R'NC(R)NHR'\}_2X]$ (R = Me, R' = Me-4-C_6H_4, X = Cl or Br) were isolated. Reaction schemes were suggested for the course of the reactions, and structures for the new complexes were proposed on the basis of spectroscopic data [104].

$[Mo(cp)(CO)_2(\mu\text{-}NNC_6H_4Me)Re(CO)_2(cp)]$ has been synthesized from $[Mo(cp)(CO)_2(\mu\text{-}NNC_6H_4Me)]$ and $[Re(cp)(CO)_2(thf)]$, and its crystal structure determined (Fig.16). The Mo-N-N group was almost linear {177.7(4) °} while the Re-N-N group was bent {118.9(3) °}, and the N-N-C angle was 113.5(4) °. Spectral data were also quoted [105].

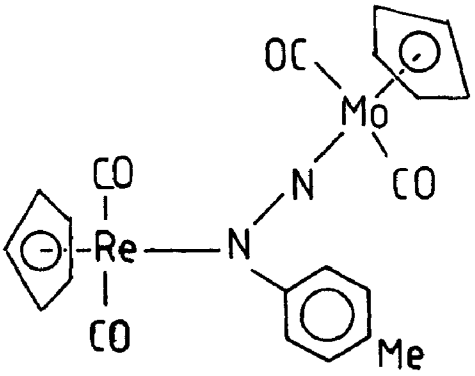
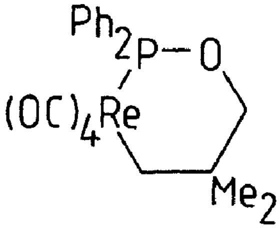


Fig.16: $[Mo(cp)(CO)_2(\mu\text{-}NNC_6H_4Me)Re(CO)_2(cp)]$.

Reaction of sulfur dioxide with (*14*) at -40°C gave (*15*), shown in

Fig.17. The X-ray analysis of *(15)* was described. Carbon monoxide substitution was afforded with the Lewis acid AlBr$_3$ to yield *(16)* [106].



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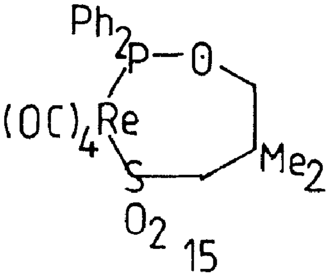

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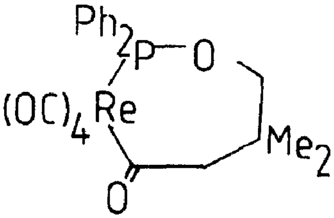

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Fig.17: *(14)*, *(15)* and *(16)*.

It was reported that, when [Fe(cp)(CO)$_2$C(=S){SRe(CO)$_5$}] (prepared from [Fe(cp)(CO)$_2$CS$_2$]$^-$ with [Re(CO)$_5$Br] at -78 °C), was allowed to react with CH$_3$SO$_3$CF$_3$, methylation of the (C=S) group occurred to yield the dithiocarbene [(cp)(CO)$_2$FeC(SMe){SRe(CO)$_5$}] [107].

A crystal structure determination of the complex tetracarbonyl-[1-(*N,N'*-dimethylaminomethyl)-7-phenyl-*m*-carboranyl-*B,N*]rhenium showed the unit cell to be monoclinic: the atomic parameters and bond lengths and angles were given. The rhenium was octahedrally bonded to the C(8)-bonded boron atom, the C(7)-bonded nitrogen atom and the four carbonyl carbon atoms, with the Re-B bond *trans* to a Re-CO bond [108]. The crystal structure of tetracarbonyl-(1-isopropyl-2-phenylazo-*o*-carboranyl-*B,N*)rhenium was also determined. The unit cell was monoclinic with two independent molecules in the unit cell [109].

4.7.6 Organometallic Complexes

The electron spin resonance and optical rotation of organometallic rhenium radical complexes have been studied [110].

The photochemistries of $[Re(cp)_2H]$, *(17)*, $[Re(cp)(CO)_3]$, *(18)*, and $[Re(cp)(\eta^2\text{-}C_5H_6)(CO)_2]$, *(19)* have been examined in low temperature matrices. *(17)* reacted by loss of the hydrogen atom, or by partial decoordination of the cyclopentadienyl ligand and addition of a ligand L to form $[Re(cp)(\eta^3\text{-}cp)LH]$ {L = CO, *(20)* or N_2, *(21)*}. Photolysis of *(18)* yielded $[Re(cp)(CO)_2]$, *(22)*, *reversibly in argon matrices, and* $[Re(cp)(CO)_2(N_2)]$, *(23)*, *irreversibly in* dinitrogen matrices. Photolysis of *(19)* in inert matrices led to reversible loss of cyclopentadiene, or oxidative hydrogen-migration to $[Re(cp)(\eta^1\text{-}cp)(CO)_2H]$, which underwent secondary photolysis to *(20)* and then to *(17)*. In reactive matrices, the photolysis of *(19)* was more complex. Much detail of the reactions was presented, together with proposed reaction mechanisms [111].

Field desorption mass spectra were reported for the salts $[Re(CO)_3(\eta\text{-}arene)][PF_6]$ (arene = methylbenzene or 1,3,5-trimethylbenzene). The spectra were simple, dominated by $[M]^+$, $[M+1]^+$ and $[M-CO]^+$ [112].

Reaction of $Na[Re(CO)_5]$ with perfluoronorbornadiene in thf solution yielded the substitution product *(24)*, shown in Fig.18:

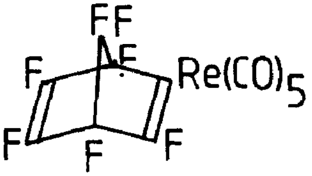

Fig.18: *(24)*.

which was characterized by analytical, IR, ^1H and ^{19}F NMR spectroscopy [113].

Cocondsensation of rhenium atoms with the arenes methylbenzene, 1,4-dimethylbenzene or 1,3,5-trimethylbenzene gave the compounds $[\{(\eta\text{-arene})Re\}_2(\mu\text{-CHR}')(\mu\text{-H})_2]$, where R′ was phenyl, 4-methylphenyl or 3,5-dimethylphenyl respectively. The structurally related compounds $[\{(\eta\text{-arene})Re\}_2(\mu\text{-CR}'R'')(\mu\text{-H})_2]$ (R′ = Me, R″ = Ph; R′ = H, R″ = CH_2Ph) were formed from the reaction between rhenium atoms and ethylbenzene. Structures were proposed on the basis of microanalytical data, mass spectra and NMR spectra [114].

Reaction of $[Re_2(\mu\text{-H})(\mu\text{-CH=CHEt})(CO)_8]$ with 3,3′-dimethylcyclopropene led to carbon-carbon bond cleavage, and formation of the .-carbene complex. $[Re_2\{\mu\text{-}(\eta^1,\eta^3\text{-CHCHCMe}_2)\}(CO)_8]$; this reacted with carbon monoxide to form $[Re_2\{\mu\text{-}(\eta^1,\eta^3\text{-CHCHCMe}_2)\}(CO)_9]$, which, on UV irradiation underwent carbon-hydrogen bond cleavage with formation of the η^1,η^2 hydride $[Re_2(\mu\text{-H})(\mu\text{-CH=CHCMe=CH}_2)(CO)_8]$ [115].

The photochemical reaction of dirhenium decacarbonyl with 1,3-butadiene yields a mixture of complexes which were separated by HPLC and characterized spectroscopically. Two allylic rhenium(I) tetracarbonyls were obtained as minor products, together with a dirhenium(I) octadienediyl derivative. A rhenium(I) dimeric hydride was also isolated at 240 K, and two rhenium(0) butadiene adducts at 183 K [116].

Dirhenium decacarbonyl was reported to react with triphenylsilyllithium to yield, after alkylation with methyl fluorosulfate or triethyloxonium tetrafluoroborate, the equatorially substituted carbene complexes *eq*-$[Re_2(CO)_9\{C(OR)SiPh_3\}]$ (where R = Me, C_4H_8OMe or Et). The crystal structure of the ethyl derivative was determined. Reaction of these carbene complexes with aluminium(III) chloride or aluminium(III) bromide yielded *ax*-$[Re_2(CO)_9(CSiPh_3)][AlX_4]$, which subsequently reacted with alcohols to give the axial isomers of the original equatorial carbenes. The axial and equatorial methoxycarbenes reacted with dialkylamines to yield the respective isomers of $[Re_2(CO)_9\{C(NR_2)SiPh_3\}]$ [117]. The reaction of the decacarbonyl with triphenylsilyllithium, followed by reaction with methyl fluorosulfate also gave $[Re_2(CO)_7\{C(OMe)SiPh_3\}_2]$ and the trimeric species (*25*). An X-ray crystal structure of (*25*) was reported (Fig.19) [118].

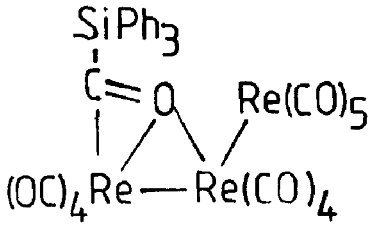

Fig.19: (*25*).

The steric and electronic effects in the molecules *cis*-$[\{Ph_3Si(RO)C:\}Re_2(CO)_9]$ (R = Me or Et) and *cis,trans*-$[\{Ph_3Si(EtO)C:\}_2Re_2(CO)_8]$ were discussed [119]. The reaction of dirhenium decacarbonyl with triphenylsilyllithium and subsequent ethylation with triethyloxonium tetrafluoroborate also yielded Re^1-*ax*,Re^2-*eq*-$[\{Ph_3Si(EtO)C\}_2Re_2(CO)_8]$. The isomeric complexes with one carbene ligand replaced by $:C(OEt)C_6H_4Me$ were obtained by reacting the monocarbene complex with methylphenyllithium, and then ethylating with triethyloxonium tetrafluoroborate [120].

While the product from the reaction of $[Mn(CO)_5(CH_2Cl)]$ with triphenylphosphine in solution in the dark at room temperature was $[Mn(CO)_3(PPh_3)_2Cl]$, the rhenium analogue did not react. Similarly, the rhenium methoxymethyl derivative did not react [121].

The preparation and characterization of the sixteen rhena-1,3-ketoimine derivatives of twelve aminoacids were reported. These rhena-labelled aminoacids were prepared by a Schiff base condensation of rhenapentane-2,4-dione with the appropriate aminoacid free base as a methyl or ethyl ester. Heteroatomic substitution did not prevent imine formation. Distal rhena-labelling of the ϵ-aminogroup of several L-lysine derivatives was also reported [122].

4.8 NITROSYL AND METHANOYL COMPLEXES

The bimetallic anionic complexes $Li[ReMn(CO)_9(CHO)]$ and $Li[Re_2(CO)_9(CHO)]$ were prepared by the action of $Li[BHEt_3]$ on the decacarbonyl. The dirhenium complex was stable over a number of days and was isolated as a thf solvate. On reaction with electrophiles such as benzaldehyde, iron(0) pentacarbonyl or iodooctane, hydride transfer occurred to the electrophile. However, treatment with methyl fluorosulfonate and strong acids did not yield methane or hydrogen gas. The heterobimetallic complex was noted to be a weaker hydride donor. Thermolysis fo the dirhenium complex yielded dirhenium decacarbonyl, but photolysis yielded $Li[Re_2(CO)_9H]$. The potassium dirhenium methanoyl complex reacted with $K[Bu_3BH]$ to form methanal and $K_2[Re_2(CO)_9]$ [123].

$[PPh_4][Re(NO)_2Br_4].2CCl_4$ was prepared by the reaction of $[Re(NO)_2Cl_4]$ with excess BBr_3 at room temperature. Treatment of the product with aluminium(III) bromide in dibromomethane gave $[Re(NO)_2Br_3]$, which is dimeric with bridging bromide ions. The nitrosyl groups in both complexes were *cis* in conformation and, in the anion, a Re=N bond was observed [124]. The reaction was reported of $[ReCl_2(NO)(PPh_3)_2]$ with an excess of thiophenol in the presence of triethylamine to yield $[Re_2(NO)_2(SPh)_7]^-$; the 4-methylphenyl derivative was also prepared. The structures of these complex anions were confirmed by IR and ^1H NMR spectroscopy, and the 4-methylphenyl derivative was studied by X-ray diffraction. The anion contained two rhenium centres each with two terminal thiotolyl groups and a terminal nitrosyl group, bridged by the remaining three thiotolyl ligands, the $\{Re_2(NO)_2\}$ unit having *syn* symmetry

(Fig.20) [125].

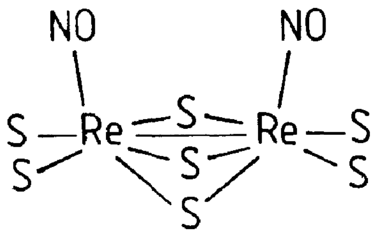

Fig.20: *syn*-{$Re_2(NO)_2$} unit.

$[AsPh_4][ReCl_4(NO)\{OC(NH_2)Me\}]$ was prepared from $[AsPh_4][ReCl_4(NO)_2]$ and ethanenitrile in the presence of water in dichlorometane solution. X-ray analysis showed that the product contained an octahedral anion, with the four chloride ions in the equatorial plane and the ethanamide ligand bound through the oxygen atom. The IR spectrum was assigned [126].

The reaction of $[(cp)Re(NO)(CO)_2][BF_4]$ with aqueous triethylamine in propanone yielded $[(cp)Re(NO)(CO)H]$, which was characterized by spectral techniques. Reaction of the hydride with tetrabromomethane, bromine or *N*-bromosuccinimide produced the bromide $[(cp)Re(NO)(CO)Br]$ in high yield, while hydride abstraction by $[CPh_3][PF_6]$ in the presence of donor ligands L (such as ethanenitrile, thf or propanone) led to $[(cp)Re(NO)(CO)L][PF_6]$. Addition of base to $[(cp)Re(NO)(CO)_2][BF_4]$ in water produced the carboxylic acid $[(cp)Re(NO)(CO)(COOH)]$, which was stable under anhydrous conditions, but was decomposed by strong bases to the hydride [127]. Reaction of $[CPh_3][PF_6]$ with $[(cp)Re(NO)(CO)H]$ also yielded the arene complex $[(cp)Re(NO)(CO)(3,4-\eta^2-C_6H_5CHPh_2)][PF_6]$. The triphenylmethane ligand was easily replaced by triphenylphosphine, and deprotonated by triethylamine to yield 3- and 4- isomers of $[(cp)Re(NO)(CO)(\eta^1-C_6H_4CHPh_2)]$. The reactions and nature of the complexes were discussed in detail [128]. The complexes $[(cp)Re(NO)(CO)R]$ (where R = Ph, 2-, 3- or 4-MeC_6H_4, 3- or 4-$CF_3C_6H_4$) have been prepared in high yield from the chloro derivative with an excess of the arylcopper reagent. When PhMgBr or PhLi were used, little or no phenylrhenium complex was formed. The complexes were characterized by IR and ^1H NMR spectroscopy [129].

Esterification of the complex $[(cp)Re(NO)(PPh_3)(CO)][BF_4]$ with sodium methoxide in methanol yielded $[(cp)Re(NO)(PPh_3)(COOMe)]$, which when allowed to react with (−)-(S)-α-(1-naphthyl)ethylamine or (+)-(R)-α-(1-naphthyl)ethylamine, yielded the amide derivative $[(cp)Re(NO)(PPh_3)(CONHCHMeC_{10}H_7)]$, the diastereoisomers of which were separated. Hydrolysis yielded pure (+)-(S)- and (−)-(R)- enantiomers of the initial carbonyl complex. Standard reactions were then used to prepare optically pure methyl, methylene, benzyl, ethyl and methanoyl derivative complexes. An X-ray crystal structure of the (−)-(R)- isomer of the benzyl derivative established the absolute configuration of all the complexes prepared. Various spectral data were presented, together with the synthesis of $[(cp)Re(NO)(PPh_3)\{CH_2P^+Ph_2(O\text{-}l\text{-menthyl})\}][PF_6]$ [130].

$[(Me_5C_5)Re(CO)_3]$ (prepared from dirhenium decacarbonyl and Me_5C_5H) reacted with $[NO][BF_4]$ to give $[(Me_5C_5)Re(NO)(CO)_2][BF_4]$. Reaction with PhIO in ethanenitrile gave $[(Me_5C_5)Re(NO)(CO)(NCMe)][BF_4]$ which, subsequently treated with triphenylphosphine or triphenylphosphite led to replacement of the ethanenitrile ligand by the phosphorus ligand. Reduction of these complexes with $Li[BEt_3H]/BH_3$ or $Na[BH_4]$ respectively yielded $[(Me_5cp)Re(NO)(Me)L]$, which deprotonated with $[CPh_3][PF_6]$ to the methylene complex. The properties of the $Re{=}CH_2$ group (bond length 0.1898(18)nm) were studied in detail. The crystal structure of the phosphine complex showed $=CH_2/NO$ disorder at −160 °C. The room temperature crystal structure of the phosphite complex was also described [131].

A number of η^2-arene complexes of the $[(cp)Re(NO)(CO)]^+$ cation have been synthesized, and observations made regarding the similarity with electrophilic aromatic substitution. The benzene, toluene and trifluoromethylbenzene adducts [(cp)Re(NO)(CO)(.^{2}-ArH)]X were prepared by reaction of the aryl complex with tetrafluoroboric acid or methylsulfonic acid at -78 °C, and the products were studied by ^{1}H NMR spectroscopy. In the presence of triethylamine, the reaction is reversible, and the 3-/4- isomeric ratios of the aryl complexes formed have been studied [132].

The complexes [(cp)Re(NO)(PPh_3)R] (where R = Et, C_3H_7, C_5H_{11}, $(CH_3)_2CHCH_2$, $(CH_3)_3CCH_2$ or $(CH_3)_2CH$) were synthesised by reaction of a Grignard or alkyllithium with an appropriate [(cp)(NO)Re(PPh_3)(=CHR')][PF_6] precursor. An acyl derivative (R = $COCH_2Ph$) was prepared from [(cp)(NO)Re(PPh_3)(CO_2Me)] with $PhCH_2MgBr$, and was reduced by excess diborane to the alkyl derivative. These alkyls, along with some previously synthesized, were treated with [CPh_3][PF_6] at -78 °C, and the regio- and stereochemistry of hydride abstraction investigated. Enthalpy and entropy changes for various equilibrations have been measured. A very detailed study was presented [133].

It was reported that [(cp)Re(NO)(CO)Me] reacted with high concentrations of trimethylphosphine to form a η^{1}-cyclopentadienyl derivative, which was then converted to a cyclopentylidene ketene complex (26) (Fig.21):

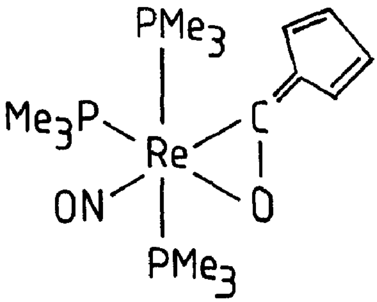

Fig.21: (26).

^{1}H NMR, ^{13}C NMR and IR spectral data were all quoted. (*26*) further reacted with propanone to insert the small molecule into the Re-O bond (Fig.22) [134]:

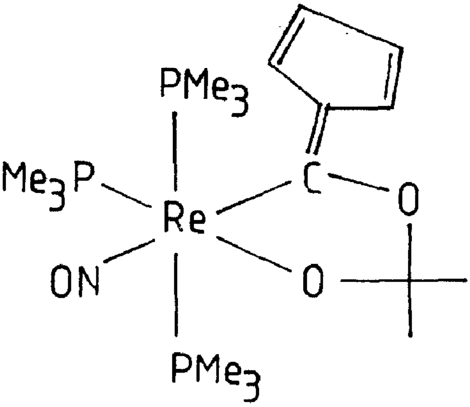

Fig.22: [Re(NO)(PMe$_3$)$_3$(OCMe$_2$OC=C$_5$H$_4$)].

A study of the mechanism of coupling of [(cp)Re(NO)(PPh$_3$)(=CH$_2$)][PF$_6$] with [(cp)Re(NO)(PPh$_3$)(CH$_2$=CH$_2$)] has been carried out, investigating the kinetics and thermodynamics of the reaction. The influence of optical purity of the reaction was also studied, and showed a notable effect on the reaction rate, and a crystal structure of the novel adduct (+)-(*SS*)-[(cp)Re(NO)(PPh$_3$){NCCH(Ph)Et}][PF$_6$] was presented [135].

The reactions of the complexes [(cp)Re(NO)(PPh$_3$)(=CHCH$_2$R)]$^+$ (R = H, Me or Pr) with K[OCMe$_3$] were studied, yielding [(cp)Re(NO)(PPh$_3$)(CH=CHR)]. The nature and further reactions of these vinylidene complexes were studied [136].

The salts [(cp)Re(NO)(PPh$_3$)(η^2-CH$_2$O)][PF$_6$], (*27*), and [(cp)Re(NO)(PPh$_3$)(η^2-CH$_2$S)][PF$_6$], (*28*), were prepared and their crystal structures determined by X-ray diffraction techniques. Oxidation of [(cp)Re(NO)(PPh$_3$)(η^2-CH$_2$)][PF$_6$] with PhIO yielded complex (*27*), while reaction with cyclohexene sulfide yielded complex(*28*) (see Fig.23):

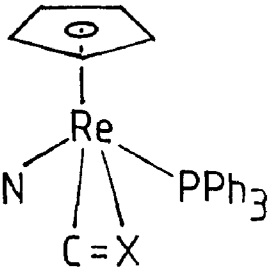

Fig.23: (*27*) X = O; (*28*) X = S.

(*27*) reacted with trideuteroethanenitrile at 51 °C after nineteen hours in 50% yield to substitute an ethanenitrile ligand for the CH_2O ligand, while (*28*) showed no reaction. Treatment of (*28*) with $Na[BH_3CN]$ in methanol resulted in reduction of the CH_2S group to CH_3S, while reaction of (*27*) with $[(cp)Re(NO)(PPh_3)(CHO)]$ yielded the carbonyl and methoxy complexes in high yield. Other reactions were noted [137].

4.9 MISCELLANEOUS BINARY COMPOUNDS

The compounds TcP_3 and ReP_3 have been prepared by the reaction of the elements in the presence of iodine, and also in a tin flux. The structures were determined by X-ray diffraction, and both compounds were shown to crystallize in the space group *Pnma*. The metal atoms were six coordinate, while the phosphorus atoms were tetrahedrally coordinated to rhenium and phosphorus atoms, with oxidation numbers of −2, −1 and 0. The metal was then deduced to have an oxidation number of +3. Metal-metal bonding between adjacent octahedra accounted for the diamagnetism in ReP_3 [138].

4.10 MIXED OXIDATION STATES

The complexes $[Re_2Cl_4L_4]$, $[Re_2Cl_4L_4][PF_6]$ and $[Re_2Cl_4L_4][PF_6]_2$ (L = PMe_2Ph) were prepared, the latter two by the oxidation of the first with $[NO][PF_6]$. The crystal structures (shown in Fig.24) were determined by X-ray diffraction techniques. Electrochemical and magnetic data were presented and the variations between the structures discussed [139].

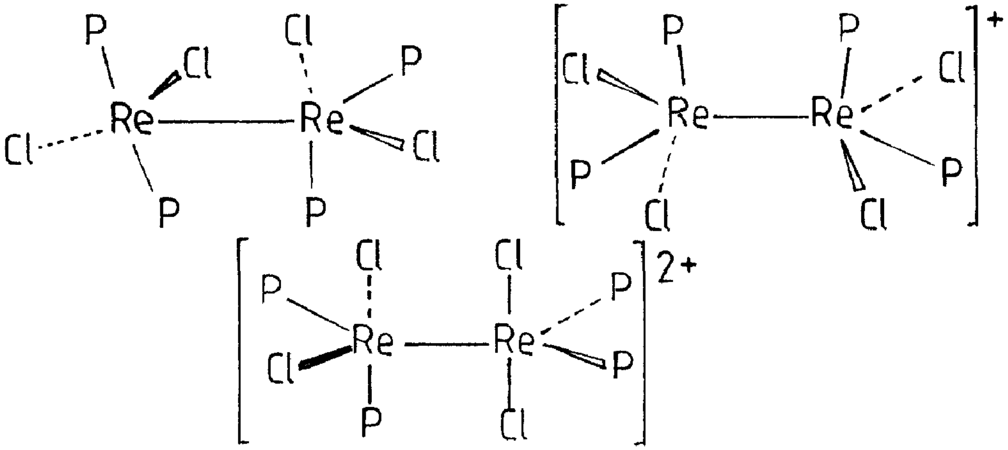

Fig.24: $[Re_2Cl_4L_4]$, $[Re_2Cl_4L_4][PF_6]$

and $[Re_2Cl_4L_4][PF_6]_2$.

The valence electronic structure of the compounds $[Re_2Cl_4(PH_3)_4]$ and $[Re_2Cl_4(PH_3)_4]^+$ has been investigated as examples of compounds with rhenium-rhenium bonds of order 3 or 3.5. Relativistic $X\alpha$-SW calculations have been performed and indicate that the two and one electrons respectively reside in the Re-Re δ^* orbital. The low temperature spectra of the $P(CHMe_2)_3$ analogues were reported and discussed [140].

The structure of the rhenium bronze $D_{1.36}ReO_3$ was determined by neutron diffraction studies. The rhenium atoms were found to lie on the special perovskite sites, and were surrounded by distorted octahedra of oxygen atoms. The deuterium atoms were statistically distributed over seventy-two possible sites in the unit cell, with O-D bonds [141].

The double oxide $Dy_5Re_2O_{12}$ has been synthesized and its crystal structure determined. The structure was shown to consist of infinite chains of

$\{ReO_6\}$ octahedra bridged by isolated $\{DyO_6\}$ octahedra, forming sheets which were linked by other dysprosium atoms [142].

Mixed oxides of rhenium with an electropositive element, such as Sr_xReO_3, $Dy_5Re_2O_{12}$ and $La_6Re_4O_{18}$, were reviewed, illustrating how structural studies contribute to solving the problem of mixed valence compounds. Eleven references were quoted [143].

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