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9. TECHNETIUM AND RHENIUM

J.E. TURP

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TECHNETIUM

RHENIUM

INTRODUCTION

The period of this review covers those publications in Volumes 92 and 93 of Chemical Abstracts. Thus, although a majority of papers covered were published in 1980, many from 1979 are also included. The major journals are covered upto the end of 1980.

The review concentrates upon the coordination chemistry of technetium and rhenium. No attempt has been made to cover work of an essentially organometallic, kinetic or catalytic nature. Two reviews of interest to rhenium chemists have been published this year. The first is a general review of rhenium chemistry [1] and the second discusses the structure of rhenium compounds containing metal-metal bonds [2].

TECHNETIUM

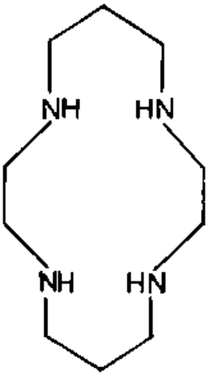
9.1 TECHNETIUM(VII)

9.1.1 Hydrides

A circular orbit model has been used to account for a coordination number greater than six in $[TcH_9]^{2-}$ [3].

9.1.2 Oxides

The crystal structure of $[NH_4][TcO_4]$ has been determined at 295, 208 and 141 K and the details observed indicate a more ordered hydrogen bonded structure than is present in $[NH_4][ReO_4]$ [4]. Reduction of $[TcO_4]^-$ by tin(II) in the presence of citrate ions initially gives a bis(citrato)technetium(IV) species; this can be further reduced to give a bis(citrato)technetium(III) complex [5], which is colourless and not purple as previously reported [6]. A similar reduction occurs in an alkaline solution of polyhydric compounds containing vicinal hydroxyl groups, giving pink-violet polyol complexes of technetium(V), which form mixed ligand complexes with cys, diethylenetriaminepentaethanoic acid and similar ligands [7]. The reduction in an alkaline solution of $[TcO_4]^-$ containing 1,4,8,11-tetraazacyclotetradecane (**1**; **cyclam**) using tin(II) tartrate shows that cyclam is a good complexing agent for technetium. The oxidation state of the product has not been determined [8].



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9.2 TECHNETIUM(V)

The species $[TcOX_4]^-$ (X = Cl or Br) have been prepared and studied in relation to their pharmaceutical application as precursors to the radiotracers $[TcOX_2(HBPz_3)]$ [9]. The reduction of $[TcO_4]^-$ by $[NCS]^-$ has been shown to give $[Tc(NCS)_7]^{2-}$ as one of the products [10].

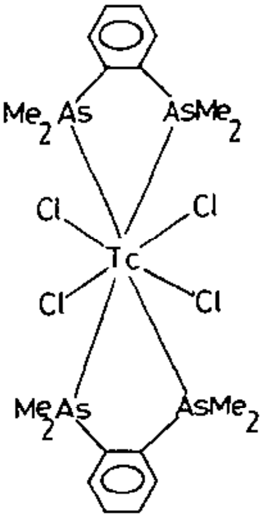
Oxobis(1,2-ethanedithiolato)technetate(V) salts have been prepared by the reduction of $[TcO_4]$ with hydrochloric acid, and precipited by the addition of $[Bu_4N]Cl$ [11,12]. $[Bu_4N][TcO(SCH_2COS)_2]$ has been prepared by the reduction of $[TcO_4]^-$ with a large molar excess (>100) of aqueous thioglycolate, $[HSCH_2CO_2]^-$. The crystal structure shows a square pyramidal structure with the sulphur atoms occupying the basal plane $\{r(TcO) = 1.672$ Å; $\bar{r}(TcS) = 2.320$ Å$\}$ [13].

Lipophilic $[TcOCl_2HCBPz_3)]$ has been prepared by the reduction of $[TcO_4]^-$ in the presence of the $[HBPz_3]^-$ ion. This is the first example of a $[HBPz_3]^-$ complex containing a metal with an oxidation state of (V): the oxidation state was deduced by the presence of Tc=0 in the crystal structure [14]. The eight coordinate $[Tc(diars)_2Cl_4]^+$ (2) complex has been prepared by oxidative addition of Cl_2 to $[Tc(diars)_2Cl_2]^+$ in alcoholic solution. The crystal structure of (2) shows D_{2d} symmetry with $r(TcCl) = 2.442$ Å and $\bar{r}(TcAs) = 2.578$ Å [15].

9.3 TECHNETIUM(IV)

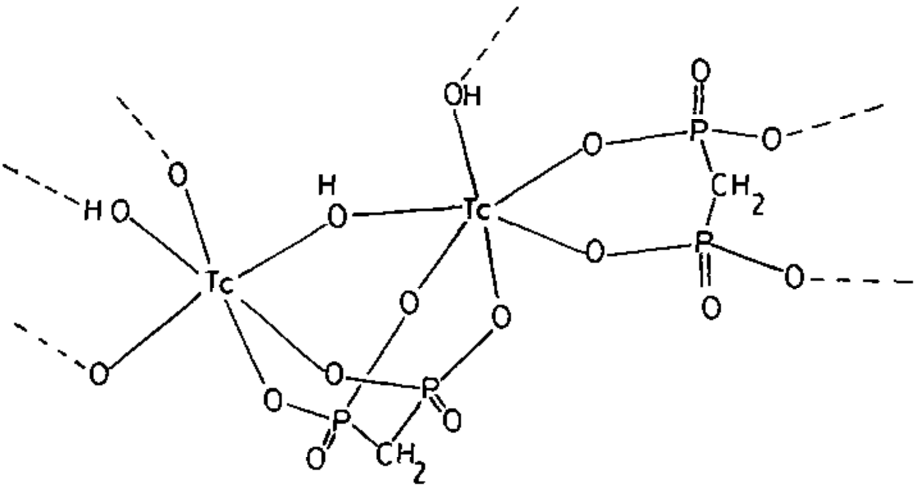
Chromatographically pure Tc(IV) has been prepared by the reduction of $[TcO_4]^-$ in concentrated hydrochloric acid [16]. The complex anion $[Tc(NCS)_6]^{2-}$ has been prepared and its crystal structure determined [17]. The reduction of $[TcO_4]^-$ by $[NCS]^-$ has also been shown to give $[Tc(NCS)_6]^{2-}$ as one of the products [10].

Copper(I) has been used to label edta with technetium(IV) [18]. A



(2)

methylenediphosphonate technetium(IV) complex, $[Li(H_2O)_3]\{Tc(mdp)(OH)\}\frac{1}{3}H_2O$ (mdp = $[O_3PCH_2PO_3]^{4-}$), has been prepared and its crystal structure shown to consist of infinite polymeric anionic chains (3). Each mdp ligand bridges two Tc atoms,



(3)

and each Tc atom is bound to two mdp ligands [19]. $[Tc(dppe)_2(N_2)]$ has been prepared by the addition of dppe to a suspension of $[TcCl_4(PPh_3)_2]$ and sodium amalgam in benzene [20]. The complex formed between Penicillamine [$PenH_2$] and technetium(IV), $[TcO(Pen)_2]^{2-}$, has been characterised by spectrometry and Sephadex column chromatography [21].

9.4 TECHNETIUM(III)

$K_4[Tc(CN)_7]2H_2O$ (4) has been prepared by treating $[NH_4]_2[TcI_6]$ with KCN under dinitrogen and the anion has D_{5h} symmetry. Aqueous solutions of (4) will oxidise in air, initially to give $K_2[Tc^{V}O(CN)_5]$, and then $K_3[Tc^{V}O_2(CN)_4]$, the anion of which possesses D_{4h} symmetry [22].

$[TcCl(CO)(MeCN)_2(PMe_2Ph)_3][ClO_4]_2$ was obtained by the two electron oxidation of $[TcCl(CO)_2(PMe_2Ph)_3]$ in MeCN; the oxidation of $[TcCl(CO)_3(PMe_2Ph)_2]$ was also studied [23]. The molecular structures of *trans*-$[TcCl_2(diars)_2]Cl$ and *trans*-$[TcCl_2(diars)_2][ClO_4]$ were reported as containing a cation of D_{2h} symmetry, with $r(TcCl) = 2.348, 2.288$ Å and $r(TcAs) = 2.518, 2.511$ Å [15,24].

9.5 COMPLEXES CONTAINING Tc-Tc BONDS

$[Tc_2Cl_8]^{2-}$ and $[Tc_2Cl_8]^{3-}$ have been prepared by reduction of $[TcCl_6]^{2-}$ with zinc in concentrated hydrochloric acid and their vibrational spectra analysed [25]. The hydrolysis of $[Tc_2Cl_8]^{3-}$ in 0-12 *M* hydrochloric acid has been studied [26]. $[Tc_2(OC_5H_4N)_4]Cl$ has been prepared by the reaction of 2-hydroxypyridine with $[NH_4]_3[Tc_2Cl_8]$. The crystal structure shows infinite chains of $\{Tc_2(OC_5H_4N)_4\}^+$ units linked by bridged chloride ions (*cf. catena*-$\{Ru_2(O_2CMe)_4Cl\}$). The technetium-technetium bond length of 2.095 Å is the shortest known, and this corresponds to a bond order of 3.5. The electronic structure of the dimetal centre, $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$ electronic absorption spectrum shows rich vibrational structure [27].

RHENIUM

9.6 RHENIUM(VII)

9.6.1 Hydrides

Circular orbit models have been described to account for a coordination number greater than six in $[ReH_9]^{2-}$ [3]. It has been shown that, in the presence of 3,3-dimethyl-but-1-ene, $[L_2ReH_7]$ ($L = PPh_3$ or PEt_2Ph) dehydrogenates cyclopentane to give the η^5-cyclopentadienyl compounds $[L_2(\eta^5\text{-}C_5H_5)ReH_2]$ [28]. This represents one of the very few known examples of a complex which can activate an alicyclic C-H bond under very mild conditions, and the system promises to yield some more exciting chemistry.

9.6.2 Oxohalides

[ReO_3F] has been prepared by the reaction of [$ReOF_5$] with [Re_2O_7] at 150–200 °C. When stoicheiometric amounts of [$ReOF_5$], [ReO_2F_3] or [ReO_3F] were reacted with AF (A = alkali metal), A[$ReOF_4$], A[ReO_2F_4] or A[ReO_3F_2] and A_2[ReO_3F_3] were formed, respectively [29]. The salts M[ReO_2F_4] (*M* = Na, K, Rb or Cs) were characterised by IR and X-ray diffraction, and their thermal behaviour studied in difluorine and dinitrogen atmospheres [30]. The reaction of [$ReOF_5$] with KF was studied and found to proceed in stages, with the formation of intermediate products which decompose partially to K[$ReOF_5$] and F_2 [31]. The electronic structures of [ReF_7], [$ReOF_5$] and [ReO_3F] have been studied in the gaseous phase by UVPES [32], and the centrifugal distortion constants and general valence force constants have been calculated for [$ReOF_5$] [33]. The heat of formation of [ReO_3Cl] has also been reported [34].

An improved preparative route for [ReO_3Cl] has been reported which involves the heating of Re_3Cl_9 to combustion [35].

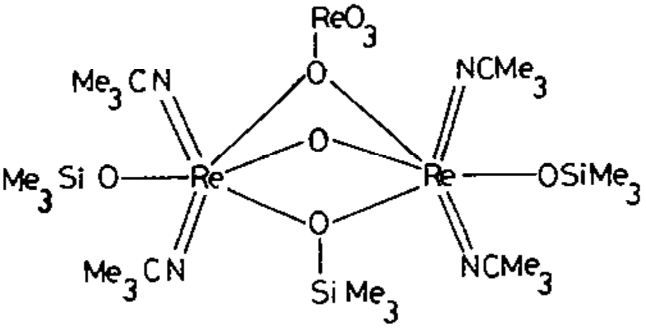
9.6.3 Oxides

XPES and thermogravimetric measurements have been used to investigate pure rhenium compounds as an aid to the understanding of their surface chemistry. Rhenium metal, ReO_2 and ReO_3 were all found to be covered by rhenium(VII) species. Re_2O_7 and [NH_4][ReO_4] were also studied [36]. No measureable hexadecapole interactions were found in solid [NH_4][ReO_4] or [ND_4][ReO_4], using rhenium NQR spectroscopy [37]. The IR absorption spectra have been measured for vapours over Re_2O_7, ReO_3 and $HReO_4$ solutions [38], and a study of complexation in the $[ReO_4]^-/[H_3O]^+/[SO_4]^{2-}/H_2O$ system has been reported [39]. $[ReO_4]^-$ in concentrated alkaline solution forms yellow 1:1 complexes with a number of polyhydric alcohols, including (*inter alia*) D-mannitol, and D-glucitol. However, polyols without vicinal OH-bearing carbons with opposing configurations (D-L) (*e.g.* glycerol) do not react and it was concluded that the adjacent O–O distance in the ligand is critical for complex formation [40]. The novel organoimido complexes [$Re(NCMe_3)_3(OSiMe_3)$] and [$Re_3(NCMe_3)_4O_5(OSiMe_3)_3$] (5) have been prepared and the latter characterised by X-ray diffraction {*r*(ReRe) = 3.165 Å} [41].

9.7 RHENIUM(VI)

9.7.1 Halides and oxohalides

A circular orbit model has been described to account for a coordination number



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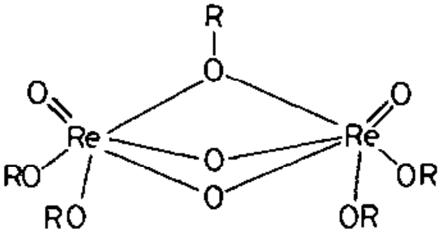
greater than six in $[ReF_8]^{2-}$ [3]. Nitrosyl salts containing $[ReF_7]^-$ and $[ReF_8]^{2-}$ have been prepared and their Raman spectra analysed [42]. A review has been published containing seventeen references to ReF_6 [43], and the electronic structure of ReF_6 has been studied in the gas phase by UVPES [32].

An improved preparative route to $[ReOCl_4]$, involving the direct oxidation of $ReCl_5$, gives yields greater than 80% [35]. The heats of formation of $[ReOCl_4]$ and $[ReOBr_4]$ have been reported [34]. The hyperfine structure of the EPR lines for $[ReOCl_5]^-$ has been studied and the parameters of the spin Hamiltonian calculated [44]. The reactions of $ReOCl_4$ in nonaqueous media, with the ligands Ph_3PO, urea, MeCN, Me_2CO, Et_2O, dimethylglyoxime or dioxane have also been studied by EPR spectroscopy [45].

9.7.2 Oxides and complexes with oxygen donor ligands

Crystals of ReO_3 have been shown by electron diffraction and electron microscopy measurements to absorb dihydrogen, and it was proposed that this phenomenon is closely related to the hygroscopic nature of this material [46]. The structural stability of the ReO_3 lattice has been related to the presence of conduction bands within the solid [47]. First and second order quadrupolar effects in the ^{187}Re NMR spectrum of ReO_3 have been used to show that the compressibility collapse transition results in a high pressure phase of symmetry lower than cubic, and to map out the phase boundary from 1-300 K [48]. At high pressures, new rhenium containing perovskites and pyrochlores of the composition $PbM^{II}ReO_6$ (M^{II} = Mg, Ni, Co, Fe, Zn, Mn, Ca or Cd) have been prepared [49].

The syntheses of $[Re_2O_3(OMe)_6]$ **(6)**, $[ReO(OCMe_3)_4]$, $Li[ReO(OCHMe_2)_5]$ and $[ReO\{N(SiMe_3)_2\}_3]$ have been reported [35,50]. The first of these complexes, **(6)**, was prepared by the dissolution of $ReOCl_4$ in MeOH in the presence of a tertiary amine, and its crystal structure was determined {r(ReRe) = 2.559 Å} [50].



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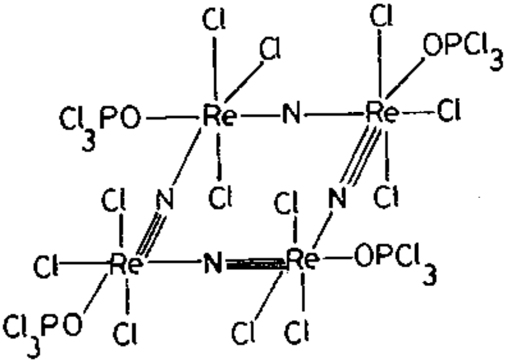
9.7.3 Complexes with Group VB donor ligands

$[\{ReNCl_3(POCl_3)\}_4].2POCl_3$ (7) has been prepared and shown to contain four Re-N-Re bridges in a tetramic square, isotypic with $[\{WNCl_3(POCl_3)\}_4].2POCl_3$



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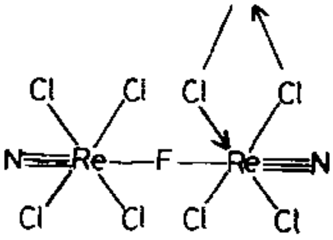
[51]. $ReCl_5$ dissolved in $POCl_3$ reacted with cyanogen chloride or trichloroethanenitrile in the presence of Cl_2 to give the alkylated nitride chlorides $[(Cl_3PO)Cl_4Re{=}N(CCl_3)]$ or $[(Cl_3PO)Cl_4Re{=}N(C_2Cl_5)]$ (8), respectively. The molecular structure of (8) shows (Re=N) = 1.69 Å [52]. $[AsPh_4]_2[Re_2FN_2Cl_7]$ has been prepared by reaction of $[ReNCl_4]$ with $[AsPh_4]F$ in MeCN. The IR spectrum indicates a bridging Re-F-Re complex anion with a terminal Re≡N moiety, and the tetrameric structure (9) was proposed [53].



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9.7.4 *Complexes with Group IVB donor ligands*

The novel methyl rhenium complexes $ReOMe_4$, $Li_2[ReMe_8]$ and $ReMe_6$ have been prepared from $ReOCl_4$ and LiMe [35].

9.8 RHENIUM(V)

9.8.1 *Halides, pseudohalides and oxohalides*

A nitrosyl salt of $[ReF_6]^-$ has been prepared and its Raman spectrum analysed [42]. The structure of $[(NH_2)_2CSSC(NH_2)_2]$ *trans*-$[ReOCl_4(H_2O)]Cl.H_2O$ has been reported $\{r(Re{=}O) = 1.66$ Å; $r(Re{-}OH_2) = 2.20$ Å; $r(ReCl) = 2.335$–2.373 Å$\}$ and shows that all the bond angles and distances are unexceptional [54] but that, there are significant differences when compared to the parameter for *trans*-$[ReOCl_4(H_2O)]$. Studies of the extraction of rhenium(V) from acid solutions in the presence of chloride and thiocyanate ions [55], and of the $[ReOCl_5]^{2-}$/$[H_4P_2O_7]$/[HCl] system [56] have been reported.

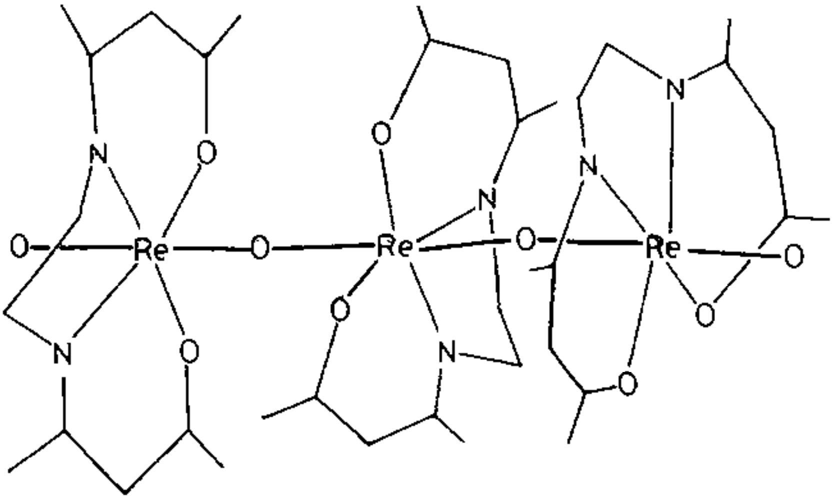
9.8.2 *Oxides*

Sr_xReO_3 ($0.4 \le x \le 0.5$) has been prepared at high pressure and temperature, and shown to have a $KSbO_3$ structure [57]. The crystal structure of the new mixed-valence rhenium(V,IV) oxide $BiRe_2O_6$ has been determined and consists of $\{Re_2O_{10}\}$ units in layers linked by corner sharing, alternating with disordered layers of Bi ions. The crystal structure of the new oxide $Bi[ReO_4]$ has also been determined and consists of corner shared octahedra linked by Bi atoms [58]. The specific heat of the pyrochlore $Cd_2Re_2O_7$ has been measured below 20 K [59].

9.8.3 *Complexes*

Stable oxobis(dithiolato)rhenium(IV) complexes, *i.e.* $[Ph_4As][ReO(SCH_2CH_2S)_2]$, $[Bu_4N][ReO(SCH_2COS)_2]$, $[Bu_4N][ReO(C_2O_2S_2)_2]$, $[Ph_3MeAs][ReO(C_2O_2S_2)_2]$, $[Ph_4As][ReO\{S_2C_2(CN)_2\}]$, $[Bu_4N][ReO(S_2C_7H_6)_2]$ have been prepared [12]. $K[ReOCl_4(tu)].2H_2O$ was prepared by the reaction of $[ReOCl_3(tu)_2]$ and $K_2[ReOCl_5]$ in HCl solution. $[NH_4]_2[C_2O_4]$ reacted with $[ReOClL_4]Cl_2$ to give the corresponding dimeric complex $[Re_2O_2L_4(C_2O_4)_3]$ (C = tu or 2-imidazolidinethione) [60].

$[ReO(H_2O)_2(N_3)_2]Cl$ was prepared by the reaction of $ReCl_3$ with $Na[N_3]$, but the reaction of $ReCl_5$ with $Na[N_3]$ yielded $Na_2[ReOCl_5]$ [61]. Cyanogen and dichlorine react with $ReCl_5$ in $POCl_3$ solution to give the $POCl_3$-solvated bis(nitrido)chloro complex $[(Cl_3PO)Cl_4\{Re{\equiv}NC_2Cl_4{-}N{\equiv}Re\}Cl_4(OPCl_3)]$ [62]. The reaction of $[ReOCl_3(PPh_3)_2]$ with $acac_2enH_2$ gave $[ReOCl(acac_2en)]$ which, when treated with O_2, gave a complex, shown by X-ray diffraction to be $[\mathrm{Re_3O_4(acac_2en)_3}][\mathrm{ReO_4}]$. This is the first example of a linear O=Re–O–Re–O–Re=O skeleton (10) {$\bar{r}(\mathrm{ReO})_{\mathrm{terminal}}$ = 1.683 Å; for the bonds *trans* to these, $\bar{r}$(ReO) = 2.076 Å; for the central bonds, $\bar{r}$(ReO) = 1.7587 Å} [63].



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Oxo complexes of rhenium(V) with $\mathrm{TPPH_2}$ or corroles as additional ligands have been prepared and the complexes discussed on the basis of their electronic, EPR, NMR and XPES spectra, and their electrochemical and magnetic properties [64]. The electrochemical properties of μ-oxobis{oxobis(*N'*,*N*-diethyldithiocarbamato}rhenium(V) have also been investigated [65].

$[\mathrm{ReOX_3L_2}]$, (X = Cl or Br; L = $\mathrm{PPh_2H}$, $\mathrm{PPh_2Et}$ or $\mathrm{PPh_3}$) $[\mathrm{ReO(OEt)Cl_2(PPh_3)_2}]$, $[\mathrm{ReOX_3(Ph_2PCH_2CH_2PPh_2)}]$ and $[\mathrm{ReOCl_3(Ph_2PCHCHPPh_2)}]$ have been prepared and their thermal oxidation to the corresponding phosphine oxides studied. $[\mathrm{ReOX_3(OPPh_3)_2}]$ and $[\mathrm{ReOX_3\{PPh_2P(O)CH_2CH_2POPh_2\}}]$ were prepared by reaction of $\mathrm{K_2[ReOX_5]}$ with the corresponding phosphine oxide ligand [66]. The reactive arylimido complex $[\{\mathrm{ReCl_3(NR)(PPh_3)}\}_2]$, which was prepared from $[\mathrm{ReCl_3(NR)(PPh_3)_2}]$ by reaction with sulphur, is readily oxidised by mild oxidants such as Me-4-$\mathrm{C_6H_4NO_2}$ to $[\mathrm{ReCl_3(RNO)(OPPh_3)}]$ (21) and readily accepts donor ligands. Reaction of (11) with a reductant, such as $\mathrm{PR_3}$, results in oxygen abstraction and reformation of the arylamido complex, $[\mathrm{ReCl_3(NR)(PPh_3)_2}]$ [67].

9.9 RHENIUM(IV)

9.9.1 Halides

As last year, the hexahalorhenates(IV) have been the subject of study by a wide range of physical techniques. A nitrosyl salt of $[ReF_6]^{2-}$ has been prepared and its Raman spectrum analysed [42]. Crystals of $K_2[ReX_6]$ (X = Cl or Br) have been studied by NMR and NQR spectroscopy, to evaluate the effect of impurities on lattice vibrations when $K_2[ReCl_6]$ is doped with $K_2[ReBr_6]$ [68]. The intensity distribution of the vibrational progressions $t_{1u} + na_{1g}$ and $t_{2u} + na_{1g}$ in a vibronically induced transition in $[ReCl_6]^{2-}$ have been investigated using crystals of $Rb_2[TeCl_6]$ or $Cs_2[TeCl_6]$ doped with $[ReCl_6]^{2-}$; it was shown that there is a Jahn-Teller distortion in the $^4T_{2g}$ excited state [69]. The phosphorescence spectra of $[ReBr_6]^{2-}$ (doped in $A_2[SnX_6]$ {A = K, Rb or Cs; X = Cl or Br}) have been measured at 10 K. The spectra consist of a weighted sum of progressions associated with the local mode of the $[ReBr_6]^{2-}$ centre, and the totally symmetric distortion of the $^2T_{2g}$ excited state relative to the $^4A_{2g}$ ground state has been determined [70]. The specific heat of a single crystal of $K_2[ReCl_6]$ at low temperature has been reported [71]. Solid solutions of $K_2[(Pt/Re)Cl_6]$ have been prepared to study the influence of lattice dimensions on the M-Cl vibrational modes. The crystals behaved as mixtures of the single species $[ReCl_6]^{2-}$ and $[PtCl_6]^{2-}$, and the changes in size of each species accounted for the changes in $\bar{\nu}$(M-Cl) and μ_{eff} [72]. The magnetic susceptibilities and effective magnetic moments were determined by the Faraday method for $A_2[ReCl_6]$ (A = $[NH_4]^+$, $[MeNH_3]^+$, $[Me_2NH_2]^+$, $[Me_3NH]^+$ or $[Me_4N]^+$) and the results discussed in terms of their structures [73]. It was found that the proton resonance line in $[NH_4]_2[ReCl_6]$ is very narrow due to rapid $[NH_4]^+$ tunnelling [74].

Enthalpies of hydrolysis or of oxidative hydrolysis for $K_2[ReCl_6]$, $K_2[ReBr_6]$, $ReCl_4$ and $ReBr_4$ have been determined, and, from these results the enthalpies of formation of the compounds were calculated. Halide ion affinities for $ReCl_4$ and $ReBr_4$ were estimated using these and other thermochemical data [75].

The effect of solvents on the initial and transition states of the Hg^{2+} catalysed aquation of $[ReCl_6]^{2-}$ have been investigated [76].

Intercalated ReF_4 can be produced by the reaction of $ReOF_5$ with graphite, liberating ReF_6 and traces of CO_2 and COF_2 [77].

9.9.2 Oxides and alkoxide complexes

The electrochemical behaviour of rhenium(IV) oxide has been studied [78], and the crystallisation of α-ReO_2 in an iodine atmosphere investigated [79].

Trans-$[Re(OPh)_4(PMe_3)_2]$ was prepared by the reaction of $[ReOCl_4]$ with lithium phenolate and trimethylphosphine and characterised by X-ray crystallography [35].

9.9.3 Complexes with sulphur donor ligands

$[Re_2O(SEt_2)_4X_6]$ (X = Cl or Br) and $[Re_2OL_2X_6]$ (L = $EtSCH_2CH_2SEt$) have been prepared by the reaction of $K_2[ReX_6]$ with the thioether [80]. The reaction of $[BH]_2[ReCl_6]$ (B = 2-aminotoluene) with thiosemicarbazide (L) in absolute ethanol gave $[Re_2(LH_2)_2Cl_8]Cl_2$. Other thiosemicarbazide derivatives (*i.e.* 5-chlorosalicylaldehyde thiosemicarbazone, quinolinaldehydethiosemicarbazone and propanone thiosemicarbazone) were used to prepare similar complexes [81].

9.9.4 Complexes with Group VB donor ligands

The solid phase thermal reactions of the rhenium(IV) triphenylphosphonium salts $[HPPh_3]_2[ReX_6]$ (X = Cl or Br) have been studied and show that PPh_3 is coordinated to give $[Re(PPh_3)_2Cl_4]$ and $[HPPh_3][Re(PPh_3)Br_5]$ respectively [82]. $[ReX_4(dppm)]$ (X = Cl or Br) was obtained by the treatment of $[ReX(CO)_3(dppm)]$ with halogens. $[ReBr_4(bipy)]$ and $[ReBr_3Cl(bipy)]$ have been isolated from the $[ReX(CO)_3(bipy)]/X_2$ system [82a].

9.9.5 Phosphides

The phosphide complexes studied this year are all mixed oxidation state complexes of Re(IV/III). The new cluster complex $Re_{12}P_{26}$ contains bitriangular Re_4 (12) clusters, linked by P-P units as pairs, as irregular zig-zag P_4 chains and as puckered P_6 rings. The crystals show metallic behaviour with rhenium having a formal oxidation state of 3.84 [83].

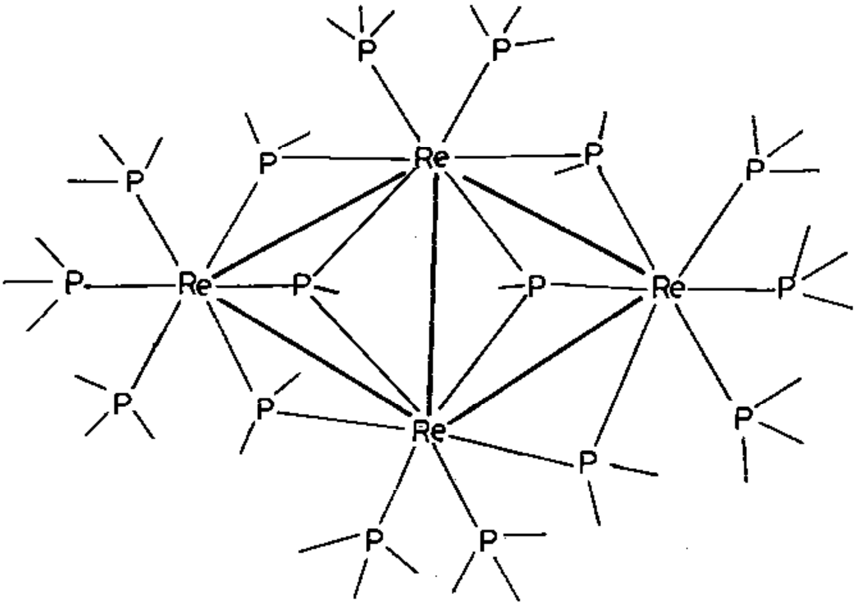
Re_6P_{13} was prepared by heating the elements in the presence of I_2 (to give a powder) or tin (to give crystals). The Re atoms are coordinated by six phosphorus atoms in a distorted octahedral manner. Four edge sharing octahedra are distorted to give Re-Re bonds of 2.76-2.94 Å [84].

9.10 RHENIUM(III)

9.10.1 Halides and pseudohalides

A nitrosyl salt containing $[ReF_6]^{3-}$ has been prepared and its Raman spectrum analysed [42].

Alternative structures for complexes of the type M_2L_{10} (*i.e.* the quadruply bonded complexes such as $[Re_2Cl_8L_2]^{2-}$ and the non-bonded, high-spin complexes



(12)

such as [$Re_2Cl_4(dppe)_2(\mu\text{-}Cl)_2$]) have been considered theoretically, and the preference of ligand sets for one of these geometries over the other discussed [85,86].

A circular orbit model has been described to account for a coordination number greater than six in $[Re_2Cl_8]^{2-}$ [3].

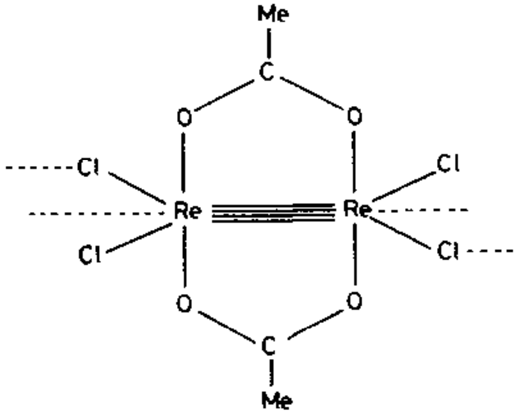
The enthalpy of formation of $Cs_2[Re_2Br_8]$ was determined by measuring its heat of oxidation by aqueous bromate. The enthalpy of formation of $[Re_2Br_8]^{2-}(g)$ was estimated from the calculated lattice energy of $Cs_2[Re_2Br_8]$. Enthalpies of formation of other Re–Br species led to estimates of the Re–Br bond energy, and hence Re–Re quadruple bond strength in $[Re_2Br_8]^{2-}$ was estimated to be 408±50 kJ mol^{-1} [87]. $[Bu_4N]_2[Re_2I_8]$ has been prepared and its resonance Raman spectrum recorded [89].

The UVPES of $[Re_3Cl_9]$ vapour has been measured [89–91]. Calculations were performed by the SCF-DV-Xα method on $[Re_3Cl_9]$ and $[Re_2Cl_8]^{2-}$ and a detailed comparison made of the valence orbitals in these two complexes [90]. In an independent study [89], the UVPES spectrum of $[Re_3Br_9]$ vapour was measured, along with that of $[Re_3Cl_9]$, and was assigned using SCF-Xα-SW and Fenske-Hall MO calculations. It was found that the results were consistent with the presence of a double bond between each pair of metal atoms. The electronic transitions for Re_3Cl_9 were calculated, and the optical absorption spectra for the general class of $[Re_3Cl_9L_3]$ trimers were also discussed and assigned [89].

The crystal structure of $K_4[Re(CN)_7].2H_2O$ has been reported and the anion shown to be a pentagonal bipyramid , with an angle between the axial ligands of 173.4° [92].

9.10.2 Carboxylates

$[Re_2Cl_4(O_2CMe)_2].2H_2O$, prepared by the reaction of $K[ReO_4]$ with HCl and ethanoic acid under H_2, reacts with L (L = Me_2SO, dma or dmf) to give $[Re_2Cl_4(O_2CMe)_2].2L$ [93]. The crystal structure of $\{Re_2Cl_4(CH_3COO)_2\}_n$ (13) has been determined, and was shown to consist of neutral dimeric metal-metal bonded dimers, which possess a *trans* configuration $\{r(ReRe) = 2.211$ Å ; and $\bar{r}(ReO) = 1.98$ Å; $\bar{r}(ReCl)_{terminal} = 2.28$ Å and $\bar{r}(R\text{-}Cl)_{bridging} = 2.35$ Å$\}$ and form chlorine-bridged chains [94]. $[Re_2Cl_4(HCO_2)_2(OCHNPh_2)_2]$ has been prepared, and consists of a quadruply-bonded Re-Re dimeric unit, bridged by the formate ligands [95]. *Trans*-$[Re_2Br_4(O_2CMe)_2]$ was prepared by thermal dehydration of *cis*-$[Re_2Br_4(O_2CMe)_2].nH_2O$ and shown to be iso-structural with (13) [96].



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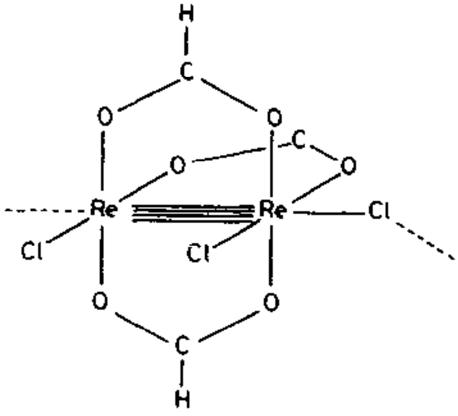

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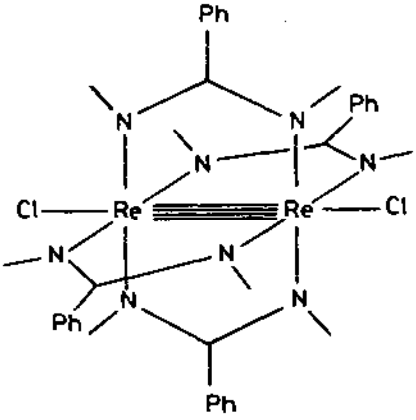
$[NH_4]_2$*cis*-$[Re_2Cl_6(HCO_2)_2]$ was heated at 70-80 °C for 3 h to give $\{Re_2Cl_3(HCO_2)_3\}_n$ (14) [97] which has a chain structure. The dimer contains three bridging $[HCO_2]^-$ groups, one inter-dimer bridging, one terminal chloride ion and a rhenium-rhenium quadruple bond [98].

The Re-Re quadruple bond in $[Re_2(O_2CMe)_4Cl_2]$ can be cleaved by the addition of excess t-butylisocyanide to the solid dimer to give $[(Me_3CNC)_5ReCl]$ [99]. $[Re_2(O_2CR)_4X_2]$ (X = Cl, Br or I) have been reduced electrochemically to give the corresponding $[Re_2(O_2CR)_4X_2]^-$ ion, and the solution properties of these species investigated. The reduction potentials depend on the halogen E° I>Br>Cl, that of iodine being the most positive [100].

9.10.3 Complexes with Group VB donor ligands

Two new complexes have been prepared, containing a Re-Re quadrupule bond and bridging diamidinato groups, $[Re_2Cl_2\{CH_3NC(Ph)CNCH_3\}_4]$ **(15)** and $[Re_2Cl_4\{PhNC(Me)NPh\}_2]$ **(16)**. The crystal structures of the materials have been determined and the constituent molecules show *r*(ReRe) of 2.208 and 2.178 Å respectively [101].



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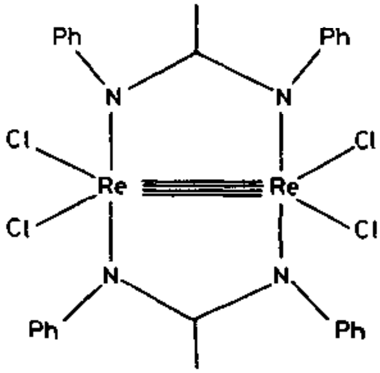


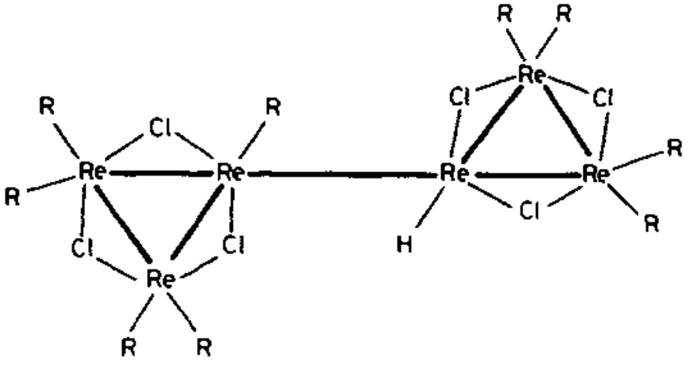
(16)

The new aryldiazenide complex, $[(\eta^5\text{-}C_5H_5)Re(CO)_2(N_2R)][BF_4]$ (R = 2-$CF_3C_6H_4$), reacts with nucleophiles, such as I^-, Cl^-, Br^-, CN^- or SCN^- to give the dinitrogen complex $[(\eta^5\text{-}C_5H_5)Re(CO)_2(N_2)]$; nucleophilic attack occurs at the singly bent aryldiazenido ligand [102].

The seven coordinate complex, $[ReX_3(CO)_2(dppm)]$ (X = Cl or Br) has been obtained by the treatment of $[ReX(CO)_3(dppm)]$ with the corresponding halogens. $[ReCl_3(CO)(bipy)]$ and $[ReX_3(CO)_2(bipy)]$ have been isolated from the $[ReX(CO)_3(bipy)]/X_2$ system [103].

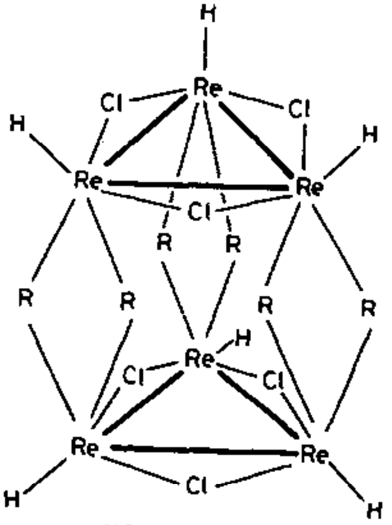
9.10.4 Organometallic clusters

The series of *triangulo*-trirhenium clusters has been extended by the preparation of $[Re_3Cl_3(CH_2Ph)_6]$, $[Re_3Cl_3(C_6H_{11})_6(PR_3)_3]$ and $[Re_3Me_9(PR_3)_n]$ (*n* = 2 or 3). Two dimeric units have been formed by the cleavage of trimers, namely $[Re_2Cl_2(CH_2SiMe_3)_2(PR_3)_4]$ and $[Re_2Me_6(PR_3)_2]$ [104]. The interaction of dihydrogen with the *triangulo*-trirhenium complex $[Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6]$ gives the new type of clusters $[Re_6(\mu\text{-}Cl)_6H(CH_2SiMe_3)_9]$ **(17)**, $[Re_6(\mu\text{-}Cl)_6H_6(\mu\text{-}CH_2SiMe_3)_6]$ **(18)** and $[Re_6(\mu\text{-}Cl)_6(CH_2SiMe_3)_6]$. The structure of **(17)** (which is formed in thf) has been determined crystallographically {$\bar{r}$(ReRe) = 2.993 Å;



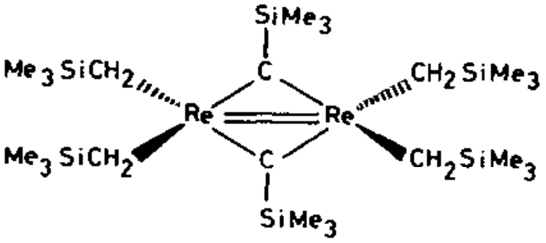
(17; R = CH_2SiMe_3)

$\bar{r}_{(triangular)}$(ReRe) = 2.390–2.420 Å}. Hydrogenolysis in benzene yields (18) [105].



(18; R = CH_2SiMe_3)

The dirhenium complex {Re_2(η-$CSiMe_3$)(CH_2SiMe_3)$_4$] (19) has been prepared (as



(19)

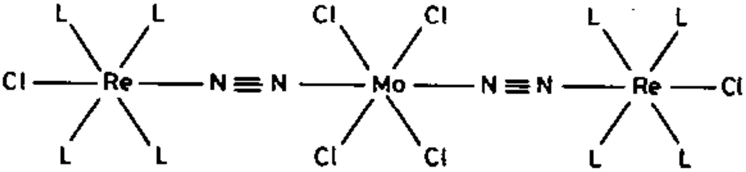
a side product) by the reaction of $[ReCl_4(thf)_2]$ and Me_2SiCH_2MgCl; its crystal structure has been determined [106].

9.11 RHENIUM(I)

As all of the rhenium(I) chemistry published this year, with the exception of a few phosphine derivatives, has concerned carbonyl containing complexes, the compounds are classified below according to the other ligands present.

9.11.1 Non-carbonyl-containing complexes

The resonance Raman spectrum of the trinuclear dinitrogen bridged complex $[Cl(PMe_2Ph)_4Re(N_2)MoCl_4(N_2)Re(PMe_2Ph)_4Cl]$ **(20)** tracks the intense absorbance



(20)

band at 23300 cm^{-1}, which was assigned to an $e_g \leftarrow e_u$ $(^1A_{2u} \leftarrow {}^1A_{1g})$ transition, resulting in a lengthening of the Re-N bond and a shortening of the N-N bonds [107].

The complexes *trans*-$[ReCl(CNR)(dppe)_2]$ (R = Me or CMe_3) were prepared by displacement of N_2 from *trans*-$[ReCl(N_2)(dppe)_2]$ by heating under reflux with excess RNC in thf: the methyl derivative reacted with $H[BF_4]$ to give the carbyne-type complex *trans*-$[ReCl\{CNH(Me)\}(dppe)_2][BF_4]$ [108].

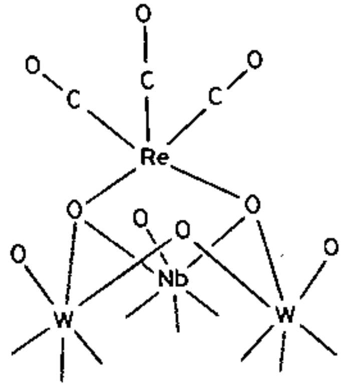
9.11.2 Halides

The kinetics of the reaction between $[Re(CO)_5Br]$ and α- or β-alanine have been shown to occur by a dissociative substitution mechanism; this is a much slower reaction than the analogous manganese complex, as expected [109]. $[BrRe(CO)_5]$ reacts with a variety of amino acids in dioxan to give $[BrRe(CO)_3L_2]$ (L = glycine, *dl*-valine, *dl*-leucine, *dl*-β-phenyl-β-alanine, *dl*-β-2-thienyl-β-alanine or β-indoylethanoic acid) with the L groups mutually *cis* [110].

9.11.3 Complexes with oxygen donor ligands

The preparation of $[NEt_4][Re_2(\mu\text{-}OMe)_3(CO)_6]$ has been reported and its crystal structure elucidated; the Re-Re distance (3.086 Å) is somewhat longer than that expected for a single Re-Re bond (*cf.* 3.02 Å in $[Re_2(CO)_{10}]$) [111].

In a fascinating example of synthetic chemistry, strongly resembling surface modification, an adduct of a rhenium tricarbonyl unit bound to the oxide surface of a polyoxoanion cluster *i.e.* $[(OC)_3Re\{Nb_2W_4O_{19}\}]^{3-}$ **(21)** has been prepared. **(21)** contains the metal tricarbonyl unit bonded to a triangle of oxygen atoms on the surface of the $[Nb_2W_4O_{19}]^{4-}$ anion. The molecular structure was determined by ^{17}O NMR spectroscopy [112].



(21)

Stable phosphinate complexes $[(\mu\text{-}R_2PO_2)Re(CO)_3L]_n$ (L = thf, py, NH_3, PPh_3, $AsPh_3$, $P(C_6H_{11})_3$ or OEt_2) are obtained by the addition of L to $[(\mu\text{-}R_2PO_2)Re(CO)_3]_n$ (R = Me or Ph): the methyl derivatives were found to be dimeric, whereas the phenyl derivative is oligomeric with the Re atoms bridged *via* the $[R_2PO_2]^-$ ligands [113].

9.11.4 Thiocarbamates, selenides and related complexes

By reaction of potassium or caesium monothiobenzoate (mtb = monothiobenzoate) with $[Re(CO)_5Br]$, the binuclear triply *S*-mtb bridged complex $[(CO)_3Re(\mu\text{-}mtb)_3Re(CO)_3]^-$ has been obtained. A crystal structure determination has shown the rhenium atoms to be inequivalent with respect to the mtb ligands [114].

Cis-$[(CO)_4Re(NH_2CH_3)(CONHCH_3)]$ reacts with CS_2 to give $[(CO)_4Re(S_2CNHCH_3)]$. The mechanism of thiocarbamate formation is thought to involve nucleophilic attack of the *N*-carbomylic atom, on the C of CS_2 [115]. A dimeric complex of the form $[\{Re(CO)_3(2\text{-}C_6H_4SN{=}NPh)\}_2]$ has been prepared by reacting $[BrRe(CO)_5]$ with the potassium salt of $[2\text{-}C_6H_4(SCN)N{=}NPh]$ in boiling dioxan. The crystal structure of the oxygen analogue has been reported [116].

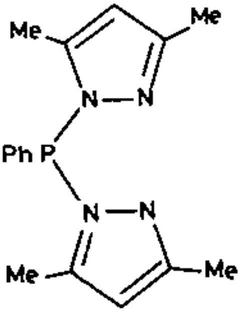
The diselenide complex $[Re_2(\mu\text{-}Br)_2(CO)_6(\mu\text{-}Ph_2Se_2)]$ has been prepared in a similar manner to its disulphide analogue: its crystal structure reveals that the diselenide unit bridges the two metal atoms with a non-bonding Re–Re distance of 3.899 Å [117].

9.11.5 Complexes with Group VB donor ligands

The electron-transfer reactivities of dirhenium complexes of the macrocyclic ligands, taa, TPP and TMTAA (where TMTAA = 5,7,12,14-tetramethyldibenzo[b,i]-[1,4,8,11]tetraaza[14]annulene), *i.e.* $[\{Re(CO)_3\}_2TAA]$, $[\{Re(CO)_3\}_2TPP]$ and $[\{Re(CO)_3\}_2TMTAA]$, were investigated by CV and polarography. The results may suggest a correlation of the oxidation potential with the degree of metal-metal bonding [118].

Trans-$[ReCl(CO)_2(N_2)(PPh_3)_2]$ reacted with MeLi/H^+ to give an unexpected hydroxy carbene dinitrogen complex – *trans*-$[ReCl\{C(OH)Me\}(CO)(N_2)(PPh_3)_2]$. *Trans*-$[ReCl(CO)_3(PPh_3)_2]$ gives *trans*-$[ReMe(CO)_2(PPh_3)_2]$ under similar conditions [119].

$[(OC)_3Re(\eta^2\text{-en})(\eta^1\text{-en})][O_2PR_2]$ and $\{(\mu\text{-}R_2PO_2)Re(CO)_3(\eta^1\text{-en})\}_n$ **(22)** are obtained from the reaction between $\{(\mu\text{-}R_2PO_2)Re(CO)_3\}_n$ (R = Me or Ph) and 1,2-diaminoethane at 110° and 20 °C, respectively. For **(21)**, $n = 2$ when R = Me, but when R = Ph, the complex is oligomeric, monomeric complexes $[\{R_2P(O)O\}Re(CO)_3(bipy)]$ are formed by the addition of bipy to the $\{(\mu\text{-}R_2PO_2)Re(CO)_3\}_n$ [120]. The crystal structure of $[Re(CO)_3(L)Br]$ {L = **(22)**} has been reported **(23)** is bidentate, with coordination *via* the two nitrogens,



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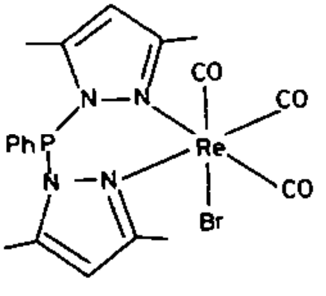


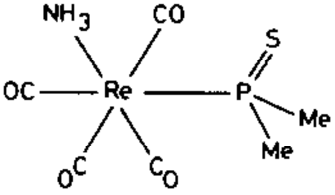
(24)

the CO groups are in a *fac* arrangement and the Br atom occupies the sixth site of an irregular octahedron **(24)** [121].

The series of complexes *fac*-$[(sol)Re(CO)_3L]^+$ {(sol) = MeCN, PhCN, py or pip; L = biquinoline or phen} have been prepared and their interligand and charge-transfer emission spectral properties studied extensively [122].

$[(OC)_5ReNC\text{-}NSF_2][AsF_6]$ and $[(OC)_5ReNC\text{-}NSOF_2][AsF_6]$ have been prepared [123]. $[Re(CO)_4\{CON(R)CH{=}NR\}]$ or $[Re(CO)_4(RNCH{=}NR)]$ (R = MeO-4-C_6H_4, Me-4-C_6H_4, C_6H_5, Cl-4-C_6H_4 or F-4-C_6H_4) have been prepared by the reaction of lithio-1,3-diaryl formamide with $[Re(CO)_5Cl]$ or $[Re_2(CO)_6Cl_2]$, respectively; the carbamoyl complexes undergo decarbonylation to produce the formamide complex in low yield [124].

$[Re(CO)_4(NH_3)\{PMe_2S\}]$ **(25)** is obtained from $[ReBr(CO)_4\{PMe_2SH\}]$ *via* the heterocycle $[\{Re(CO)_4(PMe_2S)\}_2]$ **(26)** by cleaving the Re–S bond with NH_3. The crystal structure of **(25)** was determined [125].



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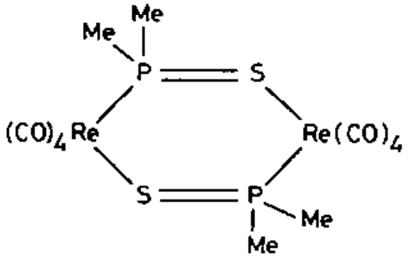


(26)

Treatment of $[ReX(CO)_3(dppm)]$ (X = Cl or Br) with halogens gives the seven coordinate $[ReX_3(CO)_2(dppm)]$ complex, as well as the expected product $[ReX_4(dppm)]$. $[ReCl_3(CO)(bipy)]$, $[ReBr_4(bipy)]$, $[ReBr_3Cl(bipy)]$ and $[ReX_3(CO)_2(bipy)]$ have been isolated from the $[ReX(CO)_3(bipy)]/X_2$ system [103].

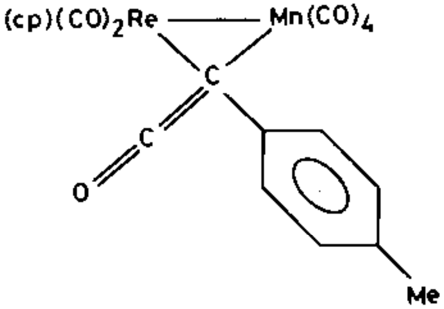
The neutral complexes $[Re(CO)_3(\eta^5\text{-}EC_4Ph_4)]$ (E = P or As) have been prepared from $[Re(CO)_5(\eta^1\text{-}EC_4Ph_4)]$ by heating at reflux in decane or xylene [126]. The complex $[Re_2(CO)_6(dppm)H_2]$ **(27)** has been prepared and its crystal structure determined $\{r(ReRe) = 2.893$ Å$\}$. When reacted with $P(OMe)_3$, RNC or MeCN, **(27)** gave 1:1 adducts; with MeCN, two products were formed, one of which was shown to be the insertion product $[Re_2(CO)_6(dppm)(NCHMe)H]$ $\{r(ReRe) = 3.035$ Å$\}$ [127].

9.11.6 Organometallic derivatives

$[Re(\eta^3\text{-}C_3H_5)(CO)_3(PPh_3)]$ and $[Re(\eta^3\text{-}C_3H_5)(CO)_2(PPh_3)_2]$ have been prepared, and are the first examples of CO ligand substitution products to be obtained from $[Re(\eta^3\text{-}C_3H_5)(CO)_4]$ [128].

The crystal structure of the metallation product of $[RePh(CO)_5]$ with benzophenone in the presence of triphenylphosphine has been reported. The product is $[Re(PPh_3)(CO)_3\{C_6H_5C(O)C_6H_4\}]$, with the orthometallated benzophenone acting as a bidentate ligand [129].

The carbyne complex $[Re(CC_6H_4Me)(CO)_2(\eta^5\text{-}C_5H_5)]$ reacts with $[(Ph_3P)_2N][Mn(CO)_5]$ to give **(28)** [130].



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9.11.7 Complexes with Group IVB donor ligands

The complexes [$(Ph_3E)Re(CO)_3(phen)$] (E = Ge or Sn) exhibit optical emission (*ca.* 750 nm) from their lowest excited states in CH_2Cl_2/CCl_4 solutions, and also undergo E-Re bond cleavage under the same conditions [131].

9.12 RHENIUM(0)

In a study of the kinetics of the substitution reactions of [$MnRe(CO)_{10}$] with PPh_3, PBu_3 or $P(OPh)_3$, it was seen that the rhenium substituted product predominates. A mechanism for substitution involving CO dissociation from the manganese centre and an intermediate with a CO bridging between Mn and Re was suggested [132]. The kinetics of thermal homolytic fission in [$Re_2(CO)_{10}$] have been studied and show that [$Re(CO)_5$] is more stable than [$Mn(CO)_5$]. It was suggested that homolytic fission is the initial step in the substitution reaction of [$Re_2(CO)_{10}$] with PPh_3 [133]. A study of the kinetics of the fragmentation reaction of [$Re_2(CO)_{10-x}(PPh_3)_x$] (x = 1 or 2) with iodine shows the initial formation of a complex/iodine species with n moles of I_2 (n = 1-4) which then leads to Re-Re bond fission [134].

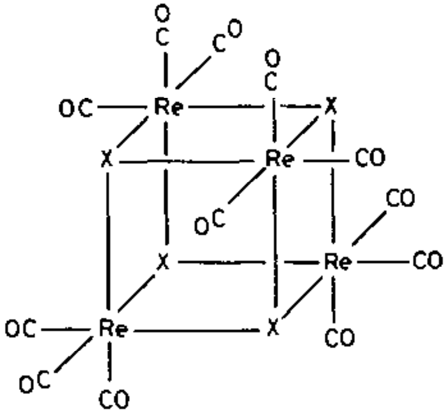
[$Re(CO)_5$] has been used to preare some metal-metal carbyne complexes of the form [$(OC)_5ReM(CO)_4CR$] (M = Cr, Mo or W; R = Ph or Me), which have been examined by Raman spectroscopy and assignments made for the ν(M-M') stretching frequency [135].

In a Raman study on a single crystal of [$Re_2(CO)_{10}$], twenty of the twenty-one Raman active modes were assigned. By consideration of the intensity ratios between the (*ZZ*) and (*YX*) tensor components of the two possible assignments of $\bar{\nu}$(ReRe) (129 or 107 cm^{-1}), the lower value was favoured [136].

9.13 CARBONYL CLUSTERS

The positions of the hydride ligands in the rhenium complexes [$H_3Re_3(CO)_8(pop)_2$] {pop = $(EtO)_2POP(OEt)_2$}, [$H_2Re_2(CO)_6(dppe)$] and [$ReH_3(dppe)_2$] have been predicted indirectly, and contrasted with other direct and indirect techniques [137].

[$X_4Re_4(CO)_{12}$] (**29**; X = Cl or Br) has been prepared by the thermal decomposition of [$ReX(CO)_3(SPh_2)_2$]. The molecule has a *pseudo*-cubane structure, with triply-bridging halides, and is isostructural with [$X_4Pt_4Me_{12}$] [138].



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The UVPES of [$H_3Re_3(CO)_{12}$] has been interpreted in terms of a three-centre two-electron bond ($M\overset{H}{\frown}M$) model, and the arguments generalised to produce a similar approach to that developed for boranes [139].

9.14 FORMYL AND NITROSYL COMPLEXES

The first crystal structure of a complex containing a formyl ligand has been reported. [$(\eta^5\text{-}C_5H_5)Re(PPh_3)(NO)(CHO)$] was prepared by reduction of the corresponding carbonyl complex with [Et_3BH]$^-$. In this complex {$r(Re\text{–}CHO)$ = 2.055 Å; $Re\hat{C}O$ = 128.1°; $Re\hat{N}O$ = 178.0°} [140]. The reactions of this complex with electrophiles have been studied and an intermediate of the form [$(\eta^5\text{-}C_5H_5)Re(=CHR)(NO)(PPh_3)$] postulated [141]. The formyl complex [$(C_5H_5)Re(CO)(NO)(CHO)$] has also been prepared, and its chemical reduction investigated [142].

[$(C_5H_5)Re(CO)(NO)(CONHCH_3)$] reacts with CS_2 to give [$(C_5H_5)Re(CO)(NO)(S_2CNHCH_3)$]. The mechanism of thiocarbamate formation has been discussed in terms of nucleophilic attack of the *N*-carbamylic atom on the C of the CS_2 [115]. The reaction of PMe_3 with [$(\eta^5\text{-}C_5H_5)Re(CO)(NO)Me$] produces a η^1-cyclopentadienyl derivative [$(\eta^1\text{-}C_5H_5)Re(CO)(NO)Me(PMe_3)_2$], the cyclopentadienyl group being *trans* to the linear nitrosyl group [143].

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