Coordination Chemistry Reviews, 37 (1981) 199—220
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

10. TECHNETIUM AND RHENIUM

K.R. SEDDON

CONTENTS

Technetium

Rhenium

The period of this review essentially coincides with the coverage of Vols. 90 and 91 of Chemical Abstracts. Thus, although a majority of the papers covered were published in 1979, many from 1978 are also included. Although the chemistry of technetium is small compared with that of rhenium, it has been treated separately in order to reflect the different interests stimulating its investigation.

This review concentrates upon the coordination chemistry of technetium and rhenium. No attempt has been made to cover work of an essentially organometallic nature (although carbonyl is treated as an inorganic ligand). Areas of especial interest this year include an extension of the chemistry of nitridorhenium(VII) systems, the preparation of Schiff base complexes of rhenium, studies upon Re—Re bonded systems, and elegant studies upon rhenium cyanide and thionitrosyl derivatives.

TECHNETIUM

10.1 TECHNETIUM(VII)

The electrochemistry of $[TcO_4]^-$ has attracted much attention. The reduction of $[TcO_4]^-$ in chloride and sulphate media has been studied by polarography, CV and coulometry, and new potential-pH diagrams at 10^{-4} M and 10^{-7} M have been reported [1]. In the presence of pyrophosphate and various other diphosphonate ligands (e.g. 1-hydroxyethane-1,1-diphosphonic acid; see also Section 10.4), the reduction of $[TcO_4]^-$ has been studied by normal-pulse polarography as a function of pH. Below pH 6, $[TcO_4]^-$ was reduced to Tc(III), which could be reoxidised to Tc(IV). At pH > 10, $[TcO_4]^-$ was reduced in two steps (n.b. but see Section 10.2) to Tc(V) and Tc(IV), each of which could be reoxidised to Tc(VII). For $6 < pH < 10$, the results obtained depended upon the ligand present [2]. In the presence of $SnCl_2$, the reduction of $[TcO_4]^-$ has been studied by polarography and electronic absorption spectroscopy (at pH 7 in 1 M sodium phosphate solution). A mixed metal complex of Tc(III), Tc(IV) and Sn(II) was observed polarographically, but fixed potential coulometry produced a Tc(III) complex, which was rapidly oxidised by air to Tc(IV) [3].

10.2 TECHNETIUM(VI)

The transient species, $[TcO_4]^{2-}$, has been detected and characterised for the first time in aqueous solution. It was produced by pulse radiolysis of

$[TcO_4]^-$ in an aqueous alkaline medium, and characterised by fast-scan cyclic voltammetry. $[TcO_4]^{2-}$ has a lifetime of the order of milliseconds and its electronic spectrum was reported [4].

10.3 TECHNETIUM(V)

Reduction of an ethanolic solution of $[NH_4][TcO_4]$ and a dithiol HS—Y—SH (Y = CH_2CH_2, CH_2CHCH_3 or $CH_2CH_2CH_2$) with $Na[BH_4]$, followed by addition of $[AsPh_4]Cl$, leads to the isolation of the orange salts $[AsPh_4][TcO(S—Y—S)_2]$, which were chemically and spectroscopically characterised [5]. The molecular structure of $[AsPh_4][TcO(SCH_2CH_2S)_2]$ reveals the anion to be square—pyramidal [6].

Reaction of $[TcO_4]^-/SnCl_2$ or $[TcOCl_5]^{2-}$ with calcium gluconate to give the same complex species in solution has been taken as evidence to indicate that the oxidation state of the Tc in the complex is (V) [7]. The gluconate complex will undergo ligand exchange reactions with *meso* or *racemic* 2,3-dimercaptosuccinic acid, to give isomeric succinatotechnetate(V) complexes [8] and, when treated with sodium 1,2-dicyanoethylenedithiolate ($Na_2[S(CN)C{=}C(CN)S]$) followed by addition of $[Et_4N]Br$, gives the brown complex, $[Et_4N][TcO\{S(CN)C{=}C(CN)S\}_2]$ [9].

10.4 TECHNETIUM(IV)

The molecular structure of $[NH_4]_2[TcCl_6]$ shows the expected octahedral environment for the metal $\{\bar{r}(TcCl) = 0.2353\ nm\}$ [10]. Thermolysis of $[pyH]_2[TcCl_6]$ gives initially $[pyH][TcCl_5(py)]$, followed by $[TcCl_4(py)_2]$ [11]. EPR studies of Tc(IV) in solution in general, and $[TcCl_6]^{2-}$ in particular, indicate that EPR will be a valuable tool for studying technetium chemistry [12]. The electrochemical behaviour of $[TcX_6]^{2-}$ (X = Cl, Br or NCS) has been investigated by cyclic voltammetry [13].

$[PPh_4]_2[TcX_6]$ (X = Cl or Br) reacts with acacH to give $[PPh_4][TcX_4(acac)]$, whereas reaction of $[TcX_4(PPh_3)_2]$ with acacH gives $[TcX_2(acac)_2]$, $[TcBr_3(acac)(PPh_3)_2]$, or Tc(III) complexes (q.v.), depending upon reaction conditions [14].

1-Hydroxyethane-1,1-diphosphonic acid ($hedpH_4$; see also Section 10.1) reacts with $K_2[TeBr_6]$ (or with $[TcO_4]^-/SnCl_2$) according to pH, to give complexes believed to be $[Tc(OH)_3(hedpH_3)]$, $[Tc(OH)_3(hedpH_2)]^-$, $[TcO(OH)(hedpH)]^{2-}$, $[Tc_2(OH)_4(hedpH_3)]^{3+}$, $[Tc_2(OH)_6(hedpH_2)]$, $[Tc(OH)_4(hedp)]^{4-}$ and $[Tc(OH)_x(hedpH_y)_2]^{(4-x-8+2y)+}$ [15].

10.5 TECHNETIUM(III)

Reaction of $[TcX_4(PPh_3)_2]$ (X = Cl or Br) with acacH gives $[TcX_2(acac)(PPh_3)_2]$, $[TcX(acac)_2(PPh_3)]$ or $[Tc(acac)_3]$, depending upon the reaction conditions [14].

10.6 TECHNETIUM(I)

The thermodynamic properties of $[TcX(CO)_5]$ (X = Cl, Br or I) have been calculated [16].

RHENIUM

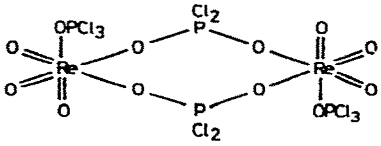
10.7 RHENIUM(VII)

10.7.1 Halides, oxohalides and nitridohalides

ReF_7 has been prepared, by the direct fluorination of ReF_6 at 400°C [17], and its force constants have been calculated [18]. It has also been characterised by photoelectron spectroscopy [17].

Reaction of $K[ReO_4]$ and IF_5 gives ReO_3F, whereas direct fluorination of ReO_2 yields a mixture of ReO_2F_3 and $ReOF_5$ [17]. The direct fluorination of ReO_2 or ReO_2F_3, in the presence of AgF_2, produces principally $ReOF_5$ [17]. The mean amplitudes of vibration and thermodynamic functions have been calculated for ReO_3F [19] and $ReOF_5$ [20]; their photoelectron spectra have also been reported [17]. The reactions of ReO_2, ReO_3, Re_2O_7, $K[ReO_4]$ and $[NH_4][ReO_4]$ with $[NH_4][HF_2]$, $K[HF_2]$ or HF, to yield various rhenium oxofluorides, have been studied [21].

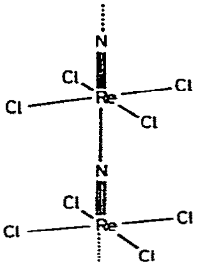
ReO_3Cl reacts with $AlCl_3$ [22], $NbCl_5$ [22], or $SbCl_5$ [23] to give the adducts $ReO_3Cl \cdot AlCl_3$, $ReO_3Cl \cdot NbCl_5$ or $ReO_3Cl \cdot SbCl_5$, respectively, which are all believed (from IR evidence) to contain $Re{=}O \rightarrow E$ (E = Al, Nb or Sb) linkages. ReO_3Cl will react with CCl_4 at 20°C, in the presence of $GaCl_3$, to give $COCl_2$, and possibly ReO_2Cl_3 [22]. $ReCl_5$ reacts with Cl_2O, in the presence of $POCl_3$, to give $ReO_3(O_2PCl_2) \cdot POCl_3$, which is postulated to have a dimeric structure (1) [24].



(1)

Unstable red-yellow crystals of $[phenH_2][ReO_3Cl_2(H_2O)]Cl$ were prepared by prolonged reaction between $[ReO_3Cl(phen)]$ and concentrated hydrochloric acid in a dessicator over P_2O_5. The molecular structure of the complex reveals the oxo-groups in the anion to be *facial*, but the parameters $\{\bar{r}(Re{=}O) = 0.173$ nm, $r(Re{-}OH_2) = 0.233$ nm, $\bar{r}(ReCl) = 0.248$ nm$\}$ are of low precision, due to disorder in the crystal [25].

$ReNCl_4$ has been prepared by the reaction of $ReCl_5$ with NCl_3. Its structure, (2), is similar to that of $WOCl_4$, having chains of $ReNCl_4$ units, linked by strongly alternated $Re{\equiv}N{-}Re$ bonds $\{r(Re{\equiv}N) = 0.158$ nm, $r(Re{-}N) = 0.248$



(2)

nm, $\bar{r}$(ReCl) = 0.227 nm} [26]. Upon heating at 170°C, $ReNCl_4$ gives $ReNCl_3$ and chlorine, whereas its reaction with $POCl_3$ yields $[ReNCl_3 \cdot POCl_3]_4 \cdot 2 POCl_3$ (and again Cl_2). Reaction of $ReNCl_4$ with $[N_3]^-$ or Cl^- gives $[ReNCl_4]^-$ and N_2 or Cl_2, respectively [26].

10.7.2 Oxides, rhenates(VII) and aqueous chemistry

Crystallographic data have been presented for a wide range of actinide, molybdenum and tungsten rhenates(VII), and many double salts thereof [27]. The thermal decomposition of $Pb[ReO_4]_2$ has been studied by mass spectrometry and ions corresponding to PbO, Re_2O_7, $Pb[ReO_4]_2$ and $Pb_2Re_2O_9$ were detected in the vapour above the solid [28]. The ternary oxides $A_3Re_2O_{10}$ (A = Ba or Sr) were prepared by heating $ACl_2 \cdot x H_2O$ with rhenium metal, whereas $A_5Re_2O_{12}$ (A = Ca or Sr; see also Section 10.9.2) were prepared by heating $ACl_2 \cdot x H_2O$ with $A[ReO_4]$; the quaternary oxides $Ca_3B_2Re_2O_{13}$ (B = La, Pr, Nd or Sm) were also characterised [29]. The structure of La_3ReO_8 has been determined [30].

The reactions between $[ReO_4]^-$ and H_2E (E = S or Se) have been reported [31]. Evidence for $[SO_4]^{2-}$ forming 1 : 1 and 2 : 1 complexes with Re(VII) in 1—10 M sulphuric acid solutions has been presented [32,33], and in neutral and acidic (H_2SO_4) solutions of $[ReO_4]^-$, interaction with thiocyanate occurs; for acid concentrations >1 M, reduction to Re(IV) is observed [34].

10.8 RHENIUM(VI)

10.8.1 Halides and oxohalides

$ReOF_4$ has been prepared by the reaction between ReF_6 and ReO_3 at 300°C [17] and by the reaction between ReF_6 and B_2O_3 [35]. The photoelectron spectra of both ReF_6 and $ReOF_4$ have been reported [17] and the mean amplitudes of vibration and thermodynamic functions of the latter have been calculated [20].

$ReOF_4$ will react with either CCl_4 or BCl_3 to give $ReOCl_4$ [35].

10.8.2 Oxides and rhenates(VI)

Fermi-surface pressure-derivative measurements upon ReO_3 at 2 K indicate that a novel second-order phase transition occurs, probably involving a tetragonal distortion of the cubic lattice; the high pressure phase is much more compressible than the low pressure phase [36]. The "open orbits" in ReO_3 have been observed by the induced torque method at 1.4 K [37] and the coefficient of linear expansion of a single crystal of ReO_3 has been measured [38].

The magnetic and structural properties of the perovskite-related oxides $A_2(BRe)O_6$ {A = Ca, Sr or Ba; B = Ca or Sr} have been re-examined; they show Curie—Weiss behaviour, having magnetic moments ~1.10 μ_B and Weiss constants ~—150 K [39]. The ternary oxides $Ba_3Re_2O_9$ and $Sr_2Re_2O_9$ have also been prepared and characterised [40].

10.9 RHENIUM(V)

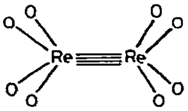
10.9.1 Fluorides

A detailed preparation of ReF_5 has been published [41], and the molecular structure of $[Re(CO)_6][F_5Re(\mu\text{-}F)ReF_5]$ (prepared by the reaction of $[ReF_6]$ with $[Re_2(CO)_{10}]$ in HF) has been determined [42].

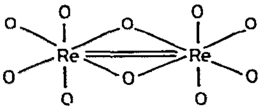
10.9.2 Oxides

The thermal decomposition of $Ca_5Re_2O_{12}$ (see Section 10.7.2) in vacuo yields single crystals of a perovskite-related phase, $Ca_3ReO_{5.5}$ (μ = 4.46 μ_B; θ = —819 K), which shows strong magnetic interactions between the Re^{5+} sites. This oxide might well be magnetically ordered at a temperature below that of the range studied (80—300 K) [39].

The structure of the mixed oxidation state {Re(V/IV)} ternary oxide $La_6Re_4O_{18}$ is of especial interest; it comprises isolated Re_2O_8 (3) and Re_2O_{10} (4) dimeric units, linked by La ions. The Re—Re separations are 0.2235 and 0.2456 nm, respectively [43].



(3)

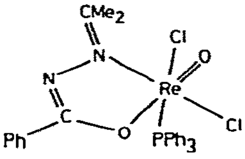


(4)

10.9.3 Complexes

The first Schiff base complexes of rhenium have been prepared by reaction of $[ReOCl_3(PPh_3)_2]$ with LH_2 (L = sal_2en, sal_2prop, sal_2phen or $acac_2en$), in the presence of Et_3N and moist air, to give $[Re_2O_3(L)_2]$. Under anhydrous conditions [ReOCl(L)] forms. In the absence of Et_3N, the products $[ReOCl_3(LH_2)]$ (L = $acac_2en$), $[Re_2O_2Cl_6(PPh_3)_2(LH_2)]$ (L = $acac_2en$) and $[Re_2O_2Cl_4(PPh_3)_2(L)]$ (L = sal_2en) were isolated [44].

The molecular structure of the propanone benzoylhydrazonido-complex, $[ReOCl_2\{PhC(O)C{=}N{-}N{=}CMe_2\}(PPh_3)]$ (5), has shown the hydrazine



(5)

moiety to be bonded in the enol form $\{r(Re{=}O) = 0.1685$ nm, $r(Re{-}O) = 0.2013$ nm, $r(ReN) = 0.2127$ nm and $\bar{r}(ReCl) = 0.2366$ nm$\}$ [45].

10.9.4 Mixed-oxidation state complexes, Re(V/IV)

A detailed study of the resonance Raman spectrum of $Cs_3[Re_2OCl_{10}]$ has been reported. The longest progression reaches $14\nu_1(a_{1g})$ $\{\nu_s(ReORe) = 228.2\ cm^{-1}\}$ and the band excitation profile maximises at ca. 19900 cm^{-1}. In total, six progressions were observed at room temperature, and eight at 80 K, thus yielding a wealth of spectroscopic data [46].

10.10 RHENIUM(IV)

10.10.1 Hexahalorhenates(IV) and related complexes

$[(C_{12}H_{25})_3NH]F$ has been used as a phase transfer reagent with $[ReX_6]^{2-}$ (X = Cl, Br or I) to form mixed halide complexes of the type $[ReF_nX_{6-n}]^{2-}$ under mild conditions [47]. Reaction of methyl isocyanide with $[NBu_4]_2[Re_2Cl_8]$ in ethanol causes oxidation to green $[NBu_4][ReCl_5(CNMe)]$, which has been characterised by X-ray crystallography [48].

Salts of the hexachlororhenate(IV) anion have been the subject of a number of varied studies. Ammonium ion tunnelling has been observed in powdered $[NH_4]_2[ReCl_6]$ [49] and the structure of this salt has been determined by neutron diffraction [50]. Variable temperature (1.5—300 K) magnetic susceptibility measurements have been made upon the series of compounds $[Me_{4-x}NH_x]_2[ReCl_6]$ (x = 0, 1, 2 or 3). The methylammonium and dimethylammonium salts show Néel temperatures at 3.8 and 9.8 K, respectively. The salts of the larger cations show no T_N, the $[Me_4N]^+$ salt being an ideal paramagnet (θ = 0 K) [51]. The reduction of $[ReCl_6]^{2-}$ has been studied polarographically [52], and the X-ray L_{III} absorption-edge structure of Re in $Cs_2[ReCl_6]$ gives an estimate of the Re—Cl bond length as 0.240 nm (cf. 0.232

nm by X-ray crystallography) [53]. Mass spectral studies of $K_2[ReCl_6]$ vapour have been reported [54] and homogeneous mixed crystals of $K_2[ReCl_6]$ and $K_2[ReBr_6]$ can be grown at *any* composition [55].

Some insight has been gained into the electronic structure of the $[ReX_6]^{2-}$ species. Near IR luminescence studies upon $[ReBr_6]^{2-}$ have detected the previously unobserved emission bands $\Gamma_7(^2T_{2g}) \rightarrow \Gamma_6(^2T_{1g}), \Gamma_8(^2E_g), \Gamma_8(^2T_{1g})$ and $\Gamma_8(^2T_{1g}) \rightarrow \Gamma_8(^4A_{2g})$ [56], and the intensity distributions in the vibronic side bands of the $\Gamma_7(^2T_{2g}) \rightarrow \Gamma_8(^4A_{2g})$ transition in the emission spectra of $[ReCl_6]^{2-}$ and $[ReBr_6]^{2-}$ have been observed [57] and calculated [58]. The electronic Raman spectrum of $[Et_4N]_2[ReI_6]$ has been observed at 80 K: the totally symmetric a_{1g} vibrational mode is coupled to the $\Gamma_8(^4A_{2g}) \rightarrow \Gamma_8(^2T_{1g})$ electronic absorption [59].

CV data for $[NBu_4]_2[Re(NCS)_6]$ have been reported [60].

10.10.2 Oxides

A series of distorted perovskites, $CaIr_xRe_{1-x}O_3$ ($x = 0.25, 0.33, 0.66$ or 0.75) has been prepared and characterised [61].

10.10.3 Complexes

$[ReCl_4(PPh_3)_2]$ reacts with LH_2 (L = sal$_2$en, sal$_2$prop, sal$_2$phen or acac$_2$en), in the presence of Et_3N, to give the novel Schiff base complexes $[ReCl_2(L)]$. In the absence of Et_3N, the products $[ReCl_4(LH_2)]$ (L = sal$_2$en or sal$_2$prop) were isolated [44]. $ReCl_5$ reacts with acetoxime, $Me_2C{=}NOH$, to give $[ReCl_4\{MeC(O)NHMe\}]$ [62].

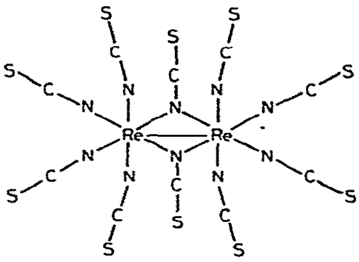
10.11 RHENIUM(III)

10.11.1 Halides and halide complexes

SCF-Xα-SW calculations (without relativistic corrections) upon Re_3Cl_9 and $[Re_3Cl_{12}]^{3-}$ have been reported, and have been used to rationalise the low energy regions of their electronic spectra [63]. Ethanolic solutions of Re_3Cl_9 react with L (L = 3-methyl-1-phenylphosphole or 3,4-dimethyl-1-phenylphosphole) to give the expected products, $[Re_3Cl_9L_3]$ [64].

The crystal structure of $[NH_4]_2[Re_2Cl_8] \cdot 2\,H_2O$ has been determined $\{r(Re{-}Re) = 0.2234$ nm$\}$ [65], and the room temperature emission spectra of $[Re_2Cl_8]^{2-}$ in CH_3CN and CH_2Cl_2 have been reported [66].

$[Bu_4N]_2[Re_2I_8]$ (see also [67]) has been prepared by the reaction between $[Bu_4N]_2[Re_2X_8]$ (X = Cl or Br) and HI in CH_2Cl_2; it is hydrolytically unstable, but stable in organic solvents and in the solid state. It has been characterised by UV, IR and Raman spectroscopy [68]. CV data have been reported for $[NBu_4]_2[Re_2(NCS)_8]$ [60]. The complex $[Bu_4N]_3[Re_2(NCS)_{10}]$ {originally believed to be $[Bu_4N]_3[Re_2(NCS)_8(CO)_2]$} has been characterised crystallographically, and shown to contain the anion (6), which contains a novel

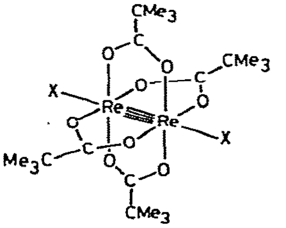


(6)

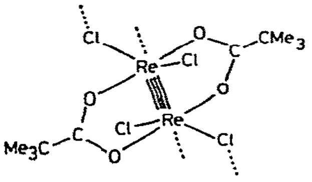
bridging mode for NCS$^-$. This Re—Re bonded species {r(Re—Re) = 0.2613 nm} is a paramagnetic, mixed-valence complex [69].

10.11.2 Carboxylates and related systems

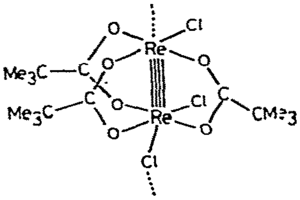
In the wake of the current interest in $M_2(O_2CR)_4$ {M = Cr or Mo}, the quadruply-bonded $Re_2(O_2CR)_4X_2$ systems, and many of their derivatives, have been the subject of extensive study. The molecular structures (7) of $[Re_2(O_2CCMe_3)_4X_2]$ (X = Cl or Br) reveal the anticipated geometry, with a linear X—Re—Re—X skeleton, and the electronic spectra of these systems have been briefly discussed [70]. Thermal decomposition of $[Re_2(O_2CCMe_3)_4Cl_2]$ at 220°C yields the complexes $[Re_2(O_2CCMe_3)_2Cl_4]$ (8) and $[Re_2(O_2CCMe_3)_3Cl_3]$ (9), which were purified by fractional sublimation. Both (8) and (9) contain chains of dimeric units, linked by halogen bridges [71]; (8)



(7)



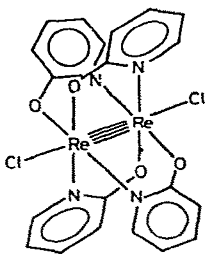
(8)



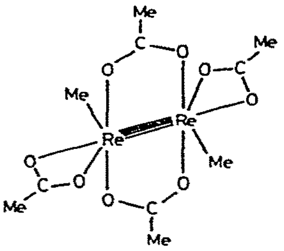
(9)

has a transoid structure (i.e. the O_2CR groups are above and below the plane of the Re_2Cl_4 unit) [71], whereas $[Re_2(O_2CR)_2Cl_4]$ (R = H or Me) are known to have cisoid structures [72,73]. *Cis*—*trans* isomerisation of mixed chlorocarboxylate dimers of dirhenium has now been reported [74] and the molecular structure of $[Re_2(O_2CMe)_2Cl_4(dmso)_2]$ (10) has been determined [75].

The reaction of $[NBu_4]_2[Re_2Cl_8]$ with 2-hydroxypyridine (py-2-OH) gives $[Re_2(py\text{-}2\text{-}O)_4Cl_2]$ (11), which has a shorter Re—Re bond than the analogous carboxylate complexes (see Table 1) [76]. On each Re atom, the N-atoms are mutually *cis*, as opposed to the more commonly occurring *trans* arrangement.



(11)



(12)

$[Re_2Me_2(O_2CMe)_4]$ (12) has been prepared by the reaction between $Li_2[Re_2Me_8] \cdot 2\ Et_2O$ and ethanoic acid [77]; its structure (12) shows an unusual mode of coordination for two of the ethanoates, in that they are chelating rather than bridging [78] and the Re—Re bond is significantly shorter than in, say, (7) (see Table 1). The complexes $[Re_2R_4(O_2CMe)_2]$ (R = CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph or CH_2Ph) were then prepared by reaction of (12) with R_2Mg. Reaction of (12) with Cl_2 gives a polymeric product $[\{ReMe(O_2CMe)Cl\}_n]$ and with MeOH gives another polymeric species $[\{ReMe(O_2CMe)(OMe)\}_n]$ [77]; the former product may be recrystallised from dmso to give $[Re_2Me_2(O_2CMe)_2Cl_2(dmso)]$ (13) [77], whose structure has been determined [78]. It seems likely that both polymeric species thus consist of $\{Re_2Me_2(O_2CMe)_2\}$ units linked by Cl or OMe bridges, respectively.

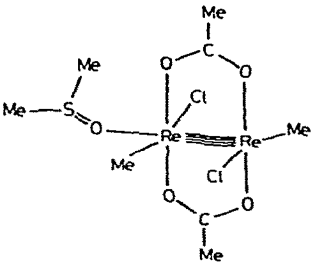
Re_3Me_9 and $[Re_3Cl_3(CH_2SiMe_3)_6]$ react with weak protonic acids (e.g. carboxylic acids, β-diketonates and diphenyltriazene) to give complete or partial loss of terminal alkyl groups as CH_4 or $SiMe_4$, respectively. The rhenium complexes thus formed retain the *triangulo*-Re_3 skeleton and may be

TABLE 1

Structural parameters

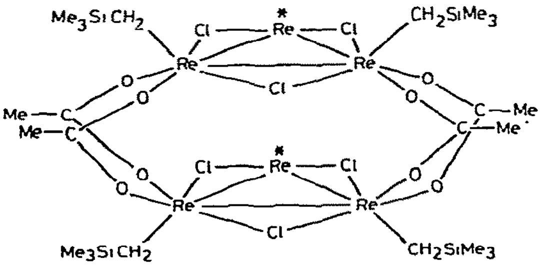
Compound	r(ReRe) (nm)	r(ReX) (nm) [a]	r(ReCl)(nm) [b]	Ref.
(7; X = Cl)	0.2236	0.2477 [c]		70
(7; X = Br)	0.2234	0.2603 [d]		70
(8)	0.2209	0.223, 0.234 [c]	0.290	71
(9)	0.2229	0.228 [c]	0.263, 0.268	71
(10)	0.2237			75
(11)	0.2206	0.2545 [c]		76
(12) [e]	0.2177			78
(13) [f]	0.2184	0.2360, 0.2432 [c]		78

[a] For terminal halide.
[b] For bridging halide.
[c] X = Cl.
[d] X = Br.
[e] r(ReMe) = 0.2099 nm.
[f] $\bar{r}$(ReMe) = 0.2127 nm.



(13)

either monomeric with respect to this unit {e.g. $[Re_3Cl_3(O_2CPh)_6]$, $[Re_3Cl_3(CH_2SiMe_3)_3(O_2CPh)_3]$, $[Re_3Me_6(dik)_3]$ or $[Re_3Cl_3(CH_2SiMe_3)_3(PhN_3Ph)_3]$} or dimeric, with two Re_3 units linked by carboxylate bridges to give an Re_6 species {e.g. $[Re_6(\mu\text{-}Cl)_6(CH_2SiMe_3)_6(\mu\text{-}O_2CMe)_6]$ (14) or $[Re_6(\mu\text{-}Me)_6Me_6(\mu\text{-}O_2CMe)_6]$} [79]. In the structure of (14) as illustrated, the coordination sphere of the atoms marked * has been left incomplete for the sake of clarity; the two parallel Re_3 planes may be eclipsed or staggered.



(14)

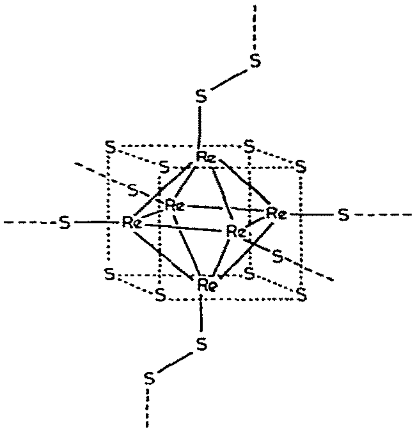
10.11.3 Pentane-2,4-dionato- complexes

Reduction of *cis*- or *trans*-$[Re(acac)_2Cl_2]$ with metallic sodium or potassium, or Tl(acac), gives green, air-sensitive $M[Re(acac)_2Cl_2]$ (M = Na, K or Tl). $K[Re(acac)_2Br_2]$ was prepared in an analogous manner. The anion has the same configuration, irrespective of the geometry of the starting material [80]. The molecular structure of $[AsPh_4][Re(acac)_2Cl_2]$ (prepared by metathesis from the K^+ salt) shows the configuration of the anion to be *trans* {$\bar{r}$(ReCl) = 0.240 nm, $\bar{r}$(ReO) = 0.201 nm} [81]. Reduction of $[Re(acac)_2Cl_2]$ with powdered zinc in acacH is a convenient preparation for $[Re(acac)_3]$ [80].

10.11.4 Sulphides

The reaction of Re, $K[ReO_4]$ or ReS_2 with an excess of A_2CO_3 (A = Na or K) and sulphur at 750°C gives red crystals of a compound, $A_4Re_6S_{12}$ (15).

The structure (**15**) consists of Re_6 octahedra located in cubes of sulphide

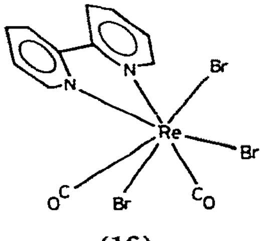


(**15**)

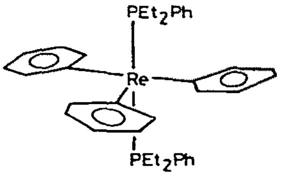
ions, which thus cap the faces of the octahedra. The four equatorial Re atoms are linked by a terminal sulphur atom to adjacent Re_6 octahedra, whilst the two axial Re atoms are similarly linked via an $(S_2)^{2-}$ bridge. The red insulating crystals turn to black semiconducting crystals upon standing in air. The identity of the black form remains to be established [82].

10.11.5 Amine and phosphine complexes

Seven-coordinate Re(III) complexes, $[ReX_3(CO)_2(LL)]$ (X = Cl or Br, LL = bipy; X = Br, LL = 2,9-Me_2phen), have been prepared by oxidation of *fac*-$[ReX(CO)_3(LL)]$ with X_2 and the molecular structure of $[ReBr_3(CO)_2(bipy)]$ (**16**) shows the Re to be in a capped-octahedral environment [83]. The structure of $[Re(^1\eta\text{-}Ph)_3(PEt_2Ph)_2]$ (**17**) reveals a trigonal bipyramidal structure,



(**16**)



(**17**)

with a near-planar array of equatorial phenyl groups, and a relatively short $\{\bar{r}(ReC) = 0.2027\ nm\}$ Re—C bond indicates the presence of significant d_π—p_{π^*} back-bonding [84].

The molecular structure of $[Re(NCS)_3(dppe)(PEt_2Ph)]$ reveals it to have a *meridional* configuration, with Re—NCS being an *iso*thiocyanato-linkage [60].

The complexes [Re(NCS)$_3$(PEt$_2$Ph)(LL)] (LL = dppe, bipy or phen) show one reversible oxidation wave (to [Re(NCS)$_3$(PEt$_2$Ph)(LL)]$^+$) and two reversible reduction waves (to [Re(NCS)$_3$(PEt$_2$Ph)(LL)]$^{-/2-}$) in their cyclic voltammograms [60].

10.11.6 Isocyanide complexes

Oxidative addition of Br$_2$ to [Re(CO)L$_4$Br] (L = CNMe or 4-CN-C$_6$H$_4$Me) gives [ReL$_4$Br$_3$]. The molecular structure of the 4-tolyl isocyanide complex shows it to be seven-coordinate, with a capped octahedral geometry; it contains three *fac* bromides, three *fac* CNR ligands, and a capping fourth CNR ligand [85].

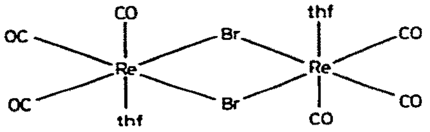
10.12 RHENIUM(I)

As all the chemistry of rhenium(I) published this year has concerned carbonyls, the compounds are classified below according to the anionic ligands present.

10.12.1 Halides

The thermodynamic properties of [ReX(CO)$_5$] (X = Cl, Br or I) have been calculated [16], and a convenient preparation of [ReI(CO)$_5$] from [Re$_2$(CO)$_{10}$] and I$_2$ has been reported [86]. IR and Raman data for [ReX(CO)$_5$] (X = Cl or Br) have also been reported [87].

Prolonged reaction between [ReX(CO)$_5$] (X = Cl, Br or I) and [NEt$_4$]X yields [NEt$_4$][(CO)$_3$Re(μ-X)$_3$Re(CO)$_3$], the presence of the triple halide bridge being deduced by vibrational analysis [88]. The presence of the double halide bridge in [Re$_2$Br$_2$(CO)$_6$(thf)$_2$] (18) has been confirmed by X-ray crystallography {r(ReRe) = 0.3967 nm} [89]. (18) is a convenient starting material for the preparation of mixed ligand complexes of type [ReBr(CO)$_3$(L)$_2$] {e.g. L = PPh$_2$Cl, PPh$_2$H or Me$_2$NH}, when L is in excess. When (18) is in excess, in the reaction with PPh$_2$H, [Re$_2$Br$_2$(CO)$_6$(PPh$_2$H)$_2$] forms, which will react with further ligand to give [ReBr(CO)$_3$(PPh$_2$H)$_2$] [89]. [ReBr(CO)$_5$] reacts with LH (LH = cysteine or threonine) to give *fac*-[ReBr(CO)$_3$(HL)$_2$], which further reacts with methanolic KOH to yield [Re(CO)$_3$L]$_n$. This, with pyridine, yields [Re(CO)$_3$L(py)], whereas *fac*-[ReBr(CO)$_3$(LH)$_2$] gives only [ReBr(CO)$_3$(py)$_2$] [90].

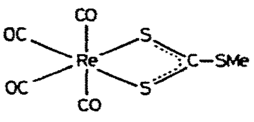


(18)

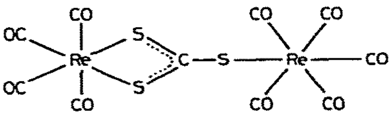
The molecular structure of [$ReBr(CO)_3(Me_2NCH_2CH_2NMe_2)$] reveals it to be in a *facial* configuration {*r*(ReBr) = 0.2636 nm} [91]. The structurally related compounds *fac*-[$ReX(CO)_3(L)_2$] (X = Cl, Br or I; L = 4-phenylpyridine or 4,4′-bipyridine) luminesce, both in solution at 298 K and at 77 K [92]; these complexes were prepared by the reaction between [$ReX(CO)_5$] and excess L at 60°C. In a similar manner, [$ReX(CO)_5$] (X = Cl or Br) reacts with various 1,4-diazabutadienes to give *fac*-[$ReCl(CO)_3(RN{=}CHCH{=}NR)$] (R = Me_3C, Me_2CH or 4-MeC_6H_4) and *fac*-[$ReBr(CO)_3(Me_3CN{=}CHCH{=}NCMe_3)$] [93]. These complexes react with [$Mn(CO)_5$]$^-$ to yield [$(CO)_5Mn$-$Re(CO)_3$-($RN{=}CHCH{=}NR$)] (R = Me_2CH or 4-MeC_6H_4) [94].

10.12.2 Dithiocarbamate, trithiocarbonate, selenides and related complexes

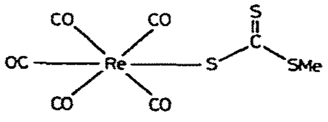
The reaction of Na[$Re(CO)_5$] with CS_2, followed by addition of MeI, gave the trithiocarbonate complexes, [$Re(CO)_4(S_2CSMe)$] (19) and [{$Re(CO)_4$}-(μ-CS_3){$Re(CO)_5$}] (20). [$Re(CO)_5${SC(S)SMe}] (21), prepared by the reaction of [$ReBr(CO)_5$] with Na[$CS_2(SMe)$], readily thermally decarbonylates to give (19). (20) can be formed in high yield by reacting Na[$Re(CO)_5$] with CS_2, followed by [$ReBr(CO)_5$]. Mixed Mn/Re analogues of (20) were also prepared by this route (i.e. using either Na[$Mn(CO)_5$] or [$MnBr(CO)_5$]) [95]. When S_8, and then CS_2, are added to Na[$Re(CO)_5$], followed by [$ReBr(CO)_5$], the complex [{$Re(CO)_5$}(μ-CS_3){$Re(CO)_5$}] (22) is formed [95].



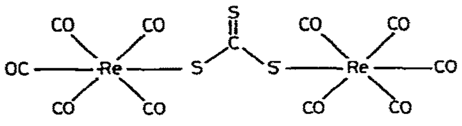
(19)



(20)



(21)

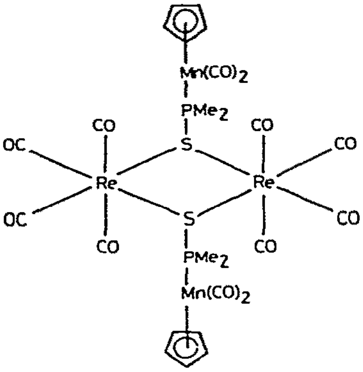


(22)

[$ReBr(CO)_3(Me_2NH)_2$] will react with CS_2/Me_2NH to give [$Re(CO)_3$-(Me_2NH)(S_2CNMe_2)]; reaction of [$Re_2Br_2(CO)_6(thf)_2$] with Et_2NH/[Et_2NCS_2]$^-$ gives [$Re(CO)_3(Et_2NH)(S_2CNEt_2)$]; treatment of [$Re_2Br_2(CO)_8$] with [$R_2NCS_2$]$^-$ (R = Me or Et) in the presence of CO gives [$Re(CO)_4(S_2CNR_2)$] [89]. [$Re(CO)_4(S_2CNMe_2)$] has also been prepared by the reaction of [ReBr-($CO)_5$] with [NMe_2H_2][S_2CNMe_2] in benzene; [$Re(CO)_4${S(O)$CNMe_2$}] and [$Re(CO)_4${Se(O)$CNMe_2$}] were formed in analogous reactions. [$Re(CO)_4$-(LL′)] {LL′ = S(Se)$CNMe_2$ or Se_2CNMe_2} were prepared by treatment of [$ReBr(CO)_5$] with [$SnMe_2Cl${S(Se)$CNMe_2$}] or [$SnMe_2(Se_2CNMe_2)_2$], respectively [96]. These complexes undergo solid state thermolysis to give the dimers [{$Re(CO)_3$[X(Y)$CNMe_2$]}$_2$] (XY = S_2, SSe, Se_2, SO or SeO) or

[{$Re(CO)_4[X(O)CNMe_2]$}$_2$] (X = S or Se) [96]. Treatment of Na[$Re(CO)_5$] with MeNCS, followed by MeI, gives a mixture of *cis*-[$Re(CO)_4I(CNMe)$], [$Re(CO)_4(S_2CNHMe)$] and *fac*-[$Re(CO)_3(S_2CNHMe)(CNMe)$] [97].

Reaction of [$ReCl(CO)_5$] with Na[(cp)$Mn(CO)_2(PMe_2S)$] yields the dimeric complex [$(CO)_4Re${(cp)$Mn(CO)_2(PMe_2S)$}$_2Re(CO)_4$] (23) [98].

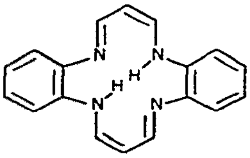


(23)

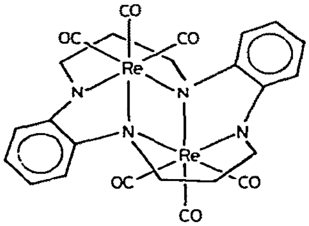
[{$(CO)_4Re(SeX)$}$_2$] (X = H or $SnMe_3$) reacts with PMe_3 to give [{$(Me_3P)(CO)_3Re(SeX)$}$_2$] and [$(Me_3P)_2(CO)_3Re(SeX)$]; treatment of the $SnMe_3$ derivative with HCl converts it to the H derivative. The structure of [{$(Me_3P)_2(CO)_3Re$}(μ-Se){$Re(CO)_3(PMe_3)_2$}], a by-product of the above preparation, has been determined by X-ray crystallography [99].

10.12.3 *Complexes with Group VB ligands*

The reaction between [$Re_2(CO)_{10}$] and 1,8-dihydrodibenzo[*b*, *i*][1,4,8,11]-tetraazaannulene ($taaH_2$; 24) gives the unusual binuclear complex [$(CO)_3Re(\mu$-taa$)Re(CO)_3$] (25), in which each Re atom is bonded to three N atoms, two of which bridge the metal atoms {r(ReRe) = 0.3345 nm} [100].



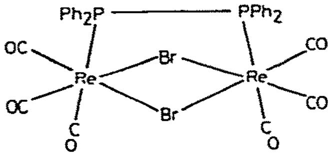
(24)



(25)

C_4Ph_4ECl (E = P, As or Sb) reacts with [$Re(CO)_5$]$^-$ to give the Re-E σ-bonded complexes, [$Re(CO)_5(EC_4Ph_4)$]. Upon heating, the phosphole and arsole derivatives lose CO to form dimeric species, [$(CO)_4Re(\mu$-$EC_4Ph_4)_2Re(CO)_4$] (E = P or As). [$Re(CO)_5(EC_4Ph_4)$] (E = P, As or Sb) react with Cl_2 or

Br_2 to reform [$ReX(CO)_5$] and C_4Ph_4EX (X = Cl or Br) [101]. $HNSOF_2$ reacts with [$Re(CO)_5(SO_2)$][AsF_6] to give the *N*-bonded complex [$Re(CO)_5(HNSOF_2)$][AsF_6] [102]. The reaction of [$ReBr(CO)_5$] or [$Re_2Br_2(CO)_6(thf)_2$] with P_2Ph_4 gives [$(CO)_3Re(\mu\text{-}Br)_2(\mu\text{-}P_2Ph_4)Re(CO)_3$] **(26)**, which has been characterised by X-ray crystallography [103], whereas the reaction of [$MnRe(CO)_{10}$] with $As_2(CF_3)_4$ gives [$(CO)_4Re\{\mu\text{-}As(CF_3)_2\}_2Mn(CO)_4$] [104].



(26)

10.12.4 Organometallic derivatives

Methyllithium reacts with [$ReX(CO)_5$] (X = Cl, Br, I or H) at −78°C, not to give the expected [$ReMe(CO)_5$], but to form the acetyl derivatives Li[*cis*-$Re(CO)_4X\{C(O)CH_3\}$]. Similar reactions of [$ReX(CO)_5$] (X = Cl, Br or I) with Li[BEt_3H] yield the corresponding formyl complexes Li[*cis*-$Re(CO)_4X\{C(O)H\}$] [86]. Reaction of [$Re(CO)_5\{C(O)R\}$] (R = Me, Me_2CH or $PhCH_2$) with two equivalents of LiMe affords the triacyl anion, *fac*-$[Re(CO)_3\{C(O)R\}\{C(O)Me\}_2]^{2-}$; analogous reactions occur with [$\{Re(CO)_5[C(O)(CH_2)]\}_2(CH_2)_n$] (*n* = 4 or 5) [105]. These species are tridentate ligands (cf. triacetylmethanide anion), and form complexes with various metal ions e.g. $[\{Re(CO)_3[C(O)R][C(O)Me]_2\}_2M]^-$ (M = Al or Ga) and [$\{Re(CO)_3[C(O)R][C(O)Me]_2\}_2M$] {M = Hf(IV) or Zr(IV)} [105].

The reaction of [$Re_2Cl_2(CO)_8$] with K[$HB(3,5\text{-}Me_2C_3HN_2)_3$] gives the expected [$Re\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(CO)_3$] (cf. [Re(cp)$(CO)_3$]), as well as the pyrazole derivative, [$ReCl(CO)_3(3,5\text{-}Me_2C_3HN_2)_2$]. Reaction of [$Re\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(CO)_3$] with Br_2 resulted, not in the oxidation of the metal, but in the bromination of the pyrazolyl rings to give [$Re\{HB(3,5\text{-}Me_2\text{-}4\text{-}BrC_3N_2)_3\}(CO)_3$] [106].

The reaction of [$ReBr(CO)_5$] with $Ph_2P(CH_2)_3MgCl$ in thf gives the unusual metallacycle [$(CO)_4Re(PPh_2CH_2CH_2CH_2)$] [107].

10.12.5 Complexes with Group IVB ligands

[$Re_2(CO)_{10}$] reacts with SnX_2 (X = Cl, Br or I) to give [$(CO)_4Re\{\mu\text{-}SnX[Re(CO)_5]\}_2Re(CO)_4$] and [$X_2Sn\{Re(CO)_5\}_2$]; [$(CO)_4Re\{\mu\text{-}GeI[Re(CO)_5]\}_2Re(CO)_4$] was formed in an analogous manner [108]. [$Re(CO)_5(SnPh_3)$] has been studied by DTA [109].

The complexes [$Re(EPh_3)(CO)_3(LL)$] (E = Ge or Sn; LL = bipy or phen) were prepared by treating $[Re(CO)_3(LL)]^-$ (formed by Na/Hg reduction of [$ReCl(CO)_3(LL)$]) with Ph_3GeBr or Ph_3SnCl in tetrahydrofuran. These complexes allow evaluation of the rate constant, k^*, associated with the excited state homolytic fission of the Re—Ge or Re—Sn bond:

i.e. $[\mathrm{E{-}Re}]^* \xrightarrow{k^*} \mathrm{E}\cdot + \mathrm{Re}\cdot$

This process competes with radiative decay of the undissociated complex [110].

10.12.6 Complexes with Group IIIB ligands

The reaction between InX (X = Cl, Br or I) and $[Re_2(CO)_{10}]$ at 150—160°C gives $[\{(CO)_5Re\}_2In(\mu\text{-}X)_2In\{Re(CO)_5\}_2]$; the molecular structure of all three products has been determined [111].

10.13 RHENIUM(0)

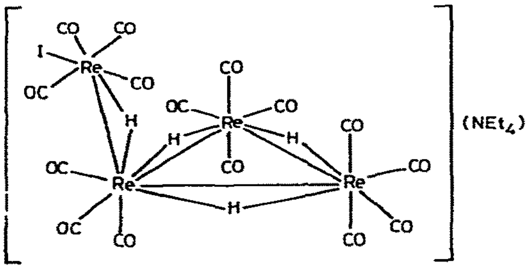
Reduction of the rhenium(I)—phosphinic acid complexes, $[ReBr(CO)_4(PR_2OH)]$ (R = Me or Ph), with Na/Hg in ether gives the dimeric rhenium(0) complexes, $Na_2[\{R_2(O)P\}(CO)_4Re\text{-}Re(CO)_4\{P(O)R_2\}]$. Further reaction of these dimers with Na/Hg in the presence of dimethylsulphate and thf gives $[MeRe(CO)_4\{P(OMe)R_2\}]$ [112].

10.14 RHENIUM CARBONYL CLUSTERS

Chemisorption of CO on the Re(0001) surface results in a non-uniform attenuation of the strongly angular dependent photoemission from the Re 5*d* bands of the pure metal [113].

The Raman spectrum of $[Re_2(CO)_{10}]$ has been the subject of a detailed investigation [114].

UV irradiation of $[(\mu\text{-}H)_3Re_3(CO)_{12}]$ in solution leads to the quantitative formation of $[(\mu\text{-}H)_2Re_2(CO)_8]$; photolysis in the presence of CO gives $[HRe(CO)_5]$ and $[(\mu\text{-}H)_2Re_2(CO)_8]$, the latter thermally reacting with CO to give $[HRe(CO)_5]$ and $[Re_2(CO)_{10}]$ [115]. Reaction of $[NEt_4]_2[H_4Re_4(CO)_{15}]$ with ethanolic iodine gave $[NEt_4][H_4Re_4(CO)_{15}I]$ (27), implying electrophilic attack of I^+ on the cluster. The structure of this complex (27) has



(27)

been determined by X-ray crystallography, but the hydrides were not located [116].

The molecular structure of $[Re_4(CO)_{12}\{\mu_3\text{-}InRe(CO)_5\}_4]$ confirms that each $\{InRe(CO)_5\}$ group caps a face of the central Re_4 tetrahedron $\{\bar{r}(ReRe) = 0.3016$ nm$\}$, each Re of which is bonded to three terminal carbonyls [117].

The reaction of either $[Re_2(CO)_{10}]$ or $[ReCl(CO)_5]$ with water at 200° C gives a compound $[Re(CO)_3(OH)]_4$. A pseudocubane structure without Re—Re bonds has been proposed, containing triply-bridging hydroxyl groups. The OH groups are acidic, reacting with $RCHN_2$ ($R = H$ or CH_3) to give $[Re(CO)_3(OCH_2R)]_4$, with D_2O in ether to give $[Re(CO)_3(OD)(OEt_2)]_4$, and with lithium to give $[Re(CO)_3O^-Li^+]_4$. $[Re(CO)_3(OH)]_4$ also forms adducts with Lewis bases, L, to give $[Re(CO)_3(OH)L]_4$ (where L = thf, $OPPh_3$ or Br^-) [118].

The unusual complexes $[(CO)_3Re\text{-}\{M(L_4)\}\text{-}Re(CO)_3]$ $\{M = Sn, Zn, Mg$ or Co; L_4 = phthalocyanine or tetraphenylporphyrin$\}$ [119] and $[(CO)_3ReC\{Sn(TPP)\}CRe(CO)_3]$ {TPP = tetraphenylporphyrin} [120] have been prepared, the latter having been structurally characterised by X-ray crystallography.

10.15 THIONITROSYL AND NITROSYL COMPLEXES

The first detailed account of thionitrosyl complexes has finally appeared. $[ReX_2N(PR_3)_3]$ ($X = Cl$ or Br; $R_3 = Me_2Ph$, Et_2Ph or $MePh_2$) and $[ReCl_2N(PR'_3)_2]$ ($R'_3 = Ph_3$ or $PrPh_2$) react with half an equivalent of S_2Cl_2 to give $[ReCl(X)(NS)(PR_3)_3]$ and $[ReCl_3(NS)(PR'_3)_2]$, respectively; with excess S_2Cl_2 ($X = Cl$), $[ReCl_3(NS)(PR_3)_2]$ is formed. Similarly, the reaction of $[ReClN(dppe)_2]Cl$ with S_2Cl_2 yields $[ReCl(NS)(dppe)_2]^+$. The reaction of $[ReCl_2(NS)(PMe_2Ph)_3]$ with $[S_2CNMe_2]^-$ or $[SCN^-]$ gave $[ReCl(S_2CNMe_2)(NS)(PMe_2Ph)_2]$ or $[ReCl(SCN)(NS)(PMe_2Ph)_3]$, respectively, whereas a similar reaction of $[ReCl(NS)(dppe)_2]Cl$ with $[S_2CNEt_2]^-$ gave only $[ReCl(NS)(dppe)_2][S_2CNEt_2]$ [121].

XPES data for $A_2[Re(NO)X_5]$, $A[Re(NO)X_4(L)]$, $[Re(NO)(PPh_3)_2X_3]$ and $[Re(NO)(dppe)_2I]I$ $\{A = Et_4N$; $X = Cl$, Br or I; L = py or 4-Me-py$\}$ have been presented [122]. The base hydrolysis of $[Re(NO)Cl_3]$ has been studied [123].

10.16 CYANIDES

The complete coordination chemistry of unsubstituted cyanorhenates has been re-investigated, in an excellent study by Griffith et al. [124]. Only the existence of salts of $[Re(CN)_6]^{5-}$ and $[Re(CN)_7]^{4-}$ has been confirmed, despite a fantastically large range of species which had previously been described in the literature. Space limitations forbid the full description which this work deserves, but the reader is urged to read this elegant example of fundamental research. Other complexes isolated in this study include salts of $[Re_4(CN)_{12}(\mu_3\text{-}S)_4]^{4-}$, $[Re_4(CN)_{12}(\mu_3\text{-}Se)_4]^{4-}$, $[Re_2(CN)_8(\mu_2\text{-}S)_2]^{4-}$ and $[Re(CN)_5(NO)]^{3-}$ [124].

REFERENCES

1 J. Grassi, J. Devynck and B. Trémillon, Anal. Chim. Acta, 107 (1979) 47.
2 C.D. Russell and A.G. Cash, J. Nucl. Med., 20 (1979) 532.
3 J. Steigman, G. Meinken and P. Richards, Int. J. Appl. Radiat. Isot., 29 (1978) 653.
4 E. Deutsch, W.R. Heineman, R. Hurst, J.C. Sullivan, W.A. Mulac and S. Gordon, J. Chem. Soc., Chem. Commun., (1978) 1038.
5 E.F. Byrne and J.E. Smith, Inorg. Chem., 18 (1979) 1832.
6 J.E. Smith, E.F. Byrne, F.A. Cotton and J.C. Sekutowski, J. Am. Chem. Soc., 100 (1978) 5571.
7 B. Johannsen and R. Syhre, Radiochem. Radioanal. Lett., 36 (1978) 107.
8 B. Johannsen, H. Spies and R. Syhre, Radiochem. Radioanal. Lett., 36 (1978) 111.
9 H. Spies and B. Johannsen, Inorg. Chim. Acta, 33 (1979) L113.
10 R.C. Elder, G.W. Estes and E. Deutsch, Acta Crystallogr., Sect. B, 35 (1979) 136.
11 A.A. Oblova, A.F. Kuzin, L.I. Belyaeva and V.I. Spitsyn, Zh. Neorg. Khim., 23 (1978) 3265.
12 W.R. Benson, G.C. Yang, M.W. Heitzmann and L.A. Ford, J. Labelled Compd. Radiopharm., Suppl. Vol., 15 (1978) 343.
13 H.S. Trop, A. Davison, G.H. Carey, B.V. De Pamphilis, A.G. Jones and M.A. Davis, J. Inorg. Nucl. Chem., 41 (1979) 271.
14 U. Mazzi, E. Roncari and G. Bandoli, Transition Met. Chem. (Weinheim, Ger.), 4 (1979) 151.
15 R. Münze, J. Labelled Compd. Radiopharm., 40 (1978) 215.
16 R.G. Behrens, J. Less-Common Met., 61 (1978) 321.
17 A.S. Dudin, V.I. Vovna, E.G. Rakov and S.N. Lopatin, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol., 21 (1978) 1564 (Chem. Abstr., 90 (1979) 65838).
18 S. Mohan, Acta Cienc. Indica, 4 (1978) 264.
19 E.J. Baran, Afinidad, 36 (1979) 219.
20 E.J. Baran, Monatsch. Chem., 109 (1978) 1337.
21 A.S. Dudin, A.A. Opalovskii, M.M. Novoselova and E.G. Rakov, Tr. Mosk. Khim. Tekhnol. Inst. im D.I. Mendeleeva, 97 (1977) 86 (Chem. Abstr., 91 (1979) 150509).
22 R. Lössberg and K. Dehnicke, Z. Naturforsch., Teil B, 34 (1979) 1040.
23 K. Dehnicke and W. Liese, Z. Naturforsch., Teil B, 34 (1979) 111.
24 M. El Essawi and K. Dehnicke, Z. Naturforsch., Teil B, 34 (1979) 746.
25 T. Lis, Acta Crystallogr., Sect. B, 35 (1979) 1230.
26 W. Liese, K. Dehnicke, I. Walker and J. Strähle, Z. Naturforsch., Teil B, 34 (1979) 693.
27 J.-P. Silvestre, Rev. Chim. Minér., 15 (1978) 412.
28 G.A. Semenov, E.N. Nikolaev and K.V. Ovchinnikov, Vestn. Leningr. Univ., Fiz., Khim., (1978) 85.
29 G. Baud, J.-P. Besse, G. Levasseur and R. Chevalier, J. Inorg. Nucl. Chem., 40 (1978) 1605.
30 G. Baud, J.-P. Besse, R. Chevalier and M. Gasperin, J. Solid State Chem., 29 (1979) 267.
31 T.Kh. Kurbanov, R.A. Dovlyatshina, T.N. Radkevich and S.I. Imamova, 13 Vses. Chugaev. Soveshch. po Khimii Kompleks Soedin., 1978, (1978) 221 (Chem. Abstr., 90 (1979) 80221).
32 G.S. Sinyakova and A. Jansone, Latv. PSR Zinat. Akad. Vestis, Kim. Ser., (1979) 175 (Chem. Abstr., 90 (1979) 211007).
33 G.S. Sinyakova and I.V. Matveeva, Latv. PSR Zinat. Akad. Vestis, Kim. Ser., (1978) 659 (Chem. Abstr., 90 (1979) 93238).
34 G.S. Sinyakova and A. Deme, Latv. PSR Zinat. Akad. Vestis, Kim. Ser., (1978) 655 (Chem. Abstr., 90 (1979) 96777).
35 R.C. Burns, T.A. O'Donnell and A.B. Waugh, J. Fluorine Chem., 12 (1978) 505.

36 J.E. Schirber and B. Morosin, Phys. Rev. Lett., 42 (1979) 1485.
37 F.S. Razavi and W.R. Datars, Can. J. Phys., 56 (1979) 860.
38 N. Matsuno, M. Yoshimi, S. Ohtake, T. Akahane and N. Tsuda, J. Phys. Soc. Jpn., 45 (1978) 1542.
39 B.L. Chamberland and G. Levasseur, Mater. Res. Bull., 14 (1979) 401.
40 B.L. Chamberland and F.C. Hubbard, J. Solid State Chem., 26 (1978) 79.
41 R.T. Paine and L.B. Asprey, Inorg. Synth., 19 (1979) 137.
42 D.M. Bruce, J.H. Holloway and D.R. Russell, J. Chem. Soc., Dalton Trans., (1978) 1627.
43 J.-P. Besse, G. Baud, R. Chevalier and M. Gasperin, Acta Crystallogr., Sect. B, 34 (1978) 3532.
44 A.R. Middleton, A.F. Masters and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1979) 542.
45 M.B. Hursthouse, S.A.A. Jayaweera and A. Quick, J. Chem. Soc., Dalton Trans., (1979) 279.
46 J.R. Campbell and R.J.H. Clark, Mol. Phys., 36 (1978) 1133.
47 A.K. Shukla and W. Preetz, Angew. Chem., Int. Ed. Engl., 18 (1979) 151.
48 F.A. Cotton, P.E. Fanwick and P.A. McArdle, Inorg. Chim. Acta, 35 (1979) 289.
49 I. Svare, A.M. Raaen and G. Thorkildsen, J. Phys. C, 11 (1978) 4069.
50 E.J. Lisher, N. Cowlam and L. Gillott, Acta Crystallogr., Sect. B, 35 (1979) 1033.
51 J. Mroziński, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 26 (1978) 789.
52 E.F. Speranskaya and L.A. Karpova, Prikl. i Teor. Khimiya, (1978) 103 (Chem. Abstr., 90 (1979) 159057).
53 P.R. Sarode, J. Chem. Soc., Dalton Trans., (1979) 993.
54 W. Lukas, Pol. J. Chem., 52 (1978) 2243.
55 H. Müller and S. Martin, Z. Anorg. Allg. Chem., 445 (1978) 47.
56 C.D. Flint and A.G. Paulusz, Chem. Phys. Lett., 62 (1979) 259.
57 R. Wernicke and H.-H. Schmidtke, Mol. Phys., 37 (1979) 607.
58 H. Kupka, R. Wernicke, W. Ensslin, and H.-H. Schmidtke, Theor. Chim. Acta, 51 (1979) 297.
59 H. Homborg, Z. Naturforsch., Teil A, 34 (1979) 778.
60 J.E. Hahn, T. Nimry, W.R. Robinson, D.J. Salmon and R.A. Walton, J. Chem. Soc., Dalton Trans., (1978) 1232.
61 B. Jezowska-Trzebiatowska, T. Nowakowski and J. Mrozinski, Mater. Sci., 4 (1978) 23.
62 A.M. Bol'shakov, M.M. Ershova, M.A. Glushkova and Yu.A. Buslaev, Koord. Khim., 4 (1978) 1767.
63 F.A. Cotton and G.G. Stanley, Chem. Phys. Lett., 58 (1978) 450.
64 D.G. Holah, A.N. Hughes, B.C. Hui and P.-K. Tse, J. Heterocycl. Chem., 15 (1978) 1239.
65 P.A. Kozimin, M.D. Surazhskaya and T.B. Larina, Koord. Khim., 5 (1979) 752.
66 C.G. Morgante and W.S. Struve, Chem. Phys. Lett., 63 (1979) 344.
67 H.D. Glicksmann and R.A. Walton, Inorg. Chem., 17 (1978) 3179.
68 W. Preetz and L. Rudzik, Angew. Chem., Int. Ed. Engl., 18 (1979) 150.
69 F.A. Cotton, A. Davison, W.H. Ilsley and H.S. Trop, Inorg. Chem., 18 (1979) 2719.
70 D.M. Collins, F.A. Cotton and L.D. Gage, Inorg. Chem., 18 (1979) 1712.
71 F.A. Cotton, L.D. Gage and C.E. Rice, Inorg. Chem., 18 (1979) 1138.
72 P.A. Koz'min, M.D. Surazhskaya and T.B. Larina, Zh. Strukt. Khim., 15 (1974) 64.
73 P.A. Koz'min, M.D. Surazhskaya and V.G. Kuznetsov, Zh. Strukt. Khim., 11 (1970) 313.
74 I.F. Golovaneva, A.S. Kotel'nikova, T.V. Misailova, N.S. Osmanov and O.N. Evstaf'eva, 13 Vses. Chugaev. Soveshch. po Khimii Kompleks. Soedin, 1978, (1978) 99 (Chem. Abstr., 90 (1979) 47699).

75 P.A. Koz'min, M.D. Surazhskaya and T.B. Larina, Koord. Khim., 5 (1979) 598.
76 F.A. Cotton and L.D. Gage, Inorg. Chem., 18 (1979) 1716.
77 R.A. Jones and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1978) 1063.
78 M.B. Hursthouse and K.M.A. Malik, J. Chem. Soc., Dalton Trans., (1979) 409.
79 P.G. Edwards, F. Felix, K. Mertis and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1979) 361.
80 C.J.L. Lock, C.N. Murphy and M.L. Turner, Can. J. Chem., 57 (1979) 1252.
81 C.J.L. Lock and C.N. Murphy, Acta Crystallogr., Sect. B, 35 (1979) 951.
82 S. Chen and W.R. Robinson, J. Chem. Soc., Chem. Commun., (1978) 879.
83 M.G.B. Drew, K.M. Davis, D.A. Edwards and J. Marshalsea, J. Chem. Soc., Dalton Trans., (1978) 1098.
84 W.E. Carroll and R. Bau, J. Chem. Soc., Chem. Commun., (1978) 825.
85 P.M. Treichel, J.P. Williams, W.A. Freeman and J.I. Gelder, J. Organomet. Chem., 170 (1979) 247.
86 K.P. Darst and C.M. Lukehart, J. Organomet. Chem., 171 (1979) 65.
87 D. Kariuki and S.F.A. Kettle, Spectrochim. Acta, Part A, 34 (1978) 563.
88 B.J. Brisdon, D.A. Edwards and J.W. White, J. Organomet. Chem., 161 (1978) 233.
89 F. Calderazzo, I.P. Mavani, D. Vitali, I. Bernal, J.D. Korp and J.L. Atwood, J. Organomet. Chem., 160 (1978) 207.
90 A.A. Ioganson, V.V. Derunov, A.M. Sladkov and N.A. Vasneva, Zh. Obshch. Khim., 49 (1979) 1438.
91 M.C. Couldwell and J. Simpson, J. Chem. Soc., Dalton Trans., (1979) 1101.
92 P.J. Giordano and M.S. Wrighton, J. Am. Chem. Soc., 101 (1979) 2888.
93 L.H. Staal, A. Oskam and K. Vrieze, J. Organomet. Chem., 170 (1979) 235.
94 L.H. Staal, G. Van Koten and K. Vrieze, J. Organomet. Chem., 175 (1979) 73.
95 I.B. Benson, J. Hunt, S.A.R. Knox and V. Oliphant, J. Chem. Soc., Dalton Trans., (1978) 1240.
96 M. Nakamoto, K. Tanaka and T. Tanaka, J. Chem. Soc., Dalton Trans., (1979) 87.
97 S.R. Finnimore, R. Goddard, S.D. Killops, S.A.R. Knox and P. Woodward, J. Chem. Soc., Dalton Trans., (1978) 1247.
98 E. Lindner, S. Hoehne and K.-W. Rodatz, Z. Naturforsch., Teil B, 34 (1979) 520.
99 V. Küllmer, E. Röttinger and H. Vahrenkamp, Z. Naturforsch., Teil B, 34 (1979) 217.
100 M. Tsutsui, R.L. Bobsein, R. Pettersen and R. Haaker, J. Coord. Chem., 8 (1979) 245.
101 E.W. Abel and C. Towers, J. Chem. Soc., Dalton Trans., (1979) 814.
102 R. Mews and H.C. Braeuer, Z. Anorg. Allg. Chem., 447 (1978) 126.
103 J.L. Atwood, J.K. Newell, W.E. Hunter, I. Bernal, F. Calderazzo, I.P. Mavani and D. Vitali, J. Chem. Soc., Dalton Trans., (1978) 1189.
104 G. Beysel, J. Grobe and W. Mohr, J. Organomet. Chem., 170 (1979) 319.
105 D.T. Hobbs and C.M. Lukehart, Inorg. Chem., 18 (1979) 1297.
106 J.A. McCleverty and I. Wołochowicz, J. Organomet. Chem., 169 (1979) 289.
107 E. Lindner, G. Funk and S. Hoehne, Angew. Chem. Int. Ed. Engl., 18 (1979) 535.
108 W. Ködel, H.-J. Haupt and F. Huber, Z. Anorg. Allg. Chem., 448 (1979) 126.
109 B.I. Kozyrkin, K.S. Gasanov, T.Kh. Kurbanov, N.E. Kolobova, S.A. Klinchikova and V.N. Khandozhko, Zh. Obshch. Khim., 48 (1978) 2408.
110 J.C. Luong, R.A. Faltynek and M.S. Wrighton, J. Am. Chem. Soc., 101 (1979) 1597.
111 H.-J. Haupt, H. Preut and W. Wolfes, Z. Anorg. Allg. Chem., 448 (1979) 93.
112 E. Lindner, G. von Au and H.-J. Eberle, Z. Naturforsch., Teil B, 33 (1978) 1296.
113 W. Braun, G. Meyer-Ehmsen, M. Neumann and E. Schwarz, Solid State Commun., 30 (1979) 605.
114 M. Arif, A.M. Cartner, D.N. Kariuki and S.F.A. Kettle, J. Chem. Phys., 70 (1979) 1031.

115 R.A. Epstein, T.R. Gaffney, G.L. Geoffroy, W.L. Gladfelter and R.S. Henderson, J. Am. Chem. Soc., 101 (1979) 3847.
116 G. Ciani, G. D'Alfonso, M. Freni, P. Romiti and A. Sironi, J. Organomet. Chem., 170 (1979) C15.
117 H. Preut and H.-J. Haupt, Acta Crystallogr., Sect. B, 35 (1979) 1205.
118 M. Herberhold, G. Süss, J. Ellermann and H. Gäbelein, Chem. Ber., 111 (1978) 2931.
119 S. Kato, I. Noda, M. Mizuta and Y. Itoh, Angew. Chem. Int. Ed. Engl., 18 (1979) 82.
120 I. Noda, S. Kato, M. Mizuta, N. Yasuoka and N. Kasai, Angew. Chem. Int. Ed. Engl., 18 (1979) 83.
121 M.W. Bishop, J. Chatt and J.R. Dilworth, J. Chem. Soc., Dalton Trans., (1979) 1.
122 V. Di Castro, D. Guisto and G. Mattogno, J. Microsc. Spectrosc. Electron., 4 (1979) 251.
123 S. Rakshit, B.K. Sen and P. Bandyopadhyay, Z. Anorg. Allg. Chem., 445 (1978) 245.
124 W.P. Griffith, P.M. Kiernan and J.-M. Brégeault, J. Chem. Soc., Dalton Trans., (1978) 1411.