Recent Advances in the Chemistry of Rhenium

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Contents

I. Introduction

Rhenium, first detected by Noddack, Tacke, and Berg in 1925 in the X-ray spectra of certain mineral concentrates,[1] was the last of the stable elements to be discovered. It is among the least abundant, both in the crust of the earth and in the solar system.[2] There are no sufficiently elevated concentrations anywhere in nature to permit economic extraction as the primary commodity, and the only commercial source is as a by-product of the molybdenum industry.[3] When molybdenite is roasted in air to molybdenum trioxide, volatile dirhenium heptoxide passes into the effluent gases and flue dusts and may be recovered by wet scrubbing or leaching with water. Rhenium is then isolated from the aqueous extracts either by selective adsorption as ReO_4^- on an anion exchanger or by solvent extraction, and it is finally precipitated as NH_4ReO_4 or Re_2S_7.[3] The free world reserves of rhenium have been estimated as *ca.* 1000 tons of which 70% are in the U.S.A. and 20–25% in Chile.[4] Substantial deposits also exist in the U.S.S.R.[5] Production in the U.S.A. rose from 600 kg in 1963[4] to 1800 kg in 1970,[6] and the total world production in 1970 was 3.75 tons.[6] The price of the metal fluctuated between \$500 and \$1500 per pound in 1970–1972[7] and is sensitive to demand since supplies are strictly limited. Unless most of the rhenium is recovered from molybdenite roasting, the small exploitable reserves will be irretrievably lost in the flue gases.

Although rhenium is the heaviest congener of manganese, the chemistry of the two elements is very different, except in the oxidation states of I and below (essentially the organometallic compounds) and in certain formal stoichiometries. Technetium[8-10] is the only element which rhenium resembles closely, and even then not to the extent that tungsten resembles molybdenum.[11] There are *distant* similarities with isoelectronic complexes of molybdenum,[11] tungsten,[12] and osmium.[13] For this reason rhenium has been studied separately from other elements, and it is perhaps legitimate to discuss its chemistry in isolation. Several monographs on the subject exist, of which three[8,9,14] are complementary and supersede the earlier texts. Review articles cover the coordination compounds through 1966,[15] the analytical chemistry,[16,17] the catalytic properties,[18-20] the metallurgy of rhenium alloys,[4,21] the halides of rhenium,[21a] and the thermodynamic functions and phase diagrams of certain systems.[22] Sections on rhenium appear in "Comprehensive Inorganic Chemistry"[23] and in the serial publications,[24,25] and the organometallic compounds have been reviewed through 1971.[26]

The present article attempts to present, in conjunction with ref 15 and 26, a fairly complete account of the chemistry of rhenium by discussing most of the developments that have occurred between January 1965 and December 1972, together with some earlier and later work. Organometallic compounds in the oxidation states I, 0, and −I are omitted since they have been recently reviewed elsewhere,[26] and the chemistry of nitrosyls and enedithiolates is best discussed with the organometallic chemistry. Nuclear properties, the physical chemistry of the metal and its alloys, heterogeneous catalysis, and the analytical chemistry are not covered. Bond distances, force constants, and thermodynamic data have been converted to SI units.

It is becoming fashionable to classify metal compounds according to the ligands. This is useful when complexes of similar ligands and a range of metal ions are to be compared. For other purposes classification according to oxidation state has decided advantages. Although it has been pointed out correctly and repeatedly that oxidation states are purely formal and may bear little resemblance to real charges,[27] it is a fact that for one reason or another every oxidation state has its own characteristic tendencies. These may include magnetic behavior, stereochemical preferences, scarcity, affinity for particular ligands, or reaction patterns. Any scheme which attempts to classify a large number of compounds inevitably creates exceptions which remain unclassified. Fewer such exceptions emerge because the oxidation state is undefined (*e.g.*, certain nitrosyls and vicinal enedithiolates) than because the ligands are mixed, and these exceptions may always be considered separately. It is hoped that the present account will illustrate how oxidation state, in spite of its limitations, provides the most logical basis for classifying the chemistry of an element, and it should therefore be retained. It is then possible to further classify the reactions of a given oxidation state as those which alter (redox reactions) or conserve it (conformational changes, association, substitution, reactions of coordinated ligands), and the chemistry of rhenium will be presented in relation to this framework.

II. General Properties of the Element

Rhenium, of atomic number 75 and atomic weight 186.2,[28] belongs to group VIIa of the periodic table. It occurs naturally as a mixture of two isotopes, ^{185}Re (37.40%) and ^{187}Re (62.60%).[29] The heavier isotope is a weak β-emitter, and the daughter ^{187}Os is present in all rhenium-bearing rocks.[30] The end-point energy of the emitted β-particles (2.62 ± 0.09 keV) is the lowest recorded for β-decay and is even lower than the difference in the atomic binding energies of Re and Os (*ca.* 13.8 keV).[31,32] The very soft β-rays are absorbed by solid rhenium compounds, but an accurate determination of the β-spectrum was achieved using gaseous π-Cp_2ReH.[32] The measured half-life for decay to continuum states, $(6.6 \pm 1.3) \times 10^{10}$ yr,[31] is longer than the total half-life, $(4.3 \pm 0.5) \times 10^{10}$ yr, estimated from $^{187}Re/^{187}Os$ ratios in geologically dated molybdenites,[33] because 50 ± 30% of disintegrations are to bound atomic states. The half-life is expected to be shorter at high temperatures (estimated as $<3 \times 10^9$ yr at 10^6 K) since bound-state decay to inner-shell vacancies of the ionized atom would occur more readily than to outer-shell vacancies of the neutral atom.[34] Thus rhenium in the sun should be depleted in ^{187}Re, and a detectably anomalous isotopic ratio might exist captured from the solar wind on the lunar surface.[35] A recent analysis of lunar material has, however, shown a slight enrichment in ^{187}Re, possibly due to neutron capture by ^{186}W.[36] The shortened half-life of ^{187}Re thus remains unconfirmed and cosmological conclusions based on $^{187}Re/^{187}Os$ ratios ought to be made with caution. The $^{187}Re/^{187}Os$ ratio has been used to determine the age of molybdenum deposits,[30] but it must be borne in mind in this connection that little is known of the detailed geochemical behavior of either element.[37]

The nuclear properties of rhenium isotopes are such as to permit accurate determination of nanogram quantities by neutron activation analysis.[35,38] The neutron capture cross sections have been measured for both natural isotopes as a function of neutron energy from 0.01 eV to 2.6 MeV.[39] Both ^{185}Re and ^{187}Re have isotopic spin $\frac{5}{2}$ and large quadrupole moments $[Q(^{185}Re) = (2.36 \pm 0.5) \times 10^{-24}$; $Q(^{187}Re) = (2.24 \pm 0.5) \times 10^{-24}\ cm^2]$.[40,41] The corresponding nmr signals have been detected in solid ReO_3 at 1-4 K[42] and in aqueous $NaReO_4$ at ambient temperatures.[43] The signals in aqueous perrhenate are extremely broad due to quadrupole relaxation of short-lived collision complexes of ReO_4^- and solvent molecules $[T_2^{-1}(^{185}Re) = 4.5 \times 10^4$; $T_2^{-1}(^{187}Re) = 4.25 \times 10^4\ sec^{-1}]$.[43] A number of nqr spectra have been recorded,[44] and a detailed study of the atomic spectrum of rhenium has yielded the hyperfine structure coupling constants for the ground state $5d^56s^2\ ^6S_{5/2}$ and for 14 excited states of the neutral atom.[45]

III. Occurrence of Rhenium

On all counts, rhenium is an exceptionally rare element. A careful search in the Fraunhofer spectrum of the sun was negative, putting an upper limit of not more than 0.5 atom per 10^{12} H.[46] Claims of rhenium lines in certain stellar spectra have not been confirmed.[46] Concentrations in iron meteorites (0.0023–4.4 ppm based on the analysis of 70 specimens)[47] are an order of magnitude less than those of osmium and iridium,[48] and the mean osmium to rhenium ratio in chondritic meteorites is 11.4 ± 1.3.[49] A sample of 32 chondrites representing all classes was found to contain 0.0311–0.0804 ppm corresponding to 0.025–0.076 atom of Re per 10^6 silicon.[49] The atomic abundance in the Orgueil meteorite, a Type I carbonaceous chondrite generally considered most nearly representative of the composition of primitive solar dust, is 0.052 (Si = 10^6), almost equal to the mean in all chondrites (0.053).[38,49] This confirms that no fractionation has occurred relative to Orgueil.[38] The abundance of rhenium in the solar system is usually taken as 0.055 and, together with that of Tb, Tm, Lu, and Ta, is the lowest among the stable elements.[50] The rhenium content of lunar volcanics (0.0016–1.6 ppb)[51] is much lower than this but is comparable to that of achondrites (0.25–0.9 ppb)[35] and of terrestrial basic rocks (*ca.* 0.5 ppb).

Rhenium is decidedly siderophilic, and concentrations in the iron phase of chondrites exceed by a factor of 30 to 300 the concentrations in the nonmagnetic phases.[38] The earth's crust is therefore depleted in rhenium. On the basis of analyses on 14 igneous and metamorphic rocks, the crustal abundance has been estimated at 0.5 ± 0.3 ppb, with the lowest values occurring in ultrabasics.[52] The element is highly dispersed within the crust, and elevated concentrations normally occur only in molybdenites.[53] A strong geochemical association with molybdenum persists through all stages of magmatic crystallization, and rhenium is finally incorporated as an isomorphous solid solution of ReS_2 in MoS_2.[54] A large number of molybdenites have now been analyzed,[53-59] and the rhenium content has been found to vary over very wide limits from <0.1 ppm to >2000 ppm (0.2%). An exceptionally high concentration (1.88%) has been reported in a sample from Armenia.[55] Of the many factors that influence the ratio of Re to Mo, two seem to be well established: molybdenites with the highest content of rhenium (*ca.* 0.1%) tend to be associated with copper in multimineral accretions.[54,55,57-60] The converse is not necessarily true and molybdenites low in rhenium (*ca.* 1 ppm) have also been found in cupriferous areas.[60] The copper minerals themselves never carry more than traces of the element.[57,61] In molybdenites of pneumatolytic–hydrothermal origin, the concentration of rhenium increases as the temperature of the ore-forming process decreases.[54,58] Very high values (0.2–0.4%) have also been recorded in some volcanic sublimates.[54]

Weathering of molybdenites results in the oxidation of both elements to their soluble highest states, but their close association ends here. Whereas molybdates are reabsorbed and in a certain locality were found to practi-

TABLE I. Characteristic Properties of the Nine Oxidation States of Rhenium

Oxidation state	Magnetic moments[a]	Characteristic features
VII (d^0)	Dia or weak TIP	Dominated by very stable ReO_4^- ion to which other species hydrolyze. All coordination numbers from 4 to 9 known. Very few complexes. Weakly oxidizing.
VI (d^1)	1.2–1.7 BM	Rare and unstable with respect to disproportionation to Re^{VII} and Re^{IV}. Several mixed oxides but few complexes. Typically distorted octahedral with a single, short Re=O bond. Main types $ReOX_4L$ and $ReOX_5^-$.
V (d^2)	Dia or weak TIP	Large number of stable octahedral complexes in which Re forms multiple bonds to oxygen or nitrogen. Main types $ReOX_5^{2-}$, $ReOX_3L_2$, $ReO_2L_4^+$, $Re(NR)X_3L_2$, $ReNX_3L_2$, etc. Rarely five-, seven-, or eight-coordinate.
IV (d^3)	3.1–3.8 BM	Very stable in association with classical ligands. Main types MX_6^{2-}, MX_5L^-, and MX_4L_2. Some compounds with Re–Re bonds. Stable ReO_2, ReS_2.
III (d^4)	TIP equivalent to 1.5–2.1 BM	(a) Mononuclear octahedral complexes of type $ReX_2L_4^+$, ReX_3L_3, and $ReX_4L_2^-$. Rarely five- or seven-coordinate. (b) Dinuclear clusters with strong Re–Re bond, mainly of type $Re_2X_8^{2-}$ and $Re_2X_6L_2$. (c) Trinuclear clusters based on a stable triangle of Re atoms, mainly of types $Re_3X_{12}^{3-}$, $Re_3X_{11}^{2-}$, $Re_3X_{10}^-$, and $Re_3X_9L_3$.
II (d^5)		Very rare. Mononuclear ReX_2L_4 and $ReXL_5^+$ and unstable di- and trinuclear species.
I (d^6)	Dia	Large number or stable octahedral carbonyl derivatives, σ-alkyls and aryls, and π-arenes. Main types $Re(CO)_6^+$, $ReL(CO)_5^+$, $ReL_2(CO)_4^+$, $Re(ArH)(CO)_3^+$, $Re(ArH)_2^+$, $ReX(CO)_5$, $ReR(CO)_5$, $ReXL(CO)_4$, $ReXL_2(CO)_3$, $ReXL_3(CO)_2$, $[ReX(CO)_4]_2$, $ReX_3(CO)_3^{2-}$, etc. Also derivatives of polynuclear carbonyls.
0 (d^7)		Mono- and binuclear derivatives of $Re_2(CO)_{10}$. Main types $Re_2(CO)_8L_2$, $Re_2(CO)_7L_3$, $Re(CO)_3L_2$, etc. Some derivatives of polynuclear carbonyls.
−I (d^8)	Dia	Confined to $Re(CO)_5^-$ and some polynuclear carbonyl anions.

[a] Effective magnetic moments of majority of mononuclear complexes at room temperature.

cally disappear from ground water at a distance of 200 m from the source, rhenium could still be detected 1 km away.[62] The greater mobility of rhenium (undoubtedly as perrhenate) is reflected in its accumulation in the sea where it attains fairly high concentrations compared to other trace elements (8.4 ng $l.^{-1}$ in surface Pacific[63] and 4.0 ng $l.^{-1}$ in intermediate Atlantic waters;[64] *cf.* Mo, 10 μg $l.^{-1}$, and Au, 11 ng $l.^{-1}$ [2]). It is removed from the sea by adsorption on clays but not on carbonates or ferromanganese minerals, and argillaceous deep sea sediments contain 1.4–19.4 ppb of Re,[64] an order of magnitude higher than the crustal abundance. This may explain the high rhenium content of certain sedimentary deposits containing fish bone detritus and its lack of correlation with the molybdenum content.[65] It would be interesting to determine rhenium in clays associated with evaporite deposits. Some rhenium has also been detected in coal-bearing sediments[5,65] and, as perrhenate, in uranium ores from Arizona.[53]

Only one rhenium mineral, dzhezkazganite, has been identified to date. It occurs in the Cu–Mo deposits of Central Kazakhstan SSR as microscopic prisms (*ca.* 100 nm long) closely associated with grains of bornite.[61,66] The mineral was once thought to be $CuReS_4$, but copper has now been shown to be a contaminant and the composition has been established as $[Re,Mo]S_2$.[61,67] Traces of ReS_2 are said to occur in the Mansfeld copper shales and of an unidentified mineral in the Prince Leopold Mines, Katanga. Both might actually be $[Re,Mo]S_2$. It does not appear to have been agreed at what point in the MoS_2–ReS_2 series the name dzhezkazganite ought to be adopted.

IV. Chemistry of Rhenium Compounds

An important feature of the chemistry of rhenium, shared to some extent with molybdenum, tungsten, technetium, and osmium, is the existence of a large number of easily accessible oxidation states which interconvert under mild redox conditions. For this reason, reactions often yield mixtures of products, and experimental conditions must be carefully controlled to obtain reproducible results. Although as many oxidation states are known for manganese, the majority are represented by a small number of species of low stability and are readily converted to Mn^{II} and MnO_2. The most accessible oxidation state is the seventh. It is obtained by mild oxidation of the metal and most of its compounds in the presence of water. Both Re^{VI} and Re^{V} disproportionate to Re^{VII} and Re^{IV} but, whereas Re^{V} is readily stabilized by a variety of ligands, Re^{VI} is apparently not, and very few complex species have been isolated. The tendency to form multiple bonds to oxygen and nitrogen remains strong but changes character from Re^{VII} to Re^{V}, then virtually disappears with Re^{IV}. Metal–metal bonding is first encountered in the ternary oxide $Nd_4Re^{V}{}_2O_{11}$ and in several solid compounds of Re^{IV}, and assumes particular significance in the chemistry of Re^{III}. In sharp contrast to manganese, the second oxidation state is the least well known. The lower oxidation states (I, 0, and −I) are represented by a large number of carbonyl derivatives and organometallic compounds similar to those of manganese, as well as by some surprisingly stable complexes such as $ReCl(N_2)(dppe)_2$. Rhenium(−I) is confined to carbonyl anions. The salient properties of the nine known oxidation states of rhenium are summarized in Table I.

A. Rhenium(VII)

The chemistry of rhenium(VII) is dominated by the great stability of the perrhenate ion to which nearly all species eventually hydrolyze. Even in the absence of water the chemistry is rather limited by the slight tendency to form complexes with ligands other than oxide. Nevertheless, all coordination numbers from four to nine have been encountered within this relatively narrow range of compounds and, under conditions which preclude formation of ReO_4^-, tetrahedral coordination does not seem to be especially favored. Technetium(VII) appears to have a more pronounced tendency to be tetrahedral. There are some striking structural similarities to analogous compounds of iodine(VII) which provide the only comparison between rhenium and the halogens. The relationship to osmium(VIII) and tungsten(VI) is rather dis-

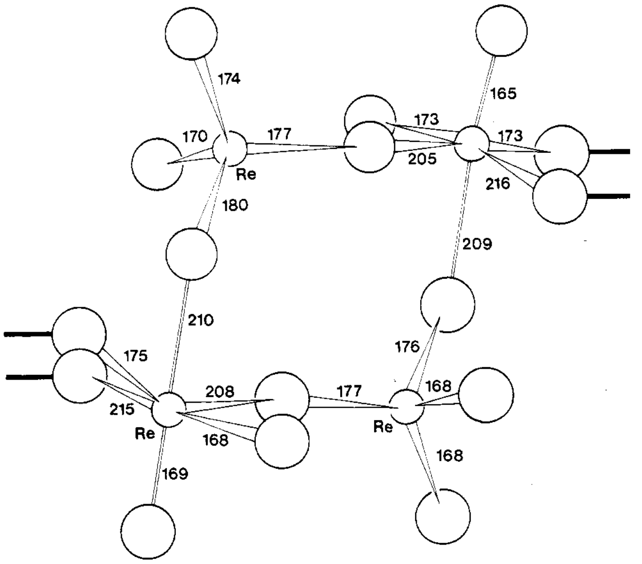


Figure 1. Ring of four polyhedra in the structure of crystalline Re_2O_7. Bond distances in pm.

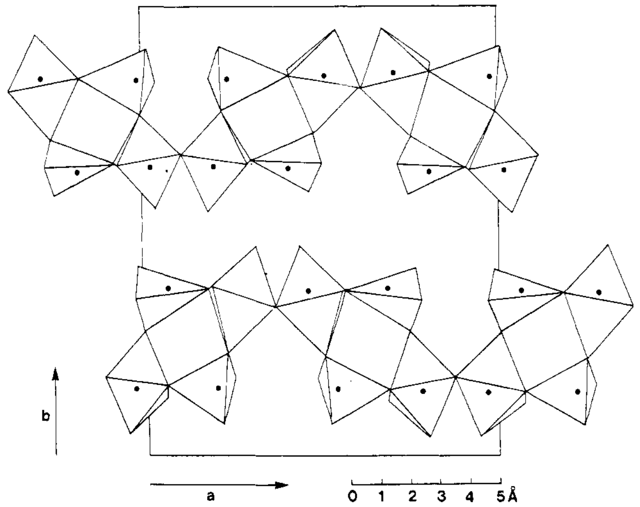


Figure 2. Projection of the structure of Re_2O_7 along the *c* axis showing the linking of rings to form sheets perpendicular to the plane of the paper.

tant, and no isopolyanions have been reported for rhenium. The highest oxidation states of the lighter actinides show many similarities to those of the corresponding metals in the d block. Very little is yet known about the newly discovered seventh oxidation state of neptunium to draw reliable comparisons with rhenium(VII), and it remains to be seen whether significant similarities persist this far along the actinide series. The oxidizing properties of rhenium(VII) are feeble as exemplified by the existence of thio and hydrido anions, and an oxobromide.

1. Dirhenium Heptoxide, Perrhenic Acid, and Perrhenates

Dirhenium heptoxide (Re_2O_7) is obtained in yellow crystals when the metal or a lower oxide is heated in oxygen[68] ($\Delta H_f° = -1263$ kJ mol^{-1}).[69] It melts at 301.5° to a colorless, mobile liquid of high vapor pressure (η = 1.161 cP at 346.0°; bp 358.5°, ΔH_{vap} = 67 kJ mol^{-1}).[70] The molecular weight and vibrational spectrum of the vapor indicate that it contains discrete $O_3Re-O-ReO_3$ molecules of symmetry C_{2v} in which the oxo bridge is probably bent and the local symmetry of each rhenium atom is C_{3v} (*i.e.*, isostructural with gaseous Cl_2O_7 and Tc_2O_7,[71] and aqueous $Cr_2O_7{}^{2-}$).[72,73] The principal species in the mass spectrum is the molecular ion.[74,75] A vibrational analysis has yielded the force constants for the terminal and bridging metal-oxygen bonds as 800 and 250 N m^{-1}, respectively, and the strongest bands in the Raman spectrum have been assigned to $\nu(ReO_3)$ 1009 vs, 972 m; $\delta(ReO_3)$ 341 m; $\rho_r(ReO_3)$ 185 ms; and $\delta(ReORe)$ 50 m cm^{-1}. Liquid dirhenium heptoxide also contains discrete dinuclear molecules since the Raman spectrum is almost identical with that of the vapor.[72] The solid, however, is polymeric and has a very different spectrum.[72,74,76] The crystal structure is unique. An equal number of nearly regular ReO_4 tetrahedra and of highly distorted ReO_6 octahedra share corners through oxygen bridges to form sheets parallel to the *ac* plane, with only oxygen-oxygen van der Waals contacts between the sheets. Each sheet is formed from rings of four polyhedra (Figure 1) perpendicular to the *ac* plane which are themselves linked through corners of octahedra (Figure 2).[77] The structure is thus reminiscent of, but not the same as, the isoelectronic $Mo_2O_7{}^{2-}$ ion in $Na_2Mo_2O_7$. It is completely different from solid ditechnetium heptoxide which contains isolated Tc_2O_7 molecules with a *linear* oxo bridge.[78] Bridging Re-O bonds (172.5-216.0 pm) are longer than terminal (165.0-174.2 pm), but still short enough to indicate a bond order higher than unity.[77]

Fusion of dirhenium heptoxide to the molecular liquid merely involves cleavage of two of the long Re-O bonds in each octahedron.[77] These must be formed again when the liquid freezes, in keeping with its tendency to remain supercooled.[70] The white amorphous oxide erroneously described as Re_2O_8 in the old literature may be the result of rapid quenching of molecular Re_2O_7.[77,188] A small proportion of the heptoxide is said to melt incongruently to $ReO_3(s)$ and oxygen.[75] Contrary to earlier reports, the pure heptoxide is either insoluble in anhydrous organic solvents or it undergoes reduction.[74,79] Moist solvents convert it to perrhenic acid, which may then dissolve. Thus Re_2O_7 dissolves in dioxane only in the presence of water. Colorless rhombic crystals of stoichiometry $Re_2O_7 \cdot 2H_2O \cdot 2C_4H_8O_2$ and unknown structure may be isolated from the solution,[74] and on heating they decompose quantitatively to pure ReO_3.[80] Olefins are oxidized by Re_2O_7 to epoxides.[81]

Dirhenium heptoxide dissolves freely in water to form a colorless, strongly acidic solution of perrhenic acid (formally $HReO_4$) from which stable metal perrhenates may be prepared. The acid is completely dissociated to the $ReO_4{}^-$ ion in solutions less concentrated than 70 wt % $HReO_4$ (*ca.* 7 *M*).[82,83] Such solutions have metal-oxygen stretching frequencies identical with those of aqueous sodium perrhenate (970 and 919 cm^{-1})[82,84] and may be concentrated without loss of rhenium in the vapor.[85] Solutions more concentrated than 80 wt % $HReO_4$ are yellow and have additional metal-oxygen stretches due to undissociated perrhenic acid.[82,84] They boil with loss of acid (*e.g.*, 92.1 wt % $HReO_4$, bp 193.5° is in equilibrium with vapor containing 7.0 wt % $HReO_4$ at the boiling point)[85] and are extremely viscous owing to hydrogen bonding.[86] The ^1H nmr spectrum consists of a single sharp peak at all concentrations due to rapid proton exchange.[82,83] Pale yellow, hygroscopic needles of anhydrous perrhenic acid are obtained by cooling a concentrated solution to −70° [87] or by allowing the heptoxide to absorb water vapor.[88] The anhydrous acid may be recrystallized from nitromethane, but it begins to dissociate *in vacuo* above 65° to Re_2O_7.[87,88] The crystal structure consists of isolated $O_3Re-O-ReO_3(H_2O)_2$ molecules in which the oxo bridge is linear and the aquo ligands are mutually cis (Figure 3).[86] Since concentrated solutions have the same vibrational spectrum as the anhydrous acid, they are also believed to contain $Re_2O_7(H_2O)_2$ molecules,[84,86] but the presence of some $ReO_3(OH)$ has not been excluded. There is some evidence that $ReO_3(OH)$ molecules may be present in the vapor above undissociated perrhenic acid.[87] Nevertheless, no rhenium compounds analogous to $ClO_3(OH)$ or $H_3O^+ClO_4^-$ have been isolated. The crystal structures of permanganic[88] and pertechnetic acids[10] have not yet been determined. Trimethylsilyl perrhenate, the only known ester of perrhenic acid, is stable in the absence of water but is rapidly hydrolyzed to ReO_4^- and Me_3SiOH.[89] The crystalline compound contains essentially tetrahedral $ReO_3(OSiMe_3)$ molecules in which the large Re-O-Si angle (164°) indicates some multiple bonding to the bridging oxygen.[90]

Perrhenic acid may be distilled from sulfuric acid solutions[91] though the actual volatile species have not been identified. Some reduction to a pink Re^{VI} species has been reported,[92,93] and a crystalline substance of uncertain structure has been isolated from concentrated sulfuric acid.[94] Perrhenic acid may be extracted from aqueous solutions into nonpolar organic solvents by tributyl phosphate (TBP), essentially as the perrhenate of a TBP–H_3O^+ complex.[95]

Nearly all metal cations form perrhenates of exceptional stability. Those formed by metals of groups Ia, IIa, IIb, Ag^I, Tl^I, Pb^{II}, Fe^{III}, and most divalent cations of the first transition series were known before 1965.[8,14] The colorless perrhenates M^IReO_4 either have a tetragonal scheelite structure (M = Na, K, Rb, NH_4, and Ag) or an orthorhombic pseudoscheelite structure (M = Cs and Tl), but high-temperature tetragonal polymorphs of both $CsReO_4$[96] and $MReO_4$[96,97] are known. The alkali perrhenates (M = Na, K, Rb, and Cs) melt and boil without decomposition (bp 1370° for M = K),[8,9,14] and the infrared spectra of the vapors are consistent with the presence of ReO_4^- ions.[73] A mass spectrometric study has shown that $NaReO_4$ and $KReO_4$ vaporize as monomers (ion pairs) and dimers (ion clusters) in comparable amounts[98] and is thus at variance with earlier electron diffraction data which indicated that the vapor consisted of $ReO_3(OK)$ molecules.[99] Ammonium perrhenate[100] begins to decompose to amorphous oxides, water, and N_2 (but not NH_3) at 230–250° (3–5% hr^{-1}) and decomposition is rapid at 325° (70% hr^{-1}). Crystalline ReO_2 is formed above 400°.[101,102] Pyrolysis of a mixture of NH_4ReO_4 and $MnCO_3$ yields $Mn(ReO_4)_2$,[103] and reduction of NH_4ReO_4 in hydrogen gives NH_3 and pure rhenium metal.[104] Aliphatic amines extract perrhenate into organic solvents as alkylammonium perrhenates[105] in which anion and cation are linked by hydrogen bonds.[106]

The thermal stability of perrhenates decreases with increasing cationic charge. Thus $Zn(ReO_4)_2$,[107] $Ni(ReO_4)_2$,[108] and $UO_2(ReO_4)_2$[109] begin to decompose at a red heat to Re_2O_7 and ZnO, NiO, and $U_3O_8 + O_2$, respectively. Anhydrous $M^{III}(ReO_4)_3$ (M = Al, Ga, and In) are obtained by heating Re_2O_7 with M_2O_3 in a sealed tube, and they dissociate to the same oxides in air above *ca.* 300°.[110] All the known hydrates of $M^{III}(ReO_4)_3$ (M = Al, Ga, In,[110,111] Bi,[112] Sc,[113] Y, and the lanthanides[114,115]) are readily soluble in water, ethanol, and acetone and may be dehydrated without hydrolysis. Yttrium and the lanthanide perrhenates crystallize from water as tetrahydrates which are either monoclinic (La to Nd) or orthorhombic (Pr to Dy). The Pr and Nd salts exist in both forms.[114] Anhydrous $La(ReO_4)_3$ loses Re_2O_7 above 700° to form a new phase, La_3ReO_8, which is itself stable up to at least 1100° and which is decomposed by water to $La(ReO_4)_3 + La_2O_3$.[115] Claims that the lanthanide perrhenates decompose at *ca.* 700° to $Ln_2O_3 + Re_2O_7$[114] thus appear to be in error. In solid $M^{III}(ReO_4)_3\cdot nH_2O$ the ReO_4^- ion is likely to be weakly coordinated to M^{III}, and a crystal structure determination on at least one of these salts would be worthwhile. The compounds $M^{IV}(ReO_4)_4\cdot nH_2O$ (M = Th and Np, n = 0 and 4;[116] M = Zr and Hf, n = 6[117]) and $M_2O(ReO_4)_6\cdot nH_2O$ (M = Zr and Hf, n = 0 and 9)[117] have been reported and almost certainly contain M^{IV}–O–Re^{VII} bridges.

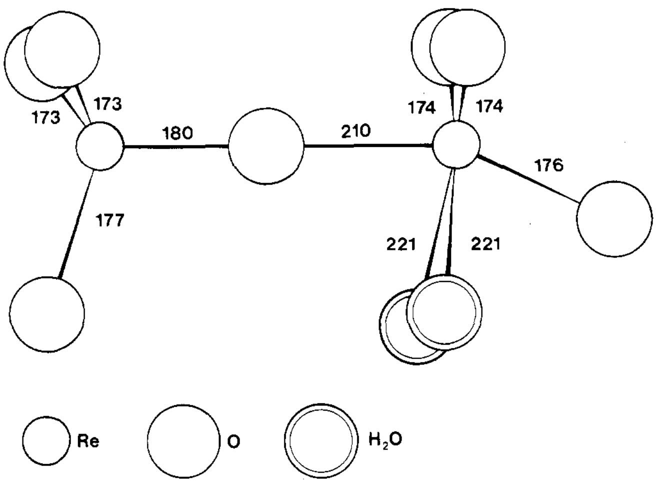


Figure 3. An isolated molecule of crystalline perrhenic acid. Bond distances in pm.

The perrhenate ion is strictly tetrahedral in solution[43,118] but may have a lower symmetry in crystalline salts.[119] A species of symmetry T_d ought to show four Raman-active fundamentals [e.g., CrO_4^{2-}(aq)]. Only three have been observed for ReO_4^-(aq) [971, $\nu_1(A_1)$; 916, $\nu_3(F_2)$; and 332 cm^{-1}, $\nu_4(F_2)$] as well as for the isoelectronic MO_4^{2-}(aq) (M = Mo[120] and W) and OsO_4(l).[118] This has been attributed to accidental coincidence of $\nu_2(E)$ and $\nu_4(F_2)$,[118] but a more plausible explanation is that $\nu_2(E)$ is too weak and broad to be seen.[120] The $\nu_3(F_2)$ fundamental is shifted closer to $\nu_1(A_1)$ than expected from T_d symmetry, apparently as a result of a close association of the anion with water molecules, and in TcO_4^-(aq) it becomes coincident with ν_1 at 912 cm^{-1} [120] The stretching force constant in ReO_4^- (755 N m^{-1}) is greater than in MnO_4^- and TcO_4^-, and the bending force constant (43 N m^{-1}) is comparable.[121] In crystalline perrhenates of the scheelite type the site symmetry of ReO_4^- is S_4, and the vibrational spectra,[120,122] including the lattice vibrations,[123] may be interpreted on this basis. Since the anion is distorted in solid $KReO_4$, it is possible to observe a pure nqr spectrum.[44]

It is generally accepted that the chemically significant energy levels in the oxo anions MO_4^- (M = Mn, Tc, and Re) occur in the order $3t_2 < t_1 < 2e < 4t_2$ and that the groundstate configuration is $(3t_2)^6(t_1)^6$.[124,125] On the other hand, there has been wide disagreement as to the separation of these levels and molecular orbital calculations have been of little help.[125] By symmetry t_1 is a nonbonding ligand orbital, and it is believed that the slightly bonding $3t_2$ has nearly pure ligand character and that the antibonding 2e assumes increasing d character from Mn to Re.[126] The first two band systems in the electronic spectra have a complicated vibrational structure both in aqueous solution[125] and in a $KClO_4$ host at 2.5 K[126] and they have been assigned to the $t_1 \rightarrow 2e$ and $3t_2 \rightarrow 2e$ transitions, respectively (both $^1A_1 \rightarrow {}^1T_2$). These assignments have recently been rationalized by an SCCC-MO calculation.[127] The first band occurs in the visible only for

MnO_4^- (18,300 cm^{-1}) and is shifted into the uv for TcO_4^- (32,200 cm^{-1}) and ReO_4^- (44,000 cm^{-1}).[124] The ReO_4^- ion exhibits slight temperature-independent paramagnetism comparable to that of MnO_4^-.[128]

Whereas OsO_4 associates with OH^- in basic solution to give $OsO_4(OH)_2^{2-}$,[13] the perrhenate ion persists as ReO_4^- even in saturated aqueous NaOH.[129] Like several other oxoanions (*e.g.*, SO_4^{2-}, NO_3^-, and MnO_4^-), it exchanges oxygen with water under acid catalysis. The rate law

$$\text{rate of exchange} = k_0[H_2O][ReO_4^-] + k_1[H_2O][ReO_4^-][H^+]^2 + k_2[H_2O][ReO_4^-][OH^-] \quad (1)$$

was proposed by Murmann, with $k_0 = 1.4 \pm 0.1 \times 10^{-8}$ M^{-1} sec^{-1}, $k_1 = 3.36 \pm 0.15 \times 10$ M^{-3} sec^{-1}, and $k_2 = 1.555 \pm 0.023 \times 10^{-4}$ M^2 sec^{-1} in 0.1 M LiCl at 25°.[130] At pH <4 this reduces to the term $k_1[H_2O]\cdot[ReO_4^-][H^+]^2$ found by other workers ($k_1 = 4.91 \times 10$ M^{-3} sec^{-1} at 30°),[131] and in this region the exchange is faster than for MnO_4^- ($k_1 = 3.0 \times 10^{-3}$ M^{-3} sec^{-1})[130] and TcO_4^- ($k_1 = 2.0$ M^{-3} sec^{-1}).[131] The dependence of each term on $[H_2O]$ had been assumed, and a kinetic study with small amounts of water in anhydrous methanol showed that the rate was in fact *independent* of $[H_2O]$ in the region of acid catalysis and only slightly dependent in the uncatalyzed region. There was no exchange with methanol. A mechanism consistent with these observations proceeds through a fast equilibrium between ReO_4^- and $ReO_3(H_2O)^+$, followed by slow dissociative exchange between $ReO_3(H_2O)^+$ and H_2O, assisted by general hydrogen bonding to the solvent.[132]

The ReO_4^- ion is a weak ligand but not as weak as ClO_4^-. Thus pyrolysis of $[Co(NH_3)_5(H_2O)][ReO_4]_3$ yields the perrhenato complex $[Co(NH_3)_5(OReO_3)][ReO_4]_2$, which is hydrolyzed by water back to the aquo complex according to first-order kinetics. Hydrolysis occurs through fission of the Re–O bond and is subject to both acid and base catalysis (first order in each).[133] The complex $UO_2(n\text{-}Bu_3PO)_2(ReO_4)_2$ of unknown structure is nonconducting in benzene but dissociates in methanol.[134] The complexes $M(py)_4(ReO_4)_2$ (M = Mn, Co, Ni, Cu, and Zn) contain coordinated perrhenate in the solid state[135] but, like the analogous perchlorato complexes,[136] give ionic species in all solvents in which they dissolve. Certain bands in the electronic spectra of the lanthanide ions shift by *ca.* 1 nm in fairly concentrated aqueous perrhenic acid (>3 M), and this has been interpreted as implying the formation of 1:1 and 1:2 complexes of ReO_4^-.[137] However, the shift does not occur in $NaReO_4$ and it might have been caused by H^+ rather than ReO_4^-. The above compounds, certain solid adducts of the lanthanides,[138] and the dinuclear Re^{III} complexes $[Re_2(RCO_2)_4](ReO_4)_2$[139] and $[Re_2Cl_2(RCO_2)_3]ReO_4$[140] are the only ReO_4^- complexes so far reported. In the last complex ReO_4^- moieties bridge dinuclear $Re^{III}{}_2$ units to form chains, but no examples of chelating perrhenate have yet been established.

Perrhenate is a weaker oxidant than pertechnetate. Reduction of aqueous solutions in the absence of complexing agents results in ill-defined hydrated oxides.[8,9,14,141] A large number of species, mostly transient and poorly characterized, are generated by chemical or electrolytic reduction in weakly complexing media under various conditions.[8,9,14,93,142-145] The first polarographic wave in 4 M sulfuric acid probably corresponds to reduction to a purple Re^{VI} species which may then disproportionate slowly to Re^{IV} and Re^{VII}, thus resulting in a three electron change.[142] In neutral 1 M KCl on a dropping mercury electrode, perrhenate is reduced irreversibly to rhenium metal and not to Re^{-I} as was once believed.[143] Various species have been implicated in polarographic reduction in HCl[144] and fused chloride media,[145] but the picture remains confused. Under strongly complexing conditions reduction leads to stable, isolable complexes which will be discussed under their oxidation states. Whereas pertechnetate inhibits steel corrosion in concentrations less than 5×10^{-5} M, perrhenate is totally inactive in this respect.[146] The chemical reactions of radiorhenium produced by irradiating crystalline perrhenates with 660-MeV protons have been studied in several laboratories.[147]

2. *Other Oxo Anions, Mixed Oxides, Thio Anions, and Chalcogenides*

Noddack and Noddack had recognized in 1933 that oxo species in addition to (meta)perrhenate (ReO_4^-) could exist in strongly basic media, but only one compound, $Ba_3(ReO_5)_2$, was isolated during the next 30 years. Recent work[148] leaves no doubt that meso- and orthoperrhenates of the alkalis and alkaline earths exist as stable, crystalline compounds in the solid state and are generally isomorphous with the corresponding compounds of osmium(VII) and iodine(VII). They are hygroscopic and are all immediately hydrolyzed to metaperrhenate and alkali. Lesser known technetium analogs have been prepared,[149] but there is no counterpart in the chemistry of manganese.[150]

The bright yellow mesoperrhenates $M^I{}_3ReO_5$ and $M^{II}{}_3(ReO_5)_2$ are obtained by heating stoichiometric quantities of the metaperrhenates with $M^I{}_2O_2$ (M^I = Na), M^IOH (M^I = K), $M^{II}CO_3$ (M^{II} = Sr), or $M^{II}(OH)_2$ (M^{II} = Ba) in dry oxygen.[148] Pure $M^I{}_3ReO_5$ (M^I = K, Rb, and Cs) may be prepared by heating rhenium dioxide and alkali superoxide to 400° for 3 hr, but if peroxide is used in place of superoxide the only product is M^IReO_4.[150,151] These compounds undergo a reversible phase transition at 374° (M^I = K), 320° (M^I = Rb), and 304° (M^I = Cs), but may otherwise be heated to 900° without change.[151] On the other hand, the lithium and calcium compounds seem to be so unstable that attempts to prepare them have resulted in mixtures of ortho- and metaperrhenates. Strontium mesoperrhenate disproportionates to such a mixture above 750°

$$2Sr_3(ReO_5)_2 \longrightarrow Sr_5(ReO_6)_2 + Sr(ReO_4)_2 \quad (2)$$

whereas the barium compound is stable up to at least 1200°.[148] The complex infrared spectra indicate low symmetry but are otherwise uninterpretable.[152] Since barium mesoperrhenate is sparingly soluble, crystals may be grown from strongly alkaline aqueous solutions[153] and then have the composition $Ba_3(ReO_5)_2\cdot{}^1\!/_3Ba(OH)_2$.[188] The X-ray crystal structure reveals discrete hydroxyl and ReO_5^{3-} ions of slightly distorted square-pyramidal geometry in which the apical Re–O bond (169 pm) is appreciably shorter than the basal bonds (180 and 185 pm).[188] Likewise, K_3ReO_5 in fused $KReO_4$ has the cryoscopic behavior of a 3:1 electrolyte, suggesting the presence of ReO_5^{3-} ions in the melt.[150] Thus mesoperrhenates appear to be simple salts of ReO_5^{3-}. It has been reported that $Ba_3(ReO_5)_2$ gives a yellow solution in concentrated alkali, and on the basis of the intensity of the shoulder on the low-energy side of the metaperrhenate absorption band it has been claimed that in 15 M NaOH about 30% of the rhenium is in the form of mesoperrhenate.[153] This conclusion seems too simple since perrhenate is the only species present in the absence of barium, even in very concentrated alkali.[129,153] Furthermore, the barium salts are unique among both meso- and orthoperrhenates in that they dissolve in absolute methanol without solvolysis.[148] It is possible that the oxo species gains stability by coordination to barium or dissolves as a heteropolyanion.

Deep orange or green orthoperrhenates $M^I_5ReO_6$ (M^I = Li and Na)[148] and $M^{II}_5(ReO_6)_2$ (M^{II} = Ca, Sr, and Ba)[148,154] are the only phases produced when the metaperrhenates are heated with the correct amount of base. No other phases appear when excess of base is used. The compounds of the heavier alkalis are unknown, mesoperrhenates being produced instead.[148,154] Lithium orthoperrhenate is obtained in hexagonal, yellow leaflets (red-brown when hot) as the only new phase in the Li_2O–$LiReO_4$ system, and the structure consists of almost cubic close-packed oxygen atoms with layers of octahedral holes filled entirely by lithium or entirely by lithium and rhenium atoms in the ratio 2:1. This results in isolated ReO_6 octahedra in which the length of the Re–O bond is 205 pm so that the compound could be regarded as the lithium salt of ReO_6^{5-}.[155] The sodium salt is isostructural. The infrared spectra of the lithium (ν(Re–O) 650 cm^{-1})[156] and barium compounds (ν(Re–O) 622 cm^{-1}, δ(Re–O) 340 cm^{-1}) are consistent with their formulation as ionic hexaoxorhenates(VII),[152] though they could equally be regarded as ternary oxides related to perovskite.[154] The mixed oxides $Ba_2M^IReO_6$ (M^I = Li and Na) are ordered perovskites,[157] and the oxides $A_4MRe_2O_{12}$ have related structures with a stacking sequence of 12 layers (A = Ba, M = Mg, Ca, Co, Zn, Cd, and In; A = Sr, M = Mg, Co, Ni, and Zn) or 24 layers (A = M = Ca; A = M = Ba; and A = Sr, M = Ca and Sr) depending on the M/A radius ratio.[154] The oxides in which A = M are probably identical with one of the polymorphs of Scholder's alkaline earth orthoperrhenates.

Mixed oxides with covalent Re–O–M bonds (M = V^V, Nb^V, Mo^{VI}, etc.) promise to have an extensive and interesting structural chemistry. Thus red $VReO_6$ (perhaps VO_2ReO_4) loses oxygen on heating to form green, hygroscopic prisms of $V_2Re_2O_{11}$. Magnetic measurements are consistent with equal numbers of V^V, V^{IV}, Re^{VII}, and Re^{VI} atoms.[158] X-Ray diffraction reveals a network of distorted VO_4 and ReO_4 tetrahedra sharing corners with an equal number of VO_5 trigonal bipyramids and distorted ReO_5 square pyramids.[159] Crystalline phases of unknown structure and stoichiometry $Ti_2Re_2O_{11}$, $Nb_4Re_2O_{17}$, $NbReO_6$,[160] La_3ReO_8,[115] and $La_8Re_6O_{33}$[161] have also been described.

All four thioperrhenates $ReO_{4-n}S_n^-$ (n = 1–4) have been reported as products of the reaction of H_2S with aqueous perrhenate under various conditions of pH. Of these, only ReO_3S^- and ReS_4^- have been rigorously characterized in crystalline salts. An additional species, probably $ReOS_3^-$, has been detected in solution at pH 11.0,[162] and it has been speculated, but without evidence, that $ReO_2S_2^-$ might also exist in solution. Investigation of this system is rendered difficult by the tendency of thioperrhenates to decompose to ReO_4^- and Re_2S_7 at a rate comparable to their formation.[162] Since many perrhenates are highly soluble in organic solvents, it would be possible to study the system under nonaqueous conditions. The isoelectronic thioanions $MO_{4-n}S_n^{2-}$ (M = Mo and W) are well known, but neither Mn^{VII} nor Os^{VIII} form analogous complexes.

Perrhenate reacts slowly with H_2S in neutral solution to form yellow ReO_3S^- [163] and in strongly alkaline solution (25% NH_3) purple ReS_4^-.[164] Cesium and thallium thioxothioperrhenates crystallize in the $BaSO_4$ structure (*cf.* $KMnO_4$) while the potassium and rubidium salts belong to a new structure type related to scheelite.[163,165] A single-crystal X-ray study has shown that the ReO_3S^- ion in $RbReO_3S$ departs slightly from C_{3v} symmetry and that the length of the Re–S bond is 214 pm. The mean length of the Re–O bonds (175 pm) is practically the same as in $KReO_4$ (177 pm).[165] A normal coordinate analysis of $CsReO_3S$ (ν(Re–S) 517 cm^{-1}) has yielded the stretching force constants for the Re–S and Re–O bonds as 425 and 750 N m^{-1}, respectively,[166] though much lower values (285 and 625 N m^{-1}) have been calculated for $TlReO_3S$ (ν(Re–S) 504 cm^{-1}).[167] The crystalline, purple-black tetrathioperrhenates $AReS_4$ (A = $AsPh_4$, PPh_4, and NMe_4) dissolve in organic solvents, but the solutions decompose within a few hours. Intense charge-transfer bands, for which assignments have been proposed, occur at 19,800 (ϵ 9.6 × 10^4), 32,050 (ϵ 1.8 × 10^4), and 44,000 cm^{-1} (ϵ 3 × 10^4). Infrared assignments include ν_s(Re–S) [501, $\nu_1(A_1)$], ν_a(Re–S) [486, $\nu_3(F_2)$], and $\delta_a(ReS_2)$ [200 cm^{-1}, $\nu_4(F_2)$]. As in ReO_4^-, ν_2(E) is either very weak or coincident with $\nu_4(F_2)$. The stretching force constant varies from 326 to 394 N m^{-1} according to the force field model assumed in the calculation.[164]

Acid solutions of perrhenate react with H_2S to give a brownish black amorphous precipitate of dirhenium heptasulfide (Re_2S_7), through a number of unidentified intermediates. It usually contains excess sulfur which is very difficult to remove. Some samples,[168] but not others,[169,170] have become microcrystalline after heating *in vacuo* for several weeks, and their magnetic properties depend on their history. This is, nevertheless, the only practical preparation since ReS_2 does not react with sulfur and Re_2O_7 is reduced by both sulfur and H_2S to impure ReO_3. The structure of Re_2S_7 is unknown. It dissociates directly to ReS_2 and sulfur when heated under argon[169] but is reduced by hydrogen at ambient temperatures to an amorphous pyrophoric substance of stoichiometry ReS_3, possibly the trisulfide.[168,169] Reduction at higher temperatures proceeds to ReS_2 and then to the metal. The intermediacy of Re_2S_5 has been proposed,[168] but not substantiated.[169] The heptaselenide has not been reinvestigated since its early preparation.[9]

3. *Rhenium Heptafluoride and the Oxohalides*

Fluorine reacts with rhenium metal to give a mixture of ReF_6 and ReF_7, but ReF_6 reacts further under 3 atm of F_2 at 400° to form pure ReF_7.[171] The heptafluoride is also obtained by treating rhenium powder with F_2 in a fluidized bed[172] and by exploding a rhenium wire in SF_6 under certain conditions.[173] Technetium does not form a heptafluoride so that IF_7 and the very unstable OsF_7 are the only other known heptahalides of the elements. Both rhenium and iodine heptafluorides have body-centered cubic unit cells at room temperature in which the molecules are disordered.[171,174] A transition to lower symmetry (orthorhombic for IF_7) occurs at *ca.* −120°.[174] A set of X-ray diffraction data for single crystals of orthorhombic IF_7 could not be refined unambiguously to a definite molecular geometry,[175] and the exercise has not been attempted yet for ReF_7.

It has been suspected for some time that both molecules might be nonrigid, with ReF_7 the less rigid of the two. Thus the ^{19}F nmr spectrum of a solution of ReF_7 in WF_6 consists of a sharp singlet at ambient temperatures, indicating fast intramolecular exchange of fluorine nuclei within the nmr timescale.[176] The vibrational spectra in the liquid and vapor phases are consistent with D_{5h} sym-

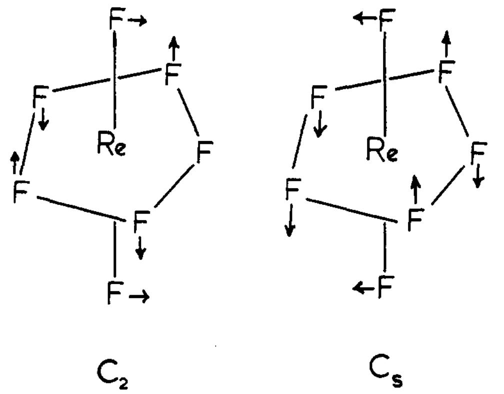


Figure 4. Stages in the pseudorotational cycle in ReF_7. Arrows indicate displacements of fluorine atoms by *ca.* 8° from the pentagonal bipyramid.

metry (excluding D_{7h} on other grounds) but the greater width of the infrared deformations of ReF_7 suggest much larger intramolecular motions in this molecule than in IF_7.[177] Experiments on the deflection of molecular beams in inhomogeneous electric fields indicate that ReF_7 has polar components which increase as the temperature is lowered. Such behavior is incompatible with a rigid structure, D_{5h} or otherwise. Similar polar components appear for IF_7 only at considerably lower temperatures.[178] An elegant electron diffraction study of ReF_7 has shown that a small but significant departure from D_{5h} symmetry occurs in the gas phase.[179] The diffraction data are consistent with puckering of the equatorial ring of five fluorines by no more than *ca.* 9° and concomitant bending of the axial fluorines by *ca.* 8° from the C_5 axis, away from the nearest equatorial fluorines (C_2 or C_s; Figure 4). Taken in conjunction with the other properties of ReF_7, these deformations are almost certainly not static but are stages in a pseudorotational cycle ($C_2 \rightarrow C_s \rightarrow C_2$) in which the equatorial pucker (E_2'' vibration) and axial bend (E_1' vibration) progress in a fixed phase relationship around the C_5 axis of the reference pentagonal bipyramid. The pucker probably originates in steric crowding of equatorial fluorines and in turn induces the axial deformation, thus leading to strong coupling of E_2'' and E_1'. The coupling and the large vibrational amplitudes render the model of independent normal vibrations inapplicable.[179] A similar situation pertains to IF_7 and XeF_6. Two independent attempts at force constant calculations on the basis of D_{5h} symmetry have yielded disparate results.[180]

Rhenium heptafluoride is stable in dry oxygen up to 500°[171] and is thus less oxidizing than PtF_6 and much more stable to dissociation than OsF_7. Surprisingly, it is only slightly more oxidizing than ReF_6 in that both fluorides are inert toward AsF_3 but oxidize PF_3 to PF_5. Generally, the reactions of ReF_7 toward halides are similar to, though more vigorous than, those of ReF_6.[181] The heptafluoride dissolves unchanged in anhydrous HF to an essentially nonconducting solution,[182] but the ReF_8^- ion is obtained as the nitronium or nitrosonium salt by heating ReF_7 with NO_2F or NOF, respectively. It is suspected to have a square antiprismatic structure.[183]

The three perrhenyl halides ReO_3X (X = F, Cl, and Br) and the oxofluorides ReO_2F_3 and $ReOF_5$ have been known for a long time. The latter is isostructural with $OsOF_5$ and IOF_5 (C_{4v})[184] and reacts with nitryl and nitrosyl fluorides to form salts of $ReOF_6^-$.[183] A mixed oxohalide of stoichiometry $Re_2O_4Cl_5$ is said to be formed by interaction of ReO_3Cl and $ReOCl_4$.[185] The only other recent work on oxohalides appears to consist of attempts at vibrational analyses.[186] A number of thiohalides such as ReS_3Cl, $ReSCl_4$, $ReSCl_2$, and $Re_2S_3Cl_4$ have been reported as products of the reactions of sulfides with chlorine or of chlorides with S_2Cl_2.[187] Although thiohalides are undoubtedly formed in such reactions, none of the above compounds have been adequately characterized.

4. Complexes

The complex species that have not been discussed above will be considered arbitrarily in this section. Four halo or oxohalo anions are known, *viz.* ReF_8^-, $ReOF_6^-$,[183] $ReO_2F_4^-$,[9] and $ReO_3Cl_2^-$,[189] and are all completely hydrolyzed by water to perrhenate. The last is obtained as the cesium salt by adding CsCl to perrhenic acid in concentrated HCl and has a vibrational spectrum consistent with the *fac* configuration. This is in keeping with the tendency of oxo ligands in octahedral d^0 complexes to occur mutually cis.[100] Although both $WO_3F_3^{3-}$ and $OsO_3F_3^-$ are known, the isoelectronic $ReO_3F_3^{2-}$ ion cannot be isolated from solutions of perrhenic acid in even anhydrous HF.[189] The salt K_2ReO_3N is formed in the reaction of potassium amide with Re_2O_7 in liquid ammonia[191] and is considered to have a Re–N triple bond (ν(Re–N) 1022 cm^{-1}; ν(Re–O) 878, 830 cm^{-1}).[192] It is intermediate between MoO_3N^{3-} and OsO_3N^- in the ease of hydrolysis to ammonia.

An anhydrous nitrate, ReO_3NO_3, is obtained by the action of N_2O_5 on ReO_3Cl and appears to be polymeric. The infrared spectrum is consistent with the presence of bridging nitrate groups, and the mass spectrum contains dinuclear species. It decomposes above 70° without melting to Re_2O_7 and NO_2.[193]

Labile, hygroscopic adducts $ReO_3Cl(dmf)_2$ and $ReO_3Cl(dmso)_2$ in which the ligands are bound through oxygen may be prepared from stoichiometric quantities of ReO_3Cl and the appropriate ligand in dry CCl_4.[194] Even less stable adducts ReO_3ClL_2 [L = py, ½dipy,[237] $MeCONMe_2$, $(Me_2N)_2CO$, and $PO(NMe_2)_3$] are formed only with an excess of L and decompose when washed with CCl_4.[195]

Perhaps the most interesting complex of rhenium(VII) is the enneahydridorhenate ion, ReH_9^{2-}, formed in the reduction of perrhenate with an alkali metal. The highest yields have been attained using $NaReO_4$ and sodium in ethanol (35% Na_2ReH_9).[196] Various erroneous formulations had been advanced until the anion was eventually characterized by Ginsberg and his coworkers by X-ray and neutron diffraction. Each rhenium atom in K_2ReH_9 is at the center of a trigonal prism of hydrogen atoms with three other hydrogens beyond the centers of the rectangular faces of the prism. The nine Re–H bonds are nearly equal with a mean length of 168 ± 1 pm and a mean H–Re–H angle between hydrogens in the same vertical mirror plane of 93.6 ± 0.6°.[197] K_2TcH_9 is isostructural.[198] Although two distinct proton environments are expected, only one nmr signal is observed in aqueous solution at τ 19.1 which suggests, but does not prove, that the ion is fluxional. Certain deformations (*e.g.*, E′) would interchange prism and equatorial hydrogens at large amplitudes though it has not been proved that this is necessarily the pseudorotation mechanism.[197] Librations about the C_3 and C_2' axes of ReH_9^{2-} have been detected in solid K_2ReH_9 at 90 K by inelastic neutron scattering spectroscopy (time scale *ca.* 10^{-11} sec), and the barriers to hindered rotation have been estimated for each of the two crystallographically distinct sites of ReH_9^{2-}.[199] Nmr relaxation studies with a much longer observation time scale (*ca.* 10^{-5} sec) reveal, by contrast, only isotropic rotations.[199,200] It is possible that the apparent isotropy is the result of pseudorotational interchange of C_3 and C_2' even in the solid state at a rate between 10^5 and 10^{11} sec^{-1}, but there are alternative interpretations.[199] Infrared Re–H stretches in solid K_2ReH_9 occur at 1931 sh, 1846 s, and 1814 sh cm^{-1} and a single deformation frequency at 735 s cm^{-1}.[196] Neutron scattering, for which no selection rules apply, reveals further overlapping deformations at 640, 760, and 810 cm^{-1}.[199]

The ReH_9^{2-} ion is fairly stable in water at high pH but loses H_2 near neutrality. It is reduced by CO in ethanol to tri-μ-hydrido-bis[tricarbonylrhenate(I)],[201] a rare example of a complex with three hydride bridges. It is possible to formally replace one[202] or two[203] hydride ligands in ReH_9^{2-} by tertiary phosphines or arsines. Thus the anions ReH_8L^- (L = PPh_3, PEt_3, P-n-Bu_3, and $AsPh_3$) are obtained, accompanied by some ReH_5L_3 (L = PPh_3 and $AsPh_3$), by heating ReH_9^{2-} with L in 2-propanol.[202] The white, neutral complexes ReH_7L_2 are found among the products of the reaction of $ReOCl_3L_2$, $ReO(OR)Cl_2L_2$, and especially $ReCl_4L_2$ with $LiAlH_4$ in tetrahydrofuran (L = PPh_3, $PEtPh_2$, PEt_2Ph, $AsEt_2Ph$, and ½dppe). They lose H_2 when heated alone to form $(ReH_xL_2)_n$ (n = 2?) and with excess L to form ReH_5L_3.[203] It is interesting that when $ReH_8(PPh_3)^-$ is treated with HCl it gives the dinuclear rhenium(III) species $[PHPh_3]_2Re_2Cl_8$[202] whereas $ReH_7(PEt_2Ph)_2$ gives $ReCl_4(PEt_2Ph)_2$.[203] As in ReH_9^{2-} itself, the protons in ReH_8L^- and ReH_7L_2 are magnetically equivalent in solution. Acid-catalyzed H–D exchange occurs between ReD_7L_2 and EtOH by an unknown mechanism, but this is slow relative to the nmr time scale. Exchange also occurs with benzene at 100° and with dihydrogen.[203]

B. Rhenium(VI)

The sixth is undoubtedly one of the least stable oxidation states of rhenium and thus parallels the behavior of osmium(VII)[13] but contrasts sharply with molybdenum(V)[11] and tungsten(V).[12,190] Rhenium(VI) occurs in a number of solid oxides in which it nearly always occupies octahedral sites, but the well-established molecular compounds are confined to ReF_6, ReF_5Cl, $ReOX_4$ (X = F, Cl, and Br), the adducts $ReOCl_4L$, and a few simple anionic complexes. Transient-colored species formed in the reduction of ReO_4^- have also been attributed to rhenium(VI).[92,93,142] All coordination numbers from four to eight are known, but octahedral coordination is definitely preferred. The five-coordinate oxotetrahalides tend to assume sixfold coordination either by association in the solid state or by forming adducts with monodentate ligands.

1. *Rhenium Trioxide, Mixed Oxides, and Oxo Anions*

Samples of rhenium trioxide obtained by reducing Re_2O_7 with CO or by heating the complex of $HReO_4$ and dioxane[80] are cubic, slightly nonstoichiometric,[204] and inert. The oxide disproportionates without melting above 400° to ReO_2 and Re_2O_7, but pure single crystals of stoichiometric ReO_3 may be prepared from the nonstoichiometric samples by vapor transport in the presence of an excess of iodine at *ca.* 370°.[204] The structure of ReO_3 is a well-known prototype,[190] formally derived from perovskite by deletion of the large cation from the center of each cubic unit cell. It is closely related to the tungsten bronzes Na_xWO_3 ($0.3 < x < 0.95$)[205] which are defect perovskites in which WO_3 assumes an ReO_3 lattice with the centers of x of the unit cells occupied randomly by sodium.[205,206]

Rhenium trioxide is a metal. The resistivity increases linearly with temperature[204] and at room temperature (18 $\mu\Omega$ cm) is only ten times greater than that of copper (1.72 $\mu\Omega$ cm).[206] The surface has a red metallic luster, and the dielectric constant derived from the optical reflectance spectrum is characteristic of free electron behavior for photon energies between 0.2 eV and the sharp plasma edge at 2.1 eV. Several interband transitions occur beyond the plasma edge, and the minimum in reflectivity in the green region at 2.30 eV (1.5% reflectivity as compared to 93% at 0.2 eV) is responsible for the red color.[206] Nmr Knight shifts and spin-lattice relaxation rates for ^{185}Re and ^{187}Re at 1–4 K indicate that the conduction bands in ReO_3 and Na_xWO_3 are essentially identical near the Fermi level and suggest that they possess strong d character.[42] Similar conclusions follow from the optical reflectance spectra.[206] These observations have an important bearing on the conduction mechanism in the cubic tungsten bronzes themselves, which thus appears to involve donation of the sodium valence electrons into empty, essentially tungsten 5d conduction bands of the insulator WO_3. Several detailed calculations of the band structure and Fermi surface of ReO_3 have given results in good agreement with experiment.[207]

The redox potential of a stoichiometric ReO_3 electrode in aqueous perrhenate varies linearly with pH from pH 1 to pH 3, but is independent of perrhenate concentration. The nature of the couple is unknown but may involve a lower oxide.[208] In alkaline solution the electrode becomes passive, apparently owing to disproportionation to ReO_4^- and an insoluble, nonconducting Re^{IV} species.[209]

Cubic rhenium bronzes, M_xReO_3 (M = Na and K, $x < 1$), are obtained by heating ReO_3 with alkali azide[210] or $MReO_4$ with rhenium metal,[211] and the solid solutions $W_{1-x}Re_xO_3$ ($0 < x < 1$) are cubic for $x > 0.25$.[211] A hexagonal bronze, K_xReO_3, is also known.[212] The hexagonal, nonstoichiometric oxide $Re_{1+x}O_3$ ($0.14 < x < 0.21$) is formed when a mixture of ReO_3 and ReO_2 is heated to 700–1400° under a pressure of 65 kbars. The structure of a single crystal (x = 0.16) was elucidated by X-ray diffraction and found to contain hexagonal close-packed oxygen with one-third of the octahedral holes completely occupied by rhenium atoms and another third (of a different type) only partially occupied. Complete filling of the latter third would have given the unknown oxide Re_2O_3, but no new phases were obtained when ReO_2 and Re were heated together under pressure. In both cubic ReO_3 and hexagonal $Re_{1.16}O_3$ rhenium is present in an octahedral oxygen environment, but the volume per formula unit is considerably smaller for the high-pressure hexagonal phase.[213] All the above substances, with the exception of the WO_3–ReO_3 solid solutions rich in tungsten, have metallic conductivity.[211-213] Unlike ReO_3 itself and the cubic rhenium bronzes, hexagonal K_xReO_3 is superconducting below 3.6 K.[212] An attempt to prepare bronzes Cu_xReO_3 by heating ReO_3 with copper led to the stoichiometric phase $CuRe_4O_{12}$.[214]

A large number of ordered perovskites $A_2M^{II}Re^{VI}O_6$ (A = Ca, Sr, or Ba; M = Ca, Sr, Ba, Mg, Mn, Fe, Co, Ni, Zn, or Cd) have been synthesized by heating mixtures of binary oxides[9,215] and in other ways.[148] The M^{II} and Re^{VI} cations occupy octahedral sites. The perovskites are cubic when M = Ba, and black, single crystals of octahedral habit may be grown by the hydrothermal technique. They are semiconductors, with the exception of Ba_2FeReO_6 which has metallic conductivity (resistivity = 1.6 mΩ cm at 370 K). The oxides Ba_2MReO_6 (M = Mn, Fe, and Ni) are ferrimagnetic and Ba_2CoReO_6 is antiferromagnetic with a Néel temperature of 40 K.[215] The only oxides in which rhenium is known to occupy tetrahedral sites are of the type $Ba_3M_2{}^{III}Re^{VI}O_9$ (M = Cr and Fe) and have the hexagonal $BaTiO_3$ structure.[9] There is no evidence for the existence of either solid rhenates or of the $ReO_4{}^{2-}$ ion in solution.

A number of other oxide phases such as La_2ReO_6,[161] Li_4MgReO_6,[216] $Ca_5Re_2O_{11}$, Sr_2ReO_5,[148,217] etc., have been claimed, but the reports lack sufficient evidence and are somewhat confusing. The mixed oxide Li_6ReO_6 has been obtained in two modifications by several routes.[218] The blue-black rhombic α form obtained above 620° is isomorphous with α-Li_6TcO_6[149] and Li_6MO_6 (M = W and Te), while the β form obtained at lower temperatures is isomorphous with β-Li_6TcO_6 and Li_6MO_6 (M = Os, Np, Pu, and Am). The X-ray powder pattern of β-Li_6ReO_6 is practically the same as of Li_5ReO_6,[155] and the structure has therefore been assumed to consist of nearly cubic close-packed oxygen with all the rhenium atoms and most of the lithium in octahedral holes. Since the available octahedral holes are too few to accommodate all the lithium, some lithium atoms would of necessity occupy tetrahedral holes but may scatter too weakly to alter the powder pattern.[218] While this theory seems entirely reasonable, it would be difficult to distinguish β-Li_6ReO_6 from Li_5ReO_6 doped with Re^{VI}. The vibrational[219] and electronic spectra of Li_6ReO_6 have been discussed.[220] Although the compound could be regarded as a salt of the $ReO_6{}^{6-}$ ion, neither this nor any other oxo anion of rhenium(VI) persists in solution.

A ternary nitride $Sr_{27}Re_5N_{28}$ is obtained, together with $Sr_9Re_3N_{10}$, by heating rhenium metal with strontium nitride under nitrogen.[221]

2. Rhenium(VI) Halides and Oxohalides

Rhenium hexafluoride is formed from the elements ($\Delta H_f{}^\circ = -1350 \pm 10$ kJ mol^{-1}),[222] along with the heptafluoride. The latter is reduced to ReF_6 by rhenium metal.[171] The hexafluoride is of theoretical interest in that it is one of the few octahedral molecules subject to dynamic Jahn–Teller effects which can be studied in the gas phase.[223] Calculations based on the model that Jahn–Teller forces originate in the electrostatic interaction between the nonbonding rhenium t_{2g} electron and the fluorine atoms predict a static tetragonal distortion of only *ca.* 0.5 pm, but a profound effect on the vibrational spectrum.[224] In keeping with these predictions, experiments with molecular beams have shown that ReF_6 is nonpolar,[225] and electron diffraction in the gas phase has established O_h symmetry within the limits of experimental error (±0.4 pm). The mean Re–F separation (183.2 ± 0.4 pm) is nearly the same as in OsF_6 (183.2 pm), which should also be subject to Jahn–Teller distortions, and in WF_6 (183.4 pm) and IrF_6 (183.2 pm), which should not.[226] As might be expected from the bond lengths, solid ReF_6 is isomorphous with MF_6 (M = W, Os, Ir; and also Mo, Tc, Ru, Rh, and Pt) both in the body-centered cubic polymorph and in the modification of lower symmetry which is stable below room temperature.[174] A molecule with O_h symmetry is expected to have three fundamentals active in the Raman [$\nu_1(A_{1g})$, $\nu_2(E_g)$, and $\nu_5(F_{2g})$] and two in the infrared [$\nu_3(F_{1u})$ and $\nu_4(F_{1u})$]. The gas-phase vibrational spectra of WF_6, ReF_6, and IrF_6 are consistent with this,[223,227] but the ν_2 and ν_5 bands in ReF_6 have broad non-Gaussian envelopes and are displaced from the frequencies deduced by interpolation. This is the result of vibronic coupling caused by dynamic Jahn–Teller effects[223,227] and has been analyzed in detail.[223,227,228] Further manifestations of the Jahn–Teller effect are apparent in the vibronic structure of electronic bands[229,230] which indicate that the distortion is trigonal,[230] and in slow electron capture experiments.[231]

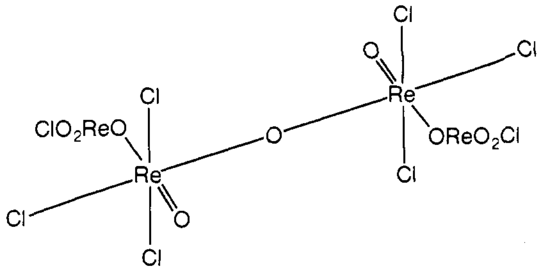
Rhenium hexafluoride is a stronger oxidant than WF_6 but is weaker than OsF_6. Thus WF_6 does not react with nitric oxide whereas both ReF_6 and OsF_6 are reduced to $(NO)MF_6$. ReF_6 reacts with nitrosyl fluoride by fluoride transfer only to give $(NO)_2ReF_8$ whereas OsF_6 gives a mixture of $(NO)OsF_7$ and $(NO)OsF_6$.[232] The reactions of TcF_6 are similar to ReF_6.[233] The hexafluoride is reduced smoothly by PF_3 (but not AsF_3) to ReF_5,[181] by BCl_3 to $ReCl_5$,[222] and by BBr_3 and PBr_3 to $ReBr_5$.[181] Like WF_6 and OsF_6 it gives nonconducting solutions in liquid hydrogen fluoride,[234] though the anions $ReF_7{}^-$ and $ReF_8{}^{2-}$ may be obtained in other ways.[9,232,233] The mixed halide ReF_5Cl is formed together with ReF_6 when $ReCl_5$ is treated with fluorine, and it decomposes even at room temperature to a mixture of ReF_6 and lower chlorides. The effective magnetic moment at 300 K (1.11 BM) is considerably higher than that of ReF_6 (0.25 BM).[235]

Although several preparations of $ReCl_6$ have been claimed,[8,236] there is serious doubt that such a compound actually exists. The action of chlorine on rhenium metal dispersed on porous brick does not yield $ReCl_6$ as was once believed, but impure $ReOCl_4$. The oxygen is derived from the ceramic material which is apparently attacked by the hot metal.[237] It is almost certain that the highest chloride formed by direct chlorination is the pentachloride, and $ReCl_5$ itself does not react with either gaseous or liquid chlorine, even under uv irradiation.[237] In view of this it would have been surprising if technetium formed a hexachloride, and a recent reinvestigation has actually shown that $TcCl_4$ is the highest chloride that can be obtained from chlorine and technetium.[238] Halogen exchange between ReF_6 and BCl_3 or PCl_3 is said to yield an extremely volatile material which readily loses chlorine and which analyzes correctly for $ReCl_6$.[181,236] However, authentic $ReCl_6$ would be expected to be much less volatile than ReF_6 (bp 33.7°) and slightly less volatile than WCl_6 (bp 346°). The reaction of ReF_6 with BCl_3 has recently been found to give only $ReCl_5$ and fluoride chlorides of boron.[222] The synthesis of $ReCl_6$ in a low-temperature matrix does not seem to have been attempted.

Three oxohalides are known. Dark blue $ReOF_4$ is formed when ReF_6 is treated with ReO_3, $W(CO)_6$, or a small amount of water. The crystal structure consists of distorted $ReOF_5$ octahedra sharing cis fluorine atoms to form infinite chains. The bridging F–Re bond trans to oxygen (230 pm) is substantially longer than the bridging F–Re bond trans to fluorine (199 pm). Oxygen is always terminal, and the short Re–O separation (165 pm) indicates a high bond order. The structure of $ReOF_4$ is thus similar to that of $TcOF_4$ and $MoOF_4$ but quite different from tetrameric WOF_4.[239] The dark brown oxotetrachloride (mp 30.0°) is the most accessible molecular compound of rhenium(VI) and is best prepared by heating $ReCl_5$ with oxygen in a Carius tube[237] or rhenium metal with sulfuryl chloride.[240] It is also formed when rhenium is heated with a mixture of chlorine and oxygen, Re_2O_7 with thionyl chloride,[8] ReO_3 with $ReCl_5$, $MoCl_5$, $MoOCl_4$, or $WOCl_4$,[241] and $ReCl_5$ with MoO_3 or MO_2Cl_2 (M = Mo, W, or U).[242] Various physical properties have been measured.[243] The crystalline solid consists of square-pyramidal $ReOCl_4$ molecules with apical oxygen (Re–O, 163 pm) and is thus entirely different from $WOCl_4$. The units are very weakly associated through distant cis Re· · · Cl interactions (355 and 365 pm).[244] The infrared spectrum in the gas phase (ν(Re–O) 1040, ν(Re–Cl) 392 cm^{-1}) is practically the same as in inert solvents (CCl_4, cyclohexane) indicating that the same species is involved.[245] It has not been possible to show whether this species is square pyramidal or trigonal bipyramidal. Two metal–chlorine stretches are expected for C_{4v} symmetry and three for D_{3h}, but only one has been observed.[245-247] In the mass spectrometer, $ReOCl_4$ fragments principally to $ReOCl_4^+$, $ReOCl_3^+$, and $ReOCl_2^+$.[248] $ReOBr_4$ has not been investigated recently.

3. Complexes

Rhenium oxotetrahalides usually react to give compounds in oxidation states other than six. Thus $ReOCl_4$ is reduced by concentrated hydrochloric acid with evolution of chlorine to $ReOCl_5^{2-}$,[247] by pyridine to $ReOCl_3(py)_2$,[237] and by thionyl chloride to $ReCl_6^{2-}$; and it disproportionates in water to ReO_2 and ReO_4^-.[8,9] Inert ligands may, however, coordinate to the vacant position in $ReOX_4$ trans to oxygen to form adducts $ReOX_4L$ of C_{4v} symmetry in which the Re–L bond is long and weak. In solid $ReOX_4$ the ligand is the halide atom of a neighboring $ReOX_4$ molecule.[239,244] Equimolar quantities of $ReOCl_4$ and water yield the bright red, crystalline complex $ReOCl_4(H_2O)$ which has been shown by X-ray diffraction to have a short Re–O bond (163 pm, the same as in $ReOCl_4$ itself) and a long $Re–OH_2$ bond (227 pm) trans to it. The four chlorine atoms are equidistant from the rhenium at 229 pm and are bent away from the terminal oxygen toward the water molecule.[249] The adducts $ReOCl_4(MeCN)$[250] and $ReOCl_4(POCl_3)$[237] are obtained from $ReOCl_4$ and the free ligands and dissociate again on heating under vacuum. $ReOCl_4(POCl_3)$ is partly dissociated even in CCl_4 solution but not in $TiCl_4$.[237] There is some spectroscopic evidence that similar adducts are formed when donors such as acetone and ether are added to solutions of $ReOCl_4$ in inert solvents.[245] The complex oxohalide $(Re_2O_3Cl_6)(ReO_3Cl)_2$ formed by uv irradiation of a mixture of $ReOCl_4$, $ReOCl_4(H_2O)$, and ReO_3Cl has a related structure (**1**) in which perrhenyl chloride donates weakly trans to each of the two terminal oxygens in the hypothetical μ-oxo-bis[oxotrichlororhenium(VI)]. Once again there is a short terminal Re–O bond (169 pm) and a long bond in the trans position (241 pm), in this case to an oxygen of ReO_3Cl. The bridging O–Re separation (184.7 pm) is intermediate.[251] It is possible that the compound $Re_2O_4Cl_5$ may consist of one-half of this molecule, *i.e.*, $ReOCl_4(OReO_2Cl)$.[185]



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Salts of the anions $ReOX_5^-$ (X = Cl and Br) separate when AX (A = $AsPh_4$, NEt_4, and acridinium, X = Cl;[247] A = PPh_4, X = Br[250]) is added to a solution of $ReOX_4$ in *anhydrous* chloroform or dichloromethane. The diethyloxonium salt of $ReOCl_5^-$ is also obtained from $ReOCl_4$ and HCl in dry ether,[252] and $ReOF_5^-$ by the partial hydrolysis of ReF_8^{2-}.[9] Partial hydrolysis of $ReOCl_4^-$ gives the mauve, almost diamagnetic anion $[Cl_4ORe–O–ReOCl_4]^{2-}$,[247] and ammonolysis of $ReOCl_4$ gives a polymeric material of stoichiometry $ReO(NH_2)_4$, said to contain Re^{VI}.[250] It was once believed that $ReOCl_5^{2-}$ in aqueous hydrochloric acid is oxidized by air to $ReOCl_6^{2-}$,[253] but subsequent work has not confirmed this.[247,254]

The tendency of rhenium(V) to form a single multiple bond to oxygen and a weak bond in the trans position is reminiscent of other d^1 ions such as V^{IV}, Cr^V, Mo^V, and W^V.[190] The Re–O stretching frequency occurs at 950–1040 cm^{-1} and the magnetic moments of all mononuclear Re^{VI} compounds except ReF_6 and ReF_7^- fall within 1.2–1.7 BM, rather lower than the spin-only values. Only three complex species are known not to have terminal Re–O bonds, *viz.* ReF_7^-, ReF_8^{2-},[9,232,233] and $Re(CN)_8^{2-}$.[15]

C. Rhenium(V)

The most characteristic feature of Re^V is the existence of a large number of stable, diamagnetic complexes in which the metal forms multiple bonds to oxygen or nitrogen. They are mostly octahedral and of the types $ReOX_5^{2-}$, $ReOX_4L^-$, $ReOX_3L_2$, $ReO_2X_4^{3-}$, $ReO_2L_4^+$, $(ReOX_2L_2)_2O$, $ReNX_2L_3$, and $Re(NR)X_3L_2$. It thus resembles Mo^V,[11] Os^V, and Os^{VI},[13] more closely than the isoelectronic Mo^{IV} and W^{IV} which form few stable oxo species. Although the tendency to form multiple bonds to nitrogen is shared with adjacent elements in their higher oxidation states (Mo^{VI}, Os^V, Os^{VI}, and Os^{VIII}), it appears to be more pronounced for Re^V than for any other transition metal. The few complexes of Re^V which lack such multiple bonds are generally eight-coordinate and diamagnetic. Paramagnetic species thus ought to be viewed with suspicion unless they have been thoroughly characterized. The reduction of Re^V to Re^{IV} and/or Re^{III} occurs with such ease that it is often encountered under conditions which might have been expected to lead to substitution.

1. Rhenium(V) Oxides and Oxo Anions

The elusive oxide Re_2O_5 has been obtained crystalline, but not pure, by the electrolytic reduction of perrhenate in 12 *M* sulfuric acid. The blue-black precipitate formed in this way retains sulfuric acid which cannot be removed by washing with water, since this results in disproportionation. The acid is lost under vacuum only at temperatures which cause partial oxidation to ReO_3 and disproportionation to ReO_2 and Re_2O_7, but some tetragonal Re_2O_5 survives these conditions.[255] A very impure form of the same oxide is apparently produced in the chemical reduction of perrhenate.[93,255] Rhenium(V) is found in the octahedral sites of the ordered perovskites $A_2M^{III}Re^VO_6$ (A = Sr, M = Cr;[9] A = Ba, M = Sc, Y, and In;[215] A = Sr and Ba, M = a lanthanide[256]), formed by heating mixtures of binary oxides. When M is a lanthanide, the perovskites obey the Curie–Weiss law down to at least 77 K,[256] and in Ba_2GdReO_6 and Ba_2ErReO_6 no magnetic ordering occurs even at 4.2 K.[215] Purple crystals of $Cd_2Re_2O_7$ with the pyrochlore structure and with rhenium in octahedral coordination (Re–O, 190 pm) are formed by the interaction of Re_2O_7 vapor and cadmium.[257]

When a lanthanide oxide is heated with an excess of ReO_2, a compound of stoichiometry $Ln_4Re^V{}_2O_{11}$ is obtained.[258,259] An X-ray diffraction study of a single crystal (Ln = Nd) has shown that the structure contains pairs of ReO_6 octahedra sharing an edge, and that NdO_4 and NdO_8 polyhedra link the Re_2O_{10} units into a three-dimensional network. The Re–Re separation (242 pm) is short, indicating strong metal–metal bonding (*cf.* 275 pm in rhenium metal and 374 pm in Re_2Cl_{10}).[259] Similar Re_2O_{10}

units (Re–Re, 242 pm) occur in the ternary oxide $La_4Re_6O_{19}$ in which rhenium has a formal oxidation state of 4⅓, but in this case the Re_2O_{10} units are linked together directly by sharing corners. Lanthanum is ten-coordinate.[260]

Other oxides said to contain Re^V include $Ca_2Re_2O_7$,[217] Li_3ReO_4, and $Li_6MgRe_2O_9$,[216,217] but they have not been described in detail. The vibrational spectrum of Li_3ReO_4 is consistent with the presence of ReO_4^{3-} ions.[261]

2. *Rhenium(V) and Halides and Oxohalides*

Rhenium pentafluoride is best prepared by reducing the hexafluoride with PF_3.[181] Rhenium pentachloride (mp 261°;[237] $\Delta H_f° = -360 \pm 3$ kJ mol^{-1} [222]) is the only product of chlorination of the metal under normal conditions and may also be obtained by heating Re_2O_7 with CCl_4.[262] The dark brown crystalline solid contains dimeric Re_2Cl_{10} molecules isostructural with M_2Cl_{10} (M = Nb, Ta, Mo, and U), but is not isomorphous with the other pentahalides since the molecules are packed differently. Each Re_2Cl_{10} unit consists of two octahedra sharing an edge in which the rhenium atoms are displaced by 20 pm from the centers of the octahedra *away* from each other, and the long Re · · · Re separation (373.9 ± 0.2 pm) precludes the existence of a metal–metal bond. The average terminal and bridging Re–Cl distances are 224.4 ± 1.2 and 246.5 ± 1.3 pm, respectively.[263] The far-infrared spectrum can be assigned to Re_2Cl_{10} in both the solid state[264,265] and in cyclohexane solution,[264] and 12 out of the 13 active fundamentals expected for D_{2h} symmetry have been observed. $ReCl_5$ vapor is presumably monomeric since the heaviest fragment detected in a mass spectrometer at 100° is $ReCl_5^+$. The major fragment is $ReCl_4^+$.[265] A number of other physical properties have been recorded, including the electronic spectrum[265] and the phase diagrams for various metal chloride systems.[266]

The reactions of $ReCl_5$ are numerous and complex. It may be distilled unchanged in an atmosphere of chlorine, but it dissociates to $ReCl_3$ and Cl_2 when heated in a stream of inert gas.[267] In a static system, $ReCl_5$ and $ReCl_3$ interact to form β-$ReCl_4$.[268,269] $ReCl_5$ is reduced quantitatively to β-$ReCl_4$ by $SbCl_3$[269] and to $ReCl_3$ by $SnCl_2$.[265] It is also reduced by tetrachloroethylene in accordance with the equation[270]

$$ReCl_5 + {}^1/_2CCl_2{=}CCl_2 \longrightarrow \beta\text{-}ReCl_4 + {}^1/_2C_2Cl_6 \quad (3)$$

When $ReCl_5$ is heated with metal oxides or oxohalides, it gives mixtures of products which always contain $ReOCl_4$[242,251,265,271] and apparently never $ReOCl_3$.[251,265] Thus As_2O_3 or SO_2 gives a mixture of $ReOCl_4$ and $ReCl_3$,[265] while ReO_3 gives ReO_3Cl, $ReOCl_4$, $Re_2O_3Cl_6(ReO_3Cl)_2$, ReO_2, $ReCl_3$, and rhenium metal.[251,271]

Rhenium pentachloride acts as a mild but efficient Friedel–Crafts catalyst and promotes the alkylation and acylation of aromatic rings.[272] It also catalyzes the oligomerization of olefins and acetylenes,[272] the condensation of acetone to mesityl oxide,[273] and the polymerization of styrene to a product of high molecular weight. The kinetics of the last reaction have been interpreted on the basis of cationic intermediates.[274] Olefin polymerization is inhibited by tetrabutyltin and a mixture of $ReCl_5$ and $SnBu_4$ catalyzes the disproportionation of pent-2-ene to but-2-ene and hex-2-ene at room temperature.[275]

The pentachloride may react with potential ligands in several ways that often depend on the solvent and on the presence of traces of moisture. "Aged $ReCl_5$" is said to react differently from freshly prepared $ReCl_5$, but since the latter is very hygroscopic and otherwise stable at ambient temperatures, "aged" samples are almost certainly partly hydrolyzed. The following reactions have been observed.

(a) Simple Substitution or Ligand Transfer. This occurs rarely and is only expected with inert ligands in the absence of water. Phosphorus pentachloride at 300°C gives the salt $[PCl_4]ReCl_6$[276] and $ReCl_5$ is said to react with fused KSCN to give $Re(SCN)_6^-$[277] and with KCNO in dimethyl sulfone to give $Re(OCN)_6^-$.[278] In view of the general behavior of Re^V, the last two reactions are rather surprising. A polymeric acetate $ReCl_3(OAc)_2$ is formed in glacial acetic acid.[279]

(b) Reduction to Rhenium(IV) by the Ligand. Under anhydrous conditions, $ReCl_5$ is reduced to complexes of the type $ReCl_4L_2$ or $ReCl_5L^-$ by a number of ligands which are not normally considered reducing. The pentahalides of molybdenum and tungsten behave in a similar way,[280,281] but $ReCl_5$ is the strongest oxidant. Anhydrous nitriles thus cause reduction to $ReCl_4(RCN)_2$ (R = Me, *n*-Pr, and Ph),[282] fused α,α'-dipyridyl to $ReCl_4$(dipy),[265] dioxane, thioxane, and tetrahydrofuran to $ReCl_4L_2$ (L = $C_4H_8O_2$, C_4H_8OS, and thf),[283] and $[NEt_4]Cl$ in CH_2Cl_2 to the salt $[NEt_4]ReCl_5$.[284] It is noteworthy that the known $ReCl_6^-$ ion[276] is not formed in the last reaction, although under similar conditions $MoCl_5$ and WCl_5 yield $[NEt_4]MCl_6$. The reaction of $ReCl_5$ with PPh_3 is complicated and in *anhydrous* acetone yields both $ReCl_4(PPh_3)_2$ and $[MeCOCH_2CMe_2PPh_3][ReCl_5(PPh_3)]$, together with traces of $Re_2Cl_8^{2-}$ and $Re_2Cl_9^{2-}$.[273] The cation is presumably formed by Michael addition of PPh_3 to mesityl oxide, itself a product of the condensation of acetone catalyzed by $ReCl_5$.[273,285] The oxidation product from the above reactions has been investigated only in the case of acetonitrile. At least a third of the chlorine atom lost by $ReCl_5$ is evolved as HCl, and at least another third appears in a highly chlorinated organic oil (58% Cl) which can be extracted into light petroleum.[282] An oil obtained in the reduction of VCl_4 by acetonitrile contains 2-methyl-4,6-bis(trichloromethyl)-1,3,5-triazine.[286]

(c) Hydrolysis to Rhenium(V) Oxo Species. In the presence of small amounts of water, $ReCl_5$ usually yields complexes of Re^V with terminal oxygen. Large cations thus precipitate $ReOCl_5^{2-}$ from solutions of $ReCl_5$ in concentrated HCl[253,254] and $ReOBr_5^{2-}$ from 48% HBr.[265] Triphenylphosphine in wet acetone gives *trans*-$ReOCl_3(PPh_3)_2$,[254,265] pyridine gives $[ReOCl_2(py)_2]_2O$,[287] and α,α'-dipyridyl gives $(ReOCl_2dipy)_2O$.[287] Aquo and hydroxo complexes are undoubtedly formed as intermediates since the Re=O moiety can be reversibly protonated to Re–OH and Re–OH_2, with equilibrium constants lying strongly to the left.[254,287] Unlike $MoCl_5$[11,190] there is no evidence that $ReCl_5$ can abstract oxygen from organic solvents or ligands. Thus $MoCl_5$ gives $MoOCl_3(POPh_3)_2$ with $POPh_3$ in acetone, whereas $ReCl_5$ disproportionates.[288]

(d) Disproportionation. $ReCl_5$ disproportionates in water above pH 7 to ReO_2 and ReO_4^-.[254] At lower pH, hydrolysis to Re^V oxo species competes with disproportionation. In wet acetone the anions ReO_4^- and $Re_2Cl_9^{2-}$ are formed through unidentified transient intermediates,[289] and the salt $[(POPh_3)_2H]_2Re_2Cl_9$ separates in the presence of $POPh_3$.[288] This is perhaps the origin of $Re_2Cl_8^{2-}$ and $Re_2Cl_9^{2-}$ formed in the complex reaction of $ReCl_5$ with PPh_3 in acetone.[273]

Rhenium pentabromide is said to be formed by direct union of the elements, but very little, if any, could be prepared by this method by later workers.[290] The compound may be obtained by treating ReF_6 with BBr_3 or PBr_3,[181,236] and $ReBr_3$ with Br_2.[291] It has not been properly characterized. No oxohalides of rhenium(V) have been established beyond doubt. Claims for the preparation of $ReOF_3$ exist in the early literature,[8,9] but all attempts to obtain $ReOCl_3$ have met with failure.[265] A report that α- and β-$ReOCl_3$ had been prepared[271] was effectively withdrawn.[251]

3. Oxo Complexes

The very stable oxo and dioxo complexes of rhenium(V) have been discussed in some detail by Fergusson.[15] They are usually prepared by reduction of perrhenate in the presence of a ligand in strongly acid solution,[283,292-299] and by ligand substitution in $ReOCl_3(PPh_3)_2$ or $ReO(OEt)X_2(PPh_3)_2$.[254,283,287,293,300-304] They have also been synthesized by solvolysis of $ReCl_5$,[254,265,287] aerial oxidation of Re^{III} [305,306] and Re^{IV},[307-310] and in other ways. The complexes fall into three categories, namely, mononuclear with one terminal oxide, mononuclear with two terminal oxides, or dinuclear with one terminal oxide on each Re^V and an oxo bridge. The metal is nearly always found in pseudo-octahedral coordination but is five-coordinate in $ReO_2I(PPh_3)_2$, $[ReOX_2(PPh_3)_2]^+$,[302] and $ReOX_4^-$ (X = Cl, Br, and I),[294] and *may* be seven-coordinate in complexes of tridentate ligands such as $ReOCl_3(tas)$[15] and $ReOCl_3(tdpme)$.[292] The five-coordinate complexes are unsaturated and readily increase their coordination number to six,[294,302] whereas $ReOCl_3(tdpme)$ dissociates to a six-coordinate isomer in which tdpme is bidentate.[292] Most well-established oxo complexes are described in Table II, but protonated species are omitted.

All Re^V oxo species are diamagnetic though weak, temperature-independent paramagnetism (TIP) equivalent to 0.3–0.8 BM usually remains when allowance is made for the diamagnetism of the ligands.[128,295,310] The infrared spectra have been tabulated[311] and discussed.[312-314] The terminal Re–O stretch in monooxo complexes and in the binuclear μ-oxo species lies within 912–995 cm^{-1}.[312] Trans dioxo species have bands at 775–835 cm^{-1} ($\nu_{as}(ReO_2)$) and 220–270 cm^{-1} ($\delta(ReO_2)$), with $\nu_s(ReO_2)$ (*ca.* 800 cm^{-1}) active only in the Raman.[312,314,315] The μ-oxo complexes have additional bands at 720–860 cm^{-1} and 200–205 cm^{-1} which have been assigned to ν_{as}(Re–O–Re) and ν_s(Re–O–Re), respectively,[312] though an alternative assignment favors a band at 660–670 cm^{-1} to be associated with ν(Re–O–Re).[300] The order of the terminal Re–O bond in monooxo complexes exceeds two since both the oxygen p_x and p_y orbitals overlap with the metal d_{xz} and d_{yz}. The two metal d electrons occupy the nonbonding d_{yz} orbital and thus account for the diamagnetism.

The anions $ReOCl_5^{2-}$ and $ReOBr_5^{2-}$ [265] are firmly established, but $ReOI_5^{2-}$ has been only briefly described.[316] Salts of $ReOCl_5^{2-}$ may be obtained by reducing perrhenic acid with HI,[8,9,295] by boiling $[ReO_2(en)_2]Cl$ with 5 *M* HCl,[254] or by dissolving $ReOCl_4$[247] or $ReCl_5$ in concentrated HCl, and adding a large cation.[253,254] The cesium salt is the most common, but many others have been described.[254,317] They are usually contaminated with ReO_4^- and $ReCl_6^{2-}$ owing to disproportionation, and magnetic moments ranging from 0.8 to 2.85 BM have been claimed.[247,253,254] In fact, pure Cs_2ReOCl_5 prepared at −10° is diamagnetic, and a correction for ligand diamagnetism reveals TIP equivalent to 0.43 BM at room temperature.[295] The salts of Cs_2ReOX_5 (X = Cl and Br) are isomorphous with the corresponding Mo and W compounds,[247,265,318] and the electronic[128,247,254,318,319] and vibrational[247,320] spectra have been recorded and analyzed.

The five-coordinate anion $ReOBr_4^-$ is formed as one of the products of aerial oxidation or $ReBr_3$ in HBr,[305] and all three anions $ReOX_4^-$ (X = Cl, Br, and I) may be prepared in high yield by reducing perrhenate with zinc in methanolic sulfuric acid and adding HX.[294] They form stable salts with large cations and may form weak solvates with water or acetonitrile. The crystal structures of both $[NEt_4]ReOBr_4(H_2O)$[305] and $[AsPh_4]ReOBr_4(MeCN)$[321] have been solved. The anion in each case consists of a square pyramidal $ReOBr_4$ moiety in which the rhenium atom is respectively 32 and 34 pm above the Br_4 plane and the Re–O separation is short (Table III). In conjunction with the high Re–O stretching frequency (1000 ± 10 cm^{-1}), this indicates unusually strong π-bonding. The solvent molecule occupies the sixth coordination position trans to oxygen to form a long, weak bond (Re–OH_2, 232 pm; Re–NCMe, 231 pm).

Perhaps the most important compound of rhenium(V) is *trans*-$ReOCl_3(PPh_3)_2$ which separates almost quantitatively when perrhenic acid in concentrated HCl is added to a suspension of PPh_3 in glacial acetic acid.[296] This and the related ethoxo complexes $ReO(OEt)X_2(PPh_3)_2$[296] have been used as intermediates in the synthesis of complexes of Re^{III},[300,306,322] Re^{IV},[301,322] and Re^{VII},[203] as well as Re^V.

The oxide ligands in *all* Re^V dioxo complexes whose configuration is known are mutually trans.[254,312-315,323-326] This is also the case for other d^2 metals (Ru^{VI} and Os^{VI}) but is in contrast to dioxo complexes of d^0 metals (V^V, Mo^{VI}, W^{VI},[313,314] and Re^{VII} [189]) in which they are cis. The trans-dioxo configuration has been confirmed by X-ray diffraction for $[ReO_2(py)_4]Cl\cdot 2H_2O$[324] and by both X-ray[326] and neutron diffraction[325] for $K_3ReO_2(CN)_4$. In the d^0 cis-dioxo complexes the ligands O_x and O_y donate exclusively into d_{xz} and d_{yz} and share only d_{xy}, whereas in the d^2 trans-dioxo complexes, O_z and O_{-z} share both d_{xz} and d_{yz} but leave d_{xy} nonbonding to accommodate the two d electrons.[313] The Re–O bond order is thus two,[315] and the Re–O bond lengths in trans-dioxo complexes are significantly longer than in monooxo complexes (Table III). It has been suggested that the ligand field exerted on the metal in trans-$ReO_2(py)_4^+$ is essentially the linear field of the oxide ligands, and the solvent effects on the electronic spectrum may then be interpreted as arising from the interaction of the solvent with the terminal oxides.[327]

The dinuclear μ-oxo complexes have a linear O=Re—O—Re=O moiety which has been established by X-ray diffraction in $Re_2O_3(Et_2dtc)_4$,[303,328] $Re_2O_3Cl_4(en)_2$,[329] and $[Pt(NH_3)_4]_2Re_2O_3(CN)_8$.[330] The structure of $Re_2O_3(Et_2dtc)_4$ (d^2) contrasts sharply with that of $Mo_2O_3(Et_2dtc)_4$ (d^1) in which each terminal oxide is cis to the oxo bridge.[328] In all three species the geometry of each rhenium atom is distorted octahedral, and in $Re_2O_3(Et_2dtc)_4$ the two Et_2dtc ligands on one metal atom are staggered by *ca.* 40° relative to the other to avoid close S···S contacts. The terminal Re–O bonds are shorter than in trans-dioxo species (Table III) and are presumed to have a bond order of three.[325,328]

Rhenium(V) oxo complexes undergo the following reactions.

(a) Ligand Substitution. Terminal oxide in $ReO_2(en)_2^+$ is inert and the complex may be dissolved in water and reprecipitated as the iodide with less than 1% exchange. The slow exchange of oxygen between $ReO_2(en)_2^+$ and labeled water obeys the equation

TABLE II. Oxo Complexes of Rhenium(V)[a]

Oxo species	Ligand (L)	Comments	Synthesis	Ref
$ReOX_4^-$		X = Cl, Br, and I	$ReO_4^- + Zn + HX$ in MeOH–H_2SO_4[b]	294
			$ReBr_3 + HBr + O_2$	305
$ReOX_5^{2-}$		X = Cl	See text	
		X = Br	$ReCl_5$ + HBr (48%)[b]	265
$ReOX_4L^-$	H_2O and MeCN	X = Cl and Br	$ReOBr_4^- + L$	294, 305
			$ReO_2(en)_2^+ + HCl$	294
	PPh_3	X = Cl; green isomer (C_s)	$ReOCl_3(PPh_3)_2$ + HCl in benzene	254
		Yellow isomer (C_{4v})	Pyrolysis of $[PHPh_3]ReOCl_5$	254
$ReOF(CN)_3L^-$	H_2O	Cation = Na^+, K^+, NH_4^+, etc.	$ReO_2(CN)_4^{3-}$ + hot 40% HF	342
$ReOX_3L_2$	PPh_3 and PEt_2Ph	X = Cl, Br, I and SCN (all combinations)	Several isomers synthesized before 1966	15
	PEt_3, P-*n*-Pr_3, $P(CH_2Cl)_3$, $AsPh_3$, $AsMe_2Ph$, $AsEt_2Ph$, $SbPh_3$, py, $^1/_2C_2H_4(PEt_2)_2$, $^1/_2$diars, $^1/_2$tas, $^1/_2$dipy	X = Cl or Br		
	PPh_3 and $AsPh_3$	X = Cl and Br; *trans*	$ReCl_5 + PPh_3$ in wet solvents	273
			$ReO_4^- + HX + PPh_3$ in AcOH[b]	296
			$ReOX_4^- + L$ in MeCN	294
	py	X = Cl	$ReO_2(py)_4^+$ + HCl under certain conditions	299
	Thioxane and dioxane	X = Cl and Br; *trans*	$ReOCl_3(AsPh_3)_2 + L$	283
	$^1/_2$dppe	X = Cl and Br	$[ReO_2(dppe)_2]X + HX$ in EtOH	293
		X = I	$ReO_2I(dppe)(PPh_3)_2 + HI$	302
	$^1/_2$tdpme	X = Cl; 6- and 7-coord isomers	$ReO_4^- + HCl + tdpme + H_3PO_2$	292
	$^1/_2$dipy	X = Cl and Br	$ReO_4^- + HX + dipy + H_3PO_2$ in EtOH	297
			$ReOCl_3(PPh_3)(POPh_3) + dipy$	306
	$^1/_2$en	X = Cl	$Re(OH)_2(en)_2^{3+}$ in 10 *M* HCl on standing	254
$ReOX_3(PPh_3)L$	dmso	X = Cl and Br	$ReOX_3(PPh_3)_2 + dmso + HCl$	254
			$ReO(OEt)Cl_2(PPh_3)_2 + dmso + HCl$	254
	$POPh_3$	X = Cl; labile $POPh_3$	$ReCl_3(MeCN)(PPh_3)_2 + O_2$ in hot C_6H_6	306
			trans-$ReOCl_3(PPh_3)_2 + O_3$ in CH_2Cl_2	290
$ReOCl_2IL_2$	PPh_3		$ReOI_2(PPh_3)_2^+ + HCl$	302
$ReOCl(NCS)_2L_2$	PPh_3		$ReO(OH)(NCS)_2(PPh_3)_2$ + hot HCl	304
$ReO(OR)X_2L_2$	PPh_3	X = Cl, Br, and I; R = Me and Et	Several isomers synthesized before 1966	15
	PPh_3, $PEtPh_2$, PEt_2Ph, P-*n*-Pr_2Ph, and $P(CH_2Cl)_3$	X = Cl, Br, or I; R = Me, Et, *n*-Pr, Bz, or $MeOC_2H_4$		
$ReO(OEt)X_2L_2$	PPh_3	X = Cl and Br	$ReO_4^- + HX + PPh_3$ in boiling EtOH[b]	296
		X = NCS (2 isomers)	$ReO(OH)(NCS)_2(PPh_3)_2$ + HCl in EtOH	304
	py	X = Cl	*trans*-$[ReO_2(py)_4]Cl$ + boiling EtOH	287
		X = NCS	$ReO(OEt)I_2(py)_2$ + NaSCN in EtOH	304
	$^1/_2$dppe	X = Cl, Br, and I	$ReO(OEt)X_2(PPh_3)_2$ + dppe in boiling C_6H_6	293
	$^1/_2$tdpme	X = Cl	ReOCl(tdpme) + boiling EtOH	292
$ReOX_2(acac)L$	PPh_3 and PEt_2Ph	X = Cl, Br, and I	$ReO(OEt)X_2L_2$ + acacH in boiling C_6H_6	301
			$ReOCl_3(PPh_3)(POPh_3)$ + warm acacH	306
$ReOX(R_2dtc)_2$	R = Me, Et, and $^1/_2(CH_2)_5$	X = Cl and Br	$ReOX_3(PPh_3)_2 + (R_2NCS)_2$	300
ReO(OH)(oxine)			$ReO_2(aq)$ + fused oxineH in air	309
$ReO(OH)(NCS)_2(PPh_3)_2$		Bonded through N	$ReO_2I(PPh_3)_2$ or $ReO(OEt)X_2(PPh_3)_2$ + NaSCN in Me_2CO	304
			$ReO_2(NCS)_2(PPh_3)_2^- + H^+$	304
$ReOX_2L_2^+$	PPh_3	X = Cl, Br, and I; anion = ReO_4^-	$ReO_2I(PPh_3)_2 + O_2$	302
			$ReO(OEt)X_2(PPh_3)_2 + HReO_4 + Me_2CO$	302
$ReOXL_4^{2-}$	tu	X = Cl and OH; anion = Cl^- or ClO_4^-	$ReO_4^- + HCl + SnCl_2 + tu$	298
$ReO_2(CN)_4^{3-}$			See ref 15	15
$ReO_2(NCS)_2L_2^-$	PPh_3	Cation = Na^+, NH_4^+, and $AsPh_4^+$	$ReO(OH)(NCS)_2(PPh_3)_2 + OH^-$ in excess SCN^-	304
ReO_2IL_3	PEt_2Ph	*mer-trans*	$ReO_2I(PPh_3)_2 + PEt_2Ph$	302

TABLE II. *(Continued)*

Oxo-species	Ligand (L)	Comments	Synthesis	Ref
$ReO_2I(dppe)(PPh_3)$			$ReO_2I(PPh_3)_2$ + 1 mol of dppe	302
$ReO_2CN(H_2O)(py)_2$			$[ReO_2(py)_4]CN$ + water on standing	299
$ReO_2(oxine)(H_2O)_2$			$ReO_2 \cdot aq$ + fused oxineH in air	309
ReO_2IL_2	PPh_3	5-Coordinate and monomeric	$ReO(OEt)I_2(PPh_3)_2 + H_2O$ in Me_2CO	302
			$ReOI_2(PPh_3)_2^+ + H_2O$	302
	dmso	Insol; *M* unknown	$ReOCl_3(PPh_3)_2$ + dmso	254
$ReO_2L_4^+$	py	Anion = Cl^-, etc.; see also ref 15	*trans*-$ReOCl_3(PPh_3)_2$ + py in hot EtOH	287
			$Re_2O_3Cl_4(py)_4$ + py in wet EtOH	287
			$ReO(OEt)Cl_2(py)_2$ + py	287
			$ReOX_4^-$ + py (X = Cl and Br)	294
			$ReOCl_3(dmso)PPh_3$ + py	254
	py, picolines	Anion = Cl^-, Br^-, and I^-	$K_2ReCl_6 + L + O_2$ in water	308
	tu	Anion = ClO_4^-	$ReO_4^- + HCl + SnCl_2$ + tu	298
	NH_3	Anion = Cl^-	$ReO(OEt)Cl_2(PPh_3)_2$ (green isomer) + concd NH_3	254
	RNH_2, $^1/_2$diamines, $^1/_2$dppe, tu		See ref 15	15
	$^1/_2$en	Anion = Cl^-, etc.	$ReOCl_3(dmso)(PPh_3)$ + en + H_2O	254
			K_2ReCl_6 + en + $H_2O + O_2$[b]	307
	$^1/_2$dipy	Anion = ClO_4^-	$ReOX_3(dipy)$ + excess dipy in hot EtOH	297
	$^1/_2$dppe	Anion = Cl^-, Br^-, I^-, ReO_4^-, etc.	ReO_4^- + HX + dppe in EtOH	293
		Anion = I^-	$ReO_2I(PPh_3)_2$ + 2 mol of dppe	302
$ReO_2(py)_3PPh_3^+$		Anion = I^- and ClO_4^-	$ReO_2I(PPh_3)_2$ + excess py at room temp	302
$ReO_2(py)_2(PPh_3)_2^+$		Anion = I^-	$[ReO_2(py)_3PPh_3]I + PPh_3$	302
$Re_2O_3(CN)_8^{4-}$		See text	$ReO_2(CN)_4^-$ + 0.5 *M* HCl	330, 340
$Re_2O_3X_4L_4$	py and $^1/_2$dipy	X = Cl or Br	$ReCl_5$ + L in wet Me_2CO	287
			$ReOCl_4$ + L	237
			$ReOX_3(PPh_3)_2$ or $ReO(OEt)Cl_2(PPh_3)_2$ + py in C_6H_6	287
	$^1/_2$en	X = Cl; see text	$ReO(OH)(en)_2^{2+}$ in HCl on standing	254
$Re_2O_3(R_2dtc)_4$	R = Me, Et, and Ph	See text	$ReOCl_3(PPh_3)_2 + NaR_2dtc$ in boiling Me_2CO	300
			$Re_2O_3Cl_4(py)_4 + NaEt_2dtc$	300
			$ReOX(R_2dtc)_2 + H_2O + Na_2CO_3$ in Me_2CO (R = Me and Et)	300

[a] Protonated dioxo species are excluded. [b] Best method of preparation.

$$\text{rate of exchange} = \{k_0 + k_1[\text{enH}_2^{2+}] + k_2[\text{en}] + k_3[\text{OH}^-]\}[\text{ReO}_2(\text{en})_2^+] \quad (4)$$

where at 50° $k_0 = 7.86 \times 10^{-5}$ sec^{-1}, $k_1 = 6.47 \times 10^{-3}$ M^{-1} sec^{-1}, $k_2 = 1.4 \times 10^{-3}$ M^{-1} sec^{-1}, and $k_3 = 3.26 \times 10^{-1}$ M^{-1} sec^{-1}.[332] Other ligands range from labile to fairly inert but are decidedly more labile than on rhenium(IV). Thus Cs_2ReOCl_5 exchanges chloride rapidly with labeled HCl even in suspension,[333] whereas $ReCl_6^{2-}$ in 7 *M* HCl does not exchange significantly in weeks.[334]

TABLE III. Rhenium-Oxygen Bond Lengths in Rhenium(V) Oxo Species

Compound	Terminal Re-O, pm	Bridging Re-O, pm	Ref
trans-$ReOCl_3(PEt_2Ph)_2$	~160		331
$[NEt_4][ReOBr_4(H_2O)]$	171 (4)		305
$[AsPh_4][ReOBr_4(MeCN)]$	173 (6)		321
$[ReO_2(py)_4]Cl \cdot 2H_2O$	176 (3)		324
$K_3ReO_2(CN)_4$	177.3 (8)		325
	178.1 (3)		326
$[Pt(NH_3)_4]_2Re_2O_3(CN)_8$	169.8(7)	191.49(4)	330
$Re_2O_3(Et_2dtc)_4$	172.2	191.0	328
$Re_2O_3Cl_4(en)_2$	167 (5)	191.2 (5)	329

Cyanide exchange with $ReO_2(CN)_4^{3-}$ and chloride exchange with $ReOCl_4(H_2O)^-$ is complete in less than a minute. Conversely, amine exchange with $ReO_2L_4^+$ (L = ½en, $MeNH_2$, and py) is slow and obeys the rate equation

$$\text{rate of exchange} = \{k_0 + k_1[\text{OH}^-]\}[\text{ReO}_2\text{L}_4^+] \quad (5)$$

where at 25° $K_0 = 8.5 \times 10^{-7}$, 9.4×10^{-6}, and 4.17×10^{-5} sec^{-1} for L = ½en, $MeNH_2$, and py, respectively; and $k_1 = 6.9 \times 10^{-2}$ for L = ½en and 4.33×10^2 M^{-1} sec^{-1} for L = $MeNH_2$. The term in $[OH^-]$ is presumably associated with an SN1-CB mechanism and is absent for L = py.[335] Since oxide creates a high electron density on the metal, bonds to σ donors ought to be weakened and to π acceptors strengthened.[335] This may explain the presence of π acceptors in the more inert mono-oxo complexes and the fact that most dioxo complexes of σ donors are cationic (Table II). In the presence of π acceptors, complexes are usually sufficiently inert to permit the isolation of geometrical isomers although these tend to equilibrate on heating in solution. The isomers of $ReO(OEt)Cl_2(PPh_3)_2$ equilibrate at room temperature in benzene within a few hours.[301] Specific ligand substitution is readily affected in the cold or on gentle warming in a suitable solvent. Thus reactions 6 (L = PPh_3, PEt_2Ph, and ½dipy)[306] and 7 (L = PPh_3 and $AsPh_3$)[294] are complete within a few minutes in the cold, and reactions 8 (L = thioxane and dithiane),[283] 9,[301] and 10[302] occur readily in hot benzene. Further examples are given in Table II.

$$ReOCl_3(PPh_3)(POPh_3) + 2L \longrightarrow ReOCl_3L_2 + PPh_3 + POPh_3 \quad (6)$$

$$ReOBr_4(MeCN)^- + 2L \longrightarrow ReOBr_3L_2 + MeCN + Br^- \quad (7)$$

$$ReOCl_3(AsPh_3)_2 + 2L \longrightarrow ReOCl_3L_2 + 2AsPh_3 \quad (8)$$

$$ReO(OEt)Cl_2(PPh_3)_2 + acacH \longrightarrow ReOCl_2(acac)(PPh_3)_2 + EtOH \quad (9)$$

$$ReO_2I(PPh_3)_2 + 2dppe \longrightarrow ReO_2dppe_2^+ + I^- + 2PPh_3 \quad (10)$$

Substitution by water or hydroxyl is often followed by deprotonation to give trans-dioxo (eq 11)[302] or μ-oxo species (eq 12).[287]

$$ReO(OEt)I_2(PPh_3)_2 + H_2O \xrightarrow{\text{cold acetone}} ReO_2I(PPh_3)_2 + HI + EtOH \quad (11)$$

$$2ReOCl_3(PPh_3)_2 + 6py + H_2O \xrightarrow{\text{cold benzene}} [ReOCl_2(py)_2]_2O + 2pyH^+ + 2Cl^- + 4PPh_3 \quad (12)$$

(b) Oxidation. Oxo species do not normally react with molecular oxygen. They are oxidized directly to perrhenate by fairly strong oxidants, and no intermediates have been detected. Labeled $ReO_2(en)_2^+$ is oxidized by ClO^- to ReO_4^- in which half the oxygen (*i.e.*, 1.91 atoms) is derived from $ReO_2(en)_2^+$ and half (*i.e.*, 2.16 atoms) from solvent water. Likewise, oxidation by MnO_4^- and by ozone gives ReO_4^- in which 1.71 and 1.95 oxygen atoms, respectively, are derived from $ReO_2(en)_2^+$.[332] Surprisingly, $ReOCl_4(H_2O)^-$ in 10 *M* HCl is oxidized rapidly by nitrate ion to ReO_4^- according to second-order kinetics (k = 2.19 M^- sec^{-1} at 25°), and the resulting nitrite ion then slowly reacts with Re^V according to eq 13 (k = 0.644 M^{-1} sec^{-1} at 25°).[336] $ReOBr_4^-$ is oxidized by dmso to ReO_4^-,[305] and the five-coordinate complex $ReO_2I(PPh_3)_2$ by oxygen to $[ReOI_2(PPh_3)_2]ReO_4$.[302]

$$5ReOCl_4(H_2O)^- + 2NO_2^- \longrightarrow 3ReO_4^- + 2ReCl_5(NO)^{2-} + 10HCl \quad (13)$$

(c) Reduction to Re^{III}. Mild reduction of monooxo species proceeds directly to mononuclear Re^{III} with removal of terminal oxide, and no Re^{IV} intermediates accumulate in detectable concentrations. This provides the usual synthetic route to octahedral complexes of Re^{III}.[306] Thus reaction 14 occurs almost quantitatively in boiling acetonitrile and $POPh_3$ is the only oxidation product. The mechanism probably involves oxide transfer between $ReOCl_3(MeCN)(PPh_3)$ and PPh_3. Reduction to the same product occurs in lower yield even in the absence of free PPh_3, but the reducing agent is still PPh_3 displaced from $ReOCl_3(PPh_3)_2$ by acetonitrile, and not acetonitrile itself.[306] Similarly dppe reduces $ReOCl_3$(dppe) to $[ReCl_2(dppe)_2]Cl$,[293] dithionite reduces $ReOCl_3$(tdpme) to $ReCl_3$(tdpme),[292] PPh_3 reduces $ReOCl_2(Et_2dtc)(PPh_3)$ to $ReCl_2(Et_2dtc)(PPh_3)_2$,[300] and PR_2Ph (R = Me, Et, *n*-Pr, and *n*-Bu) reduce *trans*-$ReOCl_3(PPh_3)_2$ to *mer*-$ReCl_3(PR_2Ph)_3$.[337] Further examples are given in Table VIII. *trans*-$ReOCl_3(PPh_3)_2$ is not reduced by PPh_3 in this way.

$$trans\text{-}ReOCl_3(PPh_3)_2 + MeCN + PPh_3 \longrightarrow trans\text{-}ReCl_3(MeCN)(PPh_3)_2 + POPh_3 \quad (14)$$

(d) Disproportionation to Re^{IV} and Re^{VII}. The unknown cations $ReO{\cdot}aq^{3+}$ and $ReO_2{\cdot}aq^+$ are presumably very unstable, and all reactions that might generate them lead instead to disproportionation. Thus $ReOBr_4^-$ disproportionates in hot water according to[305]

$$3ReOBr_4^- + 5H_2O \longrightarrow ReO_4^- + 2ReO_2 + 10HBr + 2Br^- \quad (15)$$

and the *equilibrium* 16 has been established in aqueous hydrochloric acid.[295]

$$3ReOCl_5^{2-} + H_2O \rightleftharpoons ReO_4^- + 2ReCl_6^{2-} + Cl^- + 2HCl \quad (16)$$

Very mild reducing agents under otherwise drastic conditions (for example, prolonged heating in a high boiling solvent) sometimes yield complexes of Re^{IV}, but it is not clear whether by reduction or by disproportionation. Thus $ReOBr_4^-$ gives $ReBr_6^{2-}$ in hot hydrobromic acid,[305] $ReO(OEt)Cl_2(PPh_3)_2$ gives both $ReCl_2(acac)_2$ and Re^{III}Cl(acac)$_2$PPh$_3$ in boiling acetylacetone,[301,338] and *trans*-$ReOCl_3(PPh_3)_2$ gives $ReCl_4(PPh_3)_2$ when heated in xylene or propionic acid under hydrogen chloride.[322] When *trans*-$ReOX_3(PPh_3)_2$ (X = Cl and Br) is heated with carboxylic acids in toluene, it gives a mixture of $ReX_4(PPh_3)_2$, $Re_2X_2(RCO_2)_4$, $Re_2OX_5(RCO_2)(PPh_3)_2$ (in air),[322] and $Re_2OCl_3(RCO_2)(PPh_3)_2$ (in the absence of air).[322,339]

(e) Protonation of Terminal Oxide. Mono-oxo complexes can seldom be protonated,[315] but trans-dioxo complexes readily yield oxohydroxo species. Thus yellow $ReO_2(en)_2^+$ gives a pink solution of $ReO(OH)(en)_2^{2+}$ in 2 *M* HCl[254,310] and purple needles of $[ReO(OH)(en)_2][ClO_4]_2$ separate from perchloric acid. The compound is weakly acidic with a dissociation constant of 5 × 10^{-4}.[307] Crystalline salts of the cations $ReO(OH)L_4^{2+}$ may similarly be obtained by adding acid to $ReO_2L_4^+$ (L = py[254] and ½dppe[293]), and the equilibrium

$$ReO_2(NCS)_2(PPh_3)_2^- + H^+ \rightleftharpoons ReO(OH)(NCS)_2(PPh_3)_2 \quad (17)$$

has been established.[304]

Oxohydroxo species may condense to give dinuclear μ-oxo species. The anion $ReO_2(CN)_4^{3-}$ is protonated rapidly in 0.5 *M* HCl to $ReO(OH)(CN)_4^{2-}$ (pK_a = −4.2)[340,341] which then slowly eliminates water to give $Re_2O_3(CN)_8^{4-}$;[340] and the solution of $ReO(OH)(en)_2^{2+}$ in 2 *M* HCl slowly deposits green crystals of $Re_2O_3Cl_4(en)_2$.[254] $ReOCl(R_2dtc)_2$ is converted quantitatively to $Re_2O_3(R_2dtc)_4$ by aqueous sodium carbonate, presumably because the oxohydroxo species formed initially by displacement of chloride condenses immediately.[300]

At much lower pH oxohydroxo species may be protonated further to either oxo-aquo or dihydroxo species, but substitution usually ensues. Thus $ReO_2I(dppe)(PPh_3)$ gives $ReOI_3$(dppe) when heated with HI,[302] $[ReO(OH)py_4]^{2+}$ gives $ReOCl_5^{2-}$ with boiling 5 *M* HCl,[254] and $ReO_2(CN)_4^{3-}$ gives $ReO(H_2O)(CN)_3F^-$ with hot, 40% HF.[342] $ReO_2(en)_2^+$, however, gives a blue solution of $Re(OH)_2(en)_2^{3+}$ in 10 *M* HCl,[254,310] and the strongly acidic cation may be precipitated as the hexachloroplatinate.[307] Substitution eventually occurs in hot concentrated HCl to $ReOCl_5^{2-}$ [254] or $ReOCl_4(H_2O)^-$,[294] and $Re(OH)_2Cl_4^-$ is not formed.

(f) Other Reactions. Apart from protonation, very few reactions of ligands coordinated to rhenium(V) have been reported. Ethylenediamine in $ReO_2(en)_2^+$ exchanges hydrogen rapidly with D_2O,[335] and *trans*-$ReOCl_3(PPh_3)_2$ is oxidized by ozone to $ReOCl_3(PPh_3)(POPh_3)$.[290] The Re=O moiety is reminiscent of >C=O in its reactions with arylamines[343] and aroylhydrazines[344] to form Re=N– but is otherwise quite unlike ketonic carbonyl and will not, for example, undergo the Knoevenagel condensation.[282] Reactions which generate multiple bonds to nitrogen are discussed in the next section.

4. *Nitrido and Organoimido Complexes*

A large number of compounds are now known in which rhenium(V) forms a multiple bond to a single atom of nitrogen. Most of these were discovered in Chatt's laboratory and fall into two categories: the organoimido complexes $Re(NR)X_3L_2$ (R = alkyl, aryl, etc.) *formally* contain a rhenium–nitrogen double bond and are all octahedral; the nitrido complexes, which contain a formal rhenium–nitrogen triple bond, may be five- or six-coordinate, depending on the size of the other ligands. Thus in the series of complexes $ReNCl_2(PR_3)_n$, $n = 3$ when $PR_3 = PMe_2Ph$, $PMePh_2$, etc., but $n = 2$ when $PR_3 = PPh_3$. Both types are known for $PR_3 = PEtPh_2$ and P-*n*-$PrPh_2$ and the equilibrium

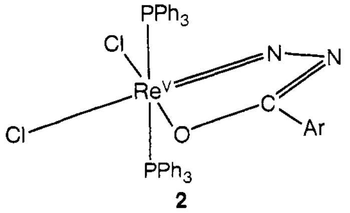
$$ReNCl_2(PEtPh_2)_3 \rightleftarrows ReNCl_2(PEtPh_2)_2 + PEtPh_2 \quad (18)$$

exists in solution.[345] The other five-coordinate nitrido complexes comprise the square-pyramidal dithiacarbamate $ReN(Et_2dtc)_2$[303,346] and the aryls $ReNAr_2(PPh_3)_2$.[347] Both yellow $K_3ReN(CN)_5$ and pink $K_2ReN(CN)_4{\cdot}H_2O$ contain six-coordinate rhenium since the latter apparently exists as the aquo ion $ReN(CN)_4(H_2O)^-$ in solution[348] and as infinite chains in the crystal, in which $ReN(CN)_4$ units are stacked so that each apical nitride is bridging. The X-ray data proved difficult to refine, and only the Re···Re separation is yet known with any certainty.[349] No complexes with either two multiply bound nitrogens or with one nitrogen and one terminal oxide are known, but the μ-oxo-bis(phenylimido) species $Re_2O(NPh)_2(Et_2dtc)_4$ has been prepared from $Re_2O_3(Et_2dtc)_4$ and aniline and from $Re(NPh)Cl_3(PPh_3)_2$ and $NaEt_2dtc$ in aqueous acetone.[300] Organoimido complexes have been synthesized by the following methods.

(a) Condensation of Rhenium(V) Monooxo Complexes with Primary Amines. Aromatic, but not aliphatic, amines in boiling benzene react according to the equation[343]

$$ReOCl_3(PR_3)_2 + ArNH_2 \longrightarrow Re(NAr)Cl_3(PR_3)_2 + H_2O \quad (19)$$

and aroylhydrazine hydrochlorides in boiling benzene-ethanol give the emerald green chelates (**2**).[344] The chelates could also be considered as formally rhenium(III) derivatives (**3**),[344,350] but their infrared spectra suggest that the canonical form (**2**) predominates. Dibenzoylhydrazine gives the same product as monobenzoylhydrazine since one benzoyl group is lost as ethyl benzoate, but acetyl, *p*-tosyl, and *N*-benzoyl-*N'*-methylhydrazine give a nitrido complex only. Under the same conditions, but in the presence of a ketone (R_2CO), the hydrochlorides of both acyl and aroylhydrazines ($R'CONHNH_2$) give complexes of the corresponding ketone hydrazones (**4**), rather than the imido complexes.[344] The cation $[Re(NMe)(MeNH_2)_4Cl]^{2+}$ has been obtained from the complex reaction of K_2ReCl_6, $MeNH_2$, water, and oxygen.[351]



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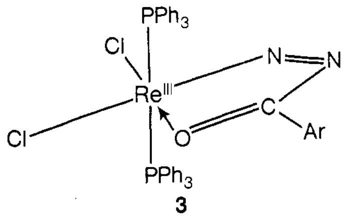

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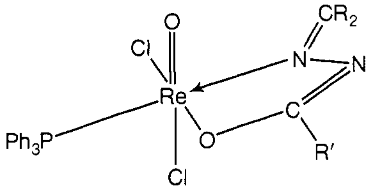

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(b) Reaction of $ReOCl_3(PPh_3)_2$ with 1,2-Disubstituted Hydrazines. The alkylimido complexes $Re(NR)Cl_3(PPh_3)_2$ (R = Me, Et, *n*-Pr, and c-C_6H_{11}) which are not available through reaction 19 may be prepared in high yield from $ReOCl_3(PPh_3)_2$, $[RNH_2NH_2R]Cl_2$, and PPh_3 in benzene–acetone. The other products are $[RNH_3]Cl$ and $POPh_3$. The choice of solvent is critical, and $ReNCl_2(PPh_3)_2$ is formed in benzene–ethanol by an obscure pathway. Under the same conditions diarylhydrazines undergo the benzidine rearrangement, but RCONHNHPh (R = Me and Ph) give $Re(NPh)Cl_3(PPh_3)_2$.[352]

(c) Reaction of $ReOCl_3(PPh_3)_2$ with Phosphinimines ($Ph_3P{=}NR$). This method provides the only route to aroylimido complexes such as $Re(NR)Cl_3(PPh_3)_2$ (R = PhCO) which cannot be made from benzamide by reaction 19 nor from dibenzoylhydrazine by method b. It gives the phenylimido complex when R = Ph.[353]

(d) Reaction of $ReOCl_3(PR_3)_2$ with Phenyl Isocyanate. Phenylimido complexes $Re(NR)Cl_3(PR_3)_2$ ($PR_3 = PPh_3$ and PEt_2Ph) are formed in boiling xylene with evolution of CO_2,[354] but the reaction is not general and the known complex $Re(NPh)Cl(Et_2dtc)_2$ cannot be obtained from $ReOCl(Et_2dtc)_2$ in this way.[300]

Nitrido complexes have been obtained in low yield by the action of sodium azide on $ReCl_3(PR_3)_3$,[345] but the only practical synthesis of the Re≡N bond involves the reaction of a rhenium(V) monooxo complex with hydrazine hydrochloride[343,345] or with certain substituted hydrazines.[344,352] The $Re^V{=}O$ moiety may be generated *in situ*, and the complexes $ReNX_2(PR_3)_n$ (X = Cl, Br, and I; n = 2 or 3) are conveniently prepared by the slow addition of Re_2O_7 in ethanol to a boiling mixture of $[N_2H_6]X_2$ and PR_3 in the same solvent.[343] $ReO(OEt)Cl_2(PR_3)_2$ appears to be an essential intermediate since $ReOCl_3(PPh_3)_2$ does *not* give a nitrido complex in either dry ethanol or in wet or dry tetrahydrofuran, but substitution to $ReO(OEt)Cl_2(PPh_3)_2$ takes place in wet ethanol, which then gives the nitrido complex. Low pH is also essential since N_2H_5Cl gives a lower yield of product than $N_2H_6Cl_2$ and N_2H_4 gives none at all. One nitrogen in hydrazine finally appears as NH_4Cl (and in $PhNHNH_3Cl$ as $PhNH_3Cl$) and terminal oxide in $Re^V{=}O$ as $POPh_3$.[345]

Once formed, the Re≡N and Re=NR moieties are extremely stable and may persist through fairly drastic substitution reactions. Thus $ReNBr_2(PPh_3)_2$ reacts with excess potassium cyanide to form $ReN(CN)_5^{3-}$,[348] $ReNCl_2(PPh_3)_2$ with aryllithium to form $ReNAr_2(PPh_3)_2$,[347] and $Re(NR)Cl_3(PPh_3)_2$ with tertiary phosphines and arsines to form $Re(NR)Cl_3L_2$.[352] $Re(NMe)Cl_3(PEtPh_2)_2$ is resistant to HCl but is converted to $ReCl_4(PEtPh_2)_2$ by chlorine.[352] Terminal nitride is sufficiently basic to coordinate to Lewis acids, and the complexes $ReNCl_2(PR_3)_3$ split the bridges in $Pt_2Cl_4(PEt_3)_2$ to give $(PR_3)_3Cl_2Re{\equiv}N{\rightarrow}PtCl_2(PEt_3)$ and form adducts with boron trihalides. They may be displaced from these adducts by pyridine.[355] The Re-N stretching frequency occurs within the range 1010-1062 cm^{-1} [345] and *rises* by up to 100 cm^{-1} on coordination. In this respect the $Re{\equiv}N$ moiety is reminiscent of $C{\equiv}N$ in organic nitriles.[355]

The complexes **2** are much more reactive than organoimido complexes, and the chelate ring is opened by a number of monodentate ligands (L) such as nitriles,[344,356] pyridine, phosphine, etc., to give the benzoylazo complexes $Re(N{=}NCOPh)Cl_2L(PPh_3)_2$, and by the more reactive tertiary phosphines to $Re(N{=}NCOPh)Cl_2L_3$.[344] These are formally derivatives of rhenium(III), but they do not possess the temperature-independent paramagnetism typical of other rhenium(III) complexes.[337] The crystal structure of $ReCl_2(N{=}NCOPh)(PMe_2Ph)_3$ has revealed an essentially linear Re-N-N moiety,[357] implying Re-N multiple bonding and consistent with the benzoylazo group acting as a three-electron donor.[344] When the benzoylazo complexes are heated with certain tertiary phosphines in methanol, the benzoyl group is removed as $PhCO_2Me$ to give stable dinitrogen complexes of rhenium(I) of the type $ReCl(N_2)L_4$ (L = PMe_2Ph, ½dppe, etc.).[358] Complex **2** (Ar = Ph) reacts with nitric oxide to give $ReCl_2(NO)(PPh_3)_2$, and with chlorine to give first $ReCl_3(N{=}NCOPh)(PPh_3)_2$ and then $ReCl_4(PPh_3)_2$, benzoyl chloride, and dinitrogen.[344]

Nitrido and organoimido complexes have been examined by X-ray diffraction in much greater detail than monooxo complexes. The more important bond lengths are given in Table IV with K_2OsNCl_5 included for comparison. The two five-coordinate nitrido complexes may be described as distorted square pyramidal with apical nitride. In $ReN(Et_2dtc)_2$ the sulfur atoms lie at the corners of a rectangular base with all four Re-S separations approximately equal at 238.8 pm and 5 pm shorter than in $Re_2O_3(Et_2dtc)_4$.[346] In both $ReN(Et_2dtc)_2$ and $ReNCl_2(PPh_3)_2$ all bond distances are significantly shorter than the corresponding distances in six-coordinate complexes.[359] The six-coordinate complexes deviate from octahedral geometry in two respects: first, the chlorine-metal distance trans to the nitrogen ligand is longer than the cis chlorine-metal distances though all distances are longer than in $ReCl_6^{2-}$ (235 pm);[360-362] secondly, ligands cis to nitrogen are bent away from it,[360-362] and in K_2OsNCl_5 the trans Cl-Os-Cl angles are 166.0 and 169.1°.[363] These distortions are steric in origin. The strong repulsions which would have operated between nitrogen and ligands in the cis position at 90° are relieved by an expansion of the cis angle. This forces the cis ligands toward the chlorine trans to nitrogen, setting up additional repulsive forces which push the trans ligand away from the metal. The strong trans influence of N^{3-} and RN^{2-} is thus predominantly steric. As the number and bulk of the phosphine ligands increases, steric crowding becomes more severe and M-L bonds lengthen further. In $ReNCl_2L_3$ crowding is so severe when L = PPh_3 that the sixth coordination position cannot be occupied.[363] It was recognized a long time ago that PPh_3 is too bulky to occupy three coordination positions on a number of metal ions including Re^{III}, Re^{V}, Rh^{III}, and Ir^{III} (except in association with hydride), and chemical reactions that would otherwise generate $MX_3(PR_3)_3$ take a different course when PR_3 = PPh_3.[364]

The Re-N-C moiety in $Re(NMe)Cl_3(PEtPh_2)_2$, $Re(NC_6H_4OMe\text{-}p)Cl_3(PEt_2Ph)_2$, and $Re(NC_6H_4Ac\text{-}p)Cl_3(PEt_2Ph)_2$[361] deviates by no more than 8° from linearity, indicating sp-hybridized nitrogen. The lengths of the formally double $Re{=}NR$ bonds are only slightly dependent on R and are *ca.* 10 pm *shorter* than the formally triple $Re{\equiv}N$ bond in $ReNCl_2(PEt_2Ph)_3$.[362] These facts suggest that the order of the Re-N bond is essentially three in both the nitrido and the organoimido complexes,[345,363] and Ibers attributes differences in Re-N bond distances predominantly to steric factors. The phosphines in $ReNCl_2(PEt_2Ph)_3$ are so crowded that they force a substantial lengthening of the Re-N bond compared to both $ReNCl_2(PPh_3)_2$ and $Re(NR)Cl_3(PR_3)_2$. Electronic effects may, of course, operate in addition, and it has been suggested that the s contribution of nitrogen to the σ component of the Re-N bond is greater in imido than in nitrido complexes, leading to increased strengthening of the Re-N bond in the former.[345] Organoimido complexes may also be formulated as nitrene complexes of rhenium(III),[353] a canonical form useful in rationalizing certain reactions, *e.g.*, with chlorine.

5. Other Complexes

Complexes of rhenium(V) lacking a terminal oxide, nitride, or imide ligand are rare and are generally rather unstable. Alkali salts of ReF_6^- are well known.[8,9] $[N_2H_6]ReF_6$ (μ = 2.13 BM) separates as yellow needles when ReF_6 is reduced with hydrazinium fluoride in liquid HF,[365] and $[NO]ReF_6$ is obtained from ReF_6 and nitric oxide.[232] Only one salt of $ReCl_6^-$ has been prepared, namely, $[PCl_4]ReCl_6$ (μ = 2.47 BM), and attempted metathesis with alkali chlorides leads to reduction to $ReCl_6^{2-}$.[276] Both $CsRe(SCN)_6$ (μ = 1.38 BM)[277] and $[AsPh_4]Re(OCN)_6$ (μ = 2.70 BM)[278] have been isolated from melts, and $[AsPh_4]Re(CN)_6$ (μ = 1.50 BM) has been claimed as a product of the reaction of KCN with K_2ReCl_6 in fused KSCN and subsequent work-up.[366] The formation of $Re(CN)_6^-$ under the above conditions does, however, require confirmation. The stable anion $Re(CN)_8^{3-}$, analogous to $Mo(CN)_8^{4-}$ and $W(CN)_8^{4-}$, can be isolated from water and has been studied extensively.[8,9,15] Halogens oxidize $ReX_2(diars)_2^+$ to the eight-coordinate cations $ReX_4(diars)_2^+$ (X = Cl and Br),[15] and $\pi\text{-}Cp_2ReH$ to $\pi\text{-}Cp_2ReX_2^+$ (X = Cl, Br, and I).[367] An eight-coordinate dithiacarbamate $Re(Et_2dtc)_4^+$, isoelectronic with $Mo(Et_2dtc)_4$, is formed as one of the products of the complex reactions of $ReCl(CO)_5$ or $ReCl_4(PPh_3)_2$ with tetraethylthiuram disulfide.[368] Neutral complexes are confined to the free pentahalides and the eight-coordinate hydrides. An adduct $ReCl_5PCl_3$ (μ = 2.37 BM) said to be formed from rhenium metal and PCl_5[369] could be $[PCl_4]_2Re_2Cl_8$[370] or $[PCl_4]_2Re_2Cl_9$ and requires confirmation.

The hydrides are best prepared by treating $ReCl_3(PR_3)_3$ with $LiAlH_4$ in tetrahydrofuran or $ReH_7(PR_3)_2$ with excess PR_3, and are also available from $ReOCl_3(PR_3)_2$. They include $ReH_5(PR_3)_3$ (PR_3 = PEt_2Ph, $PEtPh_2$, and PPh_3), $ReH_5(PPh_3)(dppe)$, and $ReH_5(dppe)_2$ in which one of the two dppe ligands is monodentate. The complexes $ReH_5(PPh_3)_2L$ (L = PEt_2Ph, $AsPh_3$, $C_6H_{11}NH_2$, py, and $C_5H_{10}NH$) are obtained by heating $ReH_7(PPh_3)_2$ with L in boiling tetrahydrofuran, and it is remarkable that PPh_3 is not displaced by PEt_2Ph. On the nmr time scale the five hydride protons are equivalent, and the ^{31}P nuclei are likewise equivalent so that the proton resonance always appears as a quartet in $ReH_5(PR_3)_3$ and as a triplet in $ReH_5(PR_3)_2L$ ($L \neq PR_3$).[203] The complexes $ReH_5(PAr_3)_3$ (Ar = Ph and C_6H_4Me-*p*) react quantitatively with halogens with evolution of hydrogen to form $ReH_4X(PAr_3)_3$ (X = Br and I) and with $SnCl_2$ to form $ReH_4(SnCl_3)(PAr_3)_3$. $ReH_4I(PPh_3)_3$ reacts further with iodine in air to give $ReO_2I(PPh_3)_2$ and with carbon monoxide to give $ReI(CO)_3(PPh_3)_2$.[371] The rhenium(III) hydrides $ReH_3(dppe)_2$ and $ReH_3(dppe)(PPh_3)_2$ may be protonated reversibly to the cations $ReH_4(dppe)_2^+$ and $ReH_3(dppe)(PPh_3)_2^+$, respectively, and may be oxidized with halogen to the same cations.[372] All known eight-coordinate complexes of rhenium(V) are diamagnetic.

D. Rhenium(IV)

The fourth oxidation state is particularly stable in association with classical ligands (*i.e.*, predominantly σ donors) and, like other d^3 ions, it normally adopts octahedral stereochemistry. Numerous very stable complexes of the types ReX_6^{2-}, ReX_5L^-, and ReX_4L_2 are known (Table V), but, in contrast to Tc^{IV} and Mo^{III}, hardly any cationic types have yet been prepared. No simple cationic species appear to exist under any conditions and, in the absence of suitable ligands, $ReO_2(aq)$ seems to be in equilibrium with water at all pH's [contrast $Mo(H_2O)_6^{3+}$]. The tendency of Re^{IV} to form oxo species has been overemphasized, and there are, in fact, no authenticated species with terminal oxide though several binuclear complexes contain an oxo bridge. Metal-metal bonding in Re^{IV} chemistry is more important than in Tc^{IV} but rather less than in W^{III}. Re-Re bonds thus occur in ReO_2, ReS_2, $ReCl_4$, and a few dinuclear molecular species. Unlike Ru^V and Os^V, redox reactions of Re^{IV} occur with greater difficulty than of adjacent oxidation states, and Re^{IV} does not normally show any tendency to disproportionate.

1. *Rhenium(IV) Oxides and Chalcogenides*

Hydrated rhenium dioxide ($ReO_2 \cdot aq$) precipitates from water as a brown to black amorphous substance as the ultimate product of hydrolysis of $ReCl_6^{2-}$, disproportionation of the halides or oxohalides of rhenium(V) and rhenium(VI), and reduction of perrhenate in the absence of strong ligands, *e.g.*, by Cr^{II} in sulfuric acid or electrolytically.[374] The product formed on a platinum, gold, or mercury cathode in 3 *M* sulfuric acid retains adsorbed hydrogen and is more easily oxidized than $ReO_2 \cdot aq$ of chemical origin.[375] The anhydrous oxide may be prepared by heating $ReO_2 \cdot aq$ in nitrogen,[374,376] by the pyrolysis of NH_4ReO_4, and by reduction of ReO_3 with rhenium at *ca.* 500°,[374,377] but some care must be taken to obtain a stoichiometric phase. Two crystalline modifications are known. Monoclinic α-ReO_2, known only as a microcrystalline powder, is formed below 300° and is isostructural with MoO_2 and WO_2 with short, pairwise Re-Re interactions at *ca.* 249 pm.[378,379] Orthorhombic β-ReO_2 ($\Delta H_f° = -447.2 \pm 8.4$ kJ mol^{-1}, $\Delta S_f° = 48.1 \pm 6.3$ J mol^{-1} deg^{-1})[380] is formed irreversibly above 300° (460° according to a recent study[376]), and large single crystals may be grown by vapor transport in the presence of iodine.[377] The structure is a prototype and consists of zigzag chains of ReO_6 octahedra sharing edges, themselves connected by sharing corners. All Re-Re separations within the chains are equal at 261 pm but are still short enough to indicate metal-metal bonding.[379] Whereas $ReO_2 \cdot aq$ is an insulator,[381] both α-ReO_2 and β-ReO_2 exhibit metallic conductivity in the form of sintered powders with the conductivity of α-ReO_2 about a third that of β-ReO_2.[382] Single crystals of β-ReO_2 have a resistivity of 100 $\mu\Omega$ cm at 300 K.[378] Both modifications possess weak Pauli paramagnetism independent of temperature,[382] and band models that account for their physical properties have been proposed.[378,382,383]

Rhenium dioxide dissolves in fused alkalis but the melts soon decompose and no oxo anions have been isolated. Ternary oxides Ln_2ReO_5 (Ln = a lanthanide) and $Ln_4Re_3O_{12}$ (Ln = La and Nd) of unknown structure are formed by heating mixtures of ReO_2 and Ln_2O_3,[161,258] and by reducing La_3ReO_8 with rhenium.[161] Substances such as Na_2ReO_3 have also been claimed.[217] The ternary nitrides $M_9Re_3N_{10}$ (M = Sr and Ba), obtained by heating rhenium with M_3N_2 under nitrogen, have metallic conductivity. Their structures are not known.[221] A number of phosphides such as Re_3P_4 have been described.[373]

The three chalcogenides ReS_2,[169] $ReSe_2$,[384] and $ReTe_2$[385] may be prepared by heating the elements together in sealed silica ampoules to *ca.* 1000° and single crystals have been grown by vapor transport.[170] The disulfide ($\Delta G_f° = -243 + 0.146T$ kJ mol^{-1} from Re(c) and S_2(g))[386] is by far the most stable phase in the rhenium-sulfur system and is also obtained by heating $KReO_4$,[387] ReO_2, or ReO_3 with sulfur, by the pyrolysis of Re_2S_7, and by the action of H_2S on aqueous $ReCl_6^{2-}$ or $ReCl_3$.[168,169] It does not react when heated with excess sulfur or with excess rhenium, and it resists aqueous hydrochloric acid, alkalis, and alkali sulfides.[169] It is oxidized by hypochlorite,[388] nitric acid, etc., to perrhenate. Dissociation to the elements begins above 700° *in vacuo*,[169] and there is some scant evidence for the existence of ill-defined intermediate phases.[168,169,389] No lower sulfides have actually been isolated, but lower tellurides[390] as well as Re_2Te_5[391] might exist. Only one modification of ReS_2 (and $ReSe_2$) exists between −180 and 1150°,[170] and this had long been thought to have the monoclinic structure of MoS_2.[169,392] A single crystal X-ray study has, however, shown that ReS_2 is triclinic with the same layer structure as $ReSe_2$ and is thus isomorphous with neither MoS_2 nor TcS_2.[170] The structure of $ReSe_2$ is a distorted version of the $CdCl_2$ layer lattice. The rhenium atoms within each layer are surrounded octahedrally by selenium and are displaced from the centers of the octahedra in such a way as to form Re_4 clusters, roughly at the corners of a rhombus. The shortest Re-Re separation, 265 ± 5 pm, is across the diagonal and the rhombi are linked into chains by relatively long Re-Re bonds at 308 ± 5 pm.[384] $ReTe_2$ is orthorhombic and thus differs from both $ReSe_2$ and $TcTe_2$.[170] When $ReSe_2$ is heated with bromine[393] or ReX_3, it forms a single, dark purple microcrystalline phase of composition $Re_3Se_2X_5$ (X = Cl and Br) and Re_2Te_5, and bromine yields $Re_3Te_2Br_5$.[391] The structures of these substances are unknown but they may be related to the trinuclear rhenium(III) clusters. All three chalcogenides of rhenium(IV) are diamagnetic[169,170,384] and behave as semiconductors.[170]

2. *Rhenium(IV) Halides and Complexes with Metal-Metal Bonds*

All four tetrahalides have been reported. Blue ReF_4 may be prepared by reducing ReF_6 with rhenium under carefully controlled conditions[393] and in other ways.[9] It dissolves in water or methanol to form transient blue solutions which persist for up to a few hours when a little H_2O_2 is added.[394] The structure of ReF_4 and the nature of the blue species in solution are unknown.

A number of substances have been described as rhenium tetrachloride but only one, black β-$ReCl_4$, has been

TABLE IV. Metal–Nitrogen and Metal–Chlorine Bond Lengths in Nitrido and Organoimido Complexes

Compound	Re–N, pm	Re–Cl (trans to N), pm	Re–Cl (cis to N), pm	Ref
K_2OsNCl_5	161	261	236–237	363
mer-trans-$Re(NMe)Cl_3(PEtPh_2)_2$	168.5 (1.1)	241.1 (6)	240.8 (6) and 242.8 (6)	360
mer-trans-$Re(NC_6H_4OMe$-*p*$)Cl_3(PEt_2Ph)_2$	170.9 (4)	243.2 (2)	242.1 (1)	361
mer-trans-$Re(NC_6H_4Ac$-*p*$)Cl_3(PEt_2Ph)_2$	169.0 (5)	241.0	239.9 and 243.3	361
mer-cis-$ReNCl_2(PEt_2Ph)_3$	178.8 (1.1)	256.3 (4)	245.4 (4)	362
$ReNCl_2(PPh_3)_2$	160.3 (9)		237.7 (2)	359
$ReN(Et_2dtc)_2$	165.6			346

TABLE V. Mononuclear Complexes of Rhenium(IV)

Complex	Ligand (X)	Ligand (L)	Comments[a]	Synthesis	Ref
ReX_6^{2-}	F, Cl, Br and I		See text	See text	8, 9, 14, 15
	Cl		Cation = NH_4^+	$ReCl_4(MeCN)_2$ + concd HCl	282
	SCN		Cs^+ (μ 3.66), Tl^+ (μ 3.36)	K_2ReCl_6 + molten KSCN	419
				$ReCl_5$ + molten KSCN	277
				$Re_2Cl_8^{2-}$ + SCN^- in Me_2CO	426
	OCN		$AsPh_4^+$ (μ 4.01); O-bonded	K_2ReCl_6 + KCNO in molten Me_2SO_2	278
$Re(OH)X_5^{2-}$	Cl			See ref 15	15
	Br		K^+ (μ 3.75; Δ_0 29,500 cm^{-1}; B, 420 cm^{-1})	Electrolytic reduction of ReO_4^- in HBr	411
	I		NEt_4^+ (μ 3.57)	ReI_6^{2-} + 20% H_2SO_4	253
$Re(OMe)X_5^{2-}$	Cl		Cs^+ (ν(MeO) 1057 cm^{-1})	$ReCl_4(MeCN)_2$ + HCl in MeOH	282
ReX_5L^-	Cl	H_2O, dmso, dmf, tu, MeCN, py, pz, PPh_3	NEt_4^+, N-*n*-Pr_4^+ μ 3.46 (MeCN)	$ReCl_5^-$ + L^b	273
				$ReCl_5$ + PPh_3 in Me_2CO (*inter alia*)	284
ReX_4L_2	Cl	thf	*trans;* μ 3.49	$ReCl_5$ + pure L	283
		Dioxane	*trans;* μ 3.39		
		Thioxane	*trans;* μ 3.28; S-bonded		
	Br	Thioxane	*trans;* S-bonded	K_2ReBr_6 + L in HBr	283
	Cl	MeCN	*cis;* μ 3.40; ν(CN) 2292 cm^{-1}	$ReCl_5$ + $MeCN^b$	282
				$ReCl_4(MeCN)_2^-$ + Fe^{3+}, etc.	282
	Cl	*n*-PrCN, PhCN		$ReCl_5$ + L	282
				$ReCl_4(MeCN)_2$ + $PhCN^b$	282
	I	py, PPh_3, $^1/_2$(*o*-phen)		ReI_4 + L	15
	Cl, Br	py		Pyrolysis of $[LH]_2ReX_6$	421
	Cl, Br	$^1/_2$dipy	μ 3.43 (Cl); 3.48 (Br)	Pyrolysis of $[L_2H]ReX_6$	297, 421
				$ReCl_5$ + molten $dipy^b$	265
	Cl	RC(=NH)NHAr	R = Me; Ar = C_6H_4Me-*p* (μ 3.54) R = Me; Ar = C_6H_4F-*m*, $C_6H_4(CO_2Et)$-*p* R = Ph; Ar = C_6H_4OMe-*p*	$ReCl_4(RCN)_2$ + $ArNH_2$	282
	Cl	MeC(=NH)OR	R = Me, Et	$ReCl_4(RCN)_2$ + ROH	282
	Cl, Br	PPh_3, PEt_2Ph	*trans;* μ 3.54 (Cl, PPh_3)	$ReOX_3(PPh_3)_2$ + boiling RCO_2H + HCl^b	322
				$ReCl_5$ + PPh_3 in dry Me_2CO (*inter alia*)	273
				Pyrolysis of $[LH]_2ReX_6$	422
				$ReCl_4(MeCN)_2$ + PPh_3	282
				$ReX_3(MeCN)(PPh_3)_2$ + CX_4^b or RCX_3	306
				ReX_3L_3 + X_2	422
	Cl	PR_2Ph	*trans;* R = Me, Et, *n*-Pr, *n*-Bu	$ReCl_3L_3$ + CCl_4	337, 423
			μ 3.4–3.7 BM	$ReCl_3L_3$ + Cl_2	337, 423
	Cl	$^1/_2$dppe		$ReH_3(dppe)(PPh_3)_2$ + Cl_2	372
	Cl	$AsPh_3$, $SbPh_3$		$ReCl_4(MeCN)_2$ + L	282
				$ReCl_3(MeCN)L_2$ + CCl_4^b	306
	Cl, Br	$^1/_2$diars		$ReX(CO)_3(diars)$ + X_2	425
$ReCl_4(py)L$		PPh_3		$ReCl_4(PPh_3)_2$ + boiling py	322
$ReCl_3XL_2$	Br	PPh_3		$ReCl_3(MeCN)(PPh_3)$ + CBr_4 in hot C_6H_6	306
	I	PPh_3		$ReH_4I(PPh_3)_3$ + HCl	371

Table V *(Continued)*

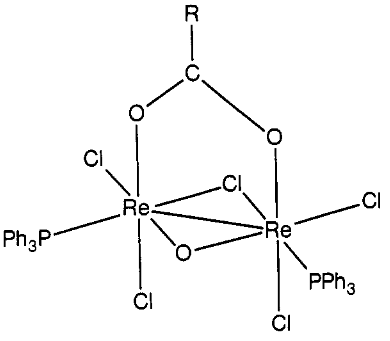
Complex	Ligand (X)	Ligand (L)	Comments[a]	Synthesis	Ref
$ReCl_2X_2L_2$	Br	PPh_3		$ReBr_3(MeCN)(PPh_3)_2 + CCl_4$	306
	I	PPh_3		$ReHI_2(acac)(PPh_3)_2 + HCl$ in boiling C_6H_6	424
$ReCl_3(N{=}NCOPh)L_2$		PPh_3	μ 2.85; $\mu(N{=}N)$ 1580 cm^{-1}	Complex **2** + Cl_2 in CCl_4	344
$ReX_2(acac)_2$	Cl		*cis* (DM, 5.5), *trans* (μ 3.32; DM, 0.0)		
	Br		*cis* (μ 3.21; DM, 4.4)	$ReOX_2(OMe)(PPh_3)_2$ + boiling acacH	301, 338
			trans (μ 3.11; DM, 0.0)	$ReCl_4(PPh_3)_2$ + boiling acacH[b]	322
$ReCl_2(PhCOCH_2COPh)_2$				$ReO(OMe)Cl_2(PPh_3)_2$ + molten $(PhCO)_2CH_2$	338
$ReCl_2(Et_2dtc)_2$				$ReCl(CO)_5 + (Et_2NCS_2)_2$	368
$ReHX_2(acac)L_2$	Cl, Br, and I	PPh_3	μ 2.21 (I)	$ReH_2(acac)L_2 + CCl_4$, $CHCl_3$, $CHBr_3$, or I_2	424

[a] μ refers to effective magnetic moments at room temperature in BM; DM refers to dipole moments in debyes. [b] Best method of preparation.

adequately characterized. It was obtained accidentally in 1966 in a preparation of the trichloride,[395] and its chemistry was elucidated using this single batch before a reproducible synthesis[268] had become available. The tetrachloride may be prepared by heating $ReCl_5$ and $ReCl_3$ in a sealed tube at 300°,[268] but, since the reaction is already reversible at that temperature, only $ReCl_3$ remains when $ReCl_5$ is heated in a stream of inert gas.[268,269,395] It is also obtained by the reaction of $ReCl_5$ with $SbCl_3$[269] or C_2Cl_4 (eq 3)[270] and rhenium metal with $SbCl_5$.[269] The crystal structure contains dinuclear Re_2Cl_9 units similar to $W_2Cl_9^{3-}$, *i.e.*, with two $ReCl_6$ octahedra sharing a face. The dinuclear units are joined into chains by sharing corners, and the Re–Re separation within each unit, 273 ± 3 pm, indicates a metal-metal bond.[396] The structure contrasts with that of technetium tetrachloride in which $TcCl_6$ octahedra share *edges* to form zigzag chains with the technetium atoms definitely not bonded at a separation of 362 pm.[397] Consequently, $TcCl_4$ exhibits ordinary paramagnetism (μ = 3.48 BM), whereas β-$ReCl_4$ exhibits TIP.[268] The black, amorphous substance obtained by heating $ReO_2 \cdot aq$ with thionyl chloride is said to be a different form of the tetrachloride, α-$ReCl_4$, and a trimeric structure has been suggested.[398] However, the composition of the product is variable, and it is evidently not a pure substance.[399,400] Its reactions are very similar to those of β-$ReCl_4$.[399] A third form, γ-$ReCl_4$, results when $ReCl_5$ is heated with hexachloropropene and transforms to β-$ReCl_4$ at high temperatures.[401] It remains to be shown that the α- and γ-tetrachlorides are not merely impure samples of β-$ReCl_4$. Apart from a new synthesis of $ReBr_4$ from $ReCl_5$ and BBr_3[401] and a report of some reactions of ReI_4 with pyridine bases,[402] the tetrabromide and tetraiodide have not been investigated in recent years. They certainly merit further attention since their structures are completely unknown and their reported preparation from aqueous mineral acid[8,9] implies unusual behavior for tetravalent rhenium. Only one oxohalide, $ReOCl_2$, has so far been established and is formed in the reaction of ReO_3 with $ReCl_5$ or $ReOCl_4$, and in the pyrolysis of $ReOCl_4(H_2O)$. It has still not been obtained pure but is believed to have a structure that includes linear oxo bridges. At 500° it disproportionates to ReO_3Cl, $ReOCl_4$, $ReCl_3$, and rhenium metal.[403] The existence of a nitride, ReNF,[394] is in doubt.[404]

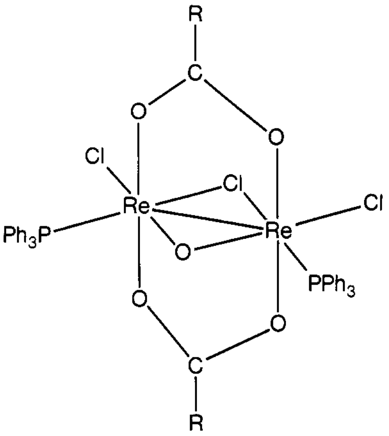
Most reactions of β-$ReCl_4$ yield complexes of Re^{III} and Re^{V} and depend markedly on conditions, but remnants of the dinuclear units usually persist. Thus β-$ReCl_4$ dissolves in weakly acidified methanol as the violet $Re_2Cl_9^{2-}$ ion in which rhenium has a formal oxidation state of 3.5. The ion is easily reduced to blue $Re^{III}{}_2Cl_8^{2-}$, and the derivatives $(ReCl_3L)_2$ (L = PPh_3, $AsPh_3$, and dth) are formed in the presence of L.[395] Rhenium(IV) complexes are obtained only under anhydrous conditions in the absence of air. Pure pyridine under nitrogen thus gives *cis*-$ReCl_4(py)_2$ and $[pyH]_2Re_2Cl_8$,[405] but in acetone in the presence of air it gives only $ReO_2(py)_4^+$, $Re_2O_3Cl_4(py)_4$, and $[pyH]_2Re_2Cl_8$.[395] Prolonged heating in dry acetonitrile gives impure $ReCl_4(MeCN)_2$ and, in the presence of PPh_3, a mixture of $ReCl_4(PPh_3)_2$, $(ReCl_3PPh_3)_2$, and some $ReCl_3(MeCN)(PPh_3)_2$.[405,406] On the other hand, PPh_3 in dry acetone yields $[CH_3COCH_2CMe_2PPh_3]_2Re_2Cl_9$ and $ReOCl_3(PPh_3)_2$, presumably by oxygen abstraction.[405]

The simplest fragment expected to be formed in the reaction of β-$ReCl_4$ with concentrated HCl would be $Re^{IV}{}_2Cl_9^-$ as this ion bears the same relation to β-$ReCl_4$ that $Re_3Cl_{12}^{3-}$ bears to $ReCl_3$. Although $Re_2Cl_9^-$ has not yet been obtained in this way, both green $[N$-n-$Bu_4]$-Re_2Cl_9 and red $[N$-n-$Bu_4]Re_2Br_9$ have been prepared by oxidizing $Re_2X_8^{2-}$ with halogen. They are readily reduced to $[N$-n-$Bu_4]_2Re_2X_9$ (μ = 1.5 BM for X = Cl and 1.7 BM for X = Br) by tin, copper, or mercury in acetone solution or even "spontaneously" when suspended in methanol. Iron carries the reduction further to $[N$-n-$Bu_4]_2Re_2X_8$.[407] The structure of $Re_2Cl_9^-$ has been shown to be similar to $W_2Cl_9^{3-}$ with a Re–Re separation of *ca.* 271 pm,[408] but that of $Re_2Cl_9^{2-}$ has not been reported. Two other series of rhenium(IV) complexes are known to contain metal-metal bonds. The first comprises the dark green diamagnetic carboxylate complexes $Re_2OX_5(RCO_2)(PPh_3)_2$ (X = Cl or Br; R = *i*-Bu, *sec*-Bu, Bz, Ph, C_6H_4OMe-*p*-, or *n*-C_nH_{2n+1} with n = 1, 2, 5, 7, 9, 11, and 15) of structure **5** in which oxide, chloride, and carboxylate bridge simultaneously despite apparent steric constraints.[322,409] The Re–Re separation is 252.2 ± 0.1 pm (for X = Cl and R = Et), much shorter than in β-$ReCl_4$ and comparable to the essentially double Re–Re bond in trinuclear Re^{III} clusters, but the bite of the bridging ligands may be partly responsible for forcing the rhenium atoms so close together.[409] The most remarkable feature of the complexes **5** is their unusual stability. Solutions in aprotic solvents resist chlorine, bromine, thionyl chloride, and boiling acetic acid for several days, and the oxo bridge is protonated *reversibly* by concentrated HNO_3 or $HClO_4$.[322] Excess sodium methoxide displaces chloride without further change to give purple



5

$Re_2OCl_4(OMe)(RCO_2)(PPh_3)_2$ in which OMe is possibly bridging.[364] The second series, purple $Re_2OCl_3(RCO_2)_2(PPh_3)_2$ (R = *sec*-Bu, *i*-Bu, *tert*-Bu, Bz, and *n*-C_nH_{2n+1} with n = 2, 3, 5, 7, and 11) of structure **6**,



6

were initially formulated without the oxygen bridge,[322] but the correct structure was established by X-ray diffraction for R = Et (Re–Re, 251.4 ± 0.1 pm) giving each rhenium atom a formal oxidation state of 3.5.[339] Like $Re_2Cl_9^{2-}$ the magnetic moments (μ = *ca.* 2.0 BM) correspond to one unpaired electron per molecule. In contrast to **5**, the complexes **6** are highly reactive and are oxidized by iodine, cold nitric acid, etc., to unstable products, and decompose slowly in the solid state.[322]

3. Complexes without Metal–Metal Bonds

Most compounds of rhenium(IV) lacking metal-metal bonds are stable neutral or anionic complexes of classical ligands with the metal in octahedral coordination. Their reactions usually give other complexes of rhenium(IV) or are destructive. Variable amounts of Re^{IV} complexes are formed as by-products in several reactions of Re^V and Re^{III} as, for example, *trans*-$ReCl_4(PPh_3)_2$ when the ligands include Cl^- and PPh_3,[364] and $ReCl_6^{2-}$ in the presence of HCl.[285,295,305] Mononuclear complexes of Re^{IV} have been synthesized by the following routes and are described in Table V.

(a) Reduction of Perrhenate in Halogen Hydracid. Whereas reduction of ReO_4^- in weakly complexing acids yields Re^V oxo species[292-299] or $ReO_2{\cdot}aq$,[374] moderately strong reducing agents (I^-, Sn^{II}) in concentrated HX lead to the formation of ReX_6^{2-} ions (X = Cl, Br, and I).[8,9,14] Yields exceed 90% when the reducing agent is hypophosphorous acid.[410] The hydroxo species $Re(OH)X_5^{2-}$ have also been isolated from such solutions, and $Re(OH)Br_5^{2-}$ is obtained, for example, by the electrolytic reduction of $KReO_4$ in HBr.[411] These species are in equilibrium with the μ-oxo dimers $Re_2OX_{10}^{4-}$, and the thermodynamic functions for the equilibrium

$$Re_2OCl_{10}^{4-} + H_2O \rightleftharpoons 2Re(OH)Cl_5^{2-} \qquad (20)$$

have been determined.[412]

The orange coloration, which develops when perrhenic acid is reduced in the presence of thiocyanate and which has long been used for the spectrophotometric determination of rhenium at the microgram level, was once attributed to Re^V oxo complexes such as $ReO_2(SCN)_4^{3-}$. The absorption spectrum is, however, identical with that of either pure $Re(SCN)_6^{2-}$ or a mixture of $Re(SCN)_6^{2-}$ and $Re(SCN)_6^-$ depending on conditions, and the orange color is evidently due to one or both of these species.[277] Although several oxo-thiocyanato complexes of Re^{IV} are mentioned in the literature,[413] none has been adequately characterized.

(b) Reduction of Rhenium(V) Compounds by Mildly Reducing Ligands. The reduction of $ReCl_5$ to $ReCl_4L_2$ was discussed in section IV.C.2(b). The salt $[NEt_4]ReCl_5$ obtained from $[NEt_4]Cl$ and $ReCl_5$ is remarkable in that the anion is polymeric and has a visible and far-infrared spectrum consistent with chains of $ReCl_6$ octahedra sharing cis edges (*i.e.*, as in $TcCl_4$). It dissolves only with reaction.[284] The reduction or disproportionation of Re^V monooxo species discussed in section IV.C.3(c) often gives mixtures of oxidation states, but *trans*-$ReCl_4(PPh_3)_2$[322] by *cis*- and *trans*-$ReX_2(acac)_2$ (X = Cl, Br, and I) are conveniently prepared by this route. The latter (X = Cl) had originally been formulated as a dimer with bridging acetylacetonates on the basis of a spurious molecular weight measurement but was later shown to be monomeric both by X-ray diffraction in the solid state and by molecular weight and mass spectral measurements in solution and in the gas phase.[338]

(c) Ligand Substitution in Rhenium(IV) Complexes. The anions ReX_6^{2-} are extremely inert to substitution.[333] Exchange with $*X^-$ ($*X$ = ^{36}Cl and ^{82}Br) is slower by a factor of 20–50 in ReX_6^{2-} than in TcX_6^{2-},[414] and for $ReCl_6^{2-}$ in 7 *M* hydrochloric acid 50% exchange occurs only after 1405 hr at 50°.[334] Attempts to fit exchange rates to a rate equation are rendered difficult by the necessity to work at high H^+ and Cl^- concentrations, and the best fit is obtained with the expression $k[ReCl_6^{2-}][H^+]$, where $k = (0.659 \pm 0.221) \times 10^{-5}$ M^{-1} sec^{-1} at 90°.[334] It is thus possible to precipitate mixed crystals K_2ReBr_6–K_2SnCl_6 and K_2ReBr_6–K_2OsCl_6 with concentrated HCl which are free from $MCl_nBr_{6-n}^{2-}$.[415] When K_2ReCl_6 is boiled with a mixture of concentrated HCl and HBr for several hours, all the mixed anions $ReCl_nBr_{6-n}^{2-}$ are obtained and may be separated chromatographically.[416] Much faster halogen exchange occurs in the solid state at 200° (10^{-1}–10^{-2} min^{-1}),[417,418] and substitutions by CNO^- [278] and SCN^- [419] have been effected in molten salts. The aquation of $ReCl_6^{2-}$ in dilute acid is exceedingly slow ($k_1 = 9 \times 10^{-9}$ sec^{-1} at 35.0°) and is catalyzed by mercury(II).[420] That of $ReBr_6^{2-}$ is rather faster ($k_1 = 1.78 \times 10^{-6}$ sec^{-1} at 35.0° in 0.2 *M* $HClO_4$) with activation parameters $\Delta H^* = 109 \pm 4.6$ kJ mol^{-1} and $\Delta S^* = -25 \pm 12$ J deg^{-1} mol^{-1}. The activation enthalpy is thus higher than for the aquation of $IrBr_6^{3-}$ ($\Delta H^* = 94.6$ kJ mol^{-1}).[420] K_2ReI_6 dissolves in 20% H_2SO_4 to give red-brown $Re(OH)I_5^{2-}$ which may be extracted with ether.[253] The anions ReX_6^{2-} are seldom used for the synthesis of other rhenium(IV) complexes, but the more labile singly charged or neutral species $[NEt_4]ReCl_5$ and $ReCl_4(MeCN)_2$, available from $ReCl_5$, are useful intermediates. The bridge splitting reaction of $[NEt_4]ReCl_5$ with L thus provides a route to $ReCl_5L^-$,[284] and the complexes

$\mathrm{ReCl_4L_2}$ are readily obtained by removing MeCN from the equilibrium[282]

$$\mathrm{ReCl_4(MeCN)_2 + 2L \rightleftarrows ReCl_4L_2 + 2MeCN} \tag{21}$$

Since the complexes $\mathrm{ReCl_4(amidine)_2}$ do not react with $\mathrm{PPh_3}$, pyridine displaces one $\mathrm{PPh_3}$ from $\mathrm{ReCl_4(PPh_3)_2}$,[322] and the equilibrium 21 lies farther to the right for L = $\mathrm{PPh_3}$ than for $\mathrm{AsPh_3}$ or $\mathrm{SbPh_3}$,[282] it follows that rhenium(IV) has an affinity for hard bases in the Pearson sense. A dimer $\mathrm{[NEt_4]_2[(ReCl_5)_2pz]}$ is obtained from $\mathrm{ReCl_5(MeCN)^-}$ and 0.5 mol of pyrazine.[284]

(d) Reactions of Ligands Coordinated to Rhenium(IV). Since complexes of rhenium(IV) are both inert and stable, reaction with bases may result in nucleophilic attack on an activated ligand rather than in substitution. The nitrile moiety in $\mathrm{ReCl_4(RCN)_2}$ is thus sufficiently polarized to add primary aromatic amines ($\mathrm{ArNH_2}$) across the triple bond giving complexes of N-substituted amidines, $\mathrm{ReCl_4[NH{=}C(NHAr)R]_2}$. Primary aliphatic alcohols likewise yield complexes of imidate esters, $\mathrm{ReCl_4[NH{=}C(OR')R]_2}$, from which the ester moiety may be displaced with $\mathrm{PPh_3}$.[282] Complexes of the type $\mathrm{ReX_4L_2}$ have been synthesized by pyrolysis of the salts $\mathrm{[LH]_2ReX_6}$, where L is a pyridine base[421] or a phosphine.[422]

(e) Oxidation of Mononuclear Rhenium(III) Compounds with Halocarbons. The octahedral complexes $\mathrm{ReCl_3(RCN)(PPh_3)_2}$ are oxidized almost quantitatively by warm carbon tetrachloride according to the equation

$$\textit{trans}\text{-}\mathrm{ReCl_3(RCN)(PPh_3)_2 + CCl_4 \longrightarrow} \textit{trans}\text{-}\mathrm{ReCl_4(PPh_3)_2 + RCN + {}^1/_2C_2Cl_6} \tag{22}$$

The formation of $\mathrm{C_2Cl_6}$ suggests that trichlorocarbene radicals are generated in the reaction and the *reacting* species promote the polymerization of styrene. However, the rate is not affected by radical initiators or scavengers but increases with $\mathrm{CCl_4}$ concentration and is retarded by free nitrile. It thus seems that the rate-determining step is displacement of RCN by $\mathrm{CCl_4}$, followed by rapid homolytic dissociation of the $\mathrm{Cl{-}CCl_3}$ bond. Mixed halide complexes $\mathrm{ReX_nX'_{4-n}L_2}$ may be prepared by heating $\mathrm{ReX_3(RCN)L_2}$ with $\mathrm{CX_4'}$ (X, X′ = Cl or Br; L = $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$, or $\mathrm{SbPh_3}$).[306] Similarly, the complexes *mer*-$\mathrm{MCl_3(PR_3)_3}$ are oxidized by $\mathrm{CCl_4}$ to *trans*-$\mathrm{MCl_4(PR_3)_2}$ when M = Re and Os, but not Ru or Ir.[337,423] Substituted trichloromethanes such as $\mathrm{C_2Cl_6}$, $\mathrm{CCl_3CO_2H}$, and $\mathrm{PhCCl_3}$ are equally effective oxidants, but dichloromethanes are generally inert. The radical fragments from $\mathrm{C_2Cl_6}$,[306] $\mathrm{CHCl_3}$, and $\mathrm{CHCl{=}CCl_2}$[423] generate $\mathrm{C_2Cl_4}$, $\mathrm{CHCl_2CHCl_2}$, and $\mathrm{C_2H_2Cl_4}$, respectively. Hydrides are well known to react with $\mathrm{CCl_4}$ (or $\mathrm{CHCl_3}$) to yield chloride complexes and $\mathrm{CHCl_3}$ (or $\mathrm{CH_2Cl_2}$) and the apparently seven-coordinate $\mathrm{ReHX_2(acac)(PPh_3)_2}$ may be obtained from $\mathrm{ReH_2(acac)(PPh_3)_2}$ in this way.[424]

(f) Other Oxidations. A number of rhenium(III)[337,372,424] and rhenium(I)[425] complexes are oxidized by halogen to rhenium(IV) (Table V), and $\mathrm{Re_2Cl_8^{2-}}$ gives $\mathrm{Re(SCN)_6^{2-}}$ with thiocyanate in acetone.[426] The anion $\mathrm{ReCl_4(MeCN)_2^-}$ is oxidized quantitatively by $\mathrm{Fe^{3+}}$, $\mathrm{Cu^{II}}$, cold $\mathrm{HNO_3}$, and $\mathrm{I_2}$ to $\mathrm{ReCl_4(MeCN)_2}$,[282] and the hydrides $\mathrm{ReH_7(PR_3)_2}$, $\mathrm{ReH_4I(PR_3)_3}$, and $\mathrm{ReHI_2(acac)(PPh_3)_2}$[424] give $\mathrm{ReX_4(PR_3)_2}$ with halogen hydracids.

The physical properties of the hexahalorhenates have been studied in considerable detail.[15] The enthalpy of formation of $\mathrm{ReCl_6^{2-}{\cdot}aq}$ has been calculated from the enthalpy of hydrolysis to $\mathrm{ReO_2{\cdot}2H_2O(s)}$ ($\Delta H° = -310 \pm 1$ kJ $\mathrm{mol^{-1}}$) and of oxidation by hypochlorite to $\mathrm{ReO_4^-{\cdot}aq}$ ($\Delta H° = -682.5 \pm 3.4$ kJ $\mathrm{mol^{-1}}$) as -765.8 ± 3.4 kJ $\mathrm{mol^{-1}}$.[427] This compares with the enthalpy of formation of $\mathrm{K_2ReCl_6(c)}$ of -1311 kJ $\mathrm{mol^{-1}}$. Single-crystal X-ray studies have shown $\mathrm{K_2ReCl_6}$ and $\mathrm{K_2ReBr_6}$ to have the cubic structure of $\mathrm{K_2PtCl_6}$ with Re–Cl, 235.3 ± 0.4 pm, and Re–Br, 248 ± 0.5 pm, and that all halogen atoms are crystallographically equivalent.[428] The structure of $[p\text{-}\mathrm{MeC_6H_4NH_3]_2ReCl_6}$ is similar (Re–Cl, 235 ± 2 pm).[429] The halogen pure nqr spectra of $\mathrm{K_2ReCl_6}$ and $\mathrm{K_2ReBr_6}$ at room temperature consist of a single resonance for each halogen isotope in keeping with O_h symmetry for the $\mathrm{ReX_6^{2-}}$ ion, but transitions to phases of lower symmetry occur on cooling and cause the resonances to split. The iodine resonance in $\mathrm{K_2ReI_6}$ is a triplet at all temperatures, implying at least three iodine environments.[430] The positive temperature coefficient of the nqr frequency in $\mathrm{WCl_6^{2-}}$ and $\mathrm{ReCl_6^{2-}}$ has been interpreted on the simple assumption that halogen to metal $p\pi{-}d\pi$ bonding is proportional to the number of vacancies in the t_{2g} set of metal 5d orbitals and is thus larger for $\mathrm{ReCl_6^{2-}}$ than for $\mathrm{PtCl_6^{2-}}$.[430] This argument has, however, been disputed,[431,432] and an alternative interpretation is based on the temperature dependence of the soft liberation mode in the solid.[431] Volume effects are also pertinent.[433] The positive charge on M in $\mathrm{MCl_6^{2-}}$ has been estimated by extended Hückel molecular orbital calculations to decrease from 1.32 on $\mathrm{Re^{IV}}$ to 0.69 on $\mathrm{Pt^{IV}}$,[434] in excellent agreement with values of 1.34 and 0.70 calculated from nqr results.[432] The $4f_{7/2}$ electron binding energy rises steadily from 44.5 eV in $\mathrm{K_2ReCl_6}$ to 75.6 eV in $\mathrm{K_2PtCl_6}$, reflecting the increasing positive charge of the *nucleus*.[435] The nqr data also show that the total (*i.e.*, $\sigma + \pi$) covalency of the M–Cl bond increases rather more rapidly than had been predicted,[434] from 0.45 in $\mathrm{ReCl_6^{2-}}$ ($t_{2g}{}^3$) to 0.55 in $\mathrm{PtCl_6^{2-}}$ ($t_{2g}{}^6$), and that the π component decreases from 0.097 to zero.[432]

The vibrational spectra of all four hexahalorhenates have been recorded in the solid state and the force constants calculated according to modified Urey–Bradley (UBFF) and valence force fields (Re–Cl, 145 and 171 N $\mathrm{m^{-1}}$, respectively.[432,436] The M–Cl force constant (UBFF) in $\mathrm{MCl_6^{2-}}$ rises slowly from 125 N $\mathrm{m^{-1}}$ for M = Hf to 159 N $\mathrm{m^{-1}}$ for M = Pt as the total covalency of the M–Cl bond increases.[432] Hexahalorhenates of long-chain aliphatic amines are readily soluble in organic solvents,[437] and the infrared active fundamentals, ν_3 and ν_4, of a solution of $\mathrm{[N(\mathit{n}\text{-}C_7H_{15})_4]_2ReX_6}$ in benzene occur at 297 and 170 $\mathrm{cm^{-1}}$, respectively, when X = Cl; and ν_3 at 208 $\mathrm{cm^{-1}}$ when X = Br.[438]

The electronic spectra of hexahalorhenates in aqueous solution,[15,439] in nonaqueous solvents and halide melts[440] and in the solid state[441] have been assigned, and the energy level diagram of $\mathrm{Re^{4+}}$ in an octahedral crystal field has been deduced from the sharp line spectra of $\mathrm{Re^{IV}}$ in crystals of $\mathrm{K_2PtCl_6}$ and $\mathrm{Cs_2ZrCl_6}$ at 4 K.[442] The crystal field parameter Δ_0 for $\mathrm{ReCl_6^{2-}}$ is 29,000 $\mathrm{cm^{-1}}$ and compares with 25,000 $\mathrm{cm^{-1}}$ for $\mathrm{TcCl_6^{2-}}$ and 18,000 $\mathrm{cm^{-1}}$ for $\mathrm{MnCl_6^{2-}}$.[128,439] Rhenium(IV) in single crystals of $\mathrm{Cs_2ZrBr_6}$,[443] $\mathrm{Cs_2ZrCl_6}$, and $\mathrm{Cs_2HfCl_6}$ shows sharp line luminescence at low temperatures which in the last two cases consists of four lines originating in $\Gamma_7({}^2T_{2g})$ and terminating in the $\Gamma_8({}^4A_{2g})$ ground state.[444] A very detailed review of the electronic and esr spectra of $\mathrm{K_2ReCl_6}$ is available.[445]

Hexahalorhenates are generally magnetically nondilute, and both $\mathrm{K_2ReCl_6}$ and $\mathrm{K_2ReBr_6}$ are ordered antiferromagnetics at 4.2 K with Néel temperatures of 11.9 and 15.3 K, respectively.[15,446] Neutron diffraction indicates that this is a result of antiferromagnetic stacking of ferromagnetic sheets along the axis perpendicular to (001).[446] Large cations may cause some dilution,[447,448] but the

Re···Re separation does not necessarily increase. The closest Re···Re separation in $[p\text{-MeC}_6H_4NH_3]_2ReCl_6$, for example, is virtually the same as in K_2ReCl_6 although the distance between layers of rhenium atoms increases from 570 pm in the potassium salt to 1252 pm in the *p*-toluidinium salt.[429]

Solutions of K_2ReCl_6 in LiCl-KCl melts are stable indefinitely at 450° although a little rhenium metal is formed by disproportionation during the dissociation process. Electrolytic reduction gives rhenium metal without accumulation of appreciable concentrations of intermediate oxidation states and the apparent standard electrode potential $E^0(Re^{IV}/Re^0)$ at t°C is $-0.389 + (5.6 \times 10^{-4})(t - 450)$ V relative to a standard Pt^{II}/Pt^0 reference electrode.[145] One-electron polarographic reduction of $ReCl_6^{2-}$ in aqueous mineral acid is now firmly established,[449] and the kinetics of the system have been carefully studied.[450] There is less evidence that the reduction product actually is $ReCl_6^{3-}$ although this seems plausible in view of the existence of the equilibrium $ReCl_4(MeCN)_2 + e^- \rightleftharpoons ReCl_4(MeCN)_2^-$.[282] Reduction of ReX_6^{2-} with formic acid generates $ReX(CO)_5$ (X = Cl, Br, and I) in high yield and thus provides one of the best available routes to compounds of rhenium(I).[451] The chemical effects of $^{185}Re(n,\gamma)^{186}Re$ reactions in solid hexahalorhenates have been investigated in detail[418,452] but will not be discussed here.

All known complexes $ReX_4(PR_3)_2$ have the trans configuration,[453,454] and the single Re-Cl stretching frequency in the far-infrared at 320 ± 2 cm^{-1} is almost independent of PR_3 but is *ca.* 20 cm^{-1} higher than in $ReCl_3(PR_3)_3$.[453,455] The stretching frequency increases from $ReCl_4(PR_3)_2$ to $PtCl_4(PR_3)_2$ by *ca.* 20 cm^{-1}.[453] A series of ligand to metal charge-transfer bands commence at *ca.* 17,000 cm^{-1}, at lower energies than in $ReCl_6^{2-}$.[455,456] The Re-Cl and Re-P bond lengths in $ReCl_4(PMe_2Ph)_2$ are 233.1 ± 0.3 and 250.5 ± 0.3 pm, respectively, and, whereas the M-Cl separations in $MCl_4(PMe_2Ph)_2$ vary by only about 1 pm from W^{IV} to Ir^{IV}, the M-P separation falls steadily by *ca.* 5 pm for each successive element.[457] This trend may be interpreted satisfactorily in terms of the form of the overlap integrals and on the plausible assumption that some chlorine to metal π-bonding is to be expected but little if any π back-bonding from the metal to phosphorus.[454] The $4f_{7/2}$ electron binding energies in $MCl_4(PR_3)_2$ are approximately the same as in MCl_6^{2-} and are independent of PR_3 but rise steadily from M = W to M = Pt.[435] The effective magnetic moments of octahedral complexes of rhenium(IV) at room temperature fall within the range 3.1–3.8 BM, rather less than the spin-only value of 3.86 BM (Table V). This range is clearly higher than for any other oxidation state (Table I), and magnetic susceptibilities can therefore be used empirically as a fairly reliable diagnostic test for mononuclear rhenium(IV).

In addition to the mononuclear complexes described above (Table V) and the polymeric $ReCl_5^-$ ion, rhenium(IV) forms a number of μ-oxo species of which only $Re_2OCl_{10}^{4-}$ has been thoroughly characterized.[15,458] The Re-O-Re moiety is linear[15] as in $Os_2OCl_{10}^{4-}$ [459] but in contrast to $W_2OCl_{10}^{4-}$,[460] and the linearity has been rationalized by molecular orbital calculations.[461] When $Re_2OCl_{10}^{4-}$ is treated with hydrogen peroxide or other oxidants in acid solution, it forms a blood-red species formulated as $Re_2(OOH)Cl_{10}^{3-}$ with a μ-hydroperoxo bridge.[458] A more plausible formulation would perhaps be as a μ-superoxo complex of Re^{IV} analogous to $[(NH_3)_5Co\text{-}O\text{-}O\text{-}Co(NH_3)_5]^{5+}$. The anion may be precipitated as the paramagnetic cesium salt (μ = 3.57 BM) and thus contrasts with the nearly diamagnetic $Re_2OCl_{10}^{4-}$.[458] Other μ-oxo species include $Re_2O(OH)_6(LL)_2^{4-}$ (LL = oxalate, citrate, tartrate, and gallate), $Re_2O(OH)_2(LL)_4^{4-}$ (LL = oxalate and ¼ EDTA),[8,14,15] $Re_2O(OH)_2(SO_4)_2(LL)_4^{4-}$,[462] and possibly $Re(OH)_4(LL)^{2-}$ (LL = oxalate and gallate),[14] but they all require confirmation. Some ill-defined phthalocyanine complexes have also been claimed.[463] Rhenium(IV) may be incorporated in heteropolyacids by treating $SiW_{11}O_{39}^{8-}$ and $P_2W_{17}O_{61}^{10-}$ with $ReCl_6^{2-}$ under nitrogen. The blue products $SiRe^{IV}W^{VI}{}_{11}O_{39}^{4-}$ and $P_2Re^{IV}W^{VI}{}_{17}O_{61}^{6-}$ are oxidized by air to the purple Re^{VI} heteropolyacids $SiRe^{VI}W^{VI}{}_{11}O_{40}^{4-}$ and $P_2Re^{VI}W_{17}O_{62}^{6-}$, but further oxidation only yields perrhenate.[464]

E. Rhenium(III)

The chemistry of Re^{III} is intermediate between its isoelectronic neighbors W^{II} and Os^{IV}. It forms a large number of mononuclear octahedral complexes similar to those of Os^{IV} and OS^{III} in which classical σ donors coexist with weak π acceptors. They are mostly of the types $ReX_2L_4^+$ and ReX_3L_3, and rarely $ReX_4L_2^-$. It also forms two types of metal atom clusters formally derived from dinuclear $Re_2X_8^{2-}$ and trinuclear $Re_3X_{12}^{3-}$. In this respect it strongly resembles Mo^{II} and W^{II} where the clusters are based on $Mo_2X_8^{4-}$ and $M_6X_8^{4+}$. Little is known about Tc^{III}, but there appear to exist important differences with Re^{III} in detail, in particular the relative reluctance of Tc^{III} to form stable cluster compounds.

It was once believed that the tendency of Re^{III} to form metal–metal bonds is so great as to virtually preclude the existence of mononuclear species. However, the synthesis of octahedral complexes by a variety of routes has now established that the most common stereochemistry of Re^{III} is monomeric octahedral and that the stability of cluster compounds is probably kinetic. Thus *both* $Re_3Cl_{12}^{3-}$ and $Re_2Cl_8^{2-}$ may be boiled with concentrated hydrochloric acid without reaction and, under drastic conditions, it is possible to convert trinuclear to dinuclear, and dinuclear to mononuclear complexes, *but not vice versa.*

No oxides of rhenium(III) have been established with certainty, but a ternary phase, $LiReO_2$, has been mentioned briefly,[217] and $La_8Re_6O_{21}$ is said to be formed in the reduction of $La_4Re_3O_{12}$ with hydrogen.[161] Hydrolysis of rhenium trichloride under nitrogen[465,466] and reduction of perrhenate with borohydride[467] gives a hydrated oxide whose composition approaches $Re_2O_3 \cdot 3H_2O$. It is slowly oxidized by water and rapidly by air to ReO_2, and it loses a molecule of water at 200° *in vacuo.* It disproportionates to ReO_2 and Re at higher temperatures,[465] and anhydrous Re_2O_3 cannot be made.[213,465] The standard enthalpy of formation of $Re_2O_3 \cdot aq$ has been calculated from the enthalpy of hydrolysis of $ReCl_3$ by base ($\Delta H^\circ = -227.2 \pm 5.9$ kJ mol^{-1}) as -498.3 kJ mol^{-1} and the free energy of formation as -425.1 ± 2.5 kJ mol^{-1}.[466]

1. Rhenium(III) Halides and Complexes of Trinuclear Clusters

The property of rhenium(III) to form stable trinuclear clusters was discovered in 1963, and a large number of such complexes were then prepared in the laboratories of Fergusson and Cotton.[15] Their structures are based on the Re_3X_9 moiety in which an equilateral triangle of rhenium atoms is held together by strong metal–metal bonds and by three coplanar halogen bridges beyond the edges of the triangle. Each rhenium atom carries one terminal halogen above and one below the Re_3X_3 plane. A third terminal position within the plane may be occupied by a

TABLE VI. Trinuclear Complexes of Rhenium(III)

Complex	Ligand (X)	Ligand (L)	Comments	Ref
ReX_3	Cl and Br		Re–Re, 248.9 pm (Cl); polymers	483
	I		Re–Re, 244.0 and 250.7 pm; polymer	469
Re_3X_9	Br		Re–Re, 246 (2) pm in vapor at 300–400°	481
$Re_3X_3Y_6$	Cl		Y = Br	477
	I		Y = Cl	477
Re_3XY_8	Cl		Y = Br	477
$Re_3X_9L_3$	Cl and Br	R_2SO, py, PPh_3 and $AsPh_3$	R = *p*-C_6H_4Me, Ph, Bz, and $(CH_2)_4$	474, 482, 489, 492
		PEt_2Ph	Re–Re, 249.3 pm (Cl)	474, 489
	Cl	$POPh_3$, thioxane, $PhNH_2$, $C_6H_4(NH_2)_2$, PhCN, MeCN, pz, subst pz, subst py, and hmpt	From $ReCl_3$ + L under mild conditions	474, 490–492
	Br	H_2O	Present in $M_2Re_4Br_{15}$ with $ReBr_6^{2-}$; Re–Re, 246.5 pm	469, 487
$Re_3X_9L_2(H_2O)$	Cl	Et_2S		494
$Re_3X_3(AsO_4)_2L_3$	Br	dmso	From $ReBr_3$ + $AgAsO_4$ + dmso	493
$Re_3X_9L_2$	Cl	$POPh_3$ and $AsOPh_3$	Possibly monohydrates	15
$Re_3X_{10}L_2^-$	Br	py		482
	Br	H_2O or absent		484
$Re_3X_3Y_7L_2^-$	Cl	H_2O	Y = Br; Re–Re, 244.9 and 245.5 in Cs^+ salt	482
$Re_3X_{11}L^{2-}$	Br	PPh_3		482
	Cl	H_2O	Re–Re, 243.5 and 248.3 in $AsPh_4^+$ salt	474, 485
	Br	L absent	Re–Re, 243.3 and 249.6 in Cs^+ salt	482, 486
$Re_3X_3Y_8^{2-}$	Cl		Y = SCN	482
$Re_3X_{12}^{3-}$	Cl		Re–Re, 247.7 pm; D_{3h} symmetry in Cs^+ salt	483
	Br		Re–Re, 249.8 pm; D_{3h} symmetry in Cs^+ salt	482, 484
$Re_3X_9Y_3^{3-}$	Cl		Y = N_3, CN, and SCN	490
			Y = NO_3	488
$Re_3X_6Y_6^{3-}$	Cl		Y = SCN and N_3	490
			Y = Br; present in $Cs_5Re_4Br_{12}Cl_6$ with $ReBr_6^{2-}$	480
$Re_3X_3Y_9^{3-}$	Cl		Y = N_3, CN, and SCN	482, 490
$Re_3X_9L_n$	Cl or Br	dipy, dppe, Et_2dtc, phen, diars, terpy, and polydentate phosphines	*n* = 1–2; structures uncertain	482, 491, 494, 496

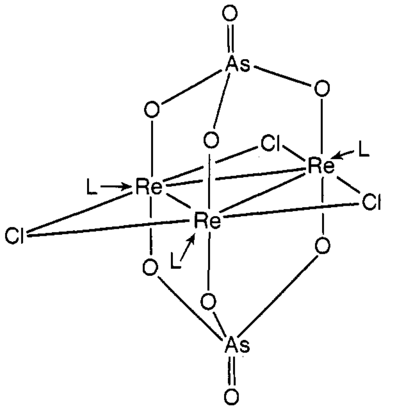
ligand L or X, or may remain vacant. Each rhenium atom is thus seven-coordinate but is six-coordinate (deficient) when the terminal in-plane ligand is missing. There thus exist derivatives such as $Re_3X_{12}^{3-}$, $Re_3X_9L_3$, $Re_3X_{11}^{2-}$ (one deficient rhenium atom), and $Re_3X_{10}^-$ (two deficient rhenium atoms). Most known trinuclear derivatives together with all the Re–Re separations that have been determined are given in Table VI. The separation of deficient from nondeficient rhenium atoms is always shorter than other Re–Re separations. In the crystalline trihalides the in-plane position is occupied by a halogen atom of a neighboring Re_3X_9 unit so that in $ReCl_3$ the units are joined to form infinite sheets[468] and in ReI_3 to form zigzag chains with a third of the rhenium atoms deficient.[469] The linking of Re_3Br_9 units in $ReBr_3$ is uncertain, and the structure of the involatile trifluoride, said to be formed when a rhenium wire is exploded in SF_6,[173] is unknown.

Derivatives of trinuclear clusters may generally be prepared only from the trihalides and have never been obtained from either mono- or dinuclear rhenium(III). Rhenium trichloride ($\Delta H_f^\circ = -264 \pm 3$ kJ mol^{-1}, $\Delta G_f^\circ = -190 \pm 3$ kJ mol^{-1})[470] is formed almost quantitatively when $ReCl_5$ is heated in a stream of nitrogen[267] and rhenium tribromide ($\Delta H_f^\circ = -164 \pm 3$ kJ mol^{-1}, $\Delta G_f^\circ = -130 \pm 3$ kJ mol^{-1})[470] is obtained by direct union of the elements at 600° under pressure,[471] but it is difficult to obtain a pure product in this way.[472] A better synthesis involves the pyrolysis of Ag_2ReBr_6.[473,474] Rhenium triodide may be prepared by reducing perrhenate with hydriodic acid,[475] by heating ReI_4 or $(NH_4)_2ReI_6$ with iodine,[475,476] and by treating $ReCl_3$ with a large excess of BI_3.[477] It loses iodine under reduced pressure to form poorly characterized lower iodides.[469] All the mixed halides $Re_3Cl_nBr_{9-n}$ and $Tc_nRe_{3-n}Cl_9$ are apparently formed when appropriate mixtures of the binary halides are heated together, and the molecular ions have been identified in the mass spectrometer.[400] Pure $Re_3Cl_3Br_9$ in which chlorine occupies the bridging positions, may be prepared by treating $ReCl_3$ with excess BBr_3, but attempted sublimation results in redistribution of the halogen atoms to give Re_3ClBr_8.[477] Only one reaction, namely the formation of $Re_3Cl_9(PR_3)_3$ in the pyrolysis of $ReOCl_3(PR_3)_2$, by-passes the intermediacy of a trihalide.

The Re_3X_9 moiety survives moderately severe physical conditions. Rhenium trichloride thus dissolves in fused dimethyl sulfone as the solvated trimer Re_3Cl_9[478] and has a molecular weight of 885 ± 60 in sulfolane.[468] The most abundant species in the mass spectrum is $Re_3Cl_9^+$.[479] The trichloride ($\Delta H_{\text{subl}} = 204 \pm 6$ kJ mol^{-1} at 277°) and tribromide ($\Delta H_{\text{subl}} = 199 \pm 8$ kJ mol^{-1} at 277°) sublime to essentially pure Re_3X_9 vapor,[480] and an electron diffraction study of Re_3Br_9 at 300–400°, reveals D_{3h} symmetry.[481] Both $ReCl_3$ and $ReBr_3$ dissolve in concentrated HX to give the ions $[Re_3X_{9+n}\cdot aq]^{n-}$ (n = 0–3), and large cations (M^+) precipitate $M_3Re_3X_{12}$,[482-484] $M_2Re_3X_{11}$,[482,485,486] and MRe_3Br_{10}.[482] In addition, oxidation of $ReBr_3$ in HBr may lead to the precipitation of M_2ReBr_6, $MReOBr_4$, $MReO(H_2O)Br_4$,[305] and $M_2Re_4Br_{15}$. The last substance contains equimolar amounts of $ReBr_6^{2-}$ and $Re_3Br_9(H_2O)_3$.[469,487] Both $Re_3Cl_{12}^{3-}$ and $Re_3Br_{12}^{3-}$ have D_{3h} symmetry in the cesium salts.[483,484] The deficient rhenium atoms may or may not be associated with a molecule of water in the crystal. Thus $Cs_2Re_3Br_{11}$ is anhydrous and the out-of-plane BrReBr angle closes from 159° at the nondeficient atoms to 133° at the deficient atom to relieve repulsive forces.[486] On the other hand, $[AsPh_4]_2Re_3Cl_{11}$ is almost certainly associated with a molecule of water, giving a ClReCl angle of 153° at the "deficient" rhenium atom,[485] similar to that in $Re_3Cl_{12}^{3-}$ (158°),[483] $Re_3Br_{12}^{3-}$ (155°),[484] and Re$_3$-

$Br_9(H_2O)_3$ (155°).[487] The anion $Re_3Cl_3Br_7(H_2O)_2^-$, precipitated by Cs^+ from a solution of $ReCl_3$ in HBr, contains two terminal in-plane water molecules and three bridging chlorines.[484,488] Neutral complexes $Re_3X_9L_3$ (X = Cl and Br) are obtained by heating solutions of ReX_3 in organic solvents with ligands such as tertiary phosphines and arsines,[474,482,489] sulfoxides,[474,490] nitriles,[491] and weak nitrogen bases.[491,492] The PEt_2Ph groups in $Re_3X_9(PEt_2Ph)_3$ occupy the terminal in-plane positions.[489]

Three terminal ligands in $Re_3X_{12}^{3-}$ may be displaced easily and another six with some difficulty, but the Re_3X_3 core is very inert. Thus a solution of $Re_3Cl_{12}^{3-}$ in hydrochloric acid containing ^{36}Cl may be boiled for 8 hr without any incorporation of ^{36}Cl in the bridging positions.[482] Similarly, treatment of $Re_3Cl_{12}^{3-}$ with thiocyanate,[482] cyanide, or azide yields complexes of the types $Re_3Cl_9X_3^{3-}$, $Re_3Cl_6X_6^{3-}$, and $Re_3Cl_3X_9^{3-}$ according to the severity of conditions, but the last three chlorines cannot be displaced.[482,490] Arsenate displaces all out-of-plane ions in the presence of dimethyl sulfoxide to give $Re_3Br_3(AsO_4)_2(dmso)_3$ of structure **7**.[493]



7

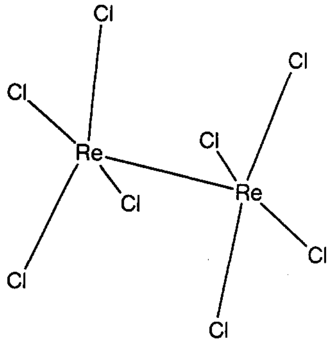
The reactions of ReX_3 with bidentate ligands are not well understood. Complexes of stoichiometry $Re_3Cl_9(LL)_{3/2}$ are obtained under mild conditions for LL = dppe, Et_2dth, and dipy and are suspected to be polymeric.[491,494,495] Under more drastic conditions excess LL has yielded substances with a higher proportion of ligand which may be ionic or polymeric,[491,494] and α,α'-dipyridyl also causes some reduction.[495] Tridentate phosphines[496] and α,α',α''-terpyridyl[494] afford compounds such as $Re_3Cl_9(LL)_n$ with n = 1, 1.33, and 2.

Destruction of the Re_3Cl_9 moiety requires severe conditions. Nitrogen bases of $pK \gtrsim 5$ such as pyridine, isoquinoline, and benzimidazole reduce $ReCl_3$ to the trinuclear rhenium(II) compounds $(ReCl_2L)_n$ (see section IV.F),[492] and liquid ammonia gives a substance of approximate composition $ReCl_3 \cdot 3NH_3$ from which $Re_3Cl_{12}^{3-}$ may be regenerated by hydrochloric acid.[497] The powerful bidentate ligands dppe and diars can, however, break up the Re_3Cl_3 core to give $[ReCl_2(LL)_2]Cl$,[494] and certain polydentate phosphines (L_p) afford green products $ReCl_3L_p$ and $[ReCl_2L_p]^+$ which may be mononuclear.[498] Molten diethylammonium chloride converts $Re_3Cl_{12}^{3-}$ to $Re_2Cl_8^{2-}$ in high yield, and dissolution of $ReCl_3$ in LiCl-KCl eutectic[478] or pyrolysis of a mixture of $ReCl_3$ and CsCl[499] results in disproportionation to $ReCl_6^{2-}$ and Re.

The bonding in trinuclear clusters has been discussed in detail elsewhere,[15,500] and the Re-Re bond order has been predicted to be two.[15] Bond lengths are in the range 243-251 pm. Derivatives of $ReCl_3$ and $ReBr_3$ are dark red or purple and absorb intensely at 500-560 and 750-950 nm. The position of the second band depends on the nature of the terminal ligands. The relevant transitions have not been identified, but the chromophore is carried by the Re_3X_3 core.[15,474,491] Some attempts have been made to assign the complex vibrational spectra and hence to calculate force constants.[501] Rhenium trichloride exhibits weak TIP with $\chi_M = 528 \times 10^{-6}$ cm³ mol⁻¹, and there appears to be a second modification which is nearly diamagnetic.[502]

2. Complexes of Dinuclear Clusters

A number of complexes are known in which two rhenium(III) atoms are held together by a strong, exceptionally short metal-metal bond. They are formally derived from the $Re_2Cl_8^{2-}$ ion (**8**) and have been thoroughly characterized by Cotton and his coworkers. Chloride may be replaced by other monodentate ligands[396,426,503-508] and by two,[508-510] three,[140] or four[139,511-513] carboxylate bridges, and the vacant axial positions trans to the Re-Re bond may be occupied by monodentates. Most known complexes of this type, together with Re-Re separations and methods of synthesis, are given in Table VII.



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The formation of dinuclear clusters is not well understood. They have been obtained by the reduction of mononuclear compounds in *higher* oxidation states and by the degradation of trinuclear clusters, but never from mononuclear rhenium(III). Reduction requires very specific conditions. Perrhenate has thus been reduced to $Re_2Cl_8^{2-}$ only by hydrogen under pressure and by H_3PO_2 in constant boiling hydrochloric acid.[506] Under different conditions $ReCl_6^{2-}$ usually results. $Re_2Cl_8^{2-}$ is also formed in the disproportionation of $ReCl_5$ in acetone,[273,288,289] and the tetra-μ-carboxylato complexes $Re_2X_2(RCO_2)_4$ (**9**) are best prepared by heating *trans*-$ReOX_3(PPh_3)_2$ with acid anhydrides (X = Cl and Br).[322] The mechanisms of these reactions are totally obscure.

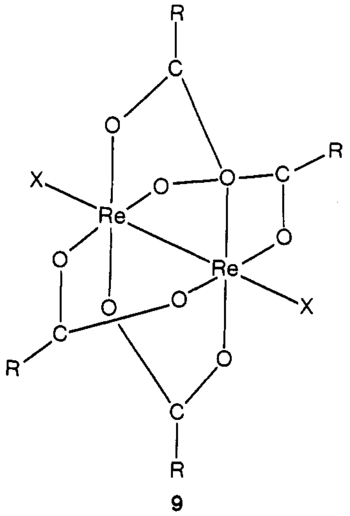

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TABLE VII. Dinuclear Complexes of Rhenium(III)

Complex	Ligand (X)	Comments	Synthesis	Ref
$Re_2X_8^{2-}$	Cl and Br	D_{4h}; Re–Re, 224.1 pm in $K_2Re_2Cl_8 \cdot 2H_2O$; Re–Re, 222.8 pm in $Cs_2Re_2Br_8$; ν(Re–Re) 275 cm^{-1}	$ReO_4^- + HCl + H_2$ (50 atm) at 290°	506, 518
			$ReO_4^- + H_3PO_2$ + const bp HCl or 40% HBr	506, 519
			$ReCl_5 + Me_2CO \pm L$ (*inter alia*)	273, 288, 289
			$ReH_8PPh_3^- + HCl$	202
			$Re_2X_9^- + 2e^-$	406
			$Re_2Cl_2(RCO_2)_4$ + hot concd HCl	506
			$ReCl_3$ + molten $[NH_2Et_2]Cl^a$	478, 514
			$Re_2Cl_8^{2-}$ + 40% HBr^a	514
	SCN	N-Bonded SCN	$Re_2Cl_8^{2-} + SCN^- + HCl$ in MeOH	426
	SeCN		$Re_2Cl_8^{2-} + SeCN^-$	503
$Re_2(mdt)_4^{2-}$			$Re_2Cl_8^{2-}$ + mdt	508
$Re_2X_8L_2^{2-}$	Cl	Equal numbers of $Re_2Cl_8^{2-}$ and $Re_2Cl_8(H_2O)_2^{2-}$ ions in $Cs_2Re_2Cl_8 \cdot H_2O$; axial L		510
$Re_2X_6L_2$	Cl or Br	No bridging ligands; L = PMe_2Ph and PR_3 with R = Et, *n*-Pr, and Ph; Re–Re, 222.2 pm in $Re_2Cl_6(PEt_3)_2$	$Re_2Cl_8^{2-} + PR_3$	396, 505, 521
$(Re_2X_4(RCO_2)_2$	Cl or Br	LL = dppe, dipy, tmtu, and dth; *n* = 2 (?)	$Re_2Cl_8^{2-}$ + LL	507, 508
$ReX_3LL)_n$	Cl	R = CCl_3	$Re_2X_8^{2-}$ + molten CCl_3CO_2H	508
	I	R = Ph; Re–Re, 219.8 pm; D_{2d} with trans iodines	$Re_2Cl_2(PhCO_2)_4$ + HI	508
			$Re_2I_2(n\text{-}PrCO_2)_4$ + molten $PhCO_2H$	510
$Re_2X_4(RCO_2)_2L_2$	Cl or Br	L = H_2O and py; R = Me; cis chlorines, two bridging RCO_2; Re–Re, 222.4 pm in $Re_2Cl_4(MeCO_2)_2(H_2O)_2$	$Re_2X_8^{2-} + Ac_2O + HBF_4$	508
			$Re_2Cl_4(RCO_2)_2(H_2O)_2$ + py	508–510
$Re_2X_3(RCO_2)_3L$	Br	L = H_2O, R = Me	$Re_2Cl_4(RCO_2)_2(H_2O)_2$ + AcOH at 100°	508
$Re_2X_2(RCO_2)_4$	Cl or Br	R = Me, Et, *n*-Pr, *i*-Pr, *t*-Bu, *n*-C_7H_{15}, CH_2Cl, Bz, Ph, Ar; Re–Re, 223.5 pm in $Re_2Cl_2(PhCO_2)_4$	$ReCl_3 + RCO_2H$ at bp	279
			$ReOX_3(PPh_3)_2 + (RCO_2)_2O$ at 120°^{a}	
			$Re_2X_8^{2-}$ + boiling RCO_2H	506, 512, 513
			$Re_2X_2(RCO_2)_4$ + fused $ArCO_2H^a$	512, 513
	I	R = *n*-Pr and Ph	$Re_2Cl_2(RCO_2)_4$ + HI	510, 512
	SCN	R = *n*-Pr and Ph	$Re_2Cl_2(RCO_2)_4$ + AgSCN	279, 512
	ReO_4	R = *n*-Pr; Re–Re, 225.1 pm	$ReCl_3$ + boiling RCO_2H in air	139, 279
$Re_2Cl_2(RCO_2)_2(CCl_3CO_2)_2$		R = Me and *t*-Bu	$Re_2Cl_2(RCO_2)_4 + CCl_3CO_2H$	508
$Re_2(RCO_2)_4(SO_4)(H_2O)_2$		R = *n*-Pr; SO_4 bridging Re_2 units (?)	$Re_2Cl_2(RCO_2)_4 + Ag_2SO_4$	279, 512
$Re_2Cl_2(RCO_2)_3(ReO_4)$		R = *i*-Pr; axial ReO_4 groups join Re^{III}_2 units into chains; Re–Re, 225.9 pm	$ReCl_3$ + boiling RCO_2H in air	140, 279

[a] Best method of preparation.

Partial disruption of the $Re^{III}{}_3Cl_9$ moiety occurs in boiling carboxylic acids to give $Re_2Cl_2(RCO_2)_4$[279] and in fused $[NH_2Et_2]Cl$ to $Re_2Cl_8^{2-}$.[478,515] When $ReCl_3$ is heated with carboxylic acids in the presence of air, partial oxidation of Re^{III} to ReO_4^- occurs and ReO_4^- then coordinates at the axial positions to give the complexes $Re_2(RCO_2)_4(ReO_4)_2$ (**9**, X = ReO_4)[139] and $Re_2Cl_2(RCO_2)_3(ReO_4)$.[140] In the latter, ReO_4 groups join $Re_2Cl_2(RCO_2)_3$ units into chains of alternate ReO_4 and Re_2 moieties.[140]

Once formed, the Re–Re bond persists through fairly severe chemical reactions. The equilibrium

$$Re_2Cl_8^{2-} + 4RCO_2H \rightleftharpoons Re_2Cl_2(RCO_2)_4 + 4HCl + 2Cl^- \quad (23)$$

may thus be traversed in either direction without disruption of the Re_2 moiety.[506,512,513] Complexes such as $Re_2X_4(RCO_2)_2(H_2O)_2$ (two bridging RCO_2, axial H_2O),[509] $Re_2X_4(RCO_2)_2$ (two bridging carboxylates, axial positions vacant),[510] and $Re_2Br_3(RCO_2)_3(H_2O)$ (three bridging carboxylates) have been isolated as intermediates.[508] Boiling 40% hydrobromic acid converts $Re_2Cl_8^{2-}$ to $Re_2Br_8^{2-}$ without further change,[514] and tertiary phosphines displace one chloride on each rhenium atom to give $Re_2Cl_6(PR_3)_2$.[507] Dinuclear clusters may also survive redox conditions in that $Re_2X_8^{2-}$ is oxidized by halogens to $Re_2X_9^-$ (X = Cl and Br)[406] and is reduced polarographically to $Re_2X_8^{3-}$ and $Re_2X_8^{4-}$ (X = Cl and SCN).[515] Although salts of the reduced species have not been isolated, $(NH_4)_3Tc_2Cl_8$ is known as a crystalline solid and the anion is isostructural with $Re_2Cl_8^{2-}$ (D_{4h}).[516] Dithiahexane reduces $Re_2Cl_8^{2-}$ to $Re_2Cl_5(dth)_2$ in which rhenium has a mean oxidation state of 2.5.[508,517]

Cleavage of the Re_2 moiety does, however, occur more easily than cleavage of Re_3X_3 in the trinuclear clusters. Thus $Re_2X_8^{2-}$ reacts with excess dppe to give $[ReX_2(dppe)_2]X$[507] and even with thiourea to give $ReX_3(tu)_3$ (X = Cl and Br).[508] Substitution of chloride in $Re_2Cl_8^{2-}$ by thiocyanate is in competition with oxidation to $Re(SCN)_6^{2-}$; and treatment of $Re_2(SCN)_8^{2-}$ with PPh_3 yields an intriguing paramagnetic species of stoichiometry $Re_2(SCN)_8(PPh_3)_2^{2-}$ (μ = 4.1 BM per Re atom) which *may* contain high-spin rhenium(III).[426]

Nine crystal structures have been determined, and in every case the conformation about the Re–Re bond has been found to be eclipsed.[139,140,505,509-511,518-520] Bond lengths lie within the narrow range of 220–226 pm (Table VII) irrespective of the presence or absence of carboxylate bridges, and it may therefore be inferred that a strong metal–metal bond is present even in the tetra-μ-carboxylato complexes (**9**). Spin pairing *via* the metal–metal bond renders the complexes essentially diamagnetic,[506] and the diamagnetic anisotropy induced by circulating electrons in the bond causes substantial deshielding of ligand protons in the nmr spectrum of $Re_2Cl_6(PR_3)_2$.[521] The Re–Re stretching frequency occurs as an intense band in the Raman spectrum at 285 ± 11 cm^{-1} and has been detected in $Re_2X_8^{2-}$, $Re_2X_4(RCO_2)_2(H_2O)_2$, and $Re_2X_2(RCO)_4$.[522,523] The $Re_2X_8^{2-}$ ions have strict D_{4h}

TABLE VIII. Mononuclear Complexes of Rhenium(III)

Complex	Ligand (L)	Comments	Synthesis	Ref
$Re(dipy)_3^+$		Anion = Cl^-	$(dipyH)_2\ ReCl_6$ + excess dipy (*inter alia*)	546
$ReX_2(dppe)_2^+$		X = Cl and Br, anion = X^-	$ReOX_3(dppe)$ + dppe in boiling EtOH	293
			$Re_2X_8^{2-}$ + excess dppe	507
			$ReH_3(dppe)_2 + Cl_2$	372
		X = I	$ReH_2I(dppe)_2 + I_2$	372
$ReX_2(diars)_2^+$		X = Cl (μ 2.14 BM), Br (μ, 2.02 BM), and I (μ, 1.74 BM)	$HReO_4$ + diars + H_3PO_2 + HX in hot EtOH	15
$ReCl_2(qas\text{-}O)^+$		μ, 2.34; anion = Cl^-	$ReCl_3$ + qas in $MeOC_2H_4OMe$	15
$ReX_2(CO)(diars)_2^+$		X = Br and I; anion = X^-	$ReX(CO)(diars)_2 + X_2$	425
$Re(OMe)(C_6H_6N_5)(NH_3)_3^+$		See text	$ReCl_3(C_6H_4N_4)(PPh_3)_2 + NH_3$ in MeOH	282
ReX_3L_3	tu	X = Cl (μ, 1.34 BM) and Br; two isomers	ReO_4^- + tu in 2 *M* HCl	298
			$Re_2X_8^{2-}$ + tu in MeOH	508
	py	X = Cl	$ReCl_3(benzil)(PPh_3)_2$ + py	306
	$P(OPh)_3$	X = I; μ, 1.65 BM	$ReH_3(PPh_3)[PO(Ph)_3]_3 + I_2$	15, 528
	$^1/_3$tdpme	X = Cl (μ, 1.68 BM) and Br (μ, 1.71 BM)	$ReOCl_3(tdpme) + Na_2S_2O_6$	292
	PMe_2Ph, PEt_2Ph, P-*n*-Pr_2Ph, P-*n*-Bu_2Ph, $PMePh_2$, $AsMe_2Ph$, As-*n*-Pr_3	All *mer;* μ, 1.5–2.0 BM; also *fac* for R = PMe_2Ph	$ReOCl_3(PPh_3)_2$ + L in boiling C_6H_6	337
			$ReCl_4(PR_3)_2 + PR_3$ in boiling EtOH	423
			$ReX_3(MeCN)(PPh_3)_2$ + L	537
	$^1/_3MeC(CH_2PPh_2)_3$	*fac*	$KReO_4$ + L + concd HCl in boil-in EtOH	527
	CO	X = F; *fac;* μ, 1.0 BM	$Re_2(CO)_{10} + ReF_6$ in liquid HF	538
$ReX_3L(PPh_3)_2$	RCN	R = Me, *n*-Pr, *i*-Bu, *n*-C_7H_{15}, and Ph; X = Cl or Br; μ, 1.6 BM	$ReOX_3(PPh_3)_2 + PPh_3$ in hot MeCN	306
			$ReCl_4(MeCN)_2^- + PPh_3$ in EtOH	282
	$C_6H_4N_4$	μ, 1.70 BM; see text	$ReOCl_3(PPh_3)_2 + CH_2(CN)_2 + PPh_3$	282
$ReX_3(MeCN)L_2$	$PEtPh_2$, P-*n*-$PrPh_2$ and P-*n*-$BuPh_2$	X = Cl or Br	$ReX_3(MeCN)(PPh_3)_2$ + L	537
	$AsPh_3$, $SbPh_3$	X = Cl	$ReCl_4(MeCN)_2^-$ + L in hot EtOH	282
$ReCl_3(dppe)(PEt_2Ph)$			$ReCl_3(PEt_2Ph)_3$ + dppe	537
$ReCl_3(py)_2PPh_3$			$ReCl_3(MeCN)(PPh_3)_2$ + py	306
$ReCl_3(LL)(PPh_3$	Benzil, dipy, phenquin	μ, 1.85 BM for benzil	$ReCl_3(MeCN)(PPh_3)_2$ + LL	306
$ReBr_3(CO)(PMe_2Ph)_2$			$Re_2(CO)_7(PMe_2Ph)_3 + Br_2$	539
$ReX_3(PPh_3)L_2$	$P(OPh)_3$	X = Cl and I	$ReH_3(PPh_3)_2L + X_2$	528
$ReCl_3(CO)(PMe_2Ph)_3$		Seven-coordinate	$ReCl_3(PMe_2Ph)_3$ + CO in EtOH	527
			$ReCl(CO)_2(PMe_2Ph)_3 + Cl_2$	527
$ReCl_3(CO)_2(PMe_2Ph)_2$		Seven-coordinate	$ReCl(CO)_3(PMe_2Ph)_2 + Cl_2$	527
$ReX_2(acac)L_2$	PPh_3	X = Cl (μ, 1.4 BM), Br (μ, 1.68 BM) and I	$ReOX_2(OEt)(PPh_3)_2$ + acacH in hot C_6H_6	301
	PEt_2Ph	X = Cl	$ReOCl_2(OEt)(PEt_2Ph)_2$ + acacH in hot C_6H_6	301
$ReCl_2(\beta\text{-diketone})(PPh_3)_2$		Various β-diketones	$ReOCl_2(acac)(PPh_3)_2$ + acacH in hot C_6H_6	301
$ReCl(acac)_2(PPh_3)$			$ReOCl_2(acac)(PPh_3)_2$ in boiling acacH	301
$Re(acac)_3$		μ, 1.81 BM	$ReCl_2(acac)_2$ + Na(acac) at 175° *in vacuo*	536
$Re(hfac)_3$		Volatile; μ, 1.74 BM	$ReCl_2(hfac)(PPh_3)_2$ + Na(hfac) at 110°	536
			$ReCl_3$ + Na(hfac) at high temp	540
$ReCl_2(PPh_2)(PHPh_2)_3$		Dia	$ReOCl_3(PPh_3)_2 + PHPh_2$ in hot C_6H_6	533
$ReCl_2(N{=}CH_2)(PMe_2Ph)_3$		*mer–trans*	$ReCl_3(NMe)(PMe_2Ph)_2 + PMe_2Ph + NEt_3$	534
$ReCl_2(N{=}CH_2)py(PRPh_2)_2$		R = Me, Et, and Ph	$ReCl_3(NMe)(PRPh_2)_2$ + py	534
$ReCl_2(Et_2dtc)(PPh_3)_2$			$ReOCl_2(Et_2dtc)(PPh_3)_2 + PPh_3$ in boiling Me_2CO	300
$Re(Ph_2dtc)_3(PPh_3)$		One monodentate Ph_2dtc	$ReCl_3(MeCN)(PPh_3)_2 + NaPh_2dtc$	300
$Re(Et_2dtc)_3$			$ReCl_3(MeCN)(PPh_3)_2 + NaEt_2dtc$	300
$Re(Et_2dtc)_3(CO)$		Seven-coordinate; dia	$ReCl(CO)_5 + (Et_2NCS)_2$	368
$ReCl_3(POPh_3)_2$		Five-coordinate	$Re_3Cl_9(PPh_3)_3 + PPh_3 + Cl_2$ in Me_2CO	315
$ReAr_3(PEt_2Ph)_2$		Ar = Ph and C_6H_4Me-*p*	$ReCl_3(PEt_2Ph)_3$ or $ReOCl_3(PEt_2Ph)_2$ + ArLi	347

TABLE VIII *(Continued)*

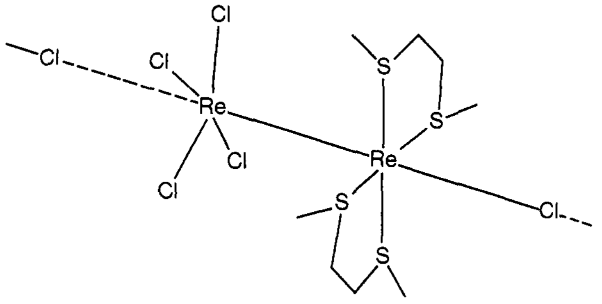
Complex	Ligand (L)	Comments	Synthesis	Ref
$ReHX(acac)(PPh_3)_3$		X = Br and I	$ReH_2(acac)(PPh_3)_2$ + HX (1 mol)	424
			$ReH_4I(PPh_3)_3$ + acacH + PPh_3 in hot EtOH	424
$ReH_2X(CO)(PPh_3)_2$		X = Br and I	$ReH_4I(PPh_3)_3$ + PPh_3 in boiling EtOH	371
$ReH_2(acac)(PPh_3)_3$			$ReH_4I(PPh_3)_3$ + Na(acac) in hot EtOH	424
$ReH_2X(dppe)_2$		X = Cl and I	$ReX_2(dppe)_2$ + $LiAlH_4$ in thf	372
			$ReO_2(dppe)_2$ + $LiAlH_4$ in thf	372
$ReH_2I(dppe)(PPh_3)_2$			$ReH_3(dppe)(PPh_3)_2$ + I_2 in C_6H_6	372
$ReH_3(dppe)_2$		Protonates reversibly	$ReH_5(PPh_3)_2$ + dppe at 180°	372
$ReH_3(PPh_3)_4$			$ReO(OEt)Cl_2(PPh_3)_2$ + PPh_3 + $NaBH_4$	372
$ReH_3(dppe)(PPh_3)_2$			$ReH_5(PPh_3)_2$ + dppe in boiling C_6H_6	372
$ReH_3(PPh_3)_2L_2$	$P(OPh)_3$	Protonates reversibly	$ReH_3(PPh_3)_4$ + L	528
$ReH_3(PPh_3)L_3$	$P(OPh)_3$	Protonates reversibly	$ReH_3(PPh_3)_4$ + L	528
$ReI_4(CO)_2^-$		Cation = NR_4^+	K_2ReI_6 + CO in Me_2CO	541
$ReCl_4(MeCN)_2^-$		Cation = Cs, Cd, Me_3NH; μ, 1.70 BM	$ReCl_4(MeCN)_2$ + NMe_3 in EtOH	282
			$ReCl_4(MeCN)_2$ + Cd/Hg in acetonitrile	282
$Re(CN)_6^{3-}$			K_2ReCl_6 + KCN	535

[a] Benzoylazo complexes and cyclopentadienides are not included.

symmetry and the Re-X distances in $K_2Re_2Cl_8{\cdot}2H_2O$[518] and $Cs_2Re_2Br_8$[519] are 229 and 247.8 pm, respectively, similar to the terminal Re-X distances in ReX_3. The salt $Cs_2Re_2Cl_8{\cdot}H_2O$ is said to contain both $Re_2Cl_8^{2-}$ and $Re_2Cl_8(H_2O)_2^{2-}$ ions.[520] Each rhenium atom in $Re_2Cl_6(PEt_3)_2$ carries one PEt_3 eclipsed with a chlorine on the opposite rhenium atom so that the two PEt_3 groups are mutually trans about the Re-Re bond.[396,505] There is, however, no virtual coupling of the proton spins to the phosphorus nuclei in the isostructural $Re_2Cl_6(PMe_2Ph)_2$.[521] The Re-Cl distance trans to PEt_3 (235.2 pm) is significantly longer than the Re-Cl distance trans to Cl (229.6 pm).[505] Axial ligands are always bound weakly, and the axial Re-Cl distance in $Re_2Cl_2(PhCO_2)_4$ (249 pm) is much longer than the meridional Re-Cl distances in related complexes (230-235 pm).[511] The axial Re-Cl stretching frequency in a range of complexes occurs at $230 \pm 10\ \text{cm}^{-1}$ as compared with $332 \pm 1\ \text{cm}^{-1}$ for the meridional.[522]

The mean Re-Re separation in dinuclear clusters is 24 pm shorter than the mean separation in trinuclear clusters and 52 pm shorter than in rhenium metal. The bond is formally quadruple and consists of a σ, two π, and a δ component which originate in overlap of a set of d_{z^2}-p_z hybrids and of the d_{xz}, d_{yz}, and d_{xy} orbitals on each rhenium atom (z-axis along C_4). Two low-lying σ orbitals (d_{z^2}-p_z hybrids; σ_n) are directed outwards along C_4 and are empty and nonbonding in $Re_2X_8^{2-}$ but bind the axial ligands in $Re_2X_2(RCO_2)_4$[524] and accommodate the additional electrons in $Re_2X_8^{3-}$ and $Re_2X_8^{4-}$.[515] It is the δ component which requires the ligands to be eclipsed and provides competition with steric forces favoring a staggered conformation with no δ overlap.[524,525] Extended Hückel calculations estimate the rotational barrier in $Re_2Cl_8^{2-}$ at 210 kJ mol^{-1}, 14% of the total Re-Re bond energy, and therefore δ-bonding decisively overcomes the repulsive forces.[526] The absorption bands in $Re_2Cl_8^{2-}$ at 14,500, 32,800, and 39,200 cm^{-1} have been tentatively assigned to $\delta \rightarrow \sigma_n$, $\delta \rightarrow \delta^*$, and $\pi \rightarrow \sigma_n$ transitions, respectively. The $\delta \rightarrow \sigma_n$ transition is absent in $Re_2X_2(RCO_2)_4$ because the σ_n orbitals are occupied.[526]

The complex $Re_2Cl_5(dth)_2$ differs from the dinuclear rhenium(III) complexes in having an extra metal valence electron per molecule and the *staggered* conformation **10.** Both axial positions are occupied since chloride ions form linear bridges between dinuclear units, but the Re-Cl separations are very unequal at 249.3 and 324 pm. In the staggered conformation δ overlap is precluded by symmetry, and three electrons must therefore occupy nonbonding d_{xy} orbitals. Such a configuration is consistent with the observed magnetic moment of 1.73 BM, independent of temperature. The Re-Re bond is thus a triple bond ($\sigma^2\pi^4$) and at 229.3 pm is 5.4 pm longer than the quadruple bond in $Re_2Cl_8^{2-}$. The difference is small because δ overlap is the weakest component of the bond in $Re_2Cl_8^{2-}$. The most plausible charge distribution in **10** is as the zwitterion $^-Cl_4Re^{III}{\equiv}Re^{II}Cl(dth)_2^+$, and a very high dipole moment would be expected. The failure of $Re_2Cl_5(dth)_2$ to be eclipsed is presumably due to the inadequately small stabilization of a $(\delta)^2(\delta^*)^1$ configuration originating in d_{xy} orbitals of very unequal energy.[517]



10

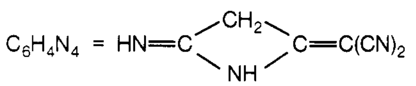
3. Mononuclear Complexes

The majority of mononuclear rhenium(III) complexes are octahedral, but several seven-coordinate complexes are also known. These include $ReX_2(CO)(diars)_2^+$,[425] $Re(Et_2dtc)_3(CO)$,[368] $ReX_3(CO)_2(PMe_2Ph)_2$,[527] $ReX_3(CO)(PMe_2Ph)_3$,[527] and a number of hydrides of the types ReH_3L_4 and ReH_2XL_4.[372,528] $ReX_3(CO)(PMe_2Ph)_3$ is obtained simply by passing CO through $ReX_3(PMe_2Ph)_3$ in boiling ethanol (X = Cl and Br).[527] The crystal structures of two seven-coordinate hydrides, namely, $ReH_3(dppe)(PPh_3)_2$[529] and $ReH_3(dppe)_2$,[530] have been solved by X-ray diffraction, and both contain nearly pentagonal bipyramidal molecules with apical phosphorus. If Cp is assumed to occupy three coordination sites, then π-Cp_2ReH is formally also seven-coordinate. This compound has two unshared electron pairs and can be protonated to π-$Cp_2ReH_2^+$ or may form adducts with boron trihalides, *e.g.*, π-$Cp_2ReH(BF_3)$.[531] When π-Cp_2ReH is treated with excess butyllithium followed by excess methyl iodide, a peculiar reaction occurs to give π-$CpReMe_2(C_5H_5Me)$ in which neutral C_5H_5Me bonds to Re^{III} through four carbon atoms as in butadiene complexes.[532] Rhenium(III) is believed to be five-coordinate in $ReCl_3(POPh_3)_2$[315] and in the aryls $ReAr_3(PEt_2Ph)_2$.[347]

Mononuclear complexes have been synthesized in a variety of ways, and most known compounds of this type are described in Table VIII. The chief preparative routes are the following.

(a) Reduction of Perrhenate. The most direct route to *mer*-$ReX_3(PMe_2Ph)_3$ is to heat $KReO_4$ in concentrated hydrochloric acid with PMe_2Ph in ethanol. The mechanism is not known but presumably involves a $Re^V{=}O$ intermediate. Overall yields are *ca.* 85%.[527]

(b) Reduction of Oxo Complexes of Rhenium(V). A large number of complexes of the type *mer*-ReX_3L_3 have been obtained in high yield by heating oxo complexes such as $ReOCl_3(PPh_3)_2$ with the appropriate ligand.[301,306,337,347,533] The reducing agent may be the ligand itself, and the mechanism has been discussed in section IV.C.3(e). A remarkable reaction occurs when *trans*-$ReOCl_3(PPh_3)_2$ is heated with excess PPh_3 and $CH_2(CN)_2$ or its dimer. The product is $ReCl_3(C_6H_4N_4)(PPh_3)_2$ where



and is presumably formed by cyclization of coordinated malononitrile dimer. It reacts with methanolic ammonia to give a complex with the six-membered chelate ring derived from the ligand $HN{=}C(NH_2)CH_2C(NH_2){=}C(CN)_2$.[282] Deprotonation of the methylimido complexes $ReCl_3(NMe)(PR_3)_2$ with bases such as pyridine gives methylenamido complexes of the type $ReCl_2(N{=}CH_2)py(PR_3)_2$ and $ReCl_2(N{=}CH_2)(PR_3)_3$.[534]

(c) Reduction of Complexes of Rhenium(IV). Although some Re^{IV} complexes are resistant to reduction, others may be reduced smoothly to Re^{III}. Thus $ReCl_4(MeCN)_2$ is reduced rapidly by ethanolic trimethylamine, aqueous ascorbic acid, or cadmium amalgam in dry acetonitrile to *cis*-$[ReCl_4(MeCN)_2]^-$. The anion can be titrated with Fe^{3+} back to $ReCl_4(MeCN)_2$.[282] Similarly *trans*-$ReCl_4(PR_3)_2$ is readily reduced by excess PR_3 in boiling ethanol to *mer*-$ReCl_3(PR_3)_3$,[423] ReI_6^{2-} by CO to $[ReI_4(CO)_2]^-$,[541] and $ReCl_6^{2-}$ by CN^- to $Re(CN)_6^{3-}$.[535]

(d) Substitution in Complexes of Rhenium(III). Whereas dinuclear and trinuclear clusters are converted to mononuclear complexes only with great difficulty, the mononuclear complexes themselves interconvert under mild conditions.[282,372,528,536,537] The readily available $ReCl_3(MeCN)(PPh_3)_2$ is an especially useful source of Re^{III} complexes, and it initially loses MeCN and one PPh_3, as in the formation of $ReCl_3(py)_2(PPh_3)$ and $ReCl_3(benzil)(PPh_3)$.[306] It reacts with tertiary phosphines (except PPh_3) to form *mer*-$ReCl_3(PR_3)_3$.[537] Steric crowding precludes the existence of $ReCl_3(PPh_3)_3$ so that $ReCl_3(MeCN)(PPh_3)_2$ dissolves in fused PPh_3 without reaction; and at higher temperatures it gives $[ReCl_3(PPh_3)]_n$.[306] The complexes $ReH_3(PPh_3)_4$ and $ReH_3(dppe)_2$ are useful intermediates in the synthesis of other seven-coordinate hydride complexes.[372,528]

(e) Oxidation of Rhenium(I) and Rhenium(0) Complexes. Many derivatives of the carbonyl halides are readily oxidized by halogens to Re^{III}, for example, $ReCl(CO)_3(PMe_2Ph)_2$ by chlorine to $ReCl_3(CO)_2(PMe_2Ph)_2$[527] and $ReCl(CO)_5$ by $(Et_2NCS)_2$ to $Re(Et_2dtc)_3(CO)$.[368] $Re_2(CO)_{10}$ is oxidized by ReF_6 to $ReF_3(CO)_3$, the only fluoride complex of Re^{III},[538] and $Re_2(CO)_7(PMe_2Ph)_3$ by bromine to $ReBr_3(CO)(PMe_2Ph)_2$.[539]

Mononuclear complexes are stable as solids but are oxidized more or less readily by air in solution. Thus air oxidizes $ReCl_3(MeCN)(PPh_3)_2$ to $ReCl_3(PPh_3)(POPh_3)$ in hot benzene,[306] and $ReCl_4(MeCN)_2^-$ to $ReCl_4(MeCN)_2$ in the presence of Cu^{2+}.[282] $Re(acac)_3$[536] and $Re(hfac)_3$[540] oxidize even in the solid state. Mild reduction affords complexes of Re^I. Thus *mer*-$ReCl_3(PR_3)_3$ gives $ReCl(CO)_3(PMe_2Ph)_2$ when treated with CO or formic acid,[527] and $ReI_4(CO)_2^-$ is reduced by CO in hot ethanol to $ReI_2(CO)_4^-$.[541]

The octahedral complexes possess paramagnetism equivalent to 1.5–2.1 BM which, however, is *independent* of the temperature. Such behavior is characteristic of low-spin d^4 systems in O_h fields (Re^{III}, Os^{IV}) and arises because the large spin–orbit coupling ($\zeta \sim 2500\ cm^{-1}$) gives a diamagnetic ground state. A small admixture of a higher state then gives the observed behavior by a second-order Zeeman effect.[537,542] Unlike other paramagnetic complexes such as $OsCl_3(PR_3)_3$, the complexes $ReCl_3(PR_3)_3$ give sharp nmr peaks which experience Knight shifts proportional to the temperature.[537,543] Since contact and pseudocontact shifts in ordinary (first-order) paramagnetic compounds are inversely proportional to the temperature, this is further evidence that the paramagnetism of $ReCl_3(PR_3)_3$ is second order.[543]

The Re–Cl distances in *trans*-$ReCl_3(MeCN)(PPh_3)_2$ are 235 pm (trans to Cl) and 240 pm (trans to MeCN),[406] and in *mer*-$ReCl_3(PMe_2Ph)_3$ 235.3 pm (trans to Cl) and 245.4 pm (trans to P).[457] They are therefore longer than the Re–Cl distance in *trans*-$ReCl_4(PMe_2Ph)_2$ (233.1 pm) and the Re–Cl stretching frequencies are lower. Thus two out of the three expected fundamentals in *mer*-$ReCl_3(PEt_2Ph)_3$ occur at 306 and 255 cm^{-1} and both expected fundamentals in *fac*-$ReCl_3(PMe_2Ph)_3$ at 298 and 262 cm^{-1}, whereas the Re–Cl stretching frequency in *trans*-$ReCl_4(PR_3)_2$ occurs at *ca.* 320 cm^{-1}.[453] The nitrile complexes of Re^{III} are remarkable in that they show no $C{\equiv}N$ stretching frequency in the infrared.[282,306] Nevertheless, there is nothing unusual in the bonding of MeCN in *trans*-$ReCl_3(MeCN)(PPh_3)_2$ and the Re–N distance is normal at 205 pm.[406] The stretch appears strongly in the Raman at 2271 cm^{-1}.[544] Although an intense $C{\equiv}N$ stretch occurs in *cis*-$ReCl_4(MeCN)_2$, there is no band at all in *cis*-$[ReCl_4(MeCN)_2]^-$. The structure of the latter has been confirmed by X-ray diffraction,[545] and there is no satisfactory explanation of why the band should be completely quenched simply by adding one electron to $ReCl_4(MeCN)_2$. The electronic spectra of $ReCl_3(PR_3)_3$ have been discussed.[455,456]

F. Rhenium(II)

The second oxidation state is the least well known and very few authentic compounds exist. This is surprising in view of the considerable stability of other d^5 systems such as Mn^{II}, W^I, and Os^{III}, and it may be that many more Re^{II} compounds will be synthesized in the future.

A difluoride is said to be formed when a rhenium wire is exploded in PF_5,[173] and ReI_3 loses I_2 to form a phase which approaches ReI_2 in composition.[469] Both trinuclear and dinuclear clusters of Re^{III} may be reduced without cleavage of the metal–metal bonds, but the products are not very stable. Thus $ReCl_3$ is reduced by nitrogen bases (L) to diamagnetic compounds of stoichiometry $(ReCl_2L)_n$ whose electronic spectra resemble those of trinuclear clusters and which may be oxidized to $Re_3Cl_{11}^{2-}$. They are believed to contain $Re_3Cl_6L_3$ units held stacked above each other by chloride bridges. $Re_3Cl_{12}^{3-}$ [547] and $Re_2Cl_8^{2-}$ [515] may be reduced to Re^{II} polarographically, and $Re_2X_8^{2-}$ by dithiahexane to $[ReBr_2(dth)]_n$ of unknown structure.[508]

The remaining complexes of Re^{II} are mononuclear. Mild oxidation of $ReCl(N_2)(dppe)_2$, $ReCl(N_2)(PR_3)_4$, and $ReCl(CO)(dppe)_2$ gives the corresponding Re^{II} cations $ReCl(N_2)(dppe)_2^+$, $ReCl(N_2)(PR_3)_4^+$, and $ReCl(CO)(dppe)_2^+$.[358] The neutral complexes $ReX_2(diars)_2$, $ReX_2(tas)$, and $ReX_2(qas)$ (X = Cl, Br, and I) are obtained by vigorous reduction of the corresponding Re^{III} cations,[15] and $ReI_4(CO)_2^{2-}$ by treating $ReI_4(CO)_2^-$ with alcoholic potash in acetone.[541] A number of cyanide complexes have been reported but have not been adequately characterized.[548]

V. Abbreviations

acacH	acetylacetone
Ar	aryl
Cp	cyclopentadienide
diars	*o*-phenylenebis(dimethylarsine)
dipy	α,α'-dipyridyl
dmf	*N*,*N*-dimethylformamide
dmpe	1,2-bis(dimethylphosphino)ethane
dmso	dimethyl sulfoxide
dppe	1,2-bis(diphenylphosphino)ethane
dth	2,5-dithiahexane
en	ethylenediamine
hfacH	hexafluoroacetylacetone
hmpt	hexamethylphosphoramide
L	any neutral monodentate ligand
LL	any neutral bidentate ligand
mdt	maleonitriledithiolate dianion
oxineH	8-hydroxyquinoline
phen	*o*-phenanthroline
phenquin	9,10-phenanthraquinone
pic	picoline
PR_3	tertiary phosphine (R may be dissimilar)
py	pyridine
pz	pyrazine
qas	tris(*o*-diphenylaminophenyl)arsine
R	alkyl or aryl
R_2dtc	dialkyldithiacarbamate
tas	bis(*o*-diphenylaminophenyl)phenylarsine
tdpme	1,1,1-tris(diphenylphosphinomethyl)ethane
terpy	α,α',α''-terpyridyl
thf	tetrahydrofuran
tmtu	tetramethylthiourea
tu	thiourea
X	any uninegative monodentate ligand

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