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4. Rhenium

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CONTENTS

INTRODUCTION

This review outlines the progress in rhenium chemistry as reported in the literature for 1991. It is based on a search of Volumes 114, 115 and 116 of *Chemical Abstracts*. In addition, major

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inorganic chemistry journals have been searched separately for the calender year 1991. In general, this review is written with coordination chemists in mind with some references to the organometallic literature. We would like to acknowledge the assistance of Heidi Mercado of the Eastern Michigan University Library with a computerized literature search for this review.

4.1 RHENIUM(VII)

4.1.1 Complexes with hydride ligands

The location of hydrides in $ReH_6(SiR_3)(PPh_3)_2$, R = alkyl or aryl, as well as $ReH_2(EPh_3)(CO)(PMe_2Ph)_3$, (E = Si or Sn) were studied using *ab initio* molecular orbital calculations employing analytical gradients [1]. The approach used was to use the X-ray structures to fit the positions of all the heavy atoms and use the energy gradient optimization technique to find the position of the H atoms. The hydride positions were easily located in the optimized geometries. Analysis of the total valence electron density shows these hydrides to exhibit significant covalent character in the region of the Re-Si bond and weak Si···H interactions. Since silicon is less electronegative, the silyl radical group (SiR_3) donates electron density to the metal-silicon bonding region thereby forming a significantly covalent bond. As a result of this transfer, silicon possesses the ability to attract hydrides in a weak bonding fashion.

4.1.2 Complexes with halide ligands

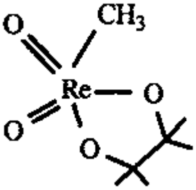
Studies on the characterization of of high oxidation-state oxide fluorides of manganese and rhenium have been reported recently [2]. In particular, MnO_3F, ReO_3F, ReO_2F_3, $ReOF_5$ and $ReOF_4$ have been isolated as molecular species in inert-gas matrices at low temperatures and studied by IR and UV-VIS spectroscopy.

4.1.3 Complexes with oxygen donor ligands

The photochemistry of methyltrioxorhenium(VII) has been reported [3]. The lowest energy ligand-to-metal charge transfer excitation involves the removal of an electron from the CH_3Re σ–bond which splits homolytically. The formation of products is achieved in two ways (i) outer-sphere back electron transfer or (ii) atom abstraction by the methyl radicals.

The preparations of $C_5H_5ReO_3$, the first example within the series $C_5H_5MX_3$ with X representing oxo or imido groups, and its monomethylated derivative have been reported [4]. In a related study [5] the structures, spectroscopy and electrochemistry of methyltrioxorhenium(VII) and trioxo(η^5–pentamethylcyclopentadienyl)rhenium(VII) have been reported. The conclusions from this study are: (i) the three oxygen ligands in ReO_3 make the fragment very flexible in its coordination facilitating stable compounds containing σ- or π- bonded ligands; (ii) the ReO_3 group behaves as a very strong electron withdrawing group and is stereoelectronically comparable with the SO_3H substituent in organic chemistry. The synthesis of the former was achieved by treating an exactly two-fold molar amount of dirhenium heptaoxide with freshly prepared, and sublimed bis(cyclopentadienyl)zinc in THF. It was characterized by ^1H, $^{13}C\{^1H\}$ and IR spectroscopies. Results from NMR spectroscopy indicate that the C_5H_5 ligand is coordinated in a π fashion and IR spectroscopic data support the presence of aromatic π-ligands. Crystal data for both compounds have been reported.

The syntheses of alkylrhenium(VII) and alkylrhenium(VI) oxides have been achieved by reacting methyltrioxorhenium(VII) and aliphatic *vic*-diols such as glycol and pinacol by redox neutral and reductive condensation reactions, respectively [6]. X-ray crystallography shows the mononuclear Re(VII) glycolato complex (**1**) possessing a rhenium atom in a distorted trigonal bipyramidal environment whereas the dinuclear Re(VI) glycolato complex (**2**) possesses an octahedral geometry about the metal atom.



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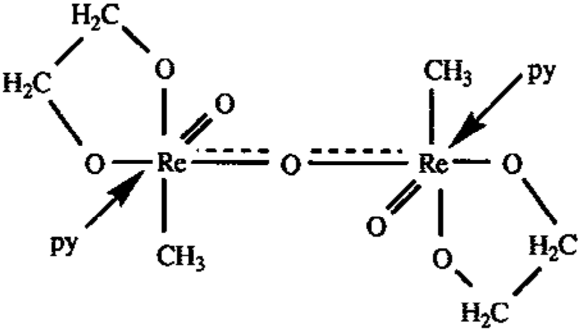

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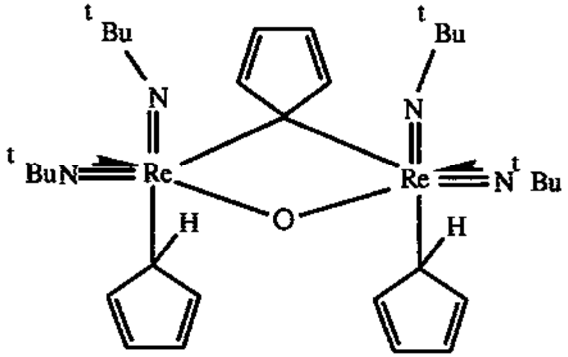
4.1.4 Complexes with oxygen and nitrogen donor ligands

The syntheses, structural characterization and reactivity of two classes of five-coordinate rhenium(VII) monoimido alkylidene complexes have been reported [7]. These complexes are of interest because of their potential as catalysts in olefin metathesis. In particular, alkylidene complexes of the general type $Re(CH^tBu)(NAr)(OAr')_3$ (where NAr = $N\text{-}2,6\text{-}C_6H_3{}^iPr_2$; OAr' = OC_6F_5, $O\text{-}2,6\text{-}C_6H_3Cl_2$, and OC_6Cl_5) were prepared. These complexes are square pyramidal with three phenoxide and one phenylimido ligand in the basal plane while the alkylidene is in the apical position. For the case where OAr' = $O\text{-}2,6\text{-}C_6H_3Cl_2$ the Re-N bond length of 1.74 (1) Å is consistent with the donation of the nitrogen lone pair to form a pseudo triple bond. Complexes of the type $Re(CH^tBu)(NAr)(OAr')Cl_2$ have also been prepared and ^1H and ^{13}C NMR spectroscopic data suggest that they are isostructural with $Re(CH^tBu)(NAr)(OAr')_3$ complexes. These two classes of complex do not react with terminal, internal or strained cyclic olefins, but addition of $GaBr_2$ to some of the halide-containing complexes yields active catalysts that metathesize *trans*-3-heptene.

The known complex $ReO_3(HB(pz)_3$ where $[HB(pz)_3]^-$ is hydrotris(1-pyrazolyl)borate has been prepared by three new methods: (i) the nitric acid oxidation of $(ReOCl_2(HB(pz)_3)$; (ii) the thermolysis of $(ReO(L)(HB(pz)_3)$, where L is ethylene glycolate; (iii) the reaction of $[NH_4][(ReO_4]$ and $[HB(pz)_3]^-$ in acidified methanol [8]. This complex has been characterized by elemental analysis, mass spectrometry, IR and ^1H NMR spectroscopies.

The reaction of NaC_5H_5 in THF with $Re(^tBuN)_3Cl$ in diethyl ether under argon at ambient temperature gave rise to orange, air-sensitive crystals of a compound $\{Re(^tBuN)_2(\eta^1\text{-}C_5H_5)\}_2(\mu\text{-}C_5H_4)(\mu\text{-}O)$ (3) [9]. An X-ray crystal structure of the molecule shows each rhenium to be five-coordinate with a distorted trigonal bipyramidal geometry, the ReCReO ring is folded with a dihedral angle of 30° about the CO direction and by 39° about the ReRe direction. The transannular Re⋯Re and C⋯O distances are 3.20 and 2.45 Å respectively. The ^tBuN groups are non-equivalent with two being a linear triply bridging and the other two bent doubly bridging groups. A unique $C_5H_4{}^{2-}$ group bridges the two Re atoms and the $\eta^1\text{-}C_5H_5$ ligands are fluxional.



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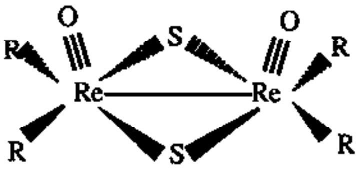
4.1.5 Complexes with nitrogen donor ligands

The synthesis and structure of $Ph_3P{=}NRe(NC_6H_3{}^iPr_2\text{-}2,6)_3$ have been documented [10]. The reaction of Ph_3PNReO_6 with three equivalents of 2,6-diisopropylphenylisocyanate occurs with the evolution of CO_2 to give the title compound. The X-ray crystal structure has been reported and shows the rhenium atom to be in a tetrahedral environment, coordinated to four nitrogen atoms.

4.2 RHENIUM(VI)

4.2.1 Complexes with oxygen and sulfur donor ligands

The syntheses of *syn*-$Re_2(\mu\text{-}O)(\mu\text{-}S)O_2(CH_2CMe_3)_4$, and the *syn*, **(4)**, and *anti*, **(5)**, isomers of $\{Re(\mu\text{-}S)O(CH_2CMe_3)_2\}_2$ have been achieved [11]. X-ray crystallography was used to characterize the isomers of $\{Re(\mu\text{-}S)O(CH_2CMe_3)_2\}_2$. The *syn*-isomer has virtual C_{2v} symmetry while the *anti*-isomer possesses C_{2h} symmetry; the rhenium atom in both isomers having a square-pyramidal geometry with the oxo ligand in the apical position and the basal plane defined by the neopentyl methylene carbons and bridging sulfide groups. The Re-Re bond is 2.871(2) Å for the syn isomer and 2.759 (3) Å for the anti form. The Re-S distances for the two isomers are similar; there is, however, a statistically significant asymmetry in the two Re-S bond distances of the *anti*-isomer: 2.289 (5) *vs* 2.247 (5) Å.



R = CH_2CMe_3

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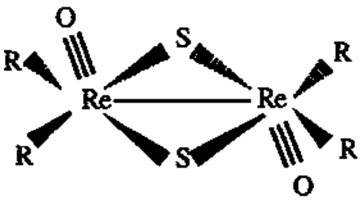


R = CH_2CMe_3

(5)

4.2.2 Complexes with nitrogen donor ligands

The first d^1 *trans*-dioxo complex, $[ReO_2(dmap)_4](PF_6)_2$, (where dmap = 4-(dimethylamino)pyridine) ever isolated has been subjected to EPR spectroscopic analysis in order to examine more closely the electronic structure of the *trans*-dioxo framework [12]. Results from EPR spectroscopy reveal a strong axially compressed tetragonal ligand field associated with the *trans*-dioxo moiety.

4.2.3 Complexes with phosphorus donor ligands

The isolation and structural characterization of the dirhenium complex $O_3ReReCl_2(dmpm)_2$, (dmpm = $Me_2PCH_2PMe_2$), has been reported. This molecule possesses both a disparity in metal oxidation states and a difference in coordination number about each rhenium atom which is unprecedented in the chemistry of metal-metal bonded dimetallic species [13]. The reaction of *cis*-$Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.20g) in ethanol with 0.46 mL of dmpm/toluene at room temperature yielded the insoluble complex, $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dmpm})_2$, which was separated by filtration. The residue was treated with a small volume of acetone yielding an orange-red mixture. This was subsequently dissolved in dichloromethane and the components were separated by column chromatography. The X-ray crystal structure of this complex shows it may be viewed as consisting of a tetrahedral four-coordinate ReO_3-unit coupled to a seven-coordinate pentagonal bipyramidal rhenium unit by means of a very short unsupported Re-Re bond of length 2.4705 (5) Å. Formally, this complex consists of Re(VI) and Re(II) centres which are coupled to give a strong σ-bond. This may be due to the smaller bite angle associated with the chelating dmpm ligand; this facilitates an expansion of the metal coordination number from six to seven, thereby leading to the formation of the metal-metal bond.

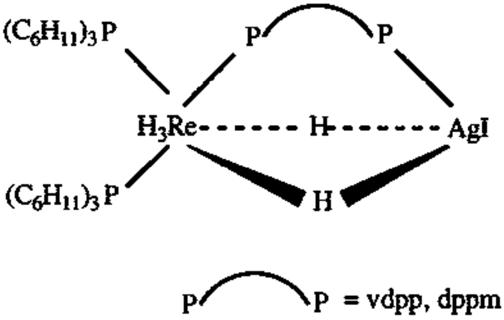
4.3 RHENIUM(V)

4.3.1 Complexes with hydride ligands

A report describing the isolation, synthesis and characterization of the linkage isomers $ReH_5(PPh_3)$(arphos-*P*), and $ReH_5(PPh_3)_2$(arphos-As) and of the analogous $ReH_5(PPh_3)$(dpae-As) where arphos is 1-(diphenylphosphino)-2-(diphenylarsino)ethane and dpae is 1,2-bis(diphenylarsino)ethane has appeared [14]. Results from NMR spectroscopy are given along with crystal data for $ReH_5(PPh_3)_2$(arphos-As) and $ReH_5(PPh_3)$(dpae-As), the latter representing the the first unambiguous determination of the solid-state geometries of complexes of the type $ReH_5(PR_3)_2(\eta^1\text{-L-L})$. The structures are distorted dodecahedra in which the H····H distances are indicative of "classical" hydrides.

The syntheses of new heterobimetallic complexes which are formed by treating a complex of the type $ReH_5\{P(C_6H_{11})_3\}_2$(L-L-*P*) with silver, copper and mercury compounds has been reported

[15]. Treatment of $ReH_5\{P(c\text{-}C_6H_{11})_3\}_2(L\text{-}L\text{-}P)$, (where L-L = $Ph_2PC(=CH_2)PPh_2$, vdpp, or $Ph_2PCH_2PPh_2$, dppm), with silver iodide gave fluxional complexes, **(6)**. Analogous complexes, (7), were prepared using CuCl or CuCN, and variable temperature $^{31}P\text{-}\{^1H\}$ and $^1H\{^{31}P\}$ NMR spectroscopic studies were performed. In contrast, mercury(II) chloride gives an adduct $HgCl_2ReH_5\{P(C_6H_{11})_3\}_2(dppm\text{-}P)$ in which the mercury atom is not complexed to the dppm ligand, but does exhibit nuclear spin-spin coupling to the phosphorus atoms complexed to the rhenium.



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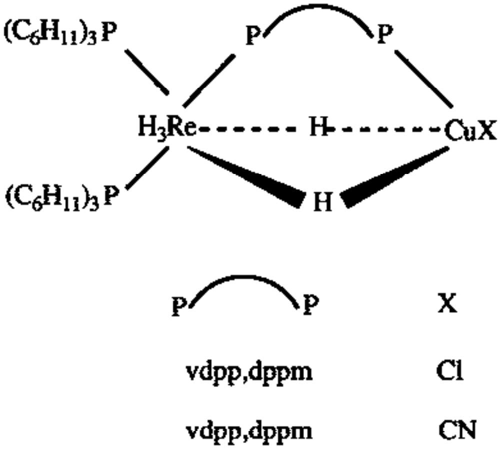

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An investigation of the replacement of phosphine ligands in a polyhydride complex with phosphites has resulted in the synthesis and characterization of several rhenium phosphite and rhenium phosphite hydride complexes [16]. The coordination chemistry of rhenium with the cyclic phosphite 2-ethyl-2,6,7-trioxa-1-phospha-bicyclo[2,2,2]octane, $P(OCH_2)_3CEt$, (ETPB), has been studied. The complexes $ReH_5(ETPB)_2(PPh_3)$ and $ReH_5(ETPB)_3$ were prepared from halide precursors and have been characterized by IR and ^1H NMR spectroscopies. Variable temperature NMR spectroscopis results and spin-lattice relaxation data for these complexes indicate that η^2-H_2 ligands are not present.

4.3.2 *Complexes with halide ligands*

The spectroscopic characterization of the octachlorodirhenate(3–) ion, $[Re_2Cl_8]^{-}$ has been reported [17]. Optical absorption, near IR and ESR spectra are presented. The results are consistent with the presence of an Re_2^{5+} core possessing the electronic configuration $\sigma^2\pi^4\delta^2(\delta^*)^1$.

The structure of $K_2[ReCl_5O]$ has recently been obtained [18]. The anion has crystallographic point symmetry *m* (C_s), with the Re-O bond length being 1.655 (6) Å. The Re-Cl bond length of 2.502 (2) Å) for the bond *trans* to the oxygen atom is longer than the Re-Cl_{cis} distances of 2.371 (2) to 2.382 (2) Å.

4.3.3 *Complexes with oxygen donor ligands*

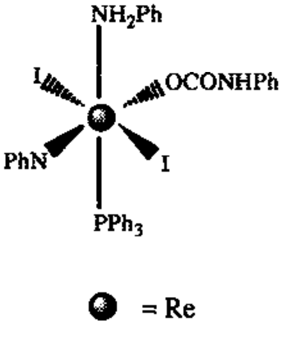
A complex of the type $MOCl_3L.H_2O$ where L is 18-crown-6 has been prepared [19]. The hydrolysis of this complex in HCl solution was studied and the hydrolysis product $(H_3O)[ReOCl_4(H_2O)]L$ was characterized by X-ray crystallography. The metal atom is in an octahedral environment with the chloride ligands in the equatorial positions and the oxo atom and the water molecule occupying the axial positions. The complex anions, cations, and crown ether molecules are linked together in a framework consisting of a branched system of hydrogen bonds.

4.3.4 *Complexes with oxygen and nitrogen donor ligands*

The synthesis and structural characterization of eight-coordinate geometrical isomers of $[ReH_2(mhp)_2(PPh_3)_2]PF_6$ where mhp represents the monoanion of 2-methyl-6-hydroxypyridine, the first reported instance where stereoisomers retain their structural identity in solution.has appeared [20]. In addition, this work is noteworthy because geometrical isomerism has been identified for a polyhydride system of a type that is more notorious for exhibiting stereochemical non-rigidity. On the basis of crystallographic data and ^1H NMR spectral data both isomers appear to be classical dihydrides. In a related paper [21], the isolation and structural characterization of the salt $[ReO(mhp)_2(PPh_3)_2]PF_6$ has been discussed. The cation is the first example of a mononuclear monooxorhenium(V) complex with a rhenium atom of coordination number greater than six. The coordination geometry is based on a distorted pentagonal bipyramid with the oxo ligand occupying a position within the pentagonal plane. In addition, the formation of Re(IV) and Re(III) hydrido complexes with hydroxypyridine and mercaptopyridine ligands has also been presented.

The reactions of iminobis(diphenylphosphine oxide), $NH(OPPh_2)$, and iminobis(diphenylphosphine sulfide), $NH(SPPh_2)_2$, with the $\{ReO\}^{3+}$ core-containing rhenium(V) complexes $ReOCl_3(PPh_3)_2$, $ReOCl_2(OEt)(PPh_3)_2$ and $[AsPh_4][ReOCl_4]$ have been investigated and the products characterized [22]. When reacted with an excess of $NH(OPPh_2)$, the complexes $ReOCl_3(PPh_3)_2$ and $ReOCl_2(OEt)(PPh_3)_2$ gave $ReOCl_2\{N(OPPh_2)_2\}(PPh_3)$. When the donor atoms were changed by using $NH(SPPh_2)_2$, the mono- and di- substituted complexes $ReOCl_2\{N(SPPh_2)_2\}(PPh_3)$ and $ReOCl_2\{N(SPPh_2)_2\}_2(PPh_3)$ were obtained. The latter complex was also prepared by using the anionic complex $[ReOCl_4]^-$ as the starting material. When this complex was crystallized from CH_2Cl_2/EtOH, the complex $ReO(OEt)\{N(SPPh_2)_2\}_2$ was obtained. X-ray crystallographic studies were performed on some of these complexes; the rhenium atoms show slightly distorted octahedral geometries.

Efficient new synthetic routes to *cis*-$[(O)_2Re(bpy\text{-}Y_2)(py\text{-}X)_2]^+$ and *trans*-$[(O)_2Re(py\text{-}Y)_2(py\text{-}X)_2]^+$, (py = pyridine, bpy = bipyridine), by means of the intermediate species $(O)_2Re(py\text{-}Y)_2(I)_2$ have been reported [23]. The most useful new features of the synthetic chemistry are (i) *trans*-species containing electron-withdrawing substituents on the pyridyl ligands can now be prepared, and (ii) mixed-ligand *trans*-dioxorhenium species can also be prepared, and (iii) a generalized *cis*-dioxorhenium preparation is now available. These complexes are useful for the study of multi-electron transfer kinetics at electrochemical interfaces.



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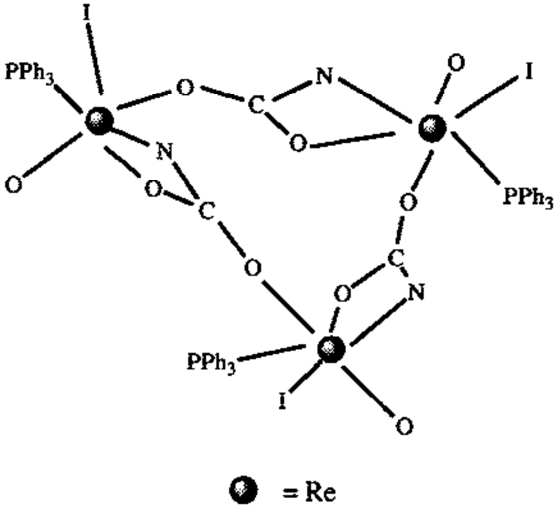
The reaction of PhNCO with oxo ligands at metal centres has been studied [24]. The reaction of PhNCO with $ReO_2I(PPh_3)_2$ gave a trimeric complex $\{ORe(OCONPh)I(PPh_3)\}_3$, (9), in which the PhNCO moiety was added to an oxo ligand to form an *N*-phenyl carbamato group. This group is a bridging ligand, chelating one rhenium atom through its *N*- and *O*-atoms, and coordinating to a second rhenium atom by means of its second *O*-atom. From the mother liquor, another compound is isolated; this is $Re(NPh)(NH_2Ph)I_2(PPh_3)(OCONHPh)$, (8), formed as a partial hydrolysis product. Here, the rhenium atom possesses octahedral coordination with the two iodine atoms in a *trans* arrangement and the phenyl nitrene *trans* to the monodentate $PhNHCO_2$

group. The coordination sphere is completed by a phosphine and an aniline ligand; the phenyl nitrene ligand is bound by an Re-N triple bond of length 1.72 Å. Upon exposure to air at room temperature, a THF solution of $\{ORe(OCONPh)I(PPh_3)\}_3$ converts to $Re(NPh)(NH_2Ph)(I)_2(PPh_3)(OReO_3)$. This complex may be viewed as an analogue of (9) in which the carbamato ligand is substituted by a perrhenato ligand.



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The reaction of $[ReOCl_4]^-$ with Schiff base ligands derived from salicyaldehyde and 1,5-diaminopentane (L) have been investigated [25]. In particular, the X-ray crystal structure of [*N,N'*-3-azapentane-1,5-diylbis(salicylideneiminato)(3–)-*O,O',N,N',N''*]oxorhenium(V) has been obtained; the complex consists of distorted ReOL-units in which one oxygen atom of the N_3O_2-pentadentate ligand is located *trans* to the rhenium-oxo oxygen bond. The remaining four coordinating atoms lie on the equatorial plane of the octahedron assuming that the oxo-oxygen atom occupies an apex. The Re-O bond lengths are 2.09 (1) and 2.14 (1) Å, while the Re-N bond lengths are 2.06 (1), 1.91 (1) and 2.04 (1) Å.

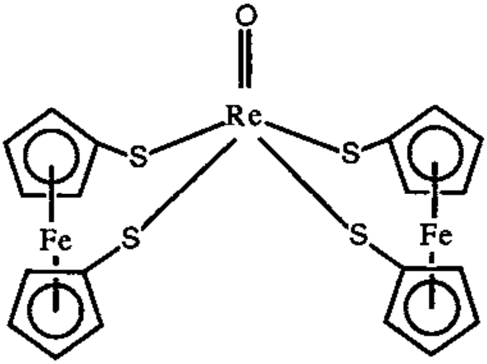
The coordination of the unsaturated N_2S_2-type ligand, *N,N'*-ethylenebis(thioacetylacetonylideneimine), (H_2L), to the $[MO]^{3+}$, M = Re or Tc, has been studied [26]. Neutral complexes of the general formulae MO(L)Cl and $\{MO(L)\}_2O$ have been synthesized and characterized by elemental analysis, IR UV-VIS, FAB mass and NMR spectroscopies. The monoxo monomeric complexes rearrange to the μ-oxo dimeric species via a charged labile intermediate in wet organic solvents or when solutions are kept in contact with air. The influence of the ligand on ^1H NMR chemical shifts is described with technetium shifting ligand protons more downfield than rhenium in agreement with the stronger acidity of the $[TcO]^{3+}$ with respect to the $[ReO]^{3+}$ core.

The reaction of *N*-{2(1*H*-pyrolylmethyl)}-*N'*-(4-pentene-3-one-2)ethane-1,2-diamine with $ReOCl_3(PPh_3)_2$, a rhenium(V) glycolato precursor, or $[Bu_4N][TcO(ethylene\ glycolate)_2]$ yielded complexes of the type ReOL or TcOL [27]. These complexes have been studied using IR, UV-VIS, and ^1H NMR spectroscopies and mass spectrometry. For the case of the complex of technetium, a crystal structure indicates a five-coordinate square based pyramidal geometry.

The reactions of $[ReOCl_4]^-$ with polydentate ligands containing sulfur or phosphorus as "soft" donor atoms in combination with aryloxo and amine or imine nitrogen as "hard" ligating sites has been studied [28]. The complex $ReOCl_2\{OC_6H_4\text{-}2\text{-}CHN{=}(CH_2)_3PPh_2\}$ and its reduced counterpart $ReOCl_2\{OC_6H_4\text{-}2\text{-}CH_2NH(CH_2)_3PPh_2\}$ have been prepared and their crystal structures determined. Both complexes are neutral monomeric compounds in which the rhenium atom is in an octahedral environment. In both cases the phenolic oxygens (Re-O = 1.943 (7) and 1.953 (9) Å respectively) coordinate *trans* to the oxo group (Re=O 1.680 (7) and 1.695 (9) Å, respectively). A lengthening of the Re-N distance occurs upon reduction of the ligand Re-N(H) = 2.224 (8) Å Re-N = 2.111 (11) Å with a concomitant decrease of 12.7° in the Re-N=C(sp^2) bond angle.

4.3.5 Complexes with sulfur donor ligands

The reaction of $ReOCl_3(PPh_3)_2$ with 1,1'-dithiolatoferrocene in refluxing methanol under nitrogen in the presence of diethylamine gave a clear orange-brown solution. Addition of $[PPh_4]Br$ and recrystallization from dichloromethane/diethylether gave brown crystals of $[PPh_4][ReO\{Fe(C_5H_4S)_2\}_2]$, **(10)** [29]. These complexes were characterized by ^1H NMR and IR spectroscopies, cyclic voltammetry and elemental analysis. The complex has been assigned a square pyramidal geometry.



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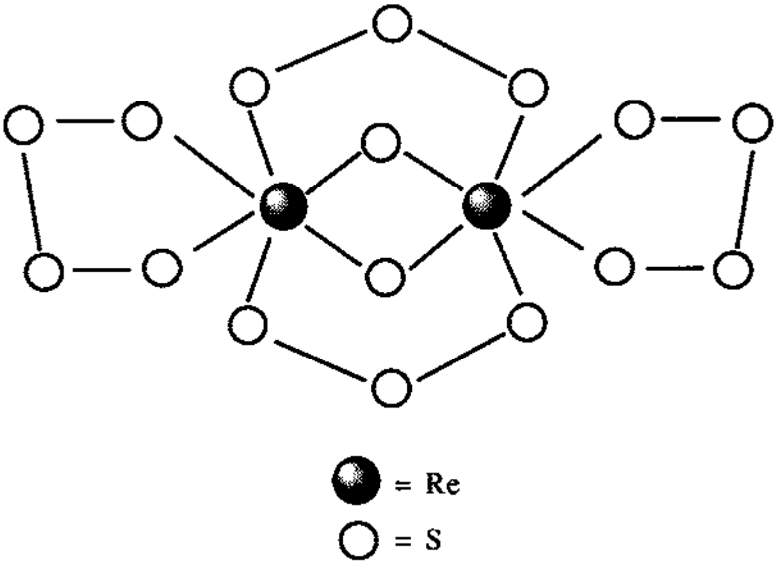
The X-ray crystal structure of the *syn-endo*-isomer of $[NEt_4][ReO(dmsa)_2]\cdot 1\frac{1}{2}H_2O$, where H_2dmsa = *meso*-2,3-dimercaptosuccinic acid, which in radiopharmaceutical form has been shown to localize in certain human tumours, has been reported [30]. The rhenium atom is in a square-pyramidal configuration. The orientation of the carboxylic acid ligands is consistent with the ^1H NMR spectrum with no evidence of any interaction between them and the metal centre trans to the oxo-ligand or of their protons with the oxo-ligand. There are significant interactions between the rhenyl oxygen atom and two methylene hydrogen atoms of the tetramethylammonium ion forming a loose ring structure with O······H contacts of 2.434 and 2.460 Å. Isomerization was studied in aqueous solution using NMR spectroscopy and HPLC and found to be pH dependent. The results suggest that thiolate ligand exchange is acid catalysed and show that the isomeric composition of radiopharmaceutical preparations can be determined which is useful for biological studies which aim to identify the biodistribution of isomers.



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The reaction of ammonium perrhenate with an aqueous ammonium poly-sulfide solution at room temperature gave black crystals of a dimorphous salt $(NH_4)[Re_2S_2(S_3)_2(S_4)_2].4H_2O$, **(11)**, a novel sulfide in which the metal-metal bond has largely double-bond character [31]. This was characterized by elemental analysis, thermogravimetry (H_2O content), UV-VIS, near IR and IR spectroscopies, X_α-MO calculations and powder diffractometry. In addition, single crystal structure analyses were carried out on two crystal modifications. The idealized symmetry in both cases is C_{2h}. The anions in both cases comprise two rhenium atoms which are linked by two μ_2-S^{2-} ions and two S_3^{2-} ligands. In addition, each rhenium atom possesses a chelating S_4^{2-} ligand to give a distorted octahedral coordination environment. The Re_2S_3-rings are present in an "envelope" conformation; the ReS_4 form approximate 'half-chair' conformations in the first modification and exact "half-chair" conformations, symmetric about the two-fold axis in the second modification. The eight-membered Re_2S_6-ring has a strong transannular interaction. It possesses unusual electronic properties owing to the very similar energies between the Re *5d* and S *3p* functions which give rise to high Re-S bond orders. In addition, all "Re-containing" molecular orbitals are so strongly stabilized that also orbitals with partial δ, δ^* and π^* character are populated and a concomitant weakening of the Re-Re π bond occurs. Its redox behaviour is in accord with considerable electronic delocalization and it is thought that the S_x^{2-} ligands probably oxidize rhenium(V) to rhenium(VII). Treatment of this compound in the presence of air at 90°C with an aqueous KCN solution gave rise to $[Re_2(SO_2)_2(CN)_6]^{6-}$ with reduction of rhenium(V) to rhenium(III).

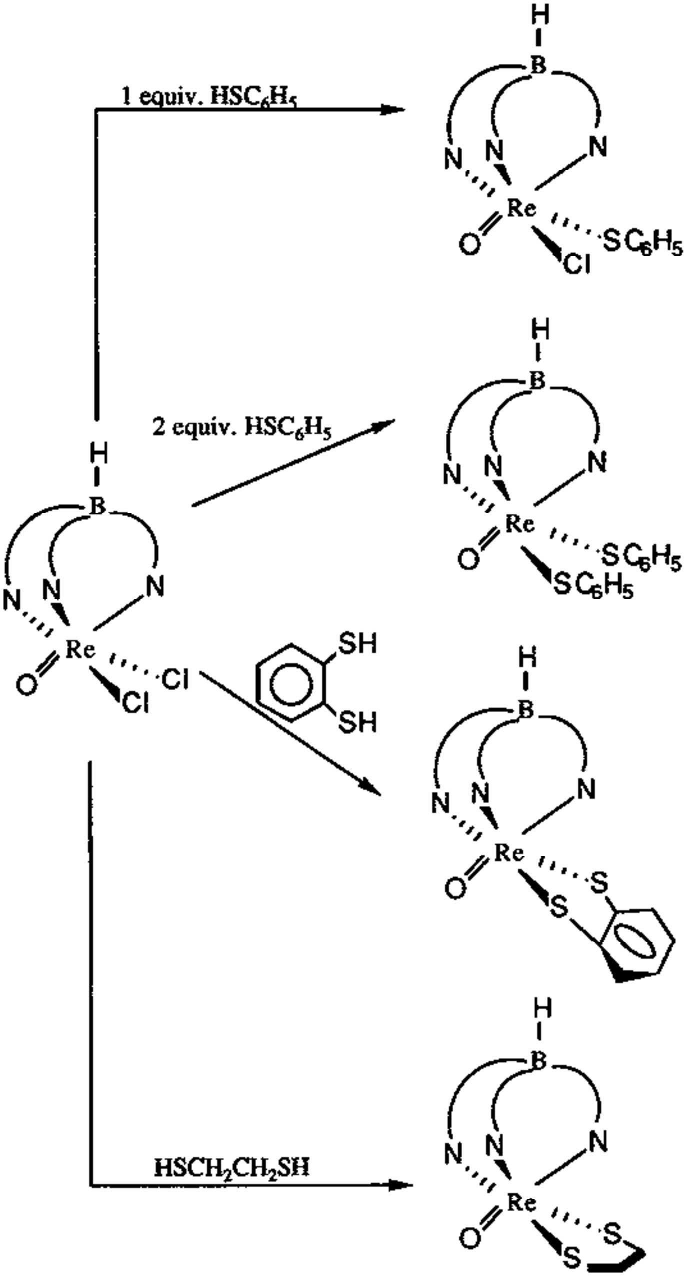
4.3.6 Complexes with nitrogen donor ligands

The coordination chemistry of rhenium(V), (IV), and (III) with the macrocyclic triamines 1,4,7-triazacyclononane (L, $C_6H_{15}N_3$) and 1,4,7-trimethyl-1,4,7-triazacyclononane (L', $C_9H_{21}N_3$) has been investigated [32]. The crystal structures of $[LReCl_3]Cl$, $[L_2Re_2Cl_2(\mu\text{-}Cl)(\mu\text{-}OH)]I_2{\cdot}2H_2O$, $[L_2Re_2I_2(\mu\text{-}O)_2]I_2{\cdot}2H_2O$, and $[L'_2Re_2Cl_4(\mu\text{-}O)][ZnCl_4]$ have been reported and all new compounds have been characterized by UV-VIS and NMR spectroscopies, magnetic susceptibility and cyclic voltammetry. The dinuclear complexes exhibit multiple metal-metal bonding with Re-Re distances which are dependent on the oxidation state of the rhenium centers and the π-donor capacity of the ligands.

High oxidation state rhenium complexes containing the Cp^*ReMe_3 core and NH_x or N_2H_y were synthesized and found to be reasonably stable [33]. It was found that N-N bond cleavage in $ReCp^*Me_3(NH_2NH_2)$ may be a controlled reaction as is the case in $MCp^*Me_3(\eta^2\text{-}NH_2NH_2)$ (M = Mo, W).

The complex $\{HB(pz)_3\}ReO$ (where $HBpz_3$ is the hydrotris(1-pyrazolyl)borato ligand) which may be viewed as an analogue of $(\eta^5\text{-}C_5Me_5)ReO$, has been used in the improved synthesis of the already known complex $\{HB(pz)_3\}ReOCl_2$, as well as the synthesis of $\{HB(pz)_3\}ReOBr_2$ [34]. In addition the syntheses of four novel thiolato derivatives from $\{HB(pz)_3\}ReOCl_2$, **(12)**, are reported.

Interest in N_3S-chelates of rhenium stems from their potential utility in radiotherapeutic applications and the first report of the structural characterization of a rhenium(V)-N_3S complex has appeared [35]. The complex was formed in the reaction of $ReO_2(en)Cl_2$ or rhenium(V) citrate with mercaptoacetylglycylglycylglycine), (MAG_3), at a pH of 10. It was isolated as salts $X[ReO(MAG_3)]$, where $X^+ = Bu_4N^+$, Ph_4As^+. The complex $[Ph_4As][ReO(MAG_3)]$ was characterized by IR and UV-VIS spectroscopy, elemental analysis and mass spectroscopy whereas $[Bu_4N][ReO(MAG_3)]$ was characterized by ^1H NMR spectroscopy and single crystal X-ray structural determination. The rhenium atom is bound to three amido nitrogen atom, a sulfur atom (thiolate) and an oxygen atom in a distorted square pyramidal geometry. The average Re-N bond distance is 2.00 ± 0.02 Å, while the Re-S bond is 2.29 (1) Å.


1 equiv. HSC$_6$H$_5$
2 equiv. HSC$_6$H$_5$
HSCH$_2$CH$_2$SH
H
B
N
Re
O
Cl
SH
SH
SC$_6$H$_5$
S

(12)

A series of new complexes of the type *trans*-[NRe(RPCH$_2$CH$_2$PR$_2$)$_2$X]$^+$ (R = Me, X = Cl, Br; R = Et, X = Cl) has been prepared. These are the first rhenium nitrido complexes to exhibit fluid-solution luminescence at room temperature [36]. These complexes were characterized by elemental analysis, IR and ^{31}P and ^{1}H NMR spectroscopies. The excitation and emission spectra of this complex in a number of solvents have been recorded and are discussed. In addition, cyclic voltammetry studies have been conducted and the data obtained permit estimates of one-electron redox potentials of the excited state to be made.

The synthesis and reactivity of the species [Re(N-2,6-C$_6$H$_3$-^{i}Pr$_2$)$_3$]$^-$ and the X-ray structure of Hg{Re(N-2,6-C$_6$H$_3$-^{i}Pr$_2$)$_3$}$_2$ have been reported [37]. The reaction of Re(N-2,6-C$_6$H$_3$-^{i}Pr$_2$)$_3$Cl with 1 equiv. of sodium amalgam gave the pentane-soluble Hg{Re(N-2,6-C$_6$H$_3$-^{i}Pr$_2$)$_3$}$_2$ in which the Hg-Re distance is 2.671 (1) Å consistent with a single bond. The linear imido ligands are arranged in a "propeller" fashion such that both ends of the molecule are staggered with respect to each other. The Re=N distances are 1.737 Å and the Hg-Re-N bond angle is 97.4° indicative of a trigonal planar geometry. The chemistry reported for the anion provides evidence for the enhanced stability of d^2 trigonal-planar tris(imido) species.

The crystal structure of (PPh$_4$)$_3$[ReN(CN)$_5$]$\cdot$7H$_2$O has been determined from three-dimensional X-ray diffraction data [38]. The rhenium atom possesses a distorted octahedral geometry and is displaced out of the plane formed by the four carbon atoms of the cyano ligands by 0.31 Å. The rhenium nitrogen triple bond length is 1.68 (1) Å which is considerably longer than in [ReN(CN)$_5$]$^{3-}$ may be attributed to the large *trans* influence of the cyano ligand. The Re-C$_{av}$(planar) = 2.12 (1) and Re-C(axial) = 2.39 (1) Å the large difference in length being due to the very strong *trans* influence of the nitrido ligand.

4.4 RHENIUM(IV)

4.4.1 Complexes with halide ligands

The electrochemical parametrization of rhenium redox couples has been reported [39]. The observed rhenium potentials for Re$^{IV/III}$, Re$^{III/II}$, and Re$^{II/I}$ reversible couples for mononuclear species have been analysed in terms of an electrochemical parametrization scheme based on Ru$^{III/II}$ couples. Two independent lines are observed for Re$^{II/I}$ couples and the lines for Re$^{III/II}$, and Re$^{II/I}$, if extended, would cross. The Re$^{IV/III}$ line is approximately parallel to one of the Re$^{II/I}$ lines. This analysis is discussed in the light of future synthetic studies.

A low temperature spectroelectrochemical study of (Bu$_4$N)[Re$_2$Cl$_9$] and (Bu$_4$N)$_2$[Re$_2$Cl$_8$] has resulted in the identification of new species [40]. In particular, [Re$_2$Cl$_8$]^0, [Re$_2$Cl$_9$]^0, [Re$_2$Cl$_9$]$^{3-}$ and transient [Re$_2$Cl$_9$]$^{4-}$ have been identified.

4.5 RHENIUM(III)

4.5.1 Complexes with hydride ligands

The complex $ReCl(H_2)(PMePh_2)_4$ was studied by means of variable-temperature ^1H and $^{31}P\{^1H\}$ NMR spectroscopies in CD_2Cl_2, CD_3COCD_3, and toluene-d_8 in an effort to gain more information about the exact nature of the dihydrogen ligand [41]. In this complex which comprises four $PMePh_2$ ligands in the equatorial plane and a chloride *trans* to an H_2 ligand, metastable conformational isomers based on rotational orientations about the Re-P bonds may arise. In this study, the percentages of conformational isomers formed was found to be a function of the solvent used. Crystallization under different conditions gave rise to $ReCl(H_2)(PMePh_2)_4 \cdot 2C_4H_8O$, (a), at 292 and 193 K, $ReCl(H_2)(PMePh_2)_4 \cdot 0.5(CH_3)_2CO$, (b), and $ReCl(H_2)(PMePh_2)_4 \cdot 0.5(CH_3)_2CO$, (c), which were studied using X-ray crystallography. In forms (a) and (b) the main molecule was ordered and the final difference maps revealed two electron density maxima near the Re atom which could be representative of two hydrogen atoms bonded to the Re atom in an η^1-H_2 mode. For both data sets for form (a), the hydrogen atoms failed to refine freely to reasonable values but the positions of these atoms from the difference maps have been reported. In form (b), refinement of the H_2 ligand proceeded satisfactorily and shows an H-H distance of 1.17 (13) Å, which is among the longest reported so far. The Re-H(1) and Re-H(2) distances of 1.49 (9) Å and 1.98 (9) Å respectively suggest an asymmetric location. Form (c) was found to have disorder between the *trans* chloride and η-H_2 ligands.

4.5.2 Complexes with halide ligands

The electrochemical reduction of Re_3Cl_9 containing the Re_3^{9+} core, in aqueous 6M HCl gave a purple oxygen-sensitive but thermally stable solution from which the singly reduced Re_3^{8+} anions $[Re_3Cl_{12-n}]^{(4-n)-}$ are isolated [42]. This was reacted with sulfuric acid to yield black crystals of a compound which, when analysed by X-ray crystallography, was found to have the formulation $Cs_3[Re_3Cl_9(SO_4)]$. This compound consists of a triangle of rhenium atoms with a sulfato ligand capping the trimetal unit, each rhenium has two terminal and two bridging chloride ligands.

The first ternary rhenium(III) halide with a chain structure has been obtained [43]. Evaporation of a hydrobromic acid solution of rhenium tribromide and rubidium bromide results in dark red-brown single crystals of $Rb[Re_3Br_{10}]$. Its crystal structure shows it to be built up of chains along [010] of $[Re_3Br_{12}]$ units that are connected by two edges anionic chains which are held together by rubidium ions. Each cation is surrounded by eight bromide ions at distances ranging from 3.32Å and 3.68Å with four additional bromide ions at 4.01 Å and 4.27 Å. In a related paper [44], dark red-brown crystals of $[Rb_2(H_2O)_2][Re_3(\mu\text{-}Cl)_3Br_7(H_2O)_2]_2 \cdot H_2O$ were obtained from a hydrobromic acid solution of $ReCl_3$ and ReBr at 0°C. This crystal has an important feature in that two anions of $[Re_3(\mu\text{-}Cl)_3Br_7(H_2O)_2]^-$ are connected *via* a water molecule to give the dimers

$\{[Re_3(\mu\text{-}Cl)_3Br_7(H_2O)_2]^{-}{}_2.H_2O\}$. The dimers are contained in slabs that are stacked in the [001] direction and are held together by Rb^+ cations and water of crystallization.

4.5.3 Complexes with oxygen donor ligands

The luminescence and absorption spectroscopic properties of $Re(O)I(C_2R_2)_2$ $R = CH_3$, C_6H_5, and $[Re(O)PPh_3(C_2(CH_3)_2)]SbF_6$ have been studied [45]. Both compounds exhibit broad, unstructured luminescences with band maxima near 15,000 cm^{-1} (20K) and lifetimes of 10 μs. The absorption spectra display three bands at 19,000, 24,000 and 28,000 cm^{-1} which have been assigned to *d-d* transitions on the basis of their intensities.

Recently, three new dicarboxylatodirhenium(III) compounds have been inadvertently prepared and their structures characterized [46]. The compound *cis*-$Re_2(O_2CPh)_2Cl_4(THF)_2.THF$, (**13**), adopts a *cisoid* disposition of the carboxylate groups. The compound *cis*-$[(n\text{-}C_4H_9)_4N][Re_2(O_2CCH_3)_2Cl_5].(CH_3)_2CO$, (**14**), is an example of a compound which appears to have a single axial ligand but in which sharing occurs to form infinite chains with the carboxylate ligands having a *cis* arrangement. The compound $[ReCl_2(dpcp)_2][Re(O_2CPh)_2Cl_6].CHCl_3$, (**15**), (where dpcp = (±)-*trans*-1,2-bis(diphenylphosphino)cyclopentane), has been structurally characterized; the dianion contains the first example of an axially coordinated species with a *transoid* arrangement of the carboxylate ligands.

4.5.4 Complexes with sulfur donor ligands

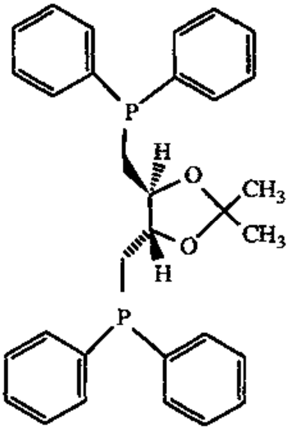
The mixed-ligand rhenium(III) complex cations *trans*-$[Re(SR)_2(R'_2PCH_2CH_2PR'_2)_2]^+$ (where $R = CH_2CH_3$, $CH_2C_6H_4\text{-}p\text{-}OCH_3$ $CH_2C_6H_5$, $C_6H_4\text{-}p\text{-}CH_3$, C_6H_5, $C_6H_4\text{-}p\text{-}Cl$, and $R' = CH_2CH_3$, C_6H_5) have been synthesized and characterized by FAB mass spectroscopy, UV-VIS spectroscopy, cyclic voltammetry and elemental analyses [47]. Single crystal analyses for three cases show that these complexes have a *trans* geometry with similar Re-S (2.303, 2.305 and 2.321 Å) and Re-P (2.45, 2.45 and 2.47 Å) bond lengths.

4.5.5 Complexes with nitrogen donor ligands

The frontier orbital approach has been used to study the structures of linear, bent and side-on dinitrogen fragments coordinated to transition metal centres [48]. The linear M-N-N structures have been discussed on the basis of $ReCl_3(PR_3)_3NNR'$; the main interactions between the $\{NNR'\}^-$ fragment and the $\{ReCl_3(PR_3)_3\}^+$ unit are between the antibonding $\pi^*_{N\text{-}N}$ and the metal d_{xz} and d_{yz} orbitals. The presence of a two-orbital four-electron interaction in bent complexes causes long M-N bond lengths in comparison to linear complexes.

4.5.6 Complexes with phosphorus donor ligands

An effort to extend the scope of reductive coupling chemistry to group 7 metals has resulted in the synthesis of mixed-halo phosphine isocyanide complexes of general formula $[ReCl_2(CNR)_3(PMePh_2)_2]^+$ [49]. The crystal structure of a representative member of this class, $[ReCl_2(CN^tBu)_3(PMePh_2)_2][SbF_6]$, has been determined and reveals a C_{2v} capped trigonal prismatic geometry with close non-bonded contacts of 2.341 (8) and 2.330 (9) Å between the coordinated isocyanide carbon atoms which suggest that this complex would be a good candidate in reductive coupling of isocyanide ligands. The synthesis of $ReCl_3(CN^tBu)_2(PMePh_2)_2$ and $ReCl_3(CN\text{-}2,6\text{-}Me_2Ph)_3(PMePh_2)$ are also described. A side product $ReCl_2O(OEt)(PMePh_2)_2$, formed during the synthesis of the starting material $ReCl_3(PMePh)_3$ was also characterized by X-ray crystallography.



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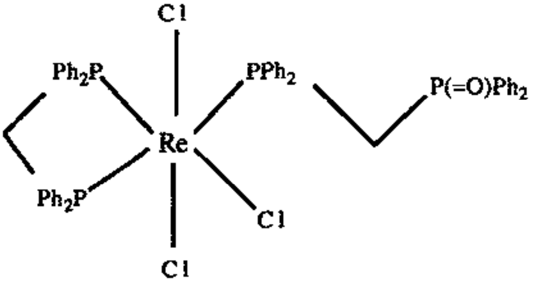
The first chiral complex containing an Re-Re quadruple bond in which a diphosphine ligand bridges the rhenium atoms in an unprecedented arrangement has been reported [50]. In particular, the reaction of $Re_2(O_2CCH_3)_2Cl_4$, $(CH_3)_3SiCl$ and (*S,S*)-diop, **(16)**, in THF at room temperature gave a yellow-green solid which, upon recrystallization from CH_2Cl_2, yielded a pink-red complex β-Re_2Cl_6(*S,S*)-isodiop. Its structure was determined by X-ray crystallography and shows that one oxygen and one phosphorus atom of the ligand are coordinated to the rhenium centres which have an Re-Re distance of 2.224 (2) Å. The Re-O distance is 1.94 (3) Å while the Re-P distance is 2.447 (11) Å. Comparison of the free and uncoordinated ligand shows that it has undergone a rearrangement which is thought to be due to the Lewis acidity of the Re^{3+} metal centers. The attack of the Re^{3+} ion on the oxygen atom promotes C-O bond breaking and the high basicity of the uncoordinated phosphorus atom with the developing charge on the carbon, results in the formation of a stabilized phosphonium-oxo Zwitterion. This rearrangement of the diop ligand to isodiop is similar to the acid catalyzed rearrangement of acetals. The UV, IR and CD spectra of this complex are discussed.

The syntheses of several new rhenium(V) trihalide oxide and rhenium(III) trichloro-complexes containing diphosphine and diphosphine monoxo ligands have been reported [51]. These complexes have been characterized by IR, and ^1H and ^{31}P NMR spectroscopies. The ^1H NMR spectra of the rhenium(III) complexes reveal large paramagnetic shifts for the methylene protons of the chelated dppm and for some of the *ortho*-protons. Some of these resonances were assigned using two-dimensional correlation and Nuclear Overhauser Effect experiments. The crystal structure of *mer*-$ReCl_3$(dppm-*P,P'*)(dppom-*P*), (**17**), (dppm = $Ph_2PCH_2PPh_2$, dppom = $Ph_2PCH_2P(=O)Ph_2$] has been determined and it shows that the rhenium atom is in an octahedral environment with a *mer* arrangement of the chlorine atoms. The dpm ligand is chelated while the dppom ligand is monodentate, coordinating through a phosphorus atom with the P=O group being uncoordinated.

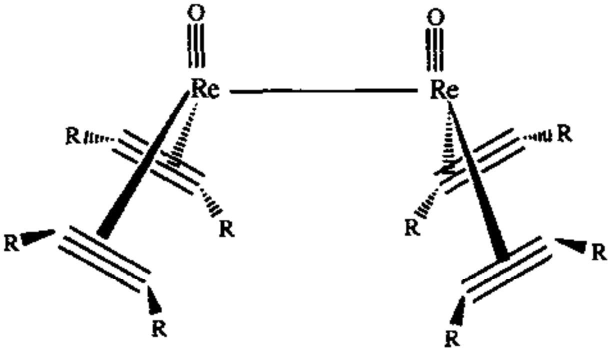


(**17**)

4.6 RHENIUM(II)

4.6.1 Complexes with oxygen donor ligands

The reduction of the rhenium(III) complexes $Re(O)I(R_2C_2)_2$ with a wide variety of reducing agents (^tBuZnCl, $NaC_{10}H_8$, and Cp_2Co) gave rise to mixtures of isomeric dimers $Re_2(O)_2(R_2C_2)_4$ [52]. One of the isomers is the symmetric complex (**18**), and comprises two $Re(O)(R_2C_2)$ fragments connected by an unsupported Re-Re bond (Re-Re = 2.686 (1) Å for R = Me). These dimers are likely to be the product of the coupling of two rhenium(II) radicals. The other isomer, which is asymmetric (R = Et), (**19**), contains a terminal and bridging oxo ligand, and an unusual twisted bridging acetylene ligand which is twisted 34° with respect to the Re-Re bond, and is best described as a mixed-valence Re(III)/Re(I) complex. Upon heating, the asymmetric form converts to the symmetric form and the latter when reacted with I_2 forms $Re(O)I(R_2C_2)$, (the initial starting reactant), all without scrambling of the acetylene ligands between rhenium centres. The acetylene ligands on the Re(I) side of the complex are fluxional displaying a "turnstile" rotation that exchanges two carbon sites.



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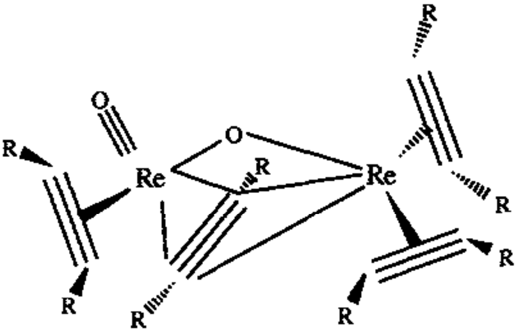

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A study examining the lability of the bridging carboxylate and axial halide ligands in *cis*-$Re_2(O_2CR)_2Cl_2(dppm)_2$ (R = CH_3, C_2H_5, dppm = $Ph_2PCH_2PPh_2$) to substitution by nitrile-containing ligands has been documented [53]. In particular, the full structural characterizations of $[Re_2Cl_3(\mu\text{-dppm})(1,2\text{-}C_6H_4(CN)_2)_2][PF_6]$ and *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2(NCBH_3)_2(\mu\text{-dppm})_2$ have been detailed. In the former, the two dinitrile ligands are bound in a monodentate fashion and the Re-Re distance is 2.265 (1) Å, while in the latter complex, the Re-Re bond length is 2.2938 (7)Å.

The preparation and characterization of several mixed-alkyl carboxylate dmpm, dmpm = $Me_2PCH_2PMe_2$ complexes that are derivatives of the dirhenium(II,II) and -(III,II) cores has been reported [54]. These complexes have been produced by the reactions between $Re_2(O_2CR)_4X_2$ (X = Cl, Br; R = CH_3, C_2H_5) and the bridging phosphine ligand dmpm in ethanol/toluene gave the diirhenium complexes $[Re_2(O_2CR)X_2(dmpm)_3]X$ which undergo anion exchange with $[^nBu_4N][PF_6]$. These complexes are formed through the intermediacy of the paramagnetic species *trans*-$[Re_2(O_2CR)_2X_2(dmpm)_2]^+$, which has been isolated as a $[PF_6]^-$ salt for the case of X = Cl and R = CH_3. A single-crystal X-ray analysis of $[Re_2(O_2CCH_3)Cl_2(dmpm)_3]Cl.2H_2O.CH_2Cl_2$ shows it to contain four bridging ligands (one acetate and three dmpm ligands) and two axially bound chlorides with an Re-Re bond distance of 2.304 (1) Å.

4.6.2 *Complexes with nitrogen and phosphorus donor ligands*

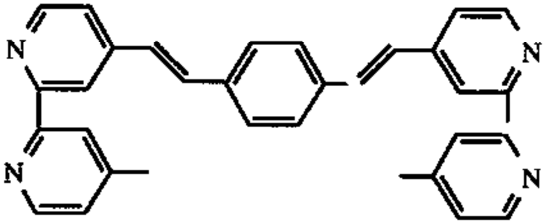
The first triply bonded dimetal species containing a nitrosyl ligand has recently been synthesized [55]. The reaction of $Re_2Cl_4(\mu\text{-dmpm})_3$, (dmpm = $Me_2PCH_2PMe_2$), with $[NO][PF_6]$ using 1:2 molar proportions in CH_2Cl_2 for four hours at room temperature folowed by recrystallization from ethanol gave dark red-brown crystals of $Re_2Cl_5(\mu\text{-dmpm})_2NO$. This complex has been characterized using IR and ^1H NMR spectroscopies, electrochemistry, and X-ray crystallography. If the nitrosyl ligand is treated as NO^+, then this complex may be viewed as a derivative of Re_2^{4+}. The Re-Re distance is 2.379 (1) Å in accord with a triple bond. The nitrosyl ligand is bound in a linear fashion: $\angle$Re-N-O = 174 (1)°. The formation of this complex requires the loss of a dmpm ligand from the starting material. It is thought that NO^+ first behaves as a one-electron oxidant oxidizing $Re_2Cl_4(\mu\text{-dmpm})_3$ to $[Re_2Cl_4(\mu\text{-dmpm})_3]^+$; then, NO becomes incorporated into the final product without a net change in the metal-metal bond order. The mechanism is a complex one in which some proportion of the dirhenium species must be sacrificed in order to provide the fifth chloride ligand in the end product. When the reaction was carried out in the presence of free chloride ion, no apparent increases in yield were observed.

The reaction of $Re_2Cl_4(\mu\text{-dppm})_2$ with the cyanotrihydridoborato ligand $[BH_3CN]^-$ proceeds with complete exchange of all four Cl^- ligands by $[BH_3CN]^-$ to produce a green complex of stoichiometry, $Re_2(NCBH_3)_4(\mu\text{-dppm})_2(H_2O)_2.2THF$ in high yield [56]. This is the first example in which the reaction of $Re_2Cl_4(\mu\text{-dppm})_2$ proceeds with complete exchange of all chloride ligands and attests to the remarkable stability of the $Re_2(\mu\text{-dppm})_2$ unit. This complex has been fully characterized by ^1H and ^{31}P NMR, and IR spectroscopies, cyclic voltammetry and X-ray crystallography. The complex consists of two bridging dppm ligands and a very short Re-Re bond 2.2874 (5) Å. Since there is no electronic barrier to rotation about the Re-Re bond the complex assumes a rotational geometry intermediate between those of a fully eclipsed and fully staggered conformation.

4.7 *RHENIUM(I)*

4.7.1 *Complexes with nitrogen donor ligands*

The photophysical properties of rhenium(I) complexes of 1,4-bis-[2-(4'-methyl-2,2'-bipyridyl-4-yl)ethenyl]benzene, (dstyb), (**20**), and 4-methyl-4'-styryl-2;2'-bipyridine, (mystb), (**21**), have been documented [57]. Weak structured phosphorescence at room temperature from an intraligand excited state was observed for the complex $[(CO)_3(CH_3CN)Re(dystb)Re(CO)_3(CH_3CN)](PF_6)_4$. This represents the first example of phosphorescence from a stilbene-like chromophore in solution at room temperature.



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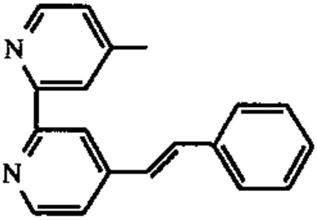

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The electronic absorption and emission spectra of a series of $(CO)_5Re\text{-}Re(CO)_3(\alpha,\alpha'$-diimine) compounds as powders and 2-methyltetrahydrofuran glasses at temperatures from 4.2 K to room temperature have been studied. Fluorescence and phosphorescence have been observed for these compounds and are discussed [58].

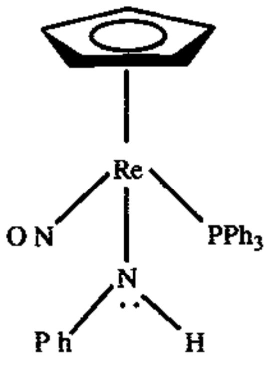
The structural, electrochemical and spectral properties of two new $ClRe(CO)_3(\alpha,\alpha'$-diimine) complexes $ClRe(CO)_3$(2-PP), (where 2-PP = *N*-(2-pyridinylmethylene)phenylamine), and $ClRe(CO)_3$(2-PC), (where 2-PC = *N*-(2-pyridinylmethylene)cyclohexylamine), have been reported. The X-ray diffraction data for both complexes are presented. The Re-N distances in these complexes are in the range 2.163 to 2.193 Å. The absorption spectra and emission specta are assigned to MLCT transitions. The correlation between electrochemical properties and absorption and emission energies are discussed [59].

The nonradiative (k_{nr}) decay rates of the low-lying emissive metal-to-ligand charge-transfer (MLCT) excited states of a series of complexes of the type $[Re(dpp)(CO)_3]^+$ (dpp = 2,3-di-2-pyridylpyrazine; L = Cl^-, *N*-methylimidazole, pyridine, 4-phenyl-pyridine, 4-methylpyridine, trimethylphosphine and acetonitrile) have been studied [60]. Results for these complexes indicate that the "energy gap law" for radiationless decay in the weak coupling limit is obeyed by this series of complexes and that dpp and bpy differ only in the relative energies of the acceptor orbitals and are vibrationally similar.

The reaction of (^{n}Bu$_4$N)[ReO$_4$] or (NH$_4$)[TcO$_4$] with the chelating organohydrazine hydralazine hydrochloride, $C_8H_5N_2NH\text{-}NH_2.HCl$, and sodium tetraphenylborate gave cationic tris-diazene complexes [M($C_8H_5N_2N\text{-}NH$)$_3$](BPh$_4$) [61]. These dark green complexes were found to be freely soluble in ethanol but decompose in solution in the absence of excess ligand. These complexes were characterized by IR, FAB MS, and NMR spectroscopies.

A novel type of photosubstitution of *fac*-Re(bpy)(CO)$_3$Br with P(OEt)$_3$, in the presence of triethylamine gave [Re(bpy)(CO)$_2${P(OEt)$_3$}$_2$]Br in 90% yield with the evolution of 0.6–0.8 equivalents of CO in CH$_3$CN, DMF, CH$_3$OH or THF [62]. This product was characterized *via* UV-VIS, FAB mass and ^{1}H, ^{13}C and ^{31}P NMR spectroscopies. The NMR spectroscopic data indicate that this species has C_{2v} symmetry with the two P(OEt)$_3$ ligands in the axial positions.

The first crystal structure of a metal complex with a pyramidal amido ligand has been reported [63]. The trifluoromethanesulfonate complex Re(η^5-C$_5$H$_5$)(NO)(PPh$_3$)(OTf) and aniline were combined in toluene resulting in [Re(η^5-C$_5$H$_5$)(NO)(PPh$_3$)(NH$_2$Ph)]$^+$[OTf]$^-$. The latter was treated with ^{n}BuLi (1.0 equiv.) in THF at –80°C and subsequently worked-up to give orange plates of the phenylamido complex Re(η^5-C$_5$H$_5$)(NO)(PPh$_3$)(NHPh), (**22**). Both of these complexes were characterized by microanalysis, IR and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies. The crystal structure of complex (**22**) shows the amido nitrogen to be distinctly pyramidalized with the sum of the three angles about the nitrogen being 345.5°. The Re-N(amido) distance is 2.076 (6) Å while the Re-N(nitrosyl) is 1.733 (6) Å. In a related paper [64] the synthesis, structure and reactivity of chiral rhenium complexes of the formula [(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(NRR'R'')]$^+$[OTf]$^-$ has been reported.



(**22**)

4.7.2 *Complexes with sulfur donor ligands*

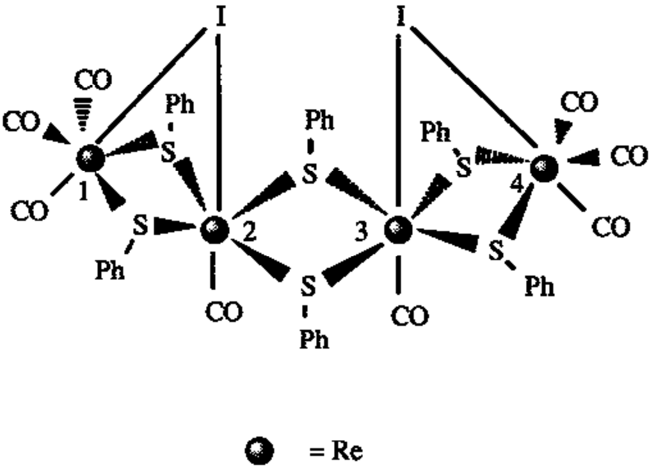
The high yield syntheses of chiral sulfide complexes $[Re(\eta^5\text{-}C_5H_5)(NO)(L)(MeSR)]^+X^-$ (L = PPh$_3$, CO, R = Me, Et, ^{i}Pr ^{t}Bu) have been reported. In addition, dynamic NMR spectroscopic studies have shown that the sulfide ligands display some of the lowest sulfur inversion barriers observed to date. The crystal structures for $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(SMe_2)]^+[OTf]^-$, and $[Re(\eta^5\text{-}C_5H_5)(NO)(CO)(S_2{}^tBu)]^+[OTf]^-$ have been elucidated, and show Re-S bonds of lengths 2.395 (3) and 2.391 (3) Å, respectively. Preliminary studies on analogous sulfoxide complexes have also been reported [65].

4.7.3 *Complexes with phosphorus donor ligands*

The reaction of *mer,trans*-ReCl(CO)$_3$(PPh$_3$)$_2$ with LiAlH$_4$ in THF at room temperature gives *mer,trans*-ReH(CO)$_3$(PPh$_3$)$_2$. The temperature dependence of the ^{1}H NMR spin-lattice relaxation rate (T_1) of the hydride resonance was studied with the aim of elucidating why greater T_1 rates are often observed for rhenium hydride complexes [66]. Two main dipole-dipole contributions have been identified, namely, proton-proton dipole-dipole (HHDD) relaxation between the hydride ligand and the protons of the phosphine ligands, and rhenium-hydride dipole-dipole (REHDD) relaxation. The two contributions can be separated by studying *mer,trans*-ReH(CO)$_3$(PPh$_3$-d_{15})$_2$.

4.7.4 *Clusters*

The oxidative addition of S$_2$Ph$_2$ to Re$_2$I$_2$(CO)$_8$ under forcing conditions gave rise to the mixed-valence cluster Re$_4$I$_2$(SPh)$_6$(CO)$_8$, **(23)** [67]. An X-ray structure determination on this molecule shows that it results from the condensation of four octahedra. The two lateral pairs of octahedra around Re(1):Re(2) and Re(3):Re(4) share a triangular face composed of two bridging sulfur and one bridging iodine atom. The two internal octahedra around Re(2):Re(3) share an edge which is the vector joining two bridging S(3) and S(4) atoms. Coordination is completed by three terminal CO ligands on each lateral rhenium and one terminal CO on each internal rhenium atom. The molecule possesses an approximate C_{2v} symmetry and the Re1-Re2, Re3-Re-4 and Re2-Re3 bond distances are 2.828 (2), 2.838 (2) and 3.892 (2) Å respectively. The oxidation state assignment proposed for this cluster is I-III-III-I with the inner Re(III) atoms achieving a closed-shell electronic configuration through dative bonding to the outer Re(I) atoms rather than Re(III)-Re(III) double bonds. The Re-S bonds involving the lateral rhenium atoms, average 2.478 (8) Å, are longer than those involving the inner rhenium atoms where those involving the bridging S atoms of the face-sharing units average 2.342 Å whereas those involving the bridging atoms of the edge-sharing units average 2.467 (7) Å. The reaction of this cluster with PPh or (cy)NC, (cy = cyclohexyl) gave Re$_4$I$_2$(SPh)$_6$(CO)$_6$L$_2$ (L = PPh$_3$ or (cy)NC) with selective substitution of the carbonyls on the inner rhenium atoms. When the cluster was reacted with CO the reductive elimination of S$_2$Ph$_2$ occurred and ReI(CO)$_5$ and Re$_2$(SPh)$_2$(CO)$_8$.



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