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COORDINATION CHEMISTRY REVIEWS

1. Rhenium 1992

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CONTENTS

INTRODUCTION

This review surveys the rhenium literature for 1992 focusing mainly on coordination compounds. In general, scant attention is given organometallic compounds and there are a couple of

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references to cluster compounds. The survey is based on a literature search of volumes 116, 117 and 118 (1–10) of *Chemical Abstracts*. Its format is similar to the 1991 review [1]. Additionally, major inorganic chemistry journals from January to December 1992 were searched separately. The assistance of Heidi Mercado of the Eastern Michigan University Library with a computer literature search is much appreciated.

1.1 RHENIUM(VII)

1.1.1 Complexes with hydride ligands

Proton nuclear magnetic resonance spin-lattice (T_1) relaxation time measurements have been carried out on the series of complexes $ReH_7[P(C_6H_4\text{-}p\text{-}X)_3]_2$ (X = CH_3, H, F, CF_3, OMe) which contain isosteric phosphine ligands [2]. Results are consistent with solution species which contain an elongated η^2-H_2 ligand with varying H-H distances depending on the electronic character of the phosphine ligands.

The synthesis, structure and reactivity of polyhydride complexes of rhenium with yttrium and lutetium have been described [3]. In particular, the complexes $(C_5H_5)_2Y(thf)H_6Re(PPh_3)_2$ and $(C_5H_5)_2Y(thf)H_4Re(PMe_2Ph)_3$ have been characterized by X-ray crystallography and contain bridging hydrides. The former was found to be unreactive toward CO, CO_2 and diphenylacetylene.

The results of *ab initio* electronic structure calculations on the model complex $ReH_7(PPh_3)_2$ as both classical nine-coordinate as well as several non-classical structures have been reported [4]. They were compared with experimental structural determination and solution NMR spectroscopic studies. The classical structure was found to be more stable than the eight-coordinate structure by 2-4 kcal mol^{-1} depending on the level of the calculation and 7-10 kcal mol^{-1} lower than the seven-coordinate forms.

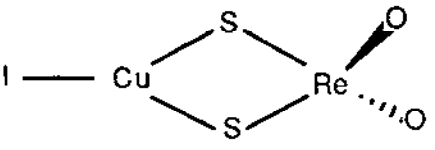
1.1.2 Complexes with oxygen donor ligands

Photo-oxidation of $Re_2(CO)_{10}$ in low temperature matrices containing O_2 generated Re_2O_7 as well as free CO and CO_2 [5]. The cleavage of the Re-Re bond appears to initiate the reaction and IR spectroscopic studies including isotopic substitution are suggestive of $(OC)_5Re\text{-}O\text{-}Re(CO)_5$ and $O{=}Re(CO)_5$ as intermediates.

The reaction of Re_2O_7 with triphenylstibin oxide and di-*n*-butyltin oxide has produced new perrhenates [6]. The crystal structure of $Ph_3Sb(OReO_3)_2$ was been obtained.

1.1.3 Complexes with oxygen and sulfur donor ligands

Synthesis of the previously unisolated oxothioperrhenate ions $[ReO_2S_2]^-$ and $[ReOS_3]^-$ has been achieved by the reaction of $(NEt_4)[ReS_4]$ with PPh_3 and CuI in acetone in the presence of $(PPh_4)I$, or with CuCl in CH_2Cl_2 in the presence of $(NEt_4)Cl$ yielding $(PPh_4)[ReO_2S_2]CuI$ (**1**) and $(NEt_4)[ReOS_3]Cu_3Cl_4$ (**2**) respectively [7]. These complexes have been characterized by X-ray crystallography, elemental analysis and IR and UV-VIS spectroscopy.



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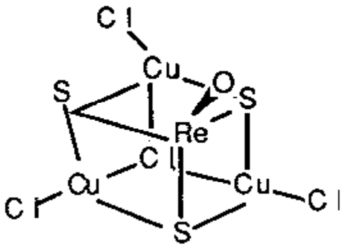

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1.1.4 Complexes with nitrogen donor ligands

The synthesis of (α-triphenylphosphonio)methylidene imido complexes of molybdenum, tungsten and rhenium having four π-donor ligands has been reported [8] The reaction of $Re(N^tBu)_3Cl$ with $Ph_3P{=}CH_2$ (2 equiv.) gave $[Re(N^tBu)_3(CHPPh_3)]$ in 90% yield, and the X-ray structure for the tungsten derivative has been reported

The synthesis and characterization of a new cationic rhenium bis(hydrazido(2–)) complex $[ReCl_2(NNMePh)_2(PPh_3)][BPh_4]$ by the reaction of $[ReOCl_3(PPh_3)_2]$ with an excess of the unsymmetrically disubstituted organohydrazine $MePhNNH_2$ in boiling methanol has been described [9]. Its $[PF_6]^-$ salt was found to be hydrolytically unstable and decomposes on attempted recrystallization yielding an oxo-hydrazido dication $[ReOCl(NNMePh)(PPh_3)_2][PF_6]_2$. This complex has a trigonal bipyramidal geometry with an Re-N distance of 1.845(6) Å and N-N being 1.261(8)Å. Reaction of the former with sulfur gave $[Re(NNMePh)_2(S_2CNMe_2)_2][BPh_4]$ which has a distorted octahedral geometry with equivalent mutually *cis*-, nearly linear hydrazido(2–) ligands with Re-N distances of 1.789(1) and 1.777(9) Å and N-N = 1.30(1)Å.

1.2 RHENIUM(VI)

1.2.1 Complexes with oxygen donor ligands

The reactions of the complexes *cis*-$Re_2(O_2CR)_2X_4L_2$ (R = CH_3, C_2H_5; X = Cl, Br; L = H_2O, py) with dmpm ($Me_2PCH_2PMe_2$) have been described and an unusual mixed-valent dirhenium complex $Re_2O_3Cl_2(dmpm)_2$ has been obtained [10]. An X-ray structure reveals a grossly unsymmetrical structure in that both Re atoms are in different environments namely tetrahedral and pentagonal bipyramidal with a very short Re-Re bond 2.4705(5) Å which is unsupported. This is the first example of a complex in which an ReO_3 unit is involved in direct metal-metal bonding.

In a related paper [11], *ab initio* two-configuration SCF and CI calculations have been carried out on $O_3ReReCl_2(H_2PCH_2PH_2)_2$ which was used as a model for the recently characterized $O_3ReReCl_2(dmpm)_2$, (dmpm = $Me_2PCH_2PMe_2$). Results from these calculations indicate that the formal oxidation states Re(VI)-Re(II) do not correspond to the distribution of the valence *d* electrons. Rather, the pentagonal pyramidal conformation of the $ReCl_2(dmpm)_2$ unit induces an important charge transfer toward the trioxorhenium fragment which corresponds to Re(V)-Re(III) states. The metal-metal bond was found to be strongly polarized which may be interpreted as σ-donation from the trioxorhenium fragment to the $ReCl_2(dmpm)_2$ unit.

1.2.2 Complexes with sulfur donor ligands

The spectroelectrochemical characterizations of ReS_4^{2-} and a trinuclear derivative $[(bpy)_2Ru(\mu\text{-}ReS_4Ru(bpy)_2]^{2+}$ have been reported [12].

1.3 RHENIUM(V)

1.3.1 Complexes with hydride ligands

Ab initio calculations have been used to study the relative stabilities of classical and non-classical isomers of polyhydride complexes of the formula $ML_{8-n}H_n$ (n = 4-7 and L = PPh_3) including $ReH_5(PPh_3)_3$ and $ReH_4(PPh_3)_4^+$ [13]. Results indicate that when twice the ionization enthalpy of an electron in the M-H bond is greater than the sum of the ionization enthalpies of an electron in the H-H bond and one in the metal *d* orbital, a classical isomer is preferential, otherwise an octahedral non-classical structure is adopted.

1.3.2 Complexes with oxygen donor ligands

The mechanisms for the electrochemical reduction of *cis*- and *trans*-dioxorhenium(V) species in acidic and neutral species have been reported [14]. Additionally, quantitative measures of electrochemical exchange kinetics at near-neutral pH have also been reported.

The solution and equilibrium behavior of the *trans*-dioxotetracyanorhenate(V) ion has been studied by ^{13}C and ^{17}O NMR spectroscopies [15]. The ^{17}O chemical shifts showed a direct relationship with X-ray and IR spectroscopic data and with electron density on the coordinated oxygen ligands.

Several new catecholato oxorhenium(V) complexes have been isolated and their infrared, Raman, and ^{31}P and ^{13}C NMR spectra are reported [16]. The X-ray crystal structures of $[N^nBu_4][ReO(OPh_2)(tccat)_2]$ and $[N^nBu_4][ReO(MeOH)(tccat)_2]$, ($H_2$tccat = tetrachlorocatechol), have been obtained. In both these complexes the rhenium atom is in a distorted octahedral environment with the catecholato ligands being bent away from the strongly bonded oxo ligand; Re-O 1.576(8)Å in the former and 1.653(11)Å in the latter complex.

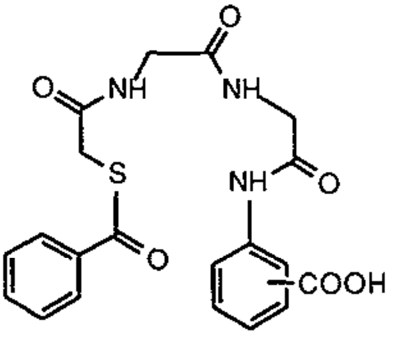
Dimethyl sulfoxide complexes of rhenium(V) were synthesized in solutions of hydrogen halide [17]. Infrared spectroscopy indicates that the dmso molecules are coordinated through the oxygen atom.

Synthetic methods have been developed and used to isolate solid onium complexes of Re(V) and Mo(V) with diaza-18-crown-6 with [18]. They have been characterized by elemental analysis, near and far IR spectroscopy, thermal analysis and conductometric and potentiometric measurements.

The emissive excited state of the d^2 ion *trans*-[$ReO_2(py)_4$]$^+$ has been studied and it has been found that pyridinium ion and other organic acids are effective quenchers of this excited state in acetonitrile by a proton-transfer mechanism [19].

1.3.3 Complexes with oxygen and nitrogen donor ligands

The synthesis and characterization of rhenium(V) oxo complexes which are models for technetium renal imaging agents have been described [20]. The complexes are derived from isomers of mercaptoacetylglycylglycylaminobenzoic acid (3) and X-ray crystallography indicates the coordination geometry to be square pyramidal in these complexes (4). Molecular mechanics calculations were carried out in order to assess the solution phase structures.



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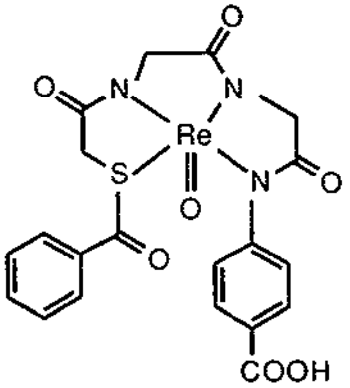
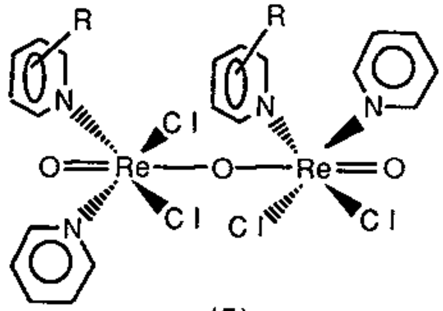


(4)

An unexpected alternative route to complexes containing the *trans*-dioxo [O=Re=O]$^+$ group has been devised [21]. The complexes $ReNCl_2(PPh_3)_2$, $ReCl_4(PPh_3)_2$,$ReCl_3(CH_3CN)(PPh_3)_2$ were found to react with didentate (L^1) and tetradentate (L^2) chelating amines and with 1,4,8,11-tetrazacyclotetradecane (cyclam) at room temperature yielding cationic complexes of the type [$ReO(L^n)_n$]$^+$ (n = 1,2) and [ReO_2(cyclam)]$^+$. The latter has been isolated with three different counterions (ReO_4^-, Cl^-, and PF_6^-) and the crystal structure of the hexafluorophosphate salt has been obtained. The complex is monomeric and the rhenium atom is in an octahedral environment with Re-O bond distances of 1.77(1) and 1.78(1) Å while Re-N distances range from 2.09(1)–2.13(1) Å. The infrared spectra of these complexes are discussed.

The cyclic voltammetry of μ-oxo-bis[*cis*-dichloro-*cis*-dipyridyloxrhenium(V)] complexes (5) has been investigated [22]. In particular, the influence of pyridine substituents has been studied;

four one-electron redox couples have been observed with the dimeric structure remaining intact for oxidation and the first reduction process.



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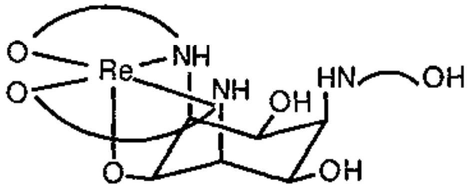
A communication has appeared describing the synthesis of 1,3,5-trideoxy-1,3,5-tris(2-hydroxybenzyl)amino)-*cis*-inositol and its Re^VO (6) complex [23]. The results demonstrate that (i) although this ligand is potentially hexadentate, the rhenium atom coordinates to only five positions, (ii) the tendency of the ReO moiety to coordinate hard oxygen donor atoms *trans* to the O_{oxo} position, and (iii) the preference for the softer amino group in the positions *cis* to the Re=O bond.



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Unusual stabilization of mutually *trans* 2,2'-bipyridine ligands in a rhenium(V) imido complex has been encountered recently [24]. The PF_6^- salt of *trans*-$[PhNRe(bpy)_2(OEt)]^{2+}$ was characterized by ^1H NMR and UV-visible spectroscopies, cyclic voltammetry, elemental analysis and X-ray diffractometry. The crystal structure reveals a pseudooctahedral coordination sphere about Re with the bpy ligands distorted in a "concerted-canted" fashion thereby minimizing steric interactions between 6 and 6' protons on adjacent bpy rings. The Re-N(Ph) distance is 1.740(6)Å while the Re-O(Et) distance is 1.895(5)Å. Attempts to convert this complex into its *cis* isomer were unsuccessful; even extended heating at reflux in EtOH for 48 hours gave no reaction.

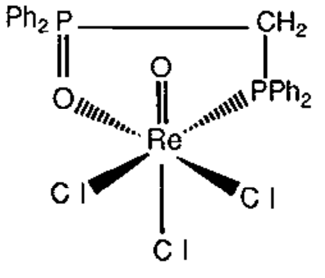
The synthesis and molecular structures of novel seven-coordinate oxo- and nitrido-rhenium complexes of 2,2':6',2",6",2'"-quaterpyridine, L, have been described [25]. The reaction of $[ReO_2(PPh_3)_2I]$ and $[ReNCl_2(PPh_3)_2]$ with L gave $[ReO(L)(OMe)_2]ClO_4$ and $[ReN(L)(PPh_3)Cl]ClO_4$ respectively. The Re-O distance was found to be 1.666(4)Å in the former and 1.647(6)Å in the latter. Cyclic voltammetry in acetonitrile has been carried out and reversible Re^{VI}-Re^Vcouples have been observed.

The reaction of Re_2O_7 with PPh_3 in the presence of bipyridine or 1,10 -phenanthroline, (L-L) has yielded the *trans*-complexes $[Re(L\text{-}L)_2O(OH)](ReO_4)_2$ and $[Re(L\text{-}L)_2O_2](ReO_4)_2$ [26]. These complexes were characterized by IR, ^1H NMR and UV-VIS spectroscopies, FAB-mass spectrometry, elemental analysis and cyclic voltammetry.

The voltammetric behaviour of compounds of the general formula $[ORe(OR)Cl_2(PPh_3)_2]$ and $[ORe(OEt)Cl_2(PPh_3)(py)]$, (R = alkyl or aryl, py = pyridine) has been studied [27]. Observations on the alkoxypyridine complex indicated that the pyridine is labile in halogenated solvents but not in Me_2CO, MeCN or CCl_4.

1.3.4 Complexes with oxygen and phosphorus donor ligands

Interest in synthesising a new genre of radiopharmaceuticals in nuclear medicine has prompted studies on the reaction of rhenium(V) precursors with mixed donor ligands containing an aryl-phosphine or -arsine in combination with a phosphine oxide within the ligand backbone [28]. In particular, the reactions of $(O)PPh_2CH_2PPh_2$ and $(O)PPh_2CH_2CH_2AsPh_2$ with $[ReOCl_2]^-$ yielded $(O)PPh_2CH_2PPh_2Re(O)Cl_3$ (7) and $(O)PPh_2CH_2CH_2AsPPh_2ReOCl_3$ (8), respectively. Monoethoxy derivatives were isolated by performing the above reactions in ethanol medium. The structure of (7) has been confirmed by X-ray crystallography. This study demonstrates a new methodology for stabilizing rhenium(V) by means of heteroatomic chelation. The extreme hydrolytic stability of the products under neutral and acidic pH conditions is important for extending such reactions to produce radioactive analogues.



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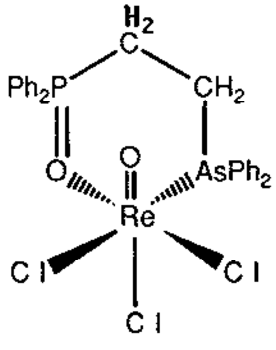

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1.3.5 Complexes with sulfur donor ligands

Complex formation of rhenium(V) with pyridinethiol-2 [29], imidazole-2-thiol [30] and 1-acetyl-3-thiosemicarbazide [31] has been studied over a range of temperatures. Thermodynamic and redox potentials are presented.

The voltammetric behavior of $ReN(S_2CN(Et)_2)_4$, $Re(S_2CN(Et)_2)_3$ and $ReOX(S_2CN(Et)_2)_2$ (where X = Cl or Br) and $Re_2O_3(S_2CN(Et)_2)_4$ were studied in five non-aqueous solvents in order to determine the effect of structure, oxidation state and solvent on their electron-transfer behavior [32]. A complex electron-transfer mechanism has been observed especially for the oxorhenium(V) case involving coupled chemical reactions and electrodeposition onto the electrode surface.

1.3.6 Complexes with selenium and phosphorus donor ligands

The reaction of $[ReOCl_3(PPh_3)_2]$ or $[AsPh_4][ReOCl_4]$ with $K[N(PPh_2Se)_2]$ generated the green complex $[ReO(Cl)\{N(PPh_2Se)_2\}_2]$ [33]. In solution this complex transformed into $[ReO(Cl)(PPh_2PNPPh_2Se)_2]$ by loss of one Se atom from each ligand. Recrystallization from CH_2Cl_2/EtOH gave $[ReO(OEt)(PPh_2PNPPh_2Se)_2]$ whose crystal structure reveals a six-coordinate geometry for the rhenium atom with two *trans* chelated didentate ligands and an Re-Se distance of 2.562(1) Å.

1.3.7 Complexes with nitrogen donor ligands

The chemical structure of azidonitridotetracyanorhenate(V) has been elucidated [34]. It was synthesized by means of the reaction shown in equation (1) and has a distorted octahedral geometry

$$[ReN(H_2O)(CN)_4]^{2-} + N_3^{3-} \rightleftharpoons [ReN(N_3)(CN)_4]^{3-} \qquad (1)$$

in which the rhenium atom is displaced by 0.34 Å out of the plane defined by the four cyano ligands and towards the nitrido ligand. The azido and nitrido ligands are coordinated *trans* to each other with Re-N(nitrido) = 1.65(2) Å and Re-N(azido) = 2.36(2) Å.

1.3.8 Complexes with phosphorus donor ligands

Inter-metal oxygen-atom transfer reactions between molybdenum, tungsten and rhenium complexes have been studied [35]. Using chloride and $PMePh_2$ as supporting ligands, $Re(O)Cl_3L_3$ reacts with $MoCl_2L_4$ or WCl_2L_4 forming $M(O)Cl_2L_3$, (M = W, Mo, L = $PMePh_2$). The above reactions were also found to yield $MoCl_3L_2$, and MCl_3L_3 which result from chlorine atom transfer. One-electron and two-electron pathways have been observed for these reactions and the competition between these pathways has been discussed.

1.3.9 Complexes with phosphorus and arsenic donor ligands

A series of new nitrido and *trans*-dioxo-rhenium(V) complexes of phosphine and arsine ligands has been synthesized recently [36]. The reaction of $[ReNCl_2(PPh_3)_2]$ and $[ReO_2(PPh_3)_2I]$ with a variety of phosphines and arsines yielded the complex cations $[ReNL_2Cl]^+$ and $[ReO_2L_2]^+$. In particular, the X-ray crystal structures of $[ReN(dpae)_2Cl]^+$ and $[ReO_2(dadpe)_2]^+$, (dpae = 1,2-bis(diphenylarsino)ethane; dadpe = 1-diphenylarsino-2-diphenylphosphinoethane) have been obtained and show an Re-N distance of 1.839(8) and Re-O distances of 1.785(8) and 1.766(8) Å.

Excitation of solid samples at 350-380 nm at room temperature gives rise to yellow-green and orange emission respectively while all *trans*-dioxo compes exhibit room temperature luminescence in MeCN. Cyclic voltammetry studies were carried out.

1.4 RHENIUM(III)

1.4.1 Complexes with halide ligands

The synthesis and crystal structures of chlororhenates with the divalent cations ethylenediammonium and piperazinium have been reported [37].

The synthesis, IR spectrum and crystal structure of the complex $[Na(15\text{-crown-}5)][ReFCl_3(NO)(CH_3CN)]$ have been reported [38]. The compound forms an ion pair by Na-F (23.44 Å) and Na-Cl (2.934 Å) contacts in which the nitrosyl ligand is *trans* to the F atom.

The synthesis, structure and thermolysis of $NH_4[Re_3Br_{10}]$ have been described [39]. The title compound crystallizes as dark brown single crystals upon slow cooling of a hot, saturated hydrobromic-acid solution of $[Re_3Br_9(H_2O)_2]$ after the addition of NH_4Br. The crystal structure reveals $[Re_3Br_{12}]^-$ ions sharing two common edges. These chains run along [010] and are held together by NH_4^+ ions each of which is surrounded by eight Br^- ions from four different chains.

1.4.2 Complexes with hydride ligands

The dirhenium polyhydride $Re_2H_8(\mu\text{-dmpm})_2$, (dmpm = $Me_2PCH_2PMe_2$) has recently been isolated and its reactivity studied [40]. The reactivity of $[Re_2(\mu\text{-}H)H_4(\mu\text{-dmpm})_3](PF_6)$ has been studied. The complex reacts with π-acceptor CO and isocyanide ligands to produce, in a stepwise fashion, a new series of lower-valent dirhenium complexes of stoichiometry $[Re_2H_{5\text{-}n}L_n(\mu\text{-dmpm})_3](PF_6)$ where n = 2 or 4, and dmpm = $Me_2PCH_2PMe_2$. The electronic unsaturation of the dirhenium unit is relieved in these complexes and the $[Re(\mu\text{-}H)(\mu\text{-dmpm})_3Re]$ unit is retained. [41]

Interest in the electrochemistry of hydride complexes has spurned investigations on the complex $[ReClH(NCR)(dppe)_2](BF_4)$ (R = $4\text{-}ClC_6H_4$ or $4\text{-}FC_6H_4$, dppe = $Ph_2PCH_2CH_2PPh_2$) in the 300 V s^{-1} to 50 mV s^{-1} scan-rate range at Pt disc electrodes in 0.3 mol dm^{-3} $[Bu_4N][BF_4]$-thf or CH_2Cl_2 [42]. These complexes were found to undergo anodically induced protonation and cathodically induced dehydrogenation. The reaction is thought to involve a bimolecular process and may be considerably more complex than simple intramolecular M-H bond cleavage.

The preparation of *cis*-$C_5H_5(CO)_2ReH_2$, its equilibration with *trans*-$C_5H_5(CO)_2ReH_2$, its direct observation in the low-temperature reaction of $C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ with diphenyacetylene and its generation from photolysis of its *trans* isomer in methylcyclohexane glass have been reported [43].

1.4.3 Complexes with oxygen and nitrogen donor ligands

A rhenium(V) oxooxalate complex $(HBpz_3)ReO(C_2O_4)$, ($HBpz_3$ = hydridotris(1-pyrazolyl)borato) has recently been synthesized [44]. It has been characterized spectroscopically and by X-ray crystallography. Photolysis of this complex yields an intermediate species $(HBpz_3)Re(O)$ and is also found to react with oxygen yielding an Re(VII) complex, $(HBpz_3)ReO_3$. Labelling studies indicate a complex mechanism in which only one oxygen comes from O_2, the others being derived from the reduction of an oxalate ligand. The failure of this intermediate to cleave dioxygen may be ascribed to a general symmetry-derived restriction on this reaction.

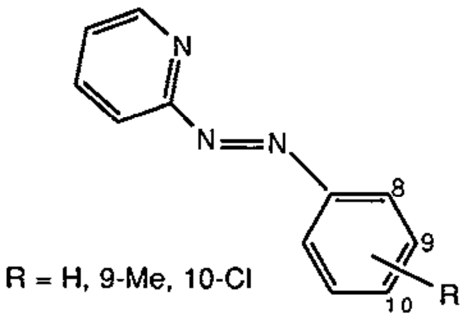
A new coordination mode for hydroxypyridinate around dimetallic centres has been elucidated recently [45]. The complex $Re_2(\mu\text{-chp})_2(\eta^2\text{-chp})Cl_3$, (Hchp = 6-chloropyridinol), was characterized by X-ray crystallography and reveals two bridging chp^- ligands in a *trans*-arrangement while the third chp^- is chelating, a finding which is unprecedented amongst dinuclear hydroxypyridinate complexes. The Re-Re bond length is 2.201(1) Å and the Re-N bond to the chelating ligand is 2.419(3) compared to values of 2.10(1) and 2.110(9) Å for Re-N in the bridging chp^- ligands.

1.4.4 Complexes with sulfur donor ligands

The first example of the 2-electron reduction of CS_2 by a multiply bonded dimetal complex has been reported [46]. Specifically the formation of the complexes $Re_2(\mu\text{-S})(\mu\text{-X})X_3(CS)(\mu\text{-LL})_2$ (LL = $Ph_2PCH_2PPh_2$ (dppm) or $Ph_2AsCH_2AsPh_2$ (dppam); X = Cl or Br) were obtained from $Re_2X_4(dppm)_2$ and $Re_2X_4(dppam)_2$ (X = Cl or Br) yielding stable edge-shared bioctahedral dirhenium species in which the CS and S^{2-} fragments have been incorporated into the dimetal unit. A salient feature for the bromide derivative is the length of the Re-Re bond (2.956(2)Å) which is some 0.3Å greater than those in authentic metal-metal bonded dirhenium(III) complexes. In a related paper [47], it was shown that the μ-S unit is readily oxygenated to $\mu\text{-SO}_2$ with no change in the remainder of the coordination geometry.

1.4.5 Complexes with nitrogen ligands

The synthesis of formamidinate complexes of dirhenium has been reported [48]. In particular, $Re_2L_4Cl_2$, and its derivatives $Re_2L_4(OMe)_2$, Re_2L_4Cl, and Re_2L_4 (HL = di-*p*-tolylformamidine) have been synthesized and characterized spectroscopically and



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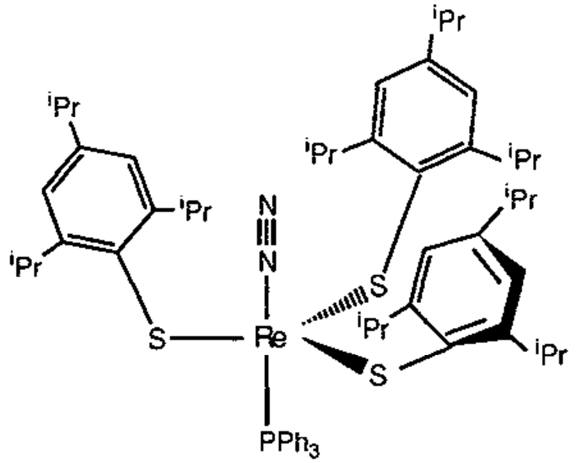
crystallographically. The Re-Re bond lengths were found to be 2.2759(3)Å for $Re_2L_4Cl_2$, 2.3045(2)Å for $Re_2L_4(OMe)_2$, and 2.344(2)Å for Re_2L_4. SCF-Xα calculations were performed on model complexes and results show that $Re_2L_4Cl_2$ and $Re_2L_4(OMe)_2$ assume classic quadruple bond configurations $\sigma^2\pi^4\delta^2$ whereas the addition of two electrons results in a novel triple bond configuration, $\sigma^2\pi^4\delta^2\pi^{*2}$ for Re_2L_4.

The synthesis of a family of complexes of the type $[ReL_2Cl_2]Cl$, L = 2-(arylazo)pyridine (**9**) has been described [49]. Spectrochemical and electrochemical studies were conducted in order to probe isomer geometry, back-bonding, charge-transfer spectra, metal oxidation and ligand reduction.

1.4.6 Complexes with nitrogen and sulfur donor ligands

Efforts aimed at modelling the dinitrogen binding site in nitrogenase have resulted in the high-yield synthesis of a d^4 fourteen-electron five-coordinate rhenium thiolato-dinitrogen complex [50]. The complex $[Re(N_2)(SC_6H_2\text{-}2,4,6\text{-}^iPr)_3(PPh_3)]$ was characterized by IR and NMR spectroscopies, CV measurements and X-ray crystallography. The overall geometry is trigonal bipyramidal with dinitrogen and phosphine ligands in axial positions. Interestingly, the aromatic groups are disposed to the same side of the equatorial plane thereby forming an umbrella-like structure (**10**) for the dinitrogen ligand which likely contributes to its stability. Two independent molecules in the crystal show Re-N distances of 1.994(10) and 2.004(12) Å.



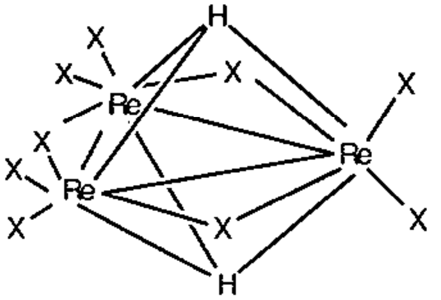
(10)

1.4.7 Complexes with phosphorus ligands

The oxidative addition of diphenylphosphine to the electron-rich triple bond in $Re_2X_4(\mu\text{-}dppm)_2$ (X = Cl or Br) has been achieved [51]. The complexes $Re_2(\mu\text{-}X)(\mu\text{-}PPh_2)HX_3(\mu\text{-}dppm)_2$ were obtained. X-ray crystallography for the chloride derivative reveals an edge-shared bioctahedral structure with an Re-Re distance of 2.5918(7) Å. Oxidation of the bromide derivative with $NOPF_6$ gave salts of an unusual dirhenium(III,II) cation $[Re_2(\mu\text{-H})(\mu\text{-Br})[P(O)Ph_2]Br_2(NO)(\mu\text{-dppm})_2]^+$ whose crystal structure reveals, yet again, a bioctahedral edge-shared geometry and an Re-Re distance of 2.6273(8) Å.

1.4.8 Clusters

The reaction of $Re_3(\mu\text{-Cl})_3Cl_6(thf)$ and 9 equivalents of $LiNMe_2$ gave *triangulo*-$Re_3(\mu_3\text{-H})_2(\mu\text{-NMe}_2)_3(NMe_2)_6$, **(11)** a 10-electron rhenium hydride cluster in low, but reproducible, yields [52]. Based on spectroscopic studies the cluster is thought to have virtual D_{3h}, D_3, or C_{3h} symmetry. Rotation about the Re-N bonds of the terminal NMe_2 groups occurs with an activation parameter $\Delta G(298\ K) = 11.1$ kcal mol^{-1}. The source of the hydride ligands is proposed to be the amido ligand methyl groups.



(11) $X = NMe_2$

Cluster excision has been used in the removal of intact clusters from the ternary phases $Re_6Se_{4+q}Cl_{10-2q}$ (q = 1-3) recently [53]. In particular, when $Re_6Se_5Cl_9$ and $Re_6Se_6Cl_6$ were treated with excess R_4NCl in hot dmf or acetonitrile, solubilization of the solid-state clusters was observed. Products isolated were in the forms $(R_4N)[Re_6Se_5Cl_9]$ (R = Et, Pr, Bu) and $(R_4N)_2[Re_6Se_6Cl_8]$ (R = Et, Pr) respectively (78-86% yields). The former contains an Re_6 octahedron which is face-capped forming a $[Re_6(\mu_3\text{-Se})_5(\mu_3\text{-Cl})_3]^{5+}$ core in which each Re atom is bonded to a terminal chloride. The latter has an $[Re_6Se_6Cl_2]^{4+}$ core. Reactions resulting in substitution of core chloride atoms have been carried out and are discussed.

1.5 RHENIUM(II)

1.5.1 Complexes with halide ligands

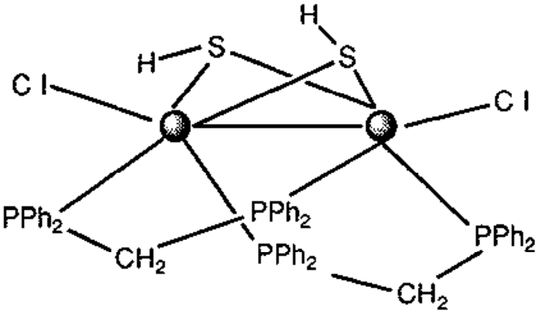
The reactivity of the $[CpRe(CO)_2(NO)]^+$ and $[Cp^*Re(CO)_2(NO)]^+$ with halides has been examined [54]. The former was found to react with halides faster than the latter, generating $[CpRe(CO)_2(NO)X]$ (X = Cl, I) upon loss of a CO ligand and $[fac\text{-}X_3Re(CO)_2(NO)]^-$ by loss of the (η^5-C_5R_5) ligand (R = H, Me). An X-ray structure for the anion has been obtained. The anion undegoes metathesis to give an intermediate $[Cp^*Re(CO)_2(NO)]I$ salt.

1.5.2 Complexes with oxygen and phosphorus donor ligands

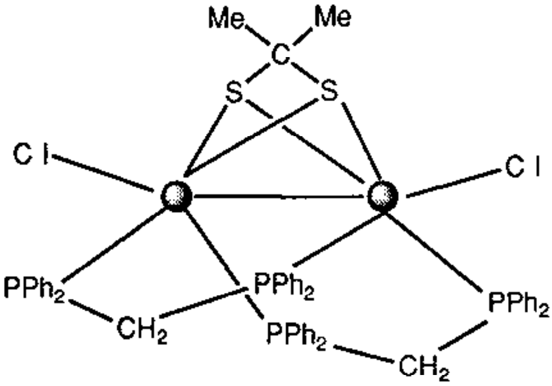
An attempt to prepare dirhenium complexes in which both $Me_2PCH_2PMe_2$ (dmpm) and CO are both present has resulted in the complex $[Re_2(\mu\text{-}X)_2(\mu\text{-dmpm})(CO)_2(dmpm)_2](H_2PO_4)_2$ [55]. This complex is characterized by a very long Re-Re bond (2.918(2) Å) for X = Cl and is striking because two of the dmpm ligands are chelating rather than bridging.

1.5.3 Complexes with sulfur donor ligands

The reaction of gaseous H_2S with *cis*-$Re_2(\mu\text{-}O_2CR)_2Cl_2(\mu\text{-dppm})_2$ (R = Me or Et) gave *cis*-$Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-dppm})_2$ when thf or CH_2Cl_2 was used as the solvent or the *gem*-dithiolato complexes *cis*-$Re_2(\mu\text{-}S_2CR^1R^2)Cl_2(\mu\text{-dppm})_2$ and *cis*-$Re_2(\mu\text{-}S_2CHR^2)Cl_2(\mu\text{-dppm})_2$ in the presence of ketones (R^1R^2CO) and aldehydes (R^2CHO) [56]. These complexes represent the first examples to contain the Re(μ-SH)Re and Re(μ-$S_2CR^1R^2$) moieties. Interestingly, this is a non-redox reaction and the dirhenium core is retained in the products. Crystal structures for the two



(12) ● =Re



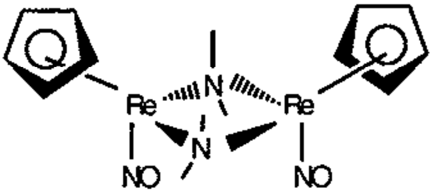
(13) ● = Re

types of complexes were obtained and reveal that both possess similar cradle-like structures in which the two μ-SH ligands in **(12)** or a bridging *gem*-dithiolate (R^1, $R^2 = CH_3$) ligand in **(13)** replace the carboxylate bridges in the precursor complex. The Re-Re bond distances of 2.2777(5)Å and 2.2544(6)Å are indicative of an Re-Re triple bond while the Re-S distances range from 2.472(2)-2.495(2)Å in **(12)** and 2.457(3)-2.485(3)Å in **(13)**.

1.5.4 Complexes with nitrogen donor ligands

Two novel strategies for the synthesis of novel solvated dinuclear cations from halide and phosphine precursors have been described [57]. The complexes $[Re_2(NCCH_3)_8](BF_4)_4$ and $[Re_2(NCCH_3)_{10}][Mo_6O_{19}]_2$ have been characterized by X-ray crystallography, IR, UV spectroscopy, electrochemical measurements, XPS and TGA. In the latter complex each rhenium atom is pseudo-octahedral, comprising four CH_3CN ligands in a near plane with the two additional vertices occupied by weakly interacting axial CH_3CN groups. The molecule reveals a staggered conformation in which the two $Re(NCCH_3)_4$ units are rotated by an average of 44.5(1)° and the Re-Re distance is 2.259(4) Å, indicative of a metal-metal triple bond with the electron rich $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration. Electrochemical measurements revealed a very accessible quasi-reversible reduction in addition to two irreversible reductions in sharp contrast to other species with this electron configuration which exhibit oxidations only. Thermogravimetric analysis results in a black amorphous mixed-metal oxide the first example of a ternary ReMo oxide.

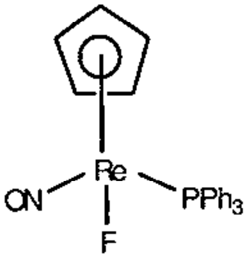
The structure and reactivity of the coordinatively saturated amido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NRR')$, R/R' = H/H, H/$CH_3$, H/$C_6H_5$, CH_3/CH_3, $CH_2CH_2CH_2CH_2$ has been described [58]. For the case R/R' = $CH_2CH_2CH_2CH_2$, it was converted upon workup into a dimeric bis(amido) complex *cis*-$[(\eta^5\text{-}C_5H_5)Re(NO)\{\mu\text{-}N(CH_3)_2\}]_2$ **(14)**. These complexes have been characterized by IR and NMR spectroscopies.



(14)

1.5.5 Complexes with nitrogen and phosphorus donor ligands

The synthesis and reactivity of chiral metal fluoride complexes derived from the rhenium fragment $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ have been described [59]. Several synthetic approaches to **(15)** have been described and it has been isolated in pure form. The rhenium-fluorine bond in this complex was found to be readily cleaved by electrophiles and nucleophiles. A related water complex **(16)** was also isolated during the course of this study.



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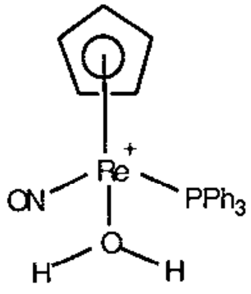


(16)

The first example of a triply bonded dimetal compound containing a nitrosyl ligand, namely, $Re_2Cl_5(\mu\text{-dmpm})_2(NO)$, has been isolated recently [60]. Its structure comprises a terminally bound linear nitrosyl ligand and a rarely encountered *cis,trans*-disposition of phosphorus donor atoms at the two metal centres. The Re-Re bond distance is 2.379(1) Å.

The reactions of $NO[BF_4]$ and NO with *trans*-$[ReCl(N_2)(dppe)_2]$ to give the complexes *trans*-$[ReCl(NO)(dppe)_2]A_2$ (A = BF_4 or NO_3) and *trans*-$[ReCl(NO)(dppe)_2][BF_4]$ have been studied [61]. The X-ray structure of *trans*-$[ReCl(NO)(dppe)_2][BF_4]_2$ has been reported and shows rhenium to be octahedrally coordinated with an Re-N bond length of 1.730(13) Å. The analysis revealed the presence of NO_3^- counterions derived from the oxidation of NO at the rhenium centre although the mechanism was not elucidated.

1.6 RHENIUM(I)

1.6.1 Complexes with oxygen donor ligands

Rhenium carbonyl complexes containing the dioxolene ligand in oxidation states other than the semiquinone radical anion have been studied recently by electrochemical and spectrochemical (resonance Raman, UV-VIS, IR) methods [62]. In particular, the complexes $[Re(CO)_2PPh_3(Diox)]^z$ and $[Re(CO)_3L(Diox)]^z$ (L = CO, PPh_3, *P*-dppe, thf, Ph_3PO, Me_3CO, py; z = −1, 0 +1) redox series were studied.

The facile rupture of the Re-Re bond in $[Re_2(CO)_{10}]$ in the presence of Me_3NO and methanol has been reported [63]. The complex $[Re_2(\mu\text{-}OMe)_2(CO)_6(\mu\text{-dppf})]$ was obtained by oxidative decarbonylation of $[Re_2(CO)_{10}]$ by $Me_3NO{\cdot}2H_2O$ in a thf-MeOH mixture at room temperature followed by phosphine addition. X-ray diffraction results show two tricarbonylrhenium(I) moieties bridged by dppf and two methoxo ligands with the axis of dppf rotated by 53.5° from a parallel position with the Re-Re axis.

A novel Re(I)-Re(VII) complex $Re(CO)_3(PPh_3)_2(OReO_3)$ has been synthesized and characterized [64]. It contains a coordinated perrhenate ion and was shown to be partially dissociated in acetone solution.

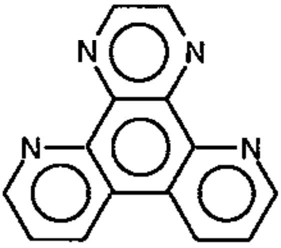
1.6.2 *Complexes with oxygen and nitrogen donor ligands*

The preparation, characterization and reactivity of *fac*-$Re(CO)_3(P\text{-}P)CO_2H$, (P-P is dppe or dppp) and their deuterio analogs have been reported [65]. X-ray crystallography was carried out on *fac*-$Re(CO)_3(dppp)CO_2D$ and shows Re to be in an octahedrally coordinated environment.

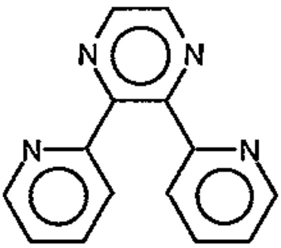
1.6.3 *Complexes with nitrogen donor ligands*

Due to the dearth of information on tetracarbonyl analogues the behaviour of a series of tetracarbonyl complexes of the type $[Re(CO)_4(L\text{-}L)]^+$, (L-L are 2,2'-bipyrimidine, 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine and 1,10-phenanthroline) have been studied and their physical and photophysical properties reported [66].

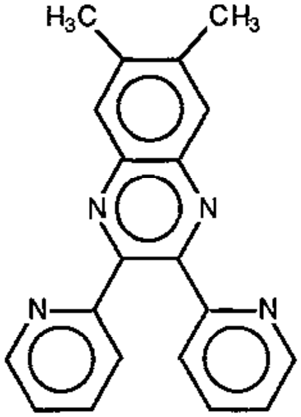
The effects of supporting ligands and secondary metal attachment on the energetics ligand-bridged dinuclear Re(I) complexes has been explored [67]. Specifically, the synthesis and properties of a series of rhenium carbonyls incorporating didentate bridging ligands (**17**), (**18**) and (**19**) have been described. All mononuclear complexes were found to be emissive in room temperature fluid solution with the luminescence originating from a MLCT excited state. Only one dinuclear complex containing (**17**) was found to be emissive. A correlation between MLCT energy and non-radiative decay has been confirmed which is in qualitative agreement with the energy gap law. In a related paper [68], the synthesis, electrochemistry and photophysical properties of a series of homodimetallic Re(I) complexes of general formula $[(LL)(CO)_3Re(BL)Re(CO)_3(LL)]^{2+}$, (LL = 2,2'-bipyridine (bpy), 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen), 2,2'-biquinoline (bqu); BL = pyrazine, 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethane or 1,3-bis(4-pyridyl)propane) have been described. An X-ray crystal structure for the derivative LL = bpy and BL = 1,2-bis(4-pyridyl)ethane show average Re-N(bpy) distances of 2.17Å whereas Re- N(pyridyl) distances were 2.213(6) Å; the intramolecular Re-Re separation was 13.540(2)Å. Oxidation potentials exhibited a weak dependence on the nature of LL ranging from +1.66 to +1.84V vs SSCE. Absorbtion and emission behaviour of these complexes indicate that ligand substitution provides an effective means for controlling the nature, energy and photodynamics of the lowest excited state.



(**17**)



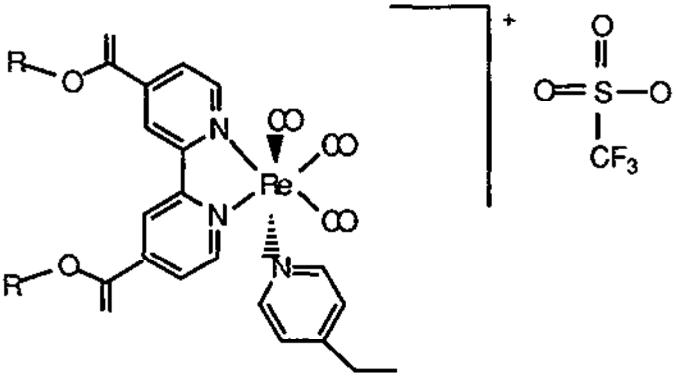
(**18**)



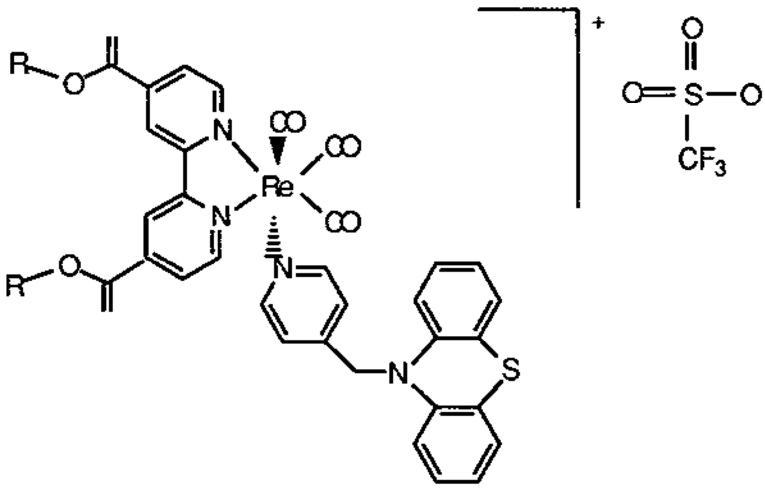
(19)

The synthesis, spectroscopy, electrochemical and photophysical properties of a homologous series of photosensitizers *fac*-[{4,4'-X_2-5,5'-Y_2-2,2'-bipyridine}Re$(CO)_3$Etpy]$^+$, (X = NEt_2, Me, OMe, H, Ph, Cl, CO_2Me, NO_2; Y = Me; Etpy = 4-ethylpyridine) have been described [69].

Approaches aimed at developing molecular-based photochemical devices have led to intermolecular and intramolecular excited-state electron transfer studies involving monolayer quantities of electrode-confined Re-carbonyl complexes (**20**) and (**21**) [70]. Surfaces derivatized with either have been characterized by electrochemical, photophysical and spectroscopic properties. Results from photoelectrochemical experiments show that sustained oxidation of triethanolamine can be brought about.



(20) R = $^{n}Pr\text{-}SiCl_3$



(21) R = ^{n}Pr-SiCl$_3$

An *in situ* infrared study of the electrochemical reduction of CO_2 which is catalysed by derivatives of rhenium carbonyl bipyridyl at carbon cathodes in acetonitrile solution has been described [71]

The spectroscopic, redox and photophysical properties of mixed-metal and homometal cyano-bridged complexes of Re(I) and Ru(I) have been reported [72]. In particular, the complexes $[(CO)_3(bpy)Re\text{-}CN\text{-}Re(bpy)(CO)_3]^+$, $[(CO)_3(bpy)Re\text{-}NC\text{-}Ru(bpy)_2\text{-}CN\text{-}Re(bpy)(CO)_3]^{2+}$ and $[(CO)_3(bpy)Re\text{-}CN\text{-}Ru(dcbpy)_2\text{-}NC\text{-}Re(bpy)(CO)_3]^{2+}$ (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) have been studied. Infrared spectroscopic studies on the trinuclear species show intense absorptions corresponding to intervalence (IT) transitions which are reported in the CT excited state and partially oxidized species. Examination of the Ru-based emission suggests efficient occurrence of energy transfer from the CT excited state of the Re-based chromophore to the Ru-based unit.

1.6.4 Complexes with nitrogen and sulfur donor ligands

The reactions of pentacarbonylhalogenorhenium(I) with 2,6-bis-(*p*-tolylthiomethyl)pyridine or 2,6-bis(methylthiomethyl)pyridine have been studied [73]. Nuclear magnetic resonance studies indicate pyramidal inversion of the coordinated sulfur atoms in addition to an intramolecular fluxional process in which coordinated and uncoordinated thioalkyl and thioaryl groups exchange.

1.6.5 Complexes with nitrogen and phosphorus donor ligands

The synthesis and molecular structure of the dinitrile complex *cis*-$[Re(NCC_6H_4Me\text{-}4)_2(Ph_2PCH_2CH_2PPh_2)_2][BF_4]$ have been described [74]. The crystal structure of the cation shows a distorted octahedral geometry with two linear nitrile ligands with average Re-N distances being

2.065(16)Å. Cyclic voltammetry studies have been carried out and results are compared with those for *trans*-[Re(NCC_6H_4Me-4)$_2$($Ph_2PCH_2CH_2PPh_2$)$_2$][BF_4].

1.6.6 Complexes with phosphorus donor ligands

A report has appeared describing the synthesis of a stable *P*-bonded phosphinidene oxide complex of Re(I) which resulted from a completely different route to any previously described [75]. It was formed by N_2 replacement by PC^{t}Bu from *trans*-[ReCl(N_2)(dppe)$_2$] in thf, presumably by addition of H_2O across the activated phosphorus carbon triple bond of the fluorophosphaalkyne-κ*P* coordinated to the bulky rhenium centre. An X-ray structure indicates that the phosphinidene is coordinated to the rhenium atom via the phosphorus lone-pair electrons with an Re-P distance of 2.203(1) Å.

The crystal structure of (η^5-C_5Me_5)Re(CO)$_3$ and micro-Raman spectra under high external pressure (up to 50 kbar) have been reported [76].

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