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Coordination Chemistry Reviews
169 (1998) 201–235

COORDINATION
CHEMISTRY
REVIEWS

Rhenium 1995

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PII S0010-8545(98)00007-1

Introduction

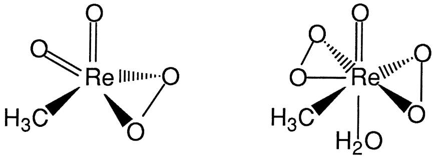
This review provides the reader with a survey of the progress in the coordination chemistry of rhenium for 1995. It is based on a search of Chemical Abstracts, Volumes 122, 123 and 124 but major inorganic chemistry journals have been searched independently for completeness.

1. Rhenium(VII)

1.1. Complexes with oxygen donor ligands

The polymerization of the simple organometal oxide CH_3ReO_3 has been described [1]. This new method presents an alternative to CVD as a means of obtaining oxides. An acidic, colourless solution of the title compound in water slowly generated a highly refractory golden-coloured precipitate at room temperature or within hours when a temperature of 70 °C was used. A 70% yield of the product was obtained; its composition after vacuum drying was found to be $\{H_{0.5}[(CH_3)_{0.92}ReO_3]\}_\infty$. revealing 8% elimination of the methyl groups during its formation. This non-stoichiometric compound, the first known of its kind, has been characterized as a two-dimensional structure containing a requisite amount of Re^{VI} centres to establish electrical conductivity. These centres are assumed to originate from the homolytic loss of methyl groups during polymer formation. Its salient physical properties are graphite-like consistency, reflectance, electrical conductivity and weak paramagnetism. In related papers, the polymer was further characterized by TGA, TEM, electron diffraction and neutron diffraction [2] and models of the polymer were investigated by the EHMO method [3]. The latter study shows the band structure of the polymer to resemble that of ReO_3 but important differences arise from its two-dimensional nature. Those rhenium atoms with missing methyl groups are oxidized rather than reduced. A variety of inclusion sites for hydrogen were explored, the hydrogen was found to be protonic providing for further reduction of the Re atom and some Re–O bonds.

The oxidation of chloride ions, by hydrogen peroxide using methylrhenium trioxide as the catalyst in acidic aqueous solutions, has been studied [4]. The active catalytic species are the monoperoxo complex $CH_3ReO_2(\eta^2-O_2)$ and the diperoxo complex $CH_3ReO(\eta^2-O_2)_2(OH_2)$, (**1**). The rate constants for reaction of these complexes with Cl^- at 25 °C in 1.0 M $HClO_4$ and $\mu = 2.0$ M were found to be 0.059 ± 0.007 and 0.124 ± 0.005 l mol^{-1}s^{-1}, respectively, which is approximately 10 000 times faster than the rate for the uncatalysed reaction. Using the initial-rate method, the reaction progress was followed by monitoring the consumption of monochlorodimedone at $\lambda = 270$ nm. The latter was found to react rapidly with chloride ion oxidation products.



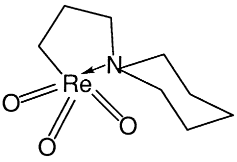
(**1**)

A mechanistic study of the coordination of hydrogen peroxide to methylrhenium trioxide with particular emphasis on the first step of peroxide binding has been carried out [5]. Activation parameters $\Delta H‡$, $\Delta S‡$ and $\Delta V‡$, for the coordination have been determined and they are indicative of a mechanism involving nucleophilic attack. Coordination of the hydrogen peroxide involves its conversion to η^2-O_2 concomitant with loss of protons which are transferred to one oxide oxygen atom which remains on the metal as an aqua ligand. The reaction rate was monitored over a range of temperature and pressure conditions and was found not to be pH dependent. The deuterium kinetic isotope effect was also determined, $k_H/k_D = 2.8$. A bromide ion reaction was used to determine the activation parameters.

1.2. Complexes with oxygen and nitrogen donor ligands

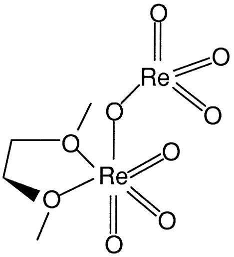
The dynamics of Lewis-base adducts (monodentate and didentate) of organorhenium(VII) oxides in solution were studied [6]. At room temperature, exchange of both the base and oxo ligands occurred which was promoted by donor solvents as revealed from ^{17}O exchange studies. The synthesis and crystal structure of the (γ-Aminoalkyl)rhenium oxide, (**2**), is reported and its crystal structure has been obtained. The Re–O distances are in the range 1.695(4) Å to 1.715(4) Å while the Re–N distance is 2.385(4) Å. Compounds of this type are intramolecular base adducts in the solid state, but rigid geometries in solution are observed only at lower temperatures.

The coordination chemistry of dirhenium heptaoxide with donor solvents and Lewis-base ligands has been studied [7]. The title compound, when dissolved in solvents such as dme, thf and CH_3CN, forms adducts of general formula $O_3ReOReO_3 \cdot 2L$ where L is monodentate. These adducts are characterized by



(2)

unsymmetrical bent oxygen bridges in the solid state as confirmed by the X-ray crystal structure for $O_3ReOReO_3 \cdot$ dme (**3**). When stronger chelating *N*-donors such as bpy, *N*,*N*-dicyclohexyl-1,4-diazabuta-1,3-dien and 2,2′-bis(pyrazolyl)propane were used rigid symmetric bridges resulted in the adducts even in solution. Thermal decomposition generates Re_2O_7 and the respective ligand. When tridentate ligands such as tris(pyrazolyl)methane (tacn), *N*,*N*′,*N*″-trimethyl1,4,7-triazacyclononane (tacn*) and 1,4,7-trithiacyclononane (ttcn) were used, breaking of the Re–O–Re bridges occurred and ionic perrhenates $[ReO_3L_3]^+[ReO_4]^-$ were formed. The crystal structure of the tacn* derivative has been obtained. Intermolecular hydrogen bridging plays a prominent role in the crystal packing of the ionic perrhenates.



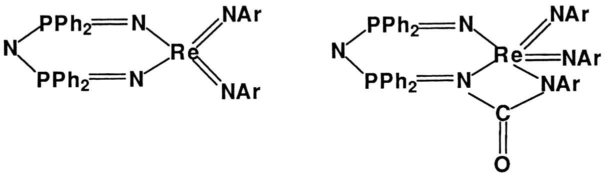
(3)

1.3. Complexes with nitrogen donor ligands

Cyclophosphazenerhenium(VII) dioxide was prepared and its reactions with aromatic isocyanates have been studied [8]. The title compound, a white solid and completely insoluble in all common solvents, was heated in toluene with various aryl isocyanates (2 mol) generated dark red–brown solutions accompanied by evolution of CO_2. The resulting products were found to be of two types; namely substitution or substitution plus addition or mixtures of both types, (**4**). They were characterized by elemental analysis, IR and NMR spectroscopies and mass sepectrometry. Efforts to separate the mixtures were unsuccessful.

1.4. Clusters

In an effort to mimic dimetallic catalysts the reaction between a rhenium oxide and a platinum cluster complex has been studied [9]. This has led to a remarkable



(4)

example of a cluster complex with a very interesting structure in which there are distinct oxide and carbonyl faces which exhibit very unusual metal–metal bonding; it may provide the best example to date for an alumina–rhenium oxide–platinum interface. The cluster $[Pt_5(\mu\text{-}CO)_5L_4Re(\mu\text{-}O)_3(\mu\text{-}OH)(ReO_4)][ReO_4]$, was produced from the complex reaction between $[Pt_3(\mu\text{-}CO)_3L_3]$, L=P(cyclohexyl)$_3$, with about a 25% yield of Re_2O_7. It was characterized by X-ray crystallography, IR and ^{1}H and ^{31}P NMR spectroscopies. The structure of the cation is best described as a central RePtCo unit with four peripheral Pt(CO)L units each being coplanar with and arranged like spokes of a wheel around the Re–Pt axis with each peripheral PtRe unit being bridged by a μ-O or μ-OH ligand. A perrhenate ligand is weakly bonded to the central rhenium atoms. If one ignores metal-metal bonding, it can be seen that the central Re atom is coordinated by hard oxygen donors while the central platinum atom is coordinated by soft carbonyl ligands, while the peripheral platinum atoms have a mixed coordination. The central Re–Pt bond is 2.584(2) Å while the bridged RePt distances are in the range 2.792(2)–3.275(2) Å with the longest being tentatively assigned to the hydroxide-bridged bond. The closest analogy with classical structures would be to consider it to have been formed by fusion of two butterfly clusters at a common edge. EHMO calculations have been carried out to rationalize the cluster bonding.

2. Rhenium(VI)

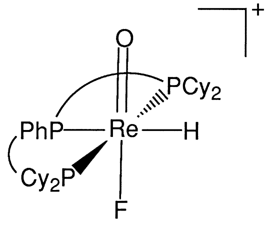
2.1. Complexes with oxygen donor ligands

The nature and strength of the metal–metal bond in the hypothetical complexes $O_3M–M(CO)_3$, (M=Re,Tc) was investigated and a comparison with previous ab initio MO studies of the dinuclear $O_3ReReCl_2(H_2PCH_2PH_2)_2$ and on monometallic O_3R-L, L=CH_3, CF_3, Cl and F has been made [10]. In particular SCF, two-configuration SCF and Cl calculations were carried out and results show that the electron withdrawing nature of ReO_3 gives rise to a highly polar hypothetical dinuclear complex. The charge transfer of 0.534 e is not as large as that in $O_3Re–ReCl_2(dmpm)_2$ which is the only presently characterized molecule. The coupling for both of these complexes may best be viewed as σ donation from the most oxidized rhenium atom to the least oxidized one. A topological analysis of the Laplacian density distribution indicates that the bonding in the ReO_3 unit is mostly ionic. Additionally the Laplacian, distribution characterized along the metal–metal bond axis is typical of a σ donation but there is some evidence of covalent character.

3. Rhenium(V)

3.1. Complexes with halide ligands

The high yield synthesis of the complex $[Re(F)(H)(O)(Cyttp)]^+$, (**5**), (Cyttp = $PhP(CH_2CH_2PCy_2)_2$) has been reported [11]. This compound was found not to react readily with either CO or SO_2 but at elevated temperatures it reacted with $NaSbF_6$ giving the difluoro-oxo complex $[ReF_2(O)Cyttp]^+$. The latter complex undergoes fluoride substitution by Cl or Br to give $[Re(X)(F)(O)Cyttp]^+$ with X=Cl or Br. In these complexes the fluoride and oxide are *trans* as inferred from spectroscopic data.

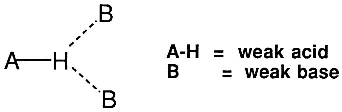


(**5**)

3.2. Complexes with hydride ligands

A new class of hydrido-alkylidyne rhenium complexes has been synthesized starting from rhenium polyhydrides [12]. The reaction of $ReH_4(mq)(PPh_3)_2$ (mq = 2-mercaptoquinoline anion) with terminal alkynes RC_2H, (R=H, Et, *n*-Pr, *i*-Pr, *n*-Bu, Ph, *p*-tolyl, CH_2Ph), in the presence of an electrophile (HPF_6(aq) or Ph_3CPF_6) in dichloromethane solvent yielded a facile and high yield route to a new class of complexes $[Re(C_2H_2R)H_2(mq)(PPh_3)_2]PF_6$. These compounds are easily deprotonated to form the neutral monohydride. When this reaction is carried out using internal alkynes the same complexes are formed. This observation in conjunction with results from deuterium labelling studies suggest that isomerization of internal to terminal alkynes occurs via η^2-allene intermediates. These alkylidyne complexes were characterized by X-ray crystallography. When $ReH_4(mq)(PPh_3)_2$ is treated with an electrophile in the absence of an alkyne, the dirhenium complex $[Re_2H_6(\mu\text{-mq})_2(PPh_3)_4](PF_6)$ is formed. Attempts to grow crystals led to $[Re_2H_6(\mu\text{-mq})_2(PPh_3)_4](H_2PO_4)_2 \cdot 2(CH_3)_2CO$, as determined by X-ray crystallography, which shows a dirhenium(V) dication containing two eight-coordinate metal centres linked through a fairly symmetrical $Re_2(\mu\text{-S})_2$ unit.

Studies aimed at elucidating the possibility of intermolecular H-bonding with a suitable H-donor have been carried out in order to probe what geometry would be adopted in the absence of geometrical constraints which are present in a chelate system [13]. Indole was chosen because of its suitable H-bond proton acceptor site. The polyhydride $[ReH_5(PPh_3)_3]$ co-crystallized with indole yielding $[ReH_5(PPh_3)_3] \cdot C_8H_6NH \cdot C_6H_6$ as large yellow crystals. In the X-ray structure determination the N–H hydrogen atom of the indole is close to two of the rhenium hydrides forming a three-centre H-bond of the type (**6**) which was later confirmed by neutron diffraction. This interaction is strong enough to hold the two components together in the crystal without complete proton transfer. From neutron diffraction studies, the two short H···H distances are very asymmetric 2.212(9) and 1.734(8)Å with the shorter one being similar to intramolecular N–H···H–M distances. These studies show that the presence of indole allows more rapid formation of much larger crystals when compared to its absence and that the structure of the complex is not significantly altered by H-bonding. Indole may therefore be a useful agent whenever a compound, which is a potential H-bond acceptor, fails to crystallize satisfactorily for crystallographic studies.

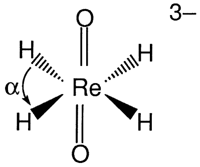


(**6**)

3.3. Complexes with oxygen donor ligands

Structural models for hydrodesulfurization catalysts have been synthesized [14]. A thf slurry of $ReOCl_3(PPh_3)_2$ was treated with thienyllithium reagents giving $Li(thf)_nReO(thienyl)_4$ where thienyl is $2\text{-}C_4H_3S$, $2\text{-}MeC_4H_2$,$2\text{-}C_8H_5$ and $2\text{-}C_{12}H_7S$. These complexes are reactive toward protic and oxidizing agents. Electrochemical studies have been carried out and show that these complexes undergo oxidation at mild potentials. X-ray crystallography has been carried out for $Li(thf)_3ReO(C_4H_3S)_4$ and $Li(thf)_4ReO(C_8H_5S)_4$ with both structures showing a square pyramidal coordination environment for the Re in which the four thienyl ligands are arranged in a pinwheel fashion.

A communication has appeared which shows how a relatively minor modification of the ligand environment in dioxo d^2 octahedral transition metal complexes may reverse the usual stability order of the diamagnetic *trans* and *cis* isomers [15]. In particular, EHMO calculations were carried out on the model complex $[ReO_2H_4]^{3-}$ in which the angle α, defined in (**7**), was varied from 90 to 60° in increments of 10° mimicking a didentate ligand with varying bite angles. For $\alpha = 90°$, the *trans* isomer was found to be more stable by 25 kcal mol^{-1}, while decreasing its value destabilizes the *trans* isomer and stabilizes the *cis* isomer. In order to check these qualitative conclusions, DFT calculations were performed on $[ReO_2He_4]^+$ and confirmed the trend shown in the EHMO calculations. In addition a triplet state for the *cis* isomer was optimized and, in agreement with experiment, was found to be higher in energy than diamagnetic ground state.



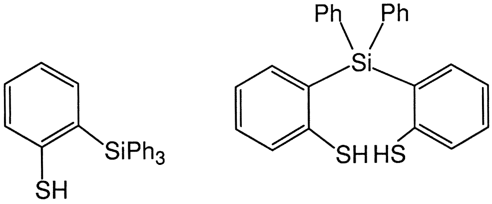
(7)

The successful preparation of a heterometallic dinuclear alkoxide cluster via addition of a higher oxidation state derivative of one metal to a lower oxidation state derivative of a second metal formed in situ has been reported [16]. The heterodimetallic methoxide [$ReMoO_2(OMe)_7$] was obtained in 62% yield by hexane extraction from the electrolyte prepared by anodic oxidation of Re metal in a methanolic solution of [$MoO(OMe)_4$] with LiCl as electrolyte. Its molecular structure exhibits the well known bioctahedral conformation with two [$MO(OMe)_5$] octahedra with three shared μ-OMe groups and possesses C_1 symmetry. The cluster is volatile and mass spectrometry indicates complete dissociation into homometallic species in the gas phase.

3.4. Complexes with oxygen and sulfur donor ligands

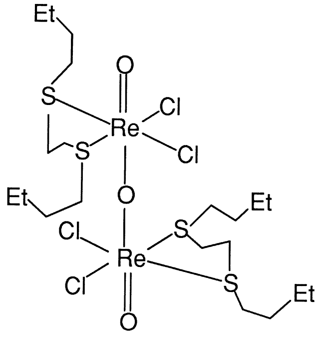
A systematic investigation of the reaction of the thiol 2-$Ph_3SiC_6H_4SH$ and the bis(thiolate) $SiPh_2(C_6H_4SH\text{-}2)_2$ (**8**), with a range of tertiary phosphine-containing complexes of transition metals including rhenium was carried out [17]. The reaction of [$ReOX_3(PPh_3)_2$], X = Cl or Br with 2-$Ph_3SiC_6H_4SH$, in methanol, under reflux, in the presence of a base, generated the dark green complex [$ReO(Cl)(SC_6H_4SiPh_3\text{-}2)_2(PPh_3)$]. When X = Br only the oxohydroxo-complex [$ReO(OH)(SC_6H_4SiPh_3\text{-}2)_2(PPh_3)$] was isolated, clearly the bromide is hydrolysed to hydroxide by adventitious water during the reaction. These complexes were characterized by IR and NMR spectroscopies. The latter complex was further studied by X-ray crystallography and reveals rhenium in a distorted trigonal bipyramidal geometry, the Re=O distance is 1.688(4) while the Re–O(H) distance is 1.931(4) Å and the Re–S distances are 2.328(2) and 2.278(1) Å. The two thiolate ligands are in a *cis* position, while the oxide and hydroxide ligands are in equatorial sites. When the reaction was carried out in the presence of $NaBH_4$ and no base, a blue thiolate polyhydride [$ReH_4(SC_6SiPh_3\text{-}2)(PPh_3)_3$] was obtained in high yield. It is moderately air stable but decomposes rapidly in solution. Its crystal structure reveals that the three P atoms and one sulfur atom are arranged in a distorted tetrahedral fashion about the Re atom. The Re–P distances are 2.289(2), 2.291(2) and 2.470(2) Å while the Re–S distance is 2.326(2) Å.

The synthesis and structure of μ-oxo bridged oxorhenium(V) complexes with mixed didentate thioether/chlorine coordination has been reported [18]. They were



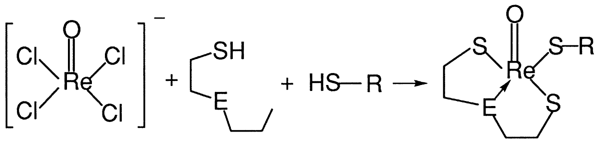
(**8**)

prepared by the reduction of ReO$_4$ with SnCl$_2$ in strongly acidic solution in the presence of thioethers with the general formula R(CH$_2$)$_2$S(CH$_2$)$_2$S(CH$_2$)$_2$R′, (R=R′=H,Et; R=S–Bu, R′=Et; R=OEt, R′=H; R,R′=OEt). Alternatively, these compounds can also be produced by ligand exchange reactions from [ReOCl$_4$]$^-$ in methanolic solution. The derivative R,R′=Et was studied using X-ray crystallography; it comprises two independent units (**9**), bridged by an oxygen atom. The O=Re–O–Re=O backbone shows considerable deviation from linearity. The molecule adopts a staggered conformation in which the ReS$_2$Cl$_2$ planes are mutually rotated by 168° about the O=Re–O–Re=O axis. The Re=O distances are 1.705(8) and 1.735(4) while the Re–O distances are 1.908(9) and 1.946(9)Å. The Re–S distances are in the range 2.410(2) to 2.439(2) Å.



(**9**)

Studies in the design and evaluation of new rhenium coordination compounds with mixed-ligands for rational tracer design have been carried out [19]. As a result of the "3 + 1" principle i.e. tridentate/monodentate coordination to oxorhenium(V), nineteen new lipophilic oxorhenium(V) complexes of the general formula [ReO(SXS)(SR)], (HSXSH = HSCH$_2$CH$_2$ECH$_2$CH$_2$SH with E = O or S; R = alkyl or aryl) have been prepared. The complexes were prepared when a 1:1 molar ratio mixture of HSXSH and the alkanethiol or substituted benzenethiol in acetonitrile was added to a stirred solution of [NEt$_3$(CH$_2$Ph)][ReOCl$_4$] in methanol at O °C as shown in (**10**). The complexes of aromatic thiols precipitate from the mixture and were purified by column chromatography with chloroform. All complexes were characterized by IR and ^{1}H NMR spectroscopies. In addition, (4-methoxybenzenethiolato)(3-oxapentane-1,5-dithiolato)oxorhenium(V) was further characterized by MS and X-ray crystallography. Its structure comprises a distorted square-pyramidal geometry in which the ether oxygen is bonded to the rhenium atom at a distance of 2.103 Å. The Re=O distance is 1.659 Å and the rhenium atom is displaced from the basal plane by 0.728 Å.



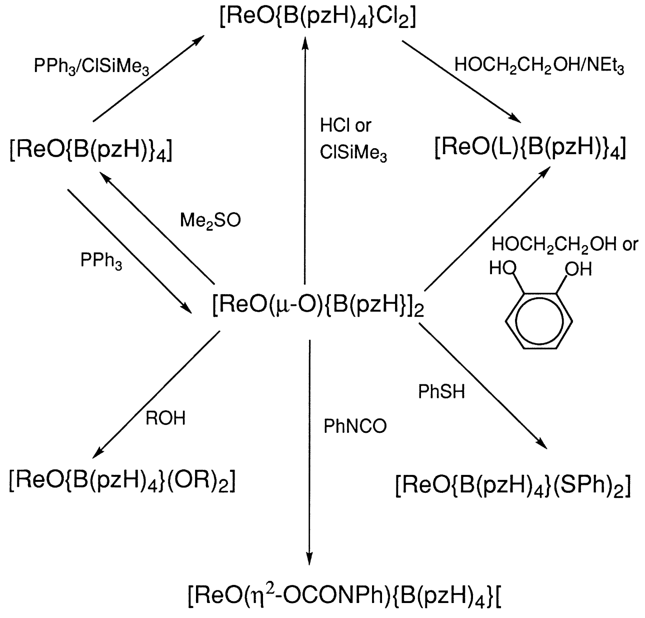
(10)

3.5. Complexes with oxygen and nitrogen donor ligands

The synthesis and characterization of a family of rhenium complexes which display the elusive oxidation state IV, at high pHs has been achieved [20]. High-valent, high-stability oxomethoxorhenium complexes can be prepared from the corresponding *trans*-dioxorhenium complexes and methyl trifiuoromethanesulfonate. The behaviours of these complexes are nearly identical to the analogous oxo and hydroxo complexes with the exception of CH_3^+ which, unlike H^+, does not dissociate from the oxo ligand and provides spectroscopic and electrochemical access to the key intermediate species *trans*-$(O)_2(HO)Re^{V}L_4^+$ and *trans*-$(O)(HO)Re^{IV}L_4^+$, L= 4-dimethylaminopyridine (dmap), 4-pyrrolidinopyridine (pyrrpy), MeOpy, 3,4-dimethylpyridine (Me_2py), methylpyridine (Mepy) and py. As a result the Re(IV) oxidation state is stabilized with respect to redox disproportionation and is observable for several complexes at high pH. The observation of this stateis useful in permitting the stepwise thermodynamics of multi-electron, multi-proton transfer reactions to be mapped.

The reduction of the compound $[ReO_3\{B(pz)_4\}]$ in thf using stoichiometric amounts of triphenylphosphine generated a very reactive compound tentatively formulated as $[ReO(\mu\text{-}O)\{B(pz)_4\}]_2$. This compound was used as a versatile material in the further synthesis of monomeric Re(V) compounds (**11**) [21]. The compounds were characterized by elemental analysis, IR and ^1H NMR spectroscopies. The compounds $[ReO\{B(pz)_4\}(OPh)_2]$ and $[ReO\{B(pz)_4\}(SPh)_2]$ were studied by X-ray crystallography. In addition, all compounds were characterized by laser desorption and electron impact Fourier transform ion cyclotron resonance mass spectrometry.

The synthesis, spectroscopic and electrochemical properties of a series of phenylimidorhenium compounds containing polypyridyl ligands has been described [22]. The reaction of $[Re(O)Cl_3(L\text{–}L)]$, L,-L=bpy, or 4,4′-dimethyl-2,2′-bipyridine, in aniline in refluxing *o*-xylene gave the phenylimido compounds *mer*-$[Re(NPh)Cl_3(L\text{–}L)]$. When they were reacted with an alcohol, the expected alkoxyimido compounds did not form but in the presence of an excess of the polypyridyl ligand salts of the cation *trans*-$[Re(NPh)(OEt)(L-L)_2]^{2+}$ were

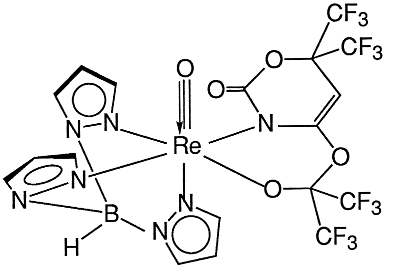


(11)

obtained. These salts represent the first example of phenylimido compounds containing two mutually *trans* polypyridyl ligands, their isolation was unexpected based upon the inertness of *mer*-[Re(NPh)Cl_3(L-L)] towards alcohols and the steric demand associated with placing two polypyridyl ligands in a *trans* position. The brown salts of *trans*-[Re(NPh)(OEt)(L – L)$_2$]$^{2+}$ were allowed to dissolve at room temperature in MeCN solutions containing a few drops of concentrated HCl and rapid reaction ensued resulting in the isolation of *mer*-[Re(NPh)Cl_3(L-L)]. A dark green intermediate was evident in these reactions and its identity and mechanism of formation is under study. The salt *mer*-[Re(NPh)Cl_2(terpy)]PF_6 was prepared by reacting *mer*-[Re(NPh)Cl_3(PPh_3)$_2$] and terpy in refluxing ethanol. It did not show any *trans* effect and is stable in alcoholic solutions containing hydrochloric acid. The spectroscopic and electrochemical properties of these compounds were studied and several structures were determined from X-ray crystallographic studies.

An alternative route to monoxorhenium(V) complexes has been established, in particular, the synthesis of the complexes [$ReOCl_2${C_5H_4N)$_2$C(O)(OH)}], [ReOCl(quin)$_2$], Hquin = 8hydroxyquinone, *cis*-[$ReOCl_2$(PPh_3)(HL), H_2L = 2,6-bis (hydroxylmethyl)pyridine and [$ReOCl_2$(PPh_3)(psal)], Hpsal = N-phenylsalicylideneirnine has been established [23]. These complexes were obtained from [$ReNCl_2$(PPh_3)$_2$] by the remarkable concomitant displacement of the nitrido by an oxo group. This displacement is thought to occur by deprotonation and coordination of a hydroxy group of the chelate ligand *trans* to the nitrido group. Axial coordination of the hard base O^- will weaken the Re–N triple bond thereby pulling the rhenium atom into the equatorial plane. Additionally the large steric requirement of the nitrido ligand will lead to additional weakening of the triple bond promoting its substitution by the smaller oxide. The crystal structure of *cis*-[$ReOCl_2(PPh_3)$(HL) was obtained and shows an unusual N, O^- didentate coordination for the potentially terdentate HL ligand. Furthermore, a surprising feature is the coordination of the pyridine nitrogen which occurs *cis* to the PPh_3 molecule which is in marked contrast to [$ReNCl_2(PPh_3)_2$] the starting complex. The Re–O(oxo) distance is 1.75(2) Å while the Re–O is 1.84(2) and Re–N 2.17(3) Å.

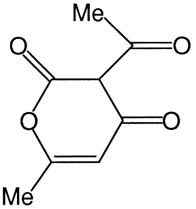
The photolysis of (Hpz_3)ReO(C_2O_4) under aerobic conditions in hexafluoroacetone and acetonitrile resulted in the self-assembly of a diamagnetic fluorinated metallacycle [24]. This new airstable complex was purified by chromatography on silica gel and isolated as violet crystals in 24% yield. From X-ray crystallography it was seen that this photoproduct incorporated two molecules of hexafluoroacetone and a molecule of acetonitrile as part of the original oxalate ligand (**12**). The chelate has surprising complexity and is formally a dianion in which the rhenium atom is bound to an alkoxide oxygen derived from hexafluoroacetone and a deprotonated nitrogen of an *N*-vinylcarbamate (derived from CH_3CN). The chelate forms two fused six-membered rings including the rhenium atom and excluding the trifluoromethyl groups it is roughly planar with rhenium situated 1.21Å above this plane and the Re–Oxo bond canted toward it by 26°. This allows the carbonyl oxygen to rest in the cleft between the two pyrazoles, *cis* to the nitrogen of the chelate. The mechanism of this transformation was probed by carrying out the photoreaction with (Hpz_3)ReO(C_2O_4) which was ^{18}O-enriched in the oxalate ligand and a suggested pathway is presented.



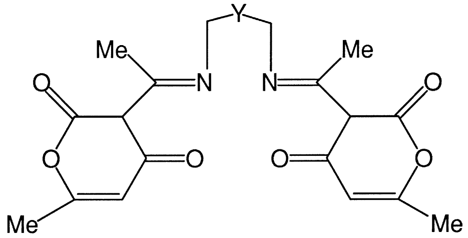
(**12**)

The near-infrared luminescence properties of single crystals of *trans*-[ReO_2(1-methylimidazole)$_4$]I have been studied [25]. The luminescence spectrum, which was obtained between 4.2 and 100 K, revealed no resolved hot bands; the analysis of the spectrum showed the first example of coupling between two metal-ligand vibrational modes involving different ligands. Those compounds with coupling between coordinates involving different ligands are promising candidates for selective photochemistry on the organic ligands via excitation of the *trans*-[ReO_2]$^+$ unit.

Rhenium and technetium complexes from pentadentate and tetradentate Schiff base ligands have been synthesized due to the interest in coordinating multidentate Schiff bases which have utility in stabilizing Re/Tc complexes for use as radiopharmaceuticals [26]. To circumvent the problem of producing lipophilic complexes, the ligand (**13**) has been synthesized; it is based on dehydroacetic acid, a potentially pentadentate ligand which contains lipophilic hydrocarbon chains and polar carbonyl groups. The complexes [ReO(apa)], [{ReO(epa)]}$_2$O] and TcOCl(epa)] were characterized by IR and ^{1}H NMR spectroscopies; H_3apa = *N′,N′*-3-azapentane-1,5-diylbis(3-(1-iminoethyl)-6methyl-2H-pyran-2,4(3H)-dione) and H_3epa = *N′,N′*-ethylenediylbis(3-(1-iminoethyl)-6-methyl-2H-pyran-2,4(3H)-dione). The complex [Re(dha)$Cl_2(OPPh_3)(PPh_3)$]·EtOH is the unexpected result of the reaction between [$ReOCl_3(PPh_3)_2$] and H_2ppa in ethanol in which one PPh_3 migrates to the oxo oxygen and the resulting vacant site filled and one chloro ligand being replaced by two oxygen donor atoms; H_2ppa = *N′,N′*-propylenediylbis[3-(1-iminoethyl)-6-methyl-2H-pyran-2 ,4(3H)-dione] and H_3epa. Its crystal structure has been obtained, the coordination geometry about the rhenium atom is distorted octahedral. The Re–O(3) and Re–O(4) distances are 1.987(20 and 2.016(3) Å, respectively, and are indicative of two oxygen donors involved in π-delocalization within the ligand. The Re to phosphine oxide distance is 2.051(2) Å and the Re–Cl bond *trans* to the phosphine is long [2.430(1) Å] while the Re–Cl bond which is *cis* to the phosphine is normal [2.362(1) Å].



dha



Y = CH_2NHCH_2 = $(dha)_2$dien
Y = none = $(dha)_2$en
Y = CH_2 = $(dha)_2$pn

(**13**)

The synthesis and properties of the complex $[Re(NPh)(OH)(PPh_3)(tacn)]^{2+}$ which has been found to mediate alkene oxidation by PhIO at room temperature has been reported [27]. The reaction of [$Re(NPh)Cl_3(PPh_3)_2$] with tacn in CH_2Cl_2

gave the title complex which was subsequendy characterized by elemental analysis, IR and UV–VIS spectroscopies, CV and X-ray crystallography. The crystal structure reveals the rhenium atom with a phenylimido and hydroxy group *cis* to one another; the tacn ligand facially coordinates to rhenium. The Re–NPh distance is 1.706(10) Å while the Re–O distance is 2.004(7) Å. Cyclic voltammetry in acetonitrile shows an irreversible reduction wave at −0.77 V assignable to the reduction of rhenium(V) to rhenium(IV).

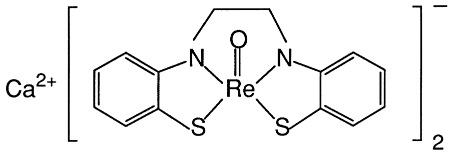
The synthesis, spectroscopy and electrochemistry of a series of novel cationic rhenium(V) methylimido pyridine phosphine complexes have been reported [28]. In particular, the reaction of $[Re(NMe)Cl_3(PPh_3)_3]$ with pyridine or 4-methylpyridine in ethanol under reflux gave *trans*-$[Re(NMe)(py)_2(PPh_3)(OEt)(Cl)]ClO_4$, $[Re(NMe)(py)_3(OEt)(Cl)]ClO_4$ and $[Re(NMe)(4\text{-}Mepy)_2(PPh_3)(OEt)(Cl)]ClO_4$. When the reaction was carried out at room temperature only *cis*-$[Re(NMe)(py)_2(PPh_3)(OEt)(Cl)]ClO_4$ was obtained. The crystal structure of $[Re(NMe)(py)_3(OEt)(Cl)]ClO_4$ was determined, each asymmetric unit is composed of two independent molecules and reveals a distorted octahedral geometry with an almost linear Re–N–Me unit consistent with a four-electron donor formulation for the methylimido unit. The ethoxy group is *trans* to the methylimido moiety Re–O(Et) distances are 1.922(8) and 1.9268(8) Å while the Re-N(Me) distances are 1.71(91) and 1.73(1) Å in each independent molecule. All complexes were characterized by ^1H NMR and IR spectroscopies, FAB-MS and magnetic susceptibility measurements. The electronic absorption spectra of these complexes have also been obtained and indicate low energy $d_{xy}\rightarrow d_{\pi*}$ electronic absorption bands at 400–500 nm. These complexes were also studied by cyclic voltammetry.

The crystal structure of $(AsPh_4)_2[Re(NO)(H_2O)(CN)_4]\cdot 5H_2O$ has been determined [29]. The ion has a distorted geometry in which the rhenium atom is displaced by 0.17 Å out of the plane formed by the four carbon atoms of the cyano ligands towards the nitrosyl ligand. The Re–NO distance is 1.732(7), Re–O = 2.165(5) and $Re–CN_{av} = 2.09$ Å.

Interest in the stereochemistry and dynamic behaviour of metal complexes ligated by lopsided and symmetrical N-donor ligands in biological systems has led to the synthesis of a series of $Re_2O_3Cl_4(L)_4$ complexes where L = 1,5,6-trimethylbenzimidazole (Me_3Bzm), 3,5-lutidine (3,5-lut) and py [30]. The complexes were prepared from $ReOCl_3(Me_2S)(OPPh_3)$ and an excess of ligand. Under stoichiometric conditions, reaction of the former with Me_3Bzm, 3,5-lut or py produced a unique family of monomeric monosubstituted complexes in which the normally labile $OPPh_3$ ligand remained coordinated. The Me_3Bzm derivative was characterized by X-ray crystallography and found to have a pseudo-octahedral coordination geometry in which the $OPPh_3$ is coordinated *trans* to the oxo ligand and *cis* to the Me_3Bzm ligand. The Re–N distance is 2.108(8) Å while the Re–O(Oxo) is 1.662(6) Å and the Re–$OPPh_3$ bond distance is 2.081(7) Å. Stacking interactions between the imidazole ring of Me_3Bzm and the aromatic ring of $OPPh_3$ are observed in the solid state and have been inferred for the 3,5-lut and py derivatives. The ability of planar *N*-heterocyclic donor ligands to interact favourably with the usually labile $OPPh_3$ ligand may explain the stability of the ligands. Further reaction of the Me_3Bzm derivative with one equivalent of 3,5-lut or py resulted in the precipitation of the mixed-ligand species $Re_2O_3Cl_4(Me_3Bzm)_2(3,5\text{-lut})_2$ and $Re_2O_3Cl_4(Me_3Bzm)_2(py)_2$. Preliminary X-ray studies imply that each Re atom has a Me_3Bzm and a py ligand *cis* to one another. The facile formation of these dimers would seem to be initiated by replacement of $OPPh_3$ with a second nitrogen ligand.

3.6. Complexes with oxygen, nitrogen and sulfur donor ligands

The crystal structure of a bis(amido)bis(thiolato)oxorhenium(V) complex which forms a methanol–solvated salt with calcium extracted from silica gel has been reported [31]. In particular, the complex (**14**) was prepared by warming the bis(*o*-mercaptoaniline) chelate with trichlorobis(triphenylphosphine)oxorhenium(V) and 2.0 ml of methanolic NaOAc at 80 °C for 15 min. A yellow solid was collected by flash chromatography and recrystallization from 50% MeOH/EtOH gave a red complex of the title compound. Its proton NMR spectrum was simple, suggesting it exists as a symmetrical anion formed by the deprotonation of both nitrogen atoms. From X-ray crystallography, the complex is seen to be in the bis(aminato) form and the counterion appears as a centre of high electron density surrounded by seven molecules of methanol in a stoichiometry of 1 to 2 with the rhenium complex. Curiously, there was no deliberate exposure of the complex to a source of calcium. Furthermore, the calcium ion is heptasolvated with a capped trigonal prism geometry in which only methanol solvates the calcium ion even though 50% MeOH/EtOH was used for crystallization of the complex. It is likely that the calcium originated from the silica gel; ICP analysis of the silica gel revealed it to contain 1.51 mg of calcium per gram.



(**14**)

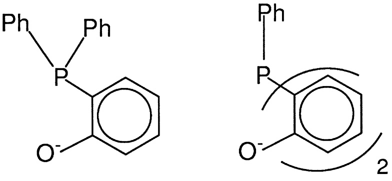
An investigation of $[M^{V}O]^{3+}$ ($M = {}^{99m}Tc$,Re) derivatives of ethylene-DL-cysteine has been carried since chirality often significantly influences renal clearance [32]. When the chiralities of the two amino acid moieties differ in $M\text{-}O(N_2S_2)$ complexes there are two expected configurations for the carboxyls namely, *syn* and *anti*. The species $ReO(DL\text{-}ECH_3)$ was obtained in a new and unexpected arrangement as the *syn*, *syn* form and studied by NMR spectroscopy and X-ray crystallography from which it can be seen that the basal coordination plane has an unusual NOS_2 coordination set.

High oxidation state rhenium complexes with the hydridotris(1-pyrazolyl) borato-oxorhenium(V) core have been synthesized [33]. The reaction of $HB(pz)_3ReOCl_3$ with hydralazine and 1,4 dihydrazineophthalazine gave $HB(pz)_3[ReO(NNHC_8H_5N_2)] \cdot CH_2Cl_2$. and $\{[HB(pz)_3ReO]_2(1\text{-}4\text{-}(NNH)_2$

$C_8H_4N_2)\}$. In the former reaction after refluxing for 2 days, the reaction mixture was filtered and a yellow-green product crystallized. It was characterized by IR, ^1H NMR and UV-VIS spectroscopies and X-ray crystallography. The Re–O distance is 1.706(7)Å while the Re–N distances to the nitrogen donors of the hydridotris(pyrazolyl)borato ligand are inequivalent: the bond *trans* to the oxo ligand is 2.258(8) while the average distance is 2.314(10) Å for the donor atoms *cis* to the terminal oxo group. A second reaction in which $HB(pz)_3ReOCl_3$ was reacted with pyridine-2-thiol giving $HB(pz)_3[ReO(2\text{-}S\text{-}py)_2]\cdot 1.5CH_2Cl_2$. It was also characterized by X-ray crystallography and displays a distorted octahedral geometry about the rhenium atom with $\{ReON_3S_2\}$ coordination. The pyridinethiolate ligand adopts a terminal monodentate coordination mode through the sulfur donor. The Re–O distance is 1.683(6) Å and the Re–N distance *trans* to the terminal oxo group is lengthened Re–N = 2.257(6) relative to the *cis* donor atoms, the average Re–N distance is 2.156(6) Å. The Re–S distances average 2.325(3) Å.

The preparation of tetradentate ligands of the type $HSCH_2CONHRNNCH$ $(2\text{-}C_6H_4OH]$, where $R=(CH_2)_2$, $(CH_2)_3$ and $(CH_2)_4$ has been achieved, these ligands were then allowed to react with $MO_2(py)_2Cl$, M=Tc and Re and $ReO(PPh_3)_2Cl_3$ in methanol to give penta and hexa-coordinated complexes [34].

3.7. Complexes with oxygen, nitrogen and phosphorus donor ligands



(15)

A modified preparation of the hydrochloride adduct of the potentially tridentate bis(hydroxyphenyl)phosphine ligand, (H_2PO_2) by a convenient large-scale route has been achieved and its coordination chemistry with pentavalent Re and Tc has been investigated (**15**) [35]. Using this ligand as well as the potentially didentate analogue (*o*-hydroxyphenyl)diphenylphosphine, HPO, PO_x^{x-} $(x=1,2)$ complexes of Re(V) and Tc(V) have been prepared by metathesis reactions with the metal precursor and/or by reduction/ligand-exchange reactions with ammonium perrhenate or pertechnetate. The complexes were of the type $MOCl(PO)_2$, $ReN(PO)_2(PPh_3)$, *fac*-$ReZCl(PPh_3)(PO_2)$, *fac*-$ReZ(PO)(PO_2)$ and $MO(PO_2)$ (HPO_2) where M is Re or Tc, Z is O or NPh. The didentate P,O monobasic ligands form oxometal complexes which are structurally analogous to the complexes of the two metals with other didentate monobasic ligands. The mono(PO_2) phenylimido complexes were isolated as *cis*- or *trans*-(*P*,*P*) geometrical isomers depending on the reaction conditions whereas for the mono(PO_2) oxo analogue a *cis*-(*P*,*P*) product was obtained. Mixed-ligand complexes containing both PO_2^{2-} and PO_2^- ligand with *cis*- or *trans*-(*P*,*P*) geometry were synthesized from mono(PO_2) complexes.

Bis(PO_2) complexes were obtained as mixtures of two diastereomers with one ligand protonated (HPO_2^-), neither of the diastereomers were interconvertible and they resisted hydrolysis. They could also be obtained by direct reduction from perrhenate or pertechnetate. Mixed(PO/PO_2) complexes or bis(PO_2) complexes could not be obtained from triphenylphosphine-containing precursors via ligand exchange reactions. All complexes were characterized by MS and IR and $^1H/^{31}P^1H$ NMR spectroscopies. X-ray crystal structures have been obtained for *fac*, *cis*-(*P*,*P*)[Re(NPh)Cl(PPh_3)(PO_2)]·$2CHCl_3$ and *fac,cis*-(P,P)-[ReO(PO)(PO_2)] from which it can be seen that the anchoring of the *o*-oxyphenyl groups strengthen the Re–P bonds significantly. In both structures a *cis*-(*P*,*P*) geometry exists with the Re atom in a distorted octahedral geometry.

3.8. Complexes with oxygen and phosphorus donor ligands

The structure of *trans*-dichloroxo(2-propoxido)bis(triphenylphosphine) rhenium(V) has been elucidated [36]. This compound crystallizes with discrete [$ReOCl_2(C_3H_7O)(C_{18}H_{15}P)_2$] units. The rhenium atom is octahedrally coordinated and the bulky phosphine ligands are *trans* to each other. The O–Re–O unit is almost linear with an angle of 174.25(9)°. The Re–O bond distance is 1.692(2) Å while for the alkoxo group the Re–O distance is 1.890(2) Å.

3.9. Complexes with nitrogen donor ligands

The synthesis and properties of some new rhenium imido complexes has been demonstrated [37]. The complex [$ReCl_2(NC_6H_4PPh_2$–2)($HNC_6H_4PPh_2$–2)] represents a new class of complex containing a *P*,*N*-chelated imide ligand; it was synthesized from [$ReCl_3O(PPh_3)_2$] and 2-$Ph_2PC_6NH_2$ in toluene under reflux yielding brown crystals in nearly quantitative yield. It was characterized by ^1H and ^{31}P NMR spectroscopies and X-ray crystallography. The rhenium atom is in a distorted octahedral environment with the principal distortions being due to the relatively small bite angles of the chelated ligands. The Re–N(imide) distance is 1.757(4) Å while the Re–N(amide) distance is 1.988(4) Å. The complex [Re-(8-$HNC_9H_6N)_2$ O(PPh_3)][BPh_4] was synthesized in high yield from the reaction between [$ReCl_3O(PPh_3)_2$] and 8-aminoquinoline under reflux in methanol. It was characterized by IR and ^1H NMR spectroscopies and X-ray crystallography. The X-ray data shows the 8-aminoquinoline ligands acting as *N*,*N*-chelated amides to the rhenium atom which is in a distorted octahedral environment. One amido nitrogen is *trans* to an oxo group while the other is *trans* to the quinoline nitrogen of the other chelated nitrogen. The quinoline-rhenium lengths are 2.183(6) and 2.157(6) Å while the Re–N(amide) lengths are 2.028(6) and 1.958(6) Å. The complexes [Re(NPh)(PPh_3)L_2][BPh_4] where L = 3-trimethylsilylpyridine-2-thiol anion, tspyt, or pyridine-2thiol anion, pyt, represents a new class of complexes containing the rhenium imido-core with pyridinethiol coligands. These were synthesized from [$ReCl_3(NPh)(PPh_3)_2$] with the appropriate ligand yielding cationic green complexes which were characterized by IR and ^1H NMR spectroscopies and X-ray crystallography. The latter reveals a distorted octahedral geometry for the tspyt derivative with an Re–N bond distance of 1.725(8) Å consistent with the imide functioning as a four-electron donor. These complexes were further studied by CV.

As part of a systematic study on the reactivity and structure of rhenium-nitrido complexes, the reaction of [ReNCl$_2$(Me$_2$PhP)$_3$] with trifluoromethane-sulfonic acid (2 h reflux in CH$_2$Cl$_2$) gave rise to the air-stable complex [ReNCl(OSO$_2$CF$_3$)(Me$_2$PhP)$_3$] in 85% yield [38]. It was characterized by elemental analysis, IR spectroscopy, FAB-MS and X-ray crystallography. The rhenium atom is in a distorted octahedral environment; the short Re–N distance of 1.642(6) Å is typical for terminal nitrido ligands. The nitrido ligand is also responsible for a strong *trans* influence which weakens the Re–O bond which is 2.403(5) Å in this compound. The Re–P distances are in the range 2.429(2) to 2.46792) Å.

The crystal structure of *trans*- bis(isothiocyanato)(methoxy)(phenylimido) bis(triphenylphosphine)rhenium(V) has been obtained [39]. The rhenium atom is in a distorted octahedral environment in which two triphenylphosphine ligands are arranged *trans* to each other while a methoxy group is *trans* to the phenylimido group. The Re–NPh distance is 1.744(4) Å and the NCS ligands are coordinated through the N atom. The Re–O distance is short [1.922(3) Å] and this results from the negligible *trans* influence of the phenylimido ligand.

The synthesis of phenylnitrene complexes with *N*-trimethylsilylanilline has been achieved [40]. In particular the complex *mer*-[Re(NPh)Cl$_3$(Ph$_3$P)$_2$] was produced from the reaction of [ReOCl$_3$(Ph$_3$P)$_2$] with *N*-trimethylsilylaniline, when allowed to react under air with excess *N*-trimethylsilylaniline the complex [Re(NPh)Cl$_3$(NH$_2$Ph)(Ph$_3$Ph)] was obtained. Crystallization from CH$_2$Cl$_2$/MeOH gave an additional product [Re(NPh)(OMe)Cl$_2$(Ph$_3$P)$_2$]. In the complex [Re(NPh)Cl$_3$(NH$_2$Ph)(Ph$_3$Ph)] the rhenium atom is in a distorted octahedral enviromnent with the Cl atoms occupying meridional positions while the phenyl nitrene ligand is coordinated with an almost linear arrangement and an Re–N distance of 1.705(6) Å. The complex [Re(NPh)(OMe)Cl$_2$(Ph$_3$P)$_2$]$\cdot$1/2CH$_2$Cl$_2$ exhibits octahedral coordination with the Cl and phosphine ligands in *trans* positions. The nitrene and methoxy ligands are also coordinated in a *trans* fashion resulting in a slight lengthening of the Re–N distance [1.732(7) Å] while the Re–O distance of 1.934(6) is short.

3.10. Complexes with nitrogen and sulfur donor ligands

A new type of reaction leading to rhenium μ-nitrido complexes has been elucidated [41]. In the first step, a rhenium(V) nitrido complex [ReN(Me$_2$PhP)(Et$_2$dtc)$_2$], Et$_2$dtc = diethyldithiocarbamato, reacts with *in situ* condensed acetone yielding a functionalized imido compound. In the second step an alkyl substituent on the multiply bonded nitrogen is replaced by triphenylboron formed by protolysis of the [BPh$_4$]$^-$ anion. The new complex [Re(NBPh$_3$)(Me$_2$PhP)(Et$_2$dtc)$_2$] is readily soluble in polar organic solvents as CH$_2$Cl, CH$_3$Cl and acetone. Crystals of the complex suitable for X-ray diffraction were obtained by the slow evaporation of a CH$_2$Cl$_2$/isopropanol solution. The structure is comprised of an octahedral rhenium atom in a distorted coordination sphere with an almost linear Re–N–B bridge and an Re–N distance of 1.653(12) Å. As a consequence of the addition of BPh_3 the structural *trans*-influence of the metal-nitrogen multiple bond is weakened. The Re–S bond trans to the Re–N bond is 2.579(4) Å while the other Re–S bonds are 2.431(3), 2.428(4) and 2.362(4) Å.

4. Rhenium(IV)

4.1. Complexes with halide ligands

The reaction of $ReOCl_3(PPh_3)_2$ in boiling propionic acid and HCl gave the compounds $ReCl_4(PPh_3)_2$ and $Re_2OCl_3(C_3H_5COO)_2(PPh_3)_2$ [42]. These compounds were characterized by visible spectroscopy and X-ray crystallography. Additionally, ligand exchange reactions with acac gave $ReCl_2(acac)_2$ and $ReCl_2(acac)(PPh_3)_2$.

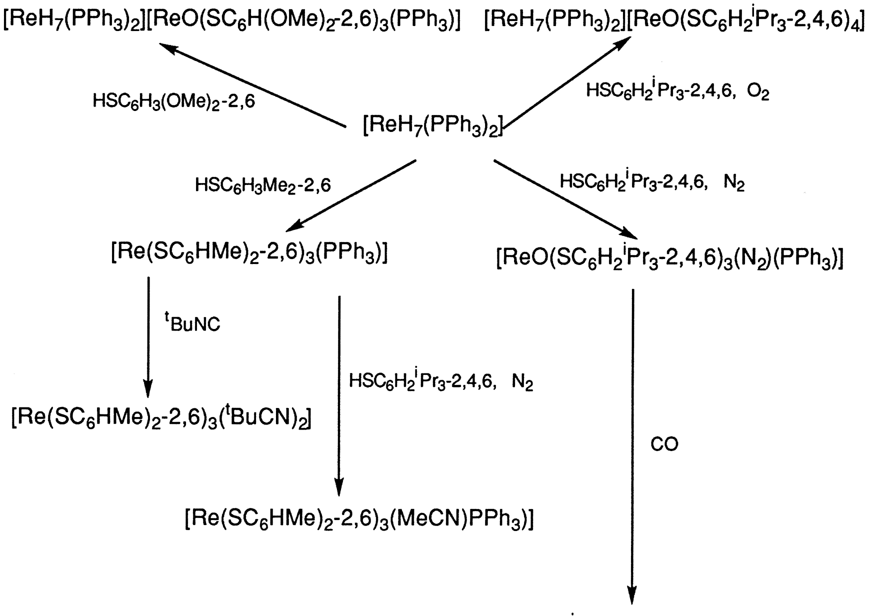
The crystal structures of $(NH_4)_2[ReCl_6]$, $[ReCl_2(CH_3CN)_4]_2[ReCl_6]\cdot 2CH_3CN$ and $[ReCl_4(18\text{-crown-6})]$ have been obtained [43]. Brown crystals of $(NH_4)_2[ReCl_6]$ were obtained from the reaction of NH_4Cl with $ReCl_5$ in a suspension of diethyl ether. The Re–Cl distance in this compound is 2.355(1) Å. From a solution of $ReCl_5$ in acetonitrile, brown crystal plates of $[ReCl_2(CH_3CN)_4]_2[ReCl_6]\cdot 2CH_3CN$ were obtained. The structure consists of two symmetry-independent $[ReCl_2(CH_3CN)_4]^+$ ions with *trans* chlorine atoms, $[ReCl_6]^{2-}$ ions and acetonitrile molecules. The Re–Cl bond lengths average 2.33 and 2.35 Å in the cation and anion, respectively. Lustrous green crystals of $[ReCl_4(18\text{-Crown-6})]$ were obtained from the reaction of 18-crown-6 with $ReCl_5$ in CH_2Cl_2 suspension. In this compound the rhenium atom is octahedrally coordinated by four chlorine atoms and two oxygen atoms of the crown ether molecule.

4.2. Complexes with oxygen donor ligands

A mechanistic study on the oxidation of the Re^{IV_2} complex $[(C_2O_2^{IV}Re(\mu{-}O)_2Re(C_2O_4)_2]^{4-}$ which afforded a good opportunity for studying in detail the progression of oxidation from Re^{IV_2} with the formation of different states has been carried out [44]. The complex was found to be stable in air at $pH=7$ for many days, at a lower pH a slow decay gave the colourless perrhenate $[ReO_4]^-$. The kinetics are indicative of a protonation step, $K=2.4\ M^{-1}$, followed by the decay process $k=4.3\times 10^{-5}\ s^{-1}$. Using the oxidants *cis*-$[VO_2(H_2O)_4]^+$(1.0 V) and $[Mo(CN)_8]^{3-}$(0.80 V) stoichiometries of 6 mol of oxidant per Re^{IV_2} are obtained indicating conversion to Re^{VIII}. Two steps were monitored with the oxidant in large excess. The reaction with V^V the first stage is dependent on $[V^V]$, $[H^+]$ and $[Re^{IV}]$ with a rate constant $k=3.31x10^{-4}\ M^{-2}\ s^{-1}$. The second stage of the reaction gives a rate law dependence $k_{2obs}=k_w[V^V]+k_{o\prime}$, whereas with the less strong Mo oxidant, $k_{2obs}=k_{o\prime}$ which is $0.20\ s^{-1}$. Using stopped-flow rapid-scan spectrophotometry the spectrum of the $Re^{IV}Re^V$ was obtained.

4.3. Complexes with sulfur donor ligands

The tendency for high-valent rhenium sulfur complexes to undergo internal electron transfer has been demonstrated (**16**) [45]. The dinuclear complex $Re_2(\mu\text{-}S)_2(S_2CNR_2)_4$ was obtained, with a high yield, from the reaction of $[Et_4N][ReS_4]$ with 1.5 mol equivalents of tetraalkylthiuram disulfide in acetonitrile. The dimer reacts with one more equivalent of the disulfide in the presence of excess Lewis acids or with 0.5 molar equivalent of the disulfide and 1 molar equivalent of $[Cp_2Fe][PF_6]$ generating the dinuclear Re(III) species $[Re_2(\mu-S-S_2CNR_2)_2(S_2CNR_2)_3]^+$ in high yield. The mononuclear species Re(V) species $[Re(S_2CN(R)_2)_4][Cl]$ was obtained from the reaction of ReS_4^- with three molar equivalents of the disulfide in a mixture of dichloromethane and acetonitrile. The above reactions involve induced internal electron transfer in which the formal oxidation state of the metal is reduced upon the addition of an oxidant, e.g. disulfide. The bound sulfide is a reductant for both metal and external oxidant. The electrochemical properties of these complexes have been investigated. The $Re_2(\mu\text{-}S)_2(S_2CNR_2)_4$ complex undergoes a reversible one-electron oxidation giving $Re_2(\mu-S)_2(S_2CNR_2)_4^+$ which in the presence of excess sulfur forms a novel Re(IV) sulfur-bridged dicationic dimer-of-dimers $[Re(\mu-S)(S_2CNR_2)_4S_4]^{2+}$. X-ray crystallography studies have been carried out on these complexes.



(16)

4.4. Complexes with oxygen, nitrogen and sulfur donor ligands

A structural analysis of the complex [3,10-diethyl-5,8-diazadodecane-3,10-dithiolato(3-)-*N*,*N*′,*S*,*S*″-oxorhenium(IV) chloroform solvate was carried out to determine whether the high solubility of the complex in chloroform was due to disruption of hydrogen bonding between complexes [46]. The N–H···O hydrogen-bonding scheme, which has been observed in the non-solvated material, persists in the chloroform solvate. The chloroform molecules occupy hydrophobic pockets created by the ethyl substituents and the hydrogen atoms are disposed towards two S atoms of one complex with H···S contacts of 2.91 and 2.93 Å. The high solubility of this complex in chloroform probably arises from the combination of hydrophobic contacts between the solvent and the ethyl groups and weak hydrogen bonding between the chloroform and the S donor atoms. The Re–O distance is 1.737(8) Å, the Re–S distances are 2.260(4) and 2.278(4) Å, while the Re–N bond lengths are 1.93(1) and 2.17(1) Å.

4.5. Complexes with oxygen, nitrogen and phosphorus donor ligands

The crystal structure of *trans*-hydroxotris(isothiocyanato)bis(triphenylphosphine)rhenium(IV) methanol solvate has been reported [47]. It consists of well-separated units of [Re(OH)(NCS)$_3$(Ph$_3$P)$_3$] complexes and MeOH solvent molecules. The rhenium atom is octahedrally coordinated with the two triphenylphosphine ligands arranged *trans* to each other. The Re–OH distance is 2.171(4) Å, while the Re–N bonds are in the range 2.002(4) to 2.024(4) Å.

5. Rhenium(III)

5.1. Complexes with halide ligands

A set of closely related ReCl$_3$(RCN)(PR$'_3$) compounds (R=Me, Et, Ph, R′=Ph, *m*-tolyl, *p*-tolyl) which are being considered as starting materials for reactions with purines have been prepared and studied by ^{1}H NMR spectroscopy to elucidate how the resonances of one ligand are affected by relatively minor changes in the other [48]. The signals were found not to be greatly affected by changes in the other ligand. For all cases the spectra were consistent with a *mer*, *trans* structure. For the case of P(*m*-tolyl)$_3$ the standard reaction with [ReO$_4$]$^-$ gave a brick red material, ReCl$_4$[P(*m*-tolyl)$_3$]$_2$ whose crystal structure was determined. In this compound the Re atom occupies a crystallographic inversion centre with Re–Cl bonds of 2.321(2) and 2.339(2) Å.

The quadruply bonded chiral anion [Re$_2$Cl$_7$PBzMePh]$^-$, Bz=CH$_2$Ph, has been synthesized and its crystal structure obtained [49]. The Re···Re distance is 2.2196(8) Å. In addition, molecular modelling was carried out in order to obtain the energy of the δ-bond by modelling non-eclipsed complexes using a torsional

M–M force constant. The energy was determined to be 9 kcal mol^{-1} which is 5% greater than the energy required to eclipse [Re$_2$Cl$_7$L]$^-$.

The crystal structure of [ReCl$_3$(PMe$_2$Ph)$_2$(CNCy)$_2$]·C$_6$H$_4$Cl$_2$ has been reported (Cy = cyclohexyl) [50]. The rhenium atom is surrounded by seven ligands in a monocapped octahedral arrangement in which three Cl atoms possess a *fac* geometry opposite the face capped by a isocyanide ligand. The *trans* axis through the metal atom exhibits remarkable deviation from linearity. The Re–Cl distances range from 2.472 (7) to 2.485(7) Å while the Re–P distances are 2.429(6) and 2.439(6) Å.

The synthesis and crystallographic characterization of compounds containing the [M$_2$Cl$_8$]$^{2-}$ (M = Mo, Re) accompanied by diprotonated diamine cations has been reported [51]. The crystal structure for [1,6-C$_6$H$_{12}$N$_{27}$H$_6$][Re$_2$Cl$_8$] has been obtained, the Re–Re bond distance is 2.2326(7) Å while the Re–Cl distances are 2.32 or 2.33 Å. All complexes were analysed for orientational disorder during which it was shown that the spatial arrangement of cations about the anion has a pronounced effect on the occurrence of disorder.

A series of complexes *trans*-[ReCl$_3$(CNR)(PPh$_3$)$_3$], (R = ^{t}C$_4$H$_9$, C–C$_6$H$_{11}$, C$_6$H$_5$, CH$_2$C(O)CH$_3$ and CH$_2$CH$_2$-(*N*-morpholinyl) has been prepared [52]. They were obtained by the reduction of *trans*-[Re(O)Cl$_3$(NCCH$_3$)(PPh$_3$)$_2$] by the isocyanide ligand. A crystal structure has been obtained for the *tert*-C$_4$H$_9$ derivative which exhibits a *trans*-octahedral geometry and reveals the weak π-acceptor qualities of the *tert*-butylisocyanide ligand.

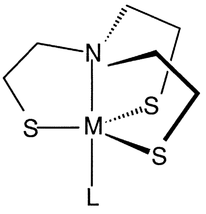
5.2. Complexes with oxygen donor ligands

The scope of the synthetic potential of bis(trimethylsilyl) reagents as molecular sources of heteroatoms including oxygen toward the modification of metal clusters under mild conditions has been extended recently [53]. In particular, the reactions of (^{n}Bu$_4$)[Re$_6$Q$^i_5$Cl$^i_3$(Cl$^i_6$)], (Q = S, Se) with [(CH$_3$)$_3$Si]$_2$E, E = O, S, Se and Te, revealed a neat, specific substitution of one inner face-bridging chloride core ligand (Cl^i). The reaction proceeded readily at room temperature in high yields and afforded a unique series of heterosubstituted rhenium cluster dianions in which three different ligands share the eight face-capping sites in the octahedral (^{n}Bu$_4$)[Re$_6$Q$^i_5$E^{i}Cl$^i_2$(Cl$^a_6$)], (Q = S, E = O, S, Se, Q = Se, E = S, Se, Te). These dianions have been fully characterized by liquid secondary negative ion mass spectrometry (LSIMS). The crystal structures of (^{n}Bu$_4$)[Re$_6$S$_5$OCl$_8$] and (^{n}Bu$_4$)[Re$_6$Se$_5$TeCl$_8$] have been obtained. In the former, a significant contraction of the single octahedron face capped by the oxygen atom is apparent. Analysis of the Re–Cl^a distances in both these clusters in addition to earlier structural studies reveals that this bond distance increases with molecular cluster charge. Extended Huckel calculations have been carried out for a variety of model cluster forms with varying chalcogen/halogen ratios and cluster charges. Results from these calculations demonstrate that the thermalized Re–Cl^a overlap population decreases with increase in cluster charge.

5.3. Complexes with sulfur donor ligands

As part of a systematic study of the reactions of bulky aromatic thiolates with rhenium polyhydrides the reactions of 2,6-dimethylbenzenethiol with

$[ReH_7(PPh_3)_2]$ to give a complex with an agostic metal hydride interaction has been reported [54]. Additionally, the reactions of the hydrides $[ReH_7(PPh_3)_2]$ and $[ReH_5(PPh_3)_3]$ with 2,4,6-triisopropylbenzenethiol, 2,6-dimethoxybenzenethiol and tris(2-sulfanylphenyl)phosphine, have also been studied. A summary of the reactions is delineated in (**17**). These complexes were characterized by IR and NMR spectroscopies and X-ray crystallography.



M = Re, L = PR_3, CNR, $CNCH_2COOH$, CO
M = Tc, L = PPh_3

(**17**)

5.4. *Complexes with selenium donor ligands*

Efforts to develop a general high-temperature technique to produce frameworks of reduced connectivity as a route of entry to inaccessible cluster chemistry have been described [55]. The dimensional reduction of $Re_6Se_8Cl_2$ has been studied. Incorporation of one equivalent of TlCl gave $TlRe_6Se_8Cl_3$ in which the overall dimensionality of the cluster was not reduced but the rigidity of the sheets with the framework has been substantially reduced. Incorporation of one more equivalent of TlCl gave $Tl_2Re_6Se_8Cl_4$ which results in a reduction of the dimensionality of the cluster framework where the phase consists of neighbouring $[Re_6Se_8]^{2+}$ cores linked to Re_2Se_2 rhombs at *trans* rhenium apices thereby fomling a one-dimensional chain. These chains are sheathed with terminal chloride atoms which ligate the remaining four rhenium atoms of the cluster core. The final step in the reduction is achieved by the incorporation of five total equivalents of TlCl to form zero-dimensional $Tl_5Re_6Se_8Cl_7$. In this phase discrete $[Re_6Se_8Cl_6]^{4-}$ clusters break down the two-dimensional framework of $Re_6Se_8Cl_2$. The parallel phases $Tl_5Re_6S_8Cl_7$ and $Cs_5Re_6S_8Cl_7$ contain unprecedented $[Re_6S_8Cl_6]^{4-}$ anions which are produced almost quantitatively. Comparison of the $[Re_6Se_8]^{2+}$ and $[Re_6S_8]^{2+}$ cores show that differences due to shorter Re–S bonds are accompanied by a subtle isotropic contraction of the Re_6 octahedron. The cluster $Cs_5Re_6S_8Cl_7$ was found to dissolve in acidic media giving a bright yellow solution, preliminary X-ray studies confirm the retention of the hexanuclear rhenium cores recovered from solution.

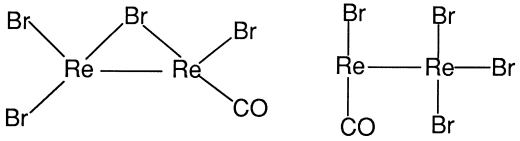
5.5. *Complexes with nitrogen donor ligands*

An investigation of a number of cationic mono and bis-diazenido complexes of rhenium(III) with the didentate ditertiary phosphine ligands dppe and dmpe with a special focus on how the subtle differences in the steric and electronic environments may impact the bonding modes and geometry of the N_2R ligand has been carried out [56]. The synthesis of rhenium diazenides from perrhenate is also presented.

The neutral Re^{III} bis-diazenido complexes $[ReCl(NNC_6H_4X\text{-}4)_2(PPh_3)_2]$, C=Cl or Me reacted with excess dppe in methanol–toluene (1:1) under reflux to give red-orange crystalline bisdiazenido cations of the type $[ReCl(NNC_6H_4X-4)_2(dppe)_2]^+$ which were precipitated easily from a solution of suitable anions. When the neutral starting material was reacted with the more reducing dmpe $[Re(NNC_6H_4X\text{-}4)_2(dmpe)_2]$, X=Cl and $[ReCl(NNC_6H_4X-4)_2(dmpe)_2]^+$ for X=Me were obtained. X-ray crystallographic studies have been carried out for $[ReCl(NNC_6H_4Me\text{-}4)_2(dppe)_2][PF_6]\cdot 2dmf$, $[Re(NNC_6H_4Cl\text{-}4)_2(dmpe)_2][PF_6]$ and $[ReCl(NNC_6H_4Me\text{-}4)_2(dmpe)_2][PF_6]$. These complexes exhibit pseudo-octahedral coordination with four P donors in a planar equatorial array and their structures have been compared and contrasted.

5.6. Complexes with nitrogen and suyur donor ligands

The synthesis and reactions of trigonal–bipyramidal rhenium and technetium complexes with a tripodal, tetradentate NS_3 ligand have been described, (**18**), [57]. These complexes although neutral, contain sterically well shielded oxo-free M(III) ions which will render them useful as radiopharmaceuticals. Rhenium complexes $[Re(N(CH_2CH_2SH)_3)(PR_3)]$ were obtained by reduction of NH_4ReO_4 with phosphines PR_3 in the presence of $N(CH_2CH_2SH)_3$; complexes containing an isocyanide co-ligand were obtained by substitution of a phosphine ligand in $[Re(N(CH_2CH_2SH)_3)(PR_3)]$ for an isocyanide or by the reaction of the isocyanide complexes $[ReCl_3(PPh_3)_2(CNR)]$ with $N(CH_2CH_2SH)_3$. Several of the complexes were characterized by X-ray crystallography.



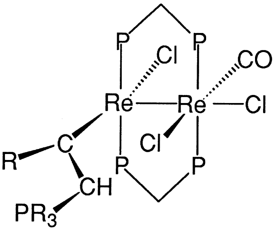
(**18**)

6. Rhenium(II)

6.1. Complexes with halide ligands

The chemistry of monocarbonyl complexes of the type $Re_2X_4(\mu\text{-dppm})_2(CO)$, X=Cl, Br has been revisited [58]. In particular, the influence of the nature of the halide ligand on reactions of complexes with various σ-donor and π-acceptor ligands was studied. The two isomeric forms of $Re_2Br_4(\mu\text{-dppm})_2(CO)$ were studied by X-ray crystallography (**19**), one was shown to have an A-frame-like structure, similar to the previously characterized chloro analogue. The second isomeric form has been identified as having an open unsymmetrical structure namely,

$Br_3Re(\mu\text{-dppm})_2ReBr(CO)$. The reactions of the bromo complex with xylyl and *tert*-butylisocyanides gave the complexes $Re_2Br_4(\mu\text{-dppm})_2(CO)(CNR)$ which have a bioctahedral structure in which the CO and RNC ligands are bound to different Re atoms and are *anti* to one another. The X-ray structure of the *tert*-butyl derivative was obtained, the Re–Re distance is 2.381(1) Å. These complexes react with TlO_3SCF_3 in dichloromethane to give triply-bonded compounds $[Re_2(Br_3(\mu\text{-dppm})_2(CO)(CNR)]O_3SCF_3$ (R=xylyl, ^{t}Bu) both of which possess an unsymmetrical structure with the two Re atoms displaying different coordination numbers with the CO and RNC ligands *trans* to one another based on conclusions from X-ray crystallography on the xylyl derivative. Its structure has been compared with the analogous chloro complex.



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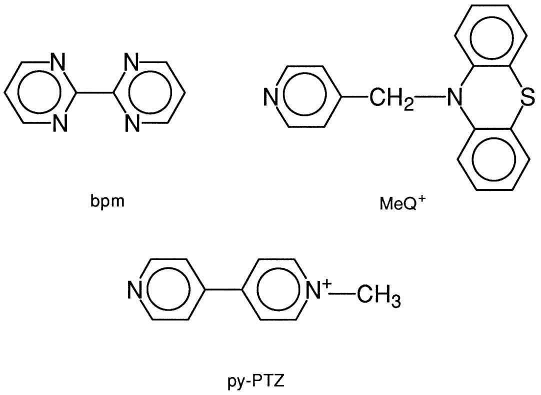
The reaction of monodentate tertiary phosphines with dirhenium(II) alkyne complexes has been investigated [59]. The reaction of the η^2-alkyne complexes $[Re_2Cl_3(\mu-\text{dppm})_2(CO)(\eta^2-RCCH)]X$ (R=H, ^{n}Pr, ^{n}Bu or Ph; X=PF_6 or O_3SCF_3) were reacted with the monodentate tertiary phosphines PR_3, (R=Me_3, Et_3, Me_2Ph or $MePh_2$), generating, in high yield (>60%), a new class of resonance stabilized ylides, the first of such to be formed at quadruply or triply bonded dimetal centres (**20**). The complexes were characterized by IR, ^{1}H NMR and $^{31}P^1H$ NMR spectroscopies and CV. The structure of the $[Re_2Cl_3(\mu-\text{dppm})_2(CO)(C(^nPr)CH(PMe_2Ph))]O_3SCF_3 \cdot 0.83C_7H_8$ was determined by X-ray crystallography, the Re–Re bond length being 2.311(1) Å indicating the retention of the rhenium-rhenium triple bond.

An example of a small but growing class of mononuelear rhenium(II) complexes possessing a *trans*-$ReCl_2P_4$ octahedral geometry has been synthesized [60]. The reaction of the ligand tris(diphenylphosphino)methane, $HC(PPh_2)_3$, with the dirhenium complexes $(^nBu_4N)_2Re_2Cl_8$ and *cis*-$Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ in ethanol, acetone or acetonitrile gave either the starting material, or intractable products. The reaction of *cis*-$Re_2(O_2CCH_3)_2Cl_4(py)_2$ with $HC(PPh_2)_3$ in acetone gave the complex *trans*-$ReCl_2(\eta^2-HC(PPh_2)_3]_2$ in a reproducibly low yield. The use of other solvents failed to give an increase in yield. Other products from this reaction were not characterized. Due to its low yield this complex was characterized by CV and single crystal X-ray crystallography; the Re–P distances are 2.411(1) and 2.402(1) Å while the Re–Cl distance is 2.402(1) Å.



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6.2. *Complexes with oxygen donor ligands*

Three prototypes of cationic [M, O_2] systems with different types of bonding have been probed by experimental and theoretical methods [61]. In particular, the coordination of dioxygen in three representative transition metal cations FeO_2^+, CrO_2^+ and $[CH_3Re(O_2)_2O]^+$ has been studied by mass spectrometry and ab initio calculations.

6.3. *Complexes with sulfur donor ligands*

The synthesis, characterization and structure of the first homoleptic thioether complex of Re, namely $[Re(9S3)]^{2+}$ (9S3 = 1,4,7-trithiacyclononane) which has the potential to be used in cancer radiotherapy, has been achieved [62]. It was obtained as a result of the reaction of $[ReO_4]^-$ and 9S3 in glacial acetic acid in the presence of Sn^{II} and $HBF_4 \cdot Et_2O$ and gave deep-red solutions of $[Re(9S3)]^{2+}$. The complex was characterized by FAB-MS, CV, magnetic susceptibility and X-ray diffraction. Solid-state magnetic measurements gave $\mu_{eff} = 1.6\mu_B$ at 300 K which decreased to $1.46\mu_B$ at 20 K. The crystal structure reveals two 9S3 rings coordinated to the metal in a tridentate fashion with the average Re–S distance of 2.37 Å; in addition, the coordinated ligand displays no conformational change from its free form. Cyclic voltammetry studies show the complex undergoes reduction to Re^I in a range typical of that found *in vivo*; the couples occur at $E_f = +0.47$ and -0.43 V relative to Fc^+/Fc, 1.02 and 0.12 V versus NHE corresponding to the $Re^{III/II}$ and $Re^{II/I}$ couples, respectively.

6.4. *Complexes with nitrogen donor ligands*

A detailed kinetic and electrochemical study of nitrile adducts of tetrachloro – *bis*(1,2-*bis*(diphenylphosphine)methane)dirhenium(II) has been reported [63]. Addition of one equivalent of nitrile to the complex $Re_2Cl_4(dppm)_2$ in CH_2Cl_2/0.1M *N*-butylammonium hexafluorophosphate solution gave the complex $Re_2Cl_4(dppm)_2(NCR)$, R = aromatic or aliphatic. Electrochemical oxidation reverses this nitrile addition. Upon addition of two or more equivalents of nitrile a slow ligand substitution takes place with the addition of a second nitrile concomitant with chloride loss to give $[Re_2Cl_3(dppm)_2(NCR)_2]^+$. The rate of nitrile addition is dependent on the electron-withdrawing or electron-donating tendencies of the ligand. Differential pulse voltammetry was used to monitor the change from monoadduct to diadduct for a range of nitrile concentrations. The kinetics indicate a first order dependence on nitrile for the addition reaction.

7. Rhenium(I)

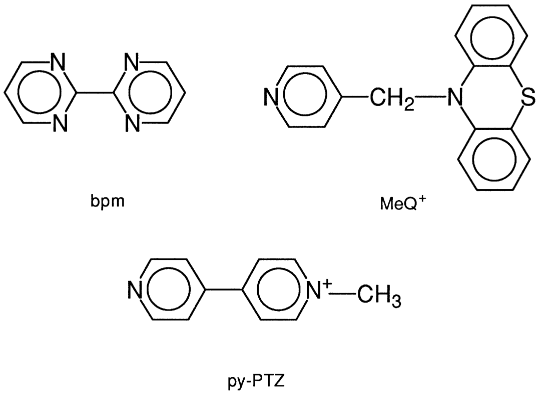
7.1. Complexes with oxygen donor ligands

A facile modular self-assembly approach to the construction of superdiamonded networks has been described [64]. The compounds $[\{M(CO)_3(\mu_3\text{-}OH)\}_4]$, M = Re or Mn, cubane-like molecules possessing four strong hydrogen-bond donor molecules rigidly directed toward the vertices of a tetrahedron co-crystallized with two equivalents of linear difunctional hydrogen-bond acceptor molecules giving 14 three-dimensional superdiamonded networks which possess varying, but predictable, extents of interpenetration as judged from X-ray crystallography. The spacer molecules benzene, toluene, *p*-xylene, *p*-fluorotoluene, naphthalene, 1-methylnaphthalene, *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine, 1,2-bis(diphenylphosphoryl)ethane and 1,4-diaminobenzene gave two-fold networks, while en and 2-chloropyrazine gave three-fold networks; 4,4′-bipiperidine gave four-fold networks. The rhenium adducts of 4,4′-bipiperidine and 1,4-diaminobenzene crystallize with enough space in the crystal lattice to enclathrate two and four acetonitrile molecules per molecule of cubane, respectively.

7.2. Complexes with nitrogen donor ligands

Studies on the temperature dependence, in fluid solution, of emission lifetimes of a series of $[Re(L-L)(CO)_3py]^+$, (L-L = 3,4,7,8-Me_4phen, 4,7-Ph_2phen, 2,9-Me_2-4,7-Ph_2phen, 4,7-Me_2phen, 5,67-,8-Me_2phen, 5-Phphen, 2,9-Me_2phen and phen) have been carried out [65]. The photophysical behaviour is very complex due to contributions from multiple emitting states. The lowest excited state is a ^{3}MLCT with a contribution from a higher-energy, shorter-lived state of unknown character. For the case of $[Re(3,4,7,8-Me_4phen)(CO)_3py^+$ the emission lifetime is seen to increase with temperature, reaching a maximum at approximately 230 K and then decreasing. This is attributed to population of the lowest ^{3}LC state lying just above the ^{3}MLCT state and below the upper state.

The synthesis, structure, physical and photophysical properties of $Re(bpm)(CO)_3L^{n+}$, bpm = 2,2′bipyrimidine, L = CH_3CN, py, *N*-methyl-4,4′-bipyri-



(20)

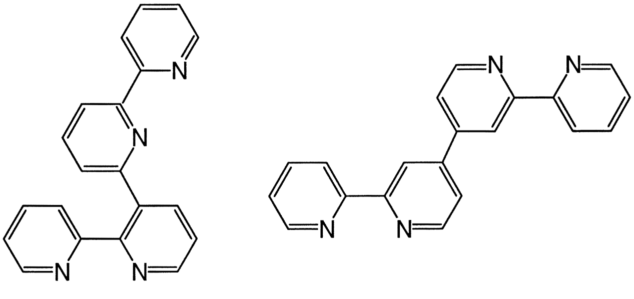
dinium, MeQ$^+$ and 10-(4-picolyl)phenothiazine, py-PTZ have been reported, (**20**), [66]. In particular this study sought to understand the photophysical features leading to the separation of charge in these complexes. The photophysical properties in the presence of an electron-accepting ligand MeQ$^+$, or the electron-donating ligand were compared to those of the model compounds Re(bpm)(CO)$_3$py$^+$ and Re(bpm)(CO)$_3$(CH$_3$CN)$^+$. The X-ray crystal structure of the [Re(bpm)(CO)$_3$(CH$_3$CN)]$^+$ derivative was obtained and reveals two independent cations in the asymmetric unit. The Re–N(bpm) distances were 2.171(9) and 2.198(10) Å for one cation and 2.161(12) and 2.187(12) Å for the other while the Re–N(CH$_3$CN) were 2.094(14) and 2.177(13) Å. The complexes underwent optical transitions in the 300–350 nm region assigned to $d\pi(\mathrm{Re})\rightarrow\pi^*(\mathrm{bpm})$ transitions and also intraligand $\pi\rightarrow\pi^*$ transitions in the 200–300 nm region. Multiple reductions were observed and were attributed to reduction of the coordinated ligands. Transient absorption spectra revealed that charge separation occurred for both MeQ and PTZ complexes and the transfer of an electron from Re(I) to MeQ$^+$ generating the Re(III) and MeQ· while in the latter the transfer was from py-PTZ to Re(II) forming the py-PTZ$^+$ radical cation and Re(I).

A series of rhenium(III), (II) and (I) terpyridyl complexes, most of which are devoid of the classical π-acids, have been synthesized [67]. Commencing with [Re^{II}(terpy)(PPh$_3$)$_2$Cl]$^+$ (Cl$^-$ or OTf$^-$) a series of Re(I) and Re(III) compounds has been obtained. The chloride analogue is oxidized in the presence of chloride generating [Re^{III}(terpy)(PPh$_3$)$_2$Cl$_2$]$^+$ or [Re^{III}(terpy)Cl$_3$]. In the presence of cyclohexenone, the triflate derivative generates Re^{I}(terpy)(PPh$_3$)$_2$Cl(η^2−cyclohexenone); the chloride undergoes facile substitution to form a series of Re(I)-terpyridyl derivatives. Electrochemical studies have been carried out and an electrochemical parameterization model has been employed in the comparison with other known rhenium compounds. A correlation between the number and strength of π-acidic ligands with deviations from observed I/II reduction potentials from predicted values has been established. The X-ray crystal structure of [Re^{II}(terpy)

$(PPh_3)_2Cl]OTf$ has been obtained with Re–N bond lengths in the range 2.017 (7)–2.113(7) Å.

The application of high resolution absorption spectroscopy to the complex $[Re(bpy)(CO)_4](PF_6)$, at cryogenic temperatures using polarized light, has facilitated the detailed analysis of electronic transitions in this complex [68]. The lowest excited electronic state has been assigned as a ^3LC transition with its electronic origin centred at 22 510 cm^{-1} on the bpy ligand. This state is weakly mixed (3%) with the lowest lying ^1CT state (31 570 cm^{-1}) giving rise to observed metal–ligand vibrational side bands, shortened luminescence decay and a large zero-field splitting of the electronic origin. Coupling arising from a large spin-orbit coupling matrix element has been invoked to postulate a mechanism for these observations.

The synthesis and electrochemical, spectroscopic and photophysical properties of a series of Ru(II), Re(I) and mixed Ru(II)/Re(I) complexes of the non-symmetric dinucleating ligand 2,2′:3′,2″:6″,2‴-quaterpyridine and the related symmetric ligand (**21**) has been reported [69]. In complexes containing the former ligand two inequivalent bpy-type chelating sites, A and B, are present and it was rationalized that these would be expected to affect to different extents the MLCT energy levels of the attached chromophores which may facilitate modulation of the directionality of the energy transfer between them. Mono- and dinuclear complexes of the asymmetric bridging ligand containing $(Ru(bpy)_2^{2+}$ and/or $(Re(CO)_3Cl\}$ fragments coordinated to the bipyridyl binding sites. In the dinuclear species Ru^{II}-AB-Re^I and Re^I-AB-Ru^{II} the luminescence is Ru- and Re-based, respectively, and photoinduced energy transfer from the higher-lying Re- and Ru-based respectively to the luminescent component chromophores takes place via an exchange mechanism. This finding corroborates the close separation distance between the metal centres and the fact that the metal centres are linked by a conjugated bridging ligand. X-ray crystallography has been carried out on the Re^I–AB–Ru^{II} complex.



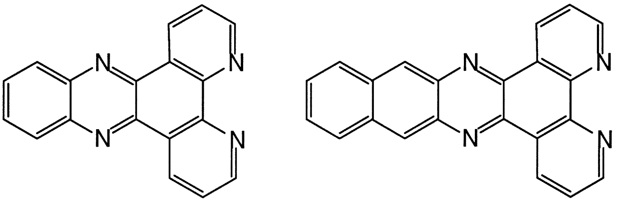
(**21**)

The photophysical properties of the complex [*fac*-(dppz) $Re(CO)_3$(4-methylpyridine), dppz = dipyrido[3,2-*a*:2′,3′-clphenazine and 4-MePy = 4-methylpyridine, were examined in protic and aprotic organic solvents and in aqueous solvents in the presence of calf thymus DNA [70]. These studies indicate that the lowest excited state in homogeneous organic solvents is a dppz-based intraligand triplet state, namely, $^3IL_{dppz}$. In degassed MeCN and MeOH weak phosphorescence was observed from the $^3IL_{dppz}$, this excited state was detected due to its characteristic and strong $T_o \rightarrow T_n$ absorption. In aqueous Tris buffer no luminescence from the complex was observed but when bound to DNA presumably due to intercalation, moderate luminescence was observed. This system differs from Re(II)- and Os(II)-dppz analogues because the $d\pi(M) \rightarrow \pi^*$(dppz) ^{3}MLCT states(s) are at a higher energy in the Re(I) system allowing the low-lying dppz-based intraligand triplet state(s) to be dominant in the photophysics of the system.

The preparation and crystal structure of the first Re(I) porphycene complex has been achieved [71]. The reaction of 2,7,12,17-tetrapropylporphycene (TPrPc) and $Re_2(CO)_{10}$ gave the complex (TPrPc)$[Re(CO)_3]_2$ which was characterized by X-ray crystallography and is analogous to its porphyrin analogue. The complex has one Re(I) above and below the porphyrin plane. The average displacement of the porphycene plane is 1.50(1)Å. Each Re(I) is coordinated to three CO ligands and three nitrogen atoms of the porphycene. Those Re–N distances in which the nitrogen atom is bonded to only one Re(I) are considerably shorter than those with the N atom bonded to two Re(I) atoms. EH calculations have been carried out on the complex and results are presented. The complex was also characterized by IR and UV–VIS spectroscopy and the EH calculated electronic transition energies were compared with those measured from UV–VIS spectroscopy. CV studies in 1,2-dichloroethane with 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte, show two reversible reduction waves at -1.16 and -1.51 V and two reversible waves at 0.69 and 0.89 V.

A communication has appeared describing the first structurally characterized luminescent rhenium nucleobase complex, $[Re(bpy)(CO)_3(EtG)]^+$ (EtG= 9-ethylguanine) whose emission is strongly dependent on the electronic properties of the nucleobase ligand [72]. It was prepared from the reaction of $[Re(bpy)(CO)_3(CH_3CN)]^+$ with 9-EtG in thf. The proton NMR spectrum of this complex differs significantly from that of the free EtG ligand. From IR spectroscopic observations, the inequivalency of all three carbonyl ligand stretching frequencies suggests that the EtG ligand breaks a plane of symmetry in the complex. An X-ray crystal structure study reveals that the guanine ligand is coordinated via nitrogen as has been observed for platinum, ruthenium and other metal complexes of the purines. Coordination of EtG alters the electronic properties of the complex as revealed in the MLCT absorption which red-shifts by 31 nm upon coordination by the ligand. In a similar vein the emission maximum shifts from 535 nm to 600 nm. The excited state is long-lived with an emission quantum yield of $\phi = 0.054 \pm 0.017$ thereby facilitating a sensitive assessment of the electronic properties of the guanine ligand using the energy-gap law. Thus, these quantitative analyses of the electronic properties of guanine ligands provides new principles for designing metal complexes which target guanine residues. The $[Re(bpy)(CO)_3]^+$ is attractive owing to the fact that the quantum yields are about an order of magnitude higher than those of related Ru(II) excited states however better ligands generate lower quantum yields providing challenges in design.

Two novel luminescent rhenium(I) complexes have been synthesized and characterized and their photophysical properties have been studied [73]. The complexes [Re(dppz)(CO)$_3$(py)](OTf) and [Re(dppn)(CO)$_3$(py)](OTf), dppz = dipyridophenazine, dppn = benzodipyridophenazine, (**22**) were characterized by elemental analysis, ^{1}H NMR spectroscopy and positive ion FAB-MS. In addition, the crystal structure of the dppn derivative has been obtained. The rhenium atom is in a distorted octahedral geometry, all atoms of the dppn ligand lie on an essentially perfect plane and exhibit ring stacking interactions. The distance between the ideal ring planes on adjacent cations was found to be approximately 3.4 Å. Both complexes exhibit low energy absorptions at 380–450 nm. In aqueous MeOH-buffer solutions containing calf thymus DNA both complexes exhibit enhanced luminescent emission intensities and is suggestive of an intercalating interaction.

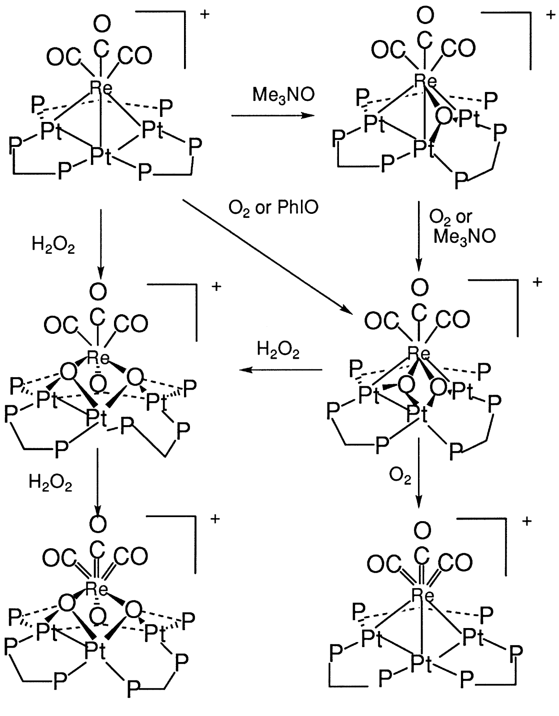


(**22**)

The regiospecific addition of the organocopper nucleophile LiCuMe$_2$ to the =CHR termini of monosubstituted rhenium alkene complexes [Re($\eta^5-C_5H_5$)(NO)(PPh$_3$)(H$_2$C=CHR)]BF$_4$ (R=H, Me, CH$_2$CH$_2$Me, Ph or CH$_2$Ph) has been studied [74]. The additions were shown to be diastereo and enantio-specific and a chemical correlation and a crystal structure, which establish attack upon the c+c face *anti* to rhenium, have been determined. Complementary results with the oxygen nucleophile NaOMe which in some instances can also affect the vinylic or allylic deprotonation of the alkene ligand have also been reported.

7.3. *Clusters*

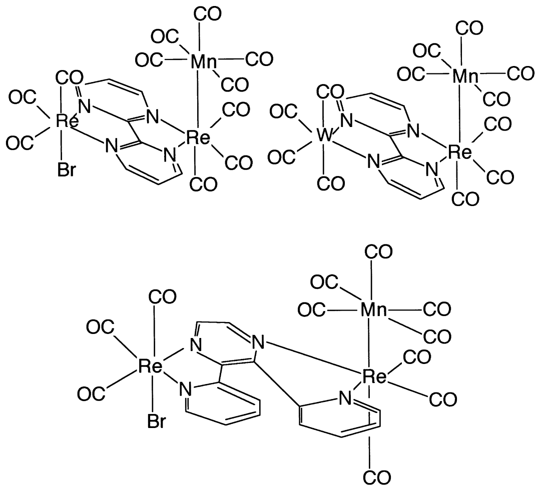
A detailed study of the oxidation of the complex [Pt$_3$Re(CO)$_3$($\mu-$dppm)$_3$]$^+$ has been carried out [75]. Its reaction with a series of oxidants Me$_3$NO, PHIO, O$_2$, or H$_2$O$_2$ under mild conditions led to a series of clusters (**23**) in which there are unprecedented increases in cluster count (up to 12 electrons) and metal oxidation states (up to 12 units). The nature of the bonding in these clusters has been analysed and is discussed on the basis of XPS spectroscopy. X-ray crystallography has been carried out for [Pt$_3$Re(CO)$_3$(μ_3-O)$_2$($\mu-$dppm)$_3$]$^+$. EHMO calculations show that the ReO$_3^+$ group is a stronger acceptor of electron density from the Pt$_3$(μ-dppm) group than is the Re(CO)$_3^+$ and an analogy between the donors C$_5$H$_5^-$ and Pt$_3$(μ-dppm).



(23)

8. Rhenium(0)

The photochemical reactivity and emissive properties of the dinuclear complexes $(CO)_5MnRe(CO)_3(L)$, (L = 2,2′-bipyrimidine (BYPM), 2,3-bis(2-pyridyl)pyrazine, (DPP)) and the bridged trinuclear complexes $(CO)_5MnRe(CO)_3(L)Re(Br)(CO)_3$ and $(CO)_5MnRe(CO)_3(BYPM)W(CO)_4$ (**24**), have been investigated [76]. The photochemistry was carried out at room temperature in different solvents with the reaction being monitored in situ by IR, UV–VIS and ESR spectroscopies. All compounds were found to undergo homolysis of the Mn–Re bond upon excitation into their MLCT absorption band(s) in the visible spectrum. In chlorinated solvents, e.g. CH_2Cl_2, CCl_4 irradiation of the complexes gave $Mn(Cl)(CO)_5$, $Re(Cl)(CO)_3(L)$ or $Re(Cl)(CO)_3(L)Re(Br)(CO)_3$. In thf, photolysis gave $Mn_2(CO)_{10}$ as well as $[Re(CO)_3(L)]^{\cdot}$ $[Re(CO)_3(L)Re(Br)(CO)_3]^{\cdot}$ or $[Re(Cl)(CO)_3(BYPM)W(CO)_4]^{\cdot}$ radicals which are presumed to have a coordinated thf molecule. The photoreactions of the dinuclear complexes proceeded with high quantum yields 0.36 for BYPM and 0.54 for DPP independent of temperature and wavelength of the excitation. The attachment of the $Re(Br)(CO)_3$ moiety to the potentially bridging ligand in $(CO)_5MnRe(CO)_3(L)$ forming the trinuclear species, was found to greatly influence the excited state dynamics of the photochemistry. In particular, there is a noticeable stabilization of the π^* LUMO of the bridging ligand and the introduction of another MLCT excited state. The Re–Mn bond homolysis is six times more efficient for the bridging DPP ligand when compared with the bridging BYPM.



(24)

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