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# Rhenium 1994

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**Contents**

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## 1. Introduction

This review reports on the advances in rhenium chemistry as described in the literature for 1994. As in previous reviews, [1], the emphasis is mainly on coordination compounds and the format is similar with some references to organometallic compounds which may be pertinent. It is based on a search of volumes 120, 121 and 122 of *Chemical Abstracts*. In addition, major inorganic chemistry journals have been searched separately for the calendar year 1994.

## 2. Rhenium(VII)

### 2.1. Complexes with hydride ligands

The complex hydride $BaReH_9$ was synthesised and characterized by IR spectroscopy, X-ray powder diffraction and X-ray crystallography [2]. Transparent, hexagonal single crystals were obtained from the slow diffusion of ethanol into an alkaline $H_2O$/methanol solution of the hydride. Each rhenium atom is surrounded by six barium atoms in a trigonal prismatic arrangement. The closest Re-Re distances are 5.287(1) Å. A tricapped trigonal prism of hydrogen atoms around the Re with H-Re distances of 1.68-1.69 Å is proposed.

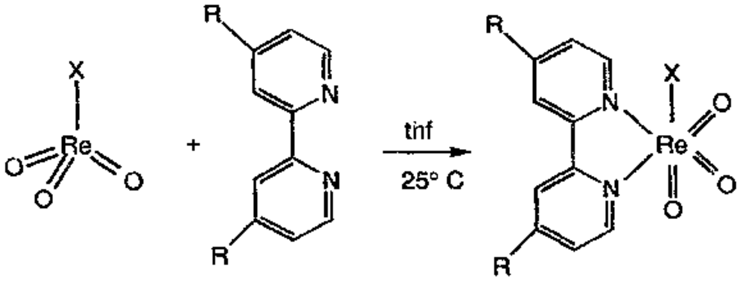
Several new multihydride complexes of rhenium containing diphosphine ligands have been synthesised [3]. Treatment of oxochloro complexes of the type $[ReOCl_3(L\text{-}L)]$, (L-L) = diphosphine, with sodium tetrahydroborate gave complexes of the type $[ReH_7(L\text{-}L)]$. The low temperature (-80°C) protonation of $[ReH_7(\text{dppen-}PP')]$ (dppen = *cis*-1,2-bis(diphenylphosphino)ethylene) with $HBF_4 \cdot Et_2O$ was studied by IR and NMR spectroscopies.

### 2.2. Complexes with oxygen donor ligands

The crystal structures of two mercury perrhenates $HgReO_4$ and $Hg_2ReO_5$ have been obtained [4]. The former crystallizes as a dimer with nearly linear $O_3Re\text{-}O\text{-}Hg\text{-}Hg\text{-}O\text{-}ReO_3$ molecular units while the latter exhibits a structure where Hg(I) and Hg(II) with oxygen form 14-membered rings which condense into two-dimensionally infinite polycationic nets. These nets are separated from each other by tetrahedral $[ReO_4]^-$ anions.

Chlorotrioxorhenium and homologues $X\text{-}ReO_3$ were generated from $Re_2O_7$ and either $ZnX_2$, $(n\text{-}C_4H_9)_3SnX$, $[(n\text{-}C_4H_9)_4N]X$ or $[(C_6H_5)_4P]X$ in clean reactions [5]. Upon addition of a free ligand, (for example) stable six-coordinate bpy adducts were formed (**1**). These adducts display characteristic thermogravimetric behaviour reflecting the volatility of the uncoordinated complexes.

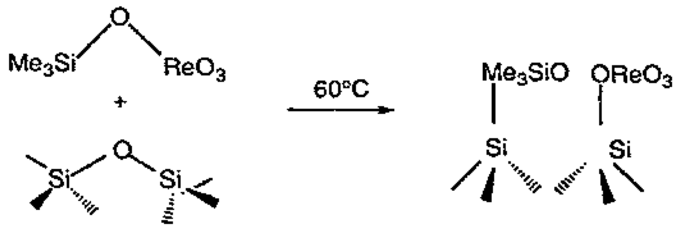
A new method for grafting Re(VII) oxide onto highly dehydroxylated oxides has been described [6]. Sublimation of $Me_3SiOReO_3$ onto $\text{silica}_{1100}$ followed by desorption at 60°C (**2**) resulted in a maximum of approximately 1 wt.% Re which corresponds to $0.14 \pm 0.01\ Re/nm^2$. This method may be applicable to the in situ



X = Cl, Br, F, CN, SCN, $OReO_3$
R = H, $CH_3$, $C(CH_3)_3$

(1)

preparation of supported metal oxides especially where the presence of water or surface hydroxyl groups would interfere with the subsequent catalytic activity.



(2)

The decomposition of methyltrioxorhenium $CH_3ReO_3$ via homolytic cleavage of the Re-C bond has been studied from the viewpoint of qualitative MO theory [7]. In particular, the pseudo-tetrahedral complex is better viewed as an 18- rather than a 14-electron species based on a detailed examination of all the orbital interactions between the metal and the coordinated atoms. The metal receives up to nine electron pairs from the oxygen atoms and the $CH_3$ moiety. The dynamics of the most critical frontier orbitals operative during the Re-C bond elongation indicate that physical separation of the $ReO_3$ and $CH_3$ fragments generates the $ReO_3$ (Re(VI)) radical which would appear to be stabilized in a planar geometry by $\sigma$ and $\pi$ interactions with the oxygen atoms. The unpaired electron which is resident in the $z^2$ orbital is quasi-degenerate with the $\sigma$ hybrid of the $CH_3$ group, due to their proximity in energy the two orbitals continue to mix (in-phase and out-of-phase combinations) such that this overlap persists even at very long Re-C separations. Of note is the avoided crossing between the HOMO and LUMO which correlates the original Re-C $\sigma$ bonding with the higher $CH_3$ $\sigma$ hybrid.

### *2.3. Complexes with oxygen and nitrogen donor ligands*

The reaction of the *cis*-dioxorhenium(VII)-catecholate complex $[Et_4N]^+[ReO_2(cat)_2]^-$ with either monosubstituted organohydrazines ($C_6H_5NHNH_2$; 4-Br-$C_6H_4NHNH_2$) or 1,1-disubstituted organohydrazines ($(C_6H_5)_2NNH_2$ generated *cis* bis(diazenido) gave the complexes $[Et_4N]^+[Re(N_2R_2)_2(cat)_2]^-$ ($R=C_6H_5$, 4-Br-$C_6H_4$ and the *cis*-bishydrazido complex $[(CH_3CH_2)_4N]^+[ReN_2R_1R_2(cat)_2]^-$, $R_1=R_2=C_6H_5$ [8]. These complexes were characterized by elemental analysis, and IR, UV-VIS and NMR spectroscopies. The complexes $[Et_4N]^+[Re(N_2Ph)_2(cat)_2]^-$ and $[Et_4N]^+[ReN_2Ph_2(cat)_2]^-$ were characterized crystallographically. In the former, the molecular anions possess a distorted octahedral geometry with the aryldiazenido ligands adopting a mutually *cis* orientation. The short Re-N [1.83(1) Å] and N-N [1.21(2) Å] distances reflect multiple bonding. In the latter, the anion exhibits a distorted octahedral geometry defined by four oxygen donors of the catecholate ligands and the nitrogen donors of the phenylhydrazido(2-) ligands. The Re-N distances range from 1.77(1) to 1.79 Å while the N-N distances are in the range 1.29-1.33 Å.

## 3. Rhenium(V)

### *3.1. Complexes with hydride ligands*

A new class of chelating bis(silyl) polyhydride complexes which show enhanced reactivity with respect to catalytic dehydrogenation of alkanes has been synthesised [9]. The reaction of $ReH_7(PPh_3)_2$ with 1,2-bis(dimethylsilyl)benzene and 1,2-bis(dimethylsilyl)ethane (disil) gave the complexes $ReH_5(disil)(PPh_3)_2$. Both complexes were characterized spectroscopically. The 1,2-bis(dimethylsilyl)benzene derivative was characterized by X-ray diffraction and possesses a dodecahedral structure. The complex is proposed to be $ReH_3(H_2)(disil)(PPh_3)_2$, containing a stretched $\eta^2$-$H_2$ ligand.

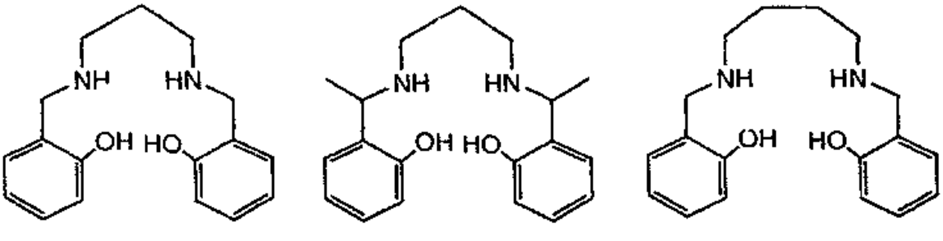
### *3.2. Complexes with halide ligands*

The preparation, vibrational spectra and normal coordinate analysis of hexachlororhenate(V) and the crystal structure of $[P(C_6H_5)_4][ReCl_6]$ have been reported [10]. The octahedral $[ReCl_6]^{6-}$ anion is compressed with Re-Cl axial bonds of 2.28 and 2.24 Å while the equatorial Re-Cl bonds are 2.31 Å.

### *3.3. Complexes with oxygen donor ligands*

The site selectivity towards ligand addition on $Pt/Re/Al_2O_3$ surfaces has been modelled using Pt/Re clusters [11]. The ligands CO, $P(OR)_3$ and $X^-$ ($X=Cl$, Br, I) were found to add selectively to the Re and $Pt_3$ sites in the coordinatively unsaturated clusters $[Pt_3\{Re(CO)_3\}(\mu\text{-dppm})_3]^+$ and $[Pt_3\{ReO_3\}(\mu\text{-dppm})_3]^-$ respectively; the selectivity displays a remarkable dependency on the oxidation state of the rhenium.

Rhenium complexes of amine phenol ligands (**3**) were synthesised [12]. They were characterized by NMR and IR spectroscopies and X-ray diffraction. They were found to be dinuclear with O=Re-O-Re=O backbones and near octahedral coordination about each rhenium atom.



(**3**)

The mutual ligand influence in monomeric octahedral Re(V) complexes and its effect on their structure has been studied [13]. In the complexes $[ReO(OEt)Cl(PPh_3)_2]$ and $[ReO(dmf)Cl_3(PPh_3)]$ the *trans* influence of the oxo ligands, the effects of the electronic configuration of the metal, and the charge on atoms in positions *trans* to the oxo group have been considered.

### 3.4. Complexes with oxygen and sulfur donor ligands

The synthesis of the oxo complex $[ReO(dmt)_3(PPh_3)]$ (dmt = 2,6-dimethylbenzenethiolate) from the reaction of $[ReOCl_3(PPh_3)_2]$ with trimethylsilyl-2,6-dimethylbenzenethiolate ($Me_3Sidmt$) has been reported [14]. This complex may also be obtained through the reaction of $[ReH_7(PPh_3)_2]$ and the disulfide derivative of dmt whereas $[Re(dmt)_3(PPh_3)(PHPh_2)]$ was isolated from the reaction of the hydride with Hdmt. An X-ray crystallographic study has been carried out for $[ReO(dmt)_3(PPh_3)]$; the rhenium atom was found to be in a distorted trigonal bipyramidal environment in which the equatorial plane comprises an oxygen and two thiolate ligands while the apical sites are occupied by phosphine and a third thiolate ligand. The Re-O distance is 1.694(6) Å while the Re-S distances range from 2.293(2) to 2.319(2) Å. The structure of $[Re(dmt)_3(PPh_3)(PHPh_2)]$ was obtained; the overall geometry about rhenium is also trigonal bipyramidal with the thiolate ligands in the equatorial plane while the phosphine ligands are in the apical positions. The thiolate ligands are oriented in a "two down, one up" orientation with respect to the apical ligands in a configuration seen for sterically hindered thiolate complexes with an $MS_3$ core. The Re-S bond distances range from 2.255(4) to 2.261(4) Å.

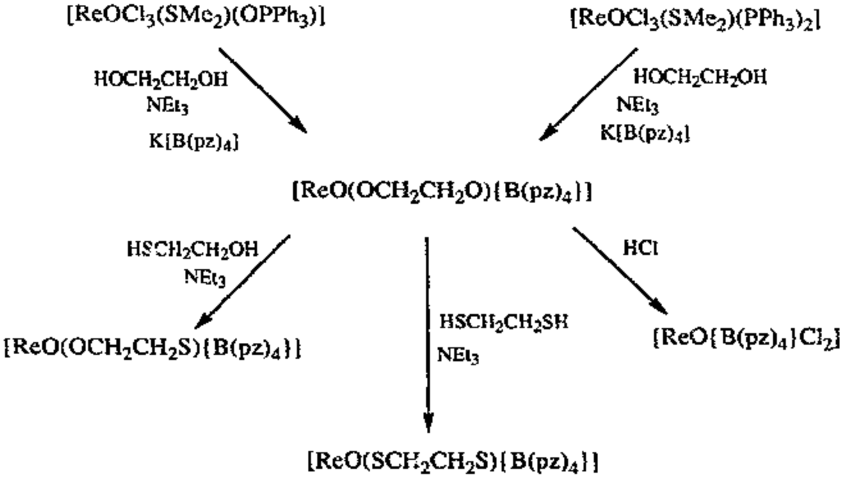
### 3.5. Complexes with oxygen and nitrogen donor ligands

The reaction of *trans*-$ReOCl_3(PPh_3)_2$ with di-(2-pyridyl)ketone, (DPK) in thf or dichloromethane under nitrogen yielded a crystalline adduct $(DPK\cdot H)^+[\{ReOCl_2(DPK\cdot OH)\}_2Cl]^-$ [15]. The compound was characterized by elemental analysis, and IR, electronic and $^1H$ NMR spectroscopy. These studies suggest that the coordinated DPK ligands have undergone the addition of water at the carbonyl carbon atom and that the $(C_5H_4N)_2C(O)(OH)$ unit acts as a uninegative, tridentate *N,O,N*-donor. An X-ray crystallographic study shows this compound to be typical of a crystalline adduct with two molecules (designated A and B) of $ReOCl_2[(C_5H_4N)_2C(O)(OH)]$ and a single molecule of DPK present in the asymmetric unit. Molecules A and B were found to be superimposable and their equatorial coordination planes are virtually parallel. The driving force for the metal-promoted hydration of the carbonyl group may have fulfilled the need to relieve angular strain. The Re-N distances (A and B) range from 2.138(9) to 2.171(9) Å whereas Re-O distances range from 1.670(6) to 1.981(5) Å.

A detailed study on the quenching of $[ReO_2(py)_4]^+$ and substituted derivatives by common organic acids over a wide range of thermodynamic acidities has been reported [16]. The emission quenching of $[ReO_2(L)_4]^+$ (L = py, 3-Cl-py and 2-OMe-py) by common nitrogen and oxygen acids are described. Marcus analysis of the free energy dependence of the quenching rate constants points to a low barrier to proton transfer (4 kcal). The results from this analysis were used to calculate a $pK_a^*$ of 11.3 for the py complex. The standard Marcus relation could also be used for 3-Cl-py. However fitting of the data for the 4-OMe complex required the use of an asymmetry parameter ε which relates to the degree of excited state distortion in the chromophore.

The synthesis, characterization and redox properties of Re(V) and Re(III) compounds with the stabilizing ligand tetrakis(pyrazol-1-yl)borate, pz, have been described [17]. The details of the syntheses of the Re(V) complexes are delineated in the scheme in (4) while those for the Re(III) are shown in the scheme in (5). The compounds were characterized by elemental analyses, IR and $^1H$ NMR spectroscopies. An X-ray crystal structure for $[ReO(OCH_2CH_2O)\{B(pz)_4\}$ shows two independent molecules in the asymmetric unit. In both molecules Re is in an approximately octahedral environment. The mean Re=O bond length is 1.69(2) Å with the Re-N bond *trans* to the oxo ligand being the longest, mean value 2.26(4) Å compared with a mean value of 2.101(1) Å for the two other Re-N distances *trans* to the ethylene glycolate ligand. The mean Re-O distance in the glycolate ligand is 1.93(2) A°. For the Re(III) complexes a crystal structure for the $L = PEt_2Ph$ derivative has been obtained. The three Re-N bond distances are equivalent with a mean value of 2.101(1) Å.

The complexation of a phenylimidorhenium complex with the multidentate ligand 1,2-bis(2,2′-bipyridyl-6-yl)ethane, (*o*-bpy) has been investigated [18]. Its synthesis, structural and electrochemical properties have been reported and reveal that the *o*-bpy ligand is capable of stabilizing *trans* bpy geometries. The complex $[Re(NPh)(o\text{-bpy})(OEt)]^{2+}$ was isolated as the hexafluorophosphate salt. The cation



(4)

$$[\mathrm{ReO\{B(pz)_4\}Cl_2}] + \mathrm{L} \xrightarrow{\text{toluene}} [\mathrm{ReO\{B(pz)_4\}Cl_2L}] + \mathrm{O{=}L}$$

$$\mathrm{L} = \mathrm{PEt_3, PEt_2Ph, PEtPh_2}\ \text{and}\ \mathrm{PPh_3}$$

(5)

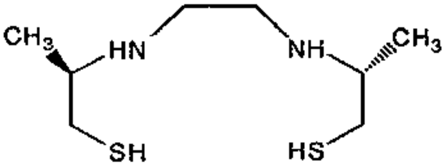
adopts a distorted octahedral geometry in which four nitrogen atoms from the two bipyridyl ligands occupy equatorial positions. The Re-N(*o*-bpy) lengths vary from 2.112(6) to 2.180(6) Å while the Re-NPh and Re-OEt lengths were found to be 1.735(5) and 1.914(5) Å. The complex exhibits three well defined reductive waves in its cyclic voltammogram.

### 3.6. *Complexes with oxygen and phosphorus donor ligands*

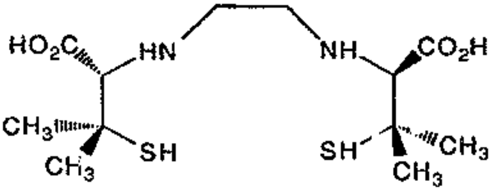
The X-ray crystal structures of [$\mathrm{ReOCl_3(OPPhEt_2)(PPhEt_3)}$] and [$\mathrm{ReOBr_3(OPPhEt_2)(PPhEt_3)}$] have been obtained [19]. Both exhibit rhenium atoms in distorted *mer*-octahedral coordination sites, with coordination to oxygen atoms of the neutral phosphine oxide ligand *trans* to the oxygen of the oxo ligand. The Re-O(oxo) bond lengths are 1.672 and 1.663 Å respectively while those for Re-O($\mathrm{OPR_3}$) are 2.063 and 2.053 Å respectively.

### 3.7. *Complexes with oxygen, nitrogen and sulfur donor ligands*

Rhenium(V) oxo analogues of technetium-99m radiopharmaceuticals containing $N_2S_2$ chelate ligands have been studied [20]. Specifically, $[\mathrm{Re(V)O}]^{3+}$ complexes prepared with the pentaanionic form of (2*R*,7*R*)-2,7-dicarboxy-3,6-diaza-1,8-octanedithiol ($ECH_6$), (**6a**), and (2*S*,7*S*)-2,7-dicarboxy-3,6-diaza-1,1,8,8-tetramethyl-1,8-octanedithiol ($TMECH_6$), (**6b**), were explored. The species $ReO(ECH_3)$ and the ammonium salt of the trianionic species $[NH_4]_3[ReO(EC)]\cdot C_4H_8O_2$ were structurally characterized by X-ray diffraction. In the former, the Re atom is in an octahedral coordination environment with the salient feature that the *anti*-carboxylate group is coordinated *trans* to the oxo ligand. In the latter complex, a distorted square pyramidal geometry is evident; notably, both nitrogen donor atoms are deprotonated. The causes for very broad $^1H$ and $^{13}C$ NMR spectra of Tc and Re complexes in aqueous solutions near physiological pH were determined using the rhenium EC and TMEC complexes and 2D NMR spectroscopy. The observed broadness was found to be due to the presence of two forms (which differ in denticity) in intermediate exchange on the NMR spectroscopic time scale. The two forms are (i) an *anti*-cys NH deprotonated, *anti*-carboxyl dissociated form and (ii) an *anti*-cys NH, coordinated *anti*-carboxyl form. The broadening is due to the coupling of the carboxyl coordination and NH proton dissociation.

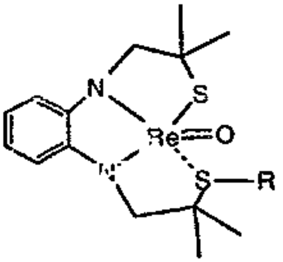


$ECH_6$ (**6a**)



$TMECH_6$ (**6b**)

Neutral rhenium(V) oxo complexes (**7**) have been synthesised by the reaction of $[ReOBr_4]^-$ and diamino-thiol-thioether ligands of the type $(RSC(CH_3)_2CH_2NH(o\text{-}C_6H_4)NHCH_2C(CH_3)_2SH$ [21]. They were produced in yields ranging from 29-97%, isolated as red-orange air-stable solids. The neutral complexes were isolated by extraction into $CH_2Cl_2$ or $CH_3Cl$, subjected to chromatography on silica and recrystallized. Characterization was by IR, UV-VIS, $^1H$ and $^{13}C$ NMR spectroscopies and FAB MS. X-Ray crystal structures for the $R=CH_2CH=CH_2$ and $CH_2CH_2CH_3$ derivatives were obtained. Both were found to possess square-pyramidal distorted geometries in which the oxo ligand is in the apical position. In contrast to aliphatic $N_2S_2$ ligands, the aromatic rings in these complexes force the base of the pyramid to be almost flat due to the coplanarity of the N-C-C-N bonds. In both complexes the side chain occupies the least sterically hindered position, *anti* with respect to the oxo ligand. Average Re-O bond distances are 1.685-1.712 Å, the Re-S(thioether) bond is 2.293(2) Å while the Re-S(thiolate) is 2.381(2) Å. Two effects of the aromatic ring were hypothesized: (i) an electronic effect, which enhances the acidity of the amine nitrogens and results in deprotonation of both nitrogens and coordination of both sides, and (ii) a steric effect which imparts rigidity to the N-C-C-N portion of the ligand resulting in an almost flat base to the square pyramidal complex by an entropy effect.



R = $CH_2CH{=}CH_2$
$CH{=}C{=}CH_2$
$CH_2CH_2CH_3$
$CH_2CH_2OH$
$CH_2Ph$
$CH_2CCH$

(7)

### 3.8. Complexes with oxygen, nitrogen and phosphorus donor ligands

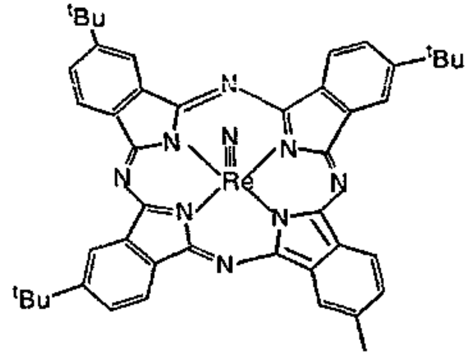
A new phase of bis[2-(diphenylphosphino-κ*P*)phenylazanido-κ*N*](ethanolato)(oxo)-rhenium(V) has been synthesised and an X-ray diffraction study carried out [22]. The coordination geometry about the Re atom is highly distorted octahedral. In the $P_2N_2O_2$ coordination polyhedron of the β-phase, the Re atom is 1.13(1) Å from the plane formed by the nitrogen and ethanolic oxygen atoms and -1.10(1) Å from the plane formed by the phosphorus and oxo oxygen atoms. The Re=O bond is 1.717(8) Å.

The structure of (*OC*-6-14)-(7-azaindole)dichloro(ethoxo)oxo(triphenylphosphine)rhenium(V) has been reported [23]. Its structure was investigated to ascertain the stereochemistry proposed from NMR spectroscopic data. The compound consists of $[ReClO(C_2H_5O)(C_7H_6N_2)\{P(C_6H_5)_3\}]$ monomers in which the Re centre has a slightly distorted geometry. The azaindole and phosphine ligands occupy *trans* positions whereas the perpendicular $ReCl_2O(OR)$ plane contains a *trans* O=Re-OR unit. The azaindole ligand forms a bifurcated intramolecular hydrogen bond with the oxo group and a Cl atom. The Re=O distance is 1.691(6) Å while the Re-N distance is 2.185(7) Å.

### 3.9. Complexes with nitrogen donor ligands

The preparation and spectroscopic characterization of nitridophthalocyaninatorhenium(V) have been described [24]. The compound was prepared by the reaction of dirheniumheptoxide with ammonium iodide in molten

1,2-dicyanobenzene resulting in a chemically and thermally stable complex. The UV-VIS spectra exhibit $\pi$-$\pi^*$ transitions typical of the $pc^{2-}$ ligand. A dominant absorption at 976 $cm^{-1}$ in the mid infrared region is due to the rhenium-nitrogen triple bond stretch. The synthesis of the first soluble nitrido(phthalocyaninato)rhenium complex $(^tBu)_4pcReN$, (**8**), has been reported [25]. The reaction of 4-*tert*-butylphthalodinitrile with ammonium perrhenate gave the complex which was characterized by IR, UV-VIS, $^1H$ and $^{13}C$ NMR spectroscopies, CV, MS and elemental analysis. It is assumed to be monomeric in solution while in the solid state dimers or higher aggregates were encountered.



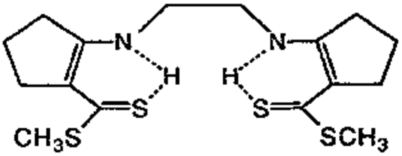
(**8**)

Ligand exchange procedures were used to prepare new rhenium isothiocyanato complexes starting from $[ReNCl_2(Me_2PhP)_3]$ and KSCN or $Me_3SiNCS$ [26]. The reaction with KSCN generated the Re(V) nitrido complex $[ReN(NCS)_2(Me_2PhP)_3]$ whereas reaction with $Me_3SiNCS$ gave the Re(I) complex $[Re(NS)(NCS)_2(Me_2PhP)_3]$. Both complexes (which are air stable) were characterized spectroscopically and by X-ray diffraction; both exhibit distorted octahedral coordination about the rhenium centre. In the Re(V) complex the Re-N bond length is 1.66 Å while the Re=NS distance in the Re(I) complex is 1.85(3) Å.

### 3.10. *Complexes with nitrogen and sulfur donor ligands*

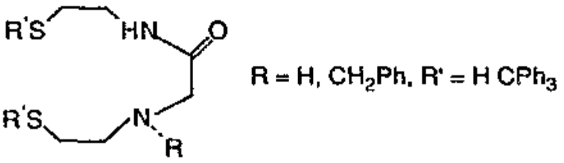
Mixed-ligand complexes of the general formula $[ReN(X)(Me_2PhP)_2(R_2tcb)]$, (X=I, $N_3$, NCS and CN; $HR_2tcb$=*N*-(*N*,*N*-dialkylthiocarbonylbenzamidines) with $R_2=Et_2$ or morpholinyl), were synthesised from $[ReN(Cl)(Me_2PhP)_2(R_2tcb)]$ complexes via ligand-exchange reactions with alkali halides or pseudohalides [27]. In the parent complex the $N^{3-}$ ligand exerts a strong *trans*-labilizing effect resulting in an extraordinarily long Re-Cl bond of 2.673 Å. The complexes prepared resulted from the preferential substitution of the chloro ligand. They were characterized by IR and NMR spectroscopy and mass spectrometry. The complex $[ReN(N_3)(Me_2PhP)_2(Et_2tcb)]$ was studied using X-ray diffraction; the geometry about the rhenium atom is distorted octahedral, and the azido ligand is coordinated *trans* to the $ReN_3$ bond which is 1.733(8) Å while the Re-N(azido) distance is 2.323(9) Å. In a related paper [28], new nitrido complexes were obtained from ligand exchange reactions starting from [ReN(Cl)$(Me_2PhP)_2$(morphtcb)], morph = morpholinyl, 2,6-dimethylthiophenol (2,6-dmtp) and disodium 1,2-dicyanoethene-1,2-dithiolate ($Na_2$mnt). The 2,6-dimethylthiophenol reacts with the parent complex with one of the $Me_2PhP$ ligands being substituted by 2,6-dmtp. The reaction proceeds with labilization of the chloro ligand and the neutral complex [ReN($Me_2PhP$)(2,6-dmtp)(morphtcb)] results. In contrast, the chelating agent $mnt^{2-}$ replaces the $morphtcb^-$ ligand in the parent complex concomitant with the abstraction of the chloro ligand generating a five-coordinate neutral complex [ReN$(Me_2PhP)_2$(mnt)]. These complexes were characterized by IR and NMR spectroscopy and by X-ray diffraction. The 2,6-dmtp derivative exhibits a strongly distorted square pyramidal geometry and the Re-N(nitrido) distance is 1.65 Å while the mnt derivative displays square pyramidal coordination and possesses an Re-N(nitrido) distance of 1.66 Å.

Substitution of $ReOCl_3(PPh_3)_2$ by a tetradentate $N_2S_2$ ligand gave a neutral complex ReO(L)Cl where L corresponds to the dianionic form of the ligand *N,N'*-ethylenebis(methyl-2-aminocyclopentane-1-dithiocarboxylate), (**9**) [29]. The complex was characterized by elemental analysis IR and NMR spectroscopy and conductimetry.



(**9**)

The design and synthesis of a novel $N_2S_2$ ligand system for the formation of Re(V) oxo and $^{99}$Tc(V) oxo complexes has been reported [30]. The synthesis of the monoamine-monoamide bis(thiol) chelate (MAMA') (**10**) was achieved as follows: cysteamine hydrochloride was *S*-trityl-protected by allowing it to react with triphenylmethanol in trifluoroacetic acid to yield an amine. The amine was *N*-acylated with bromoacetyl bromide in the presence of triethylamine and then reacted with an additional equivalent of amine under more vigorous conditions to yield *S,S'*-bis(trityl) monoamine-monoamide ligand. Upon nucleophilic displacement of the methanesulfonate of benzyl alcohol, this yielded the *S,S'*-bis(trityl) *N*-benzyl monoamine-monoamide ligand. Incorporation of this ligand into the metal(V) oxo core required deprotection of the sulfur atoms by mercury salt formation followed by cleavage of the salt with $H_2S$. Rhenium(V) oxo incorporation consisted of incubation of the ligand in basic methanolic solution with trichlorobis(triphenylphosphine)rhenium(V) oxide which yielded the *syn* and *anti* products which were separated by flash chromatography. An X-ray crystallographic study was carried out; Re=O distances were 1.683(4) (*syn*) and 1.680(2) (*anti*) while Re-N distances were 2.182(5) and 2.151(3) Å respectively. These complexes were also characterized by NMR spectroscopy.



**(10)**

## 4. Rhenium(IV)

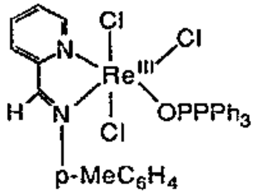
### 4.1. Complexes with oxygen and nitrogen donor ligands

The structure of the compound $[Re_2(\mu\text{-}O)_2(C_{18}H_{18}N_4)_2](PF_6)_4 \cdot 2(CH_3)_2CO \cdot 4H_2O$ has been obtained [31]. It comprises a dinuclear unit (tpa)Re (μ-O)Re (tpa), tpa = tris(2-pyridylmethyl)amine, which has a crystallographically imposed centre of symmetry at the midpoint of the rhenium-rhenium triple bond. The coordination about each rhenium atom is pseudo-octahedral, the rhenium-rhenium, rhenium-oxygen(average) and rhenium-nitrogen distances are 2.364(1), 1.950(6) and 2.105(7)-2.150(6) Å respectively.

The transformation of a chelated *N*-aryl-pyridine-2-aldimine to the corresponding deprotonated *N*-aryl-2-picolinamide has been demonstrated in rhenium and ruthenium systems [32]. The oxidation by hydrogen peroxide of an MeCN solution of the red Re (III) complex (**11**) at room temperature gave the Re (IV) amide complex (**12**) as a toluene adduct. Its X-ray crystal structure was obtained and shows the rhenium atom to be at the centre of a distorted octahedral $ReOCl_3N_2$ coordination sphere in which the pyridine nitrogen lies *trans* to $OPPh_3$ oxygen and the $Cl_3$ fragment is meridional. The Re-N distances range from 2.066(14) to 2.101(12) Å. These complexes were further studied using cyclic voltammetry. In a related paper [33], the synthesis of the analogous benzene adducts are described along with results from X-ray crystallography and cyclic voltammetry.

### 4.2. Complexes with sulfur donor ligands

The crystal structure of rhenium disulfide has been obtained and observations on this structure refute the notion that it is isostructural with the previously published structure of $ReSe_2$ [34]. The asymmetric unit of rhenium disulfide consists of two $Re^{4+}$ and four $S^{2-}$ ions. Layers of nearly hexagonal-close-packed arrays of sulfur atoms stack along the *a* axis and are nearly parallel to the *bc* plane of the unit cell. The Re atoms occupy the octahedral sites between every other pair of these hexagonal-close-packed layers of sulfur atoms. Each rhenium is coordinated to six sulfur atoms in an approximately octahedral geometry and each trigonal pyramidal sulfur is bonded to three Re atoms. As a result of participation by each Re atom in metal-metal bond formation to three neighbours in the layer of cations, $Re_4$ parallelograms are formed. Rhenium-rhenium bond distances range from 2.695(2) to 2.895(2) Å whereas non bonding separations range from 3.560(1) to 3.770(2) Å.



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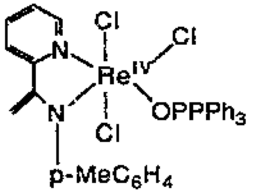


**(12)**

The reaction of $[Re^{IV}S_4(S_3)_6]^{4-}$ or amorphous $Re_2S_7$ with aqueous cyanide ions has been studied in an effort to glean more insight into nucleophilic attack on the stability of these clusters [35]. The reaction between the aforementioned chalcogenides and aqueous $CN^-$ solution at 85°C gave rise to $K_4[Re_4^{IV}S_4(CN)_{12}]\cdot 4H_20$, $K_4[Re_4^{IV}S_4(CN)_{12}]\cdot 6H_20$ and $K_8[Re_2^{III}Re_2^{IV}S_2(SO_2)_4(CN)_{10}]\cdot 5H_20$ which were characterized by IR and electronic spectroscopy in addition to X-ray crystallography. In the reaction of $[Re^{IV}S_4(S_3)_6]^{4-}$ with cyanide ions the $K_4[Re_4^{IV}S_4(CN)_{12}]\cdot 4H_20$ is generated; the central $Re_4S_4$ core maintains it integrity while the reaction involving the amorphous $Re_2S_7$ generates $K_8[Re_2^{III}Re_2^{IV}S_2(SO_2)_4(CN)_{10}]\cdot 5H_20$ which exhibits a novel, electron-rich mixed-valence tetranuclear cluster anion. This rhombic anion has approximately $C_{2h}$ symmetry and may be viewed as being formally obtained from the condensation of two trinuclear $\{Re_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(CN)_9\}$ units with the anion being formed from the "intermediate product" $[Re_4(\mu_3\text{-}S)_2(\mu_2\text{-}S)(CN)_{10}]^{8-}$ as a result of the oxidation of the four $(\mu_2\text{-}S)^{2-}$ ligands which display a higher electron density than the $(\mu_3\text{-}S)^{2-}$ ligand. Metal clusters with planar $M_4$ rhombuses have interesting electronic properties since the planarity of the four-membered ring of metal atoms bestows on them the potential for very strong metal-metal interactions while strong transannular interactions will cause non-equivalent metal centres to be present. In the present cluster, the short transannular Re-Re distance is indicative of considerable double-bond character Re-Re = 2.740(1) Å. Calculations using the EH-SCCC method confirm this and also show an increase in negative charge on the two central rhenium atoms relative to the others concomitant with a pronounced delocalization of the HOMOs over the Re centres. The $Re_4S_6$ fragment is shown to correspond with a section of the $ReS_2$ or $ReSe_2$ lattice and the results of this investigation are discussed in the light that cyanolysis supplements other physical methods for the characterization of amorphous metal sulfide phases of early transition elements and relevant catalysts and metalloenzymes.

## 5. Rhenium(III)

### 5.1. Complexes with halide ligands

A new synthetic route to ternary Re(III) bromides and to $ReBr_3$ has been established [36]. For the first time the substitution of bridging and terminal chloride for bromide ions was observed in rhenium clusters $[Re_3(\mu\text{-}Cl^{i,b})_3(Cl^{o,t})_6(Cl^{i,t})_{(3\text{-}x)}(H_2O^{i,t})_x]^{(3\text{-}x)-}$, (x=0-3) as a result of the reaction of "$ReCl_3 \cdot 2H_2O$" in hot hydrobromic acid solution under an inert gas atmosphere. The ternary Re(IV) bromides were found to dominate in the presence of oxygen with the Re(III) bromides as by-products.

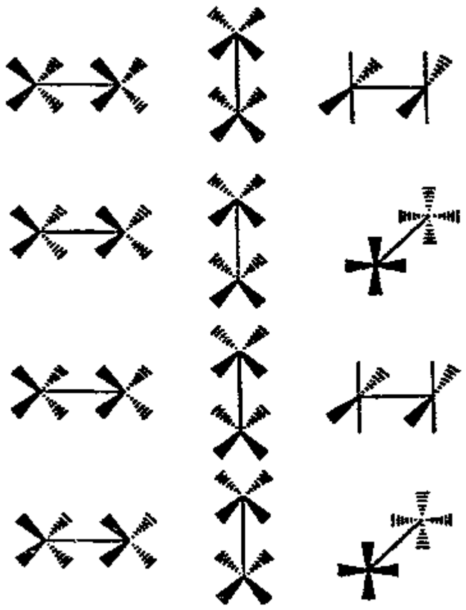
An unusual salt $[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$ has been synthesised and structurally characterized [37]. This salt represents the first example where the octachlorodirhenate unit is present in three different crystallographic environments in the same unit cell. The asymmetric unit contains two independent $[Rh_2]^{2+}$ cations held together with one $[Re_2Cl_8]^{2-}$ anion at full occupancy and two dirhenium anions each at half-occupancy. The Re-Re separations in the three different anions are 2.225(4), 2.216(3) and 2.215(4) Å. Inspection of the unit cell packing-diagram reveals the influence of the cation shape on the packing of the three different anion types. The first type of anion is involved in parallel stacking of the M-M units in a large channel bordered by acetate groups of the surrounding dirhodium cations. The second type stacks in an end-to-end fashion and the third type packs with perpendicularly aligned metal units in a second slightly smaller star-shaped channel as shown in structure (**13**).

### 5.2. Complexes with oxygen and phosphorus donor ligands

A systematic study of the reactivity of bis(diphenylphosphino)-amine $NH(PPh_2)_2$ with $[AsPh_4][ReOCl_4]$ was undertaken and the results have been reported [38]. The reaction of the aforementioned species in a 1:1 molar ratio in boiling degassed chloroform gave a green octahedral complex $[ReCl_3(H_2O)\{NH(OPPh_2)PPh_2\text{-}P,O\}]$ as a solid in 80% yield. The same reaction when carried out in anhydrous degassed chloroform gave a yellow-green precipitate which was further crystallized from dried and degassed solvents ($CH_2Cl_2$-$CCl_4$). Its X-ray structure confirmed it to be octahedral $[ReCl_4\{NH(OPPh_2)PPh_2\text{-}P,O\}]$. When this complex was reacted further with an excess of ligand in anhydrous chloroform the ionic octahedral complex $[AsPh_4][[ReCl_4\{N(OPPh_2)PPh_2\text{-}P,O\}]$ was obtained in low yield and which exhibits the ligand in its deprotonated form. This deprotonation is ascribed to the excess of ligand which may form its hydrochloride salt. The Re-O distances in these complexes range from 2.054(3) to 2.071(6) Å and are indicative of the presence of neutral or partially negatively charged oxygen atoms. Magnetic studies were carried out on these complexes.

### 5.3. Complexes with sulfur donor ligands

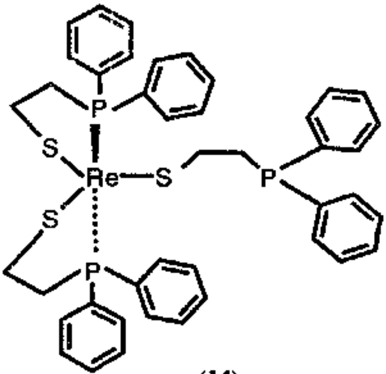
The syntheses and properties of the carbonyl-containing complexes $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(dppm)_2(CO)]PF_6$ (X=Cl or Br), and their conversion to



**(13)**

the analogous μ-$SO_2$ compounds have been reported [39]. Specifically, the reaction of $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(dppm)_2]$ (X=Cl or Br) with $TlPF_6$ and CO in dichloromethane resulted in the labilization of one of the Re-X bonds and gave green complexes of the type $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_2(CS)(dppm)_2(CO)]PF_6$ (X=Cl or Br) in 55-60% yield. Results from NMR spectroscopy suggest that the carbonyl containing complex has an unsymmetrical edge-sharing bioctahedral structure displaying separate ligand environments about each rhenium atom. The analogous μ-$SO_2$ compounds $[Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_2(CS)(dppm)_2(CO)]PF_6$ were formed by the reaction of $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_2(CS)(dppm)_2(CO)]PF_6$ and $NOPF_6$ in dichloromethane. These reactions were found to occur only when oxygen is present and evolve $NO_2$ as the actual oxygen transfer reagent. The complexes were further characterized by IR spectroscopy and by cyclic voltammetry.

The synthesis and physiochemical characteristics of a new series of five-coordinate $Re^{III}P_2S_3$ complexes containing the 2-(diphenylphosphino)ethanethiolate ligand together with a monothiol RSH, $R=Ph_2P(O)CH_2CH_2$, $PhCH_2$, Ph or $^nPr$ has been achieved [40]. The complexes were characterized by elemental analysis, NMR spectroscopy and positive-ion fast atom bombardment mass spectroscopy and found to be diamagnetic, neutral and stable. An X-ray crystal structure of bis-[2-(diphenylphosphino)ethanethiolato-κS-κP](phenylmethanethiolato-κS)rhenium(III), **(14)** has been obtained. The complex comprises two monomeric, neutral and well separated molecules with the rhenium atom is in a trigonal bipyramidal environment in both. The Re-S distance in both molecules ranges from 2.236(4) to 2.387(5) Å.



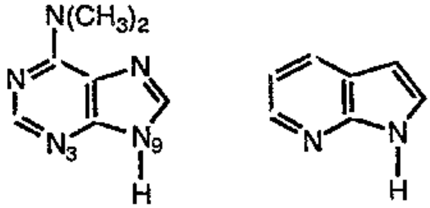
**(14)**

The first syntheses of Re (III) complexes with both thiolato and arsine ligands have been reported [41]. Reaction of the Re (V) species $[ReOCl_3(PPh_3)_2]$ with excess thiol and diarsine at 100°C gave the cationic complexes *trans*-$[Re(SCH_2CH_3)_2(DIARS)_2]^+$ and *cis*- and *trans*-$[Re(SC_6H_5)_2(DIARS)_2]^+$ where DIARS = *o*-phenylenebis(dimethylarsine). The complexes were characterized by FAB mass spectroscopy, UV-visible spectroscopy, elemental analysis and cyclic voltammetry. An X-ray crystallographic study has been carried out; the *trans*-$[Re(SC_6H_5)_2(DIARS)_2](C_3H_5O_2) \cdot H_2O$ structure consists of two independent half-cations, an anion and a water solvent molecule. Both benzenethiolate ligands are arranged in a *trans* fashion. The Re-S bond lengths are 2.298(5) Å and 2.497(10) Å for Re-S. The SEt derivative, *trans*-$[Re(SEt)_2(DIARS)_2]PF_6$, exhibits octahedral coordination about the Re atom; the Re-S distances are 2.284(3) Å while the Re-As length averages 2.480(4) Å.

### 5.4. Complexes with nitrogen donor ligands

Dirhenium complexes with *N*6,*N*6-dimethyladenine (dmad⁻) and 7-azaindole, aza have been synthesised, (**15**) [42]. Refluxing $Re_2Cl_2(CH_3CO_2)_4$ and a small excess of *N*6,*N*6-dimethyladenine in ethanol for 24 hr led to the replacement of about 90% of the acetate ligands by bridging N3/N9 adenine units generating $Re_2Cl_2(dmad)_2$. Four different stereoisomers were observed in the $^1H$ NMR spectrum due to the different relative orientations of the dissymmetric ligands about the rhenium-rhenium axis. When $(Bu_4N)_2[Re_2Cl_8]$ and 7-azaindole were heated together in the absence of solvent, a brown material, $Re_2Cl_2(aza)_2$, which exhibited several stereoisomers due to different orientations of the N1/N7-bridging ligand was obtained. Both complexes were characterized by $^{13}C$ NMR spectroscopy.

The first seven-coordinate rhenium bis(terpyridine) complexes $[Re(terpy)_2X]^{2+}$, (X = OH, Cl, NCS) have been prepared [43]. They were prepared from

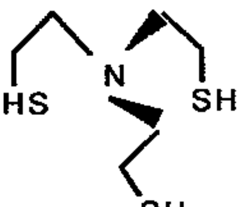


**(15)**

$[Re^{V}O_2(py)_4]^+$ and a 2 molar equivalent of terpyridine via a reduction/substitution route. In addition $[ReO_4]^-$ was also produced thereby implicating a disproportionation as a component of the preparative route. The replacement of the hydroxo ligand in this complex by $Cl^-$ or $NCS^-$ was found to be more rapid at low pH. The X-ray crystal structures of all three complexes were reported, all three complexes exhibit similar structures in which Re is seven-coordinate bonding to three nitrogen donors from each of the terpy ligands and a seventh bond to the hydroxo, chloride or thiocyanate-*N* in a distorted capped trigonal prismatic coordination. The Re-N bond lengths range from 2.040(9) to 2.157(7) Å while Re-OH is 1.969(5), Re-Cl is 2.281(5) Å and Re-NCS is 2.046(9) Å. The complexes were also characterized by elemental analysis, UV-VIS, mass spectrometry and IR, and $^1$H NMR spectroscopies. A kinetic study of the substitution reaction producing $[Re(terpy)_2NCS]^{2+}$ from $[Re(terpy)_2OH]^{2+}$ was carried out, results indicate that a rapid protonation equilibrium occurs generating a reactive species which subsequently reacts with $SCN^-$ in the rate determining step. The derived equilibrium and rate constants at 25°C and $\mu = 1.00$ M are $pK_a = 1.4(8)$ and $k = 45(4)\ M^{-1}\ s^{-1}$.

### 5.5. *Complexes with nitrogen and sulfur donor ligands*

The syntheses, structures and properties of trigonal bipyramidal $Re^{III}$ and $Tc^{III}$ complexes containing the tetradentate tripod ligand 2,2,2′-nitrilotris(ethanethiol), **(16)** and a triphenylphosphane or isocyanide ligand has been reported [44].



**(16)**

## 6. Rhenium(II)

### 6.1. Complexes with halide ligands

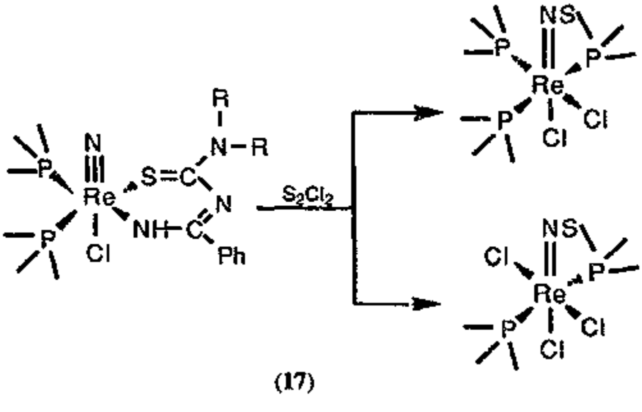
An unusual crystallographic disorder of $M_2$ units in $Re_2Cl_4(PEt_3)_4$ has been studied [45]. The Re-Re bond distance of 2.250(4) Å is indicative of a triple bond between the two rhenium atoms.

The aminocarbyne complex *trans*-$[ReCl(CNH_2)(dppe)_2][BF_4]$ underwent (by cyclic voltammetry in 0.2M $[NBu_4][BF_4]$/NCMe at a Pt electrode) a single-electron oxidation by an induced anodic deprotonation generating the hydrogen isocyanide compound *trans*-$[ReCl(CNH)(dppe)_2][BF_4]$ [46]. The latter exhibits a similar anodic process at a higher potential. The mechanism of these anodic processes has been investigated by digital simulation of the cyclic voltammograms. Rate constants of deprotonation reactions induced by electron transfer and acid dissociation constants for the aminocarbyne species and its oxidized form were estimated.

The synthesis, NMR spectroscopic properties and reactivity of the unstable pentamethylcyclopentadienyl chlorohydrocarbon complexes $[(Cp^*)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ and $[(Cp^*)Re(NO)(PPh_3)(ClC_6H_5Cl)]^+BF_4^-$ have been reported [47]. Both compounds may be generated in enantiomerically enriched form and serve as functional equivalents for the chiral Lewis acid $[Cp^*)Re(NO)(PPh_3)]^+$. Alkene binding selectivities were studied and compared to those in the Cp series.

### 6.2. Complexes with nitrogen and phosphorus donor ligands

The reaction of rhenium(V) mixed-ligand complexes of the general formula $[ReN(Cl)(Me_2PhP)_2(R_2tcb)$, $HR_2tcb = N$-(N,N-dialkylthiocarbamoyl)benzamidine), with disulfur dichloride has led to Re(II) and Re(I) thionitrosyl complexes *trans*-$[Re(NS)Cl_3(Me_2PhP)_2]$ and *mer*-$[Re(NS)Cl_2(Me_2PhP)_3]$, (17) [48].



(17)

## 7. Rhenium(I)

### 7.1. Complexes with hydride ligands

Molecular complexes of the form $ReCl(\eta^2-H_2)(PR_3)_4$, where $PR_3$ is a tertiary phosphine ligand, were studied in order to assess the influence of the ancillary ligands on dihydrogen coordination [49]. The syntheses and structural characteristics of $ReCl(\eta^2-H_2)(dppe)_2$ and $ReCl(\eta^2-H_2)(dppee)_2$, dppee = $Ph_2PCH=CHPPh_2$, extend the number of compounds known to contain long H-H interactions. The metal-bonded H atoms in these complexes display $T_1$ (min) of 43(5) and 29(4) ms at 200 MHz which would be on the order of 1.23 Å (fast Rotation) to 1.56 Å (slow Rotation) for the dppe complex and 1.11 Å (fast Rotation) to 1.41 Å (slow Rotation) for the dppee complex. In addition, the complex $[ReO_2(dppee)_2][ReO_4]$ was synthesised and its crystal structure reported. The Re-O distance in the cation is 1.788(6) Å.

### 7.2. Complexes with selenium ligands

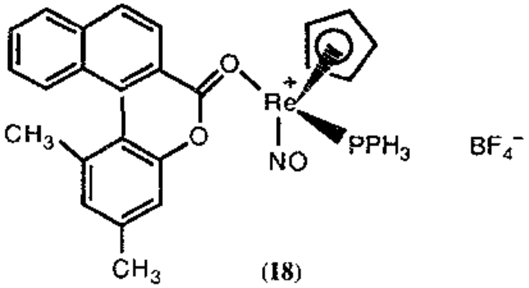
The synthesis of $[Re_2I_2(CO)_6(Se_7)]$, a coordination compound of elemental selenium with a transition metal, has been achieved [50]. The compound has been characterized by NMR spectroscopy and X-ray diffraction studies. Each of the rhenium atoms is coordinated to three terminal carbonyl ligands, two bridging iodide groups and one selenium atom of the *cyclo*-heptaselenium ligand. The Re···Re non-bonding distance is 4.077(3) Å and the Re-Se distances average 2.586 Å; the apical selenium atoms are bonded at a distance of 2.588(3) Å and the heptaselenium ligand adopts a chair-like conformation.

### 7.3. Complexes with oxygen and nitrogen donor ligands

Extended X-ray absorption fine structure (EXAFS) studies have been carried out on a chiral rhenium complex possessing an "axially prostereogenic" biaryl lactone ligand, (**18**). Its precursors have been studied in $CH_2Cl_2$ and acetone solutions [51]. In addition, multiple scattering calculations have been carried out. This study was conducted in order to understand the mechanism for the stereoselective reduction and alkylation of aldehydes and ketones and the prediction of the outcome of nucleophilic attack at the activated carbonyl group, not only in the crystalline state, but also in homogeneous solution. The EXAFS results were compared with those already obtained from X-ray crystallography.

### 7.4. Complexes with oxygen and phosphorus donor ligands

An NMR spectroscopic conformational analysis has been carried out to assess the dynamics of the ligand 1,1′-bis(diphenylphosphino)ferrocene in the complex $Re_2(\mu-OMe)_2(\mu-dppf)(CO)_6$ at 228 K [52]. At this temperature, the fluxionality of the dppf ligand ceases whereas the dynamics of the phenyl rings is rapid on the NMR spectroscopic timescale down to -85°C. The $[Re_2(\mu-OMe)_2]$ core is static



(18)

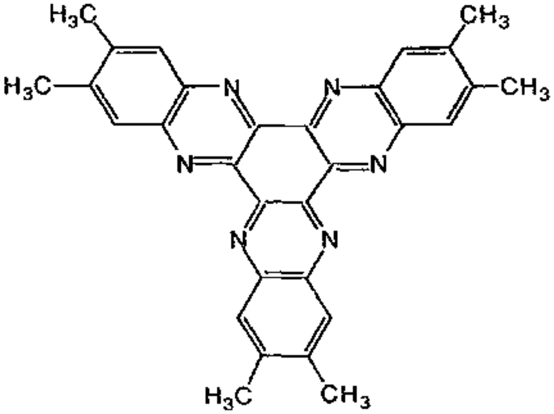
during the temperature lowering process. The rotations of the phenyl rings in conjunction with the ferrocenyl mobilities permit the dppf ligand to attain the most suitable conformation between the metal centres.

### 7.5. Complexes with nitrogen donor ligands

Mononuclear and dinuclear Pd(II)/Re(I) complexes containing a sterically hindered trinucleating ligand 2,3,8,9,14,15-hexamethyl-5,6,11,12,17,18-hexaazatrinaphthalene (hhtn), (**19**) have been synthesised [53]. The trinucleating ligand was first synthesised in an efficient one-pot synthesis from the condensation of hexaketocyclohexane with 4,5-dimethyl-1,2-phenylenediamine. Addition of Re$(CO)_5$Cl to hhtn in refluxing toluene gave red-brown crystals of *fac*-Re$(CO)_3$Cl(hhtn) after 6 hr. When a dichloromethane solution of the latter was reacted with 1 equivalent of Pd$(PhCN)_2Cl_2$, the resulting complex {Re$(CO)_3$Cl}$PdCl_2$(hhtn) was isolated as a brown solid upon the addition of diethyl ether. The structure of Re$(CO)_3$Cl(hhtn) has been obtained and comprises a nearly octahedral Re centre which is deflected from the hhtn plane by an angle of 19.5°. The Re-N distances are 2.203(6) and 2.222(6) Å. In {Re$(CO)_3$Cl}$PdCl_2$(hhtn), the rhenium atom is in a nearly octahedral coordination environment while palladium is square planar; both are coordinated to a highly distorted hhtn ligand. The $PdCl_2$ fragment is bent out of the ligand plane by 40.2° while the Re unit is distorted by 10.4°. This latter complex forms π-π stacks with the 1,2-dichlorobenzene solvate molecules.

The preparation of the cationic imido rhenium complex [Tp*Re$(N^tBu)_2$Cl]$PF_6$, Tp* = $\kappa^3$-HB$(3,5\text{-}Me_2pz)_3$ (**20**), has been described [54].

The exchange of an azine ligand in *fac*-Re$(CO)_3L_2$Cl, L = 4-cyanopyridine or quinoline has been investigated [55]. The substitution of 4-cyanopyridine by 4-phenylpyridine in *fac*-Re$(CO)_3$(4-cyanopyridine)$_2$Cl was achieved in the preparation of *fac*-Re$(CO)_3$(4-cyanopyridine)(4-phenylpyridine)Cl. The kinetics of mixed-ligand complex formation were investigated and a mechanism has been proposed. These mixed-ligand complexes are of interest in photochemical studies due to the coordination to Re(I) by two different pyridine ligands each with its own electron donating and accepting ability which may have utility in the control of photochemical reactions.



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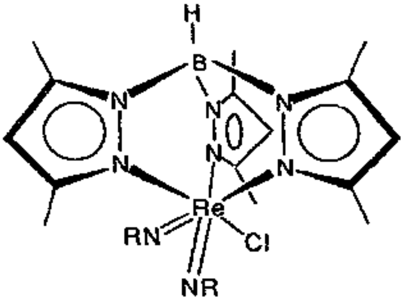

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A novel type of 1,4-M-N fluxional shift in rhenium(I) tricarbonyl halide complexes of pyrazolylpyridine ligands has been investigated through a detailed NMR spectroscopic study [56]. In particular, variable temperature one- and two-dimensional NMR spectroscopic studies on the solution fluxionality of the complexes *fac*-[ReX(CO)$_3$L] (L = bppy or tmbppy, X = Cl, Br or I; L = dmbppy, X = Br; bppy = 2,6-bis(pyrazol-1-yl)pyridine, dmbppy = 2,6-bis(3,5-dimethylpyrazol-1-yl)-6-(pyrazol-1-yl)pyridine, tmbppy = 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine) are reported. In addition, NMR spectroscopic data for the complex *cis*-[ReBr(CO)$_2$(tmbppy)] formed from the tricarbonyl complex under more forcing reaction conditions was also presented. For the bppy complexes in which the bppy ligand is acting as a bidentate chelate, these complexes were found to be fluxional in solution with the bppy ligand oscillating between equivalent bidentate modes by a twist mechanism which involves the breaking and making of Re-N bonds. The dmbppy and tmbppy derivatives were found to exhibit analogous fluxional complexes. Under more severe conditions the complex *cis*-[ReBr(CO)$_2$(tmbppy)] was formed and the ligand exhibits its more usual tridentate behaviour. The activation energies were found to be dependent upon the relative donor strengths of the nitrogen atoms $\Delta G^*(298.15\ K) = 55\text{-}56$ (bppy), *ca* (dmbppy) and 70-77 kJ $mol^{-1}$ (tmbppy).

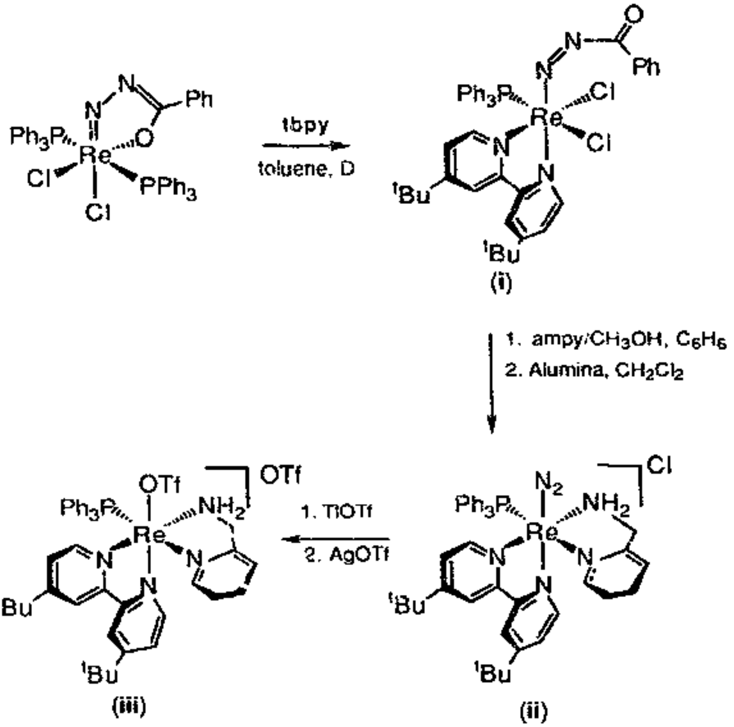
A versatile synthetic approach for the preparation of chiral rhenium(I) -amine complexes has been communicated [57]. As shown in (**21**) the compound $Re(=NN=C(Ph)O\text{-})(PPh_3)_2Cl_2$ undergoes a two electron reduction of the metal when refluxed in toluene with 4,4′-di-*tert*-butyl-2,2′-bipyridine (tbpy) or bpy to form rhenium(III) complex (**i**) as shown. When the complex (**i**) is refluxed in benzene along with MeOH and ampy reduction to the Re (I) complex (**ii**) occurs concomitant with elimination of methyl benzoate. The dinitrogen stretch in (**ii**) occurs at 1940 $cm^{-1}$ indicative of an electron rich metal centre. An X-ray crystal structure indicates an N-N bond length of 1.13(1) Å. Anion exchange of (**ii**) with TlOTf to generate $[ReN_2(ampy)(tbpy)PPh_3]OTf$ (90% yield) followed by oxidation of the rhenium atom with AgOTf resulted in dinitrogen loss giving an Re (II) precursor (**iii**). Subsequent reduction of (**iii**) in dme by $Mg^0$ in the presence of a variety of ligands gave a new series of complexes of the form $[Re(ampy)(tbpy)(PPh_3)(L)]^+$ where $L = N_2$, ethene, benzaldehyde, *tert*-butyl isocyanide or CO. The benzaldehyde complex was characterized by NMR and shows an aldehyde proton resonating at 5.98 ppm indicative of $\eta^2$-coordination, suggesting that it forms as a single diastereomer. This complex was studied by cyclic voltammetry.

Fast time-resolved infrared spectroscopy, TRIR, was used to probe the lowest MLCT excited state of $ClRe(CO)_3(4,4'\text{-bipyridyl})_2$ [58]. The three ground-state ν(CO) bands shift up in frequency but not by the same amount. Employing $^{13}CO$-enrichment, the energy-factored force field of the ground state was obtained. Based on these results a new interpretation of the resonance Raman spectrum of the compound has been postulated.

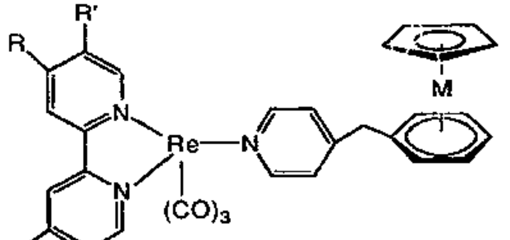
The photochemistry and photophysics of a series of dinuclear complexes $(L)Re^{I}(CO)_3[CpM^{II}(arene)]^{2+}$ (**22**) where L is one of the diimine ligands bpy, dmb, tmb and deab (deab = 4,4′-bis(diethylamino)-2,2′-bipyridine, tmb = 4,4′,5,5′-tetramethyl-2,2′-bipyridine, dmb = 5,5′-dimethyl-2,2′-bipyridine) and M = Fe or Ru, and the corresponding mononuclear complexes $(L)Re(CO)_3$ have been explored [59]. The energy of the Re→diimine MLCT excited state varied over a 2000 $cm^{-1}$ range. Near-UV photoexcitation of the dimers indicates that the Re→diimine MLCT chromophore transfers electronic excitation to the CpM(arene) unit generating a reactive $^3$d-d state. The intramolecular exchange energy transfer $E_NT$ is moderately exothermic for M = Fe and weakly endothermic for M = Ru. The rate of intramolecular $E_NT$ was estimated from the quantum efficiency for CpM(arene) loss from the dimers and from MLCT emission lifetimes.

### *7.6. Complexes with nitrogen and phosphorus donor ligands*

The photophysical behaviour of a new carbon dioxide reduction catalyst $[Re(CO)_2(bpy)\{P(OET)_3\}_2]^+$, $(P^+)$ has been examined by time-resolved infrared spectroscopy (TRIR) of the ν(CO) absorption bands, by UV/visible flash photolysis



(21)



(22)

in both emission and absorption and by spectroelectrochemistry in both infrared and UV/visible regions. [60]. These techniques have established that photolysis of the title complex promotes it into an excited state $P^{+*}$ which has a lifetime of 250 ns. The observed shifts in ν(CO) bands from the ground to excited state are indicative that this state is an MLCT state with the charge localized on the bpy ligand. Reaction of the excited state with 1,4-diazabicyclo[2,2,2]octane (DABCO) reduces $P^{+*}$ to P with a shift in IR bands below those of $P^{+}$. The back-reaction of DABCO with P was found to be fast and preliminary experiments suggest that further activation of P is required before the reduction of $CO_2$ occurs.

### 7.7. *Complexes with phosphorus donor ligands*

The synthesis of the "metalloligand" *fac*-$ReBr(CO)_3(\eta^1\text{-dmpm})_2$ has been reported and its use in the synthesis of heterodimetallic complexes has been demonstrated [61]. When *fac*-$ReBr(CO)_3(MeCN)_2$ was heated with a 3-fold excess of dmpm in toluene overnight, complete conversion to the title complex occurs. The heterodimetallic complexes formed were characterized by elemental analysis, $^1H$ and $^{31}P$ NMR spectroscopies and X-ray crystallography.

### 7.8. *Clusters*

A non-carbide-stabilized octahedral rhenium cluster has recently been synthesised [62]. It was obtained from the reaction between $[Re_4H_4(CO)_{12}]$ and $NEt_4BF_4$ in dichloromethane with or without acetone giving $[NEt_4][Re_6H_7(CO)_{18}]$. An X-ray crystal structure has been obtained; the Re-Re distances fall into three distinct groups and range from 3.051(1) to 3.263(1) Å and are consistent with all hydrides occupying face-bridging positions.

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