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Rhenium 1996

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1. Introduction

This review centers around the progress in the coordination chemistry of rhenium for the calendar year 1996. Its style is as in previous reviews [1], with sparse attention to the organometallic literature. It is based on a survey of Chemical Abstracts, volumes 123, 124 and 125. In addition, an independent search of pertinent journals has been conducted to ensure completeness.

2. Rhenium(VII)

2.1. Complexes with hydride ligands

The synthesis, fluxionality and structural characterization of $ReMo_3H_4(CO)_{12}^{3-}$ have been reported [2]. The hydrides, although not located directly, were inferred from spectroscopic studies to be present on each tetrahedral face. Variable temperature NMR spectroscopic studies showed a fluxional process for some of the carbonyl ligands, but not for the hydrides.

2.2. Complexes with oxygen donor ligands

The syntheses of $ReO_2(OTeF_5)_3$ from ReO_2F_3 and the *cis*-$ReO_2(OTeF_5)_4^-$ anion have been reported [3]. They have been characterized in solution by ^{19}F and ^{125}Te NMR spectroscopy and in the solid state by Raman spectroscopy. From NMR and vibrational spectroscopic studies, a trigonal bipyramidal arrangement has been inferred in which the oxygen atoms and an $OTeF_5$ group are in the equatorial plane. In addition, axial and equatorial $OTeF_5$ groups are fluxional and are consistent with intermolecular exchange by means of pseudo-rotation.

Phenyl-to-oxo migration in an electrophilic rhenium dioxo complex has been elucidated [4]. Oxygen atom transfer to $(HBpz_3)ReO(Ph)OTf$ gave the dioxo-phenyl complex $[(HBpz_3)ReO_2(Ph)]OTf$. The use of pyridine *N*-oxide facilitated the observation of the dioxo-phenyl complex at low temperatures. Using Me_2SO, the adduct

[(HBpz$_3$)ReO(Ph)(Me$_2$SO)]OTf was found to be stable at room temperature, albeit in rapid equilibrium with the dioxo complex as a result of Me$_2$S loss. For both cases the phenyl ligand migrates to the oxo group, generating a phenoxide complex. The half-life for the process [(HBpz$_3$)Re$_2$(OPh)]OTf→[(HBz$_3$)ReO(OPh)]OTf was found to be 4 min at 25 °C. This demonstrates the first example of the thermal migration of a ligand from a metal center to an oxo ligand. The kinetics of this migration have been measured and these, together with mechanistic studies, attest to the fact that this is a unimolecular rearrangement. The oxo ligands in the dioxo complex are implicated to be highly electrophilic, given that the complex reacts very rapidly with Me$_2$S, 1.7×10^5 M^{-1} s^{-1}, and this electrophilicity is suggested to be the salient feature instrumental in metal-to-oxo migration.

The oxygen-transfer reaction of methylrhenium oxides has been studied from a kinetic and thermodynamic perspective [5]. Methylrhenium trioxide, when reacted with hypophosphorus acid in an acidic aqueous medium, generates methylrhenium dioxide. The kinetic isotope effect was studied using D$_3$PO$_2$ in D$_2$O for H$_2$P(O)H, $k = 0.028$ l mol^{-1} s^{-1}; D$_2$P(O)OH, $k = 0.039$ l mol^{-1} s^{-1}. Methylrhenium dioxide reduces perchlorate and other inorganic oxoanions at a rate that is controlled by the first oxygen abstraction from perchlorate to give chlorate and a second-order rate constant (at pH 0 and 25 °C) of 7.3 l mol^{-1}. The reaction of V^{2+} and methylrhenium trioxide and the reduction of VO^{2+} with methylrhenium dioxide facilitated the determination of the free energy for methylrhenium dioxide/methylrhenium trioxide. The oxygen-atom transfer from donors occurs via nucleophilic attack on the electrophilic Re(V) center of methylrhenium dioxide through the intermediacy of a [methylrhenium dioxide:XO] adduct, X = Cl, Br or I.

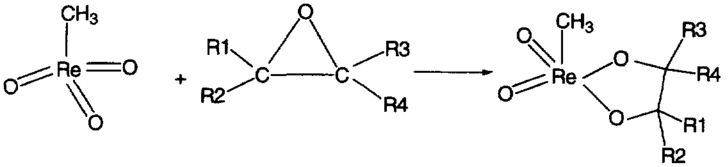
The structure of hydrated strontium perrhenate has been redetermined [6]. From crystal chemical analysis its composition obtained under identical crystallization conditions was found to be Sr(ReO$_4$)$_2$ · 2H$_2$O. The structure comprises two independent formula units and a disordered ReO$_4$ group. The Re atoms are surrounded by four oxygen atoms in a regular tetrahedron with Re–O distances in the range 1.689(11) to 1.747(9) Å.

A rare case of two-dimensional polytopism of crystalline (Cp*)ReO$_3$ has been reported [7]. The crystals comprise a polytopic packing in the *bc* plane of ordered polar chains of a three-legged piano stool; Cp*ReO$_3$ molecules stacked head-to-tail along the *a* axis. This polytopism is a generalized example of the more common polytopic, monodimensional stacking of 2D layers. It originates in Cp*ReO$_3$ because of the possibility of building a similar motif with both two-fold screw axes and the packing of neighboring chains of equal or different polarity.

The Raman and infrared spectra of gas phase Re$_2$O$_7$ have been reported [8]. Pure Re$_2$O$_7$ was prepared from rhenium wire while attempts at its preparation from rhenium powder and oxygen led to IR spectral contamination from a species containing an –OH linkage which was later identified as HReO$_4$. The experimental vibrational spectra have been compared with the calculated spectra for Re$_2$O$_7$ and Tc$_2$O$_7$. Results indicate a non-linear M–O–M bridge in the gas phase.

A more convenient method for the synthesis of rhenium complexes containing a chelated bis(diolate) ligand has been reported [9]. Five epoxides, namely

2,3-dimethylbut-2-ene epoxide, styrene epoxide, *cis*-cyclodecane epoxide, *cis*-stilbene oxide and *trans*-stilbene oxide, were used and all except the last react with trimethylrhenium trioxide to give the rhenium complexes in quantitative yield (**1**).

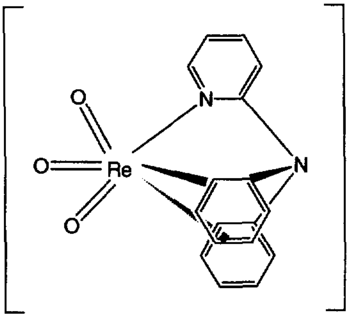


(1)

Solvolysis of Re_2O_7 with 1,4-dioxane in the presence of small quantities of water gave the products $Re_2O_6(OH)_2 \cdot$ 1,4-dioxane and $Re_2O_7(OH)_2 \cdot 2H_2O \cdot 2$(1,4-dioxane) [10]. X-ray crystallography reveals that the structure of the latter crystalline phase comprises a supramolecular arrangement of $Re_2O_7(OH_2)_2$ units with 1,4-dioxane molecules associated through O–H…O hydrogen bridges. One of the rhenium atoms is in a tetrahedral environment while the other has distorted octahedral coordination.

2.3. Complexes with nitrogen donor ligands

The ligand tri-2-pyridylamine (tripyam) was found to form a variety of stable complexes with metals, including rhenium [11]. The complex $[ReO_3(tripyam)]ReO_4$ (**2**) was synthesized and characterized by IR and ^1H NMR spectroscopies. Alkene dihydroxylation using two strained alkenes, norbornene and norbornadiene, was attempted but no glycolate complexes were isolated or detected by ^1H NMR spectroscopy. The complexes $[ReO(OCH_2CH_2O)_2(PPh_3)(\eta^3\text{-tripyam})]Cl$ and $ReCl_3$(tripyam) were also synthesized. All complexes are remarkably thermally resistant.



(2)

2.4. Clusters

The reactions of the cluster cation $[Pt_3\{ReO_3\}(\mu\text{-dppm})_3]^+$ with CO, $P(OMe)_3$, Hg and Tl(acac) have been studied [12]. In particular, the reaction with Hg produced the cation $[Pt_3\{ReO_3\}(\mu_3\text{-Hg})(\mu\text{-dppm})_3]^+$ which contains a distorted trigonal bipyramidal Pt_3ReHg metal core. The mean Pt–Re distance is 2.780 Å while the mean Re–O distance 1.687 Å. When the latter was oxidized in the presence of mercury and $NH_4[ReO_4]$, the bis(mercury) cluster $[Pt_3(\mu_3\text{-Hg})_2(\mu\text{-dppm})_3][ReO_4]_2$, whose crystal structure has been reported, was obtained. Its inner core comprises a slightly distorted trigonal bipyramid of metal atoms Pt_3Hg_2 where both faces of the Pt triangle are capped by Hg atoms in a μ_3 fashion. Repetition of the $[Pt_3(\mu_3\text{-Hg})_2(\mu\text{-dppm})_3][ReO_4]_2$ unit gives a cluster polymer.

3. Rhenium(VI)

An improved synthesis for the rhenium complex $[Re(N^tBu)_2(\mu\text{-}N^tBu)_2]$ involving Na/Hg reduction of $Re(N^tBu)_3I$ and its reaction with electrophiles has been reported [13]. In particular its reaction with trifluoromethanesulfonic acid gave the crystalline product $[(^tBuN)(^tBuHN)Re(\mu\text{-}N^tBu)_2Re(^tBuN)_2][CF_3SO_3]$ which was analyzed by X-ray crystallography; the geometry about the two rheniums differs significantly. The terminal Re–N(^{t}Bu) distances are short but unequal, 1.719(7) and 1.773(7) Å. The bridging Re–N distances reveal an unsymmetric bridge. The interaction of the $[Re(N^tBu)_2(\mu\text{-}N^tBu)_2]$ with silver triflate gave a silver complex $\{[(^tBuN)Re(\mu\text{-}N^tBu)]_2(\mu\text{-}N^tBu)_2Ag(\mu\text{-}O_3SCF_3)\}_2$ in which N^tBu groups bridge rhenium and silver atoms. A copper complex has also been obtained from the reaction of the starting rhenium complex with $Cu(O_3SCF_3)\cdot 0.5C_6H_6$.

The substitution kinetics of the aqua ligand in $[Re(NO)(H_2O)(CN)_4]^{2-}$ by monodentate nucleophiles including SCN^-, N_3^- and thiourea have been studied [14]. These studies revealed that both the aqua and hydroxo ligands are substituted by SCN^- with rate constants of $3.6(1)\times 10^{-3}$ and $1.57(5)\times 10^{-3}\,M^{-1}\,s^{-1}$, respectively. One of the products of these substitution reactions was isolated and its crystal structure was obtained. The structure of the product $(AsPh_4)_2[Re(NO)(SC(NH_2)_2)(CN)_4]$ reveals an anion with a distorted octahedral geometry, interestingly the thiourea ligand is *cis* with respect to the nitrosyl group. The Re–N(O) distance is 1.736(11) Å while the Re–S distance is 2.503(4) Å.

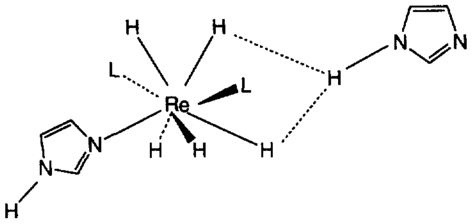
4. Rhenium(V)

4.1. Complexes with hydride ligands

The reactions of $ReH_5(Cyttp)$, $Cytpp = PhP(CH_2CH_2CH_2PCy_2)_2$, with heterocumulenes [$X=C=S$, $X=S$, $p\text{-}O_2NC_6H_4N$ and $EtOC(O)N$] MeI and $[C_7H_7]BF_4$ in the presence of several ligands have been investigated [15]. The solid state structure of the title complex was also determined by X-ray crystallography. It adopts a classical triangulated dodecahedral structure with three phosphorus atoms and a hydrogen atom occupying the four five-neighbor B sites, the remaining hydrogen atoms occupy four four-neighbor A sites in the polyhedron. Protonation by $HSbF_6$ gave $[ReH_4(\eta^2\text{-}H_2)(Cyttp)]SbF_6$ which displays a non-classical hydride triangulated structure in the solid. Its X-ray structure has been determined, Re–H distances were found to be in the range 1.45(3) to 1.73(4) Å. The complex $ReH_5(Cyttp)$ was found to insert one molecule of heterocumulenes generating tetrahydride products $ReH_4(SCH{=}X)(Cytpp)$. Reaction with MeI cleaves an Re–H bond giving $ReH_4I(Cytpp)$ while a hydride abstraction substitution reaction with $[C_7H_7]BF_4$ in the presence of L gave $[ReH_4L(Cytpp)]BF_4$, L = MeCN, ^tBuCN, CyCN and $P(OMMe)_3$. All tetrahydride species are stable classical polyhydrides and apparently adopt triangulated dodecahedral structure with hydrogens occupying the A sites while the other donor atoms occupy the B sites. These complexes were characterized by ^1H and $^{31}P\{^1H\}$ NMR and IR spectroscopy.

A series of eight-coordinate metal polyhydrides was prepared and shown to be fluxional by NMR spectroscopy [16]. They were obtained from the reactions of $[ReH_7(PPh_3)_2]$ with the ligand L = 4-carbomethoxypyridine, pyridine, 4-picoline and 4-(dimethylamino)pyridine and found to be rigid on the NMR timescale at low temperature, but two coalescence processes were observed upon warming. The low temperature spectrum has been assigned by ROESY NMR studies and a turnstile motion of three hydrides has been proposed while a pseudo-rotation of the coordination dodecahedron for the high temperature process has been proposed. Exchange barriers for the process have been measured and are dependent on the properties of the ligand. Quantum exchange has not been observed.

Intermolecular N–H...H–Re hydrogen bonding has been explored [17]. A strategy in which the donor and acceptor are covalently linked in such a way that intramolecular interactions are not favored was sought. The reaction of $[ReH_7(PPh_3)_2]$ with imidazole in benzene at 20 °C for 20 h followed by recrystallization from benzenes–hexanes gave a yellow product which was obtained as a mixture of powder and single crystals. Spectral data of the powdered product suggested the structure $[ReH_5(PPh_3)_2(ImH)]$, X-ray diffraction of a single crystal showed that the crystals are $[ReH_5(PPh_3)_2(ImH)]\cdot 0.5ImH\cdot 1.5C_6H_6$. The packing diagram shows that the N–H of one coordinated imidazole comes very close to two of the hydride ligands of a neighboring molecule in the lattice, but that the H...H distances are 3.55(7) and 2.60(8) Å and can be regarded as weak interactions. In addition to the coordinated imidazole, 0.5 molecules of free imidazole were found in the cell unit. One nitrogen atom of this imidazole was found to be close in distance to two of the hydride ligands at a distance suitable for a H...H interaction (**3**). IR spectroscopy of the crystal reveals a broad band at 3154 cm^{-1} shifted by 302 cm^{-1} to a lower wavenumber, relative to a sharp band which is observed for the $\upsilon(NH)$ of a dilute CH_2Cl_2 solution of pure imidazole, and is indicative of dihydrogen bonding. The overall strength of the H...H interaction was estimated to be 22 kJ mol^{-1} based on the IR shift seen in the crystal.



(3)

An integrated molecular orbital molecular mechanics (IMOMM) method has been used to obtain optimized geometries for rhenium hydrides [18]. The complexes $[ReH_5(PPh^iPr_2)_2(SiHPh_2)_2]$ and $[ReH_5(PCyp_3)_2(SiHPh_2)_2]$ have been studied and compared with experimentally obtained diffraction data.

4.2. Complexes with oxygen donor ligands

The reactivity of $[ReO(CH_2SiMe_3)_3(PMe_3)]$ with the cyanide, bipyridine and trimethylmethylenephosphorane has been studied [19]. The products $[ReO(CH_2SiMe_3)_3(CN)]$, $[ReO(CH_2SiMe_3)_3(bpy)]$ and $[ReO(CH_2PMe_3)(CH_2SiMe_3)_3]$ were characterized by IR and ^1H and ^{13}C NMR spectroscopies.

4.3. Complexes with sulfur donor ligands

The stepwise complex formation of rhenium(V) with 3-methyl-4-phenyl-1,2,4-triazole-5-thiol (3-Met-4-PTT) in 6 M HCl at various temperatures has been studied potentiometrically [20]. Thermodynamic functions have been determined.

4.4. Complexes with oxygen and sulfur donor ligands

The chiral dithiolato complex $[ReO\{(S)(SCH_2)C_5Me_4\}(C_5Me_5)$ has been synthesized recently [21]. Introduction of hydrogen gas into solutions containing either $[ReCl_4(C_5Me_5)]$ or $[Re(O)Cl_2(C_5Me_5)]$ in chloroform–pyridine (20:1) at room temperature gave the title compound as a red product and a violet dinuclear product $[Re_2S_6(C_5Me_5)]$ which could be isolated as the main components of the reaction mixture. A single crystal structure analysis of the mononuclear complex reveals that rhenium is in a distorted octahedral environment with a planar Cp* ligand; the oxo ligand and two sulfur atoms of the dithiolato ligand are in a three-legged piano stool arrangement. The average Re–S bond length is 2.268 Å.

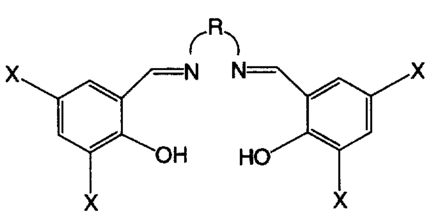
4.5. Complexes with oxygen and nitrogen donor ligands

Rhenium(V) oxo alkyl triflate complexes $(HBpz_3)ReO(R)OTf$, R = Me, Et and ^{n}Bu were found to be oxidized by oxygen atom donors pyridine *N*-oxide and Me_2SO, generating $(HBpz_3)ReO_3$ and the corresponding aldehyde [22]. The reactions were found not to proceed through the intermediacy of the alkoxides; the data suggest that oxidation involves the displacement of the triflate ligand with an oxygen atom to generate an Re(VII) dioxo alkyl cation. Subsequent transfer of an α-hydrogen from the alkyl group to an oxo group generates a carbene which is trapped to form an ylide complex which have been observed by NMR at low temperatures.

The synthesis and characterization of monomeric and dimeric(V) complexes in which the tetrakis(pyrazolyl)borate $B(pz)_3$ ligand demonstrates differing coordination modes have been reported [23]. Starting from the compound $[ReO\{\eta^3\text{-}B(pz)_3]^-\}(OMe)_2]$ and with judicious choice of the protic substrate allows modulation of the denticity of the tetrakis(pyrazolyl)borate ligand. Complexes where this ligand is didentate were obtained through the use of monoanionic protic substances, whereas potentially dianionic protic substances generated complexes where this ligand is tridentate. Characterization was achieved by IR and ^1H NMR spectroscopies and X-ray crystallography; NMR spectroscopy proved to be invaluable in assessing the coordination geometry about the metal center, in addition to the denticity of the $B(pz)_3$ ligand.

The preparation of several *trans*-$[ReO_2L_4]^+$ salts with ImH and its 1-methyl (1-MeImh), 2-methyl (2-MeImH), 4-methyl [4(5)-MeImH] and 1,2-dimethyl (1,2-Me_2Im) methylated derivatives has been carried out [24]. Stable salts were isolated for $X^- = I^-$ and L = ImH, 1-MeIm and 1,2-Me_2Im and $X^- = [B(C_6H_5)_4]^-$, L = 1-MeIm, 2-MeIm and 5-MeImH. These complexes were characterized by IR, Raman, ^1H and ^{13}C NMR and UV–vis spectroscopies. X-ray crystallography studies were carried out. Protonation studies in methanol and water were conducted and the $[ReO(OH)(1,2\text{-}Me_2Im)_4](I_3)_{0.5}(ReO_4)_{1.5}$ crystal revealed octahedral dications with a *trans* disposition for the oxo and hydroxo ligands and the Re–N bonds displaced to the Re–OH side due to the steric effect of the Re–oxo bond.

Studies on the reactions of $[NBu_4][ReOCl_4]$ with potentially terdentate bis(salicylidene)amine salen$_2$en ligands (**4**) have been studied [25].



	a	b	c	d
X	^tBu	Cl	H	^tBu
R	CH_2CH_2	CH_2	$C(CH_3)_2$	CH_2

(**4**)

The dimetallic complex $[NBu_4]_2[Re_2O_2Cl_6(L)]$ was formed provided the H_2L ligand contained two CH_2 units bridging the imino groups of the salen$_2$en fragments while, when three carbon atoms comprise the bridge, mononuclear compounds of general formula [ReOCl(L)] were obtained. Interestingly, the Schiff base ligands do not coordinate in a symmetric fashion in the mononuclear compounds, instead there is a C_s symmetry in which the ligand coordinates in all equatorial positions, and complexes of C_1 symmetry in which the two *N,O* units coordinate asymmetrically. The ^1H NMR spectroscopic data support this asymmetric arrangement and were assigned by means of $^1H,^1H$ NMR-COSY experiments. These complexes were also characterized by IR spectroscopy.

An EHMO study has been carried out in order to assess whether a didentate ligand might favor an unusual *cis* isomer in d^2 octahedral transition metal complexes [26]. The calculations have been carried out on model experimental complexes including $ReO_2(HN{=}CHC{=}NH)(NH_3)_2^+$ and reveal that a small bite angle, σ donor and π acceptor properties might reverse the usual stability of the *cis* and *trans* isomers. In a related paper [27], gradient-corrected density functional theory calculations have been carried out. Using only σ donors in $ReO_2(NH_3)_4^+$ the *trans* isomer is the most stable. Model complexes containing a chelating didentate ligand, e.g. $OsO_2(OCH_2CH_2O)(NH_3)_2$ and $ReO_2(HN{=}CHC{=}NH)(NH_3)_2^+$, have shown that in the case of the former, the *trans* isomer is more stable than the *cis* isomer, whereas in the latter, the *cis* isomer is favored by 29 kcal mol^{-1} and has been traced to the geometric and electronic properties of the didentate ligand. When a chelating didentate with weaker π acceptor abilities is used, i.e. $ReO_2(bpy)(NH_3)_2^+$, the *cis* isomer is favored by only 7.5 kcal mol^{-1}.

A study of metal complexes of naturally occurring chelators has been carried out and bis(ligand) complexes of rhenium and technetium obtained [28]. Complexes of the formula $MOXL_2$, M = Re, Tc, X = Br, Cl and HL = 2-(2′-hydroxyphenyl)-2-oxazoline (Hoz), 2-(2′-hydroxy-3′-methylphenyl)-2-oxazoline (Hmoz), 2-(2′-hydroxyphenyl)-2-thiazoline (Hthoz) and 2-(2′-hydroxyphenyl)-2-benzoxazoline (Hhbo) have been obtained. An X-ray crystal structure for the $ReOBr(oz)_2$ derivative has been obtained and reveals a distorted octahedral geometry in which the halide ligand is bound in a *cis* fashion and the phenolate oxygen atom from the ligand in a *trans* fashion to the metal–oxo bond. The Re–Br length is 2.5804(7) Å, the Re–O distances are 1.681(4), 1.988(4) and 2.013(4) Å while the Re–N distances are is 2.098(5) and 2.045(5) Å.

4.6. Complexes with oxygen and phosphorus donor ligands

A detailed study of the reactivity of the potentially didentate hybrid ligand (*o*-hydroxyphenyl)diphenylphosphine (POH) with pentavalent oxo–rhenium precursors has been carried out [29]. The monosubstituted derivatives $[ReOCl_3(PO)]^-$ and $[ReOCl_2(PO)(PPh_3)]$ were isolated and found to be key intermediates in the further synthesis of bis-substituted compounds including a rare example of an anionic dioxo–Re(V) complex $[ReO_2(PO)_2][A]$, A = NBu_4, $AsPh_4$ and neutral monooxo $[ReOX(PO)_2]$, X = Cl, Br and I, and [ReOX(PO)(PNH)], PNH = (*o*-amidophenyl)-

diphenylphosphine, X = Cl, Br and I. In the monosubstituted complexes the P,O-donors of the didentate ligand span equatorial and apical positions *trans* to the Re=O linkage in a distorted octahedral arrangement. In the bis-substituted monooxo compounds, the second POH ligand is coordinated on the equatorial plane and is almost orthogonally oriented with respect to the first one and the two phosphorus atoms are in a *cis*-(P,P) orientation. These complexes were characterized by IR, MS and $^1H/^{31}P\{^1H\}$ NMR spectroscopy and X-ray crystallography. Detailed IR analysis of these complexes has facilitated the distinction between symmetrical and asymmetrical bis-substituted complexes.

The synthesis and characterization of rhenium complexes derived from novel water-soluble (hydroxymethyl)phosphines have been documented [30]. Monophosphine $P(CH_2OH)_3$ and bisphosphines $(HOH_2C)PC_6H_4P(CH_2OH)_2$ and $(HOH_2C)PCH_2CH_2P(CH_2OH)_2$ were obtained by the addition of formaldehyde to the appropriate P–H compounds in the presence of a platinum catalyst. The reactions of these phosphines with $ReO_2I(PPh_3)_2$ in biphasic media or with $[ReO_2(NC_6H_5)_4]Cl$ in aqueous media gave the water-soluble $[ReO_2\{P(CH_2OH)_3\}_4]^+$, $[ReO_2\{(HOH_2C)PC_6H_4P(CH_2OH)_2\}_2]^+$, and $[ReO_2\{(HOH_2C)PCH_2CH_2P(CH_2OH)_2\}_2]^+$ in near quantitative yield. These complexes have been characterized by X-ray crystallography.

4.7. Complexes with nitrogen donor ligands

The synthesis and characterization of Re(V) organoimido complexes have been described [31]. When $[ReCl_3(NAr)(PPh_3)_2]$, NAr = NC_6H_4Me-4, $NC_6H_3Me_2$-2,6, was reacted with ^tBuNC in methanol the complexes $[ReCl(NAr)(OMe)(^tBuNC)_2(PPh_3)][BPh_4]$ were obtained. X-ray crystallography for the NC_6H_4Me-4 derivative revealed that the rhenium atom is in a distorted octahedral environment with a *cis* disposition of the isocyanide ligands while the phosphine and chloride ligands are *trans*. The Re–N distance is 1.739(3) Å. Reactions between the tolylimido complex $[ReCl_3(NC_6H_4Me\text{-}4)(PPh_3)_2]$ and aroylhydrazones Ar(O)CHNHNCRR′, Ar = Ph, R = R′ = Me; Ar = 4-ClC_6H_4, R = H, R′ = Ph in a 1:1 toluene/ethanol mixture under reflux gave the complexes $[ReCl_2(NC_6H_4Me\text{-}4)(PPh_3)]$ {Ar(O)CNNCRR′-O,N}, Ar = Ph, R = R′ = Me or Ar = 4-ClC_6H_4, R = H, R′ = Ph. X-ray crystallography for the latter indicates a distorted octahedral geometry in which the oxygen and nitrogen atoms of the chelated hydrazone (1 −) ligand are *cis*.

A report describing the synthesis and spectroscopic characterization of the first heterodimetallic complex formed as a result of incomplete nitrogen atom transfer between nitridorhenium(V) and chlorochromium(III) porphyrins has appeared [32]. Electronic spectral changes during the course of the reaction between an equimolar mixture of NRe(OEP) and ClCr(TPP) in DCE have been monitored. The intensity of the Soret bands for the two reactants diminished as the intensity of a new band at 400 nm increased. Isosbestic points were observed at 401, 419 and 429 nm indicating the absence of any long-lived intermediates. A Soret band for the expected product of complete nitrogen transfer, namely NCr(TPP), was not observed. Vibrational spectroscopy and FAB MS were also used in the characterization. From a kinetic analysis complex, formation was proposed to occur via the following sequence:

$$\mathrm{XCr(POR)} \rightleftharpoons [\mathrm{Cr(POR)}]^+ + \mathrm{X}^- \tag{1}$$

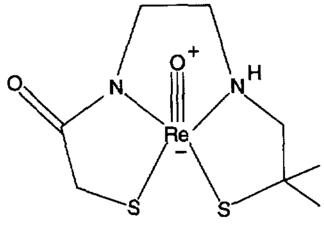
$$\mathrm{NRE(POR)} + [\mathrm{Cr(POR)}]^+ \rightleftharpoons [\mathrm{(POR)Re{\equiv}N{\rightarrow}Cr(POR)}]^+ \tag{2}$$

Rhenium imido and amido complexes of hydrotris(pyrazolyl)borate (Tp) have been synthesised [33]. Reactions of $\mathrm{TpRe(O)X_2}$ with amines resulted in either replacement of the oxo ligand to give imido complexes or substitution of a chloride ligand to form oxo–amido compounds. Reaction involving *p*-toluidine gave the imido complexes $\mathrm{TpRe(NTol)X_2}$ on refluxing in toluene, whereas in reactions conducted at room temperature the oxo–amido complex TpReO(NHTol)Cl and the amido complex were formed. The amide complexes reveal restricted rotation about the Re–N bond while the imido complexes were found to be photochemically active.

4.8. Complexes with nitrogen and sulfur donor ligands

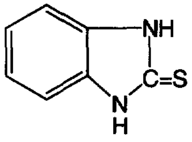
A detailed study of the role of the ligand $\mathrm{H_2NNMeC(S)SMe}$ ($\mathrm{H_2L}$) in the formation of the metal–nitrido core in rhenium or technetium complexes has been carried out [34]. In particular, the reaction of $[\mathrm{ReOCl_3(PPH_3)_2}]$ with the ligand under mild conditions gave the complex $[\mathrm{ReO(HL)_2}]\mathrm{Cl}$ which was subsequently transformed to the corresponding nitrido complexes under reflux in the presence of HCl and $\mathrm{PPh_3}$. The crystal structure of this complex shows a distorted square-pyramidal geometry in which the oxygen atom is in an apical position. The chloride ion is bound to the NH groups by means of hydrogen bonds. The Re–O distance is 1.706(5) while the Re–S distances are 2.328(2) are 2.327(2) Å and the Re–N distances are 1.943(6) and 1.936(6) Å.

The first example of a rhenium complex bearing an asymmetric monoamine dithiol $\mathrm{N_2S_2}$ ligand has been prepared [35]. The complex oxo(1,1-dimethyl-1,8-dimercapto-3,6-diazaoctan-7-onatoN^3,N^6,S^1,S^8)rhenium(V) (**5**) was examined by X-ray crystallography and reveals that the rhenium atom sits above [0.747(5) Å] a square pyramid defined by the $\mathrm{N_2S_2}$ ligand atoms. The Re=O bond distance, at 1.681(5) Å, is long and was postulated to be brought about by competitive π-bonding between the deprotonated amidic nitrogen atom and the rhenium atom, as is evident from the short Re–N distance of 1.997(6) Å as compared with the distance from the amine nitrogen of 2.151(4) Å.



(**5**)

A new series of rhenium complexes has been obtained from the reaction of 2-benzimidazolethione (**6**) with $H_2[ReOCl_5]$ [36].



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Depending on the metal:ligand molar ratio and HCl concentration, either mononuclear such as $[ReOLCl_3(OH_2)]$, $[ReOL_2(OH_2)_3]Cl_3$, and $[ReOLCl(OH_2)_3]Cl_2$ or dinuclear complexes such as $[Re_2O_3L_2Cl_4]\cdot 2H_2O$ and $[Re_2O_2L_3Cl_6]\cdot 2H_2O$ were obtained. These complexes have been characterized by IR, electronic spectroscopies, magnetic measurements and molar conductivity.

The reaction of diamines with several isothiocyanates leading to the formation of novel symmetrical dithiourea N_2S_2 ligands has been explored [37]. These ligands were then used to prepare novel rhenium oxo complexes via ligand exchange reactions with Re(V) precursors. The structure of ([1-phenyl-3-(3-phenylthioureido)]thioureato)oxorhenium was obtained by X-ray crystallography. Its structure comprises a pseudo-square-pyramidal geometry with an N_2S_2 basal and an apical donor set. Both coordinated nitrogen atoms were deprotonated, remarkably one of the uncoordinated nitrogen atoms of the thiourea ligand was deprotonated in spite of the fact that it is three bonds away from the metal atom. The Re–N distances are 2.008(7) and 1.942(7) Å while the Re–S distances are 2.355(2) and 2.343(3) Å, the Re–O distance is 1.677(6) Å. NMR spectroscopic studies in methanol showed that the neutral complex with a deprotonated uncoordinated nitrogen atom was favored in neutral and basic solutions while under acidic conditions a cationic form with both uncoordinated N atoms protonated was favored.

The reaction of the rhenium hydride $[ReH_5(PMe_2Ph)_3]$ with 2-mercaptopyridine (pySH) in the presence of HBF_4 gave the complexes $[ReH(pyS)(PMe_2Ph)_4]BF_4$ and $[ReHF(pyS)_2(PMe_2Ph)_2]BF_4$ [38]. Their structures have been determined by X-ray crystallography. In the former, rhenium possesses a distorted pentagonal bipyramidal geometry with an Re–N distance of 2.196(5) Å and Re–S bond length of 2.513(2) Å. In the latter, rhenium is in a distorted pentagonal bipyramidal environment with Re–N distances of 2.152(6) Å and 2.168(5) Å, while the Re–S distance is 2.544(2) Å and the Re–F length is 1.701(4) Å.

Rhenium(V) and technetium(V) complexes with S-substituted diamide-dithiol ligands have been synthesized [39]. They have been characterized by IR and NMR spectroscopies and X-ray crystallography.

5. Rhenium(IV)

5.1. Complexes with halide ligands

A crystallographic and computational characterization of $[Re_2Cl_9]^-$ and $[Re_2Cl_9]^{2-}$ has been carried out [40]. On going from the monoanion to the dianion a contraction of the Re–Re distance from 2.704(1) to 2.473(4) Å is observed, and the metal–metal bond order decreases from 3.0 to 2.5 Å. Using SCF–Xα–SW molecular orbital calculations it has been determined that, although $[Re_2Cl_9]^-$ possesses a $\{d^3d^3\}$ configuration, it is more realistic to regard the Re–Re bond as being single in character. The observed contraction in the Re–Re distance in the dianion is due to the radial expansion of the Re t_{2g} orbitals in the lower oxidation state, thereby bringing about a more effective overlap between neighboring metal centers and diminishing their electrostatic repulsion. This leads to stronger σ- and δ-bonding. Transition energies have been computed for both anions and compared with electronic spectra. Both halide to metal charge transfer, XMCT and σ–σ* transitions contribute to absorption in these complexes.

The complex *trans*-tetrachlorobis(triphenylphosphine)rhenium(IV) has been partially oxidized (14–25%) by aerial oxidation resulting in the formation of $[ReCl_4(C_{18}H_{15}P)_2]_{0.86}[ReCl_3O(C_{18}H_{15}P)_2]_{0.14}$ and subject to X-ray structural analysis [41]. There are 1.5 molecules in the asymmetric unit and one molecule sits at a center of symmetry. The independent molecules differ in the orientation of the triphenylphosphine groups with respect to the $ReCl_4$ plane. The average Re–Cl distances are 2.322 Å and Re–P lengths are 2.571 Å for the Re(IV) complex, while for the Re(V) molecule the Re–Cl distances are 2.390 Å for the monoclinic form and 2.360 Å for the ordered molecule. The Re–O distance is 1.73(2) Å.

The X-ray crystal structures of several complexes containing the $Re^{IV}Cl_4$ unit have been obtained [42]. In particular, complexes of the type $ReCl_4L_2$ including *cis*-$(HN{=}CMeNHPh)_2ReCl_4$, *cis*-$(HN{=}CMeNHPh)_2ReCl_4{\cdot}2MeCN$, *cis*-fw[$HN{=}CMeNH(p\text{-}C_6H_4Me)_2ReCl_4$], *cis*-$(thf)_2ReCl_4$ and *trans*-$(Me_2PhP)_2ReCl_4$ were obtained. The Re–Cl distances in these complexes have been analyzed and no *trans* effect of the donor atom on the chlorine atoms was seen either in these complexes or in examples of complexes containing a chelate ligand from the literature.

5.2. Complexes with hydride ligands

A note has appeared describing examples in which mixed phosphine/arsine ligands have been used to stabilize rhenium polyhydrides [43]. The first rhenium polyhydride, $Re_2H_8(arphos)_2$ (arphos = $Ph_2PCH_2CH_2AsPh_2$) was prepared by reacting $Re_2Cl_4(\mu\text{-arphos})_2$ with $LiAlH_4$ in THF followed by hydrolysis of the reaction and workup. It may also be prepared by refluxing a mixture of mononuclear $ReOCl_3(arphos)$ with $NaBH_4$ in ethanol. It has been characterized by ^1H and ^{31}P NMR spectroscopy and CV studies. Attempts to obtain single crystals were unsuccessful. In addition, another hydride, $ReH_7(arphos)$, was obtained in moderate yield from the reaction of $ReCl_3$(arphos) with $NaBH_4$ in ethanol and has been characterized by ^1H and ^{31}P NMR spectroscopy and CV studies.

5.3. Complexes with oxygen donor ligands

The structure of $[ReClO(C_{18}H_{14}OP)_2]$ has been elucidated [44]. It contains severely distorted octahedra with a *cis,cis,cis* configuration. Steric hindrance between the phosphine groups results in a departure from octahedral geometry. One of the phenolate oxygen atoms is *trans* to the Re=O bond. The Re=O distance is 1.686(4) Å, the Re–Cl length is 2.394(2) Å, while the Re–P distances are 2.433(2) and 2.451(2) Å. The Re–O(phenolate) distances are 2.003(4) and 1.987(4) Å.

The structures and properties of the bis(μ-oxo)dirhenium(III,IV) and dirhenium(IV) complexes $[Re_2(\mu\text{-}O)_2(L)_2](PF_6)_n$, L = tris(2-pyridylmethyl)amine (tpa), [(6-methyl-2-pyridyl)methyl]bis(2-pyridylmethyl)amine (Metpa) and bis[(6-methyl-2-pyridyl)methyl](2-pyridylmethyl)amine (Me_2tpa) have been reported [45]. X-ray crystallographic determinations were made for L = Metpa, $n = 3$; L = Metpa, $n = 4$; and L = Me_2tpa, $n = 4$ and represent the first structural determinations of: (i) a bis(μ-oxo)-$Re^{III}Re^{IV}$ complex and (ii) a pair of $Re^{III}Re^{IV}$ and Re_2^{IV} complexes. Each complex displays a centrosymmetric structure indicative of the fact that the mixed-valent complex is of a structurally delocalized type. The increase in Re–Re bond length [2.368(1) and 2.383(1) to 2.426(1) Å] on going from the (IV,IV) state to the (III,IV) oxidation states is concordant with a decrease in bond order from 3 to 2.5. Cyclic voltammetry studies have been carried out; two reversible one-electron redox waves at 0.77 V (III,III)/(III,IV) and at −0.09 V (III,IV)(IV,IV) vs. Ag/AgCl in acetonitrile.

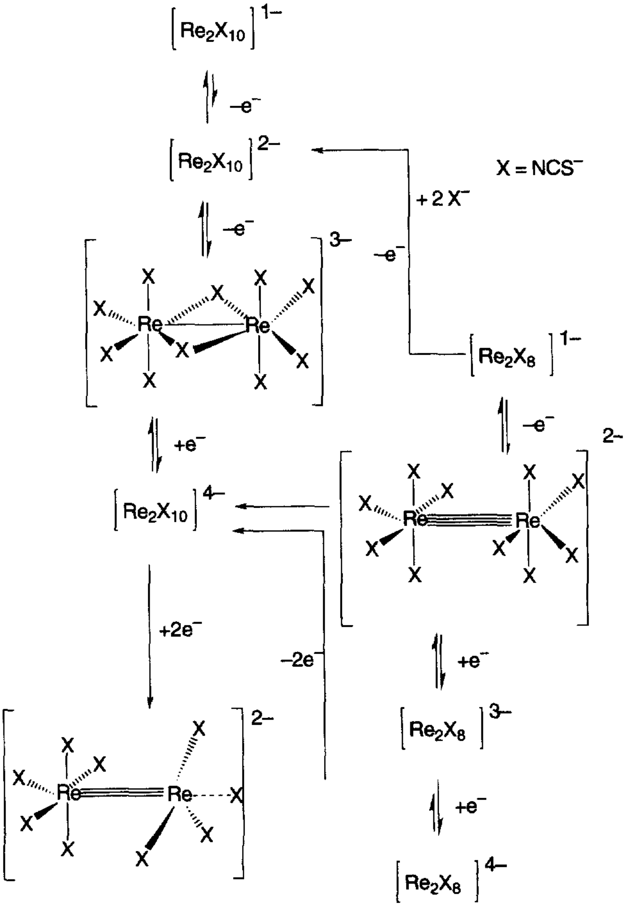
5.4. Complexes with sulfur donor ligands

A single crystal of the tetrahedral cluster compound $Re_4S_4Te_4$ was grown as a result of the high temperature reaction of stoichiometric amounts of rhenium and sulfur in molten tellurium [46]. Using X-ray diffraction its structure has been elucidated. The structure comprises tetrahedral Re_4 clusters with sulfur atoms capping each of the four faces in a triply bridging fashion; tellurium atoms bridge the $[Re_4S_4]$ units to form a three-dimensional structure. The Re–Re distances are 2.785(3) Å, while the Re–S distances are 2.337(10) Å.

The reaction of $[Re_3S_7Br_6]Br$ with an aqueous solution of KCN has been explored. This has resulted in the production of a cuboidal species $Cs_2K_2[Re_4S_4(CN)_{12}]\cdot 2H_2O$ in 78% yield [47]. It has been characterized by X-ray crystallography; the central core comprises a regular tetrahedron of four rhenium atoms with a mean Re–Re distance of 2.746(6) Å, while the mean Re–S distances are 2.346(8) Å.

5.5. Complexes with nitrogen donor ligands

The redox behavior of the edge-shared bioctahedral (ESBO) complex $[Re_2(NCS)_{10}]^{3-}$ has been investigated [48]. This complex displays extensive redox chemistry in non-aqueous solvents in which a series of sequential one-electron processes was observed in addition to an overall two-electron process. Each of these processes was studied spectroelectrochemically and the measurements obtained indicate remarkable structural stability in the oxidized and reduced products which retain the ESBO structure. More redox changes generate more reactive species in which structural rearrangement leads to an unsupported metal–metal bonded complex in the case of $[Re_2(NCS)_{10}]^{4-}$ (7).



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6. Rhenium(III)

6.1. Complexes with halide ligands

Electronic absorption spectra have been obtained in pulsed magnetic fields for $(Bu_4N)[Re_2Cl_8]$ at 3.8 K [49]. Using a pulse duration of 10 ms and field strengths up to 50 T, spectra were measured in the 530–600 nm and 435–500 nm band regions. No Zeeman splitting was observed; the bands have been tentatively assigned as being due to transitions to two ^1E_g excited states [$^1(\pi,\delta^*)$ and $^1(\delta^*,\pi^*)$] and to two formally doubly excited states $^1A_{1g}$ [$^1(\delta\delta,\delta^*\delta^*$] and ^1E_u [$^1(\pi,\delta,\delta^*\delta^*)$].

6.2. Complexes with hydride ligands

The reactions of $ReH_7(dppe)$ with organic ligands including pyridine-2-carboxylic acid, 1-isoquinolinecarboxylic acid, 2-hydroxy-6-methyl-pyridine and 2-mercaptoquinoline have been studied [50]. Complexes of the type $ReH(L)_2(dppe)$ have been obtained as highly orange–purple complexes and are soluble in a range of solvents. They were characterized by IR, conductivity measurements and CV; ^1H and ^{31}P NMR spectroscopy reveals that these complexes are stereochemically rigid at room temperature. X-ray crystallography studies on the 2-hydroxy-6-methyl-pyridine and 2-mercaptoquinoline derivatives have been carried out.

6.3. Complexes with sulfur donor ligands

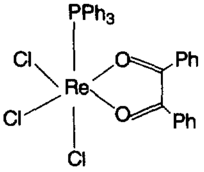
A dimensional reduction approach has been used to deconstruct extended solid frameworks [51]. In particular, the phases $[Re_6Q_6Cl_2]$, Q=S or Se, have been deconstructed through the stoichiometric solid state reactions in which TlCl supplements the core with additional ligands, thereby producing less connected frameworks, e.g. two-dimensional $[Re_6Se_8Cl_3]^{1-}$ sheets, one-dimensional $[ReQ_8Cl_4]^{2-}$ chains and isolated $[Re_6Q_8Cl_6]^{4-}$ clusters. Using cesium halide as a reduction agent generated unprecedented molecular clusters in water-soluble form as phases $Cs_5Re_6S_8X_7$ (X= Cl, Br), $Cs_5Re_6S_8I_8$ and $Cs_4Re_6S_8I_6$.

Extended X-ray absorption studies have been carried out at the rhenium L_{III}-edge in order to gain information on local coordination around rhenium and X-ray absorption studies at the sulfur K-edge to glean information regarding the oxidation state of sulfur in Re_2S_7 [52]. Results from this study indicate that the amorphous compound contains Re_4 rhomboidal clusters as the basic structural block with rhenium in oxidation state 3.5 and sulfur in oxidation state 1.

6.4. Complexes with nitrogen donor ligands

Access to a variety of Re^{III} and Re^{II} polypyridyl complexes from $Re^{III}(benzil)(PPh_3)Cl_3$ (**8**) has been demonstrated [53]. The complex *cis*-$[Re^{III}(bpy)_2Cl_2]^+$ has proved to be of utility in the synthesis of complexes of the type $[Re(bpy)_2L_x]^{n+}$ which are six- or seven-coordinate Re^{III} or octahedral Re^{II} or Re^I complexes (**9**). The redox properties of these complexes have been studied and are discussed with respect to the observed π-acidity of the polypyridyl ligands.

As part of an ongoing study of paramagnetic rhenium(III) complexes, monomers of the type $ReCl_3L_n(PPh_3)_{3-n}$, $n=1$, 2 and 3, L=py, 3-picoline, 4-picoline and



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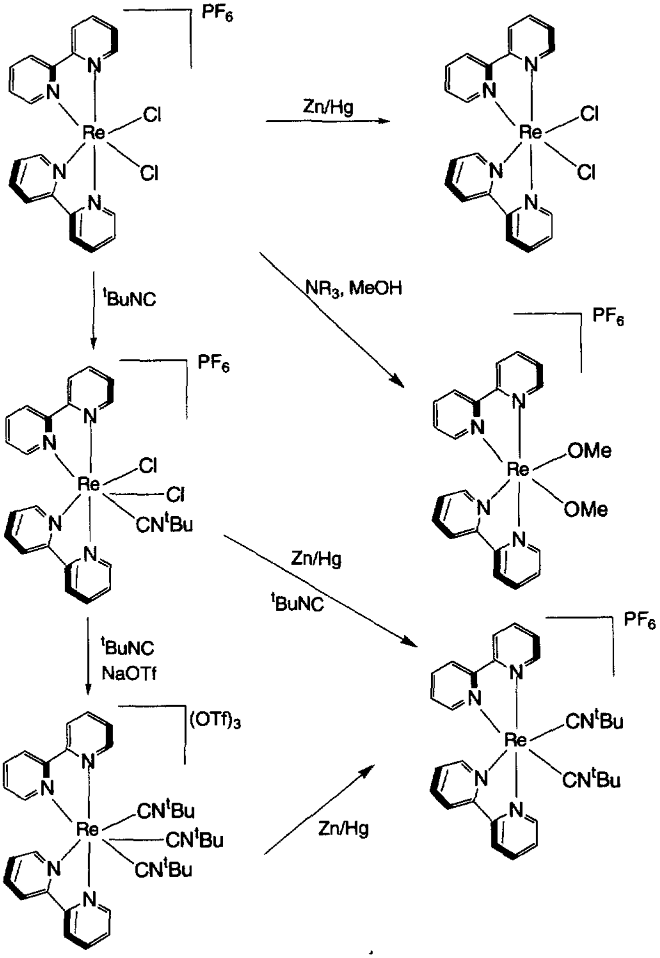

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1-methylimidazole, have been synthesized and characterized by ^1H NMR and IR spectroscopies [54]. Using methylated pyridines the ^1H NMR signals of these paramagnetic compounds were assigned. For complexes of the type $ReCl_3L_2(PPh_3)$, the 3-picoline, pyridine and 1-methylimidazole adopt a *mer,cis* geometry as seen from

X-ray crystallographic studies. This geometry also exists in solution for these complexes as inferred from ^1H NMR data. The Re–Cl distances *trans* to a Re–N bond (2.390 Å average) are longer than the mutually *trans* Re–Cl bonds (2.369 Å). The Re–N distances also show significant differences, i.e. those *trans* to Cl have a proclivity to be ~0.03 Å shorter than those *trans* to the phosphine.

The reductive nitrosylation of $[ReOBr_3(PPh_3)_2]$ with gaseous NO gave $[Re(NO)(Ph)Br_3(PPh_3)]$ as a by-product [55]. It has been characterized by X-ray diffraction; the nitrosyl ligand is coordinated in a linear fashion, the Re–N distance is 1.830 Å, Re–P distance 2.492(3) Å and Re–Br distances in the range 2.4817(14)–2.5484(14) Å.

Mixed halogeno–pyridine–rhenates $[ReX_{6-n}(py)_n]^{(3-n)-}$, X = Br, Cl, $n = 1$–3 have been prepared [56]. X-ray crystallography has been conducted on the *mer*-$[ReX_3(Py)_3]$ complexes, showing the stronger *trans* influence of pyridine. The Re–N distances are 2.12 Å.

6.5. Complexes with phosphorus donor ligands

The solid state structures and carbon-13 magnetic resonance spectra in solution of several paramagnetic rhenium complexes have been obtained [57]. The ^{13}C NMR spectra of the complexes $[ReCl_3(PEt_2Ph)_3]$ and $[ReCl_3(P^nPr_2Ph)_3]$ were assigned by means of ^{13}C–^1H correlation spectroscopy experiments. They display sharp and broad lines and no ^{13}C and ^{31}P coupling was observed in the spectra. Measured relaxation T_1^1 and T_2^1 and linewidths in three different magnetic fields were found to increase with increasing strength. The structure of $[ReCl_3(PEt_2Ph)_3]$ was determined by X-ray crystallography; ^{13}C NMR chemical shifts were compared with corresponding bond lengths in the crystal.

Further studies of the isomeric 1,2,7- and 1,3,6-$Re_2Cl_5(PMe_3)_3$ compounds have been conducted [58]. Using PhI, Cl_2 and $Re_2Cl_4(PMe_3)_4$ in a 2:1 molar ratio in the presence of free PMe_3 gave a red crystalline product 1,3,6/1,2,7-$Re_2Cl_5(PMe_3)_3$ which contains both isomers in the unit cell. An additional product 1,3,6-$Re_2Cl_5(PMe_3)_3 \cdot 1/2CH_2Cl_2$ was always found as a reaction product. The reaction of $[(^nBu)_4N]_2Re_2Cl_8$ with PMe_3 in propanol at room temperature gave 1,2,7-$Re_2Cl_5Re_2Cl_5(PMe_3)_3 \cdot (^nBu)_4NCl$. Upon heating a dichloromethane solution of the latter, pure 1,2,7-$Re_2Cl_5(PMe_3)_3$ was obtained. All the molecules possess a rhenium–rhenium bond order of 3.5 and Re–Re distances are in the range 2.210–2.227 Å. The average Re–P distance in 1,3,6/1,2,7-$Re_2Cl_5(PMe_3)_3$ is 2.437 Å, 2.451 Å for 1,3,6-$Re_2Cl_5(PMe_3)_3 \cdot 1/2CH_2Cl_2$, 2.451 Å and 2.407 Å for 1,2,7-$Re_2Cl_5Re_2Cl_5(PMe_3)_3 \cdot (^nBu)_4NCl$.

6.6. Clusters

An attempt at developing a high temperature technique for the synthesis of Te-containing Re_6 cluster compounds has resulted in the preparation of $Re_6Te_6Cl_6(TeCl_2)_2$ and $[Re_6Te_8(TeBr_2)_6]Br_2$ containing the new ligands $TeCl_2$ and $TeBr_2$ [59]. The former comprises an Re_6 octahedron which is resident inside a

Te_6Cl_2 pseudo-cube. Six corners of the cube are occupied by tellurium atoms while the remaining two corners are occupied by Cl atoms. The Re–Te distances range from 2.634(3) to 2.711(3) Å, while the Re–μ_3-Cl distances are in the range 2.476(7) to 2.502(8) Å. Four rhenium atoms that are bonded to μ_3-Cl ligands are also bonded to terminal Cl ligands with distances in the range 2.349(9)–2.407(8) Å. Two rhenium atoms which are bonded to μ_3-Te are also bonded to $TeCl_2$ groups with Re–Cl_2 distances of 2.634(3) and 2.667(3) Å. The latter complex comprises an Re_6 core inscribed inside a cube and each Re atom is ligated by a neutral $TeBr_2$. The Re–Re distances are 2.666(3)–2.677(4) Å and Re–μ_3-Te distances 2.638(5)–2.668(3) Å. In comparison with the former cluster, all six Re atoms are bonded to μ_3-Te ligands and the cluster also contains a terminal $TeBr_2$ ligand with an Re–$TeBr_2$ distance of 2.634(3) Å.

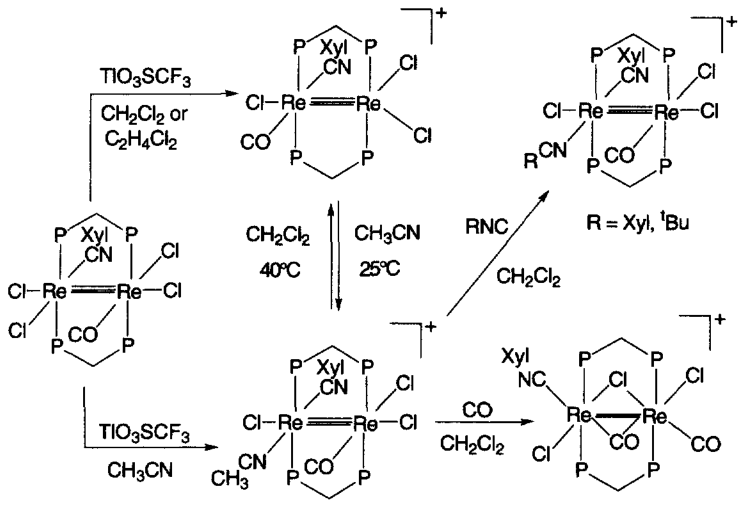
Reaction of $ReCl_5$ with elemental tellurium in an evacuated sealed fused silica tube at 773 K yielded $Re_6Te_4Cl_{10}$ [60]. The structure is composed of two independent Re_6 octahedral units each possessing a crystallographic center of symmetry. Each rhenium atom is coordinated to four Te atoms in a μ_3 fashion while four μ_3-Cl ligands are distributed equally over the faces of the metal polyhedron. The remaining six chlorine ligands are coordinated to the apices of the octahedron. The Re–Re distances are 2.618(1)–2.638(1) Å, Re–Cl(terminal) 2.325(6)–2.353(5) Å.

Using high temperature methods the preparation of octahedral sulfidobromide Re_6 cluster complexes has been achieved [61]. The reaction of Re_3Br_9 with PbS in the presence of KBr generated a salt of $[Re_6S_6Br_8]^{2-}$ while the reaction between $Re_6S_4Br_{10}$ and KNCS gave rise to a salt of $[Re_6S_7Br_7]^{3-}$. Both salts are octahedral clusters displaying terminally ligated bromine atoms. Additional bromine and sulfur atoms occupy face capping positions. Both clusters have been characterized by X-ray crystallography.

7. Rhenium(II)

The deprotonation reactions of the aminocarbyne complex *trans*-$[ReCl(CNH_2)(dppe)_2][BF_4]$ with NBu_4OH under N_2 or CO have been investigated [62]. This reaction generated the complex *trans*-$[Re(CN)L(dppe)_2]$ while in the presence of an organonitrile or phenylacetylene (under argon) the nitrile or the vinylidene complexes *trans*-$[Re(CN)L(dppe)_2]$, L = NCMe, NCPh, NCC_6H_4Me-4 or C=CHPh were obtained. These complexes were characterized by IR, NMR, FAB MS and electrochemically. The structure of *trans*-$[Re(CN)(NCMe)(dppe)_2]\cdot{}^iPrOH$ has been reported, the Re–P distances are in the range 2.380(1) to 2.393(1) Å and the Re–N distance is 2.085(4) Å.

The reactions of the bioctahedral complex $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNxyl)$ with $TlOSCF_3$ in acetonitrile gave the dirhenium complex $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNxyl)(NCCH_3)]O_3SCF_3$ [63]. The crystal structure of the latter reveals that the rhenium–rhenium triple bond is retained and a chloride *trans* to the xylNC ligand has been removed. The reactivity of this complex has been studied (**10**).



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In a related paper [64], the reactions of $Re_2Cl_4(\mu\text{-dppm})(CO)$ and $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNxyl)$ with xylNC in the presence of Tl^+ have given rise to yellow and green isomers of the salts $Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNxyl)_2]Y$, Y = Cl, ReO_4, SO_3CF_3 or PF_6. These isomers have been characterized by IR, NMR and conductivity. Crystals of none of the yellow isomers could be obtained; single crystals of the perrhenate salt of the green isomer $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNxyl)_2](ReO_4)_{0.82}Cl_{0.18}$ were obtained and X-ray studies confirm that it possesses an all *cis* arrangement of ligands about the $[Re_2Cl_3(\mu\text{-dppm})_2]^+$ core, the Re–Re bond length is 2.576(1) Å.

The reactions of salts of $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)]Y$, Y = PF_6, O_3SCF_3, with carbon monoxide and xylyl isocyanide (XylNC) have been studied [65]. The reaction of the title complex has resulted in the formation of three isomeric forms of the cation $[Re_2Br_2(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$. Two forms have a very similar bis(μ-halo)-bridged edge-sharing bioctahedral structure, while the third form displays an open bioctahedron arrangement. The reaction of the title complex with CO gave the salt $[Re_2Br_2(\mu\text{-dppm})_2(CO)_2(CNXyl)_2]O_3SCF_3$ in which the cation displays an all *cis* arrangement of π-acceptor ligands. The Re–Re distances were found to be 3.04456(8), 2.3792(7) and 2.5853(13) Å, respectively, consistent with Re–Re bond orders of 1, 3 and 2, respectively. These complexes were characterized by IR, ^1H and ^{31}P NMR, CV and X-ray crystallography.

8. Rhenium(I)

8.1. Complexes with halide ligands

The first unaided displacement of chloride by H_2 forming a novel cationic dihydrogen complex $[Re(CN^tBu)_3(PCy_3)_2(H_2)]Cl$ has been reported [66]. Thermodynamic parameters for the equilibrium system $Re(CN^tBu)_3(PCy_3)_2Cl + H_2 \rightleftharpoons [Re(CN^tBu)_3(PCy_3)_2(H_2)]Cl$ were obtained; ^1H NMR and $^{31}P\{^1H\}$ NMR studies over the temperature range 286–316 K gave $\Delta H = -18.0 \pm 0.7$ kcal mol^{-1}, $\Delta S = -44 \pm 2$ eu and $\Delta G_{298} = -4.8 \pm 1.3$ kcal mol^{-1} for the equilibrium. The molecular structure of the chloro complex revealed an unusually long Re–Cl distance of 2.596(2) Å. Variation of the ratio of phosphines and isonitriles on Re was studied in an effort to explore the utility of isonitriles as ligands for stabilizing dihydrogen complexes. Complexes of the form $[ReL_5H_2]^+$ were found to adopt either the formally Re^{III} dihydride structure ($L = PMe_3$) or the Re^I dihydrogen structure ($L = CN^tBu$). The use of phosphines favored the dihydride structure while π-acid ligands such as CO and CNR favored a dihydrogen structure and at least three isonitrile ligands are necessary for the formation of the latter structure.

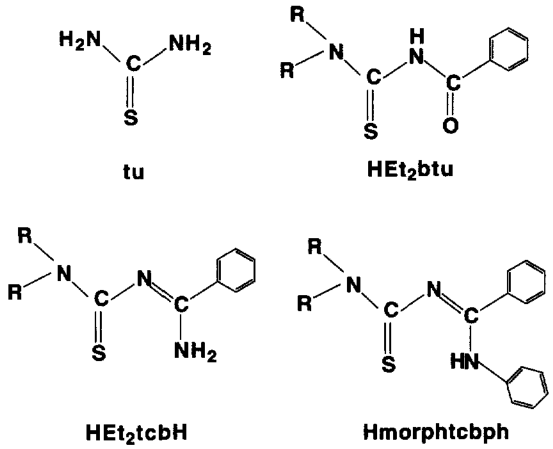
8.2. *Complexes with oxygen donor ligands*

The hydroxymetalate $[Re_3(CO)_9(\mu\text{-}OH)_3(\mu_3\text{-}OH)]^-$ has been shown to function as a novel tripodal ligand for a wide range of metals [67]. Divalent manganese and copper formed heterodimetallic electrically neutral complexes with this ligand in near quantitative yields which are air- and water-stable crystalline compounds of formula $[MRe_6(CO)_{18}(\mu_3\text{-}OH)_8]$, $M = Mn^{II}$ and Cu^{II}. A single crystal of the manganese derivative shows a double-cubane type structure with the divalent metal ion occupying the common corner site. The Re–O distances, 2.182(8) Å (average), are increased when compared with the free ligand. Of note is the unusual geometry for the Mn atoms resembling trigonal prismatic more than octahedral, while in the copper derivative the Cu^{II} center is octahedral with a tetragonal distortion, average Re–O distances 2.187(10) Å. Both complexes exhibit a layered arrangement.

A comprehensive spectroscopic and electrochemical study of the rhenium and manganese complexes of the 3,5-di-*tert*-butyl-1,2-benzosemiquinone (DBSQ) ligand $[M(CO)_4(DBSQ)]$, *fac*-$[M(CO)_3(L)(DBSQ)]$ and *cis,trans*-$[M(CO)_2(L)_2(DBSQ)]$, where M = Re, Mn, L = thf, Me_2CO, MeC(O)Ph, NEt_3, Ph_3PO, $SbPh_3$, $AsPh_3$, PCy_3, $P(OPh)_3$, PPh_3, dppe, PPh_2Et, $P(OEt)_3$ and PEt_3, has been carried out [68]. A particular focus of this study was to assess how the extent of increasing electron density on the metal atom influences the extent of electronic delocalization within the metal semi-quinone ring. Evidence from IR, EPR and resonance Raman studies led to the characterization of these complexes as valence-localized molecules containing the radical-anionic DBSQ ligand bound to the metal atoms with a small delocalization of the singly occupied MO of the DBSQ ligand over the metal atom. This delocalization may be modulated by changing co-ligands, although in a limited way since the DBSQ ligand is a weak π-acceptor.

8.3. *Complexes with sulfur donor ligands*

The reactions of $(Et_4N)_2[Re(CO)_3Br_3]$ with various ligands containing a thiocarbonyl donor site (**11**) have been explored [69].



(11)

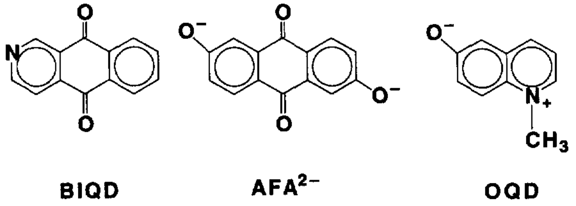
The complex *fac*-$[Re(CO)_3(tu)_3](NO_3)$ was formed from the bromo complex by precipitation after addition of $AgNO_2$ and subsequent reaction with urea. The mean Re–S distance is 2.529 Å. Dialkylbenzoylthioureas react to form neutral $[Re(CO)_3Br(HR_2tu)]$ complexes, coordinated in a didentate fashion without deprotonation which is unusual for chelate ligands of this type. Significant deviations from planarity in the chelate ring are evident. In the case of the *N*,*N*-diethylthiocarbamoylbenzamidinate ligand of the dinuclear compound $[Re_2(CO)_6(Et_2tcbH)_2]$, both rhenium atoms are coordinated by three facially oriented carbonyls and a singly deprotonated Et_2tcbH^- ligand. The sulfur atoms of these ligands act as bridges between the metal centers, forming a four-membered Re_2S_2 ring. The Re–S lengths are 2.507(2) and 2.545(2) Å. The mononuclear anionic complex $(Et_4N)[Re\{3Br(morphtcbph)\}]$ has an Re–S bond distance of 2.476(2) Å.

8.4. Complexes with selenium donor ligands

A low energy $d_{\sigma*}$ MLCT transition from Re^I to Se_2Ph_2 in the absorption spectrum of $[Re_2Br_2(CO)_6(Se_2Ph_2)]$ has been observed [70]. The absorption at $\lambda_{max} = 434$ nm (in CH_2Cl_2) is due to a transition from the rhenium atom into the σ^*(Se–Se) orbital of the bridging diphenyl diselenide ligand.

8.5. Complexes with oxygen and nitrogen donor ligands

Emission measurements have been used to calculate rate constants for electron transfer in polypyridyl complexes of rhenium [71]. The complexes $[(4,4'-(Me)_2bpy)Re(CO)_3](BIDQ)[(OTf)]$, $[(4,4'-(Me)_2bpy)Re(CO)_3]_2(AFA)$ and $[(4,4'-(^tBu)_2bpy)Re(CO)_3(OQD)](OTf)$, BIDQ = benz[*g*]isoquinoline-5,10, Otf = $CF_3SO_3^-$, AFA^{2-} = 2,6-dioxyanthraquinone dianion, OQD = 1-methyl-6-oxyquinoline (**12**) were studied. They were chosen because they exemplify complexes where electron transfer acceptor ligands and a metal-to-ligand charge transfer (MLCT) chromophore are linked with moderate to weak electronic coupling.



(12)

A novel tetranuclear compound has been obtained from the reaction of $Re_2(C_6H_5NCOCH_3)_4Cl_2$ with water in air [72]. The blue compound $[Re_4(C_6H_5NCOCH_3)_6(Cl)(\mu\text{-}O)(\mu\text{-}OH)(MeOH)_3][ReO_4]_2$ was analyzed by X-ray crystallography and comprises two quadruply bonded dirhenium units which are connected by an oxygen and a hydroxy ligand thereby forming a five-membered ring containing three rhenium atoms. The oxo ligand is tightly bonded to both rhenium atoms it bridges at distances of 1.88(2) and 1.94(2) Å. In contrast, the hydroxo ligand is bound more strongly to one rhenium atom at a distance of 2.06(3) Å, while its distance to the other rhenium atom is 2.29(2) Å. Notably the *cis* arrangement of the amidato ligands present in the starting reactant has changed to *trans* in the product. The product has been further characterized by mass spectroscopy.

8.6. Complexes with nitrogen donor ligands

Luminescence and transient absorption studies have been carried out on the salt $[(bpy)Re(CO)_3(py)^+][C_6H_5CH_2BPh_3^-]$ in THF and acetonitrile solvents [73]. From UV–visible absorption and steady state emission spectroscopy it was determined that this salt exists primarily as an ion pair in THF. A weak absorption band was assigned to an optical ion pair charge transfer transition. Quenching studies have shown that $BzBPh_3^-$ quenches the luminescent $d\pi(Re)\rightarrow\pi^*(bpy)$ metal-to-ligand charge transfer excited state of the chromophore. The quenching is attributed to electron transfer from the benzylborate anion. Laser and quantitative laser flash photolysis studies were used to further study electron transfer quenching and the quantum efficiency of this process.

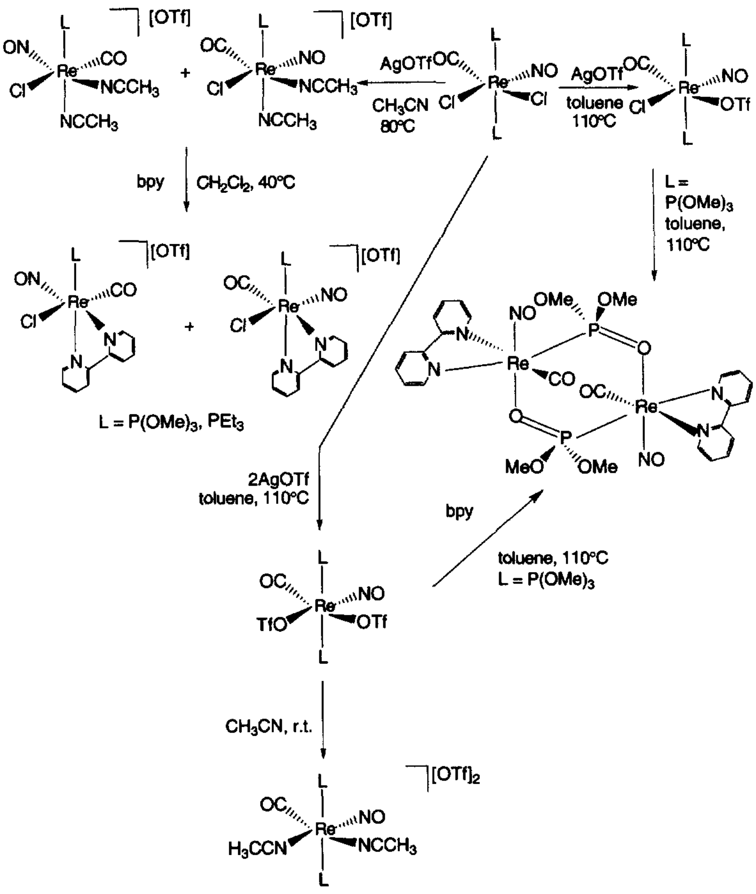
Solution NMR studies of the 1:1 complexes *fac*-$[ReX(CO)_3L]$ [X = Br, L = 2,4,6-tris(pyrazolyl-1-yl)pyrimidine, tpzp, or 2,4,6-tris(4-methylpyrazolyl-1-yl)pyrimidine, tmpzp; X = Cl, Br or I, L = 2,4,6-tris(3,5-dimethylpyrazolyl-1-yl), tdmpzp] and of the 2:1 complexes $[\{ReBr(CO)_3\}_2(tmpzp)]$ and $[\{ReBr(CO)_3\}_2(tdmpzp)]$ have been conducted [74]. Complexes involving coordination with the 2-pyrazolyl ring nitrogen strongly predominate. A fluxional exchange between two types of coordination species was observed for the tmpzp and tdmpzp derivatives. Measured activation energies for the fluxional processes were in the range 53–74 kJ mol^{-1}. The structure of the non-fluxional dinuclear complexes was deduced from NMR. In a related paper [75], the synthesis and fluxional properties of complexes *fac*-[ReX(CO)$_3$L], X = Cl, Br, L = 2,4,6-tris(4-methylpyrazol-1-yl)-1,3,5-triazine (tmpzt), 2,4,6-tris(3,5-dimethylpyrazoly-1-yl)-1,3,5-triazine (tdmpzt) have been documented. Using dynamic NMR methods the activation energies for the process have been measured and are in the range 46–72 kJ mol^{-1} and are dependent on the steric requirements of the pyrazole ligands. Low temperature NMR studies reveal spectral changes which are interpreted in terms of varying rates of rotation of one of the uncoordinated pyrazole rings.

A monohelical dimetallic rhenium(I) and monohelical rhenium(III) complexes of quinquepyridine (qpy) have been prepared and characterized electrochemically, by photophysical means and X-ray crystallography [76]. The dimetallic complex [(py)(OC)$_3$Re(qpy)Re(CO)$_3$(py)][ClO$_4$] generated two types of crystals but only the needle shaped ones were analyzed. From its X-ray crystal structure it is apparent that each rhenium atom is in a distorted octahedral geometry. The Re–N distances range from 2.154(8) to 2.225(8) Å. No π–π interactions within the complex are operative and the two pyridine, two bipyridine and central 1,3-pyridyl spacer are planar. The Re...Re separation is 7.723 Å. In the mononuclear complex rhenium is in a pentagonal-bipyramidal geometry with two Cl atoms which are *trans* to each other with long Re–Cl distances of 2.430(5) Å. Both complexes display photoluminescence in the spectral range 560–600 nm.

The absolute lability of triflate ligands coordinated to the *trans*-{ReL$_2$(CO)(NO)} unit where L = phosphorus donors and the relative *trans* labilization effects of the nitrosyl and carbonyl ligands have been investigated [77]. The reactions are delineated (**13**). These complexes have been characterized by ^{1}H,^{31}P, ^{19}F NMR and IR spectroscopies, elemental analysis and X-ray crystallography.

Using resonance Raman, time-resolved absorption and emission spectroscopy it has been shown that the character and dynamics of the lowest excited state in Re(X)(CO)$_3$(α-diimine), α-diimine = bpy, pyridine-2-carbaldehyde *N*-isopropylimine (^{i}Pr-PyCa), 1,4 diazabutadience *N*-isopropylimine (^{i}Pr-DAB) complexes may be finely tuned by varying the halide and α-diimine ligands [78]. For the case where X = Cl$^-$, the lowest excited state was characterized as MLCT; while changing to Br$^-$ and I$^-$ in particular the lowest excited state comprises more halide character and is best described as an X→π*(α-diimine) XLCT excitation. The extent of mixing of the rhenium d π and halide p π orbitals determines the halide influence on this excited state and increases with increasing π halide orbital energy. The XLCT state has a longer lifetime owing to slower non-radiative decay to the ground state. Additionally, this state is a better luminophore owing to higher emission quantum yields.

In a related paper [79], the character and picosecond dynamics of the excited states of [Re(Br)(CO)$_3$(α-diimine)] complexes, α-diimine = 4,4′-dimethyl-2,2′-bipyridine (bpy′), *N*,*N*-di-*p*-tolyl-1,4-diaza-butadiene and *N*,*N*-di-*p*-anisyl-1,4-diaza-butadiene have been investigated by time-resolved absorption spectroscopy over the time range 50–250 ps. The nature of the α-diimine ligand was found to affect the character

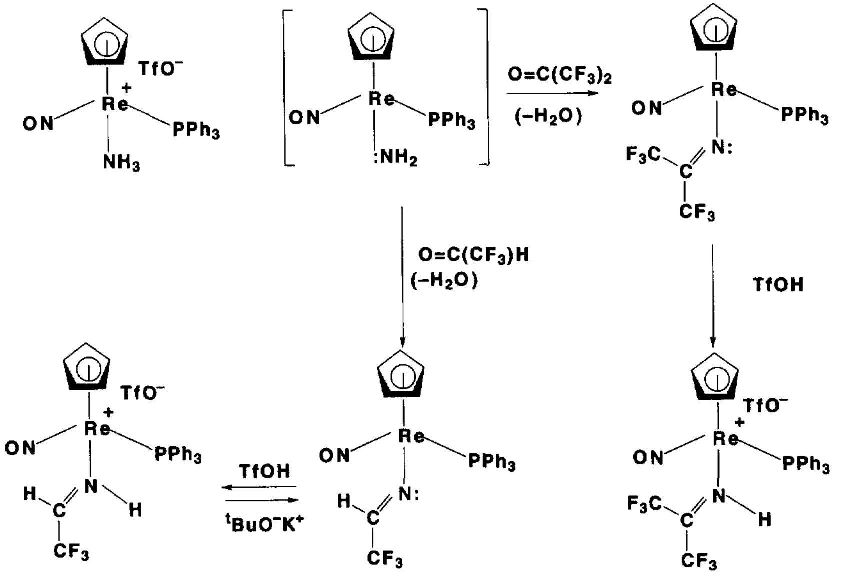


(13)

and dynamics of the lower excited states, substituting bpy′ for either of the diazabutadiene ligands alters the excited state from being MLCT to ligand-to-ligand charge transfer (LLCT). The MLCT state in the diazabutadiene complexes lies above the LLCT state and population of this state may be possible at higher excitation energies.

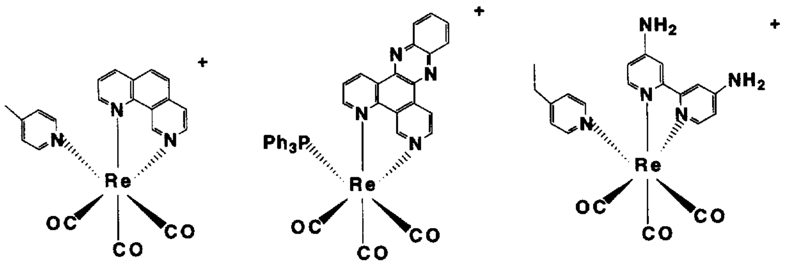
A comparative spectroelectrochemical study of the reduction of [Re(X)(CO)$_3$(R′-DAB)], X=TfO$^-$, Br$^-$, DAB=diazabutadiene, R′=^{i}Pr, *p*-Tol, pAn, and [Re(R)(CO)$_3$(^{i}Pr-DAB)], R=Me, Et, Bz complexes has been carried out at variable temperatures [80]. The electrochemical and spectroelectrochemical data were obtained by application of cyclic voltammetry, bulk electrolysis and electrolysis in optically transparent thin-layer electrolytic cells at variable temperature. The one-electron reduction of [Re(Br)(CO)$_3$(R′-DAB)] resulted in an equilibrium between [Re(Br)(CO)$_3$(R′-DAB)]$^-$ and [Re(^{n}Pr)(CO)$_3$(R′-DAB)] with the position of the equilibrium being dependent on the R′ substituent and temperature. The [Re(R)(CO)$_3$(^{i}Pr-DAB)], R=Me, Et and Bz complexes were reduced with one electron generating radical anionic products $[\mathrm{Re(CO)_3(^iPr\text{-}DAB)}]^{-}\cdots\mathrm{R}^{\cdot}$. Furthermore, this reduction was found to be both chemically and electrochemically reversible. The radicals were further reduced, yielding five-coordinate anions $[\mathrm{Re(CO)_3(R'\text{-}DAB)}]^{-}$ whose bonding properties were assessed by means of a qualitative MO diagram.

Imine and methyleneamido complexes of the chiral rhenium Lewis acid $[\mathrm{CpRe(NO)(PPh_3)}]^{+}$ have been prepared (**14**) [81]. It was hoped that σ/π equilibria might be observed with respect to ligands with C=N linkages. No evidence for π-isomers was found. These complexes were studied by IR and NMR spectroscopies.



(**14**)

Time-resolved step-scan Fourier-transform infrared spectroscopy has been used to probe the excited state electronic structure in rhenium(I) polypyridyl complexes (**15**) [82].

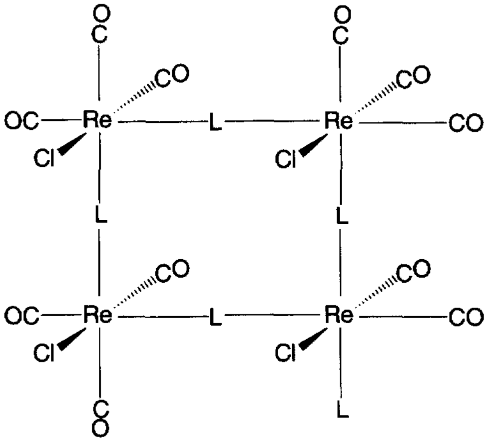


(**15**)

Typically, there is a complicated interplay between MLCT and ligand-based excited states in these complexes. The υ(CO) shifts for *fac*-$[Re(phen)(CO)_3(4\text{-}Mepy)]^+$ are consistent with the oxidation of Re(I) to Re(II) and formation of an MLCT excited state. For the case of *fac*-$[Re(dppz)(CO)_3(4\text{-}Mepy)]^+$ the υ(CO) shifts are lower in energy, which is consistent with a lowest ligand-localized excited state thought to be $^3\pi\pi^*$(dppz). The υ(CO) shifts in *fac*-$[Re(4,4'\text{-}(NH_2)_2bpy)(CO)_3(4\text{-}Etpy)]^+)(CO)_3(4\text{-}Mepy)]^+$, $(4,4'\text{-}(NH_2)_2bpy)$ = 4,4′-diamino-2,2′-bipyridine, are comparable with those of the phen derivative, and can be attributed to an MLCT excited state and an additional ligand-based state.

An infrared rigidochromic effect in the IR spectra of the excited state of $[Re(CO)_3Cl(bpy)]$ has been described [83]. The magnitude of the υ(CO) shift in the MLCT excited state of the title compound in the glass-forming solution butyronitrile–propionitrile PrCN–EtCN 5:4 v/v solution as compared to the ground state spectrum was found to decrease on cooling from fluid to glass. This effect is likely due to changes occurring in the MLCT state as a result of glass formation.

The self-assembly of luminescent molecular squares featuring octahedral rhenium corners has been reported [84]. The products are depicted in (**16**), giving yields in excess of 95%, and the products were characterized using FAB$^+$ mass spectrometry, NMR spectroscopy and X-ray crystallography, all indicating that molecular squares are formed.

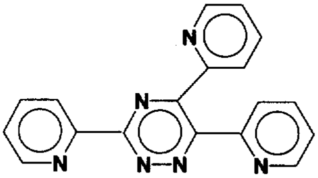


L = pyrazine, bpy′, 1,2-bis(4-pyridyl)ethylene

(**16**)

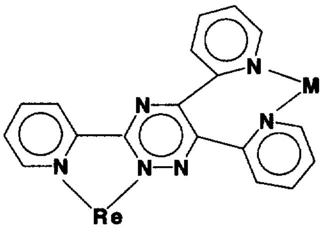
X-ray crystals of the 4,4′-bipyridine and pyrazine derivative were grown by solubilizing the samples in acetone and then layering with *n*-hexanes. Solvent exclusion from the small pyrazine square cavity gave rise to a more highly ordered structure than in the bipyridine derivative. However, a slight distortion from a strictly square cavity was observed in the pyrazine derivative. Electronic spectra of all three derivatives exhibit two bands in the UV and visible regions and were assigned to bridging-ligand-localized π–π* and MLCT transitions. The bpy and pyrazine derivatives luminesce at room temperature while the third derivative does not.

The synthesis and characterization of a novel mononuclear species [ReCl(CO)$_3$(L)], L=(**17**) has been described [85].



(17)

Coordination to the metal atom occurs via a pyridyl and a triazine nitrogen atom. In addition, the reaction of [M(Hfac)$_2$] (M=Mn, Fe, Co, Ni, Cu, Zn) generated the heterodimetallic products [(CO)$_3$ClRe(tpt)M(hfac)$_2$]. These complexes have been characterized by IR and visible spectroscopy, magnetic measurements and electrochemically. In addition, 2D COSY ^{1}H–^{1}H NMR spectroscopy has been used to study these complexes. In the heterodimetallic complexes the tpt-M binding mode was found to be atypical (**18**), only two free pyridyl nitrogen atoms of the [ReCl(CO)$_3$(tpt)] complex are involved.

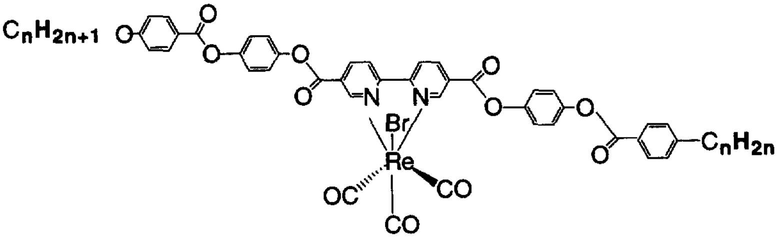


(18)

Studies on mesomorphic bipyridine complexes of rhenium(I) have been conducted with a view to designing metal-based liquid crystals comprising highly coordinated metal centers [86]. Using larger bipyridines containing six aromatic rings which were then reacted with an equimolar amount of [ReBr(CO)$_5$] in toluene–heptane (3:2 v/v) at reflux under N_2 for 3.5 h gave the desired complex in isolated yields which were quantitative (**19**). The butoxy and octyloxy derivatives gave nematic phases while the S_c phase seen in the dodecyl ligand was retained in the complex.

8.7. Complexes with phosphorus donor ligands

The structure of [ReBr(CO)$_3${NH(PPh$_2$)$_2$}] has been determined [87]. It is composed of discrete molecules in which the rhenium atom is in an octahedral environment with the carbonyl groups in a facial position. Constraints imposed by the



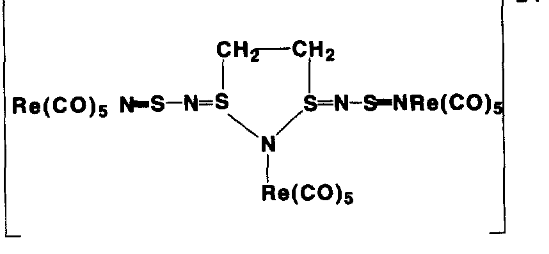
(19)

didentate diphenylphosphino ligand cause some deviations from idealized symmetry. The Re–Br distance is 2.644(2) Å.

Phosphorus longitudinal relaxation times in mono $[Re(CO)_3Cl(PPh_3)_2]$ *fac* and *trans–mer* and polynuclear $Re_3(\mu\text{-}H)_3(CO)_{11}PR$, $L=PPh_3$, $PMePh_3$, PMe_2Ph, PMe_3 and $P(OMe)_3$ and *eq,eq*-$[Re_3(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]^-$ have been studied [88]. The scalar coupling of the second kind (sc) mechanism is operative at low fields. In some instances a comparison of the ^{31}P longitudinal relaxation times which are sensitive to $^1J(P\text{–}Re)$ revealed that they may be used in the assignment of the relative P-coordination geometry in rhenium compounds. The absolute value of T_1 has been found to be affected by several factors such as bulkiness of ligands, charge of the compound, viscosity of the solvent and temperature.

8.8. Complexes with nitrogen and sulfur donor ligands

The reactions of *trans*-$[Re(CO)_4(MeCN)(NS)][AsF_6]_2$ with CsCl and CsF have been studied [89]. Addition of the chloride results in exchange of the MeCN group generating *trans*-$[Re(CO)_4Cl(NS)][AsF_6]\cdot MeCN$ in 78% yield. Its structure reveals a short ReN distance of 1.87(2) Å and indicates strong π acceptor abilities of the NS ligand. In the reaction with CsF no products with Re–F bonds were observed. Based on ^{19}F NMR studies the primary product is suggestive of the formation of *trans*-$[Re(CO)_4(MeCN)(NSF)]AsF_6$, but attempts to recrystallize this were futile. Single crystals of (**20**) were obtained. It is an unusual trinuclear complex with an anionic tridentate ligand whose formation cannot easily be explained. The Re–N distances are in the range 2.09(1) to 2.205(9) Å.



(20)

9. Rhenium(0)

The photophysics and photochemistry of metal–metal bonded complexes L_nM'–$Re(CO)_3$(α-diimine), $L_nM' = Ph_3Sn$, $(CO)_5Mn$, $(CO)_5Re$, α-diimine = 4,4′-dimethyl-2,2′-bipyridine (bpy′), pyridine-2-carbaldehyde *N*-isopropylimine (^{i}Pr-PyCa), 1,4-diazabutadience *N*-isopropylimine (^{i}Pr-DAB) have been studied by time-resolved emission and absorption spectroscopies [90]. The lowest excited state of the metal–metal bonded complexes was found to have a $^3\sigma(M'\text{–}Re)\pi^*$ character. In a low temperature glass, the emission of these complexes is longer lived than the MLCT emission of analogous halide complexes. In solution the homolysis is strongly promoted by a nucleophilic or chlorinated solvent.

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