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Variable-Valent Rhenium Chemistry of Conjugated Nitrogenous Ligands: Structure and Reactivity

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The valence states of particular concern in this review are VI–I and the ligand types are diimine, azoimine, imineamide and azooxime all bidentate and *N*,*N*-coordinating. Metal reduction potentials and stability of oxidation states are subject to control via variation of the nature and extent of *N*,*N*-chelation and coligation. Back-bonding plays a major role in determining stability and isomer specificity, particularly in the valence domain III–I. Three types of mediated oxygen atom transfer processes have been scrutinized and modeled: from $Re^{V}O$ to tertiary phosphanes and variable-spacer diphosphanes, from water to diimine and from oxime to metal/coligand. Other reactivity topics include isomerizations associated with ligand substitution, stable azo anion radical generation and azo cleavage.

1. Introduction

Named after the river Rhine, rhenium ($6s^2 5d^5$) occurs in very low abundance (0.7 ppb) in earth's crust. It was indeed the last of the naturally occurring chemical elements to be discovered (1925).[1] Progress in the chemistry of rhenium which spans the oxidation states –1 to +7 has been comprehensively reviewed from time to time.[2–4] But for a short earlier involvement,[5] our sustained activity in rhenium chemistry dates from the early nineties when we were attracted by the prevalence of the $Re^{V}O$ motif[2,3] and its documented ability to transfer oxygen atoms.[6–9] Since then the chemistry of $Re^{V}O$-promoted transfer reactions has been enriched in several laboratories[4,10–16] including ours (vide infra).

Conjugated nitrogen donor organic molecules constitute a large family of chelating ligands that have been widely used for binding transition metal ions. However, reactive $Re^{V}O$ species incorporating such ligands have been relatively rare[2,3] and this provided the initial lead for us. Our endeavour in this area would eventually lead us to a rich arena of variable-valent rhenium chemistry encompassing interesting reactions, structures and bonding situations. The salient features of this chemistry will be outlined in this article.

2. Ligands, Coligands and Coordination Types

Three bidentate chelating moieties widely used in our work and generally represented as (NN) are diimine, **1**, azo-

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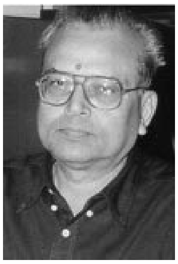
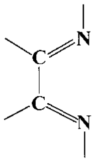
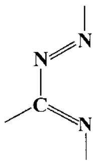


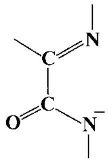
Animesh Chakravorty was born in Mymensingh, Bangladesh, in 1935. He received his PhD degree from Calcutta University and did postdoctoral work at M.I.T. and Harvard University. He was Professor and Head of the Department of Chemistry at I.I.T. Kanpur and subsequently of the Department of Inorganic Chemistry at Indian Association for the Cultivation of Science, Kolkata, where he is now an Emeritus Professor. He is also a Chair Professor of the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore. His research interest lies in design and structure of reactive d-block complexes and organometallics, variable valence phenomena and redox transformations. Recent highlights include carbohydrate ligation, crystalline anion radical complexes, metal promoted oxygen atom transfer and insertion into small metallacycles. He has authored 300 papers with his students, sixty of whom have graduated. He has been on the Editorial/Advisory Boards of Inorganic Chemistry, Dalton Transactions, Inorganica Chimica Acta, Comprehensive Coordination Chemistry II and Indian Journal of Chemistry. He is the current President of the Chemical Research Society of India and had been a Golden Jubilee Research Professor of the Indian National Science Academy.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

imine, **2** and anionic imineamide, **3** which is derived from **1**. All of these are excellent σ-donors (nitrogen lone pairs); **1** and **2** are also potentially good π-acceptors, **2** being superior in this respect [low-lying π*(azo) orbital].[17,18]


diimine
1


azoimine
2


imineamide
3

By regulating this duality of bonding with the help of coligands multiple oxidation states of rhenium have been realized. The majority of ligand systems of types **1**–**3** used by us are listed in Table 1 along with abbreviations. Other ligands such as azooximes will be considered in due course.

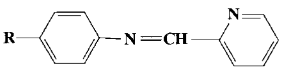
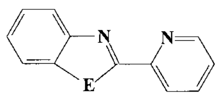
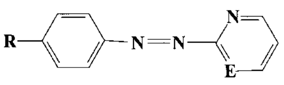
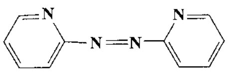
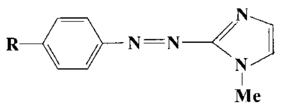
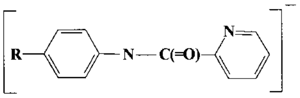
The majority of coordination types encountered are set out in Table 2. These are uniformly hexacoordinate and generally belong to the (NN)-monochelated [ReQ(NN)] class [chloride ligand(s) omitted] wherein the coligand Q is a good handle for modulation of metal reduction potential and valence. Thus O^{2-} and NAr^{2-} (strong σ-and π-donor)

Table 2. Coordination types.

Complex	Q[a]	(NN)
$[Re^{VI}QCl_3(NN)]$	NAr	**3**
$[Re^{V}QCl_3(NN)]$	O, NAr	**1**, **2**
$[Re^{IV}QCl_3(NN)]^{z+}$	z = 1: OP, OPnP	**1**
	z = 0: OP, P	**3**
$[Re^{III}QCl_3(NN)]$	OP, OPnP, OPnPO, P, PnPO	**1**, **2**
$[Re^{II}Cl_2(NN)_2]$	–	**1**, **2**
$[Re^{I}(NN)_3]^+$	–	**2**
$[Re^{I}QCl(NN)]$	$(CO)_3$	**2**
$[Re^{I}Q(MeCN)(N^{\cdot-})]$[b]	$(CO)_3$	**2**

[a] P is tertiary phosphorus and n is a spacer between two P atoms. [b] $(NN^{\cdot-})$ is the azoimine anion radical.

Table 1. Ligands, functions and their abbreviations.

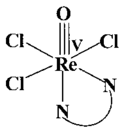
Ligand	Function	Abbreviation
Diimines		
	pyridinealdimine	Rpyal
	E = O, pyridyloxazole E = S, pyridylthiazole	pyox pyth
R—N=C(H)—C(H)=N—R	diazabutadiene	Rdabd
Azoimines		
	E = CH, azopyridine E = N, azopyrimidine	Razpy Razpm
	azobipyridine	azbp
	azoimidazole	Razim
Iminoamides		
	picolinamide	Rpiam
$[R—N—C(=O)—C(H)=N—R]^-$	iminoacetamide	Riaam

are suited for Re^{VI}/Re^{V}; OP (σ-donor) and P (σ-donor and π-acceptor) for Re^{IV}/Re^{III}; $(CO)_3$ (strong σ-donor and π-acceptor) for Re^{I} and azo anion radicals. Bis- and tris-chelation of azoimines (strong σ-donor and π-acceptor) respectively support Re^{II} and Re^{I} without assistance from any special coligand. These can also be formally looked upon as [ReQ(NN)] species where Q stands for (NN) and $(NN)_2$ in bis- and tris-chelates, respectively.

3. The Parent $Re^{V}O$ Systems and $Re^{V}(NAr)$ and $Re^{III}(OPPh_3)$ Derivatives

3.1 Synthetic Methods

The diimine ligands Rpyal, pyox and pyth react with $[Re^{V}OCl_3(PPh_3)_2]$ in nonpolar solvents under mild conditions (to avoid phosphane oxide formation) furnishing oxo species of type **4**.[19,20] In the case of Rdabd phosphane oxide formation is fast even under mild conditions and $[Re^{V}OCl_3(AsPh_3)_2]$ is the convenient (weaker oxygen affinity of $AsPh_3$) starting material.[21]



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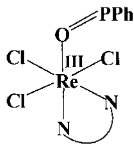
On the other hand azoimine ligands react with $KReO_4$ in hot concentrated hydrochloric acid (reducing agent and source of chloride ligand) furnishing **4**.[22–24] Spontaneous aryl chlorination may, however, occur[22,23] as in the formation of $[Re^{V}OCl_3(Clazpy)]$ from Hazpy and $KReO_4$.[22]

The phosphane oxide system **5** can be generally prepared by the reaction of **4** with PPh_3 (other tertiary phosphanes behave similarly) or of the (NN) ligand with $[Re^{V}OCl_3(PPh_3)_2]$ in a polar solvent.[19–27] The imido system **6** is formed via oxide (water) elimination from **4** in presence of $ArNH_2$ which also reacts with **5** in air to furnish **6**.[20–24,29–31]



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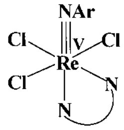

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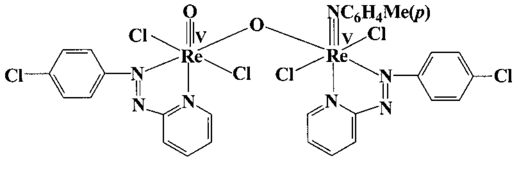
Two observations, both relating to Razpy are noteworthy. First, is the otherwise rare[32] metal-promoted splitting of the azo function, see Equation (1), leading to an imido complex, where the PhN fragment of Hazpy binds to the metal and the pyridyl fragment dimerizes to 2,2′-azobispyridine(azbp).[22] Second, is the synthesis of the first binuclear oxo-imido dimer **7** by the reaction of $[Re^{V}OCl_3(Clazpy)]$ with *p*-toluidine.[22,33]

$$[Re^{III}(OPPh_3)Cl_3(Hazpy)] + Hazpy \rightarrow [Re^{V}(NPh)Cl_3(Hazpy)] + azbp + OPPh_3 \quad (1)$$



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3.2 Structural Features

The structures (for a selection see Table 3 and Table 4) of a number of systems of type **4**,[19–24] **5**[22–25,28] and **6**[5,20–24,29–31] are known. All of these have meridional geometry. It is convenient to discuss **4** and **6** together (Table 3). Here the metal atom is systematically shifted from the equatorial plane (Cl_3N) towards the oxo oxygen atom by 0.30–0.35 Å in **4** and towards the imido nitrogen by 0.27–030 Å in **6**. In **4** the Re–O distances generally lie in the range 1.65–1.67 Å representing approximate triple bonding. Idealized $Re^{V}{\equiv}O$, $Re^{V}{=}O$ and $Re^{V}{-}O$ distances

Table 3. Bond lengths [Å] in $Re^{V}O$ and $Re^{V}(NAr)$ complexes.

Compound	Re–O/[N][a]	Re–N[b]	Re–N[c]	Re–Cl[d]	Ref.
$[Re^{V}OCl_3(Mepyal)]$	1.668	2.295	2.072	2.343	[19]
$[Re^{V}OCl_3(pyth)]$	1.607	2.270	2.118	2.311	[20]
$[Re^{V}OCl_3(NN)]$[e]	1.646	2.171	2.070	2.298	[21]
$[Re^{V}OCl_3(Clazpy)]$	1.663	2.247	2.071	2.341	[22]
$[Re^{V}OCl_3(Hazim)]$	1.660	2.174	2.086	2.339	[24]
$[Re^{V}OCl_3(NN)]$[f]	1.666	2.218	2.072	2.330	[23]
$[Re^{V}OCl(PPh_3)_2(NN)]^{+}$[g]	1.616	2.384	2.002	2.375	[52]
$[Re^{V}(NC_6H_4Cl)Cl_3(Mepyal)]$	1.679	2.224	2.033	2.369	[30]
$[Re^{V}(NC_6H_5)Cl_3(pyox)]$	1.698	2.266	2.075	2.338	[20]
$[Re^{V}(NC_6H_5)Cl_3(Phdabd)]$	1.704	2.194	2.032	2.356	[21]
$[Re^{V}(NC_6H_4Cl)Cl_3(Clazpy)]$	1.719	2.173	2.017	2.371	[22]
$[Re^{V}(NC_6H_4Me)Cl_3(Meazim)]$	1.723	2.140	2.024	2.363	[24]
$[Re^{V}(NC_6H_4Cl)Cl_3(Clazpm)]$	1.719	2.173	2.003	2.358	[23]
$[Re^{V}(NC_6H_5)Cl_3(NN)]$[h]	1.691	2.117	1.998	2.356	[52]
$[Re^{V}(NC_6H_4Me)Cl_2(PPh_3)(NN)]$[i]	1.725	2.191	2.099	2.392	[52]

[a] Oxo O/imido N. [b] N *trans* to O/N. [c] N *cis* to O/N. [d] Average value. [e] (NN) ligand is Schiff base of diacetyl and aniline. [f] (NN) ligand is 2-(*o*,*p*-dichlorophenylazo)pyrimidine. [g] Complex **22** (R = H). [h] Complex **23** (R = Cl). [i] Complex **24**.

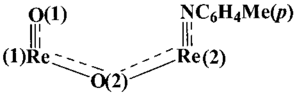
Table 4. Bond lengths [Å] in Re^{III}(phosphane oxide) complexes.

Compound	Re–O	Re–N[a]	Re–N[b]	Re–Cl[c]	Ref.
$[Re^{III}(OPPh_3)Cl_3(Mepyal)]$	2.080	2.030	2.033	2.367	[25]
$[Re^{III}(OPPh_3)Cl_3(Clazpy)]$	2.033	2.032	1.987	2.352	[22]
$[Re^{III}(OPPh_3)Cl_3(Clazim)]$	2.039	1.999	1.978	2.356	[24]
$[Re^{III}(OPPh_3)Cl_3(Hazpm)]$	2.021	2.022	1.957	2.334	[23]
$[Re^{III}(OP2P)Cl_3(Clazim)]$	2.048	2.000	2.002	2.367	[43]
$[Re^{III}(OP1PO)Cl_3(Clazpy)]$	2.030	2.026	1.966	2.369	[27]
$[Re^{III}(OP1PO)Cl_3(Clazim)]$	2.033	1.993	1.985	2.368	[43]
$[(Mepyal)Cl_3Re^{III}(OP2PO)Re^{III}Cl_3(Mepyal)]$[d]	2.068	2.032	2.020	2.368	[27]

[a] Heterocyclic N *trans* to O. [b] Azo/imine N *cis* to O. [c] Average value. [d] Re···Re distance is 8.222(1) Å.

have been estimated to be 1.60, 1.76 and 2.05 Å respectively.[22,34,35] In **6** the Re–N(imido) distance, 1.68–1.72 Å, again corresponds to triple bonding (estimated Re≡NAr, Re=NAr and Re–NAr lengths are 1.69, 1.84 and 2.14 Å respectively).[5,22,36,37] The Re–N bond lying *trans* to Re≡O or Re≡NAr is uniformly longer by 0.1–0.2 Å compared to the other Re–N bond.

In the unique oxo-imido dimer **7**[22] the Re–N(imido) [1.735(10) Å] and Re–O(oxo) [1.685(8) Å] distances are slightly longer than those in **6** and **4**. The oxygen bridge, highlighted in **8**, is unsymmetrical: Re(1)–O(2), 1.849(7) Å and Re(2)–O(2), 1.945(7) Å. Thus the Re(1)–O(2) bond has a large double bond character and this diminishes the bond order of Re(1)–O(1), as depicted by dotted lines in **8**.



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The same applies to the O(2)Re(2)N fragment but to a smaller degree. In simple terms, **7** can be described as a complex in which the rare *cis*-Re^VO_2 moiety acts as a monodentate oxygen donor ligand forming a coordinate bond with the Re^V(NAr) moiety.

In the $[Re^{III}(OPPh_3)Cl_3(NN)]$ species, (Table 4) Re–O (2.02–2.08 Å) is a single bond and the metal is no longer shifted towards the oxygen atom. Significant Re(NN) back-bonding is present particularly in the azoimine system. The Re–N(azo) bond is generally shorter than the Re–N(heterocyclic) bond (Table 4) implying involvement of π*(azo) orbitals. Indeed, the N–N(azo) distance in the complexes span the range 1.32–1.35 Å[22–24,27,43] as compared to 1.25 Å in free azo ligands. In the Re^VO and Re^V(NAr) complexes of azoimines back-bonding is expected to be unimportant but the N–N(azo) distance (1.25–1.31 Å) is still somewhat long possibly due to azo←Re←NAr type interactions.[5,22–24,31]

3.3 Metal Redox

The Re^{VI}/Re^V reduction potentials in $[Re^VOCl_3(NN)]$[19–24] and $[Re^V(NAr)Cl_3(NN)]$[5,20–24,29–31] span the ranges 1.5–2.2 and 0.8–1.5 V, respectively. The Re^{IV}/Re^{III} couple in $[Re^{III}(OPPh_3)Cl_3(NN)]$[19–25] occur in the domain 0.2–1.2 V. Representative data are collected in Table 5. The azo group is electron-withdrawing and in general azoimine complexes have higher $E_{1/2}$ values than diimine complexes. For a given (NN) ligand the Re^{VI}/Re^V reduction potential of an Re^V(NAr) complex is 0.6–0.8 V lower than that in the Re^VO congener reflecting the superior donor ability of NAr^{2-}. Although the $Re^{VI}O$ species are too unstable for chemical/electrochemical generation in solution in bulk quantities, it has been possible to obtain certain Re^{VI}(NAr) species such as $[Re^{VI}\{NC_6H_4Me(p)\}Cl_3(Meazpy)]^+$ in solution. It displays a six-line EPR spectrum (see Section 5.3) with $g = 1.96$ and $A = 540$ G.[5]

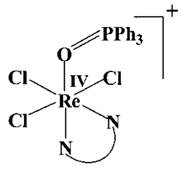
3.4 Bond Lengths Trends in a $Re^{III}(OPPh_3)/Re^{IV}(OPPh_3)$ Pair

The $[Re^{IV}(OPPh_3)Cl_3(NN)]^+$ system **9** can be generated by coulometric or dilute nitric acid oxidation of **5**.

Table 5. Reduction potential data [V vs. SCE] for $[Re^VOCl_3(NN)]$, $[Re^V(NAr)Cl_3(NN)]$, $[Re^{III}(OPPh_3)Cl_3(NN)]$, and $[Re^{III}(PPh_3)Cl_3(NN)]$ in acetonitrile solution at 298 [K].

(NN) ligand	Re^{VI}/Re^V [ReO][a]	Re^{VI}/Re^V [Re(NAr)][a],[b]	Re^{IV}/Re^{III} $[Re(OPPh_3)]$[a]	Re^{IV}/Re^{III} $[Re(PPh_3)]$[a]	Ref.
Mepyal	1.72[c]	0.96	0.30	0.62	[19,30,61]
C_6H_{11}dabd	1.72[c]	1.08[d]	0.69	–	[21]
Pyox	1.64	0.85	0.26[e]	0.59	[20,28]
Pyth	1.54	0.81	0.23[e]	0.57	[20,28]
Clazpy	1.91	1.38	0.98	1.20	[22,27]
Clazim	1.88[c]	1.21	0.82	1.08	[24]

[a] Chloride and (NN) ligand not shown. [b] Unless otherwise stated Ar = Ph. [c] Anodic peak potential. [d] Ar = $C_6H_4Cl(p)$. [e] Unpublished results.



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The complex $[Re^{IV}(OPPh_3)Cl_3(pyth)]^+$ has been isolated and characterized as the nitrate salt.[28] Its metal–ligand distances are compared with those of $[Re(OPMe_2Ph)Cl_3(pyth)]$ in Table 6. The lengths of the Re–O and Re–Cl bonds decrease by 0.06 Å due to radial contraction upon metal oxidation. On the other hand oxidation increases the average Re–N distance by 0.06 Å, reflecting considerable weakening of back-bonding in the $Re^{IV}(OPPh_3)$ system.

Table 6. Bond lengths [Å] in a pair of rhenium(IV)-rhenium(III) phosphane oxide complexes.[28]

	$[Re^{IV}(OPPh_3)Cl_3(pyth)]^{+[a]}$	$[Re^{III}(OPMe_2Ph)Cl_3(pyth)]$
Re–O	2.018	2.078
Re–N(py)	2.119	2.054
Re–N(azole)	2.123	2.063
Re–Cl[b]	2.310	2.376

[a] The asymmetric unit consists of two molecules and the lengths are average values. [b] Average value.

4. Oxygen Atom Transfer from Re^VO to Tertiary Phosphanes

4.1 Monophosphanes: Reactivity Trends and Reaction Model

Oxygen atom transfer reactions involving iron, molybdenum and tungsten sites are important in the chemistry of life.[38,39] Rhenium is not a biometal, but as an element in an adjacent periodic group transfer processes of Re^VO are of potential interest as reaction models. The reaction of interest here is stated in Equation (2). In dichloromethane solution the reaction follows second-order kinetics.

$$Re^V{\equiv}O + PPh_3 \rightarrow Re^{III}{-}O{=}PPh_3 \qquad (2)$$

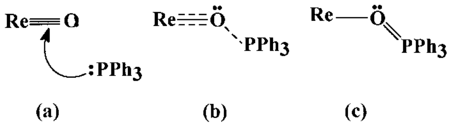
Selected rate data[19,20] are set out in Table 7. An increase in phosphane basicity makes the transfer reaction more facile, and PPh_2Me reacts nearly six times faster than PPh_3. Electron withdrawal from the Re^VO moiety via ligand modification hastens the transfer process. Thus, for $[ReOCl_3(Rpyal)]$ log *k* increases linearly with the Hammett constant of R (Me<H<Cl).[19] Finally, the $[ReOCl_3(pyox)]$ complex reacts nearly twice as fast as $[ReOCl_3(pyth)]$ which is qualitatively consistent with the heteroatom electronegetivity order O>S.[20]

Table 7. Rates of reactions of $[Re^VOCl_3(NN)]$ with phosphanes in dichloromethane solution.

(NN) Ligand	Phosphane	*T* [K]	10^3 *k* [$M^{-1}s^{-1}$][a]	Ref.
Mepyal	PPh_3	299	7.96	[19]
Hpyal	PPh_3	299	12.26	[19]
Clpyal	PPh_3	299	24.02	[19]
Pyox	PPh_3	302	4.18	[20]
Pyth	PPh_3	302	2.00	[20]
Mepyal	PPh_2Me	295	47.00	[19]
Pyox	PPh_2Me	302	24.80	[20]
Pyth	PPh_2Me	302	10.65	[20]
Pyox	$Ph_2P(CH_2)_4PPh_2$	308	30.67	[28]
Pyth	$Ph_2P(CH_2)_4PPh_2$	308	14.17	[28]

[a] Estimated standard deviation lie in the range 0.02–0.06.

For the ligands Mepyal, pyox and pyth the activation enthalpies (kcal mol^{-1}) are 8.91, 13.49 and 14.31 respectively while the activation entropies (cal K^{-1} mole^{-1}) are –38.69, –24.15 and –23.32 respectively.[19,20] The large and negative $\Delta S{\neq}$ values imply close association of $[Re^VOCl_3(NN)]$ and PPh_3 in the transition state. A model[20] of this association and subsequent events are stylized in **10** which has common features with oxygen atom transfer reactions of $Mo^{VI}O_2$ and $W^{VI}O_2$.[40–42]

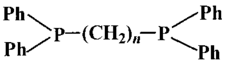


10

In **10** the full and broken lines, respectively, represent coordinate covalent bonds and weak links. In structurally characterized $[Re^{III}(OPPh_3)Cl_3(NN)]$ complexes the phosphorus atom uniformly lie within 2.8 Å from the centroids of one or both of the triangular OCl_2 faces (see **5**) whereas the distances from the two OClN centroids is greater than 3 Å. It is believed that phosphane attack occurs from the side away from the (NN) chelate ring.

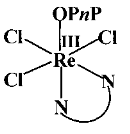
4.2 Diphosphanes: Single and Double Oxygen Atom Transfer

The diphosphanes used are of type **11** abbreviated as P*n*P (*n* = 1–4). The reaction of $[Re^VOCl_3(NN)]$ with excess P*n*P follows second-order kinetics[28] (Table 7) affording **12** which has a dangling phosphane function. The (NN) ligands examined include Mepyal,[27] pyox,[28] pyth,[28] Clazpy[27] and Clazim.[43] Spontaneous solution isomerization is an interesting feature of **12**, vide infra.



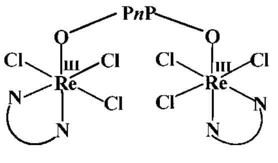
P*n*P

11



12

The reaction of excess $[Re^VOCl_3(NN)]$ with P*n*P leads to successive oxygen atom transfer furnishing binuclear **13** when $n > 1$.[27,43] In the case of P1P two atom transfer furnishes only mononuclear $[Re^{III}(OP1PO)Cl_3(NN)]$ (**14**). The dangling phosphane oxide function strongly implicates transient binucleation on the reaction pathway.



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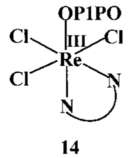


14

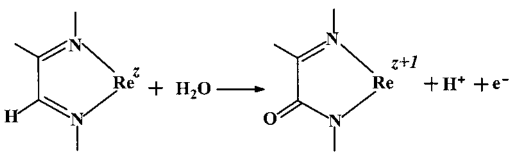
The instability of the binuclear intermediate leading to dissociation of one of the $ReCl_3(NN)$ fragment is due to the excessive steric crowding imposed by the short spacer ($n = 1$).[27]

Metal–ligand bond lengths in the species of type **12**–**14** are very similar to those in $[Re^{III}(OPPh_3)Cl_3(NN)]$ (Table 4). This close similarity extends to other properties including Re^{IV}/Re^{III} reduction potentials.[27,28,43]

5. Oxygen Atom Transfer from Water: Imine→Amide Oxidation

5.1 Re^{IV}(imineamide) Species: Synthesis and Reaction Model

The general reaction is stated in Equation (3) where the imineamide ligand in the product complex is monoanionic (Table 1). This reaction was first encountered in the case of $[Re^{III}(OPPh_3)Cl_3(Rpyal)]$ which afforded $[Re^{IV}(OPPh_3)Cl_3(Rpiam)]$.[19,25,26] The required oxidation equivalents could be provided electrochemically and/or chemically.[19]

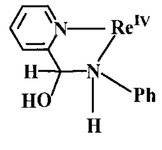


(3)

The quasireversible Re^{IV}/Re^{III} couple in $[Re^{III}(OPPh_3)Cl_3(Rpyal)]$ lie near 0.3 V (Table 5). The rhenium(IV) cation $[Re^{IV}(OPPh_3)Cl_3(Rpyal)]^+$, the actual reactive intermediate, is quantitatively afforded upon coulometry (0.5 V in dry MeCN). Upon regulated addition of H_2O to be the oxidized solution (after completion of coulometry) the spontaneous imine→amide reaction [Equation (3)] occurred and the final solution is found to contain $[Re^{III}(OPPh_3)Cl_3(Rpyal)]$ and $[Re^{IV}(OPPh_3)Cl_3(Rpiam)]$ in the mol ratio 2:1. Of the three electrons of Equation (3), one is accounted by the cathodic process corresponding to the anodic $Re^{III}\rightarrow Re^{IV}$ oxidation. The remaining two electrons are consumed by $[Re^{IV}(OPPh_3)Cl_3(Rpyal)]^+$ regenerating two mol of the precursor.

The imineamide complexes were isolated in excellent yields by oxidizing $[Re^{III}(OPPh_3)Cl_3(Rpyal)]$ with excess of chemical oxidants such as Ce^{IV} or H_2O_2 in wet solutions.[19] Here the aldimine→amide conversion proceed quantitatively since it is no longer necessary for $[Re^{IV}(OPPh_3)Cl_3(Rpyal)]^+$ to act as oxidant. Imineamide complexes of type $[Re^{IV}(OPPh_3)Cl_3(Riaam)]$ have been similarly prepared by oxidising the corresponding $[Re^{III}(OPPh_3)Cl_3(Rdabd)]$ precursors with H_2O_2.[21]

In the case of $[Re^{III}(OPPh_3)Cl_3(Hpyal)]$ the reaction rate was found to be first-order with respect to both $[Re^{IV}(OPPh_3)Cl_3(Hpyal)]^+$ and H_2O.[19] The $\Delta H\neq$ and $\Delta S\neq$ parameters are 13.4 $kcal\,mol^{-1}$ and –27.3 $cal\,K^{-1}\,mol^{-1}$, respectively.[19] Water attack is believed to occur on the aldimine π*-orbital furnishing the α-hydroxy amine intermediate **15** (Cl^- and $OPPh_3$ ligands not shown).



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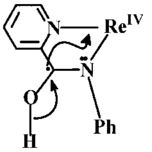

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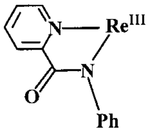

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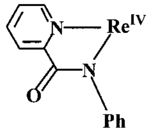


18

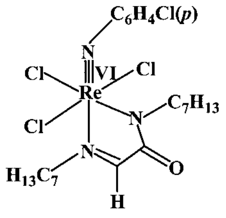
Instances of aqua adduct formation by aldimines have been documented.[44,45] The adduct **15** is however unstable and can undergo rapid transformation via induced transfer of two electrons.[46] The rational steps are: **15**→**16** (oxidative radical formation and proton dissociation), **16**→**17** (internal redox and proton dissociation), and **17**→**18** (metal oxidation). The net result is the imineamide complex **18**.[19]

The crucial requirement for realizing the imine→amide oxidation is the facile accessibility of two oxidation states (here Re^{III} and Re^{IV}) such that the higher state is able to affect sufficient electron withdrawal from the aldimine function to promote nucleophilic water attack. Aldimine→amide oxidation has earlier been documented in ruthenium[47] and iron[48,49] chemistry.

5.2 Re^{VI}(imineamide) Complexes: Regiospecificity and Steric Blockade

The reaction of Equation (3) has provided an elegant way for stabilizing the otherwise rare $Re^{VI}(NAr)$ moiety in the form of $[Re^{VI}(NAr)Cl_3(Rpiam)]$[29,30,50] and $[Re^{VI}(NAr)Cl_3(Riaam)]$[21] which have been isolated via chemical oxidation of $[Re^{V}(NAr)Cl_3(Rpyal)]$ and $[Re^{V}(NAr)Cl_3(Rdabd)]$ in wet solvents.

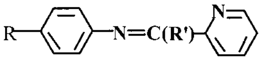
In the oxidation of the Rdabd complex there are two imine functions to choose from but structure determination of $[Re^{VI}(NC_6H_4Cl)Cl_3(C_7H_{13}iaam)]$ has revealed that the amide nitrogen lie exclusively *trans* to a chloride ligand as in **19** and not to the NAr ligand.[21] This is consistent with the reaction model considered in the previous section of this article. We recall that in $Re^{V}(NAr)$ complexes (see Section 5.1) the Re–N bond lying *trans* to the NAr group is elongated (*trans* influence) compared to the other Re–N bond.



19

The imine function supporting the shorter Re–N bond will thus be more polarized and subject to more facile nucleophilic attack by water. It is indeed this function that is selectively oxidized to amide.

The ketimine analogues, **20**, of Rpyal affords [Re^{V}(NAr)-Cl$_3$(NN)] type systems.[29] The R′ = Me complex was readily converted into the same amide chelate [Re^{VI}(NAr)-Cl$_3$(Rpiam)] obtained from [Re^{V}(NAr)Cl$_3$(Rpyal)]. But the R′ = Ph system failed to afford any amide complex. Space-filling structural models have revealed that the C=N function in the R′ = Ph system is greatly hindered due to aryl crowding making it inaccessible to nucleophilic water attack. In contrast the function is well exposed in the R′ = H/Me complexes.[29]



R' = Me, Ph

20

5.3 Structure and Properties

The structures of one Re^{IV}(OPPh$_3$) and a few Re^{VI}(NAr) imineamide complexes are known (Table 8). These have meridional geometry as in their precursors and the amide group, C–C(=O)–N is uniformly planar. In going from [Re^{III}(OPPh$_3$)Cl$_3$(Mepyal)] (Table 4) to [Re^{IV}(OPPh$_3$)-Cl$_3$(Mepiam)] (Table 8) the Re–O and Re–Cl distances decrease while the Re–N distances increase very significantly, reflecting decrease of both radius and extent of back-bonding upon metal oxidation (see also Section 3.3).

In the Re^{VI}(NAr) species[21,30] the metal atom is shifted from the Cl$_3$N plane towards the imido nitrogen by ca. 0.3 Å and the Re–N bond *trans* to the imide function is lengthened by 0.15 to 0.20 Å (Table 8). The radial changes between rhenium(v) and rhenium(vi) species are relatively small. The Re^{VI}–N(imide) length (1.70–1.72 Å) imply triple bonding as in Re^{V}–N(imide) (see Section 3.2). Outside our work structures of very few Re^{VI}N(imide) complexes are known.[29,51]

In [Re^{V}(NAr)Cl$_3$(diimine)] species the Re^{VI}/Re^{V} couple occur near 1.0 V (Table 5). In the corresponding imineamide complexes two one-electron couples (Re^{VI}/Re^{V} and Re^{VII}/Re^{VI}) occur near 0.2 and 1.5 V (Table 9).[21,19] The Re^{VI}/Re^{V} reduction potential is thus dramatically lowered upon imine oxidation reflecting stabilization of the hexavalent state by the amide function. A similar relationship applies to the Re^{IV}/Re^{III} and Re^{V}/Re^{IV} couples among diimine and imineamide complexes of Re(OPPh$_3$)Cl$_3$ (Table 5 and Table 9).[19]

Table 9. Reduction potentials [V vs. SCE] of Re(imineamide) species in MeCN at 298 [K].

Compound	Re$^{(z+1)+}$/Re^{z+}	Re$^{(z+2)+}$/Re$^{(z+1)+}$	Ref.
[Re^{IV}(OPPh$_3$)Cl$_3$(Mepiam)][a]	–0.46	1.26	[19]
[Re^{IV}(OPPh$_3$)Cl$_3$(C$_6$H$_{11}$iaam)][a]	–0.38[c]	1.66	[21]
[Re^{IV}(PPh$_3$)Cl$_3$(Mepiam)][a]	–0.15	1.19	[61]
[Re^{VI}(NC$_6$H$_4$Me)Cl$_3$(Mepiam)][b]	0.13	1.50	[29]
[Re^{VI}(NC$_6$H$_4$Cl)Cl$_3$(C$_6$H$_{11}$iaam)][b]	0.20	1.56	[21]

[a] $z = 3$. [b] $z = 5$. [c] Cathodic peak potential.

The Re^{VI}(NAr) complexes (t$_2$g^1) display six-line EPR spectra in fluid solution[21,29,30] corresponding to the $I = 5/2$ nuclei ^{185}Re and ^{187}Re which have nearly equal nuclear moments. The centre-field g value and average hyperfine splitting lie near 1.91 and 440 G, respectively.

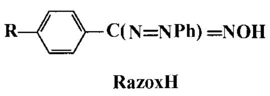
6. Oxygen Atom Transfer from Azooximes: Oxime→Imine Reduction

In this third type of transfer reaction a preoxidized imine i.e., an oxime function gives up the oxygen atom either to a metal site or to an oxophilic substrate.[52] The concerned oxime ligands are of type **21**, RazoxH (the terminal H is the dissociable oxime proton). Treatment of [Re^{III}(MeCN)-Cl$_3$(PPh$_3$)$_2$] with the silver salt of **21** in cold affords the azoimine complex **22** isolated as the PF$_6^-$ salt. On the other hand the reaction of [Re^{V}(NPh)Cl$_3$(PPh$_3$)$_2$] with **21** furnished the deprotonated azoimine chelated complex **23**. In contrast to **21** the oxime of 2-acetylpyridine reacts with [Re^{V}(NAr)Cl$_3$(PPh$_3$)$_2$] without oxygen atom transfer affording stable oximato complexes such as **24**. Bond parameters of **22**–**24** are listed in Table 3.

Table 8. Bond lengths [Å] in Re^{IV}(imineamide) and Re^{VI}(imineamide) complexes.

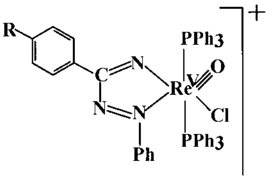
Compound	Re–O/N[a]	Re–N[b]	Re–N[c]	Re–Cl[d]	Ref.
[Re^{IV}(OPPh$_3$)Cl$_3$(Mepiam)]	2.003	2.091	2.070	2.345	[25]
[Re^{VI}(NC$_6$H$_4$Me)Cl$_3$(Mepiam)]	1.699	2.231	2.026	2.346	[29]
[Re^{VI}(NC$_6$H$_4$Cl)Cl$_3$(Mepiam)]	1.722	2.208	2.058	2.339	[30]
[Re^{VI}(NC$_6$H$_4$Cl)Cl$_3$(C$_7$H$_{13}$iaam)]	1.717	2.214	2.035	2.342	[21]

[a] Phosphane oxide O/imido N. [b] N atom *trans* to O/N. [c] N atom *cis* to O/N. [d] Average value.



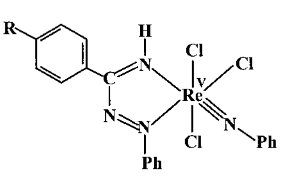
RazoxH

21



22

The azoimine ligand in **22** and **23** are not known in the free state. There is a report on the chelation of such ligands to bivalent palladium achieved via azooximates reduction.[53] The formation of **22** involves oxidative addition of the oxime function. Instances of such addition are in general rare,[54,55] particularly in rhenium chemistry.[56] Oxime→imine reduction by PPh_3 as in the formation of **23** has been documented in salicylaldoxime chemistry.[57,58] Outside certain dioximates,[59] **24** appears to be the only other structurally characterized oximato complex of rhenium.



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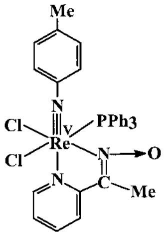
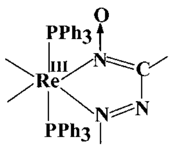


24

The system **25** involving the usual[60] azooxime chelation has been proposed as a possible intermediate in the formation of **22**. The crucial event is activation of oximato oxygen by the electron-withdrawing azo group leading to oxygen atom transfer to the metal site with concomitant displacement of a chloride ligand in *cis* position.[52]



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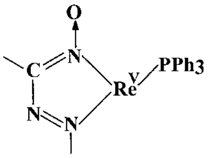


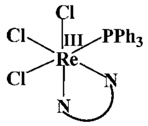
26

In analogy with **24**, the moiety **26** has been proposed to be the possible intermediate in the formation of **23**. Here, rhenium(V) acts as a Lewis acid activator[7] promoting oxygen atom transfer to PPh_3 followed by displacement of $OPPh_3$ by chloride. The relatively weak electron withdrawal by the imine function ensures stability of **24**.

7. Reaction of $[Re^{III}(OPPh_3)Cl_3(NN)]$ with PPh_3

7.1 Geometrical Isomerization

Meridional $[Re^{III}(OPPh_3)Cl_3(NN)]$ (**5**) undergoes facile displacement of coordinated $OPPh_3$ by PPh_3 furnishing facial $[Re^{III}(PPh_3)Cl_3(NN)]$ (**27**).[24,27,28,61] Metal–ligand bond parameters in selected species are listed in Table 10.



27

Table 10. Bond lengths in Re^{III}(phosphane) complexes.

Compound	Re–N[a]	Re–N[b]	Re–Cl[c]	Re–P	Ref.
$[Re^{III}(PPh_3)Cl_3(Hpyal)]$	2.103	2.083	2.379	2.463	[61]
$[Re^{III}(PPh_2Me)Cl_3(pyox)]$	2.110	2.098	2.383	2.414	[28]
$[Re^{III}(PPhMe_2)Cl_3(pyox)]$	2.089	2.060	2.365	2.373	[28]
$[Re^{III}(PPh_3)Cl_3(Clazpy)]$	2.077	1.994	2.359	2.510	[27]
$[Re^{III}(PPh_3)Cl_3(Clazim)]$	1.997	2.035	2.363	2.476	[24]
$[Re^{III}(P1PO)Cl_3(Clazpy)]$	2.072	2.007	2.363	2.479	[27]
$[Re^{III}(P1PO)Cl_3(Clazim)]$	2.050	2.055	2.375	2.476	[43]

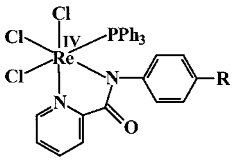
[a] Pyridine/imidazole N. [b] Imine/azo N. [c] Average value.

In **27** two π-acceptor ligands [PPh_3 and (NN)] are present and the net back-bonding is maximized in the facial geometry which ensures minimum competition between the acceptor sites for the same metal orbital. On the other hand in **5** the (NN) ligand can occupy any two *cis* positions and the net geometry is controlled by steric and electrostatic factors. Thus logical stable geometries of **5** and **27** are respectively meridional and facial as observed. Interestingly, the average Re–N distance in a phosphane complex is longer (by upto 0.06 Å) than that in the corresponding $OPPh_3$ complex (see Table 4 and Table 10) where (NN) alone does all the back-bonding. The geometrical selectively is strong and exclusive and in no case isomers have been observed. We recall that $[Re^{V}OCl_3(NN)]$ and $[Re^{V}(NAr)Cl_3(NN)]$ are meridional as expected.

7.2 Metal Redox, Imine→Amide Oxidation and Facial Re^{IV}(imineamide) Species

The Re^{IV}/Re^{III} reduction potential in **27** lie near 0.6 and 1.0 V for diimine and azoimine ligands respectively. These values are higher than those of the corresponding $OPPh_3$ complexes by 0.2–0.3 V (Table 5) reflecting the superior net back-bonding in the PPh_3 complexes.

The complex $[Re^{IV}(PPh_3)Cl_3(Rpyal)]^+$, electrogenerated in solution reacts spontaneously with water affording the corresponding facial imineamide system $[Re^{IV}(PPh_3)Cl_3(Rpiam)]$, **28**. In **28** (R = Cl) the Re–N(py), Re–N(amide), Re–P and Re–Cl(av) distances are 2.123, 2.061, 2.549 and 2.325 Å respectively.[61]



28

The average Re–Cl distance is thus shorter by 0.05 Å and the Re–P distance is longer by 0.1 Å than those in

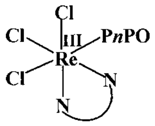
$[Re^{III}(PPh_3)Cl_3(Hpyal)]$ (Table 10) consistent with decrease of metal radius and the degree of back-bonding upon oxidation. The Re^{IV}/Re^{III} reduction potential in $[Re^{IV}(PPh_3)Cl_3(Mepiam)]$ is –0.15 V (Table 9)[61] again signifying the dramatic stabilizing influence of imineamide chelation as opposed to diimine chelation on higher oxidation states (see Section 5.3).

8. Twin Isomerization of $[Re^{III}(OP\mathit{n}P)Cl_3(NN)]$

8.1 The Reaction and Its Pathway

The meridional $[Re^{III}(OP\mathit{n}P)Cl_3(NN)]$ species, **12** undergo spontaneous intramolecular twin isomerization (linkage and geometrical), Equation (4), in solution furnishing facial $[Re^{III}(P\mathit{n}PO)Cl_3(NN)]$, **29**.[27,28,43] The metal–ligand bond lengths in type **29** complexes are very similar to those in **27** (Table 10), also **27** and **29** have very similar Re^{IV}/Re^{III} reduction potentials.[27,28,43]

$$[Re^{III}(OP\mathit{n}P)Cl_3(NN)] \rightarrow [Re^{III}(P\mathit{n}PO)Cl_3(NN)] \qquad (4)$$



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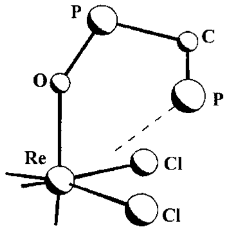
The reaction of Equation (4) follows first-order kinetics and is characterized by strongly negative entropy of activation (–20 to –40 cal K^{-1} mol^{-1}). A model for the association of the dangling phosphane function in the transition state (n = 1) is stylized in **30**.



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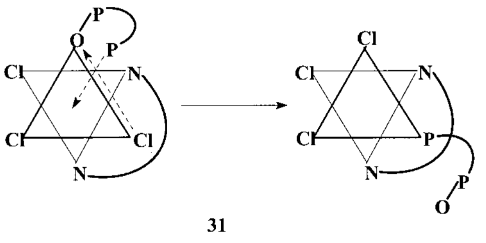
Subsequent attack by the P atom on the triangular face with concomitant edge displacement of a chloride ligand and Re–OP bond cleavage affords the facial complex as depicted in **31**.[27]



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8.2 Effect of Spacer Length and Metal Oxidation State

For the $[Re^{III}(OP\mathit{n}P)Cl_3(pyox)]$ and $[Re^{III}(OP\mathit{n}P)Cl_3(pyth)]$ complexes the rate of the twin isomerization reaction has been determined over the domain n = 1–4[28] (Table 11). The rate decreases approximately exponentially as n increases. The number of possible conformations of the dangling $(CH_2)_nPPh_2$ fragment is indeed expected to increase exponentially with increase of n,[62] but only a few of the conformations will be spatially suited (proximal metal and phosphane site) for the reaction to occur.

Table 11. Rate constants for the twin isomerization of $[Re^{III}(OPnP)Cl_3(pyox/pyth)]$ in CH_2Cl_2 at 308 [K].[28]

N	10^5 k [s^{-1}][a]	
	Pyox	pyth
1	8.42	3.62
2	4.07	1.80
3	1.58	0.72
4	0.67	0.25

[a] Estimated standard deviation lie in the range 0.02–0.05.

In the system $[Re^{IV}(OP1P)Cl_3(pyox/pyth)]^+NO_3^-$ prepared by treating the trivalent congener with dilute nitric acid (see also Section 3.4) the isomerization process is completely arrested even though it is n = 1 case which corresponds to maximum reactivity before oxidation. This is consistent with the kinetic inertness of rhenium(IV) ($5d^3$). Other factors also work in the same direction. Thus rhenium(IV) is a harder acceptor than rhenium(III) and oxygen is a harder donor than phosphorus. This as well as the weaker back-bonding ability of rhenium(IV) is expected to disfavor the attack of the metal by the dangling phosphane function.[28]

9. Bis and Tris Chelation: Rhenium(II) and Rhenium(I)

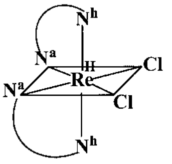
9.1 Ligand Choice, Synthesis, Magnetism and Metal Redox

Metal π-basicity would increase progressively upon reduction: $Re^{III}<Re^{II}<Re^{I}$. In designing (NN)-chelated complexes of the latter two oxidation states it is imperative that good π-acids are chosen. Azoheterocycles are excellent π-acceptors with low-lying π*(azo) orbitals.[17,18,63,64] These have indeed afforded bis and tris chelates of coordination types $[Re^{II}Cl_2(NN)_2]$, **32** and $[Re^{I}(NN)_3]^+$, **33** for the first time in rhenium chemistry.[31,65] In **32** and **33** N^a and N^h are azo and heterocyclic nitrogen atoms respectively. A remarkable feature is the exclusive occurrence of the geometrical forms depicted in **32** and **33**. For synthesis, $[Re^{V}OCl_3(PPh_3)_2]$ and/or $[Re^{V}O(OEt)Cl_2(PPh_3)_2]$ were used as starting materials. For assembling bis and tris chelates the Re:(NN) ratio used was 1:2.5 and 1:6 respectively.[31,65] In most cases the tris chelates were isolated as ReO_4^- salts.

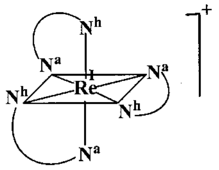
Table 12. Bond lengths[a] in rhenium(II) and rhenium(I) species and their reduction potentials [V vs. SCE] in MeCN.

Compound	Bond length [Å]			$Re^{(z+1)+}/Re^{z+}$	Ref.
	Re–N[b]	Re–N[c]	N=N		
$[Re^{II}Cl_2(Meazim)_2]$	2.003	2.051	1.34	0.44[d]	[65]
$[Re^{II}Cl_2(Clazpy)_2]$	1.99	2.07	1.33	0.70[d]	[65]
$[Re^{II}Cl_2(azbp)_2]$	2.00	2.06	1.35	0.50[d]	[31]
$[Re^{I}(Hazpy)_3]^+$	1.99	2.10	1.32	0.93[e]	[65]
$[Re^{I}(azbp)_3]^+$	1.98	2.11	1.34	0.60[e]	[31]
$[Re^{I}(CO)_3Cl(Clazpy)]$	2.158	2.153	1.273	1.65[e]	[68]
$[Re^{I}(CO)_3Cl(Hazpm)]$	2.173	2.136	1.271	1.60[e]	[70]
$[Re^{I}(CO)_3Cl(Clazim)]$	2.150	2.166	1.281	1.45[e]	[70]

[a] Average values in bis and tris chelates. [b] Azo N. [c] Heterocyclic N. [d] $z = 2$. [e] $z = 1$.



32



33

The bis-chelates are paramagnetic (t_{2g}^5) and in fluid solution these display well-resolved EPR spectra with six hyperfine lines. The centre-field g value and the average hyperfine splitting lie near 2.10 and 280 G, respectively[31,65] [compare with the Re^{VI}(NAr) case, see Section 5.3]. The tris chelates are diamagnetic (t_{2g}^6) and their ^{1}H NMR spectra reveal that the three chelate rings are magnetically equivalent consistent with the facial geometry. The bis and tris chelates display well defined Re^{III}/Re^{II} and Re^{II}/Re^{I} couples respectively (Table 12).

9.2 Structure, Back-Bonding and Isomer Specificity

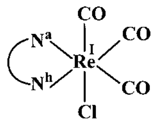
Selected average bond lengths[31,65] are listed in Table 12. The Re–N^a length is uniformly shorter than Re–N^h length by 0.05–0.1 Å and the average N–N distance is longer by 0.1 Å than that in uncoordinated azo ligands (1.25 Å). Clearly strong d(Re)-π*(azo) back-bonding is present [compare with rhenium(III) species, Section 3.2].

The observed geometrical disposition of the ClCl–N^{h}N^h–N^{a}N^a donor sites in $[ReCl_2(NN)_2]$ is uniformly *cis*-*trans*-*cis*, see **32**. Four other isomers are possible but none of these have been observed.[65] Similarly the tris-chelates were isolated exclusively in the facial form (no meridional isomer observed). The *cis* (as opposed to *trans*) disposition of two N^a donor sites as in **32** ensures maximum back-bonding. Further, **32** is sterically more favorable than other possible isomers. In facial **33** the three N^a atoms represent a model situation for back-bonding which more than offsets the steric disadvantage of the facial geometry.

Two comparisons are relevant. First, $[Os(N^aN^h)_3]^{2+}$ which is isoelectronic with $[Re(N^aN^h)_3]^+$ occur in isomeric forms, primarily meridional,[64] reflecting the π-basicity order $Re^I >> Os^{II}$. Second, tris chelation of 2,2′-bipyridine stabilizes the rhenium(II)[66] as opposed to rhenium(I) showing that azoheterocycles are superior π-acceptors than bipy.

10. Monochelation of $Re^I(CO)_3$ by (NN) and ($NN^{·-}$)

The $[Re^I(CO)_3Cl(NN)]$ system, **34**, results from the reaction of $[Re(CO)_5Cl]$ with azoimines.



34

The Re–N^a and Re–N^h distances (2.15 ± 0.02 Å) are nearly equal and the azo N–N distance lie close to 1.27 Å (Table 12).[67–70] Thus carbon monoxide does most of the back-bonding and the t_{2g} shell is greatly stabilized as reflected in the high Re^{II}/Re^{I} reduction potential (Table 12). A second one-electron couple (–0.6 to –0.1 V) assignable to azo reduction is also observed and the $[Re^I(CO)_3Cl(NN^{·-})]$ species so generated have been spectrally characterized in solution.[71]

The chloride ligand in $[Re^I(CO)_3Cl(NN^{·-})]$ is labile furnishing $[Re^I(CO)_3(MeCN)(NN^{·-})]$ in acetonitrile solution. These anion radical complexes, as well as $[Re^I(CO)_3(PPh_3)(NN^{·-})]$ and $[Re^I(CO)_3(imidazole)(NN^{·-})]$ derived from them have been isolated. These are EPR-active in solution with g values lying near 2.003. Six hyperfine lines representing a small metal contribution to the spin-bearing orbital are observed. Thus in $[Re^I(CO)_3(D)(Clazim^{·-})]$ coupling constants are 27.25, 28.75 and 39.1 G for D = MeCN, imidazole and PPh_3, respectively.[70]

11. Conclusion

New families of rhenium complexes incorporating chelation of conjugated (NN)-donors have been assembled in a rational manner. Systematic structural and electrochemical studies have revealed interesting trends of bond lengths and reduction potentials. Three types of oxygen atom transfer reactions have been encountered and their pathways scrutinized using rate and structural data. Unusual redox induced oxygen atom transfers from water and from the oximato function have respectively provided access to rare tetra-/hexa-valent imineamide and pentavalent azoimine systems. π-Basicity and back-bonding is a dominant feature of the lower oxidation states ($Re^{III} < Re^{II} < Re^{I}$) as reflected in bond parameters. This gets expressed in spontaneous isomerization upon substitution of phosphane oxide by phosphane, in the isomer specificity of bis/tris chelates of di-/mono-valent rhenium and in the stabilization of anion radical species. A concern of ongoing studies is the search for active complexes of new (NN) ligands and unusual atom transfer reactions.

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