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Article

Rhenium Chemistry of Azooximes: Oxygen Atom Transfer, Azoimine Chelation, and Imine–Oxime Contrast

Indranil Chakraborty,[†] Bikash Kumar Panda,[†] Jaydip Gangopadhyay,[†] and Animesh Chakravorty*,[†,‡]

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science,
Kolkata 700 032, India, and Jawaharlal Nehru Centre for Advanced Scientific Research,
Bangalore 560 064, India

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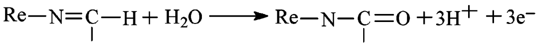
The concerned azooximes (L^1OH, **1**) are of type *p*-X-$C_6H_4C(N_2Ph)(NOH)$ (X = H, Me, Cl). The reaction of [Re(MeCN)$Cl_3(PPh_3)_2$] with [Ag(L^1OH)(L^1O)] in cold dichloromethane–acetonitrile solvent has furnished the green colored ionized azoimine complex [Re^V(O)Cl$(PPh_3)_2(L^1)$](PF_6), **2**. In effect L^1O^- has undergone oxidative addition, the oxygen atom being transferred to the metal site. Upon treatment of [Re^V(NPh)$Cl_3(PPh_3)_2$] with L^1OH in solution, the neutral azoimine complex [Re^V(NPh)$Cl_3(L^1H)$], **3**, resulted due to the spontaneous transfer of the oxime oxygen atom to a PPh_3 ligand, which is eliminated as $OPPh_3$. In contrast, the oxime of 2-acetylpyridine (L^2OH, **4**) did not undergo oxygen atom transfer and simply afforded the imine–oxime complex [$Re^V(NC_6H_4Y)Cl_2(PPh_3)(L^2O)$], **5**, upon reacting with [$Re^V(NC_6H_4Y)Cl_3(PPh_3)_2$] (Y = H, Me, Cl). The spectral and electrochemical properties of **2**, **3**, and **5** and the structures of three representative compounds are reported. In the cation of **2** (X = H) the two PPh_3 ligands lie trans to each other and the equatorial plane is defined by the five-membered azoimine chelate ring and the oxo and chloro ligands. The oxo ligand which forms a model triple bond (Re–O length 1.616(6) Å) lies cis to the imine-N atom. In **3** (X = Cl) the $ReCl_3$ fragment has meridional geometry and the imido nitrogen lies trans to the imine nitrogen of the planar azoimine chelate ring. In **5**·H_2O (Y = Me), the Cl, oximato-N, and P atoms define an equatorial plane and the pyridine-N lies trans to the imido-N. The water of crystallization is hydrogen bonded to the oximato oxygen atom (O···O, 2.829(5) Å). Reaction models in which chelation of the azooxime precedes oxygen atom transfer are proposed on the basis of oxophilicity of trivalent rhenium, Lewis acid activity of pentavalent rhenium, electron withdrawal by the azo group, and observed relative disposition of ligands in products.

Introduction

This work stems from our interest in variable-valent rhenium chemistry of conjugated nitrogen donor ligands especially α-diimines and azoimines.[1–4] A central concern has been oxygen atom transfer processes either from oxorhenium species to oxophilic substrates,[1,3b,5] eq 1, or from solvent water to an activated imine function leading to amide formation,[1a,e,2] eq 2. As a sequel to these studies, we have initiated search into the possible oxygen atom transfer behavior of rhenium systems based on ligands in which one of the donor sites is a preoxidized imine, i.e., an oxime function.

$$\mathrm{Re{\equiv}O + PR_3 \rightarrow Re{-}OPR_3} \qquad (1)$$



$$\mathrm{Re{-}N{=}\underset{|}{C}{-}H + H_2O \longrightarrow Re{-}N{-}\underset{|}{C}{=}O + 3H^+ + 3e^-} \qquad (2)$$

We were encouraged in this endeavor by the fact that rhenium–oxime coordination chemistry has so far witnessed

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* Author to whom correspondence should be addressed at the Indian Association for the Cultivation of Science. E-mail: icac@mahendra.iacs.res.in.

[†] Indian Association for the Cultivation of Science.

[‡] Jawaharlal Nehru Centre for Advanced Scientific Research.

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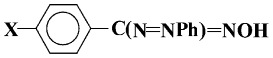
only limited attention. Oximes have been used for analytical separation and colorimetric estimation of rhenium.[6] In recent patents oxime complexes of rhenium have been scrutinized for diagnostic and therapeutic values.[7] However, structurally authenticated oxime-coordinated rhenium systems are very rare and little is known beyond a family of tris(dioximates).[8] In a di-2-pyridyl ketoxime complex of known structure, the oxime group is not coordinated to the metal.[9] Rhenium complexes have recently been shown to be potent catalysts for aldoxime dehydration[10] and to be good couplers of oximes with polar unsaturates such as nitriles.[11] But in these reactions rhenium−oxime coordination is not involved.

In this work we explore the rhenium chemistry of azooxime ligands characterized by the −N═N−C═NOH function. No complex incorporating chelation of the intact function could, however, be isolated. Instead depending on the metal oxidation state and coligands present, the oxime function was found to transfer the oxygen atom either to the metal site itself or to an oxophilic substrate like PPh_3 furnishing hitherto unknown azoimine chelates of pentavalent rhenium. An imine−oxime ligand bearing the −N═C−C═NOH function has also been examined. In striking contrast to the isoelectronic azooxime function it was found to engage in straightforward oxime chelation. The structures and properties of the new systems are reported, and attempts are made to rationalize the observed transfer reactions.

Results and Discussion

(A) Azooximes and Rhenium Reagents. 2-Arylazooximes are known to be versatile metal chelators.[12] Three of these (**1**, general abbreviation L^1OH) have been employed in this work either as such or as silver salts of type $[Ag(L^1O)(L^1OH)]$.[13]

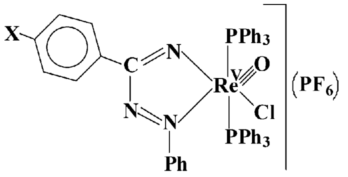


	X
$L^{1a}OH$	H
$L^{1b}OH$	Me
$L^{1c}OH$	Cl

1

To observe the effect of metal oxidation state and coligands, the reactions of L^1OH and its silver salt have been examined with a number of rhenium reagents. Stable complexes representing two kinds of oxygen atom transfer from the azooxime ligands have been observed in the cases of $[Re^{III}(MeCN)Cl_3(PPh_3)_2]$ and $[Re^V(NPh)Cl_3(PPh_3)_2]$.

(B) Transfer to Metal: Oxidative Addition. This has been realized in the case of the trivalent metal. Upon treatment of $[Re(MeCN)Cl_3(PPh_3)_2]$ with $[Ag(L^1O)(L^1OH)]$ taken in slight excess of 2 mol in *cold* mixed dichloromethane−acetonitrile solvent, a rapid reaction occurs. It is associated with color change from yellow to deep green and precipitation of silver chloride. From the reaction solution the green complex of composition $[Re^VOCl(PPh_3)_2(L^1)]PF_6$, **2**, was isolated in excellent yields upon addition of NH_4PF_6.



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No tractable product could be isolated by reacting $[Re(MeCN)Cl_3(PPh_3)_2]$ with L^1OH. Evidently Ag^+ facilitates halide displacement thus promoting ligand chelation, eq 3, which formally represents the oxidative addition of L^1O^- to the metal. Low temperature (<−5 °C) is crucial for the success of the reaction of eq 3; otherwise only a brown insoluble mass of uncertain nature resulted. The reaction of eq 3 proceeded unhindered in oxygen-free inert atmosphere (N_2/Ar) as it did in air, and dry solvents were as effective as the partially wet variety. The source of the oxo oxygen in **2** is thus the oxime function of the ligand.

$$[Re^{III}(MeCN)Cl_3(PPh_3)_2] + 2Ag^+ + L^1O^- \rightarrow [Re^V(O)Cl(PPh_3)_2(L^1)]^+ + 2AgCl \quad (3)$$

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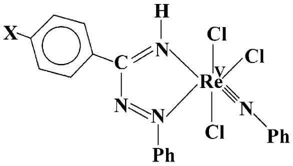
Known instances of oxidative addition of oximes to metal centers are very rare.[14] In rhenium chemistry the only known example[15] is the addition of acetoxime to $[\mathrm{Re^{I}Cl(N_2)(dppe)_2}]$ furnishing $[\mathrm{Re^{III}(OH)(N{=}CMe_2)(dppe)_2}]^+$, where dppe is 1,2-bis(diphenylphosphino)ethane.

(C) Transfer to Coligand. This happened upon reacting the pentavalent imido complex $[\mathrm{Re^{V}(NPh)Cl_3(PPh_3)_2}]$ with $\mathrm{L^1OH}$ in 1:1 ratio. The reaction, eq 4, could be carried out in dichloromethane solution at room temperature or more conveniently (faster, better yield) in boiling toluene. The resultant green solution afforded $[\mathrm{Re^{V}(NPh)Cl_3(L^1H)}]$, **3**, in good yield upon chromatographic workup. The crude solid before chromatography revealed the presence of $\mathrm{PPh_3O}$ both in IR ($\nu_{\mathrm{P-O}}$, 1180 cm^{-1}) as well as in ^{31}P NMR (δ, 28.918 ppm).

$$[\mathrm{Re^{V}(NPh)Cl_3(PPh_3)_2}] + \mathrm{L^1OH} \rightarrow [\mathrm{Re^{V}(NPh)Cl_3(L^1H)}] + \mathrm{OPPh_3} + \mathrm{PPh_3} \tag{4}$$



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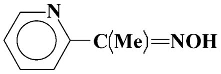
To our knowledge the only precedence of $\mathrm{PPh_3}$-promoted oxime → imine reduction in rhenium chemistry occurs in the reaction of $[\mathrm{Re^{V}OCl_3(PPh_3)_2}]$ with salicylaldoxime,[16] and a similar reaction has been documented in the case of ruthenium.[17]

(D) Imine−Oxime Chelation. With the hope of understanding the nature of the spontaneous atom transfer processes involving azooximes, we have investigated the behavior of an imine−oxime ligand, viz., the oxime of 2-acetylpyridine, **4** ($\mathrm{L^2OH}$). We found **4** to be unreactive toward $[\mathrm{Re(MeCN)Cl_3(PPh_3)_2}]$ in dichloromethane−methanol mixture even the presence of halide scavengers ($\mathrm{Ag^+}$ and $\mathrm{Tl^+}$). On the other Hand, $\mathrm{L^2OH}$ reacted smoothly with $[\mathrm{Re^{V}(NC_6H_4Y)Cl_3(PPh_3)_2}]$ (Y = H, Me, Cl) in dichloromethane solution at room temperature resulting in straightforward substitution of a chloride and a phosphine ligand via imine−oximato chelation affording the green complex $[\mathrm{Re^{V}(NC_6H_4Y)Cl_2(PPh_3)(L^2O)}]$, **5**, in very good yield.

(E) Spectra and Electrochemistry. The complexes (**2**, **3**, **5**) are uniformly diamagnetic (Re(V), 5d^2; $S = 0$). In dichloromethane solution both **2** and **3** display two moderately intense bands in the visible region (near 640 and 400 nm in **2** and near 600 and 440 nm in **3**). In **5** a relatively weak band near 700 nm is associated with a stronger band near 420 nm. Complexes of type **2** are characterized by single Re−Cl and Re−O stretches near 330 and 1000 cm^{-1}, respectively. On the other hand, in both **3** and **5** two Re−Cl stretches occur (near 350 and 320 cm^{-1} in **3** and near 320 and 300 cm^{-1} in **5**). Complexes **2** and **3** are characterized by an N═N stretch near 1420 cm^{-1} while in **5** C═N and N−O stretches occur near 1600 and 1230 cm^{-1}, respectively. The ^{1}H NMR spectra of the complexes are dominated by complex aromatic multiplets (6.5−8.2 ppm). The N−H group in **3** is observed both in IR (sharp band near 3250 cm^{-1}) and ^{1}H NMR (singlet near 9.60 ppm).



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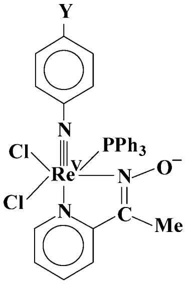

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All the complexes are electroactive in acetonitrile solution. An irreversible oxidation peak presumably corresponding to the $\mathrm{Re^{VI}/Re^{V}}$ couple is observed with anodic peak potential of ∼1.2 V vs SCE in **2** and ∼1.6 V in **3**. In **5** the corresponding response is quasireversible and occurs near 1.20 V. The potentials generally follow the Hammett order (Cl > H > Me).

(F) Structures. The X-ray structures of two azoimine complexes, $[\mathrm{ReOCl(PPh_3)_2(L^{1a})}]\mathrm{PF_6}$, **2** (X = H), and $[\mathrm{Re(NPh)Cl_3(L^{1c}H)}]$, **3** (X = Cl), and the imine−oxime complex, $[\mathrm{Re(NC_6H_4Me)Cl_2(PPh_3)(L^2O)}]\cdot\mathrm{H_2O}$, **5**$\cdot\mathrm{H_2O}$ (Y = Me), have been determined. Selected bond parameters are listed in Tables 1−3, and perspective views are shown in Figures 1−3.

In the cation of **2** (X = H) (Figure 1, Table 1), the O1, Cl1, N1, and N3 atoms along with the metal make a good equatorial plane (mean deviation 0.03 Å) and the phosphine ligands define the axis (P1−Re−P2, 174.68(7)°). The chelate ring itself makes a nearly perfect plane (mean deviation 0.005 Å) to which the pendent phenyl rings at C37 and N1 make the dihedral angles of 13.9 and 33.6°, respectively. The oxo atom lie cis to the imine nitrogen.

The Re−N1 bond (2.384(6) Å) lying trans to the oxo oxygen is much longer than the Re−N3 bond (2.022(6) Å) consistent with the strong trans influence of the oxo group. At 1.616(6) Å, the Re−O(oxo) bond is quite short as in only a few other $\mathrm{Re^{V}O}$ systems.[18] The idealized $\mathrm{Re^{V}{\equiv}O}(\sigma^2\pi^4)$ bond length is estimated to be 1.60 Å. In the majority of $\mathrm{Re^{V}O}$ complexes the Re−O distance however lies in the range 1.68 ± 0.03 Å[1a,3b,18a] corresponding to a bond order between two and three. The double-bonded $\mathrm{Re^{V}{=}O}$ distance is ∼1.76 Å.[19]

In **3** (X = Cl) (Figure 2, Table 2), the three chloride ligands are meridionally disposed as is usual in [Re$^{\mathrm{V}}$(NAr)-

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Table 1. Selected Bond Distances (Å) and Angles (deg) for Compound **2**$^+$ (X = H)

Distances			
Re−O1	1.616(6)	Re−P2	2.490(3)
Re−N1	2.384(6)	N1−N2	1.313(8)
Re−N3	2.022(6)	N2−C37	1.367(10)
Re−Cl1	2.375(2)	N3−C37	1.324(9)
Re−P1	2.521(3)		

Angles			
O1−Re−N3	90.5(3)	O1−Re−Cl1	105.0(2)
N3−Re−Cl1	164.5(2)	O1−Re−N1	159.2(3)
N3−Re−N1	68.9(3)	Cl1−Re−N1	95.7(2)
O1−Re−P2	90.5(2)	N3−Re−P2	92.9(2)
Cl1−Re−P2	86.12(8)	N1−Re−P2	93.0(2)
O1−Re−P1	91.8(2)	N3−Re−P1	91.8(2)
Cl1−Re−P1	88.67(8)	N1−Re−P1	86.4(2)
P2−Re−P1	174.68(7)	N3−C37−N2	118.4(7)

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound **3** (X = Cl)

Distances			
Re−N4	1.691(10)	Re−Cl2	2.347(4)
Re−N1	2.117(12)	Re−Cl3	2.392(4)
Re−N3	1.998(11)	N2−N3	1.293(14)
Re−Cl1	2.328(4)		

Angles			
N4−Re−N3	94.2(5)	N4−Re−N1	166.4(5)
N3−Re−N1	72.3(4)	N4−Re−Cl1	106.5(4)
N3−Re−Cl1	159.1(3)	N1−Re−Cl1	87.1(3)
N4−Re−Cl2	95.5(4)	N3−Re−Cl2	94.7(3)
N1−Re−Cl2	84.9(4)	Cl1−Re−Cl2	86.6(2)
N4−Re−Cl3	94.9(4)	N3−Re−Cl3	89.3(3)
N1−Re−Cl3	86.1(3)	Cl1−Re−Cl3	85.9(2)
Cl2−Re−Cl3	168.6(2)	C14−N4−Re	176.2(10)

Table 3. Selected Bond Distances (Å) and Angles (deg) for **5**·H_2O (Y = Me)

Distances			
Re−N3	1.725(3)	Re−Cl1	2.4003(12)
Re−N1	2.191(3)	Re−Cl2	2.3840(11)
Re−N2	2.099(3)	O1−N2	1.319(4)
Re−P	2.4521(11)		

Angles			
N3−Re−N2	90.6(2)	N3−Re−N1	163.95(14)
N2−Re−N1	73.41(12)	N3−Re−Cl2	106.15(12)
N2−Re−Cl2	162.38(10)	N1−Re−Cl2	89.89(8)
N3−Re−Cl1	97.62(12)	N2−Re−Cl1	86.04(9)
N1−Re−Cl1	82.82(9)	Cl2−Re−Cl1	86.34(5)
N3−Re−P	93.89(12)	N2−Re−P	101.24(9)
N1−Re−P	88.15(9)	Cl2−Re−P	83.38(5)
Cl1−Re−P	166.33(4)		

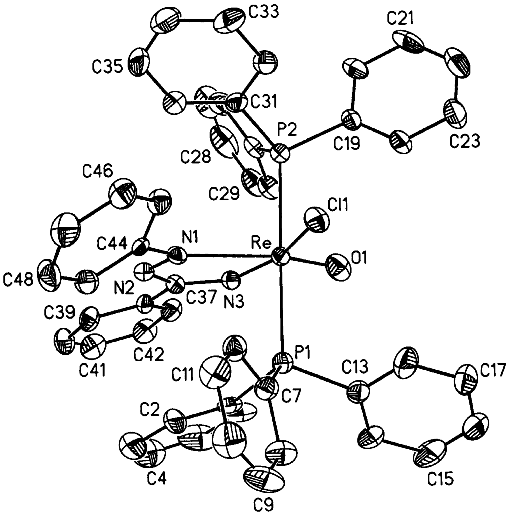

Figure 1. Perspective view and atom-labeling scheme of $[ReOCl(PPh_3)_2(L^{1a})]^+$, **2**$^+$ (X = H). All non-hydrogen atoms are represented by their 30% thermal probability ellipsoids.

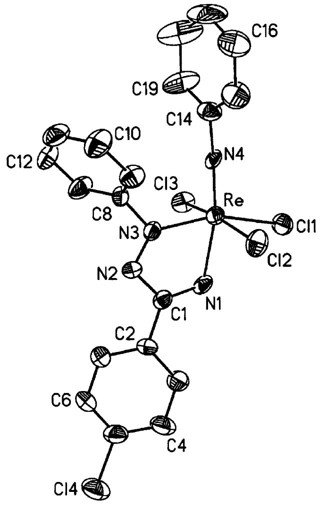

Figure 2. Perspective view and atom-labeling scheme of $[Re(NPh)Cl_3(L^{1c}H)$, **3** (X = Cl). All non-hydrogen atoms are represented by their 30% thermal probability ellipsoids.

Cl_3(NN)] type complexes.[1a−b,2b−c,3a−c] The N1, N3, N4, and Cl1 atoms define a good plane (mean deviation 0.03 Å) and the metal atom lies on it. The chelate ring is planar (mean deviation 0.03 Å), and the pendent aryl groups at C1 and N3 made dihedral angles of 17.8 and 61.4°, respectively, with it. The Re−N4−C14 fragment is approximately linear. The Re−N4 distance of 1.691(10) Å nearly corresponds to an idealized triple bond.[1a,b,2b,c,3b,20] The trans influence of the imido group is expressed in the lengthening of the Re−N1 bond by ~0.12 Å over the Re−N3 bond.

The ligand L^2O in **5**·H_2O (Y = Me) (Figure 3, Table 3) is chelated at the oximato and pyridine nitrogen atoms, and the $Re(L^2O)$ fragment (excluding methyl hydrogen atom) defines a satisfactory plane with mean deviation of 0.03 Å. The oximato and pyridine nitrogen atoms lie trans to Cl2 and imide N3, respectively. The Cl1, Cl2, N2, and P atoms define an approximate equatorial plane (mean deviation 0.05 Å) from which the metal is displaced toward N3 by 0.27 Å.

The Re−N1 distance, 2.191(3) Å, is significantly longer than that of the Re−N2 length, 2.099(3) Å, consistent with the trans influence of the imide nitrogen. The Re−N3 distance, 1.725(3) Å, is slightly longer than the corresponding Re−N(imido) distance in $[Re(NPh)Cl_3(L^{1c}H)]$. The water of crystallization is hydrogen bonded to the oximato oxygen atom, the O···O distance being 2.829(5) Å. Last, we note that outside tris(dioximates),[8] the present complex appears to be the only other structurally characterized oximato complex of rhenium.

(G) Reaction Models. Numerous light and heavy transition metal ions (3−5d) are known to undergo facile five-membered azooxime chelation.[12] It is logical to assume that similar binding precedes the transformations of eq 3 and 4.

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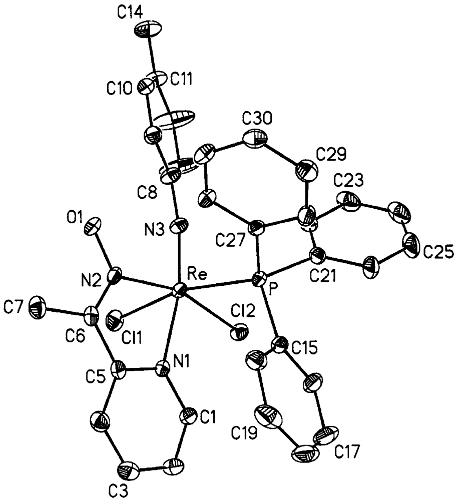
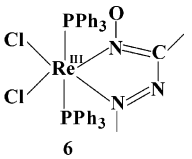


Figure 3. Perspective view and atom-labeling scheme of [Re(NC_6H_4Me)Cl_2(PPh_3)(L^2O)], **5** (Y = Me). All non-hydrogen atoms are represented by their 30% thermal probability ellipsoids.

We consider the reaction of eq 3 first. Trivalent rhenium is a good π-donor,[1c,2a,21] and the initial azooxime attack on $Re(MeCN)Cl_3(PPh_3)_2$ is expected to proceed via displacement of $MeCN/Cl^-$ ligands leaving the π-accepting PPh_3 ligands in place. In this model a possible reaction intermediate is **6**. Interestingly a stable 2,2′-bipyridine analogue of **6** is known.[22] The oxophilicity of rhenium(III) is well-documented.[23] This combined with the augmented oxygen atom transfer ability of the oxime function due to the pronounced electron-withdrawing character of the azo group[3b−c,24] is believed to promote the transfer reaction which results in the displacement of a chloride ligand from **6** by the newly formed oxo ligand affording **2**. Two observations are significant in this context. First, in **2** the imine and the oxo ligand lie cis to each other as expected. Second, in rhenium(III) chelates of N,N-coordinating azoheterocycles of type [Re^{III}(N,N)Cl_3(OPR_3)] the Re−Cl bond lying trans to the Re−N(azo) bond is invariably longer than the other Re−Cl bonds.[1c,d,3a−c] The transformation **6** → **2** would thus have the favorable feature that the weaker Re−Cl bond is displaced. (A reviewer of this work has observed that an O,N-bidentate chelate might be the intermediate instead of **6** and that the observed stereochemistry might only represent the thermodynamic structure.)



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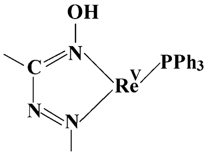
The structure of the acetylpyridine oxime complex **5** provides insight about the probable intermediate in the reaction of eq 4. The crucial feature is that the oxime and PPh_3 ligands lie cis to each other—the necessary relative placement for facile oxygen transfer to take place. In analogy an intermediate incorporating the moiety **7** is proposed to be the precursor to the azoimine complex **3**. The essential gross steps are oxygen atom transfer and displacement of $OPPh_3$ by Cl^- present in the reaction solution furnishing **8**, which is a fragment of **3**. In this transformation the rhenium(V) atom essentially acts as a Lewis acid activator[5b] and the electron-withdrawing azo group plays its part in facilitating oxygen atom transfer. Poor electron withdrawal by the imine function deactivates the imine−oxime complex **5**.



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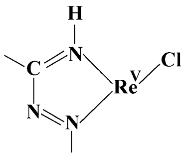

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Last, we note that the azoimine ligands as in **2** and **3** generated via metal-promoted oxygen atom transfer from oximato precursors are not known in the free state. There is one report on azoimine chelation of bivalent palladium achieved via ascorbic acid reduction of otherwise stable azooximates.[25]

Concluding Remarks

The main findings of this work will be briefly highlighted. Notable instances of metal-promoted oxime reactivity have been revealed. In reactions with rhenium reagents, the oxime function of 2-arylazooxime (L^1OH, L^1O^-) is found to be in a state of inherent redox activation leading to spontaneous oxygen atom transfer.

In the case of [Re^{III}(MeCN)Cl_3(PPh_3)$_2$], transfer occurs to the metal site furnishing [Re^V(O)(PPh_3)$_2$(Cl)(L^1)]$^+$, which incorporates a short Re≡O bond. Transfer occurs to a PPh_3 ligand (eliminated as $OPPh_3$) in the formation of [Re^V(NPh)Cl_3(L^1H)] from [Re^V(NPh)Cl_3(PPh_3)$_2$]. Authentic instances of azoimine (L^1H, (L^1)$^-$) chelation are rare in general and unprecedented in rhenium chemistry. In contrast to L^1OH, the imine−oxime ligand L^2OH engages rhenium in stable chelation as in [Re^V(NC_6H_4Y)Cl_2(PPh_3)(L^2O)].

A qualitative reaction model based on initial azooxime chelation has been developed on the basis of the considerations of oxophilicity of trivalent rhenium, Lewis acid activity of pentavalent rhenium, electron withdrawal by the azo group, and the observed relative dispositions of ligands in products.

Experimental Section

Materials. [Re(MeCN)Cl_3(PPh_3)$_2$],[23a] [Re(NC_6H_4Y)Cl_3(PPh_3)$_2$],[26] and 2-arylazooximes[27] and their silver salts[13] were prepared by

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reported methods. The oxime of 2-acetylpyridine was prepared by reaction of the ketone with hydroxylamine hydrochloride in aqueous alkaline solution.

Physical Measurements. UV−vis spectral measurements were carried out with a Shimadzu UV-1601 PC spectrophotometer. IR spectra were measured with Nicolet Magna IR 750 series II and 550 FAR IR and Perkin-Elmer L-0100 spectrometer. Proton NMR spectra were recorded on a Bruker FT 300 MHz spectrometer. The atom-numbering scheme used for ^{1}H NMR is the same as that used in crystallography. Spin−spin structure is abbreviated as follows: s, singlet. Electrochemical measurements were performed under nitrogen atmosphere using a model 620A electrochemical analyzer of CH Instruments with platinum working electrode. The supporting electrolyte was tetraethylammonium perchlorate (TEAP), and the potentials are referenced to the saturated calomel electrode (SCE) without junction correction. Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 series II elemental analyzer.

Synthesis of Complexes. Synthesis of [ReOCl(PPh$_3$)$_2$(L^1)]PF$_6$, 2. The two complexes were prepared by the same general procedure on the basis of the reaction of $[Re(MeCN)Cl_3(PPh_3)_2]$ with $[Ag(L^1O)(L^1OH)]$. Details are given below for a representative case.

[ReOCl(PPh$_3$)$_2$(L^{1a})]PF$_6$. To a solution of $[Re(MeCN)Cl_3(PPh_3)_2]$ (100 mg, 0.120 mmol) in 20 mL of dichloromethane−acetonitrile (1:1) was added $[Ag(L^{1a}O)(L^{1a}OH)]$ (128 mg, 0.260 mmol) at −7 °C (ice−salt mixture). The resulting solution was then stirred for 10 min affording a deep green solution that was filtered to remove AgCl, and to the stirred filtrate an excess of NH_4PF_6 (49 mg, 0.30 mmol) was added. The solvent was then removed under reduced pressure, and the solid thus obtained was thoroughly washed with water to free any excess of NH_4PF_6. The product was dried under vacuo over fused calcium chloride and then recrystallized from a dichloromethane−hexane mixture. Yield: 92 mg (71%). Anal. Calcd for $C_{49}H_{40}N_3OP_3F_6ClRe$: C, 52.76; H, 3.61; N, 3.77. Found: C, 52.83; H, 3.55; N, 3.81. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}); CH_2Cl_2 solution): 640 (7760); 400 (7700); 325 (13 300). IR (KBr, cm^{-1}): ν(Re−Cl) 330; ν(Re≡O) 1000; ν(N═N) 1416; ν(P−F) 850. ^{1}H NMR (δ (J, Hz); $CDCl_3$ solution): 6.76−7.66 (aromatic multiplets). E_{pa} (vs SCE, CH_3CN solution, scan rate 50 mV s^{-1}): 1.32 V.

[ReOCl(PPh$_3$)$_2$(L^{1b})]PF$_6$. Anal. Calcd for $C_{50}H_{42}N_3OP_3F_6ClRe$: C, 53.17; H, 3.75; N, 3.72. Found: C, 53.25; H, 3.70; N, 3.67. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}); CH_2Cl_2 solution): 640 (5700); 400 (6500); 325 (11 200). IR (KBr, cm^{-1}): ν(Re−Cl) 330; ν(Re≡O) 1000; ν(N═N) 1415; ν(P−F) 840. ^{1}H NMR (δ (J, Hz); $CDCl_3$ solution): 6.72−7.72 (aromatic multiplet); C(41)-Me, 2.58 (s). E_{pa} (vs SCE, CH_3CN solution, scan rate 50 mV s^{-1}): 1.18 V.

Synthesis of [Re(NPh)Cl$_3$(L^{1}H)], 3, Complexes. The two complexes were prepared by the same general procedure on the basis of the reaction of $[Re(NPh)Cl_3(PPh_3)_2]$ with L^{1}OH. The reaction took place in dichloromethane solution at room temperature, but best yields were rapidly obtained using boiling toluene as the solvent. Details of the reaction in toluene are given below for a representative case.

[Re(NPh)Cl$_3$(L^{1a}H)]. To a suspension of $[Re(NPh)Cl_3(PPh_3)_2]$ (100 mg, 0.110 mmol) in 25 mL of toluene was added 24 mg (0.110 mmol) of L^{1a}OH. The resulting mixture was heated to reflux for 1 h affording a green solution. The solvent was then removed under reduced pressure. The residue was extracted with toluene at room temperature and the extract concentrated to 5 mL and then subjected to chromatography on a silica gel column (20 × 1 cm, 60−120 mesh). Following elution with pure toluene, a green band was eluted with a toluene−acetonitrile (25:1) mixture. Solvent removal from the elute under reduced pressure afforded $[Re(NPh)Cl_3(L^{1a}H)]$ in pure form which was dried under vacuo over fused calcium chloride. Yield: 43 mg (66%). Anal. Calcd for $C_{19}H_{16}N_4Cl_3Re$: C, 38.49; H, 2.72; N, 9.45. Found: C, 38.40; H, 2.79; N, 9.54. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}); CH_2Cl_2 solution): 606 (1040); 445 (2600); 324 (7900). IR (KBr, cm^{-1}): ν(Re−Cl) 322, 350; ν(N═N) 1415; ν(N−H) 3250. ^{1}H NMR (δ (J, Hz); $CDCl_3$ solution): 7.21−8.03 (aromatic multiplet); 9.63 (s, N−H). E_{pa} (vs SCE, CH_3CN solution, scan rate 50 mV s^{-1}): 1.62 V.

[Re(NPh)Cl$_3$(L^{1c}H)]. Anal. Calcd for $C_{19}H_{15}N_4Cl_4Re$: C, 36.38; H, 2.41; N, 8.93. Found: C, 36.47; H, 2.47; N, 8.86. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}); CH_2Cl_2 solution): 605 (1300); 443 (3900); 327 (9000). IR (KBr, cm^{-1}): ν(Re−Cl) 320, 350; ν(N═N) 1416; ν(N−H) 3251. ^{1}H NMR (δ (J, Hz); $CDCl_3$ solution): 7.22−7.97 (complex multiplet); 9.59 (s, N−H). E_{pa} (vs SCE, CH_3CN solution, scan rate 50 mV s^{-1}): 1.66 V.

Synthesis of [Re(NC$_6$H$_4$Y)Cl$_2$(PPh$_3$)(L^{2}O)] Complexes. The three complexes were prepared by the same general procedure on the basis of the reaction of $[Re(NC_6H_4Y)Cl_3(PPh_3)_2]$ with L^{2}OH in dichloromethane solution. Details are given below for a representative case.

[Re(NC$_6$H$_4$Me)Cl$_2$(PPh$_3$)(L^{2}O)]. To a solution of $[Re(NC_6H_4Me)Cl_3(PPh_3)_2]$ (100 mg, 0.109 mmol) in 25 mL of dichloromethane was added 24 mg (0.174 mmol) of L^{2}OH. The resulting solution was stirred for 3 h at room temperature, during which the color of the solution become yellowish green. The solution was concentrated and then subjected to chromatography on a silica gel column (25 × 1 cm, 60−120 mesh). Excess L^{2}OH was first eluted with dichloromethane, and then a yellowish green band was eluted with benzene−acetonitrile (25:1) mixture. Solvent removal from the latter elute under reduced pressure afforded $[Re(NC_6H_4Me)Cl_2(PPh_3)(L^2O)]$ as a yellowish green solid, which was dried under vacuo over fused calcium chloride. Yield: 67 mg (82%). Anal. Calcd for $C_{32}H_{29}N_3OPCl_2Re$: C, 50.59; H, 3.85; N, 5.53. Found: C, 50.64; H, 3.89; N, 5.58. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}); CH_2Cl_2 solution): 690 (400); 422 (4800); 338 (9100). IR (KBr, cm^{-1}): ν(Re−Cl) 300, 320; ν(C═N) 1600; ν(N−O) 1235. ^{1}H NMR (δ (J, Hz); $CDCl_3$ solution): 6.19−8.02 (complex multiplet); 2.94 (s, C6−Me); 2.11 (s, C11-Me). $E_{1/2}$ (vs SCE, CH_3CN solution, scan rate 50 mV s^{-1}): 1.16 V (ΔE_p = 80 mV).

[Re(NC$_6$H$_5$)Cl$_2$(PPh$_3$)(L^{2}O)]. Anal. Calcd for $C_{31}H_{27}N_3OPCl_2Re$: C, 49.93; H, 3.65; N, 5.64. Found: C, 50.00; H, 3.62; N, 5.60. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH_2Cl_2 solution): 696 (430); 414 (5200); 339 (8800). IR (KBr, cm^{-1}): ν(Re−Cl) 292, 315; ν(C═N) 1599; ν(N−O) 1241. ^{1}H NMR (δ (J, Hz) $CDCl_3$ solution): 6.20−8.02 (complex multiplet): 2.96 (s, C6−Me). $E_{1/2}$ (vs SCE, CH_3CN solution, scan rate 50 mVs^{-1}): 1.17 V (ΔE_p = 80 mV).

[Re(NC$_6$H$_4$Cl)Cl$_2$(PPh$_3$)(L^{2}O)]. Anal. Calcd for $C_{31}H_{26}N_3OPCl_3Re$: C, 47.73; H, 3.36; N, 5.39. Found: C, 47.78; H, 3.41; N, 5.35. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}); CH_2Cl_2 solution): 692 (440); 415 (4600); 338 (7900). IR (KBr, cm^{-1}): ν(Re−Cl) 295, 318; ν(C═N) 1605; ν(N−O) 1229. ^{1}H NMR (δ (J, Hz); $CDCl_3$ solution): 6.20−8.01 (complex multiplet); 2.99 (s, C6−Me). $E_{1/2}$ (vs SCE, CH_3CN solution, scan rate 50 mV s^{-1}): 1.18 V (ΔE_p = 80 mV).

X-ray Structure Determination. Single crystals of **2** (X = H) (0.30 × 0.25 × 0.20 mm^3), **3** (X = Cl) (0.40 × 0.30 × 0.20 mm^3), and **5**·H_2O (Y = Me) (0.35 × 0.25 × 0.20 mm^3) were grown by slow diffusion of hexane into dichloromethane solutions at room temperature. Cell parameters were determined by a least-squares fit of 30 machine-centered reflections (2θ = 14−28°). Data were collected with the ω-scan technique on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Two check reflections measured after every 198

Table 4. Crystal Data for Complexes **2** (X = H), **3** (X = Cl), and **5**·H_2O (Y = Me)

param	**2** (X = H)	**3** (X = Cl)	**5**·H_2O (Y = Me)
formula	$C_{49}H_{40}ClF_6N_3OP_3Re$	$C_{19}H_{15}Cl_4N_4Re$	$C_{32}H_{31}Cl_2N_3O_2PRe$
M	1116.41	627.35	777.67
system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	10.928(4)	12.502(7)	10.785(2)
b/Å	12.915(6)	10.023(5)	10.884(2)
c/Å	17.026(10)	17.870(9)	14.212(3)
α/deg	100.88(4)	90	78.63(3)
β/deg	93.53(4)	105.13(5)	78.53(3)
γ/deg	99.78(3)	90	74.49(3)
V/Å^3	*2315(2)*	*2162(2)*	*1557.0(5)*
Z	2	4	2
D/mg m^{-3}	*1.602*	*1.928*	*1.659*
T/K	293(2)	293(2)	293(2)
μ/mm^{-1}	2.851	6.129	4.159
tot. reflcns	5138	3982	5326
unique reflcns (R_{int})	4993 (0.0307)	3779 (0.0682)	5326 (0.0000)
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0374, 0.0801	0.0629, 0.1496	0.0261, 0.0666
all data	0.0518, 0.1059	0.0971, 0.1847	0.0280, 0.0726

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum(F_o^2)^2]^{1/2}$.

reflections showed no significant intensity reduction in any case. All data were corrected for Lorentz−polarization effects, and an empirical absorption correction[28] was done on the basis of the azimuthal scan of six reflections for the crystals.

The metal atom was located from Patterson maps, and the rest of the non-hydrogen atoms emerged from successive Fourier syntheses. The structures were refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms (except H1 for **3** (X = Cl), which was emerged from successive Fourier syntheses and refined isotropically) were added at calculated positions. Calculations were performed using the SHELXTL, version 5.03,[29] program package. Significant crystal data are listed in Table 4.

Acknowledgment. We thank the Department of Science and Technology, Council of Scientific and Industrial Research, New Delhi, India, for financial support. Thanks are due to Dr. Sangeeta Banerjee for performing preliminary experiments.

Supporting Information Available: For $[ReOCl(PPh_3)_2(L^{1a})]PF_6$, **2** (X = H), $[Re(NPh)Cl_3(L^{1c}H)]$, **3** (X = Cl), and $[Re(NC_6H_4Me)Cl_2(PPh_3)(L^2O)]\cdot H_2O$, **5**·$H_2O$ (Y = Me), crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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