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Article

Rhenium Chemistry of Diazabutadienes and Derived Iminoacetamides Spanning the Valence Domain II–VI. Synthesis, Characterization, and Metal-Promoted Regiospecific Imine Oxidation

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The reaction of diazabutadienes of type R′N═C(R)─C(R)═NR′, L (R = H, Me; R′ = cycloalkyl, aryl) with $\mathrm{Re^{V}OCl_3(AsPh_3)_2}$ has furnished $\mathrm{Re^{V}OCl_3(L)}$, **1**, from which $\mathrm{Re^{III}(OPPh_3)Cl_3(L)}$, **2**, and $\mathrm{Re^{V}(NAr)Cl_3(L)}$, **3**, have been synthesized. Chemical oxidation of **2**(R = H) by aqueous H_2O_2 and of **3**(R = H) by dilute HNO_3 has yielded $\mathrm{Re^{IV}(OPPh_3)Cl_3(L')}$, **5**, and $\mathrm{Re^{VI}(NAr)Cl_3(L')}$, **4**, respectively, where L′ is the monoionized iminoacetamide ligand $\mathrm{R'N{=}C(H){-}C({=}O){-}NR'^{-}}$. Finally, the reaction of $\mathrm{Re^{V}O(OEt)X_2(PPh_3)_2}$ with L has furnished bivalent species of type $\mathrm{Re^{II}X_2(L)_2}$, **6**(X = Cl, Br). The X-ray structures of **1** (R = Me, R′ = Ph), **3** (R = H, R′ = Ph, Ar = Ph), and **4** (R = H, R′ = cycloheptyl, Ar = C_6H_4Cl) are reported revealing meridional geometry for the $ReCl_3$ fragment and triple bonding in the ReO (in **1**) and ReNAr (in **3** and **4**) fragments. The *cis* geometry (two Re–X stretches) of $\mathrm{ReX_2(L)_2}$ is consistent with maximized $\mathrm{Re^{II}}$–L back-bonding. Both $\mathrm{ReX_2(L)_2}$ and $\mathrm{Re(NAr)Cl_3(L')}$ are paramagnetic ($S = {}^1/_2$) and display sextet EPR spectra in solution. The *g* and *A* values of $\mathrm{Re(NAr)Cl_3(L')}$ are, respectively, lower and higher than those of $\mathrm{ReX_2(L)_2}$. All the complexes are electroactive in acetonitrile solution. The $\mathrm{Re(NAr)Cl_3(L)}$ species display the $\mathrm{Re^{VI}/Re^{V}}$ couple near 1.0 V versus SCE, and coulometric studies have revealed that, in the oxidative transformation of **3** to **4**, the reactive intermediate is $\mathrm{Re^{VI}(NAr)Cl_3(L)^+}$ which undergoes nucleophilic addition of water at an imine site followed by induced electron transfer finally affording **4**. In the structure of **3** (R = H, R′ = Ph, Ar = Ph), the Re–N bond lying *trans* to the chloride ligand is ∼0.1 Å shorter than that lying *trans* to NPh. It is thus logical that the imine function incorporating the former bond is more polarized and therefore subject to more facile nucleophilic attack by water. This is consistent with the regiospecificity of the imine oxidation as revealed by structure determination of **4** (R = H, R′ = cycloheptyl, Ar = C_6H_4Cl).

Introduction

Prototypic of a large family of conjugated nitrogen-donor ligands, 1,4-diazabutadienes[1] are of abiding interest in transition metal chemistry. Recent studies have concerned topics such as unusual compound types,[2] coordinated radical anions,[3] redox-promoted transformations,[4] and polymerization catalysis,[5] as well as photophysical and photochemical phenomena.[6] The present work has originated from our interest in the rhenium chemistry of conjugated nitrogen-donor ligands.[7−12] As for 1, 4-diazabutadienes, the activities reported so far from different laboratories have been mostly limited to tricarbonyl species incorporating monovalent rhenium.[6e,13−15] This has prompted us to probe the scope of variable-valent diazabutadiene chemistry of the metal with special reference to higher oxidation states.

Herein we report the first diazabutadiene monochelates incorporating the $\mathrm{Re^{V}O}$ core from which the corresponding $\mathrm{Re^{V}NAr}$ and $\mathrm{Re^{III}OPPh_3}$ species have been synthesized. Regiospecific metal-promoted ligand oxidation of the $\mathrm{Re^{V}}$-

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NAr and $\mathrm{Re^{III}OPPh_3}$ complexes have, respectively, afforded the $\mathrm{Re^{VI}NAr}$ and $\mathrm{Re^{IV}OPPh_3}$ cores monochelated by iminoacetamide ligands. Finally, bis diazabutadiene chelates of bivalent rhenium have been obtained via reduction of $\mathrm{Re^{III}}$-$\mathrm{OPPh_3}$ species. Representative compounds have been structurally characterized. The spectral and electrochemical features of this remarkable variable-valent family are scrutinized, and rationales are proposed for the transformations observed.

Results and Discussion

(A) Synthesis. The diazabutadiene ligands $\mathrm{L^1}$− $\mathrm{L^7}$ (general abbreviation, L) used in the present work and the types of complexes (**1**−**3**, **6**) synthesized are listed in Scheme 1. Also listed in the scheme are the monoionized iminoacetemide ligands $\mathrm{L'^1}$−$\mathrm{L'^4}$ (general abbreviation, L′) which have been isolated only in their coordinated form as complexes of type **4** and **5**. A summary of the syntheses of complexes arranged according to metal oxidation state is given in Scheme 2.

Scheme 1

Ligands

$\mathrm{R'N{=}C(R)\text{-}C(R){=}NR'}$ (L)

$\mathrm{R'N{=}C(R)\text{-}C({=}O)\text{-}\overline{NR'}}$ (L′)

R	R′		
H	cyclopentyl	$\mathrm{L^1}$	$\mathrm{L'^1}$
H	cyclohexyl	$\mathrm{L^2}$	$\mathrm{L'^2}$
H	cycloheptyl	$\mathrm{L^3}$	$\mathrm{L'^3}$
H	phenyl	$\mathrm{L^4}$	$\mathrm{L'^4}$
Me	phenyl	$\mathrm{L^5}$	
Me	p-tolyl	$\mathrm{L^6}$	
Me	p-chlorophenyl	$\mathrm{L^7}$	

Types of Complexes

$\mathrm{ReOCl_3(L)}$, **1**

$\mathrm{Re(OPPh_3)Cl_3(L)}$, **2**

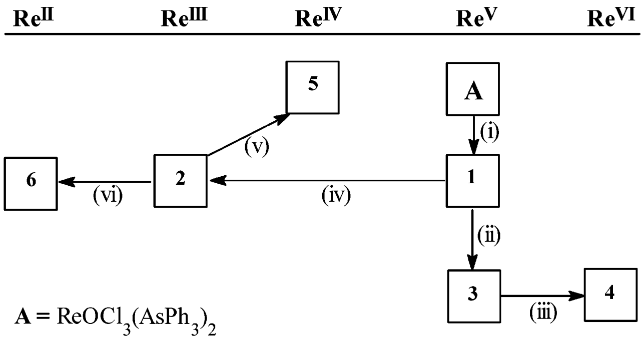
$\mathrm{Re(NAr)Cl_3(L)}$, **3**

$\mathrm{Re(NAr)Cl_3(L')}$, **4**

$\mathrm{Re(OPPh_3)Cl_3(L')}$, **5**

$\mathrm{ReX_2(L)_2}$, **6**

Scheme 2 [a]



[a] Summary of syntheses: (i) L, benzene; (ii) $\mathrm{ArNH_2}$, toluene; (iii) dil $\mathrm{HNO_3}$, acetonitrile; (iv) $\mathrm{PPh_3}$, benzene; (v) $\mathrm{H_2O_2}$, acetonitrile; (vi) L/$\mathrm{PPh_3}$, benzene.

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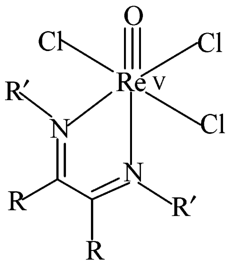
The golden yellow oxo complexes of type $Re^VOCl_3(L)$, **1**, were prepared in excellent yields by reacting $ReOCl_3(AsPh_3)_2$ with L in boiling benzene, eq 1. Use of the arsine precursor is crucial. The reaction of the more common phosphine analogue $ReOCl_3(PPh_3)_2$ with L yielded only the phosphine oxide complex $Re^{III}(OPPh_3)Cl_3(L)$, **2**, evidently due to facile oxygen atom transfer between the initially generated $ReOCl_3(L)$ and liberated PPh_3. Indeed, preformed $ReOCl_3(L)$ was found to rapidly oxidize PPh_3 in solution, eq 2. Under the same conditions $AsPh_3$ is unreactive to $ReOCl_3(L)$.



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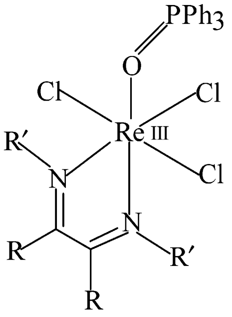


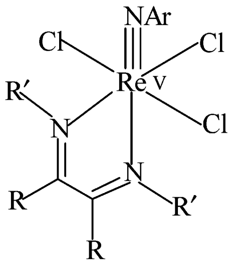
2

$$ReOCl_3(AsPh_3)_2 + L \rightarrow ReOCl_3(L) + 2AsPh_3 \qquad (1)$$

$$ReOCl_3(L) + PPh_3 \rightarrow Re(OPPh_3)Cl_3(L) \qquad (2)$$

In this context, we note that pyridylaldimines[7] and pyridylazoles[16] which bear a formal analogy of L in terms of the α-diimine function react relatively slowly with PPh_3, and their oxo complexes are readily accessible from $ReOCl_3(PPh_3)_2$.

The reaction of $ReOCl_3(L)$ with excess primary aromatic amines ($ArNH_2$) yielded pink imido species of type $Re(NAr)Cl_3(L)$, **3**, via the acid−base reaction of eq 3. In the case of R′ = aryl ligands (L^4−L^7), the imido complexes could also be prepared by simply reacting $ReOCl_3(PPh_3)_2$ with excess L in boiling toluene, the imido group originating from partial break-up of L. Indeed, this is the best method for the synthesis of $Re(NC_6H_5)Cl_3(L^4)$ for which the oxo precursor was difficult to isolate.



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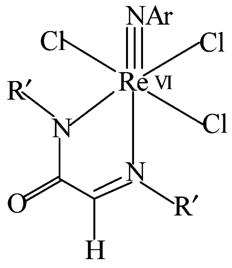


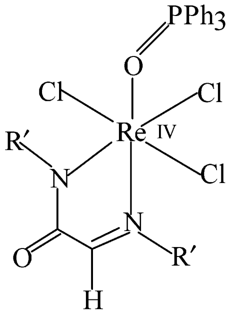
4

$$ReOCl_3(L) + ArNH_2 \rightarrow Re(NAr)Cl_3(L) + H_2O \qquad (3)$$

The type **3** complexes having R = H (ligands L^1−L^4) undergo facile oxidation of one of the imino groups to an amide function upon treatment with dilute nitric acid. The product is the iminoamide rhenium(VI) system, **4**. The net reaction involves a molecule of water as stated in eq 4 (the electrons are consumed in the reduction of nitric acid). The nature of the reaction will be scrutinized in a latter section.

$$Re(NAr)Cl_3(L) + H_2O \rightarrow Re(NAr)Cl_3(L') + 3e^- + 3H^+ \qquad (4)$$

The phosphine oxide complexes of type **2** having R = H also undergo a similar reaction furnishing $Re^{IV}(OPPh_3)Cl_3(L')$, **5**. Here, hydrogen peroxide is the most convenient oxidizing agent.



5

Transition metal chelates of ligands of type L′ are rare, and to our knowledge, only a few iron[17] and ruthenium[4b] systems have been reported so far.

In the presence of free L, $Re(OPPh_3)Cl_3(L)$ is reduced by PPh_3, furnishing the bis chelates $Re^{II}Cl_2(L)_2$, **6**(X = Cl). Both the X = Cl and X = Br analogues are also obtainable from

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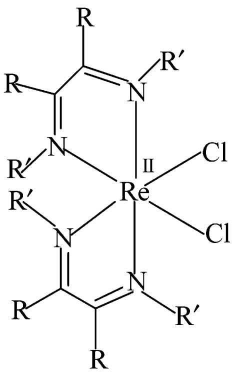
ReO(OEt)X$_2$(PPh$_3$)$_2$. Bivalent rhenium is a relatively rare 5d^5



6

oxidation level.[18,19] The first examples of the ReX$_2$(NN)$_2$ coordination sphere to which **6** also belongs were realized only recently.[19,20]

Meridionally disposed ReCl$_3$ is expected to give rise to three Re−Cl stretches of which all or at least two are observed (300−360 cm^{-1}) in the compounds of type **1**−**5**. On the other hand, the bis chelate ReCl$_2$(L^6)$_2$ and its bromo analogue display two well-resolved Re−X stretches at 317, 304 and 229, 213 cm^{-1}, respectively, consistent with *cis* geometry. The Re$\equiv$O stretch in **1** and P=O stretch in **2** and **5** occur as strong bands near 1000 and 1120 cm^{-1}, respectively. Complexes **1**−**3** and **6** generally show two C=N stretches (1450−1500 and 1570−1600 cm^{-1}). Two amide bands in the regions 1550−1580 and 1610−1630 cm^{-1} occur in **4** and **5**. The diamagnetic (5d$_{xy}^2$) ReOCl$_3$(L) and Re(NAr)-Cl$_3$(L) species exhibit normal ^{1}H NMR spectra while the spectra of Re(OPPh$_3$)Cl$_3$(L) are paramagnetically shifted.[11,16] Spectral data of the complexes are listed in the Experimental Section.

(B) Structures. Three compounds furnished single crystals suitable for structure determination: ReOCl$_3$(L^5), Re(NC$_6$H$_5$)-Cl$_3$(L^4), and Re(NC$_6$H$_4$Cl)Cl$_3$(L′^{3}). Molecular views are shown in Figures 1−3, and selected bond parameters are listed in Tables 1 and 2.

In all three compounds, the distorted octahedral coordination sphere incorporates meridional disposition of the chloride ligands. The Cl1, Cl2, Cl3, and N2 atoms define a nearly perfect plane in Re(NC$_6$H$_4$Cl)Cl$_3$(L′^{3}) and good planes (mean deviation ~0.02 Å) in both ReOCl$_3$(L^5) and Re(NC$_6$H$_5$)Cl$_3$-(L^4). The metal atom is uniformly displaced from the plane by 0.28−0.30 Å toward the O/N3 atom. In both ReOCl$_3$-(L^5) and Re(NC$_6$H$_5$)Cl$_3$(L^4), the five-membered chelate ring is excellently planar (mean deviation ~0.02 Å), and the pendent phenyl groups of the L ligand make dihedral angles in the range 50−80° with the chelate planes. On the other hand, in Re(NC$_6$H$_4$Cl)Cl$_3$(L′^{3}) the chelate ring is only roughly planar, primarily due to a 0.26 Å shift of the amide N2 atom from the otherwise good plane (mean deviation, 0.02 Å) defined by the remaining four atoms. The two cycloheptyl rings are puckered in two different ways (inset in Figure 3). The amide atoms C15, C16, O, and N2 make a perfect plane. The C15−C16 and C16−N2 bonds are both longer by ~0.07

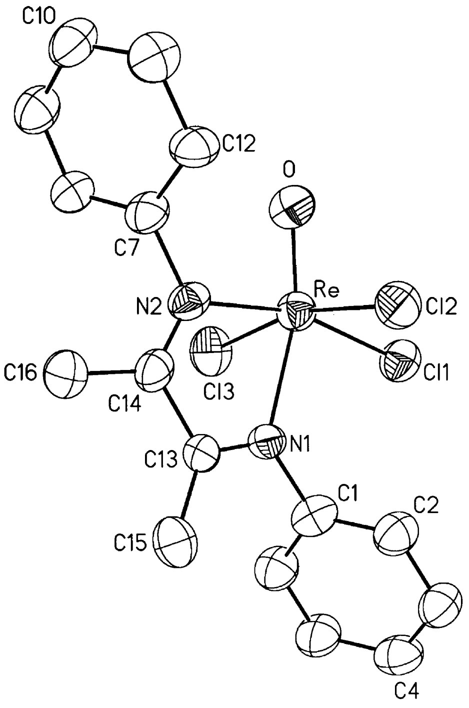


Figure 1. Perspective view and atom-labeling scheme of ReOCl$_3$(L^5). All non-hydrogen atoms are represented by their 30% thermal probability ellipsoids.

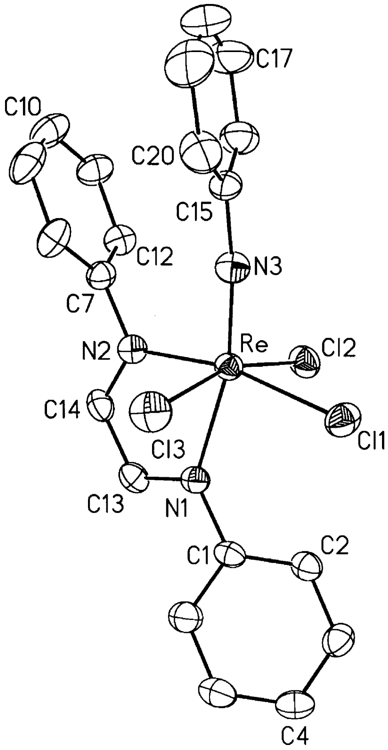


Figure 2. Perspective view and atom-labeling scheme of Re(NC$_6$H$_5$)Cl$_3$-(L^4). All non-hydrogen atoms are represented by their 30% thermal probability ellipsoids.

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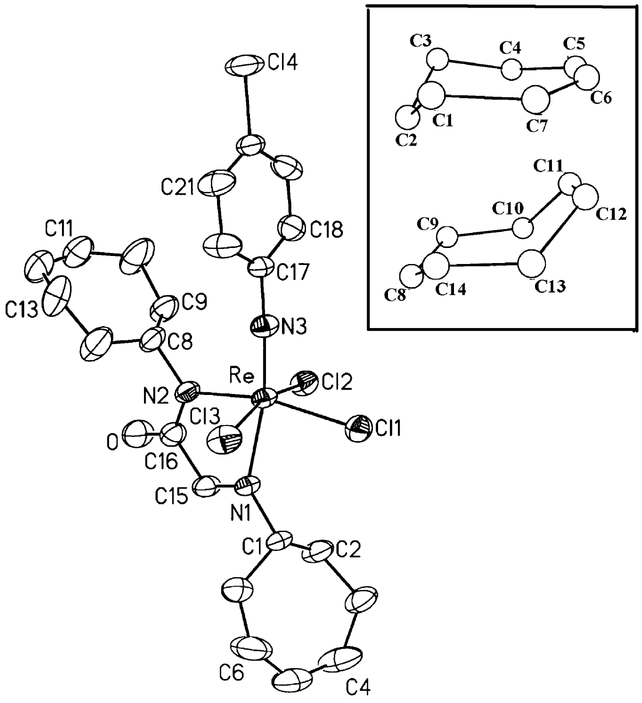

Figure 3. Perspective view and atom-labeling scheme of $Re(NC_6H_4Cl)Cl_3(L'^3)$. All non-hydrogen atoms are represented by their 30% thermal probability ellipsoids. The inset shows conformations of the two cycloheptyl rings.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Compound $ReOCl_3(L^5)$

	Distances		
Re−O	1.646(13)	Re−Cl3	2.303(5)
Re−N1	2.171(14)	N1−C13	1.29(2)
Re−N2	2.07(2)	N2−C14	1.26(2)
Re−Cl1	2.257(5)	C13−C14	1.43(2)
Re−Cl2	2.335(5)		
	Angles		
O−Re−N2	88.9(6)	O−Re−N1	160.4(6)
N2−Re−N1	71.6(6)	O−Re−Cl1	107.7(5)
N2−Re−Cl1	163.4(4)	N1−Re−Cl1	91.8(4)
O−Re−Cl3	99.2(5)	N2−Re−Cl3	90.1(4)
N1−Re−Cl3	82.7(4)	Cl1−Re−Cl3	87.2(2)
O−Re−Cl2	95.0(5)	N2−Re−Cl2	91.0(4)
N1−Re−Cl2	84.1(4)	Cl1−Re−Cl2	87.7(2)
Cl3−Re−Cl2	165.7(2)		

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds $Re(NC_6H_5)Cl_3(L^4)$ and $Re(NC_6H_4Cl)Cl_3(L'^3)$

	$[Re(NC_6H_5)Cl_3(L^4)]$	$[Re(NC_6H_4Cl)Cl_3(L'^3)]$
	Distances	
Re−N3	1.704(6)	1.717(4)
Re−N1	2.194(6)	2.214(3)
Re−N2	2.032(6)	2.035(4)
Re−Cl1	2.343(2)	2.3460(13)
Re−Cl2	2.377(3)	2.3397(13)
Re−Cl3	2.347(2)	2.3409(14)
N1−C13	1.306(10)	
N2−C14	1.294(9)	
C13−C14	1.406(10)	
N1−C15		1.259(6)
N2−C16		1.345(6)
C15−C16		1.492(6)
	Angles	
N3−Re−N2	90.8(3)	94.6(2)
N2−Re−N1	73.4(2)	75.85(13)
N2−Re−Cl1	166.8(2)	164.12(10)
N3−Re−Cl3	97.8(2)	96.33(13)
N1−Re−Cl3	82.5(2)	81.04(10)
N3−Re−Cl2	97.8(2)	97.76(13)
N1−Re−Cl2	83.3(2)	85.51(10)
Cl3−Re−Cl2	164.07(8)	165.66(5)
N3−Re−N1	164.2(3)	169.8(2)
N3−Re−Cl1	102.4(2)	100.65(14)
N1−Re−Cl1	93.4(2)	89.18(10)
N2−Re−Cl3	91.1(2)	93.90(12)
Cl1−Re−Cl3	86.46(9)	88.88(6)
N2−Re−Cl2	91.6(2)	87.58(12)
Cl1−Re−Cl2	87.25(9)	85.97(5)

Å, and the C15−N1 bond is shorter by ~0.05 Å than the corresponding bonds in $Re(NC_6H_5)Cl_3(L^4)$. This is consistent with the loss of conjugation in going from the diimine to the iminoamide function.

In $ReOCl_3(L^5)$, the Re−O length, 1.646(13) Å, lies within the range 1.68 ± 0.03 Å observed in most structurally characterized Re^VO species.[7,11a,21] Idealized $Re^V{\equiv}O$ and $Re^V{=}O$ distances have been estimated to be approximately 1.60 and 1.76 Å, respectively.[11a,21,22] The observed bond length in the present complex is thus indicative of a bond order lying close to three as idealized in **1**. In $Re(NC_6H_5)Cl_3(L^4)$, the Re−N3 distance, 1.704(6)Å, lies close to the idealized triple bond (Re≡NAr) length of 1.69 Å.[8,9,16,23] The Re−N3−C15 fragment is approximately linear. The *trans* influence of the oxo and the NAr groups is evident in the lengthening of the Re−N1 bond compared to the Re−N2 bond by ~0.10 Å in both $ReOCl_3(L^5)$ and $Re(NC_6H_5)Cl_3(L^4)$.

An increase of the metal oxidation state in going from $Re(NC_6H_5)Cl_3(L^4)$ to $Re(NC_6H_4Cl)Cl_3(L'^3)$ only marginally affects metal−ligand bond lengths: the average Re−Cl distance decreases by ~0.02 Å while the Re−N3 and Re−N1 lengths increase by ~0.02 Å. The Re−N3 bond length, 1.717(4)Å, and the linearity of the ReNAr fragment in $Re(NC_6H_4Cl)Cl_3(L'^3)$ imply triple bonding, $Re^{VI}{\equiv}NAr$. Very few imido complexes of rhenium(VI) have so far been structurally characterized.[8,9,24,25]

The compounds of type $Re(OPPh_3)Cl_3(L)$, $Re(OPPh_3)Cl_3(L')$, and $ReX_2(L)_2$ did not afford single crystals. The former two are believed to retain the meridional geometry of the parent oxo complex on the basis of previous results on other species.[7,11,16] For $ReX_2(L)_2$, the *cis* geometry for **6** is expected to be more stable than the *trans* form due to superior Re−L back-bonding.[19,20] IR spectral data are indeed consistent (vide supra) with the *cis* configuration of the isolated compounds.

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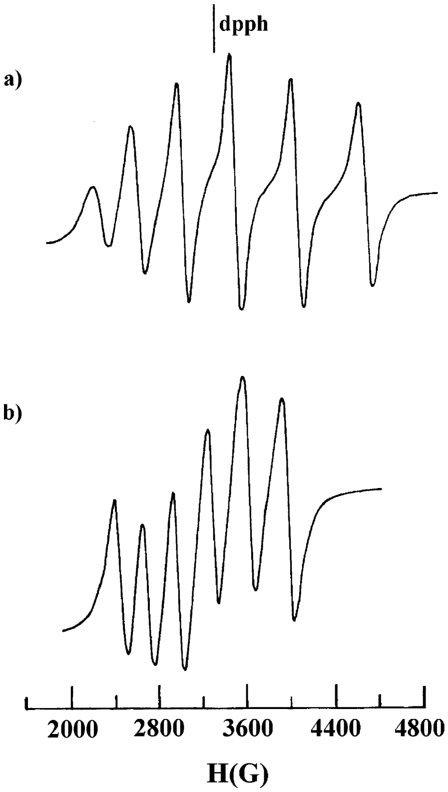

Figure 4. X-band EPR spectrum of (a) $Re(NC_6H_4Cl)Cl_3(L'^3)$ and (b) $ReBr_2(L^6)_2$ in dichloromethane solution (300 K). Instrument settings: power, 30dB; modulation, 100 kHz; sweep center, 3200 G.

(C) Magnetism and EPR Spectra of $Re^{VI}(NAr)Cl_3(L')$ and $Re^{II}X_2(L)_2$. The $Re(NAr)Cl_3(L')$ complexes have one unpaired electron (idealized $t_{2g}{}^1$) although the observed magnetic moment is smaller than the spin-only value due to strong orbital coupling.[8,26] Representative room temperature (300 K) magnetic moment values are $Re^{VI}(NC_6H_4Cl)Cl_3(L'^1)$, 1.50 μB, and $Re^{VI}(NC_6H_4Cl)Cl_3(L'^3)$, 1.45 μB. The EPR-active complexes are unusual[8,9,26b] in displaying well-resolved hyperfine lines in solution at room temperature (Figure 4). The sextet spectrum ($I = {}^5/_2$) is due to both ^{185}Re (37.07%) and ^{187}Re (62.93%), the nuclear moments of which differ only slightly (1%), leaving isotopic fine structure unresolved. The separation between adjacent hyperfine lines is variable (320−640 G) due to second order effects.[27] Center-field *g* values and average hyperfine splittings are listed in Table 3. The magnetic moment of $ReCl_2(L^6)_2$ is 1.89 μB (300 K) corresponding to the idealized $t_{2g}{}^5$ configuration. The bis chelates also show sextet EPR spectra in solution with an average hyperfine splitting of ~330 G (variable splitting range 260−440 G). A representative spectrum is shown in Figure 4, and the relevant parameters are listed in Table 3. Significantly, the *g* and *A* values of the lower valent complex ($t_2{}^5$) are, respectively, higher and lower than those of the higher valent complex ($t_2{}^1$).

Table 3. EPR Spectral Data at 300 K in Dichloromethane Solution

compd	g^a	A^b
$Re(NC_6H_4Cl)Cl_3(L'^1)$	1.917	484
$Re(NC_6H_4Cl)Cl_3(L'^2)$	1.910	483
$Re(NC_6H_4Cl)Cl_3(L'^3)$	1.912	484
$Re(NC_6H_4Cl)Cl_3(L'^4)$	1.899	483
$ReCl_2(L^2)_2$	2.090	330
$ReCl_2(L^6)_2$	2.085	345
$ReBr_2(L^6)_2$	2.091	305

[a] At center field. [b] Average values.

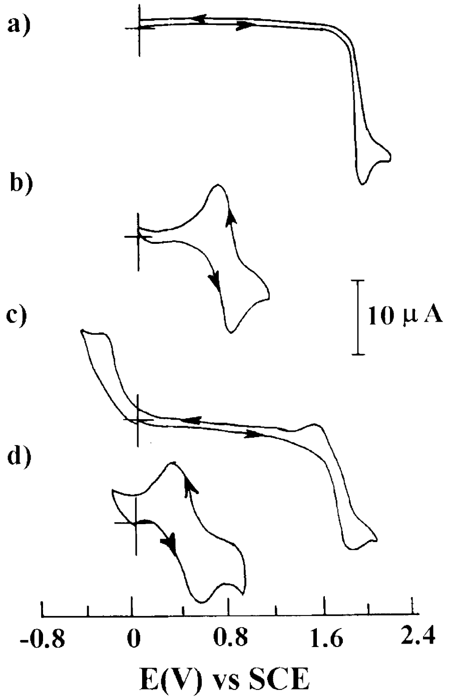

Figure 5. Cyclic voltammograms of ~10^{-3} M solutions of (a) $ReOCl_3(L^7)$, (b) $Re(OPPh_3)Cl_3(L^1)$, (c) $Re(OPPh_3)Cl_3(L'^2)$, and (d) $ReCl_2(L^6)_2$ in acetonitrile solution.

(D) Ligand Control of Valence and Reduction Potentials. All the complexes are electroactive in acetonitrile solution. Cyclic voltammetric reduction potential data are given in the Experimental Section, and representative voltammograms are shown in Figures 5 and 6.

The strong donor (σ and π) O^{2-} and NAr^{2-} coligands are suited for stabilizing (multiple dative bonds) higher oxidation states, and in combination with L, the state isolated is rhenium(V). In $ReOCl_3(L)$, an anodic response occurs near 1.7 V, believed to be due to $Re^VO \rightarrow Re^{VI}O$ oxidation, the oxidized complex being too reactive to survive for the cathodic scan. The NAr^{2-} ligand imparts better redox stability to the hexavalent state (see also the next section), and $Re(NAr)Cl_3(L)$ displays a quasireversible Re^{VI}/Re^V couple near 1.0 V. The $OPPh_3$ ligand is a much weaker donor (σ only) than the oxo group and is suited for the stable binding of rhenium(III). The quasireversible Re^{IV}/Re^{III} couple in $Re(OPPh_3)Cl_3(L)$ occurs near 0.6 V. The L ligand is a good σ donor, and it is also a π acceptor.[3] In the absence of strongly donor coligands, it can thus support low oxidation states as in the bis chelate, $ReX_2(L)_2$, which displays the Re^{III}/Re^{II} couple near 0.4 V. On the other hand, the anionic iminoamide ligand L′ is a stronger σ donor and much weaker π acceptor

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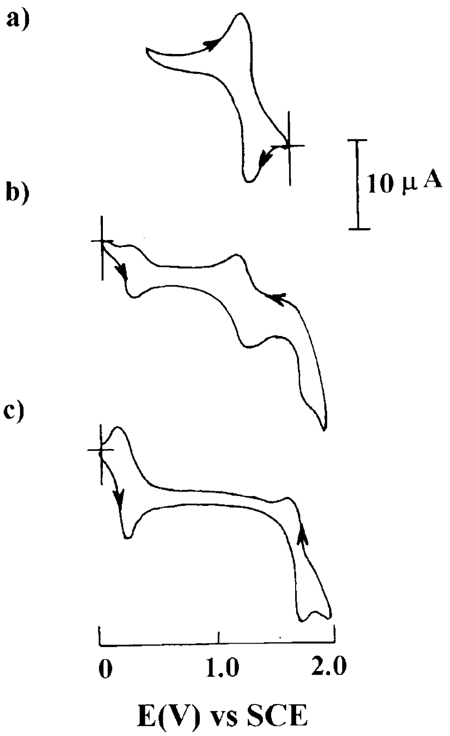


Figure 6. Cyclic voltammograms (in dry acetonitrile) of (a) coulometrically generated $Re(NC_6H_4Cl)Cl_3(L^2)^+$, (b) the product obtained after solvent removal following the reaction of $Re(NC_6H_4Cl)Cl_3(L^2)^+$ with water (see text), (c) $Re(NC_6H_4Cl)Cl_3(L'^2)$.

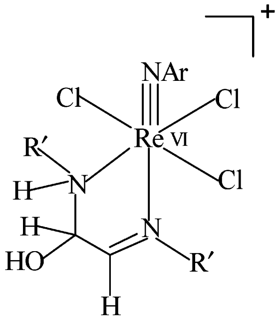
than L. Consistent with this, the isolated oxidation level increases by one unit in going from L to L′ chelation for both the Re(NAr) and $Re(OPPh_3)$ species. In $Re(NAr)Cl_3(L')$, quasireversible Re^{VI}/Re^{V} and Re^{VII}/Re^{VI} couples are observed near 0.2 and 1.5 V, respectively. Compared to the parent L complex, there is a remarkable ∼0.8 V decrease in the Re^{VI}/Re^{V} reduction potential. In $Re(OPPh_3)Cl_3(L')$, the Re^{IV}/Re^{III} and Re^{V}/Re^{IV} couples occur near −0.4 and 1.7 V, respectively.

In summary, the increase of metal reduction potentials with ligands/coligands can be categorized in three groups: $L' \ll L$; $L \ll (L)_2$; $NAr^{2-} < O^{2-} \ll OPPh_3$. These trends are generally consistent with donor−acceptor properties of the ligands/coligands and with the observed stabilization of the different oxidation states under ambient conditions.

(E) Imine Oxidation and Its Regiospecificity. The representative case of $Re^{V}(NC_6H_4Cl)Cl_3(L^2)$ will be considered first. Constant potential coulometry of this complex at 1.2 V in dry acetonitrile furnished the cation $Re^{VI}(NC_6H_4Cl)Cl_3(L^2)^+$ whose cyclic voltammogram (Figure 6a; initial scan cathodic) is the same as that of the parent complex (initial scan anodic). Upon making the solvent moist, the cation is transformed to the amide complex $Re^{VI}(NC_6H_4Cl)Cl_3(L'^2)$ but with regeneration of a part of the parent complex. The residue obtained by removal of the solvent at the end of the transformation was subjected to cyclic voltammetry, and current height data revealed that $Re^{VI}(NC_6H_4Cl)Cl_3(L'^2)$ ($E_{1/2}$; 0.19 V) and $Re^{V}(NC_6H_4Cl)Cl_3(L^2)$ ($E_{1/2}$; 1.08 V) are present in 1:2 proportion (Figure 6b). The absorption spectrum of the product in the visible region was also consistent with that of a 1:2 mixture of the two compunds. The other $Re(NAr)Cl_3(L)$ complexes behaved similarly, and the formation of the amide complex from the reactive intermediate $Re(NAr)Cl_3(L)^+$ can be logically represented by the reaction of eq 5. When the oxidation is carried out by an external oxidant like aqueous nitric acid the regenerated $Re(NAr)Cl_3(L)$ is reoxidized to react again as in eq 5, thus increasing the net yield of the amide complex.

$$3Re(NAr)Cl_3(L)^+ + H_2O \rightarrow Re(NAr)Cl_3(L') + 2Re(NAr)Cl_3(L) + 3H^+ \quad (5)$$

It is logical to propose[4b,7−9,10a] that the crucial step in the reaction is the nucleophilic addition of water to $Re(NAr)Cl_3(L)^+$, the site of addition being an imine function polarized by the oxidized metal. The α-hydroxylamine intermediate, **7**, thus generated can react via an induced electron transfer route[28] finally furnishing the $Re(NAr)Cl_3(L')$. Instances of stable aqua adduct formation by aldimines have been documented.[29]



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In the observed structure of $Re(NC_6H_4Cl)Cl_3(L'^3)$, the amide nitrogen lies *trans* to a chloride ligand and not to the imide ligand. The close similarity of spectral, magnetic, and electrochemical properties of all the four isolated $Re(NAr)Cl_3(L')$ complexes strongly suggests that the whole family belongs to the same structural type, viz. **4**. During synthesis, we found no evidence indicating that the possible isomer incorporating the amide nitrogen *trans* to the imide function is formed at all. This regiospecificity of the oxidation reaction is fully consistent with the proposed pathway. We recall that in $Re(NC_6H_5)Cl_3(L^4)$ the Re−N1 bond is significantly longer than the Re−N2 bond due to the *trans* influence of the NC_6H_5 group. This trend is expected to continue even after metal oxidation. The imine function incorporating the N2 atom will thus be more polarized and subject to more facile nucleophilic attack by water. It is, indeed, this imine function that is selectively oxidized to the amide function as is evident in the structure of $Re(NC_6H_4Cl)Cl_3(L'^3)$.

Since complexes of types $Re(OPPh_3)Cl_3(L)$ and $Re(OPPh_3)Cl_3(L')$ failed to afford single crystals, the site of

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oxidation could not be established directly. However, structural data on other $Re(OPPh_3)Cl_3(NN)$ type complexes have revealed that the Re−N bond *trans* to chloride is generally shorter than that *trans* to $OPPh_3$ by 0.01−0.05 Å.[11,12] It is therefore very probable that the oxidation is regiospecific here as well, as implied in drawing **5**.

Concluding Remarks

The diazabutadiene chemistry and the corresponding iminoamide chemistry of rhenium have been developed in the valence domain II−VI. The compounds isolated and characterized belong to the types $Re^{II}X_2(L)_2$, $Re^{III}(OPPh_3)Cl_3(L)$, $Re^{IV}(OPPh_3)Cl_3(L')$, $Re^{V}OCl_3(L)$, $Re^{V}(NAr)Cl_3(L)$, and $Re^{VI}(NAr)Cl_3(L')$. The ultimate parent of the family is $Re^{V}OCl_3(L)$ from which the other members are derived. The observed oxidation states and reduction potentials are consistent with the combined donor−acceptor potency of the ligands and coligands. The iminoamide species are formed by metal-promoted ligand oxidation of the corresponding diazabutadiene complexes via nucleophilic aquation of the more tightly bound imine function followed by induced electron transfer.

Ongoing studies include oxidation of chelated diacetyldiimine ligands and photophysical and photochemical behavior of $ReOCl_3(L)$, $Re(NAr)Cl_3(L)$, and $Re(NAr)Cl_3(L')$ which have been found to fluoresce in the visible region.

Experimental Section

Materials. $ReOCl_3(AsPh_3)_2$,[30] $ReOCl_3(PPh_3)_2$,[30] $ReO(OEt)X_2(PPh_3)_2$[31] ($X = Cl$, Br), and diazabutadienes[32] were prepared by reported methods. For electrochemical work, HPLC grade acetonitrile was used. All other chemicals and solvents were of reagent grade and were used as received.

Physical Measurements. UV−vis spectral measurements were carried out with a Shimadzu UVPC 1601 spectrophotometer. IR spectra were measured with Nicolet Magna IR 750 series II and 550 FAR IR and Perkin-Elmer L-0100 spectrophotometers. 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 structures are abbreviated as follows: s, singlet; d, doublet; t, triplet. EPR spectra were recorded on a Varian E-109C X-band spectrometer. Magnetic susceptibilities were measured on a PAR 155 vibrating-sample magnetometer. A Perkin-Elmer 2400 series II elemental analyzer was used for microanalysis (C,H,N). Electrochemical measurements were performed under nitrogen atmosphere using a CH 620A electrochemical analyzer, 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.

Preparation of Complexes. Preparations of $ReOCl_3(L)$, 1. These complexes were prepared in 80−85% yield by the same general procedure based on the reaction of $ReOCl_3(AsPh_3)_2$ with L in benzene. Details are given here for a representative case.

$ReOCl_3(L^5)$. To a suspension of $ReOCl_3(AsPh_3)_2$ (100 mg, 0.109 mmol) in 25 mL of benzene was added 26 mg (0.109 mmol) of L^5. The resulting mixture was heated to reflux for 15 min producing a pink solution. The reaction mixture was then cooled, and the solvent was removed under reduced pressure. The solid mass thus obtained was repeatedly washed with *n*-hexane to remove the liberated $AsPh_3$. The solid was then dissolved in 5 mL of dichloromethane and subjected to chromatography on a silica gel column (10 cm × 1 cm, 60−120 mesh) prepared with toluene. The pink complex was eluted out with pure toluene. Solvent removal from the eluate under reduced pressure afforded $ReOCl_3(L^5)$ in pure form which was dried under vacuum over fused calcium chloride. Yield: 50 mg (85%). Anal. Calcd for $C_{16}H_{16}N_2Cl_3ORe$: C, 35.27; H, 2.96; N, 5.14. Found: C, 35.37; H, 2.91; N, 5.21. UV−vis (λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$) CH_2Cl_2 solution): 278 (5770); 505 (3200); 746 (540). IR (KBr, cm^{-1}): ν(Re−Cl) 304, 329, 354; ν(Re≡O) 998; ν(C=N) 1485, 1587. ^{1}H NMR (δ (*J*, Hz) $CDCl_3$): 2.20 and 4.57 (C(13)-Me, s and C(14)-Me, s); 7.25−7.50 (aromatic multiplet). E_{pa} (Re^{VI}/Re^{V} couple): 1.70 V.

$ReOCl_3(L^1)$. Anal. Calcd for $C_{12}H_{20}N_2Cl_3ORe$: C, 28.78; H, 4.02; N, 5.59. Found: C, 28.84; H, 4.10; N, 5.65. UV−vis (λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$) CH_2Cl_2 solution): 260 (5720); 503 (2370); 737 (260). IR (KBr, cm^{-1}): ν(Re−Cl) 320, 336, 357; ν(Re≡O) 992; ν(C=N) 1480, 1587. ^{1}H NMR (δ (*J*, Hz) $CDCl_3$): 6.62 and 8.24 (C(13)-H, s and C(14)-H, s); 1.42−5.06 (aliphatic multiplet). E_{pa} (Re^{VI}/Re^{V} couple): 1.70 V.

$ReOCl_3(L^2)$. Anal. Calcd for $C_{14}H_{24}N_2Cl_3ORe$: C, 31.79; H, 4.57; N, 5.30. Found: C, 31.86; H, 4.51; N, 5.36. UV−vis (λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$) CH_2Cl_2 solution): 263 (5140); 500 (3300); 745 (360). IR (KBr, cm^{-1}): ν(Re−Cl) 317, 333, 355; ν(Re≡O) 993; ν(C=N) 1481, 1583. ^{1}H NMR (δ (*J*, Hz) $CDCl_3$): 6.58 and 8.27 (C(13)-H, s and C(14)-H, s); 1.01−4.52 (aliphatic multiplet). E_{pa} (Re^{VI}/Re^{V} couple): 1.72 V.

$ReOCl_3(L^3)$. Anal. Calcd for $C_{16}H_{28}N_2Cl_3ORe$: C, 34.50; H, 5.07; N, 5.03. Found: C, 34.57; H, 5.12; N, 5.07. UV−vis (λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$) CH_2Cl_2 solution): 262 (5870); 498 (2250); 737 (250). IR (KBr, cm^{-1}): ν(Re−Cl) 325, 340, 360; ν(Re≡O) 995; ν(C=N) 1480, 1580. ^{1}H NMR (δ (*J*, Hz) $CDCl_3$): 6.52 and 8.22 (C(13)-H, s and C(14)-H, s); 1.10−4.58 (aliphatic multiplet). E_{pa} (Re^{VI}/Re^{V} couple): 1.71 V.

$ReOCl_3(L^6)$. Anal. Calcd for $C_{18}H_{20}N_2Cl_3ORe$: C, 37.73; H, 3.52; N, 4.91. Found: C, 37.61; H, 3.58; N, 4.85. UV−vis (λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$) CH_2Cl_2 solution): 279 (4900); 507 (3500); 747 (570). IR (KBr, cm^{-1}): ν(Re−Cl) 310, 330, 357; ν(Re≡O) 990; ν(C=N) 1478, 1586. ^{1}H NMR (δ (*J*, Hz) $CDCl_3$): 2.23 and 4.55 (C(13)-Me, s and C(14)-Me, s); 7.27−7.56 (aromatic multiplet). E_{pa} (Re^{VI}/Re^{V} couple): 1.60 V.

$ReOCl_3(L^7)$. Anal. Calcd for $C_{16}H_{14}N_2Cl_5ORe$: C, 33.90; H, 2.21; N, 4.39. Found: C, 34.00; H, 2.27; N, 4.49. UV−vis (λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$) CH_2Cl_2 solution): 275 (5200); 510 (3700); 745 (630). IR (KBr, cm^{-1}): ν(Re−Cl) 315, 328, 352; ν(Re≡O) 994; ν(C=N) 1480, 1588. ^{1}H NMR (δ (*J*, Hz) $CDCl_3$): 2.21 and 4.58 (C(13)-Me, s and C(14)-Me, s); 7.26−7.54 (aromatic multiplet). E_{pa} (Re^{VI}/Re^{V} couple): 1.75 V.

Preparation of $Re(OPPh_3)Cl_3(L)$, 2. The same general method was used for the four complexes (yield, 80−85%). The case of $Re(OPPh_3)Cl_3(L^1)$ is detailed here.

$Re(OPPh_3)Cl_3(L^1)$. To a solution of $ReOCl_3(L^1)$ (100 mg, 0.200 mmol) in benzene (15 mL) was added 105 mg (0.400 mmol) of PPh_3. The pink solution turned brown instantly, and the reaction mixture was stirred for 20 min at room temperature. The solvent was then removed under reduced pressure. The solid thus obtained was washed several times with *n*-hexane, and finally, it was

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dissolved in 5 mL of dichloromethane and subjected to chromatography on a silica gel (15 cm × 1 cm, 60−120 mesh) prepared in benzene. Following elution with pure benzene, a yellowish brown band was eluted out with a benzene−acetonitrile (50:3) mixture. Solvent removal from the eluate under reduced pressure afforded Re(OPPh$_3$)Cl$_3$(L^1) in pure form. Yield: 122 mg (80%). Anal. Calcd for C$_{30}$H$_{35}$N$_2$Cl$_3$OPRe: C, 47.22; H, 4.62; N, 3.67. Found: C, 47.30; H, 4.56; N, 3.77. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH$_2$Cl$_2$ solution): 408 (600); 459 (1100). IR (KBr, cm^{-1}): ν(Re−Cl) 310, 320, 335; ν(O═P) 1123; ν(C═N) 1472, 1595. $E_{1/2}$ (Re^{IV}/Re^{III} couple): 0.66 V (ΔE_p, 62 mV).

Re(OPPh$_3$)Cl$_3$(L^2). Anal. Calcd for C$_{32}$H$_{39}$N$_2$Cl$_3$OPRe: C, 48.58; H, 4.97; N, 3.54. Found: C, 48.65; H, 5.02; N, 3.47. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH$_2$Cl$_2$ solution): 388 (900); 449 (1700). IR (KBr, cm^{-1}): ν(Re−Cl) 320, 336; ν(O═P) 1121; ν(C═N) 1470, 1596. $E_{1/2}$ (Re^{IV}/Re^{III} couple): 0.69 V (ΔE_p, 66 mV).

Re(OPPh$_3$)Cl$_3$(L^5). Anal. Calcd for C$_{34}$H$_{31}$N$_2$Cl$_3$OPRe: C, 50.59; H, 3.87; N, 3.47. Found: C, 50.62; H, 3.92; N, 3.52. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH$_2$Cl$_2$ solution): 352 (4200); 453 (2000). IR (KBr, cm^{-1}): ν(Re−Cl) 319, 340; ν(O═P) 1121; ν(C═N) 1487, 1590. ^{1}H NMR (δ (J, Hz) CDCl$_3$): −27.96 and −30.64 (C(13)-Me, s and C(14)-Me, s); ligand protons, 21.68 (d, 7.2), 15.54 (d, 7.2), 12.53 (t, 7.1), 11.65 (t, 7.2), 8.26 (t, 7.5), 6.14 (t, 7.2); PPh$_3$ protons, 6.08−7.38. $E_{1/2}$ (Re^{IV}/Re^{III} couple): 0.54 V (ΔE_p, 80 mV).

Re(OPPh$_3$)Cl$_3$(L^6). Anal. Calcd for C$_{36}$H$_{35}$N$_2$Cl$_3$OPRe: C, 51.77; H, 4.22; N, 3.35. Found: C, 51.85; H, 4.26; N, 3.42. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH$_2$Cl$_2$ solution): 358 (3100); 456 (1550). IR (KBr, cm^{-1}): ν(Re−Cl) 310, 318, 335; ν(O═P) 1122; ν(C═N) 1504, 1600. ^{1}H NMR (δ (J, Hz) CDCl$_3$): −27.00 and −29.80 (C(13)-Me, s and C(14)-Me, s); ligand protons, 21.27 (d, 9.0), 15.65 (d, 6.0), 12.11 (d, 9.0), 11.22 (d, 6.0); 2.34 and 2.39 (C(4)-Me, s and C(10)-Me, s); PPh$_3$ protons, 6.42−7.54. $E_{1/2}$ (Re^{IV}/Re^{III} couple): 0.49 V (ΔE_p, 100 mV).

The Re(OPPh$_3$)Cl$_3$(L^1) complex was also synthesized by the reaction of ReOCl$_3$(PPh$_3$)$_2$ with L^1. To a suspension of ReOCl$_3$(PPh$_3$)$_2$ (100 mg, 0.120 mmol) in 15 mL of benzene was added 15 mg (0.176 mmol) of L^1, and the mixture was stirred for 30 min at room temperature. The solvent was then removed under reduced pressure. The solid thus obtained was processed in the same manner as described in previous paragraphs. Yield: 64 mg (70%). All the phosphine oxide complexes of L ligands reported in this work can be prepared by this method in similar yields.

Preparation of Re(NAr)Cl$_3$(L), 3. These complexes were synthesized in 80−85% yield by the same general procedure, and details are given here for a representative case.

Re(NC$_6$H$_4$Cl)Cl$_3$(L^2). To a solution of ReOCl$_3$(L^2) (100 mg, 0.190 mmol) in 15 mL of toluene was added an excess of *p*-chloroaniline (121 mg, 0.950 mmol), and the mixture was heated to reflux for 5 h. The solvent was then removed under reduced pressure, and the solid thus obtained was subjected to column chromatography as for ReOCl$_3$(L^5). Following elution with pure toluene (to remove the excess *p*-ClC$_6$H$_4$NH$_2$), a reddish pink band was eluted out with a toluene−acetonitrile (25:1) mixture. Solvent removal from the eluate under reduced pressure afforded the imido complex which was dried under vacuo over fused calcium chloride. Yield: 97 mg (80%). Anal. Calcd for C$_{20}$H$_{28}$N$_3$Cl$_4$Re: C, 37.23; H, 4.42; N, 6.58. Found: C, 37.15; H, 4.46; N, 6.63. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH$_2$Cl$_2$ solution): 306 (4250); 511 (2200); 742 (600). IR (KBr, cm^{-1}): ν(Re−Cl) 317, 338; ν(C═N) 1481, 1572. ^{1}H NMR (δ (J, Hz) CDCl$_3$): 5.96 and 8.04 (C(13)-H, s and C(14)-H, s); *p*-ClC$_6$H$_4$N protons, 7.40 (d, 8.7), 7.65 (d, 8.7); 0.84−5.06 (aliphatic multiplet). $E_{1/2}$ (Re^{VI}/Re^V couple): 1.08 V (ΔE_p, 70 mV).

Re(NC$_6$H$_4$Cl)Cl$_3$(L^1). Anal. Calcd for C$_{18}$H$_{24}$N$_3$Cl$_4$Re: C, 35.42; H, 3.96; N, 6.88. Found: C, 35.50; H, 3.92; N, 6.98. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH$_2$Cl$_2$ solution): 308 (4500); 512 (2700); 743 (400). IR (KBr, cm^{-1}): ν(Re−Cl) 320, 330; ν(C═N) 1482, 1574. ^{1}H NMR (δ (J, Hz) CDCl$_3$): 5.93 and 8.06 (C(13)-H, s and C(14)-H, s); *p*-ClC$_6$H$_4$N protons, 7.42 (d, 8.4), 7.64 (d, 8.2); 1.02−5.10 (aliphatic multiplet). $E_{1/2}$ (Re^{VI}/Re^V couple): 1.02 V (ΔE_p, 63 mV).

Re(NC$_6$H$_4$Cl)Cl$_3$(L^3). Anal. Calcd for C$_{22}$H$_{32}$N$_3$Cl$_4$Re: C, 39.64; H, 4.84; N, 6.30. Found: C, 39.57; H, 4.89; N, 6.37. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH$_2$Cl$_2$ solution): 307 (5400); 507 (2900); 739 (730). IR (KBr, cm^{-1}): ν(Re−Cl) 300, 315, 336; ν(C═N) 1486, 1571. ^{1}H NMR (δ (J, Hz) CDCl$_3$): 5.87 and 8.03 (C(13)-H, s and C(14)-H, s); *p*-ClC$_6$H$_4$N protons, 7.40 (d, 8.7), 7.66 (d, 8.4); 1.04−5.15 (aliphatic multiplet). $E_{1/2}$ (Re^{VI}/Re^V couple): 1.07 V (ΔE_p, 75 mV).

Re(NC$_6$H$_5$)Cl$_3$(L^5). Anal. Calcd for C$_{22}$H$_{21}$N$_3$Cl$_3$Re: C, 42.62; H, 3.41; N, 6.78. Found: C, 42.69; H, 3.46; N, 6.83. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH$_2$Cl$_2$ solution): 344 (8460); 517 (4300); 751 (1500). IR (KBr, cm^{-1}): ν(Re−Cl) 300, 316, 332; ν(C═N) 1485, 1595. ^{1}H NMR (δ (J, Hz) CDCl$_3$): 2.36 and 4.57 (C(13)-Me, s and C(14)-Me, s); 6.29−7.47 (aromatic multiplet). $E_{1/2}$ (Re^{VI}/Re^V couple): 0.97 V (ΔE_p, 70 mV).

Re(NC$_6$H$_4$Me)Cl$_3$(L^6). Anal. Calcd for C$_{25}$H$_{27}$N$_3$Cl$_3$Re: C, 45.35; H, 4.11; N, 6.34. Found: C, 45.39; H, 4.17; N, 6.27. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH$_2$Cl$_2$ solution): 341 (9500); 515 (5100); 749 (1600). IR (KBr, cm^{-1}): ν(Re−Cl) 317, 331; ν(C═N) 1505, 1592. ^{1}H NMR (δ (J, Hz) CDCl$_3$): 2.34 and 4.53 (C(13)-Me, s and C(14)-Me, s); 6.79−7.23 (aromatic multiplet). $E_{1/2}$ (Re^{VI}/Re^V couple): 0.93 V (ΔE_p, 65 mV).

Re(NC$_6$H$_4$Cl)Cl$_3$(L^7). Anal. Calcd for C$_{22}$H$_{18}$N$_3$Cl$_6$Re: C, 36.54; H, 2.51; N, 5.81. Found: C, 36.60; H, 2.55; N, 5.75. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH$_2$Cl$_2$ solution): 347 (8660); 521 (4750); 750 (1450). IR (KBr, cm^{-1}): ν(Re−Cl) 320, 340; ν(C═N) 1492, 1598. ^{1}H NMR (δ (J, Hz) CDCl$_3$): 2.40 and 4.69 (C(13)-Me, s and C(14)-Me, s); 6.95−7.42 (aromatic multiplet). $E_{1/2}$ (Re^{VI}/Re^V couple): 1.07 V (ΔE_p, 70 mV).

Preparation of Re(NC$_6$H$_5$)Cl$_3$(L^4) from ReOCl$_3$(PPh$_3$)$_2$. To a suspension of ReOCl$_3$(PPh$_3$)$_2$ (100 mg, 0.120 mmol) in 15 mL of toluene was added 62 mg (0.300 mmol) of L^4, and the mixture was heated to reflux for 1 h. During this time, the color changed to reddish pink. The solvent was then removed under reduced pressure, and the solid thus obtained was subjected to chromatographic workup as in the case of Re(NC$_6$H$_4$Cl)Cl$_3$(L^2). Yield: 46 mg (65%). Anal. Calcd for C$_{20}$H$_{17}$N$_3$Cl$_3$Re: C, 40.58; H, 2.89; N, 7.10. Found: C, 40.50; H, 2.94; N, 7.18. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH$_2$Cl$_2$ solution): 335 (19200); 514 (5250); 749 (2400). IR (KBr, cm^{-1}): ν(Re−Cl) 305, 315, 335; ν(C═N) 1503, 1590. ^{1}H NMR (δ (J, Hz) CDCl$_3$): 6.01 and 7.89 (C(13)−H, s and C(14)−H, s); 7.08−7.51 (aromatic multiplet). $E_{1/2}$ (Re^{VI}/Re^V couple): 1.10 V (ΔE_p, 120 mV).

Preparation of Re(NAr)Cl$_3$(L′), 4. The R′ = alkyl complexes were synthesized in 55−65% yield by the same general method based on the reaction of Re(NAr)Cl$_3$(L) with dilute nitric acid in acetonitrile. Details are given here for a representative case.

Re(NC$_6$H$_4$Cl)Cl$_3$(L′^{3}). The complex Re(NC$_6$H$_4$Cl)Cl$_3$(L^3) (100 mg, 0.150 mmol) was dissolved in acetonitrile (20 mL), and 0.5 N nitric acid (2 mL) was added. The solution was then stirred for 10 h at room temperature during which time the color turned brown. Solvent evaporation under reduced pressure afforded a dark solid which was repeatedly washed with water. The product was then dried in vacuo over P$_4$O$_{10}$ and finally extracted with *n*-hexane. The extract was evaporated to dryness under reduced pressure, and the solid so obtained was further dried in vacuo. Yield: 61 mg (60%). Anal. Calcd for C$_{22}$H$_{31}$N$_3$Cl$_4$ORe: C, 38.77; H, 4.58; N, 6.17.

Found: C, 38.87; H, 4.64; N, 6.28. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH_2Cl_2 solution): 293 (3900); 363 (6700); 579 (1260). IR (KBr, cm^{-1}): ν(Re−Cl) 304, 326, 342; ν(amide) 1566, 1621. $E_{1/2}$ (Re^{VI}/Re^{V} couple): 0.20 V (ΔE_p, 72 mV). $E_{1/2}$ (Re^{VII}/Re^{VI} couple): 1.58 V (ΔE_p, 90 mV).

$Re(NC_6H_4Cl)Cl_3(L'^1)$. Anal. Calcd for $C_{18}H_{23}N_3Cl_4ORe$: C, 34.56; H, 3.71; N, 6.72. Found: C, 34.62; H, 3.76; N, 6.67. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH_2Cl_2 solution): 290 (4000); 359 (6200); 577 (1200). IR (KBr, cm^{-1}): ν(Re−Cl) 310, 325, 340; ν(amide) 1567, 1622. $E_{1/2}$ (Re^{VI}/Re^{V} couple): 0.18 V (ΔE_p, 62 mV). $E_{1/2}$ (Re^{VII}/Re^{VI} couple): 1.55 V (ΔE_p, 100 mV).

$Re(NC_6H_4Cl)Cl_3(L'^2)$. Anal. Calcd for $C_{20}H_{27}N_3Cl_4ORe$: C, 36.76; H, 4.16; N, 6.43. Found: C, 36.66; H, 4.21; N, 6.49. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH_2Cl_2 solution): 294 (3600); 364 (6100); 580 (1100). IR (KBr, cm^{-1}): ν(Re−Cl) 325, 342; ν(amide) 1569, 1624. $E_{1/2}$ (Re^{VI}/Re^{V} couple): 0.19 V (ΔE_p, 74 mV). $E_{1/2}$ (Re^{VII}/Re^{VI} couple): 1.64 V (ΔE_p, 80 mV).

The syntheses of R′ = aryl complexes require certain modifications. A representative case is given here.

$Re(NC_6H_5)Cl_3(L'^4)$. The complex $Re(NC_6H_5)Cl_3(L^4)$ (100 mg, 0.169 mmol) was dissolved in acetonitrile (20 mL), and 0.5 N nitric acid (2 mL) was added. The solution was then stirred for 3 h during which the color turned brown. Solvent evaporation afforded a dark product which was repeatedly washed with water and dried in vacuo over P_4O_{10} followed by recrystallization from dichloromethane. Yield: 62 mg (60%). Anal. Calcd for $C_{20}H_{16}N_3Cl_3ORe$: C, 39.58; H, 2.66; N, 6.92. Found: C, 39.63; H, 2.71; N, 6.97. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH_2Cl_2 solution): 328 (14300); 511 (4600). IR (KBr, cm^{-1}): ν(Re−Cl) 306, 323, 338; ν(amide) 1574, 1620. $E_{1/2}$ (Re^{VI}/Re^{V} couple): 0.16 V (ΔE_p, 60 mV). $E_{1/2}$ (Re^{VII}/Re^{VI} couple): 1.52 V (ΔE_p, 70 mV).

Preparation of $Re(OPPh_3)Cl_3(L')$, 5. The two complexes reported were prepared in 70% yield by the same general procedure. Details are given here for a representative case.

$Re(OPPh_3)Cl_3(L'^1)$. The complex $Re(OPPh_3)Cl_3(L^1)$ (100 mg, 0.131 mmol) was dissolved in 20 mL of acetonitrile, and 0.5 mL of H_2O_2 (30%) was added. The solution was stirred for 2 h at room temperature, during which time the color become yellowish orange. Evaporation of the solution under reduced pressure gave a brown solid, which was repeatedly washed with water and dried in vacuo over P_4O_{10}. The product was recrystallized from dichloromethane. Yield: 71 mg (70%). Anal. Calcd for $C_{30}H_{34}N_2Cl_3O_2PRe$: C, 46.31; H, 4.40; N, 3.60. Found: C, 46.38; H, 4.46; N, 3.55. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH_2Cl_2 solution): 492 (1000). IR (KBr, cm^{-1}): ν(Re−Cl) 325, 338; ν(O═P) 1120; ν(amide) 1552, 1612. E_{pc} (Re^{IV}/Re^{III} couple): −0.40. $E_{1/2}$ (Re^{V}/Re^{IV} couple): 1.67 V (ΔE_p, 100 mV).

$Re(OPPh_3)Cl_3(L'^2)$. Anal. Calcd for $C_{32}H_{38}N_2Cl_3O_2PRe$: C, 47.67; H, 4.75; N, 3.47. Found: C, 47.62; H, 4.81; N, 3.43. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH_2Cl_2 solution): 495 (600). IR (KBr, cm^{-1}): ν(Re−Cl) 323, 334; ν(O═P) 1121; ν(amide) 1558, 1613. E_{pc} (Re^{IV}/Re^{III} couple): −0.38 V. $E_{1/2}$ (Re^{V}/Re^{IV} couple): 1.66 V (ΔE_p, 100 mV).

Preparation of $ReX_2(L)_2$, 6. $ReCl_2(L^2)_2$. To a solution of $Re(OPPh_3)Cl_3(L^2)$ (100 mg, 0.126 mmol) in 25 mL of benzene was added 42 mg (0.190 mmol) of L^2 and 3 mg (0.011 mmol) of PPh_3. The resulting mixture was heated to reflux for 1 h affording a brown solution. The solvent was then removed under reduced pressure, and the mass thus obtained was dissolved in 5 mL of dichloromethane and subjected to chromatography on a silica gel column (15 cm × 1 cm, 60−120 mesh). Following elution with pure benzene, a brown band was eluted out with a benzene−acetonitrile (25:2) mixture, and solvent removal from the latter eluate under reduced pressure afforded $ReCl_2(L^2)_2$ in pure form. Yield: 57 mg (65%). Anal. Calcd for $C_{28}H_{48}N_4Cl_2Re$: C, 48.19; H, 6.93; N, 8.03. Found: C, 48.24; H, 6.87; N, 8.09. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH_2Cl_2 solution): 449 (3800). IR (KBr and polyethylene, cm^{-1}): ν(Re−Cl) 305, 321; ν(C═N) 1454, 1627. $E_{1/2}$ (Re^{III}/Re^{II} couple): 0.41 V (ΔE_p, 100 mV).

Table 4. Summary of the Crystal and Refinement Data for $ReOCl_3(L^5)$, $Re(NC_6H_5)Cl_3(L^4)$, and $Re(NC_6H_4Cl)Cl_3(L'^3)$

	$ReOCl_3(L^5)$	$Re(NC_6H_5)Cl_3(L^4)$	$Re(NC_6H_4Cl)$-$Cl_3(L'^3)$
formula	$C_{16}H_{16}Cl_3N_2$-ORe	$C_{20}H_{17}Cl_3N_3Re$	$C_{22}H_{31}Cl_4N_3ORe$
fw	544.86	591.92	681.50
system	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/c$	$P2_1/n$
a (Å)	20.196(8)	14.991(11)	11.257(2)
b (Å)	8.227(6)	7.139(3)	12.922(3)
c (Å)	20.880(11)	19.717(11)	18.295(4)
α (deg)	90	90	90
β (deg)	90	104.72(5)	104.99(3)
γ (deg)	90	90	90
V ($Å^3$)	3470(4)	2041(2)	2570.8(9)
Z	8	4	4
D_{calcd} (mg m^{-3})	2.086	1.926	1.761
temp (K)	293	293	293
μ (mm^{-1})	7.471	6.356	5.162
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0673, 0.1648	0.0372, 0.0903	0.0306, 0.0703
GOF on F^2	1.137	1.101	1.026

[a] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

$ReCl_2(L^6)_2$. To a suspension of $ReO(OEt)Cl_2(PPh_3)_2$ (100 mg, 0.119 mmol) in 25 mL of benzene was added 79 mg (0.298 mmol) of L^6. The resulting mixture was heated to reflux for 1 h affording a yellowish brown solution. The solvent was then removed under reduced pressure, and chromatographic workup in the same manner as described for $ReCl_2(L^2)_2$ afforded $ReCl_2(L^6)_2$ in pure form. Yield: 61 mg (65%). Anal. Calcd for $C_{36}H_{40}N_4Cl_2Re$: C, 55.02; H, 5.14; N, 7.13. Found: C, 54.97; H, 5.09; N, 7.17. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH_2Cl_2 solution): 464 (5000). IR (KBr and polyethylene, cm^{-1}): ν(Re−Cl) 304, 317; ν(C═N) 1454, 1627. $E_{1/2}$ (Re^{III}/Re^{II} couple): 0.40 V (ΔE_p, 66 mV).

$ReBr_2(L^6)_2$. This complex was synthesized by the same procedure as described from $ReO(OEt)Br_2(PPh_3)_2$ in similar yield. Anal. Calcd for $C_{36}H_{40}N_4Br_2Re$: C, 49.43; H, 4.61; N, 6.40. Found: C, 49.37; H, 4.65; N, 6.34. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}) CH_2Cl_2 solution): 476 (7950). IR (KBr and polyethylene, cm^{-1}): ν(Re−Br) 213, 229; ν(C═N) 1454, 1632. $E_{1/2}$ (Re^{III}/Re^{II} couple): 0.38 V (ΔE_p, 70 mV).

X-ray Structure Determination. Single crystals of the complexes $ReOCl_3(L^5)$ and $Re(NC_6H_5)Cl_3(L^4)$ were grown by slow diffusion of hexane into dichloromethane solutions of the respective compounds. Single crystals for the complex $Re(NC_6H_4Cl)Cl_3(L'^3)$ were grown by slow evaporation of a solution of dichloromethane−heptane (1:2). Data for the compounds $ReOCl_3(L^5)$ and $Re(NC_6H_5)Cl_3(L^4)$ were collected on a Nicolet R3m/V four circle diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) by the ω-scan technique in the 2θ ranges 3−50° and 3−47°, respectively. Data for the compound $Re(NC_6H_4Cl)Cl_3(L'^3)$ were collected on a Bruker SMART diffractometer having CCD area detector by ϕ- and ω-scan technique in the 2θ range 3−55°. All the data were corrected for Lorentz-polarization and absorption. The metal atoms were 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 procedure on F^2. All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were included in calculated positions [$U = 0.08 Å^2$]. Calculations were performed using the SHELXTL V5.03[33] program package. Significant crystal data are listed in Table 4.

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Supporting Information Available: For $ReOCl_3(L^5)$, $Re(NC_6H_5)Cl_3(L^4)$, and $Re(NC_6H_4Cl)Cl_3(L'^3)$, crystallographic data, in CIF and PDF formats. This material is available free of charge via the Internet at http://pubs.acs.org.

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