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Articles

Chemistry of the Rhenium−Azopyridine Family: An Oxo Parent and Derivatives Thereof Including a Novel Oxo−Imido Dimer

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The concerned azo ligands are 2-(phenylazo)pyridine (HL) and 2-((*p*-chlorophenyl)azo)pyridine (ClL). The reaction of $KReO_4$ with HL in hot concentrated HCl is attended with metal reduction and ligand chlorination affording the oxo complex $Re^{V}OCl_3(ClL)$, **2**, which furnishes $Re^{III}(OPPh_3)Cl_3(ClL)$, **3**, upon treatment with PPh_3. Aromatic amines, $ArNH_2$, convert **2** to the imido complex $Re^{V}(NAr)Cl_3(ClL)$, **5**, and the unusual oxo−imido dimer $(ClL)Cl_2(O)Re^{V}ORe^{V}(NAr)Cl_2(ClL)$, **7**. The complex $Re^{III}(OPPh_3)Cl_3(HL)$, **4**, has been generated from $Re^{V}OCl_3(PPh_3)_2$ and HL. Reaction of **4** with HL has yielded $Re^{V}(NPh)Cl_3(HL)$, **6**, via azo splitting. The complexes have been characterized with the help spectral, magnetic, and X-ray structural data (**2**, **3**, **5c** ($Ar = p\text{ClC}_6H_4$) and **7**·CH_2Cl_2 ($Ar = p\text{MeC}_6H_4$)). In **2**, **3**, and **5c** the $ReCl_3$ fragment is meridionally disposed, and in **7** the $ReCl_2$ fragments have a trans configuration. The Re−O(oxo) bond, 1.663(6) Å, in **2** and Re−N(imido) bond, 1.719(5) Å, in **5c** are triple bonds. The corresponding bonds are slightly longer in **7** wherein the (O)Re(1)−O(2)−Re(2)(NAr) bridge is angular (151.0(5)°) and unsymmetrical, the Re(1)−O(2) bond, 1.849(7) Å, having a large double-bond character (Re(2)−O(2), 1.954(7) Å). In effect, *cis*-$Re^{V}O_2$ acts as a monodentate oxygen ligand toward $Re^{V}NAr$ in **7**. In all cases the pyridine nitrogen binds trans to the oxo, $OPPh_3$, or NAr donor. Bond length data are consistent with the presence of substantial d(Re)−π^*(azo) back-bonding. In acetonitrile solution the complexes display electrochemical one-electron metal (Re^{VI}/Re^{V} or Re^{IV}/Re^{III}) and azo redox. The imido ligand in **5** stabilizes the Re^{VI} state ($E_{1/2} \sim 1.4$ V) better than the oxo ligand in **2** ($\sim$1.9 V). Parallely it is more difficult to reduce the azo group in **5** (~ -0.4 V) than in **2** ($\sim$0.0 V). In **7** the metal ($\sim$1.0 V) and azo (~ -0.4 V) couples correspond to the imido and oxo halves, respectively. The significantly higher (by 0.2−0.6 V) metal reduction potentials of the azopyridine compared to pyridine-2-aldimine complexes is ascribed to the superior π-acidity and electron-withdrawing character of the azo function relative to the aldimine function. This also makes the transfer of the $Re^{V}O$ oxygen function much more facile under azopyridine chelation as in **2**. For the same reason, $ReOCl_3(PPh_3)_2$ reacts with HL affording only **4** while it reacts with pyridine-2-aldimines furnishing oxo species. Crystal data for the complexes are as follows: **2**, empirical formula $C_{11}H_8Cl_4N_3ORe$, crystal system triclinic, space group $P\bar{1}$, $a = 7.118(4)$ Å, $b = 8.537(4)$ Å, $c = 13.231(9)$ Å, $\alpha = 79.16(5)°$, $\beta = 78.03(5)°$, $\gamma = 70.96(4)°$, $V = 737.2(7)$ Å^3, $Z = 2$; **3**, empirical formula $C_{29}H_{23}Cl_4N_3OPRe$, crystal system monoclinic, space group $P2_1/n$, $a = 11.264(2)$ Å, $b = 15.221(3)$ Å, $c = 17.628(4)$ Å, $\beta = 94.21(3)°$, $V = 3014(1)$ Å^3, $Z = 4$; **5c**, empirical formula $C_{17}H_{12}Cl_5N_4Re$, crystal system triclinic, space group $P\bar{1}$, $a = 9.683(3)$ Å, $b = 10.898(3)$ Å, $c = 11.522(3)$ Å, $\alpha = 63.67(2)°$, $\beta = 71.24(2)°$, $\gamma = 86.79(2)°$, $V = 1026(1)$ Å^3, $Z = 2$; **7**·CH_2Cl_2, empirical formula $C_{30}H_{25}Cl_8N_7O_2Re_2$, crystal system triclinic, space group $P\bar{1}$, $a = 12.522(6)$ Å, $b = 12.857(8)$ Å, $c = 13.182(7)$ Å, $\alpha = 67.75(4)°$, $\beta = 88.30(4)°$, $\gamma = 82.09(4)°$, $V = 1945(2)$ Å^3, $Z = 2$.

Introduction

Oxo−metal chemistry is of abiding import in inorganic research. Species incorporating the oxorhenium moiety $Re^{V}O$[1−12] and derivatives thereof have concerned us.[2,13−18] 2-(Arylazo)pyridines are versatile nitrogen donor ligands[19−40] with notable

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(1) Selected $Re^{V}O$ literature was cited in a previous paper.[2] Some further developments are cited below.[3−12]

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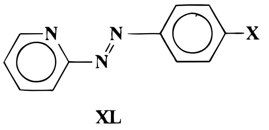
π-acidic properties,[35−40] and their $Re^{V}O$ chemistry should be potentially interesting.[41,42] This prompted the present research and the first $Re^{V}O$ system is described here. It undergoes facile reactions with PPh_3 and aromatic amines generating a family of azopyridine chelates incorporating the phosphine oxide $Re^{III}OPPh_3$, the imido $Re^{V}NAr$, and the unprecedented binuclear oxo−imido $ORe^{V}ORe^{V}NAr$ moieties.

The synthesis, structure, and properties of the four systems are described. This endeavor coupled with our previous work on pyridine-2-aldimine species[2,15,16] has provided an opportunity for observing the effect of azopyridine π-acidity on metal reduction potentials and on $Re^{V}O$ oxygen transfer potency.

Results and Discussion

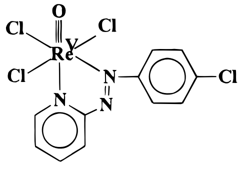
A. Synthetic Studies. a. Oxo Chelate. The azo ligand used is 2-(phenylazo)pyridine, HL; see **1**. It reacts, eq 1, smoothly and quantitatively with $KReO_4$ in hot concentrated hydrochloric acid medium affording the oxo complex **2**. In this synthesis the metal is reduced from the +7 to the +5 state and the pendent aryl group is regiospecifically chloro substituted at the para position presumably by incipient chlorine generated via HCl oxidation. The ligand in **2** is thus ClL and not HL. The mechanism of the process is unclear at present. That the substitution occurs para to the electron-withdrawing azo function militates against an electrophilic pathway.



XL

X = H, Cl

1



ReOCl$_3$(ClL)

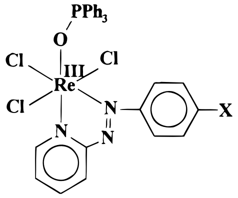
2

$$KRe^{VII}O_4 + HL + 5HCl \longrightarrow \underset{\mathbf{2}}{ReOCl_3(ClL)} + 3H_2O + KCl \qquad (1)$$

b. Phosphine Oxide Complexes. The $Re^{V}O$ moiety of the oxo complex **2** undergoes very facile and quantitative transfer of the oxygen function formally as an atom[2,43−49] to PPh_3 in solution, eq 2. The phosphine oxide so formed remains coordinated to the reduced metal site affording $Re^{III}(OPPh_3)Cl_3(ClL)$, **3**, as a golden brown solid. The complex **4**, incorporating unsubstituted HL, has been synthesized from $ReOCl_3(PPh_3)_2$ and HL, eq 3. This reaction will be scrutinized further; vide infra.

$$\mathbf{2} + PPh_3 \longrightarrow \underset{\mathbf{3}}{Re^{III}(OPPh_3)Cl_3(ClL)} \qquad (2)$$

$$Re^{V}OCl_3(PPh_3)_2 + HL \longrightarrow \underset{\mathbf{4}}{Re^{III}(OPPh_3)Cl_3(HL)} + PPh_3 \qquad (3)$$



Re(OPPh$_3$)Cl$_3$(XL)

3 X = Cl

4 X = H

Formation of phosphine oxide via oxygen atom transfer from $Re^{V}O$ to tertiary phosphines has received attention,[2,43−49] but instances where the phosphine oxide remains firmly coordinated to the reduced metal site generating the $Re^{III}OP$ moiety are relatively sparse.[2,43]

c. Imido Species. The violet colored imido complexes of type **5** are quantitatively formed by the reaction of **2** with excess of aromatic primary amines, $ArNH_2$, eq 4. Here the $Re^{V}O$ oxygen function is transferred formally as oxide to $ArNH_2$ protons affording H_2O.

$$\mathbf{2} + ArNH_2 \longrightarrow \underset{\mathbf{5}}{Re^{V}(NAr)Cl_3(ClL)} + H_2O \qquad (4)$$

$$\mathbf{4} + HL \longrightarrow \underset{\mathbf{6}}{Re^{V}(NPh)Cl_3(HL)} + OPPh_3 + L' \qquad (5)$$

The unsubstituted imido complex **6** is furnished by the unusual reaction of eq 5, in which the HL ligand is split at the

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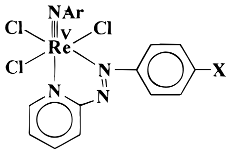
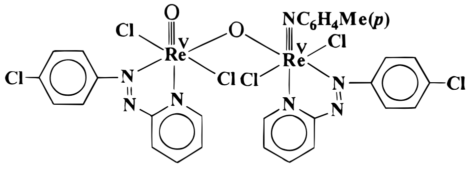


Re(NAr)Cl$_3$(XL)

	X	Ar
5a	Cl	Ph
5b	Cl	$C_6H_4Me(p)$
5c	Cl	$C_6H_4Cl(p)$
6	H	Ph

azo function. The PhN fragment binds to the metal, and the C_5H_4NN fragment dimerizes to 2-(pyridylazo)pyridine, L′. All the products of eq 5 have been isolated. Instances of transition metal promoted azo splitting reactions as in eq 5 are relatively rare.[50−53] We have earlier reported the formation of **6** in poor yield by an ill-understood reaction between K_2ReCl_6 and L, the latter being the source of the imido fragment.[41]

d. Oxo−Imido Dimer. To drive the reaction of eq 4 to completion a 5-fold excess of $ArNH_2$ is required. Upon decreasing the relative proportion of $ArNH_2$, (the case of Ar = $C_6H_4Me(p)$ is reported here) the bluish violet binuclear complex **7** is produced, eq 6, along with **5**. For optimum yield of **7**, (isolated as dichloromethane adduct, **7**·CH_2Cl_2), **2** and $MeC_6H_4NH_2$ should be taken in equal proportions. The mechanism of formation of **7** is not known. Our attempts to assemble it from equal proportions of preformed **2**, **5**, and water have not succeeded so far.



Re$_2$O$_2$(NC$_6$H$_4$Me)Cl$_4$(ClL)$_2$

7

$$2\,\mathbf{2} + 3\,p\text{-}MeC_6H_4NH_2 \longrightarrow \underset{\mathbf{7}}{Re_2O_2(NC_6H_4Me)Cl_4(ClL)_2} + 2\,MeC_6H_4NH_3Cl \quad (6)$$

A number of complexes incorporating the bridged oxo−oxo moiety, ORe^{V}ORe^{V}O, have been synthesized and characterized.[54−58] Complexes of the bridged imido−imido dimer, ArNRe^{V}ORe^{V}NAr, have also been described.[60,61] To our knowledge **7** represents the first example of the mixed oxo−imido system ORe^{V}OReNAr.

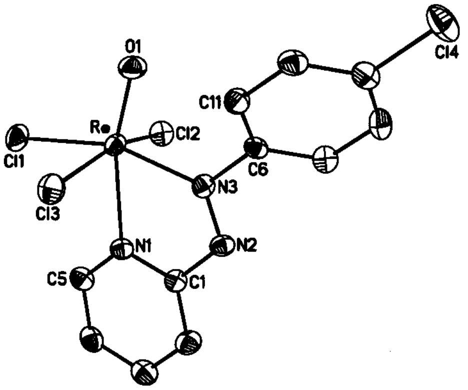


Figure 1. Molecular view and atom-labeling scheme of ReOCl$_3$(ClL), **2**. All non-hydrogen atoms are represented by 30% probability ellipsoids.

B. Spectra and Magnetism. Spectral and magnetic characterization data are listed in the Experimental Section. Of the three expected Re−Cl stretches for the meridional $ReCl_3$ moiety in **2**−**6** all or at least two are resolved (300−370 cm^{-1}). The Re≡O (**2** and **7**), Re−O−Re (**7**), P−O (**3**, **4**), and N=N stretches occur near 1000, 780, 1120, and 1330 cm^{-1}, respectively. The complexes have characteristic intense (ϵ > 2000 M^{-1} cm^{-1}) absorption bands in the visible region with maxima near 530 nm (**2**), 470 nm (**3**, **4**), 500 and 660 nm (**5**, **6**), and 540 and 660 nm (**7**).

The rhenium(V) complexes (**2**, **5**, **7**) are diamagnetic ($5d_{xy}^2$) and display normal ^1H NMR spectra. The rhenium(III) complexes (**3**, **4**) have magnetic moments near 1.7 μ_B, which is much lower than the spin-only t_{2g}^4 (idealized octahedral geometry) value as is common for trivalent rhenium.[62,63] The ^1H NMR lines are paramagnetically shifted[62,64−67] spreading over a wide ppm range (azopyridine protons, +41 to −30 ppm; $OPPh_3$ protons, 2−7 ppm).

C. Structures. The structures of four representative complexes **2**, **3**, **5c**, and **7**·CH_2Cl_2 have been determined. Molecular views are shown in Figures 1−4, and selected bond parameters are listed in Tables 1 and 2.

a. Geometrical Features. In all the cases the coordination spheres are highly distorted octahedral. In **2**, **3**, and **5c** the $ReCl_3$ fragment has meridional geometry. The Cl(1), Cl(2), Cl(3), and N(3) donors define a good equatorial plane in both **2** (mean deviation, md, 0.02 Å) and **5c** (md, 0.04 Å). The metal atom is displaced from this plane by 0.35 Å toward O(1) in **2** and 0.29 Å toward N(4) in **5c**. In the order from **2** to **3** the metal atom descends on to the equatorial plane (here planarity is only approximate: md, 0.13 Å). Of the four octahedral faces having O(1) as vertex in **3**, the P(1) atom lies closest to the Cl(1), Cl(2), O(1) face, the P(1)···f distance being 2.80 Å (f, centroid of face). The other three P(1)···f lengths span the range 3.0−3.2 Å.

In complex **7** each $ReCl_2$ fragment has trans geometry. The chloride ligands and the bridging oxygen are meridionally

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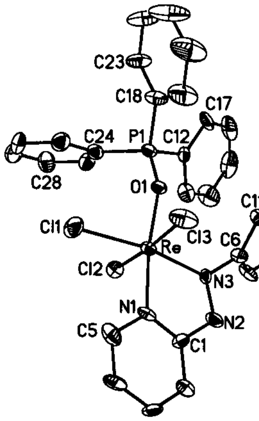

Figure 2. Molecular view and atom-labeling scheme of Re(OPPh$_3$)Cl$_3$(ClL), **3**. All non-hydrogen atoms are represented by 30% probability ellipsoids.

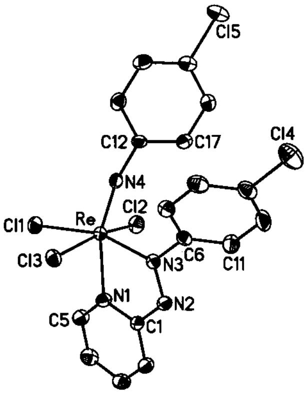

Figure 3. Molecular view and atom-labeling scheme of Re(NC$_6$H$_4$-Cl-*p*)Cl$_3$(ClL), **5c**. All non-hydrogen atoms are represented by 30% probability ellipsoids.

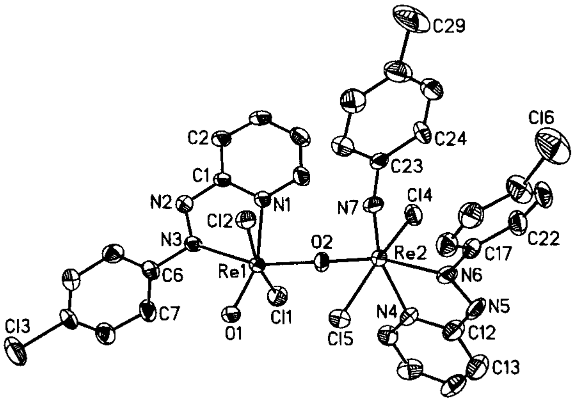

Figure 4. Molecular view and atom-labeling scheme of Re$_2$O$_2$(NC$_6$H$_4$-Me-*p*)Cl$_4$(ClL)$_2$, **7**. All non-hydrogen atoms are represented by 30% probability ellipsoids.

Table 1. Selected Bond Distances (Å) and Angles (deg) for **2**, **3**, and **5c**

	2	**3**	**5c**
	Distances		
Re−O(1)	1.663(6)	2.033(9)	
Re−N(4)			1.719(5)
Re−N(1)	2.247(6)	2.032(11)	2.173(5)
Re−N(3)	2.071(6)	1.987(11)	2.017(4)
Re−Cl(1)	2.316(2)	2.360(5)	2.351(2)
Re−Cl(2)	2.368(2)	2.353(4)	2.404(2)
Re−Cl(3)	2.338(2)	2.342(4)	2.358(2)
N(2)−N(3)	1.268(8)	1.33(2)	1.298(6)
	Angles		
O(1)−Re−N(3)	93.1(3)	96.9(4)	
N(4)−Re−N(3)			93.3(2)
O(1)−Re−N(1)	163.9(2)	172.0(5)	
N(4)−Re−N(1)			160.9(2)
O(1)−Re−Cl(1)	106.6(2)	92.8(3)	
N(4)−Re−Cl(1)			104.67(14)
O(1)−Re−Cl(2)	97.1(2)	88.5(3)	
N(4)−Re−Cl(2)			88.1(2)
O(1)−Re−Cl(3)	99.6(2)	87.5(3)	
N(4)−Re−Cl(3)			104.7(2)
N(3)−Re−N(1)	71.0(2)	75.3(5)	72.7(2)
N(3)−Re−Cl(1)	160.3(2)	169.9(4)	161.80(13)
N(3)−Re−Cl(3)	88.7(2)	93.6(4)	87.20(12)
N(1)−Re−Cl(1)	89.3(2)	95.1(4)	90.34(12)
N(1)−Re−Cl(3)	83.6(2)	91.2(3)	87.96(13)
N(3)−Re−Cl(2)	92.4(2)	88.8(3)	95.26(12)
N(1)−Re−Cl(2)	80.9(2)	93.0(3)	80.49(13)
Cl(1)−Re−Cl(3)	86.89(9)	89.7(2)	85.50(6)
Cl(3)−Re−Cl(2)	163.24(8)	175.6(2)	166.86(5)
Cl(1)−Re−Cl(2)	86.50(9)	88.6(2)	88.30(6)
P(1)−O(1)−Re		156.0(6)	
C(12)−N(4)−Re			164.4(4)

Table 2. Selected Bond Distances (Å) and Angles (deg) for **7**·CH$_2$Cl$_2$

	Distances		
Re(1)−O(1)	1.685(8)	Re(1)−O(2)	1.849(7)
Re(1)−N(3)	2.044(9)	Re(1)−N(1)	2.169(9)
Re(1)−Cl(1)	2.359(4)	Re(1)−Cl(2)	2.366(3)
N(2)−N(3)	1.300(13)	O(2)−Re(2)	1.954(7)
Re(2)−N(4)	2.162(10)	Re(2)−N(6)	2.014(10)
Re(2)−N(7)	1.735(10)	N(5)−N(6)	1.307(14)
Re(2)−Cl(5)	2.364(3)	Re(2)−Cl(4)	2.388(4)
	Angles		
O(1)−Re(1)−O(2)	114.4(4)	O(1)−Re(1)−N(3)	86.9(4)
O(2)−Re(1)−N(3)	158.6(4)	O(1)−Re(1)−N(1)	157.8(4)
O(2)−Re(1)−N(1)	87.8(4)	N(3)−Re(1)−N(1)	71.0(4)
O(1)−Re(1)−Cl(1)	94.8(3)	O(2)−Re(1)−Cl(1)	85.6(3)
N(3)−Re(1)−Cl(1)	95.3(3)	N(1)−Re(1)−Cl(1)	86.6(3)
O(1)−Re(1)−Cl(2)	95.1(3)	O(2)−Re(1)−Cl(2)	87.2(3)
N(3)−Re(1)−Cl(2)	88.7(3)	N(1)−Re(1)−Cl(2)	85.6(3)
Cl(1)−Re(1)−Cl(2)	169.56(12)	Re(1)−O(2)−Re(2)	151.0(5)
N(7)−Re(2)−O(2)	106.5(4)	N(7)−Re(2)−N(6)	92.6(4)
O(2)−Re(2)−N(6)	160.9(4)	N(7)−Re(2)−N(4)	162.7(4)
O(2)−Re(2)−N(4)	88.6(4)	N(6)−Re(2)−N(4)	72.5(4)
N(7)−Re(2)−Cl(5)	102.1(4)	O(2)−Re(2)−Cl(5)	85.4(3)
N(6)−Re(2)−Cl(5)	91.0(3)	N(4)−Re(2)−Cl(5)	87.2(3)
N(7)−Re(2)−Cl(4)	90.7(4)	O(2)−Re(2)−Cl(4)	87.0(3)
N(6)−Re(2)−Cl(4)	92.6(3)	N(4)−Re(2)−Cl(4)	81.6(3)
Cl(5)−Re(2)−Cl(4)	166.57(13)	C(23)−N(7)−Re(2)	168.1(9)

disposed at each metal site. The displacement of the Re(1) and Re(2) atoms toward O(1) and N(7) away from the planes of Cl(1), Cl(2), N(3), O(2) (md, 0.09 Å) and Cl(4), Cl(5), N(6), O(2) (md, 0.04 Å) are 0.27 and 0.29 Å respectively. The dihedral angle between the O(1), Re(1), O(2) and N(7), Re(2), O(2) planes is 64.1°, and the corresponding O(1), Re(1), Re(2), N(7) torsion angle is 114.5°.

b. Metal−Oxo and Metal−Imido Bonds. The Re−O(1) length in **2**, 1.663(6) Å, lies within the span 1.68 ± 0.03 Å, applicable to the majority of structurally characterized Re^{V}O species.[1−12,68] The minimum Re−O(oxo) distances observed lie around 1.60 Å.[68−70] This distance can therefore be taken to correspond more or less to triple bonding, Re≡O ($\sigma^2\pi^4$). The double bonded Re^{V}=O length observed in *trans*-Re^{V}O$_2$ species

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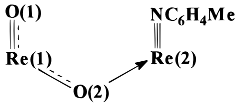
is ~1.76 Å.[68,71−73] The Re−O(oxo) bond in **2** is thus more triple than double in character and is simply represented as Re≡O in this work.

In **5c** the Re−N(4) length, 1.719(5) Å, lies close to the idealized triple bond value of 1.69 Å, the corresponding double bond value being 1.84 Å.[74,75] In hexacoordinated rhenium(V) imido species the Re−N bond is generally highly triple in character, its length spanning the range 1.67−1.74 Å (Re−N−C angle, 160−180°).[15,16,41,74−84]

c. Bridge in 7. The Re−N(imido) length and especially the Re−O(oxo) length in **7** are slightly longer than those of **5c** and **2**. The oxygen bridge is very unsymmetrical: Re(1)−O(2), 1.849(7) Å, and Re(2)−O(2), 1.954(7) Å. The bridge angle is 151.0(5)°. The length of the $\mathrm{Re^V}$−O single bond is estimated to be ~2.05 Å,[69,85,86] and the $\mathrm{Re^V}$═O length is ~1.76 Å (vide supra). Thus the Re(1)−O(2) bond has a large double-bond character and correspondingly the Re(1)−O(1) bond is longer here than that in **2**. This effect is stylized in **8** where the dotted line represents a partial bond. The Re(2)−O(2) bond also has significant double-bond character, but it is much less than that of Re(1)−O(2) and is not explicitly shown in **8**. The corresponding slight decrease in Re−NAr bond order is also not shown. In this simplified version, **7** can be conveniently described as a complex in which the rare[87,88] *cis*-$\mathrm{Re^VO_2}$ moiety acts as a monodentate oxygen-donor ligand forming a coordinate bond with the $\mathrm{Re^V}$NAr moiety.



8

No other oxo−imido dimer is available for comparison with **7**. In structurally characterized complexs of the oxo−oxo moiety $\mathrm{ORe^VORe^VO}$, the Re−O(oxo) and Re−O(bridging) distances and the Re−O−Re angle span the ranges 1.68−1.76 Å, 1.90−1.95 Å, and 174−180°, respectively.[54−59]

d. Chelate Ring and Back-Bonding. The chelate ring along with the pyridine ring constitute an excellent plane (md, 0.01−0.04 Å) in each complex. The Re−N(pyridine) bond invariably lies trans to the Re≡O or Re≡NAr function in **2**, **5c**, and **7** and is lengthened by trans influence. The two metal electrons occupy the $5d_{xy}$ orbital which can back-bond the azo-π^* orbital. The shortness (by ~0.1 Å) of the Re−N(azo) bond in **2**, **5c**, and **7** compared to the Re−N single bond (2.14 Å;[74,75] vide supra) and the lengthening (by up to 0.05 Å) of the N═N bond from the free ligand value (1.25 Å[89−91]) corroborate the presence of such back-bonding. This also provides a plausible clue for the geometric disposition of the ClL ligand. Significantly, in **3** the shortening of the Re−N(azo) bond and the lengthening of N═N bond are even more pronounced in agreement with the superior back-bonding ability of trivalent rhenium.[13] The Re−N(pyridine) bond is shorter in **3** than in the other complexes due to the weak, if any, trans influence of the Re−$\mathrm{OPPh_3}$ function.

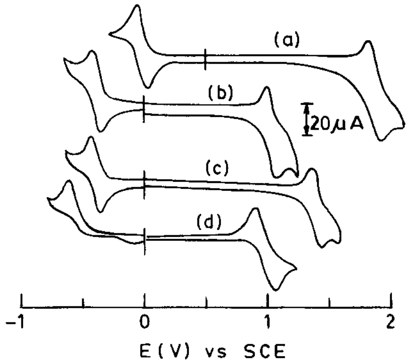


Figure 5. Cyclic voltammograms of a 10^{-3} M solution of (a) **2**, (b) **7**, (c) **5c**, and (d) **3** in acetonitrile (0.1 M $\mathrm{Et_4NClO_4}$) at a platinum electrode with a scan rate of 50 mV $\mathrm{s^{-1}}$.

Table 3. Cyclic Voltammetric Formal Potentials at 298 K in Acetonitrile (0.1 M $\mathrm{Et_4NClO_4}$) at a Platinum Electrode[a−e]

	$E_{1/2}$, V (ΔE_p, mV)			$E_{1/2}$, V (ΔE_p, mV)	
compd	az/az$^-$	$\mathrm{Re^{n+1}/Re^n}$	compd	az/az$^-$	$\mathrm{Re^{n+1}/Re^n}$
2	0.0 (100)	1.91 (120)	**5b**	−0.37 (80)	1.38 (80)
3	−0.60[f]	0.98 (80)	**5c**	−0.37 (80)	1.39 (80)
4	−0.62[f]	0.93 (80)	**6**	−0.44 (80)	1.35 (70)
5a	−0.38 (80)	1.38 (80)	**7**	−0.38 (80)	1.03 (80)

[a] $n = 5$ for **2** and **5**−**7**; $n = 3$ for **3** and **4**. [b] Scan rate 50 mV $\mathrm{s^{-1}}$. [c] $E_{1/2} = {}^1/_2(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. [d] $\Delta E_p = E_{pc} - E_{pa}$. [e] Reference elctrode SCE. [f] E_{pc}.

D. Redox Behavior. a. Electrochemistry: Metal Oxidation and Ligand Reduction. The complexes are electroactive in acetonitrile solution. A representative set of cyclic voltammograms are shown in Figure 5, and reduction potential data are listed in Table 3. A quasireversible one-electron oxidative response occurring at positive potentials is assigned to the metal site ($\mathrm{Re^{VI}/Re^V}$ in **2** and **5**−**7** and $\mathrm{Re^{IV}/Re^{III}}$ in **3** and **4**). A second response observed at negative potentials is due to the az/az$^-$ couple where az and az$^-$ represent the azo and azo anion radical moieties, respectively.[35−37]

In the redox sense, the imido ligand stabilizes the rhenium(VI) state better than the oxo ligand, the $\mathrm{Re^{VI}/Re^V}$ $E_{1/2}$ of **5** (~1.4 V) being much less than that of **2** (~1.9 V). Parallely, it is more difficult to reduce the azo group in **5** (~−0.4 V) than in **2** (~0.0 V). The bridging oxygen ligand in **7** stabilizes rhenium(VI) and destabilizes az$^-$ relative to cases of **2** and **5** which have the

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chloride ligand instead. The responses of **7** near 1.0 and −0.4 V are accordingly assigned to Re^{VI}/Re^{V} and az/az^{-} couples in the imido and the oxo halves, respectively. The voltage gap (∼1.4 V) between the two responses is much less than that (∼2.0 V) in **2** and **5** where the Re^{VI}/Re^{V} and az/az^{-} processes occur within the same monomer. The expected Re^{VI}/Re^{V} couple of the oxo half and the az/az^{-} couple of the imido half of **7** could not be experimentally accessed.

b. Azo−Aldimine Contrast: Reduction Potential and Oxygen Transfer. The metal reduction potentials of **2**−**6** are 0.2−0.6 V higher than those of similar pyridine-2-aldimine (pal) species.[2,15,16] This is qualitatively consistent with the superior electron-withdrawing ability of the azo function compared to the aldimine function. A significant orbital interaction can also be defined. The azo π^* orbital lies much lower than the aldimine π^* orbital.[35,92] Thus d(Re)−π^*(XL) back-bonding is stronger than d(Re)−π^*(pal) back-bonding. The d(Re) orbital is thus better stabilized in the XL complexes. The metal reduction potential is therefore higher. The relatively high energy of the π^*(aldimine) orbital gets expressed in another way: the pal complexes do not display any couple near the az/az^{-} couples of the XL species.

The π-acceptor order XL > pal finds chemical expression in the relative ease of $Re^{V}O$ reaction leading to the transfer of the oxygen function either as "O" to PPh_3, eq 2, or as "O^{2-}" to $ArNH_2$, eq 4. The transfer process is generally initiated by nucleophilic substrate attack on the $Re^{V}{\equiv}O$ π^* orbital and is therefore facilitated by the presence of electron-withdrawing ligands. Indeed the reaction of eq 2 is at least 100 times faster than the corresponding reaction between $ReOCl_3$(pal) and PPh_3.[2] Similarly the reaction of eq 4 is much more facile than the corresponding pal reaction.[15,16]

A dramatic expression of the very different oxygen atom transfer potency of the XL and pal complexes of $Re^{V}O$ can be seen in reactions of $ReOCl_3(PPh_3)_2$ with the ligands. In the case of XL the reaction of eq 3 affording the phosphine oxide complex occurs even when the reaction solution is cold. On the other hand the reaction of pal with $ReOCl_3(PPh_3)_2$ constitute the method for synthesis of the oxo complex $ReOCl_3$(pal).[2] It is very likely that $ReOCl_3$(XL) is formed as an intermediate in the reaction of eq 3 but only to react rapidly with the liberated PPh_3 forming **4** which alone is isolated.

Concluding Remarks

The findings of this work can now be stated along with indications of future prospects. The first $Re^{V}{\equiv}O$ complex incorporating 2-(arylazo)pyridine chelation, $ReOCl_3$(ClL), **2**, has been synthesized. It has provided rational access to the phosphine oxide and imido complexes $Re^{III}(OPPh_3)Cl_3$(ClL), **3** and $Re^{V}(NAr)Cl_3$(ClL), **5**. In all of the three systems the $ReCl_3$ fragment is meridionally disposed and the pyridine nitrogen of the ClL chelate ring lies trans to oxo/$OPPh_3$/NAr ligand.

An unexpected finding is the dimer **7** incorporating the unprecedented oxygen-bridged oxo−imido motif **8**. The bridge is angular and unsymmetrical such that **8** can be approximately described as a complex of *cis*-$Re^{V}O_2$ and Re^{V}NAr. The Re−O(oxo) and Re−N(imido) bond orders in **7** are somewhat smaller than those in **2** and **5**.

A notable feature of the complexes is the sizable d(Re)−π^*(azo) back-bonding, and this is expressed in bond parameter and metal reduction potential values. It is chemically expressed in the potency of $Re^{V}O$ oxygen transfer either as "atom" to PPh_3 (**2** → **3**) or in oxidic form to $ArNH_2$ protons (**2** → **5**). The back-bonding factor makes the transfer process far more facile in the case of **2** compared to pyridine-2-aldimine species.

The phosphine oxide complexes **3** and **4** are themselves reactive and act as precursors to several other systems. We have noted in this work that **4** can cleave the azo group affording **6**, eq 5. The $OPPh_3$ ligand is replaceable by PPh_3 apparently with a change in isomeric geometry. It is also replaceable by azopyridine ligands with concomitant metal reduction leading to bis and tris chelates. Such findings will constitute a subject matter of future reports on the remarkably rich chemistry of rhenium−azopyridine systems.

Experimental Section

Materials. $ReOCl_3(PPh_3)_2$[93] and 2-(arylazo)pyridines[41,94] were prepared by reported methods. The purification and drying of dichloromethane and acetonitrile for synthesis as well as electrochemical and spectral work were done as before.[95,96] Toluene was distilled over sodium before use. All other chemicals and solvents were of reagent grade and were used as received.

Physical Measurements. Spectral measurements were carried out with Perkin-Elmer 783 (IR; KBr disk) and Hitachi 330 (UV−vis; CH_2Cl_2 solution) spectrophotometers. Proton NMR spectra ($CDCl_3$ solvent) were recorded on a Bruker FT 300 MHz spectrometer. The numbering scheme used for ^1H NMR is the same as in crystallography. Spin−spin structures are abbreviated as the following: s, singlet; d, doublet; t, triplet; m, multiplet. Electrochemical measurements were performed (acetonitrile solution) on a PAR model 370-4 electrochemistry system as described elsewhere[97] using a platinum working electrode under dinitrogen atmosphere. The supporting electrolyte was tetraethylammonium perchlorate (TEAP), and potentials are referenced to the saturated calomel electrode (SCE) without junction correction. Magnetic susceptibilities were measured on a PAR 155 vibrating-sample magnetometer, and microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 Series II elemental analyzer.

Preparation of Complexes. a. $ReOCl_3$(ClL), 2. To a hot suspension of $KReO_4$ (250 mg, 0.86 mmol) in 10 mL of concentrated hydrochloric acid was added 785 mg (4.3 mmol) of 2-(phenylazo)pyridine, HL. The resulting mass was stirred magnetically and heated to reflux for 30 min. A dark crystalline solid starts depositing from the solution, which was then cooled to room temperature. The solid collected by filtration was made acid free by washing several times with water. It was finally washed with hexane and then dried in vacuo over P_4O_{10}. Yield: 385 mg (85%). Anal. Calcd for $C_{11}H_8Cl_4N_3ORe$: C, 25.09; H, 1.50; N, 7.98. Found: C, 25.18; H, 1.60; N, 7.90. UV−vis (λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)): 700 (710); 525 (5010); 365 (9120). IR (cm^{-1}): ν_{Re-Cl}, 325, 345, 365; $\nu_{Re{\equiv}O}$, 995. ^1H NMR (δ (J, Hz)): 7.84 (H(2), d, 8.5); 8.22 (H(3), t, 7.6); 6.74 (H(4), t, 6.6); 8.70 (H(5), d, 6.0); 7.90 (H(7), H(11), d, 8.7); 7.53(H(8), H(10), d, 9.0) (compare with free ClL: 7.34 (H(2), d, 7.9); 7.83 (H(3), t, 7.5); 7.34 (H(4), t, 6.8); 8.68 (H(5), d, 6.0); 7.93 (H(7), H(11), d, 8.7); 7.43 (H(8), H(10), d, 8.7).

b. $Re(OPPh_3)Cl_3$(ClL), 3. Reaction of 2 with PPh_3. To a solution of **2** (100 mg, 0.19 mmol) in 10 mL of dichloromethane was added 250 mg (0.96 mmol) of PPh_3. The pink solution turned brown instantly, and it was stirred for 5 min at room temperature. The solvent was then removed under reduced pressure. The golden brown crystalline solid was washed several times with hexane and finally dried in vacuo over P_4O_{10}. Yield: 130 mg (87%). Anal. Calcd for $C_{29}H_{23}Cl_4N_3OPRe$: C, 44.16; H, 2.92; N, 5.33. Found: C, 44.32; H, 2.82; N, 5.20. UV−vis (λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)): 780^{sh} (115); 650 (480); 470 (6280); 395^{sh}

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Table 4. Crystallographic Data for 2, 3, 5c, and **7**·CH_2Cl_2

	2	**3**	**5c**	**7**·CH_2Cl_2
empirical formula	$C_{11}H_8Cl_4N_3ORe$	$C_{29}H_{23}Cl_4N_3OPRe$	$C_{17}H_{12}Cl_5N_4Re$	$C_{30}H_{25}Cl_8N_7O_2Re_2$
fw	526.20	788.47	635.76	1171.57
cryst size, mm	0.35 × 0.30 × 0.25	0.4 × 0.35 × 0.3	0.35 × 0.3 × 0.3	0.4 × 0.35 × 0.25
cryst system	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	7.118(4)	11.264(2)	9.683(3)	12.522(6)
b, Å	8.537(4)	15.221(3)	10.898(3)	12.857(8)
c, Å	13.231(9)	17.628(4)	11.522(3)	13.182(7)
α, deg	79.16(5)		63.67(2)	67.75(4)
β, deg	78.03(5)	94.21(3)	71.24(2)	88.30(4)
γ, deg	70.96(4)		86.79(2)	82.09(4)
V, Å^3	737.2(7)	3014(1)	1026(1)	1945(2)
Z	2	4	2	2
ρ_{calcd}, g cm^{-3}	2.371	1.738	2.057	2.001
μ, cm^{-1}	89.63	44.67	65.80	68.06
R^a, wR2^b [$I > 2\sigma(I)$], %	3.19, 7.83	6.16, 13.55	3.39, 7.65	4.69, 10.68

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

(4980). IR (cm^{-1}): $\nu_{\mathrm{Re-Cl}}$, 320, 330; ν_{OPPh3}, 1120; $\nu_{\mathrm{N=N}}$, 1335. μ: 1.69 μ_B. ^{1}H NMR (δ (J, Hz)): C_5H_4N, 27.69 (H(2), d, 9.0); −27.96 (H(3), t, 7.4); 40.85 (H(4), t, 6.1); −11.11 (H(5), d, 6.1); ClC_6H_4, 30.97 (H(7), H(11), d, 8.7); 10.65 (H(8), H(10), d, 7.8); PPh_3, 2.18 (H(o), d, ill-resolved); 6.90 (H(m), t, 7.1); 6.32 (H(p), t, 7.1).

c. Re(OPPh$_3$)Cl$_3$(HL), 4. Reaction of ReOCl$_3$(PPh$_3$)$_2$ with HL. To a suspension of $ReOCl_3(PPh_3)_2$ (100 mg, 0.12 mmol) in 10 mL of toluene was added 30 mg (0.16 mmol) of HL, and the mixture was warmed (40 °C) under dinitrogen atmosphere with stirring for 10 min. The solvent was then removed under reduced pressure. The solid thus obtained was dissolved in 5 mL of dichloromethane, and the solution was subjected to chromatography on a silica gel column (20 × 1 cm; 60−120 mesh, BDH). Upon elution with benzene, a small red band separated out, which was rejected. A golden yellow band was then eluted out with benzene−acetonitrile (25:1) mixture. The required complex was obtained by slow evaporation of the eluate as shining golden yellow microcrystals. Yield: 35 mg (∼ 40%). Anal. Calcd for $C_{29}H_{24}Cl_3N_3OPRe$: C, 46.18; H, 3.19; N, 5.58. Found: C, 46.05; H, 3.10; N, 5.50. UV−vis ($\lambda_{\max}$, nm (ϵ, M^{-1} cm^{-1})): 780$^{\mathrm{sh}}$ (115); 635 (310); 470 (3320); 400$^{\mathrm{sh}}$ (2740). IR (cm^{-1}): $\nu_{\mathrm{Re-Cl}}$, 310, 340; ν_{OPPh3}, 1120; $\nu_{\mathrm{N=N}}$, 1335. μ: 1.66 μ_B.

d. Re(NAr)Cl$_3$(ClL), 5. Reaction of 2 with Excess ArNH$_2$. The complexes were prepared in 75−80% yield by the same general method. Details are given for $Re(NC_6H_4Me)Cl_3(ClL)$, **5b**. To a warm solution of **2** (100 mg, 0.19 mmol) in 10 mL of toluene was added an excess of p-toluidine (102 mg, 0.95 mmol), and the mixture was heated to reflux for 1 h. During this time the color changed from pink to violet. The solvent was then removed under reduced pressure, and the solid thus obtained was subjected to column chromatography. The violet band was eluted using benzene−acetonitrile (20:1) mixture, and from the eluate **5b** was obtained in ∼80% yield by slow evaporation. Anal. Calcd for $C_{18}H_{15}Cl_4N_4Re$: C, 35.12; H, 2.43; N, 9.11. Found: C, 35.25; H, 2.50; N, 9.05. UV−vis ($\lambda_{\max}$, nm (ϵ, M^{-1} cm^{-1})): 660 (2700); 500 (8090); 340 (14 700). IR (cm^{-1}): $\nu_{\mathrm{Re-Cl}}$, 340, 350; $\nu_{\mathrm{N=N}}$, 1320. ^{1}H NMR (δ (J, Hz)): 7.63 (H(2), d, 8.3); 8.04 (H(3), t, 7.8); 6.71 (H(4), t, 6.9); 9.15 (H(5), d, 6.0); 7.41 (H(7), H(11), d, 8.2); 7.15 (H(8), H(10), d, 8.7); 7.09 (H(12), H(14), H(16), H(17), m); 2.49 (Me(15), s).

Re(NC$_6$H$_5$)Cl$_3$(ClL), 5a. Anal. Calcd for $C_{17}H_{13}Cl_4N_4Re$: C, 33.94; H, 2.16; N, 9.32. Found: C, 34.05; H, 2.05; N, 9.20. UV−vis ($\lambda_{\max}$, nm (ϵ, M^{-1} cm^{-1})): 660 (2540), 500 (7960), 335 (10 425). IR (cm^{-1}): $\nu_{\mathrm{Re-Cl}}$, 320, 340, 365; $\nu_{\mathrm{N=N}}$, 1320.

Re(NC$_6$H$_4$Cl)Cl$_3$(ClL), 5c. Anal. Calcd for $C_{17}H_{12}Cl_5N_4Re$: C, 32.08; H, 1.88; N, 8.88. Found: C, 32.30; H, 1.96; N, 8.98. UV−vis ($\lambda_{\max}$, nm (ϵ, M^{-1} cm^{-1})): 660 (2700), 510 (8100), 340 (15 680). IR (cm^{-1}): $\nu_{\mathrm{Re-Cl}}$, 325, 345; $\nu_{\mathrm{N=N}}$, 1320.^{1}H NMR (δ (J, Hz)): 7.63 (H(2), d, 8.1); 8.09 (H(3), t, 7.5); 6.96 (H(4), t, 6.8); 9.16 (H(5), d, 6.0); 7.46 (H(7), H(11), d, 8.2); 7.20 (H(8), H(10), H(13), H(14), H(16), H(17), m).

e. Re(NC$_6$H$_5$)Cl$_3$(HL), 6. Reaction of 4 with HL. To a solution of $Re(OPPh_3)Cl_3(HL)$, **4** (400 mg, 0.53 mmol), in 30 mL of toluene was added 97 mg (0.53 mmol) of HL, and the mixture was allowed to reflux for 30 min. The resulting violet solution was evaporated under reduced pressure. The solid mass thus obtained was dissolved in 5 mL of benzene and was subjected to chromatography on silica gel column successively using benzene−hexane (1:1), benzene, and benzene−acetonitrile (20:1) as eluants (**A**−**C** fraction, respectively). Solvent removal from **A** (colorless) afforded $OPPh_3$ as white solid (103 mg, 0.37 mmol, mp 154 °C). Similarly **B** afforded orange colored 2-(pyridylazo)pyridine[98] (yield: 23 mg, 0.25 mmol, mp. 86 °C). Finally **C** furnished $Re(NC_6H_5)Cl_3(HL)$[41] as a dark shiny product (yield: 223 mg, 0.39 mmol).

f. Re$_2$O$_2$(NC$_6$H$_4$Me)Cl$_4$(ClL)$_2$, 7. Reaction of 2 with *p*-MeC$_6$H$_4$NH$_2$ (1:1). To a warm solution of **2** (100 mg, 0.19 mmol) in 10 mL of toluene was added p-toluidine (20 mg, 0.19 mmol), and the mixture was refluxed for 1 h. Evaporation of the solvent under reduced pressure gave a dark solid which was dissolved in a minimum volume of dichloromethane and subjected to chromatography. A blue violet band was eluted with benzene−acetonitrile (20:1) mixture. It was found to be a mixture of **5b** and **7** in 1:2 mole ratio. From this **7** was obtained in pure form after several recrystallizations from 1:1 dichloromethane−hexane mixture as the dichloromethane adduct **7**·CH_2Cl_2. Yield: 52 mg (50% with respect to metal). Anal. Calcd for $C_{30}H_{27}Cl_8N_7O_2Re_2$: C, 30.69; H, 2.30; N, 8.35. Found: C, 30.5; H, 2.4; N, 8.5. UV−vis ($\lambda_{\max}$, nm (ϵ, M^{-1} cm^{-1})): 670$^{\mathrm{sh}}$ (5030), 540 (10 390), 340 (19 100). IR (cm^{-1}): $\nu_{\mathrm{Re-Cl}}$, 330, 345; $\nu_{\mathrm{Re\equiv O}}$, 990; $\nu_{\mathrm{Re-O-Re}}$, 785. ^{1}H NMR (δ (J, Hz)): 7.62 (H(2), d, 7.2); 7.91 (H(3), t, 6.1); 6.68 (H(4), t, 6.8); 9.78 (H(5), d, 6.2); 7.80 (H(7), H(11), d, 7.5); 7.48 (H(8), H(10), H(13), m); 8.02 (H(14), t, 6.0); 6.35 (H(15), t, 6.8); 9.92 (H(16), d, 6.6); 7.41 (H(18), H(22), d, 6.9); 7.16 (H(19), H(21), d, 7.8); 7.02 (H(24), H(25), H(27), H(28), m); 2.43 (Me(26), s).

X-ray Structure Determination. Single crystals of complexes were grown by slow diffusion of hexane into dichloromethane solutions of the complexes. Cell parameters were determined by a least-squares fit of 30 machine-centered reflections ($14 \le 2\theta \le 28°$). Data were collected by the ω scan technique in the range $3 \le 2\theta \le 50°$ for **2**, $3 \le 2\theta \le 45°$ for **3** and **7**, and $3 \le 2\theta \le 55°$ for **5c** on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation at 25 °C. Two check reflections after each 198 reflections showed no intensity reduction for any of the crystals. All data were corrected for Lorentz−polarization effects and absorption.[99]

Totals of 2635 (**2**), 4237 (**3**), 5032 (**5c**), and 5192 (**7a**) reflections were collected, of which 2606, 3962, 4749, and 5108 were respectively unique; of these 2364, 2648, 4118, and 3855 were observed ($I > 2\sigma(I)$). The metal atoms were located from Patterson maps, and the rest of the

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non-hydrogen atoms emerged from successive Fourier synthesis. The structures were refined by full-matrix least-squares procedures on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms for **2** were directly located from X-ray data; others were included at calculated positions. Calculations were performed using the SHELXTL V 5.03[100] Program package. Significant crystal data are listed in Table 4.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **2**, **3**, **5c**, and **7**·CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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