

Oxygen Atom Transfer from Nitrogenous Re^{VO} Reagents to Diphosphines and Subsequent Transformations. Rhenium(III) Products and Reaction Models

Sibaprasad Bhattacharyya, Indranil Chakraborty, Bimal Kumar Dirghangi, and Animesh Chakravorty*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

Received June 1, 2000

The concerned diphosphines are Ph₂P(CH₂)_nPPh₂ (**1**), abbreviated P_nP, and the Re^{VO} reagents are ReOCl₃L (**2**) and ReOCl₃L' (**3**), where L and L' are the azopyridine and pyridine–imine ligands *p*-ClC₆H₄N=NC₅H₄N and *p*-MeC₆H₄N=CHC₅H₄N, respectively. One atom transfer from **2** to **1** has afforded Re(OP_nP)Cl₃L (**4a**, *n* = 1; **4b**, *n* = 2; **4c**, *n* = 3). Of these **4b** and **4c** are stable, but **4a** undergoes spontaneous isomerization to Re(PIPO)Cl₃L (**5**) in solution. Two-atom transfer studied with both **2** and **3** has afforded binuclear LC₃Re(OP_nPO)ReCl₃L (**8a**, *n* = 2; **8b**, *n* = 3) and L'Cl₃Re(OP_nPO)ReCl₃L' (**9a**, *n* = 2; **9b**, *n* = 3) for *n* = 2, 3 and mononuclear Re(OP₁PO)Cl₃L (**11**) and Re(OP₁PO)Cl₃L' (**12**) for *n* = 1. The mixed system L'Cl₃Re(OP₂PO)ReCl₃L (**10**) has been prepared from **3** and **4b**. The complex Re(PPh₃)Cl₃L (**7a**) is furnished by the reaction of Re(OPPh₃)Cl₃L (**6a**) or **4b** or **11** with PPh₃. The species have been characterized with the help of spectral, electrochemical, and X-ray structural data. All the complexes have *mer* geometry except **5** and **7a**, which have *fac* geometry. The latter is best suited for concurrent Re–N and Re–P back-bonding. Variable-temperature rate data of the reaction **4a** → **5** are consistent with an intramolecular strongly associative transition state (ΔS[‡], –22.6 eu) in which the dangling phosphine function lies close to the metal. Two-atom transfer to PIP is believed to proceed via a transient binuclear intermediate which undergoes cleavage at one end due to steric crowding, affording **11** and **12**. Crystal data for the complexes are as follows: **5**·1.5 C₆H₆, empirical formula C₄₅H₃₉Cl₄N₃O₂Re, crystal system triclinic, space group P1̄, *a* = 10.034(2) Å, *b* = 10.737(2) Å, *c* = 20.357(4) Å, α = 89.38(3)°, β = 87.79(3)°, γ = 80.22(3)°, *V* = 2159.7(7) Å³, *Z* = 2; **7a**·CH₂Cl₂, empirical formula C₃₀H₂₅Cl₆N₃PRE, crystal system monoclinic, space group P2₁/*n*, *a* = 11.695(6) Å, *b* = 17.745(7) Å, *c* = 15.459(9) Å, β = 100.94(5)°, *V* = 3150(3) Å³, *Z* = 4; **9a**, empirical formula C₅₂H₄₈Cl₆N₄O₂P₂Re₂, crystal system monoclinic, space group C2/*c*, *a* = 19.769(12) Å, *b* = 12.864(6) Å, *c* = 22.20(2) Å, β = 101.76(6)°, *V* = 5530(6) Å³, *Z* = 4; **11**, empirical formula C₃₆H₃₀Cl₄N₃O₂P₂Re, crystal system monoclinic, space group I2/*a*, *a* = 16.866(6) Å, *b* = 12.583(6) Å, *c* = 34.78(2) Å, β = 99.22(4)°, *V* = 7285(7) Å³, *Z* = 8.

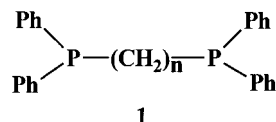
Introduction

This work stems from our interest in rhenium-promoted ligand oxidations.^{1–8} The Re^{VO} moiety is a potentially excellent oxygen atom transfer reagent, as in eq 1, where the oxophilic



substrate is a tertiary phosphine.^{1–3,9–17} Chelation of nitrogenous

π -acidic ligands to Re^{VO} facilitates the transfer process via electron withdrawal from the metal.^{1–3} The progress in the case of monophosphines has now prompted us to explore the reactions of such chelates with linear diphosphines of type **1**, abbreviated P_nP (*n* = 1–3). The serial atom transfer reactions,



eq 2 and 3, have been realized. Of major interest is the spontaneous solution reactivity of the *n* = 1 products, in contrast

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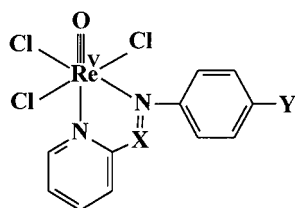
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with the indefinite stability of the $n > 1$ species. The binuclear complex of eq 3 could not be isolated in the $n = 1$ case; instead mononuclear ReOPIPO is afforded. On the other hand, the ReOP1P system (eq 2, $n = 1$) is found to undergo a remarkable twin isomerization. The nature of these transformations and the origin of the $n = 1$ singularity have been scrutinized with the help of rate data and structural models. Certain related reactions with monophosphines have also been examined. The family of rhenium(III) compounds defining this fascinating chemistry has been characterized. A few reactions of Re^{VO} species with diphosphines leading to phosphorus-coordinated end products have been reported in the literature.^{18–20}

Results and Discussion

A. Isolation of Products. a. The Reactants. In most of the reactions with PnP , the oxo complex ReOCl_3L , **2**, has been used as the transfer reagent in view of its efficacy endowed by the π -acidic azopyridine ligand (L).¹ In a few studies the relatively sluggish pyridine-2-alimine (L') complex³ $\text{ReOCl}_3\text{L}'$, **3**, has

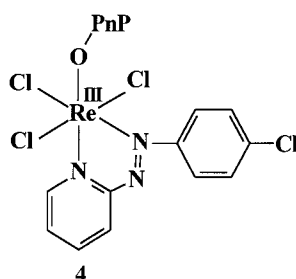


2 (X = N, Y = Cl)

3 (X = CH, Y = Me)

been employed to achieve superior product quality. The products concerning us in this work are listed and numbered in Chart 1.

b. Complexes 4, 5, and 7. Transfer of one oxygen atom from **2** to PnP afforded **4** in good yield, eq 4. The reaction proceeded

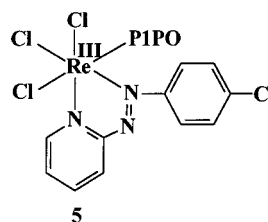


rapidly at room temperature upon mixing **2** with excess PnP in benzene solution. All the type **4** complexes are stable in the solid state, and **4b** and **4c** are also stable in solution. In contrast **4a** spontaneously isomerizes to **5**, which has been isolated by simply leaving a benzene solution of **4a** for a few hours at room temperature followed by chromatographic workup.

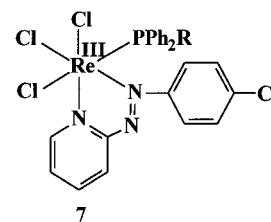
The monophosphine complex **7**, which belongs to the same geometrical type as **5**, was furnished upon reacting the phosphine

Chart 1

4a	$\text{Re}(\text{OP1P})\text{Cl}_3\text{L}$	8a	$\text{LCl}_3\text{Re}(\text{OP2PO})\text{ReCl}_3\text{L}$
4b	$\text{Re}(\text{OP2P})\text{Cl}_3\text{L}$	8b	$\text{LCl}_3\text{Re}(\text{OP3PO})\text{ReCl}_3\text{L}$
4c	$\text{Re}(\text{OP3P})\text{Cl}_3\text{L}$	9a	$\text{L}'\text{Cl}_3\text{Re}(\text{OP2PO})\text{ReCl}_3\text{L}'$
5	$\text{Re}(\text{P1PO})\text{Cl}_3\text{L}$	9b	$\text{L}'\text{Cl}_3\text{Re}(\text{OP3PO})\text{ReCl}_3\text{L}'$
6a	$\text{Re}(\text{OPPh}_3)\text{Cl}_3\text{L}$	10	$\text{LCl}_3\text{Re}(\text{OP2PO})\text{ReCl}_3\text{L}'$
6b	$\text{Re}(\text{OPPh}_2\text{Me})\text{Cl}_3\text{L}$	11	$\text{Re}(\text{OP1PO})\text{Cl}_3\text{L}$
7a	$\text{Re}(\text{PPh}_3)\text{Cl}_3\text{L}$	12	$\text{Re}(\text{OP1PO})\text{Cl}_3\text{L}'$
7b	$\text{Re}(\text{PPh}_2\text{Me})\text{Cl}_3\text{L}$		



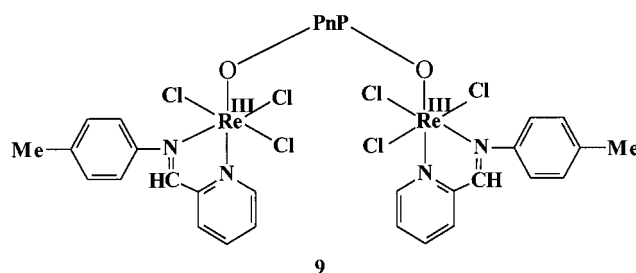
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7

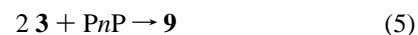
oxide complex¹ **6** with excess PPh_2R (R = Ph, Me) in boiling benzene. Under this drastic condition, the imide complex $\text{Re}(\text{NC}_6\text{H}_4\text{Cl})\text{Cl}_3\text{L}'$ is invariably formed as a byproduct.

c. Complexes 8–12. Oxygen atom transfer to both ends of PnP has been achieved by reacting it with excess **2** or alternatively by reacting **4** with **2**. In the $n = 2, 3$ cases binuclear complexes of type **8** are isolated. However lack of solubility and single crystals have vitiated their characterization. Fortunately **9**, the pyridine-2-alimine analogue of **8**, is readily formed



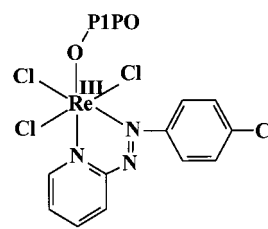
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by the reaction of eq 5, and it is soluble and crystalline. The



mixed L,L' dimer **10** isolated by the reaction of **3** with **4b** was found to be insoluble like **8**.

In contrast with the $n = 2, 3$ cases, successive oxygen atom transfer from **2** to PIP afforded the mononuclear complexes **11** incorporating a dangling phosphine oxide function. Similarly **3** and P1P furnished **12**.



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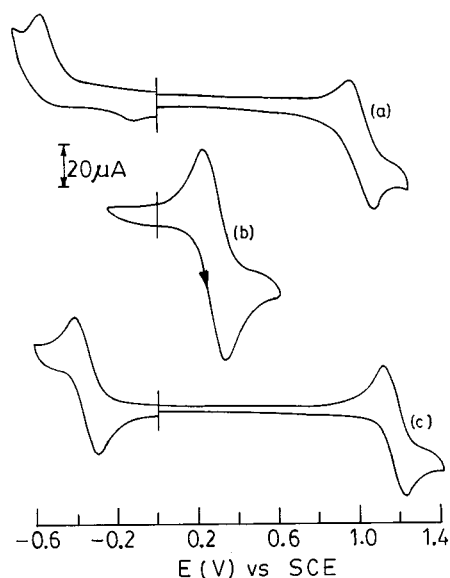
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Table 1. Cyclic Voltammetric Potentials at 298 K in Acetonitrile (0.1 M Et₄NClO₄) at a Platinum Electrode^{a-d}

compd	$E_{1/2}$, V (ΔE_p , mV)		compd	$E_{1/2}$, V (ΔE_p , mV)	
	L/L ^{•-}	Re ^{IV} /Re ^{III}		L/L ^{•-}	Re ^{IV} /Re ^{III}
4a	-0.56 ^e	0.96 (90)	7b	-0.26 (80)	1.18 (80)
4b	-0.60 ^e	1.01 (100)	9a		0.27 (100)
4c	-0.56 ^e	0.99 (100)	9b		0.33 (100)
5	-0.35 (100)	1.16 (120)	11	-0.55 ^e	0.93 (70)
6b	-0.59 ^e	0.99 (120)	12		0.30 (100)
7a	-0.27 (70)	1.20 (70)			

^a Scan rate 50 mV s⁻¹. ^b $E_{1/2} = 1/2(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. ^c $\Delta E_p = E_{pc} - E_{pa}$. ^d Reference electrode SCE. ^e E_{pc} .

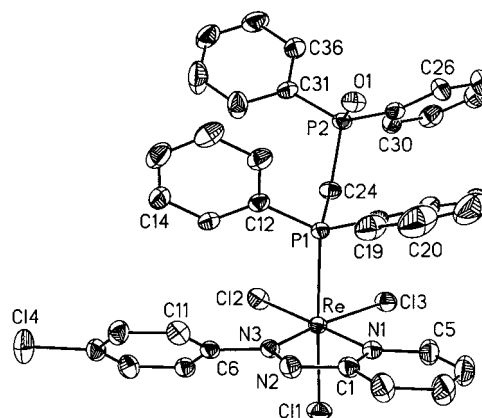
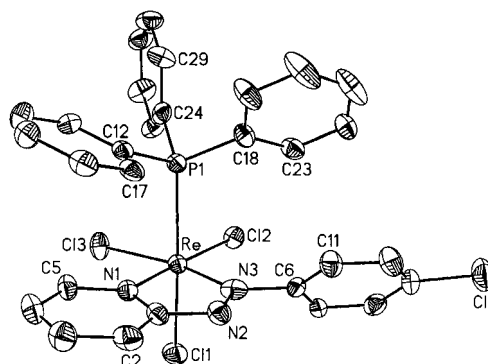
**Figure 1.** Cyclic voltammograms of a 10⁻³ M solution of (a) **4a**, (b) **9a**, and (c) **5** in acetonitrile (0.1 M Et₄NClO₄) at a platinum electrode with a scan rate of 50 mV s⁻¹.

B. Characterization. a. Spectra. Data are collected in the Experimental Section. The complexes display Re–Cl stretches in the range 300–340 cm⁻¹. Coordinated O–P (**4**, **6**, **8–12**), free P–O (**5**, **11**, **12**), azo (**4–8**, **10**, **11**), and azomethine (**9**, **10**, **12**) vibrations occur near 1120, 1200, 1330, and 1600 cm⁻¹, respectively.

The ¹H NMR lines of the complexes in CDCl₃ are paramagnetically (Re^{III}, t_{2g}⁴) shifted.^{1,2,8,10,21} The chemical shifts of the chelating ligands are particularly widely spread: L, +47 to -35 ppm, and L', +30 to -33 ppm. The large difference in chemical shifts of the proton ortho to the pyridine nitrogen is useful for isomer identification: **4a**, -9.94 ppm, and **5**, -19.50 ppm. The corresponding resonances in **4b**, **4c**, and **11** expectedly lie close to that of **4a**. Further, the aromatic protons of the phosphorus ligand have distinctive spreads in the Re–OP (**4**, **6**, **9**, **11**, **12**) and Re–P (**5**, **7**) species: 1–8 and 3–21 ppm, respectively.

b. Electrochemistry. The species of Chart 1 are generally electroactive in acetonitrile solution (**8** and **10** are too insoluble). Reduction potential data are collected in Table 1 and representative voltammograms are shown in Figure 1. The $E_{1/2}$ values and the voltammograms are diagnostic of Re–OP (**4**, **6**, **11**) and Re–P (**5**, **7**) species as well as of Re–L (**11**) and Re–L' (**12**) species.

The Re–L species uniformly display two responses, one at positive potential assigned to the Re^{IV}/Re^{III} couple (redox orbital t_{2g})^{1,3} and one at negative potential due to the L/L^{•-} couple (redox orbital primarily azo-π*).^{1,22–24} As expected, the latter

**Figure 2.** Molecular view and atom-labeling scheme for Re(PiPO)-Cl₃L, **5**. All non-hydrogen atoms are represented by 30% thermal probability ellipsoids.**Figure 3.** Molecular view and atom-labeling scheme for Re(PPh₃)-Cl₃(L), **7a**. All non-hydrogen atoms are represented by 30% thermal probability ellipsoids.

response does not occur in the Re–L' species. On going from **4a** to **5** the $E_{1/2}$ values of both the couples increase significantly, suggesting better stability of the t₂ as well as of azo-π* orbitals in **5**. This is consistent with bonding consideration, vide infra.

The $E_{1/2}$ of the Re^{IV}/Re^{III} couple in Re–L' species is lower than that of the corresponding Re–L species because of the π-acidity order L ≫ L'. Dinuclear species of type **9** display only a single Re^{IV}/Re^{III} couple, the current height being approximately twice that for one-electron transfer as in **5** and **11** (Figure 1). There is thus little or no communication between the two widely separated (>8 Å) metal atoms.

C. Structures. The structures of **5**·1.5 C₆H₆, **7a**·CH₂Cl₂, **9a**, and **11** have been determined. Molecular views and atom-numbering schemes are shown in Figures 2–5, and selected bond parameters are listed in Tables 2–4.

a. Coordination Spheres. All the complexes have severely distorted octahedral geometries, the coordination spheres being either RePCl₃N₂ (**5**, **7a**) or ReOCl₃N₂ (**9a**, **11**). In **5** the N(1), N(3), Cl(2), and Cl(3) atoms along with the Re atom form an excellent equatorial plane (mean deviation 0.01 Å) to which the nearly linear P(1), Re, Cl(1) fragment is more or less perpendicularly disposed. The coordination sphere in **7a** is similar.

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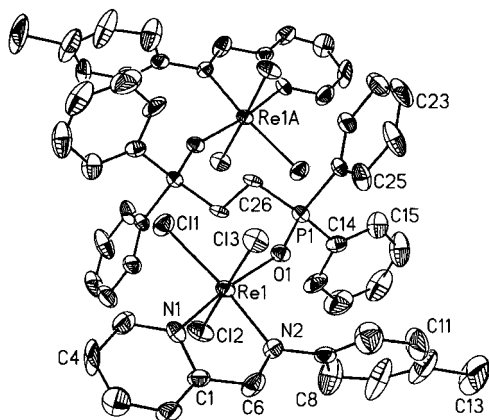


Figure 4. Molecular view and atom-labeling scheme for $L'Cl_3Re(OP_2PO)ReCl_3L'$, **9a**. All non-hydrogen atoms are represented by 30% thermal probability ellipsoids

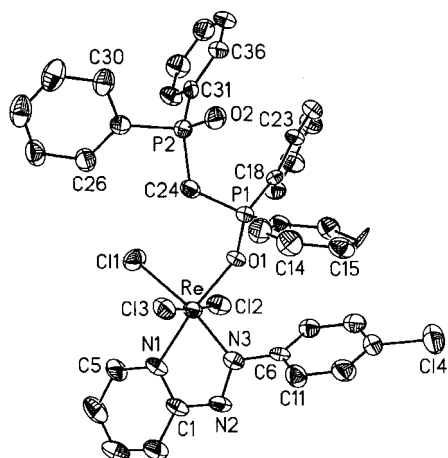


Figure 5. Molecular view and atom-labeling scheme for $Re(OPiPO)Cl_3L$, **11**. All non-hydrogen atoms are represented by 30% thermal probability ellipsoids

In **11** the N(1), N(3), O(1), and Cl(1) atoms define a good equatorial plane (mean deviation 0.02 Å), and the Cl(2), Re, and Cl(3) atoms constitute an approximately perpendicular axis. The corresponding geometrical situation in **9a** is very similar. The two halves of the later molecule are related by a crystallographic inversion center. The two metal atoms are widely separated ($Re \cdots Re$, 8.222(1) Å).

b. Isomeric Geometries. The $ReCl_3$ fragments have *fac* and *mer* geometries in **5**, **7a** and **9a**, **11**, respectively. Tertiary phosphines are π -accepting ligands, the acceptor orbital being a mixture of $3d\pi$ and $P-C \sigma^*$ -components.^{25,26} The azopyridine ligand is also an excellent π -acid, especially at the azo site.¹ Trivalent rhenium is prone to back-bonding,^{1,27} which can thus have (idealized octahedral geometry assumed) both $t_{2g}(Re) \rightarrow \pi(P)$ and $t_{2g}(Re) \rightarrow \pi^*(L)$ components in **5** and **7a**. The bonding would be stronger in the *fac* geometry, in which competition between $\pi(P)$ and $\pi^*(L)$ for identical metal orbitals is minimal.

Back-bonding is believed to sustain the *fac* geometry in **5** and **7a** by more than offsetting the steric and electrostatic advantages of the *mer* geometry, as has been observed in related species.^{2,8} Phosphine oxides are purely donor in character and

Table 2. Selected Bond Lengths [Å] and Angles [deg] for $5 \cdot 1.5C_6H_6$ and **7a**· CH_2Cl_2

	5	7a
Distances		
Re–N(3)	2.007(4)	1.994(10)
Re–N(1)	2.072(4)	2.077(9)
Re–Cl(2)	2.345(2)	2.332(3)
Re–Cl(3)	2.365(1)	2.370(3)
Re–Cl(1)	2.380(2)	2.375(3)
Re–P(1)	2.479(2)	2.510(3)
N(2)–N(3)	1.322(6)	1.333(13)
P(2)–O(1)	1.480(4)	
Angles		
N(3)–Re–N(1)	74.1(2)	74.2(4)
N(3)–Re–Cl(2)	103.2(1)	101.1(3)
N(1)–Re–Cl(2)	177.0(1)	175.2(3)
N(3)–Re–Cl(3)	166.0(1)	165.4(3)
N(1)–Re–Cl(3)	92.1(1)	91.5(3)
Cl(2)–Re–Cl(3)	90.6(1)	93.3(1)
N(3)–Re–Cl(1)	92.5(1)	88.9(3)
N(1)–Re–Cl(1)	89.9(1)	89.8(2)
Cl(2)–Re–Cl(1)	91.4(1)	91.1(1)
Cl(3)–Re–Cl(1)	89.7(1)	88.4(1)
N(3)–Re–P(1)	93.0(1)	94.8(3)
N(1)–Re–P(1)	92.5(1)	91.7(2)
Cl(2)–Re–P(1)	86.4(1)	87.7(1)
Cl(3)–Re–P(1)	85.2(1)	88.1(1)
Cl(1)–Re–P(1)	174.4(1)	176.3(1)

Table 3. Selected Bond Lengths [Å] and Angles [deg] for **9a**

	Distances	
Re(1)–N(2)	2.020(11)	Re(1)–N(1) 2.032(11)
Re(1)–O(1)	2.068(8)	Re(1)–Cl(3) 2.357(4)
Re(1)–Cl(2)	2.378(4)	Re(1)–Cl(1) 2.370(4)
N(2)–C(6)	1.32(2)	O(1)–P(1) 1.506(8)
Angles		
N(2)–Re(1)–N(1)	78.0(5)	N(1)–Re(1)–O(1) 171.6(4)
N(2)–Re(1)–O(1)	94.1(4)	N(1)–Re(1)–Cl(3) 88.5(3)
N(2)–Re(1)–Cl(3)	87.9(3)	N(1)–Re(1)–Cl(1) 95.1(4)
N(2)–Re(1)–Cl(1)	173.0(3)	N(1)–Re(1)–Cl(2) 94.6(3)

Table 4. Selected Bond Lengths [Å] and Angles [deg] for **11**

	Distances	
Re–N(3)	1.966(11)	Re–N(1) 2.026(10)
Re–O(1)	2.030(7)	Re–Cl(2) 2.357(4)
Re–Cl(3)	2.368(4)	Re–Cl(1) 2.382(4)
N(2)–N(3)	1.316(13)	P(1)–O(1) 1.523(8)
P(2)–O(2)	1.469(9)	
Angles		
N(3)–Re–N(1)	75.3(5)	N(3)–Re–O(1) 96.5(4)
N(1)–Re–O(1)	171.8(4)	N(3)–Re–Cl(2) 94.7(3)
N(1)–Re–Cl(2)	93.6(3)	O(1)–Re–Cl(2) 87.7(3)
N(3)–Re–Cl(3)	88.5(3)	N(1)–Re–Cl(3) 90.6(3)
O(1)–Re–Cl(3)	88.4(3)	Cl(2)–Re–Cl(3) 175.2(1)
N(3)–Re–Cl(1)	170.1(3)	N(1)–Re–Cl(1) 95.2(4)
O(1)–Re–Cl(1)	93.0(2)	Cl(2)–Re–Cl(1) 88.5(2)
Cl(3)–Re–Cl(1)	89.0(2)	P(1)–O(1)–Re 146.7(5)

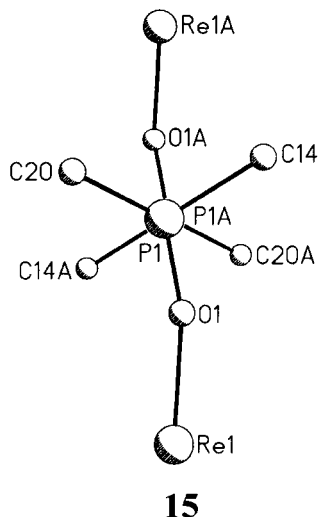
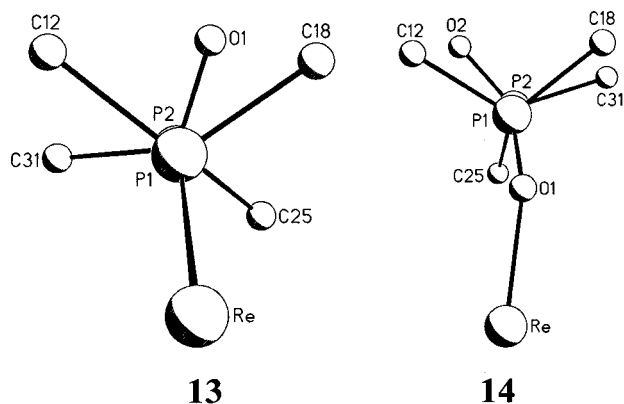
lack acceptor properties. Hence **9a** and **11** like **6**¹ and some related species³ have the *mer* geometry. The Re–N distances in the present complexes are consistent with the above bonding consideration, see below.

c. The Re(PiPO) and Re(OPiPO) Fragments. Two geometrical features that are useful in the scrutiny of $n = 1$ reactions to be considered later will be described. First, we compare **5** and **11** (immediate environment of P atoms only) viewed down the $P \cdots P$ axis, as in **13** and **14**, respectively. For angular ZP_2 type species ($Z =$ one atom bridge; CH_2 in the present case) viewed down the $P \cdots P$ axis, the staggered conformation of substituents on the P atoms is energetically most favorable.^{26,28,29} On this basis the conformation **13** (in **5**) is more relaxed than

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14 (in **11**). For comparison, the conformation of the Re(OP2PO)-Re fragment in **9a**, viewed down the P...P axis, is depicted in **15**: here the two P atoms are separated by two C atoms.

Second, the pendent P(1), C(24), P(2), O(2) fragment of **11** is positioned relatively close to one (Cl(1), Cl(3), O(1)) of the four octahedral faces having O(1) as the common vertex. The distances of the P(1), C(24), and P(2) atoms from the centroid of this face are 2.67, 2.66, and 4.45 Å, respectively. The corresponding distances from the other three faces lie in the ranges 2.90–3.23, 3.47–4.17, and 5.23–5.97 Å, respectively.

d. Chelate Ring, Re–N Distances, and Back-Bonding. In each of the four species, the five-membered chelate ring along with the adjacent pyridine ring constitute a good plane with mean deviation in the range 0.02–0.03 Å. The dihedral angle of this plane with the pendent aryl group is 40.9° in **5**, 49.6° in **7a**, 81.3° in **9a**, and 51.2° in **11**.

The Re–N lengths are in general shorter than the estimated single bond value^{30,31} of 2.14 Å. The double bond character is assigned to Re–L back-bonding, especially of the $t_{2g}(\text{Re})-\pi^*$ -(azo) type.¹ Consistent with this, the Re–N(3) bond in **5**, **7a**, and **11** is ~0.06 Å shorter than the Re–N(1) bond. Further, the N=N bond is lengthened to 1.32 Å from the free ligand value^{32–34} of 1.25 Å. In **5** and **7a** Re–P type back-bonding is also present and the Re–N lengths are correspondingly longer than those in **11**, where L is the lone π -acid (the case of **6a** is

Table 5. Rate Constants and Activation Parameters^a for the Reaction **4a** → **5** in Benzene^b

T, K	10 ⁴ [4a], M	10 ³ k, min ⁻¹
298	2.54	1.92 (1)
303	2.54	2.68 (1)
308	2.54	4.53 (2)
313	2.54	6.27 (3)
313	1.89	6.32 (3)
313	1.27	6.30 (3)

^a ΔH^\ddagger , 14.6 (1.2) kcal mol⁻¹; ΔS^\ddagger , -22.6 (1.7) eu. ^b Least-squares deviations are given in parentheses.

analogous¹). In **9** the Re–N(1) and Re–N(2) lengths are nearly equal, reflecting similar π -acidities at the two nitrogen sites which form parts of the α -diimine fragment in L'.

D. Nature of Reactions. The primary reaction in the present work is oxygen atom transfer (eqs 4 and 5). The nature of such transfer has already been elaborated in the case of monophosphines.³ The transformations that occur after oxygen atom transfer are scrutinized below.

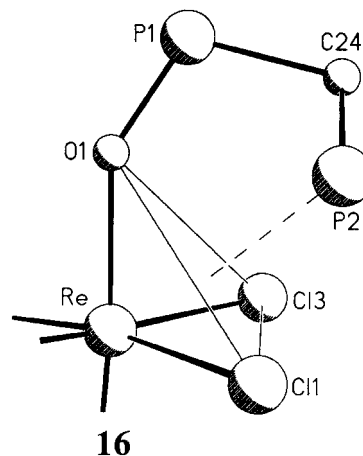
a. Intramolecular Twin Isomerization of 4a. The reaction of eq 6 embodies twin isomerization: linkage (Re–OP1P → ReP1PO) and geometrical (*mer* → *fac*). The rate of the reaction



$$\text{rate} = k[\mathbf{4a}] \quad (7)$$

has been spectrophotometrically monitored in benzene solution in the temperature range 298–313 K using the absorbance at 468 nm (decay of **4a**). The time evolution spectra are characterized by several isosbestic points (see Supporting Information). The reaction follows the first-order rate law of eq 7. Rate constants and activation parameters are listed in Table 5. The rate law and the large negative entropy of activation are suggestive of an intramolecular pathway with strong association of the dangling phosphine function with the metal. In effect a septacoordinated transition state is implicated.

Although **4a** did not afford single crystals, the structure of **11** provides a credible model. The pendent phosphine oxide fragment in **11** lies relatively close to the Cl(1), Cl(3), O(1) face from which the P(2) atom is 4.45 Å away. However a simple rotation around the P(1)–C(24) bond can bring P(2) to within 2.5 Å of the face as in **16**, which is thus a plausible



model of the transition state. Attack by P(2) on the face with concomitant edge displacement^{35,36} of a chloride ligand and Re–OP(1) bond cleavage can afford **5**, as depicted in eq 8. In **5** the

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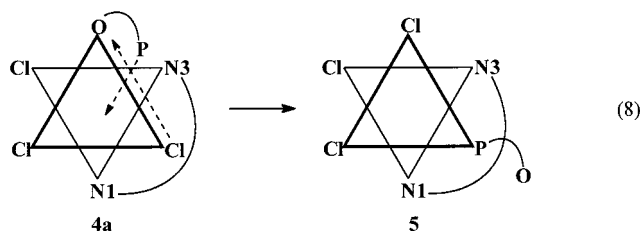
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RePIPO fragment has the sterically relaxed conformation **13**, wherein the *fac* geometry is sustained by back-bonding.



Unlike **4a**, complexes **4b** and **4c** fail to isomerize even in boiling benzene. The longer interphosphorus bridges evidently make the facial approach of the pendant phosphorus site improbable (synchronous rotation around more than one bond required). However **4b** and **4c**, again unlike **4a**, are reactive to externally added phosphines.

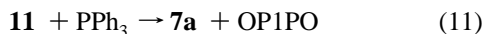
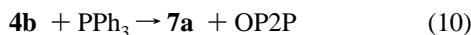
b. Stereodynamic Substitution by External Phosphines.

We first refer to the reaction of eq 9, which is an intermolecular analogue of that of eq 6. In **6a**¹ the meridional disposition of the coordinated phosphine oxide fragment with respect to octahedral faces is very similar to that in **11** and by inference to that in **4a**. The approach of external PPh₃ to the reactive



face can thus be expected to be hindered. Significantly, the required reaction conditions of eq 9 are relatively drastic (large PPh₃ excess, boiling solvent).

As anticipated, the reaction of eq 9 works as well upon replacing **6a** by **4b** or by **11** as in eqs 10 and 11. Complex **4c**



behaves similarly. In contrast, **4a** is rapidly converted to **5** under the same reaction conditions and no **7a** is formed, implying complete dominance of the intramolecular isomerization pathway of eq 6.

c. Bond Cleavage Following Two-Atom Transfer. Two-atom transfer to PIP furnishes only mononuclear **11** and **12**, and no binuclear complexes could be isolated. The dangling phosphine oxide function in **11** and **12**, however, strongly implicates transient binucleation on the reaction pathway.

The instability of such a binuclear intermediate is consistent with the crowding near the O(2) atom of **11**, as expressed in the ReOP1PO conformation **14**. The relatively short nonbonded distances such as O(2)⋯P(1), 3.55 Å, and O(2)⋯C(12), 3.48 Å, reflect that stable coordination of an ReCl₃L fragment to the O(2) site is not viable. This difficulty disappears upon lengthening the P⋯P bridge as in **9a**; see **15**.

The dissociation of the Re–OP bond after oxygen atom transfer from Re^{VO} to a tertiary phosphines is a well-documented phenomenon.^{11,13,16,17,19,37} However the ReCl₃L and ReCl₃L' moieties, like a few others,^{2,12,14} are unusual in

sustaining strong Re–OP bonds until other factors destabilize them, as in the formation of **11** and **12**.

Concluding Remarks

Transfer of one and two oxygen atoms between the azopyridine reagent ReOCl₃L and Ph₂P(CH₂)_nPPh₂ (*PnP*) has been realized via regulation of the relative ratio of the two reactants. The products are mononuclear Re(OP*n*P)Cl₃L, **4** (*n* = 1–3), and binuclear LCl₃Re(OP*n*PO)ReCl₃L', **8** (*n* = 2, 3), respectively. The latter are insoluble, but two-atom transfer and binucleation have been authenticated with the help of pyridine-2-alimine dimers L'Cl₃Re(OP*n*PO)ReCl₃L', **9** (*n* = 2, 3) generated from ReOCl₃L' and *PnP*.

A remarkable reactivity singularity of products occurs for *n* = 1. Thus **4** (*n* = 1) alone undergoes a spontaneous intramolecular linkage-cum-geometrical isomerization to Re(PIPO)Cl₃L, **5**, via an associative pathway characterized by a large negative entropy of activation. Again in the *n* = 1 case alone, two-atom transfer furnishes only mononuclear Re(OP1PO)Cl₃L, **11**, with a dangling phosphine oxide function, which is a vestige of the transient binucleation that must be occurring on the reaction path. The steric and electronic scenario promoting these *n* = 1 transformations following oxygen atom transfer has been analyzed.

Ongoing studies concern the effects of variation of the chelating nitrogenous ligand on reactivity and the structure and properties of systems incorporating fragments such as Re(*PnP*), Re(*PnP*O) (*n* > 1), and Re(*PnP*O)Re, which are not covered in the present work.

Experimental Section

Materials. ReOCl₃L, Re(OPPh₃)Cl₃L, and ReOCl₃L' were prepared by reported methods.^{1,3} Dichloromethane and acetonitrile for electrochemical, spectral, and synthetic work were purified as before.^{38,39} Benzene was distilled over sodium before use. All other chemicals and solvents were of reagent grade and were used as received.

Physical Measurements. UV–vis spectra (CH₂Cl₂ solution), IR spectra (KBr disk), and ¹H NMR spectra (CDCl₃) were recorded on a Shimadzu UVPC 1601 spectrophotometer fitted with thermostated cell compartments, a Perkin-Elmer 783 spectrophotometer, and a Bruker FT 300 MHz spectrometer, respectively. 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; i, ill-resolved. Cyclic voltammetry (in MeCN, 0.1 M TEAP) was done at a platinum working electrode under nitrogen atmosphere on a PAR model 370-4 electrochemistry system.²⁶ Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 Series II elemental analyzer.

Preparation of Complexes. Re(OPIP)Cl₃L, 4a. To a solution of PIP (220 mg, 0.57 mmol) in 10 mL of dichloromethane was added a solution of ReOCl₃L (100 mg, 0.19 mmol) in 10 mL of dichloromethane at room temperature. The solution color rapidly turned from pink to golden yellow. The solvent was quickly (to avoid isomerization) removed under reduced pressure, and the yellow solid was repeatedly washed with hexane to remove excess PIP and then dried in vacuo over P₂O₁₀. Yield: 150 mg (87%). Anal. Calcd for C₃₆H₃₀Cl₄N₃OP₂Re: C, 47.47; H, 3.29; N, 4.62. Found: C, 47.32; H, 3.22; N, 4.51. UV–vis (λ_{max}, nm (ε, M⁻¹ cm⁻¹)): 637 (307); 473 (6340); 284 (14 220). IR (cm⁻¹): ν_{Re–Cl}, 310, 330; ν_{O–P}, 1120; ν_{N=N}, 1330. ¹H NMR (δ (J, Hz)): C₅H₄N, 27.12 (H(2), d, 8.4); –28.08 (H(3), t, 7.2); 39.75 (H(4), t, 6.6); –9.94 (H(5), d, 6.3); ClC₆H₄, 30.77 (H(7), H(11), d,

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6.9); 10.68 (H(8), H(10), d, 7.9); P1P, -14.39 (H(24), s); 2.80 (i); 4.12 (t, 7.8); 6.74 (m); 7.08 (t, 7.5); 7.29 (m); 7.36 (m).

Re(OP2P)Cl₃L, 4b. To a solution of P2P (227 mg; 0.57 mmol) in 10 mL of benzene was added a solution of ReOCl₃L (100 mg, 0.19 mmol) in 10 mL of benzene at room temperature, leading to a change of solution color from pink to golden yellow. The solvent was stripped under reduced pressure. The residue was dissolved in 5 mL of dichloromethane and then subjected to chromatography on a silica gel column. Excess P2P was removed using benzene as the eluant, and the golden yellow band of **4b** was then eluted with a benzene-acetonitrile (25:1) mixture. Slow evaporation of the eluate afforded **4b** as a golden yellow solid. Yield: 125 mg (71%). Anal. Calcd for C₃₇H₃₂-Cl₄N₃OP₂Re: C, 48.05; H, 3.46; N, 4.55. Found: C, 48.11; H, 3.39; N, 4.46. UV-vis (λ_{\max} , nm (ϵ , M⁻¹ cm⁻¹)): 650 (675); 475 (6390); 283 (16 365). IR (cm⁻¹): $\nu_{\text{Re-Cl}}$, 310, 335; $\nu_{\text{O-P}}$, 1120; $\nu_{\text{N=N}}$, 1330. ¹H NMR (δ (J, Hz)): C₅H₄N, 27.30 (H(2), d, 8.1); -27.87 (H(3), t, 7.2); 40.35 (H(4), t, 6.6); -10.45 (H(5), d, 6.8); ClC₆H₄, 30.45 (H(7), H(11), d, 6.6); 10.72 (H(8), H(10), d, 7.2); P2P, -7.53 (H(24), i); -4.21 (H(25), i); 1.62 (i); 3.03 (i); 5.95 (t, 7.0); 6.82 (t, 7.2); 7.34 (m).

Re(OP3P)Cl₃L, 4c. was similarly prepared from ReOCl₃L and P3P. Yield: 73%. Anal. Calcd for C₃₈H₃₄Cl₄N₃OP₃Re: C, 48.61; H, 3.62; N, 4.48. Found: C, 48.53; H, 3.55; N, 4.43. UV-vis (λ_{\max} , nm (ϵ , M⁻¹ cm⁻¹)): 640 (610); 475 (4940); 295 (12 300). IR (cm⁻¹): $\nu_{\text{Re-Cl}}$, 310, 320; $\nu_{\text{O-P}}$, 1120; $\nu_{\text{N=N}}$, 1330.

Re(PIPO)Cl₃L, 5. A 50 mg (0.055 mmol) sample of **4a** was dissolved in 20 mL of benzene, and the solution was kept for 8 h at room temperature. The solvent was then removed under reduced pressure, and the residue was dissolved in 5 mL of dichloromethane and subjected to chromatography on a silica gel column. A yellow band was eluted with a benzene-acetonitrile (25:2) mixture. The slow evaporation of the eluate afforded microcrystals of **5**. Yield: 42 mg (84%). Anal. Calcd for C₃₆H₃₀Cl₄N₃OP₂Re: C, 47.47; H, 3.29; N, 4.62. Found: C, 47.52; H, 3.21; N, 4.55. UV-vis (λ_{\max} , nm (ϵ , M⁻¹ cm⁻¹)): 630 (630); 477 (5465); 298 (11 305). IR (cm⁻¹): $\nu_{\text{Re-Cl}}$, 300, 320; $\nu_{\text{Re-P}}$ 510, 720; $\nu_{\text{P-O}}$, 1200; $\nu_{\text{N=N}}$, 1330. ¹H NMR (δ (J, Hz)): C₅H₄N, 26.30 (H(2), i); -34.50 (H(3), i); 46.19 (H(4), i); -19.50 (H(5), i); ClC₆H₄, 41.38 (H(7), H(11), i); 12.44 (H(8), H(10), i); P1P, 23.51 (H(24), s); 3.02 (i); 6.37 (t, 7.2); 6.85 (m); 6.95 (t, 6.9); 7.19 (m); 7.29 (i); 7.65 (t, 9.0); 7.77 (t, 6.9); 11.10 (i); 13.29 (d, 6.0); 15.97 (i).

Re(OPPh₂Me)Cl₃L, 6b. This was prepared from ReOCl₃L and PPh₂Me in the same way as Re(OPPh₃)Cl₃L. Yield: 85%. Anal. Calcd for C₂₄H₂₁Cl₄N₃OPRe: C, 39.67; H, 2.89; N, 5.79. Found: C, 39.61; H, 2.83; N, 5.72. UV-vis (λ_{\max} , nm (ϵ , M⁻¹ cm⁻¹)): 660 (380); 467 (8145); 288 (13 540). IR (cm⁻¹): $\nu_{\text{Re-Cl}}$, 300, 320; $\nu_{\text{O-P}}$, 1120; $\nu_{\text{N=N}}$, 1325. ¹H NMR (δ (J, Hz)): C₅H₄N, 26.99 (H(2), d, 8.4); -27.85 (H(3), t, 7.5); 39.61 (H(4), t, 6.3); -9.50 (H(5), d, 6.0); ClC₆H₄, 30.37 (H(7), H(11), d, 7.8); 10.76 (H(8), H(10), d, 7.8); PPh₂Me, -4.58 (H(Me), s); 2.15 (H(o), i); 7.10 (H(m), t, 7.5); 6.60 (H(p), t, 7.5).

Re(PPh₃)Cl₃L, 7a. To a solution of **6a** (100 mg, 0.13 mmol) in benzene (15 mL) was added PPh₃ (350 mg, 1.34 mmol), and the mixture was heated to reflux under pure nitrogen for 1 h. The resulting solution was evaporated to dryness, and the residue was washed several times with hexane (to remove excess PPh₃) and then subjected to chromatography on a silica gel column. Benzene-acetonitrile mixtures of compositions 50:1, 25:1, and 10:1, respectively, eluted out Re(NC₆H₄-Cl)Cl₃L (and OPPh₃), unreacted **6a**, and **7a**, which was isolated by evaporation of the solvent from last fraction. Yield: 50 mg (48%). Anal. Calcd for C₂₉H₂₃Cl₄N₃PRe: C, 45.08; H, 2.98; N, 5.44. Found: C, 45.19; H, 2.92; N, 5.53. UV-vis (λ_{\max} , nm (ϵ , M⁻¹ cm⁻¹)): 640 (610); 475 (4980); 295 (12 100). IR (cm⁻¹): $\nu_{\text{Re-Cl}}$, 300, 320; $\nu_{\text{Re-P}}$, 500, 710; $\nu_{\text{N=N}}$, 1325. ¹H NMR (δ (J, Hz)): C₅H₄N, 21.21 (H(2), d, 9.0); -31.66 (H(3), i); 40.08 (H(4), i); -19.80 (H(5), i); ClC₆H₄, 31.66 (H(7), H(11), i); 11.94 (H(8), H(10), d, 6.0); PPh₃, 13.76 (H(o), i); 8.72 (H(m), i); 9.04 (H(p), i).

Re(PPh₂Me)Cl₃L, 7b. It was similarly prepared from Re(OPPh₂Me)Cl₃L and PPh₂Me. Yield: 50%. Anal. Calcd for C₂₄H₂₁Cl₄N₃PRe: C, 40.56; H, 2.96; N, 5.92. Found: C, 40.47; H, 2.89; N, 5.99. UV-vis (λ_{\max} , nm (ϵ , M⁻¹ cm⁻¹)): 637 (580); 470 (5020); 289 (10 500). IR (cm⁻¹): $\nu_{\text{Re-Cl}}$, 310, 320; $\nu_{\text{Re-P}}$, 500, 710; $\nu_{\text{N=N}}$, 1330. ¹H NMR (δ (J, Hz)): C₅H₄N, 23.05 (H(2), d, 8.1); -33.14 (H(3), t, 6.9); 41.10 (H(4), i); -19.16 (H(5), i); ClC₆H₄, 32.23 (H(7), H(11), d, 7.8); 12.20 (H(8),

H(10), d, 7.5); PPh₂Me, -8.35 (H(Me), s); 16.63 (H(o), d, 7.5); 20.55 (H(o), d, 7.5); 8.98 (H(m), t, 7.5); 11.11 (H(m), t, 7.2); 9.59 (H(p), t, 7.5); 10.51 (H(p), t, 7.5).

LCl₃Re(OP2PO)ReCl₃L, 8a. To a benzene (10 mL) solution of P2P (40 mg, 0.10 mmol) was added ReOCl₃L, **2** (160 mg, 0.30 mmol), under stirring. The solvent was then removed under reduced pressure, and the yellow residue was washed repeatedly with benzene, affording **8a**, which was insoluble in all common organic solvents. Yield: 130 mg (85%).

8a was also synthesized by mixing a solution of **4b** (100 mg, 0.11 mmol) in benzene (10 mL) with ReOCl₃L, **2** (100 mg, 0.19 mmol). Yield: 120 mg (80%). Anal. Calcd for C₄₈H₄₀Cl₈N₆O₂P₂Re₂: C, 39.72; H, 2.76; N, 5.79. Found: C, 39.60; H, 2.71; N, 5.69. IR (cm⁻¹): $\nu_{\text{Re-Cl}}$, 300, 320; $\nu_{\text{O-P}}$, 1120; $\nu_{\text{N=N}}$, 1320.

LCl₃Re(OP3PO)ReCl₃L, 8b. It was similarly prepared from ReOCl₃L and P3P. Yield: 85%. Anal. Calcd for C₄₉H₄₂Cl₈N₆O₂P₃Re₂: C, 40.16; H, 2.87; N, 5.74. Found: C, 40.30; H, 2.78; N, 5.65. IR (cm⁻¹): $\nu_{\text{Re-Cl}}$, 310, 320; $\nu_{\text{O-P}}$, 1120; $\nu_{\text{N=N}}$, 1325.

L'Cl₃Re(OP2PO)ReCl₃L', 9a. A benzene solution (15 mL) containing P2P (40 mg, 0.10 mmol) and ReOCl₃L', **3** (150 mg, 0.30 mmol), was stirred for 3 h at 40 °C. The color changed from orange to pink, and the solvent was removed under reduced pressure. The residue thus obtained was dissolved in 5 mL of dichloromethane and subjected to chromatography on a silica gel column. A band containing Re(OP2P)-Cl₃L' was first eluted out with a benzene-acetonitrile (25:1) mixture. The pink band of **9a** was then eluted with a benzene-acetonitrile (15:1) mixture. The solvent was then stripped off under reduced pressure, and the solid mass was dried in vacuo. Yield: 80 mg (57%). Anal. Calcd for C₅₂H₄₈Cl₆N₄O₂P₂Re₂: C, 44.35; H, 3.41; N, 3.98. Found: C, 44.29; H, 3.46; N, 3.93. UV-vis (λ_{\max} , nm (ϵ , M⁻¹ cm⁻¹)): 675 (3390); 525 (5700); 425^{sh} (3370). IR (cm⁻¹): $\nu_{\text{Re-Cl}}$, 310; $\nu_{\text{O-P}}$, 1120; $\nu_{\text{C=N}}$, 1600. ¹H NMR (δ (J, Hz)): C₅H₄N, 12.26 (H(2), d, 7.9); -5.88 (H(3), t, 7.5); 28.73 (H(4), t, 6.6); 13.43 (H(5), i); CH=N, -32.13 (H(6), s); MeC₆H₄, 19.88 (H(8), H(12), d, 7.1); 10.39 (H(9), H(11), d, 7.2); 4.04 (H(p-Me), s); P2P, -11.87 (H(26, 26A), i); 5.43 (H(o), i); 8.56 (H(m), t, 7.4); 7.85 (H(p), t, 7.4).

L'Cl₃Re(OP3PO)ReCl₃L', 9b. It was prepared similarly to **9a**. Yield: 65%. Anal. Calcd for C₅₃H₅₀Cl₆N₄O₂P₃Re₂: C, 44.76; H, 3.52; N, 3.94. Found: C, 44.69; H, 3.57; N, 3.87. UV-vis (λ_{\max} , nm (ϵ , M⁻¹ cm⁻¹)): 675 (3100); 525 (5800); 425^{sh} (3300). IR (cm⁻¹): $\nu_{\text{Re-Cl}}$, 310; $\nu_{\text{O-P}}$, 1125; $\nu_{\text{C=N}}$, 1600. ¹H NMR (δ (J, Hz)): C₅H₄N, 12.63 (H(2), i); -6.62 (H(3), t, 7.8); 29.92 (H(4), i); 12.73 (H(5), d, 9.0); CH=N, -30.02 (H(6), s), MeC₆H₄, 21.13 (H(8), H(12), d, 9.0); 11.20 (H(9), H(11), d, 6.0); 4.51 (H(p-Me), s); P3P, -9.92 (H(26, 26A), i); -6.70 (H(27), i); 5.17 (H(o), i); 7.98 (H(m), t, 7.5); 7.45 (H(p), t, 7.5).

LCl₃Re(OP2PO)ReCl₃L', 10. To a yellow-colored solution of **4b** (60 mg, 0.06 mmol) in 15 mL of benzene was added **3** (40 mg, 0.08 mmol). The mixture became brick red in color upon stirring for 2 h at 40 °C. The solvent was removed under reduced pressure, and the residue was washed several times with benzene and finally dried under vacuo. Yield: 60 mg (67%). Anal. Calcd for C₅₀H₄₄Cl₇N₅O₂P₂Re₂: C, 42.00; H, 3.08; N, 4.90. Found: C, 42.12; H, 3.15; N, 4.97. IR (cm⁻¹): $\nu_{\text{Re-Cl}}$, 310, 320; $\nu_{\text{O-P}}$, 1140; $\nu_{\text{N=N}}$, 1325; $\nu_{\text{C=N}}$, 1600.

Re(OPIPO)Cl₃L, 11. A solution of P1P (50 mg, 0.13 mmol) and **2** (200 mg, 0.38 mmol) in 15 mL of benzene was stirred for 30 min at room temperature. The solvent was then stripped off under reduced pressure, and the solid mass was subjected to chromatography on a silica gel column. The golden yellow band of **11** was eluted out with a benzene-acetonitrile (16:1) mixture, and the microcrystalline complex was isolated by slow evaporation. (At best **11** can account for 50% of the total rhenium. The remaining metal remains adsorbed on the column in the form of one or more intractable species.) Yield of **11**: 90 mg (75%). Anal. Calcd for C₃₆H₃₀Cl₄N₃O₃P₂Re: C, 46.65; H, 3.24; N, 4.54. Found: C, 46.74; H, 3.29; N, 4.59. UV-vis (λ_{\max} , nm (ϵ , M⁻¹ cm⁻¹)): 650 (430); 470 (5395); 294 (11 420). IR (cm⁻¹): $\nu_{\text{Re-Cl}}$, 310, 330; $\nu_{\text{O-P}}$, 1120 (coordinated to metal); $\nu_{\text{P-O}}$, 1200 (free) $\nu_{\text{N=N}}$, 1325. ¹H NMR (δ (J, Hz)): C₆H₄N, 26.98 (H(2), d, 8.0); -27.40 (H(3), t, 7.2); 38.62 (H(4), t, 6.0); -9.01 (H(5), d, 7.2); ClC₆H₄, 30.41 (H(7), H(11), d, 7.2); 10.64 (H(8), H(10), d, 7.6); P1P, -14.40 (H(24), s); 3.42 (i); 4.52 (t, 7.2); 6.66 (t, 7.2); 7.08 (m).

Table 6. Crystallographic Data for $5 \cdot 1.5\text{C}_6\text{H}_6$, $7\mathbf{a} \cdot \text{CH}_2\text{Cl}_2$, $9\mathbf{a}$, and 11

	$5 \cdot 1.5\text{C}_6\text{H}_6$	$7\mathbf{a} \cdot \text{CH}_2\text{Cl}_2$	$9\mathbf{a}$	11
empirical formula	$\text{C}_{45}\text{H}_{39}\text{Cl}_4\text{N}_3\text{O}_2\text{P}_2\text{Re}$	$\text{C}_{30}\text{H}_{25}\text{Cl}_6\text{N}_3\text{PRe}$	$\text{C}_{52}\text{H}_{48}\text{Cl}_6\text{N}_4\text{O}_2\text{P}_2\text{Re}_2$	$\text{C}_{36}\text{H}_{30}\text{Cl}_4\text{N}_3\text{O}_2\text{P}_2\text{Re}$
fw	1027.73	857.40	1407.98	926.57
cryst size, mm	$0.45 \times 0.30 \times 0.20$	$0.45 \times 0.25 \times 0.10$	$0.25 \times 0.20 \times 0.15$	$0.4 \times 0.4 \times 0.2$
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$C2/c$	$I2/a$
a , Å	10.034(2)	11.695(6)	19.767(12)	16.866(6)
b , Å	10.737(2)	17.745(7)	12.868(6)	12.583(6)
c , Å	20.357(4)	15.459(9)	22.20(2)	34.78(2)
α , deg	89.38(3)			
β , deg	87.79(3)	100.94(5)	101.76(6)	99.22(4)
γ , deg	80.22(3)			
V , Å ³	2159.7(7)	3150(3)	5530(6)	7285(7)
Z	2	4	4	8
ρ_{calcd} , g cm ⁻³	1.58	1.81	1.69	1.69
μ , cm ⁻¹	31.73	44.44	47.64	37.54
R , $wR2^b$ [$I > 2\sigma(I)$], %	3.03, 6.90	5.85, 14.03	6.35, 11.12	5.71, 10.19

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

Re(OP1PO)Cl₃L', 12. It was prepared in the same manner as **11** from **3** and P1P. Here stirring has to be done for 3 h at 40 °C, and the color of the complex is pink. Yield: 70%. Anal. Calcd for $\text{C}_{38}\text{H}_{34}\text{Cl}_3\text{O}_2\text{P}_2\text{Re}$: C, 50.41; H, 3.76; N, 3.10. Found: C, 50.49; H, 3.71; N, 3.16. UV-vis (λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)): 675 (2300); 525 (4250); 425^{sh} (2790). IR (cm⁻¹): $\nu_{\text{Re-Cl}}$, 310; $\nu_{\text{O-P}}$, 1120 (coordinated to metal); $\nu_{\text{P-O}}$, 1160 (free) $\nu_{\text{C-N}}$, 1600. ¹H NMR (δ (J, Hz): $\text{C}_6\text{H}_4\text{N}$, 13.23 (H(2), d, 6.8); -5.42 (H(3), i); 30.30 (H(4), i); 13.88 (H(5), i); CH=N, -30.51 (H(6), s); MeC_6H_4 , 21.23 (H(8), H(12), d, 6.0); 11.15 (H(9), H(11), d, 9.0); 4.19 (H(*p*-Me), s); P1P, -11.43 (H(26), s); 2.36 (i); 3.24 (t, 9.0); 6.82 (t, 7.2); 7.00 (i); 7.36 (i).

Other Reactions. a. Reaction of 4b with PPh₃. To a solution of **4b** (50 mg, 0.06 mmol) in dry benzene (10 mL) was added PPh₃ (160 mg, 0.61 mmol). The mixture was then heated to reflux in nitrogen atmosphere for 45 min. The complex **7a** was then isolated from the reaction mixture using the procedure described earlier. Yield: 12 mg (28%).

b. Reaction of 11 with PPh₃. The above reaction was repeated with **11** in place of **4b**, affording **7a** (Yield: 34%).

c. Reaction of 4a with PPh₃. To a solution of **4a** (50 mg, 0.06 mmol) in dry benzene (10 mL) was added PPh₃ (160 mg, 0.61 mmol). The mixture was then heated to reflux in nitrogen atmosphere for 45 min. The solvent was then removed under reduced pressure, and the residue was washed several times with hexane and then subjected to chromatography on a silica gel column. Benzene-acetonitrile mixtures of compositions 50:1 and 10:1, respectively, eluted out $\text{Re}(\text{NC}_6\text{H}_4\text{Cl})\text{Cl}_3\text{L}$ and **5** (yield: 25 mg, 50%).

Rate Measurements. Benzene solutions of **4a** were used, and the rate was followed spectrophotometrically at 468 nm. The absorbance A_t was recorded as a function of time t , and A_∞ was measured when the reaction was complete (24 h). Values of the first-order rate constants were obtained from the slopes of the linear plots of $-\ln(A_t - A_\infty)$ versus t . The rate constant was independent of concentration (range used $(1-3) \times 10^{-4}$ M) within experimental error. The activation enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) parameters were calculated from the Eyring equation (eq 12) utilizing rate constant data obtained over the temperature range 298–313 K.

$$k = (k_B T/h) [\exp(-\Delta H^\ddagger/RT) \exp(\Delta S^\ddagger/R)] \quad (12)$$

X-ray Structure Determination. Single crystals were grown either by slow diffusion of hexane into benzene solution ($5 \cdot 1.5 \text{C}_6\text{H}_6$, **11**) or dichloromethane solution ($7\mathbf{a} \cdot \text{CH}_2\text{Cl}_2$) or by slow evaporation of benzene solution (**9a**). Cell parameters were determined by a least-squares fit of 30 machine-centered reflections ($14^\circ \leq 2\theta \leq 28^\circ$). Data were collected by the ω scan technique in the range $3^\circ \leq 2\theta \leq 47^\circ$ for $5 \cdot 1.5 \text{C}_6\text{H}_6$, $3^\circ \leq 2\theta \leq 50^\circ$ for $7\mathbf{a} \cdot \text{CH}_2\text{Cl}_2$ and **9a**, and $3^\circ \leq 2\theta \leq 48^\circ$ for **11** on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo K α ($\lambda = 0.71073$ 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.⁴⁰

The metal atoms were located from Patterson maps, and the rest of the 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 were included at calculated positions. In $5 \cdot 1.5 \text{C}_6\text{H}_6$ the solvent of crystallization lies on a center of symmetry and in a general position. Calculations were performed using the SHELXTL V 5.03⁴¹ program package. Significant crystal data are listed in Table 6.

Acknowledgment. We thank the Department of Science and Technology, Indian National Science Academy, and the Council of Scientific and Industrial Research, New Delhi, for financial support. Affiliation with the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India, is acknowledged.

Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of $5 \cdot 1.5 \text{C}_6\text{H}_6$, $7\mathbf{a} \cdot \text{CH}_2\text{Cl}_2$, **9a**, and **11**, and kinetic results (time-dependent spectra, linear $-\ln(A_t - A_\infty)$ versus t plot, Eyring plot) for **4a**. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

IC0005893

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