

# Synthesis and Structures of New Six-Coordinate 16- and 17-Valence-Electron Rhenium Phosphine Complexes and Their Use in Preparing Seven-Coordinate Mixed RNC/CO Rhenium(III) Compounds

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When  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_3(\text{PMePh}_2)_2]\text{SbF}_6$  in toluene is heated to reflux, the paramagnetic 16-electron all-trans isomer of  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_2(\text{PMePh}_2)_2]\text{SbF}_6$  (**1**) is formed. This complex has been characterized by IR and NMR spectroscopies, elemental analysis, and a single-crystal X-ray structure determination. Addition of two-electron donors L (L = CO, CN-*i*-Pr) to **1** results in the formation of  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_2\text{L}(\text{PMePh}_2)_2]\text{SbF}_6$ . Reaction of  $[\text{ReCl}_3(\text{CO})_2(\text{PMePh}_2)_2]$  with “(Cp\*)<sub>2</sub>Zr”, formed in situ from Mg dust and  $[(\text{Cp}^*)_2\text{ZrCl}_2]$ , gives rise to the paramagnetic 17-electron compound  $[\text{ReCl}_2(\text{CO})_2(\text{PMePh}_2)_2]$  (**2**). This complex has been characterized by both spectroscopy and X-ray crystallography. The octahedral coordination sphere in **2** is comprised of two cis chloride, two cis carbonyl, and two trans phosphine ligands. Crystallographic details are as follows: **1**,  $\text{ReSbCl}_2\text{P}_2\text{F}_6\text{N}_2\text{C}_{34}\text{H}_{40}$ ,  $P2_1/n$ ,  $a = 6.9456(8) \text{ \AA}$ ,  $b = 20.301(4) \text{ \AA}$ ,  $c = 28.428(8) \text{ \AA}$ ,  $\beta = 92.54(2)^\circ$ ,  $Z = 4$ ; **2**,  $\text{ReCl}_2\text{P}_2\text{O}_2\text{C}_{28}\text{H}_{26}$ ,  $P2_12_12$ ,  $a = 9.628(2) \text{ \AA}$ ,  $b = 13.013(3) \text{ \AA}$ ,  $c = 11.131(3) \text{ \AA}$ ,  $Z = 2$ .

## Introduction

Structurally characterized Re(II)-d<sup>5</sup> 17-valence-electron mononuclear complexes are rare.<sup>1,2a,3-5</sup> In contrast, Re(III)-d<sup>4</sup> 16-valence-electron mononuclear coordination complexes are relatively common.<sup>2b</sup> Our interest in the reductive coupling of linear ligands<sup>6</sup> and the dealkylation of isocyanides<sup>7</sup> in seven-coordinate early-transition-metal complexes led us to explore the structure and reactivity of  $[\text{ReX}_2(\text{CNR})_3(\text{PMePh}_2)_2]\text{X}$  complexes, as described previously.<sup>6e,8</sup> The recently discovered reductive coupling of two carbonyl ligands in a seven-coordinate Ta(I) complex using “Zr(Cp\*)<sub>2</sub>” as the reducing agent<sup>6d</sup> further stimulated a parallel investigation of the reactivity of  $[\text{ReCl}_3(\text{CO})_2(\text{PMePh}_2)_2]$  with “Zr(Cp\*)<sub>2</sub>”. Here we describe details of the isolation of the mononuclear paramagnetic 16-electron Re(III) and 17-electron Re(II) complexes  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_2(\text{PMePh}_2)_2]\text{SbF}_6$  (**1**) and  $[\text{ReCl}_2(\text{CO})_2(\text{PMePh}_2)_2]$  (**2**), respectively, that have been obtained from seven-coordinate Re(III) 18-electron compounds. We also report the preparation and preliminary characterization of new seven-coordinate mixed isocyanide/carbonyl Re(III) complexes obtained from **1** and **2**.

## Experimental Section

**Materials and Methods.**  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_3(\text{PMePh}_2)_2]\text{SbF}_6$  and  $[\text{ReCl}_3(\text{CO})_2(\text{PMePh}_2)_2]$  were supplied by Tulip.<sup>8b</sup> Methyl isocyanide<sup>9</sup>

and isopropyl isocyanide<sup>10</sup> were prepared by literature procedures. Mg powder (Baker), I<sub>2</sub> (Baker),  $[(\text{Cp}^*)_2\text{ZrCl}_2]$  (Strem), and CP grade carbon monoxide (Matheson) were obtained from commercial sources and used without further purification. Dichloromethane used for electrochemical measurements was obtained from Burdick and Jackson Laboratories and used as received. Tetrahydrofuran was predried over potassium hydroxide and then distilled from potassium benzophenone ketyl under nitrogen. Diethyl ether, *n*-pentane, and toluene were distilled from potassium benzophenone ketyl under nitrogen. Dichloromethane was predried over calcium chloride and then distilled from calcium hydride under nitrogen. Reactions and all manipulations were carried out by using standard Schlenk techniques or in a Vacuum Atmospheres drybox, all under nitrogen.

**A. Decomposition of  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_3(\text{PMePh}_2)_2]\text{SbF}_6$  To Form  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_2(\text{PMePh}_2)_2]\text{SbF}_6$  (**1**).** A yellow toluene (~20 mL) solution of  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_3(\text{PMePh}_2)_2]\text{SbF}_6$  (0.12 g, 0.11 mmol) was heated and stirred at reflux for ~8 h. The solution turned orange, and the toluene was removed under reduced pressure while the mixture was still warm. The residue was extracted with dichloromethane, and the mixture was filtered. Recrystallization by vapor diffusion of diethyl ether into a dichloromethane solution at -30 °C yielded 0.075 g (0.073 mmol, 67%) of  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_2(\text{PMePh}_2)_2]\text{SbF}_6$  (**1**). Occasionally, it was observed that stirring of  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_3(\text{PMePh}_2)_2]\text{SbF}_6$  in acetonitrile at room temperature would also lead to the formation of **1**. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ -5.96 (s, 6 H, PCH<sub>3</sub>), 2.14 (m, 2 H, CNCHMe<sub>2</sub>), 8.17 (d, 12 H, *J* = 6.8 Hz, CNCH(CH<sub>3</sub>)<sub>2</sub>), 9.16 (t, 8 H, *J* = 7.3 Hz, *m-H*), 9.95 (t, 4 H, *J* = 7.8 Hz, *p-H*), 15.04 (d, 8 H, *J* = 7.8 Hz, *o-H*). IR (KBr): 3064 (w), 3001 (w), 2932 (w), 2182 (s), 1587 (w), 1573 (w), 1489 (m), 1437 (m), 1334 (m), 1118 (m), 1095 (m), 899 (m), 889 (s), 758 (m), 747 (m), 738 (m), 694 (m), 657 (s), 507 (m), 479 (w), 458 (w), 320 (m), 285 (s) cm<sup>-1</sup>. Cyclic voltammetry (CH<sub>2</sub>Cl<sub>2</sub> vs Ag/AgCl): *E*<sub>1/2</sub>(redn 1), -0.165 V; *E*<sub>1/2</sub>(redn 2), -1.198 V. Anal. Calcd for C<sub>34</sub>H<sub>40</sub>N<sub>2</sub>ReP<sub>2</sub>Cl<sub>2</sub>SbF<sub>6</sub>: C, 39.59; H, 3.91; N, 2.72. Found: C, 39.34; H, 3.87; N, 2.88.

**B. Reaction of  $[\text{ReCl}_3(\text{CO})_2(\text{PMePh}_2)_2]$  with “Zr(Cp\*)<sub>2</sub>” To Form  $[\text{ReCl}_2(\text{CO})_2(\text{PMePh}_2)_2]$  (**2**).** A solution containing 3.403 g (140 mmol) of Mg, 0.178 g (0.70 mmol) of I<sub>2</sub>, and 50 mL of THF was stirred. The initial brown coloration faded, upon gentle warming, to leave a clear, colorless solution. A 0.443-g (1.02-mmol) portion of  $[(\text{Cp}^*)_2\text{ZrCl}_2]$  was added, and the resulting solution was stirred for 15 min. This solution was then filtered, and 1.116 g (1.49 mmol) of  $[\text{ReCl}_3(\text{CO})_2(\text{PMePh}_2)_2]$  was added to the filtrate. This mixture was stirred for 12 h. The resulting red solution was filtered and the solvent removed under reduced pressure. The residue was taken up in ~5 mL of THF and chromatographed on a silica gel column (2 × 12 cm, 15% H<sub>2</sub>O by weight) under nitrogen. Elution with ether led to the isolation of a red-orange material, which was recrystallized by layering pentane onto a saturated dichloromethane solution at -40 °C and allowing the solvents to diffuse over

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several days. Red crystals of  $[\text{ReCl}_2(\text{CO})_2(\text{PMePh}_2)_2]$  (**2**) were isolated: 0.46 g (0.64 mmol, 43%).  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -4.00 (s, 6 H,  $\text{PCH}_3$ ), 9.31–9.39 (m, 12 H, *m,p-H*), 16.70 (d, 8 H,  $J = 6.1$  Hz, *o-H*). IR (KBr): 1974 (w, sh), 1946 (s), 1887 (s), 1845 (w, sh), 1434 (m), 889 (s), 743 (m), 699 (s), 504 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{28}\text{H}_{26}\text{ReCl}_2\text{P}_2\text{O}_2$ : C, 47.13; H, 3.67. Found: C, 47.29; H, 3.58.

Use of a 1:1 mixture of ether/THF as eluant led to the isolation of a yellow mixture. This mixture was not completely characterized; however, a small amount of starting  $[\text{ReCl}_3(\text{CO})_2(\text{PMePh}_2)_2]$  complex was identified on the basis of its  $^1\text{H NMR}$  and IR spectroscopic properties. Some  $[(\text{Cp}^*)_2\text{Zr}(\text{CO})_2]$  was also identified in this mixture by  $^1\text{H}$  and IR spectroscopy, as well as by comparison of its unit cell parameters to those of the known compound.<sup>11</sup> Omission of the zirconium reagent from the above reaction led to an inseparable mixture of products.

**C. Reaction of  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_3(\text{PMePh}_2)_2]\text{SbF}_6$  with CO To Form  $[\text{ReCl}_2(\text{CO})(\text{CN-}i\text{-Pr})_2(\text{PMePh}_2)_2]\text{SbF}_6$  (**3**).** Carbon monoxide was vigorously bubbled through a solution containing 0.290 g (0.26 mmol) of  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_3(\text{PMePh}_2)_2]\text{SbF}_6$  in 100 mL of toluene. This solution was heated to reflux for ~1 h and then stirred at ~23 °C for ~12 h. The toluene was removed under reduced pressure, and the residue was recrystallized from 1:1 dichloromethane/pentane at -40 °C. Yellow crystals of starting material formed and were separated by filtration. The remaining orange solution was filtered and the solvent removed under reduced pressure. The orange-brown residue that remained was not further purified and was identified as mainly  $[\text{ReCl}_2(\text{CO})(\text{CN-}i\text{-Pr})_2(\text{PMePh}_2)_2]\text{SbF}_6$  (**3**): 0.204 g (~74%).  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.02 (d, ~12 H,  $J = 7.0$  Hz,  $\text{CNCH}(\text{CH}_3)_2$ ), 2.30 (virtual t, ~6 H,  $^2J_{\text{PH}} \approx ^4J_{\text{PH}} \approx 4.7$  Hz,  $\text{PCH}_3$ ), 4.10 (septet, ~2 H,  $J = 6.5$  Hz,  $\text{CNCHMe}_2$ ), 7.48 (br, ~27 H, *Ph*).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -11.4 (s). IR (KBr): 3058 (w), 2988 (w), 2935 (w), 2197 (s, sh), 2165 (s), 1946 (m), 1864 (w), 1436 (s), 1392 (w), 1374 (w), 1332 (s), 1164 (w), 1120 (s), 1100 (m), 893 (s), 745 (m), 694 (s), 658 (s)  $\text{cm}^{-1}$ .

**D. Addition of CO or CN-*i*-Pr to **1**.** A 1-mL  $\text{CD}_2\text{Cl}_2$  solution containing 0.07 g (0.07 mmol) of **1** was placed in an NMR tube. To this tube was added 0.006 mL (0.11 mmol) of CN-*i*-Pr. Proton and phosphorus NMR spectra were recorded at  $t = 30, 105,$  and 145 min. The formation of  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_3(\text{PMePh}_2)_2]\text{SbF}_6$  was evident by the growth of a  $^{31}\text{P}$  NMR signal at  $\sim\delta$  -10.7 and by an unshifted  $^1\text{H}$  NMR spectrum identical with that of an authentic sample of  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_3(\text{PMePh}_2)_2]\text{SbF}_6$ . After 145 min, there was ~97% conversion. An analogous experiment using CO gas in place of CN-*i*-Pr led to the formation of **3**, which was identified by its spectroscopic properties.

**Physical Measurements.**  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  (36.6 MHz) NMR spectra were recorded on a JEOL-90X Fourier transform instrument in dichloromethane- $d_2$ . The residual proton resonance of dichloromethane- $d_2$  ( $\delta$  5.28 vs  $\text{Me}_4\text{Si}$ ) was used as the internal proton NMR calibrant, and 85%  $\text{H}_3\text{PO}_4$  ( $\delta$  0.00) was used as the external phosphorus-31 calibrant. Infrared spectra were recorded in the 4000–400- $\text{cm}^{-1}$  range on an IBM IR/32 FTIR spectrometer or in the 4000–200- $\text{cm}^{-1}$  range on a Perkin-Elmer Model 283B spectrometer using samples prepared as KBr pellets and calibrated with polystyrene film. Electrochemical measurements were made at  $20 \pm 2$  °C on a  $\sim 1.3 \times 10^{-3}$  M dichloromethane solution containing 0.2 M tetra-*n*-butylammonium perchlorate (TBAP, Southwestern Analytical Chemicals) as supporting electrolyte. Cyclic voltammetry experiments were carried out by using a Princeton Applied Research Model 173 potentiostat and a Model 175 universal programmer, and the voltammograms were recorded on a Houston Instruments Omnigraphic 2000 X-Y recorder. Voltammetry was done at a platinum-disk (1-mm diameter) electrode in deoxygenated solutions. Elemental analyses were performed by either Galbraith Laboratories, Knoxville, TN, or Spang Microanalytical Laboratory, Eagle Harbor, MI.

**Collection and Reduction of X-ray Data.** (i)  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_2(\text{PMePh}_2)_2]\text{SbF}_6$  (**1**). An orange crystal grown from the vapor diffusion of diethyl ether into a saturated dichloromethane solution of **1** at -30 °C was used for the diffraction study. The crystal, a parallelepiped, was bound by the faces {100}, 0.66 mm apart, {010}, 0.20 mm apart, and {001}, 0.30 mm apart, and was mounted on a glass fiber under epoxy. Study on the diffractometer indicated  $2/m$  Laue symmetry and systematic absences ( $h0l$ ,  $h + l \neq 2n$ ;  $0k0$ ,  $k \neq 2n$ ), consistent only with space group  $P2_1/n$  ( $C_{2h}^2$ , No. 14, derived from  $P2_1/c$ ).<sup>12</sup> A primitive orthorhombic unit cell, found by a unit cell check using the program TRACER,<sup>13</sup> was ruled out by axial photographs, which showed only  $2/m$  Laue symmetry, and by inspection of the structure factor amplitudes of several

**Table I.** Experimental Details of the X-ray Diffraction Studies of  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_2(\text{PMePh}_2)_2]\text{SbF}_6$  (**1**) and  $[\text{ReCl}_2(\text{CO})_2(\text{PMePh}_2)_2]$  (**2**)<sup>a</sup>

	1	2
formula	$\text{ReSbCl}_2\text{P}_2\text{F}_6\text{N}_2\text{C}_{34}\text{H}_{40}$	$\text{ReCl}_2\text{P}_2\text{O}_2\text{C}_{28}\text{H}_{26}$
fw	1031.50	713.57
<i>a</i> , Å	6.9456 (8)	9.628 (2)
<i>b</i> , Å	20.301 (4)	13.013 (3)
<i>c</i> , Å	28.428 (8)	11.131 (3)
$\beta$ , deg	92.544 (2)	
<i>V</i> , Å <sup>3</sup>	4004.5	1394.6
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_12_12$
<i>Z</i>	4	2
$\rho_{\text{calcd}}$ , g $\text{cm}^{-3}$	1.711	1.699
$\rho_{\text{obsd}}$ , g $\text{cm}^{-3}$ <sup>b</sup>	1.68 (1)	1.69 (1)
linear abs coeff, $\text{cm}^{-1}$ <sup>c</sup>	37.55	44.67
scan range, deg	$2 \leq 2\theta \leq 50$	$3 \leq 2\theta \leq 58$
no. unique data colld	7035	2138
no. rflns with $F > 4\sigma(F)$	4483	1711
$R_1$ <sup>d,e</sup>	0.029	0.059
$R_2$ <sup>d,e</sup>	0.034	0.071
no. of observns	4483	1711
no. of params	419	148

<sup>a</sup>Data were collected by  $\omega$ (crystal)- $2\theta$ (counter) scans at room temperature by using an Enraf-Nonius CAD-4  $\kappa$ -geometry diffractometer employing Mo  $K\alpha$  (0.701 69 Å) radiation and a graphite monochromator. For procedures used in our laboratory, see ref 14. <sup>b</sup>By neutral buoyancy in bromoform/carbon tetrachloride. <sup>c</sup>Absorption corrections were performed with the Wehe-Busing-Levy ORABS program. <sup>d</sup>All calculations were performed on a DEC VAX 11/780 computer using SHELX-76.<sup>16</sup> <sup>e</sup> $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ .

reflections  $hkl$  and  $\bar{h}kl$ , which were found to be inequivalent. Open-counter  $\omega$  scans of several strong, low-angle reflections showed no structure ( $\Delta\omega_{1/2} = 0.20^\circ$ ) and acceptable crystal quality. Data collection and reduction proceeded by methods standard in our laboratory,<sup>14</sup> the details of which are given in Table I.

(ii)  $[\text{ReCl}_2(\text{CO})_2(\text{PMePh}_2)_2]$  (**2**). A red crystal grown by the slow diffusion of pentane into a dichloromethane solution of **2** at -40 °C was used for the diffraction study. The crystal was a parallelepiped bound by the faces {100}, 0.52 mm apart, {010}, 0.13 mm apart, and {001}, 0.15 mm apart, and was mounted on a glass fiber under epoxy. Study on the diffractometer indicated an orthorhombic crystal system and systematic absences ( $h00$ ,  $h \neq 2n$ ;  $0k0$ ,  $k \neq 2n$ ) consistent only with space group  $P2_12_12$  ( $D_{2h}^2$ , No. 18).<sup>15</sup> A unit cell check using the program TRACER<sup>13</sup> failed to reveal any higher symmetry, and axial photographs confirmed the *mmm* Laue symmetry. Open-counter  $\omega$  scans of several strong, low-angle reflections showed no structure but were quite broad ( $\Delta\omega_{1/2} = 0.50$ – $0.60^\circ$ ). Our inability to obtain better crystals coupled with the relatively small unit cell lengths convinced us that we could collect data on this crystal with a large scan width. Details of the data collection are given in Table I.

**Determination and Refinement of the Structures.** (i)  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_2(\text{PMePh}_2)_2]\text{SbF}_6$  (**1**). The structure was solved in space group  $P2_1/n$  by using standard Patterson and difference Fourier methods. Anisotropic temperature factors were assigned to all non-hydrogen atoms. Hydrogen atoms of the methyl groups were placed at calculated positions [ $d(\text{C-H}) = 0.95$  Å] and constrained to "ride" on the carbon atoms to which they were attached. These hydrogen atoms were refined with a common isotropic thermal parameter. Hydrogen atoms of the phosphine phenyl groups and the two methyne hydrogen atoms of the isopropyl isocyanide groups were handled in an analogous manner and refined with separate, but common, isotropic thermal parameters. Calculations were performed by using SHELX-76,<sup>16</sup> with neutral-atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms obtained from ref 17

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**Table II.** Final Non-Hydrogen Atom Positional Parameters for  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_2(\text{PMePh}_2)_2]\text{SbF}_6$  (1)<sup>a</sup>

atom	x	y	z
Re	1.22594 (3)	0.234100 (10)	0.129460 (10)
Sb	1.01190 (7)	0.18590 (3)	0.37561 (2)
Cl1	0.9552 (2)	0.16745 (8)	0.13583 (6)
Cl2	1.4959 (2)	0.30078 (8)	0.12444 (5)
P1	1.3480 (2)	0.15846 (7)	0.06904 (5)
P2	1.1060 (2)	0.31304 (7)	0.18780 (5)
F1	0.5291 (8)	0.4016 (3)	0.8901 (2)
F2	0.2454 (7)	0.3198 (3)	0.8737 (3)
F3	0.4876 (12)	0.2260 (3)	0.8611 (3)
F4	0.7745 (8)	0.3092 (4)	0.8785 (3)
F5	0.5087 (10)	0.2947 (4)	0.93950 (19)
F6	0.5194 (11)	0.3322 (3)	0.81250 (19)
N1	1.0000 (8)	0.3135 (3)	0.04636 (17)
N2	1.4409 (9)	0.1521 (3)	0.21204 (19)
C1	1.0817 (8)	0.2857 (3)	0.0759 (2)
C2	1.3662 (9)	0.1815 (3)	0.1825 (2)
C10	0.9053 (2)	0.27966 (7)	0.22100 (5)
C11	0.9047 (8)	0.3469 (3)	0.00515 (16)
C12	0.7390 (8)	0.3882 (3)	0.02301 (16)
C13	1.0632 (8)	0.3892 (3)	-0.01520 (16)
C20	1.5667 (6)	0.1895 (2)	0.04217 (15)
C21	1.5255 (9)	0.1138 (3)	0.25202 (17)
C22	1.7037 (9)	0.0808 (3)	0.23499 (17)
C23	1.3683 (9)	0.0642 (3)	0.26421 (17)
C31	1.2813 (8)	0.3365 (3)	0.23453 (18)
C32	1.3720 (9)	0.3964 (3)	0.2368 (2)
C33	1.5100 (11)	0.4095 (4)	0.2736 (3)
C34	1.5556 (11)	0.3640 (5)	0.3066 (3)
C35	1.4656 (11)	0.3042 (4)	0.3045 (2)
C36	1.3316 (10)	0.2912 (4)	0.2695 (2)
C41	1.1814 (8)	0.1476 (3)	0.01809 (18)
C42	1.0496 (8)	0.0965 (3)	0.0156 (2)
C43	0.9217 (9)	0.0921 (3)	-0.0237 (2)
C44	0.9242 (10)	0.1385 (4)	-0.0591 (2)
C45	1.0551 (11)	0.1883 (4)	-0.0561 (2)
C46	1.1858 (10)	0.1926 (3)	-0.0183 (2)
C51	1.0185 (9)	0.3907 (3)	0.16230 (19)
C52	1.1375 (10)	0.4271 (3)	0.1345 (2)
C53	1.0772 (13)	0.4872 (3)	0.1160 (2)
C54	0.8944 (12)	0.5092 (4)	0.1241 (3)
C55	0.7709 (11)	0.4731 (3)	0.1498 (3)
C56	0.8316 (6)	0.4133 (2)	0.17042 (15)
C61	1.4091 (8)	0.0743 (3)	0.0876 (2)
C62	1.3087 (11)	0.0417 (3)	0.1205 (2)
C63	1.3544 (13)	-0.0225 (4)	0.1332 (3)
C64	1.5021 (12)	-0.0547 (4)	0.1136 (3)
C65	1.6020 (13)	-0.0238 (4)	0.0805 (4)
C66	1.5593 (11)	0.0412 (4)	0.0675 (3)

<sup>a</sup>Numbers in parentheses are errors in the last significant digit(s).

and hydrogen atom scattering factors from ref 18. Least-squares refinement minimized the function  $\sum w(|F_o| - |F_c|)^2$ , where weights were set at  $w = 1.5909[\sigma^2(F_o) + 0.000625F_o^2]^{-1}$ , and this refinement converged to the *R* values reported in Table I.

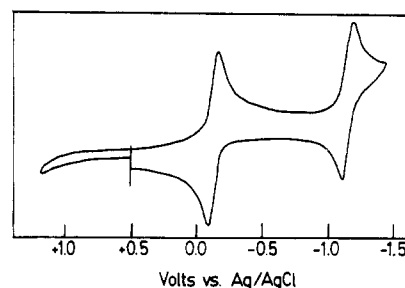
A final difference electron density map revealed a residual peak of  $1.33 \text{ e } \text{\AA}^{-3}$  at  $0.97 \text{ \AA}$  from the antimony atom. Final non-hydrogen atom positional and thermal parameters are given in Tables II and S1 (supplementary material), respectively. Final hydrogen atom positional and thermal parameters and a listing of observed and calculated structure factors are given as supplementary material in Tables S2 and S3, respectively.

(ii)  $[\text{ReCl}_2(\text{CO})_2(\text{PMePh}_2)_2]$  (2). This structure was solved and refined in space group  $P2_12_12$  by methods analogous to those reported for 1. The molecule sits on a 2-fold symmetry axis. Anisotropic temperature factors were assigned to all non-hydrogen atoms except for the carbon and oxygen atoms of the carbon monoxide group. Hydrogen atom positions were calculated as in 1 and included in the refinement. The carbon and oxygen atoms of the carbon monoxide group were located in a difference Fourier map, and only their isotropic temperature factors were refined. A large peak in the final difference Fourier map ( $\sim 7 \text{ e } \text{\AA}^{-3}$  at

**Table III.** Final Non-Hydrogen Atom Positional Parameters for  $[\text{ReCl}_2(\text{CO})_2(\text{PMePh}_2)_2]$  (2)<sup>a</sup>

atom	x	y	z
Re	0.0000	0.5000	0.19972 (8)
Cl	0.6646 (6)	0.0501 (4)	0.9513 (5)
P	0.4095 (5)	0.1775 (4)	0.8233 (5)
O1	0.7051	0.0652	0.5976
C1	0.6332	0.0394	0.6846
C10	0.396 (2)	0.2141 (15)	0.9816 (19)
C21	0.518 (2)	0.2787 (13)	0.7552 (16)
C22	0.585 (2)	0.3498 (15)	0.8232 (18)
C23	0.663 (2)	0.4268 (19)	0.768 (2)
C24	0.672 (3)	0.4295 (18)	0.645 (2)
C25	0.607 (3)	0.356 (2)	0.582 (3)
C26	0.531 (2)	0.2777 (17)	0.6314 (17)
C31	0.231 (2)	0.2046 (16)	0.769 (2)
C32	0.196 (2)	0.2971 (16)	0.722 (2)
C33	0.059 (3)	0.3178 (19)	0.684 (3)
C34	-0.040 (2)	0.2462 (18)	0.704 (2)
C35	-0.009 (3)	0.1536 (17)	0.757 (2)
C36	0.130 (2)	0.1323 (16)	0.788 (2)

<sup>a</sup>Numbers in parentheses are errors in the last significant digit(s).

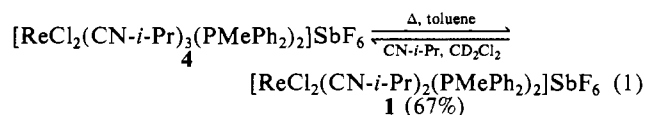


**Figure 1.** Cyclic voltammogram (scan speed = 200 mV/s; Pt-disk electrode) for a 0.2 M TBAP/dichloromethane solution of  $1.3 \times 10^{-3} \text{ M}$   $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_2(\text{PMePh}_2)_2]\text{SbF}_6$  (1).  $\Delta E_p \sim 76, 77 \text{ mV}$ .

$0.77 \text{ \AA}$  from C1 and  $0.60 \text{ \AA}$  from O1) located between the carbon and oxygen atoms of the carbon monoxide ligand appears to be due to a chlorine for carbon monoxide disorder. Unfortunately, this disorder could not be properly modeled, since the peaks due to partially occupied CO and Cl could not be resolved. The precision of the measurements associated with the carbon monoxide ligand is severely limited by the disorder discussed above, and therefore the distances and angles associated with this CO ligand will not be further discussed. The overall structure of this molecule and the distances and angles associated with the rest of the atoms should be reliable, however. Unit weights were used, and least-squares refinement converged to the *R* values reported in Table I. The initial assignment of enantiomorph was confirmed by refinement of the other enantiomorph, which led to an increase in the *R*<sub>2</sub> value by 0.0130. Final non-hydrogen atom positional and thermal parameters are given in Tables III and S4 (supplementary material), respectively. Final hydrogen atom positional and thermal parameters and a listing of observed and calculated structure factors are given as supplementary material in Tables S5 and S6.

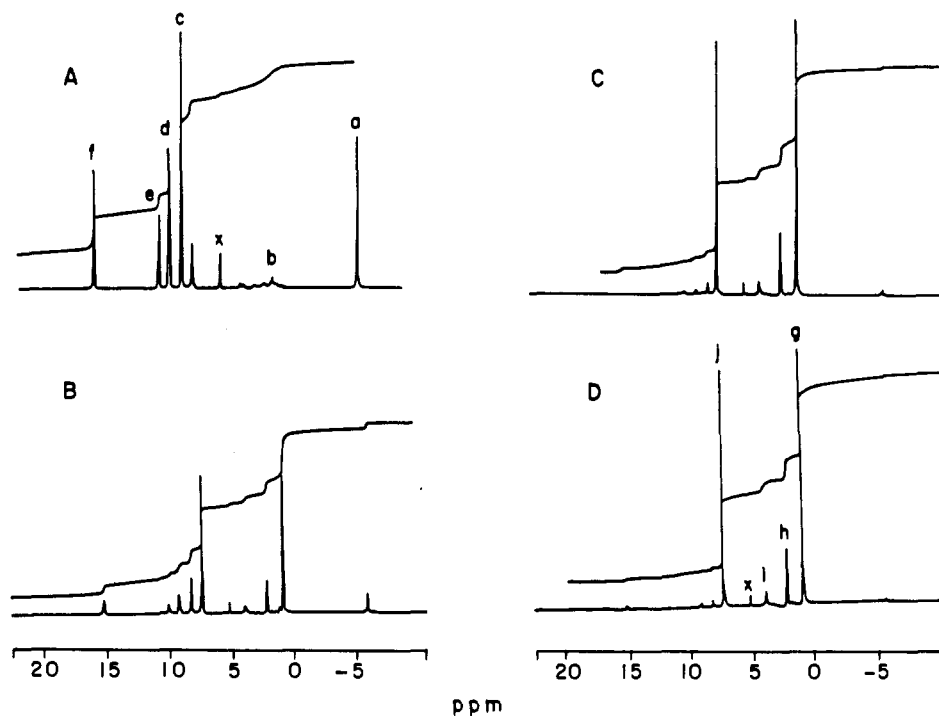
## Results and Discussion

**Syntheses.** When  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_3(\text{PMePh}_2)_2]\text{SbF}_6$  (4) is stirred in acetonitrile during its purification, some paramagnetically shifted <sup>1</sup>H NMR resonances along with the signals of complex 4 are observed. Furthermore, recrystallization of 4 occasionally yields some orange crystals along with the yellow crystals of 4. These orange crystals exhibit rather sharp, shifted proton resonances and no <sup>31</sup>P NMR resonance. A cyclic voltammogram (Figure 1) shows two relatively accessible reversible reductions for the orange crystals, suggesting that it is a 16-electron Re(III) complex. A single-crystal X-ray structure determination revealed the composition to be  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_2(\text{PMePh}_2)_2]\text{SbF}_6$  (1). Complex 1 can also be prepared by heating a toluene solution of 4 (eq 1). Addition of 1 equiv of isopropyl isocyanide to 1 results



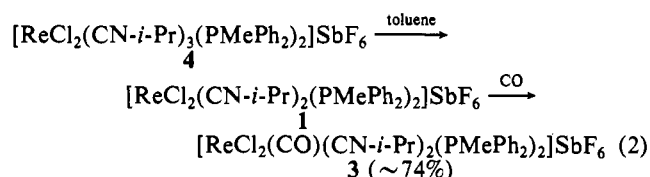
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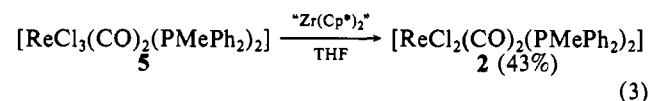


**Figure 2.** Time-dependent study of the reaction of isopropyl isocyanide with  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_2(\text{PMePh}_2)_2]\text{SbF}_6$  (**1**) as followed by  $^1\text{H}$  NMR spectroscopy (90 MHz). (A)  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_2(\text{PMePh}_2)_2]\text{SbF}_6$  (**1**),  $t = 0$  min: (a)  $-5.96$  (s, 6 H,  $\text{PCH}_3$ ), (b)  $2.14$  (m, 2 H,  $\text{CNCHMe}_2$ ), (c)  $8.17$  (d, 12 H,  $J = 6.8$  Hz,  $\text{CNCH}(\text{CH}_3)_2$ ), (d)  $9.16$  (t, 8 H,  $J = 7.3$  Hz,  $m\text{-H}$ ), (e)  $9.95$  (t, 4 H,  $J = 7.8$  Hz,  $p\text{-H}$ ), (f)  $15.04$  ppm (d, 8 H,  $J = 7.8$  Hz,  $o\text{-H}$ ), (x)  $\text{CDHCl}_2$ . (B)  $t = 80$  min. (C)  $t = 105$  min. (D)  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_3(\text{PMePh}_2)_2]\text{SbF}_6$  (**4**): (g)  $1.00$  (d, 18 H,  $J = 6.9$  Hz,  $\text{CNCH}(\text{CH}_3)_2$ ), (h)  $2.28$  (virtual t, 6 H,  $^2J_{\text{PH}} \approx ^4J_{\text{PH}} \approx 4.9$  Hz), (i)  $4.05$  (m, 3 H,  $\text{CNCHMe}_2$ ), (j)  $7.47$  ppm (br, 20 H,  $\text{Ph}$ ), (x)  $\text{CDHCl}_2$ .

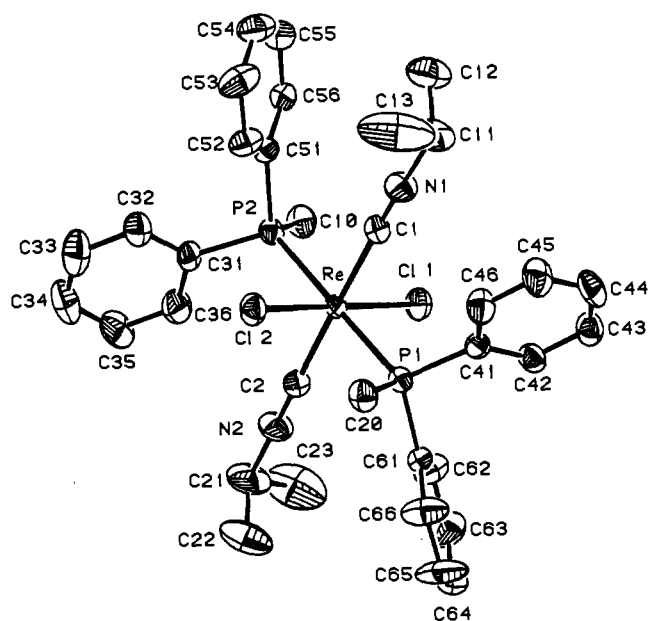
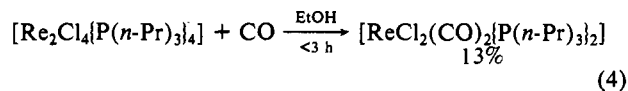
in the appearance of the  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectral signals of **4**. The time course of this reaction (eq 1) is displayed in Figure 2. Bubbling gaseous CO through a  $\text{CD}_2\text{Cl}_2$  solution of **1** leads to the formation of **3**. Passing CO gas through a refluxing toluene solution of **4** also results in **3** (eq 2).



Recently, the reductive coupling of two CO ligands in  $[\text{Ta}(\text{CO})_2(\text{dmpe})_2\text{Cl}]$  to form coordinated bis(trimethylsiloxy)ethyne has been accomplished.<sup>6d</sup> The reaction of  $[\text{ReCl}_3(\text{CO})_2(\text{PMePh}_2)_2]$  (**5**) with various reducing agents under different conditions was studied in the hope of observing an analogous reductive coupling of two carbon monoxide ligands. No rhenium-ethyne complex was observed; however, a ubiquitous red product formed, having a  $^1\text{H}$  NMR spectrum suggestive of paramagnetism and an IR spectrum consistent with two cis carbon monoxide ligands. A six-coordinate 17-electron Re(II) complex was proposed and later confirmed by X-ray crystallography. This material can be prepared, as shown in eq 3. As discussed earlier,



mononuclear Re(II) complexes are quite rare. Only two such examples (but see ref 3c) have been structurally characterized, all-trans isomers of  $[\text{Re}(\text{CN-}t\text{-Bu})_2(\text{NCMe})_2(\text{PPh}_3)_2](\text{BF}_4)_2$ <sup>3a</sup> and  $[\text{ReCl}_2(\text{CO})_2(\text{PET}_3)_2]$ .<sup>5</sup> The first member of the general class  $[\text{ReX}_2(\text{CO})_2(\text{PR}_3)_2]$ ,  $[\text{ReCl}_2(\text{CO})_2\{\text{P}(n\text{-Pr})_3\}_2]$ , was prepared as shown in eq 4 and postulated also to have an all-trans geometry.<sup>3b</sup>



**Figure 3.** Structure of the cation in **1** showing the atom-labeling scheme and 40% thermal ellipsoids.

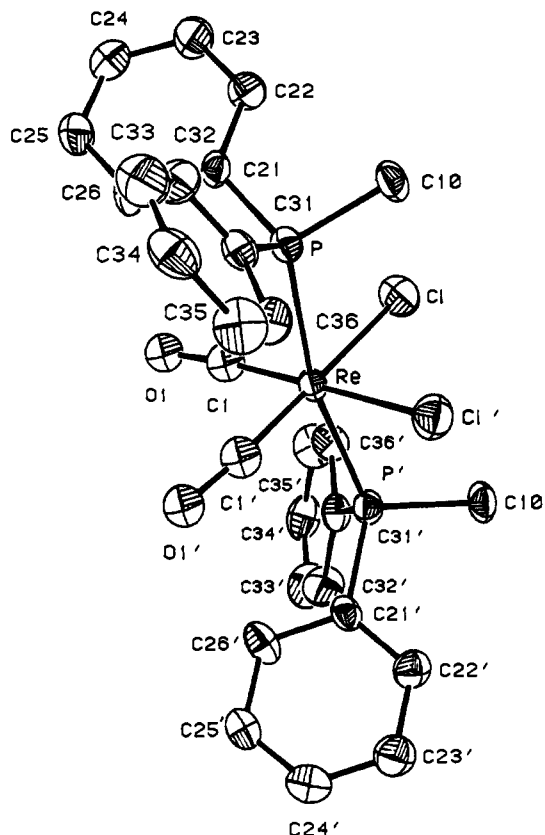
**Structural and Spectroscopic Properties of 1–3.** (i)  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_2(\text{PMePh}_2)_2]\text{SbF}_6$  (**1**). The structure of **1** is shown in Figure 3, and bond distances and angles are reported in Table IV. There is little distortion of this cation from regular octahedral geometry, and the ligands, two chlorides, two isopropyl isocyanides, and two methylphenylphosphines, are in the all-trans configuration. This example is the first crystal structure report of a mononuclear 16-electron rhenium isocyanide complex. The Re–C1 and Re–C2 distances are significantly longer than the Re–C(isocyanide) distances in seven-coordinate  $[\text{ReCl}_2(\text{CN-}t\text{-Bu})_3(\text{PMePh}_2)_2]\text{SbF}_6$  (1.948 (8)–2.013 (6) Å),<sup>8</sup> not the result expected solely on the basis of coordination number. The lesser degree of back-bonding in six-coordinate 16-electron **1**, compared with  $[\text{ReCl}_2(\text{CN-}t\text{-Bu})_3(\text{PMePh}_2)_2]\text{SbF}_6$ , however, and the trans dis-

**Table IV.** Interatomic Distances (Å) and Angles (deg) for  $[\text{ReCl}_2(\text{CN-}i\text{-Pr})_2(\text{PMePh}_2)_2]\text{SbF}_6$  (1)<sup>a</sup>

Coordination Sphere				
Bond Distances				
Re-Cl1	2.331 (3)	Re-Cl2	2.322 (3)	
Re-P1	2.48 (1)	Re-P2	2.48 (1)	
Re-C1	2.07 (1)	Re-C2	2.06 (1)	
Bond Angles				
C11-Re-Cl2	179.1 (1)	C11-Re-P1	89.8 (6)	
C11-Re-P2	91.5 (6)	C12-Re-P1	90.9 (6)	
C12-Re-P2	87.7 (6)	P1-Re-P2	177.90 (5)	
C1-Re-Cl1	89.1 (6)	C1-Re-Cl2	91.5 (6)	
C2-Re-Cl1	89.9 (6)	C2-Re-Cl2	89.5 (6)	
C1-Re-P1	88.5 (2)	C1-Re-P2	89.9 (2)	
C2-Re-P1	91.2 (2)	C2-Re-P2	90.4 (2)	
C1-Re-C2	179.0 (2)			
Ligand Geometry				
(i) Isopropyl Isocyanide Groups				
Bond Distances				
C1-N1	1.14 (1)	C2-N2	1.14 (1)	
N1-C11	1.48 (1)	N2-C21	1.48 (1)	
C11-C12	1.53 (1)	C21-C22	1.51 (1)	
C11-C13	1.53 (1)	C21-C23	1.537 (9)	
Bond Angles				
Re-C1-N1	179.1 (5)	Re-C2-N2	178.9 (6)	
C1-N1-C11	175.1 (6)	C2-N2-C21	176.1 (7)	
N1-C11-C12	107.7 (6)	N1-C11-C13	104.6 (6)	
N2-C21-C22	106.9 (7)	N2-C21-C23	104.8 (7)	
C12-C11-C13	112.6 (5)	C22-C21-C23	112.5 (5)	
(ii) Diphenylmethylphosphine Groups				
Bond Distances				
P1-C20	1.84 (1)	P2-C10	1.85 (1)	
P1-C41	1.83 (2)	P2-C31	1.83 (2)	
P1-C61	1.833 (6)	P2-C51	1.829 (7)	
mean C(ring)-C(ring)	1.38 (1)	range C(ring)-C(ring)	1.35-1.41	
Bond Angles				
Re-P1-C20	112.9 (6)	Re-P2-C10	112.9 (5)	
Re-P1-C41	113.6 (2)	Re-P2-C31	115.0 (2)	
Re-P1-C61	117.4 (2)	Re-P2-C51	114.1 (2)	
C41-P1-C20	102.6 (4)	C10-P2-C51	105.9 (2)	
C41-P1-C61	104.2 (3)	C31-P2-C10	102.6 (3)	
C61-P1-C20	104.7 (2)	C31-P2-C51	105.2 (4)	
mean C(ring)-C(ring)-P	120.7 (5)	range C(ring)-C(ring)-P	118.7-123.8	
mean C(ring)-C(ring)-C(ring)	120.0 (8)	range C(ring)-C(ring)-C(ring)	117.0-122.6	
Anion Geometry				
Hexafluoroantimonate				
Bond Distances and Angles				
mean Sb-F	1.840 (6)	range Sb-F	1.827-1.860	
mean cis F-Sb-F	90.0 (6)	mean trans F-Sb-F	178.8 (3)	
min cis F-Sb-F	88.4 (4)	min trans F-Sb-F	178.5 (3)	
max cis F-Sb-F	92.2 (4)	max trans F-Sb-F	179.0 (4)	

<sup>a</sup>Distances reported have not been corrected for thermal motion. Standard deviations, quoted for mean values, are the average of the standard deviations for the individual values.

position of the isopropyl isocyanides both contribute to this bond lengthening. Table V compares some Re(III,IV)-P and Re(III,IV)-Cl bond lengths in related compounds. The Re-P bond lengths in 1 are in the range, albeit the high side, of other Re(III)-P determinations. The Re-Cl bond lengths of 1 are shorter than those in  $[\text{ReCl}_2(\text{CN-}i\text{-Bu})_3(\text{PMePh}_2)_2]\text{SbF}_6$ . The relief of steric strain that one might expect in going from a seven-coordinate complex to a six-coordinate complex is in part responsible for this bond shortening. The Re-Cl distances are in the range of the Re-Cl lengths of *trans*- $[\text{ReCl}_4(\text{PMe}_2\text{Ph})_2]$ . This result may be due to the cationic nature of 1. The infrared spectrum of 1 shows a strong absorbance at  $\sim 2182\text{ cm}^{-1}$ , assignable to  $\nu(\text{C}\equiv\text{N})$ , and a strong single absorbance at  $295\text{ cm}^{-1}$ ,

**Figure 4.** ORTEP view of 2 showing the atom-labeling scheme and 40% thermal ellipsoids.

assigned to  $\nu(\text{Re-Cl})$  stretching bands.<sup>23</sup> Both assignments are consistent with the all-*trans* geometry of 1. The <sup>1</sup>H NMR spectrum of 1 exhibits sharp and well-defined resonances, behavior consistent with d<sup>4</sup> Re(III) complexes that exhibit interpretable <sup>1</sup>H NMR spectra even though they are paramagnetic.<sup>2a,3a,20-22,26</sup> The shifts associated with the <sup>1</sup>H NMR spectrum of 1 are best described as Knight shifts,<sup>2a,3a,22b,26</sup> rather than contact shifts, since the latter implies a specific shift mechanism, whereas the former does not. Surprisingly, the complex  $[\text{ReCl}_3(\text{CN-mesityl})_3]$  does not exhibit Knight shifting.<sup>26</sup>

(ii)  $[\text{ReCl}_2(\text{CO})_2(\text{PMePh}_2)_2]$  (2). An ORTEP view of 2 is shown in Figure 4, and interatomic bond distances and angles are summarized in Table VI. This 17-electron d<sup>5</sup> octahedral Re(II) complex has two cis carbonyls, two cis chlorides, and two *trans* methylphenylphosphines as its ligand set. There is a distortion of the P-Re-P bond angle so as to bend the phosphines away from the cis carbonyl ligands and toward the cis chlorides, probably indicating the steric preference of the *trans* phosphine ligands. The phenyl groups are rotated toward the carbonyl ligands, another reflection of internal packing preferences. The Re-P and Re-Cl bond distances in 2 agree well with those determined for *all-trans*- $[\text{ReCl}_2(\text{CO})_2(\text{PEt}_3)_2]$ ; viz, Re-P = 2.470 (4) Å and Re-Cl

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Table V. Comparison of Selected Re-P and Re-Cl Bond Distances (Å)

complex	Re-P	Re-Cl	ref
[ReCl <sub>2</sub> (CN- <i>t</i> -Bu) <sub>3</sub> (PMePh <sub>2</sub> ) <sub>2</sub> ]SbF <sub>6</sub>	2.486 (2)	2.473 (2)	8
<i>all-trans</i> -[ReCl <sub>2</sub> (CN- <i>i</i> -Pr) <sub>2</sub> (PMePh <sub>2</sub> ) <sub>2</sub> ]SbF <sub>6</sub> (1)	2.510 (2)	2.447 (2)	this work
	2.48 (1)	2.331 (3)	
<i>mer</i> -[ReCl <sub>3</sub> (PMe <sub>2</sub> Ph) <sub>3</sub> ]	2.48 (1)	2.322 (3)	this work
	2.458 (6)	2.353 (6)	19
<i>trans</i> -[ReCl <sub>4</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> ]	2.401 (6)	2.454 (6)	19
	( <i>trans</i> to Cl)	( <i>trans</i> to P)	
	2.505 (3)	2.331 (3)	

Table VI. Interatomic Distances (Å) and Angles (deg) for [ReCl<sub>2</sub>(CO)<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>] (2)<sup>a</sup>

Coordination Sphere			
Bond Distances			
Re-Cl	2.400 (6)	Re-P	2.481 (5)
Re-Cl	1.88		
Bond Angles			
Cl-Re-Cl'	91.1 (3)	Cl-Re-P	84.7 (2)
Cl-Re-Cl	87.4 (1)	Cl-Re-P'	87.1 (2)
Cl'-Re-Cl	178.5 (1)	P-Re-P'	168.2 (2)
Cl-Re-P	93.2 (1)	Cl'-Re-P	94.9 (1)
Cl-Re-Cl'	94		
Ligand Geometry			
(i) Carbonyl Group			
Bond Distances and Angles			
Cl-O1	1.24	O1-Cl-Re	171
(ii) Diphenylmethylphosphine Groups			
Bond Distances			
P-C10	1.83 (2)	P-C21	1.85 (2)
P-C31	1.86 (2)		
mean C(ring)-C(ring)	1.37 (3)	range C(ring)-C(ring)	1.34-1.41
Bond Angles			
C10-P-Re	111.5 (7)	C21-P-Re	115.0 (7)
C31-P-Re	117.9 (7)	C10-P-C21	104.4 (9)
C10-P-C31	102 (1)	C21-P-C31	105 (1)
mean C(ring)-C(ring)-P	120 (2)	range C(ring)-C(ring)-P	117-122
mean C(ring)-C(ring)-C(ring)	120 (2)	range C(ring)-C(ring)-C(ring)	116-124

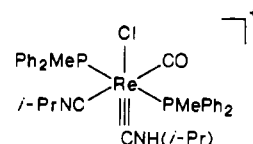
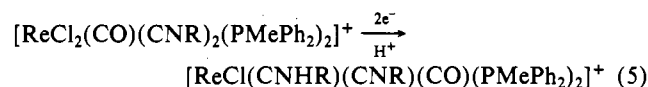
<sup>a</sup>Distances reported have not been corrected for thermal motion. Standard deviations, quoted for mean values, are the average of the standard deviations for the individual values.

= 2.407 (4) Å. The infrared spectrum is consistent with the *cis* disposition of the carbonyls, and the paramagnetic <sup>1</sup>H NMR spectrum is readily assignable, as was the case for **1**. *all-trans*-[ReCl<sub>2</sub>(CO)<sub>2</sub>(P-*n*-Pr<sub>3</sub>)<sub>2</sub>] is yellow and has a strong IR absorption at ~1901 cm<sup>-1</sup> ( $\nu$ (CO)), whereas **2** is red and has strong  $\nu$ (CO) absorptions at 1946 and 1887 cm<sup>-1</sup>.

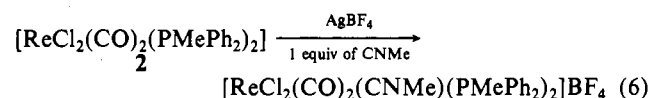
(iii) [ReCl<sub>2</sub>(CO)(CN-*i*-Pr)<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>]SbF<sub>6</sub> (**3**). The infrared spectrum of **3** shows the presence of both CO and isocyanide ligands. A single resonance in the phosphorus-31 NMR spectrum and a virtual triplet observed for the phosphine methyl groups in the proton NMR spectrum are consistent with a *trans* disposition of phosphines. We propose a capped trigonal-prismatic geometry, analogous to that of [ReCl<sub>2</sub>(CN-*t*-Bu)<sub>3</sub>(PMePh<sub>2</sub>)<sub>2</sub>]-

SbF<sub>6</sub>,<sup>8</sup> in which the carbonyl ligand would occupy one of the isocyanide sites on either the quadrilateral face or the unique edge *trans* to chloride. Occasionally, the weak absorption at ~1864 cm<sup>-1</sup> in the infrared spectrum of **3** was observed to have greater intensity. Integration of the <sup>1</sup>H NMR spectrum also revealed too many phosphine protons. Both of these observations are consistent with the presence of some amount of impurity, possibly [ReCl<sub>2</sub>(CO)<sub>2</sub>(CN-*i*-Pr)(PMePh<sub>2</sub>)<sub>2</sub>]SbF<sub>6</sub> formed in reaction 2. Further purification is required to separate these two similar compounds.

**Relation to Reductive Coupling Chemistry.** In compound **3**, like [ReCl<sub>2</sub>(CN-*t*-Bu)<sub>3</sub>(PMePh<sub>2</sub>)<sub>2</sub>]SbF<sub>6</sub>, there are likely to be close nonbonded contacts between linear ligands. Such a geometry would facilitate formation of a six-coordinate aminocarbene complex (eq 5), from which further nucleophilic attack of X<sup>-</sup> at



the rhenium atom could lead to aminocarbene-isocyanide or -carbonyl coupling (eq 5).<sup>6d,e</sup> These reactions must await further purification of **3**, however. As discussed previously, carbonyl-carbonyl coupling to form C-C bonds via ligand addition to tungsten complexes is well-known.<sup>24,25</sup> Preliminary attempts to prepare another mixed CO/isocyanide seven-coordinate Re(III) complex (eq 6) generated a mixture of products. AgBF<sub>4</sub> may not



be the best choice of one-electron oxidizing agents for this system, since the silver ion can also abstract a chloride in a competitive reaction. Further studies of this chemistry are planned.

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**Supplementary Material Available:** Tables S1, S2, S4, and S5, reporting non-hydrogen atomic thermal parameters and hydrogen atom positional and thermal parameters for **1** and **2** (3 pages); Tables S3 and S6, listing observed and calculated structure factors for **1** and **2** (33 pages). Ordering information is given on any current masthead page.