shift/esd ratio of 0.1 for III and 0.3 for IV. No unusually high correlations were noted between any of the variables in the last cycles of full-matrix least-squares fitting. All calculations were made by using Nicolet's SHELXTL (1987) series of crystallographic programs. The pertinent crystallographic data for III and IV are summarized in Table IV, and the final atomic coordinates are listed in Tables V and VI, respectively.

Acknowledgment. We thank the University of Wroclaw for a leave of absence for S.W., J. D. Korp for crystallographic assistance, and the National Science Foundation, the Robert A. Welch Foundation, and the Texas Advanced Research Program for financial support.

Supplementary Material Available: For $[Et_4N][TpMoO_3]\cdot 3H_2O$ (III) and $(TpMoO_2)_4\cdot 2H_2O$ (IV), tables of anisotropic displacement parameters, bond lengths and angles, H atom coordinates, and isotropic displacement parameters (7 pages); listings of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of Seven-Coordinate Rhenium(III) Mixed Halo–Phosphine Isocyanide Complexes

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The synthesis of mixed halo–phosphine isocyanide complexes of general formula $[ReCl_2(CNR)_3(PMePh_2)_2]^+$ is described. The crystal structure of a representative member of this class, $[ReCl_2(CN\text{-}t\text{-}Bu)_3(PMePh_2)_2](SbF_6)$ (**1**), has been determined. This complex adopts the C_{2v} capped trigonal prismatic geometry with close nonbonded contacts of 2.341 (8) and 2.330 (9) Å between coordinated isocyanide carbon atoms. Such distances in seven-coordinate compounds reveal that they are good candidates for reductive coupling of the isocyanide ligands, a reaction previously studied for **1**. The syntheses of $[ReCl_3(CN\text{-}t\text{-}Bu)_2(PMePh_2)_2]$ and $[ReCl_3(CN\text{-}2,6\text{-}Me_2Ph)_3(PMePh_2)]$ are also reported. Red crystals of $[Re(O)(OEt)Cl_2(PMePh_2)_2]$ (**2**) were isolated in 25% yield as a side product during the preparation of $[ReCl_3(PMePh_2)_3]$ starting material from $AgReO_4$. The identity of **2** was established by IR spectroscopy, elemental analysis, and X-ray crystallography. The Re–O bond distance of 1.699 (5) Å is characteristic of a metal–oxygen triple bond. Crystal data: for **1**, a = 10.486 (2) Å, b = 13.201 (2) Å, c = 17.559 (2) Å, α = 76.21 (1)°, β = 89.73 (1)°, γ = 87.05 (1)°, triclinic, $P\bar{1}$ (C_i^1; Z = 2); for **2**, a = 11.015 (1) Å, b = 12.745 (1) Å, c = 21.035 (3) Å, β = 105.19 (1)°, monoclinic, $P2_1/n$ (C_{2h}^5; Z = 4).

Introduction

Our interest in seven-coordinate early-transition-metal isocyanide complexes stems from their propensity to undergo reductive coupling to form coordinated bis(alkylamino)acetylenes (eq 1).[2,3] Mechanistic studies, currently in progress, indicate that

$$[M(CNR)_6X]^+ \xrightarrow[H^+]{Zn(s)} [M(RHNC{\equiv}CNHR)(CNR)_4X]^+ \quad (1)$$

$$M = Mo, W$$

this reaction proceeds by a sequence of steps involving reduction to $[M(CNR)_6]$ followed by protonation to form an aminocarbyne species and, ultimately, the coupled product (eq 2).[4] A parallel

$$[M(CNR)_6X]^+ \xrightarrow[-X^-]{Zn(s)} [M(CNR)_6] \xrightarrow{H^+}$$

$$[M{\equiv}CNHR(CNR)_5]^+ \xrightarrow{HX}$$

$$[M(RHNC{\equiv}CNHR)(CNR)_4X]^+ \quad (2)$$

series of reactions occurs in the reductive coupling of CO ligands in $[M(CO)_2(dmpe)_2X]$ (M = Nb, Ta; dmpe = 1,2-bis(dimethylphosphino)ethane; X = halide)[3,5] to afford disiloxyacetylene complexes and, in the case of mixed CO/CNR coupling, to form $[M(R_3SiOC{\equiv}CN(SiR_3)R')(dmpe)_2Cl]$ (M = Nb, Ta; R, R′ = alkyl groups).[6]

The present study was undertaken as part of a systematic investigation to extend the scope of the reductive coupling chemistry to group VII metals. Previously we showed that, with $[M(CNR)_6X]^{2+}$ cations (M = Tc, Re, R = *t*-Bu, Me, and X = Br; M = Tc, R = *t*-Bu, and X = Cl), these conditions afford only $[M(CNR)_6]^+$ by reductive elimination, analogous to the first step in eq 2.[7] Since mechanistic studies revealed that increasing the electron density at the metal center favors the reductive coupling reaction,[8] the more electron-rich complexes $[ReCl_2(CNR)_3(PMePh_2)_2]^+$ were examined.[9] Here we report a general synthetic route to cations in this class, the crystal structure of one member, $[ReCl_2(CN\text{-}t\text{-}Bu)_3(PMePh_2)_2]SbF_6$, and the preparation and structure of $[ReCl_2(O)(OEt)(PMePh_2)_2]$, a side product formed during the synthesis of the $[ReCl_3(PMePh_2)_3]$ starting material.

Experimental Section

Materials and Methods. $AgReO_4$ (Alfa), diphenylmethylphosphine (Strem), $KSbF_6$ (Strem), and 37% hydrochloric acid (Mallinckrodt) were obtained from commercial sources and used as received. $[ReCl_3(PMePh_2)_3]$[10] and $[ReCl_2I(PMePh_2)_3]$[11] were prepared by literature procedures. Dichloromethane was predried over calcium chloride and then distilled from calcium hydride under nitrogen, or it was purified by

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transfer from 4-Å molecular sieves. Hexane was filtered through alumina. Diethyl ether, toluene, and *n*-pentane were distilled from sodium or potassium/benzophenone ketyl under nitrogen. Methanol was distilled under nitrogen from magnesium turnings that were activated by iodine. Reactions and all manipulations were carried out by using standard Schlenk techniques or a Vacuum Atmospheres drybox, all under nitrogen.

[ReCl$_2$(CN-*i*-Pr)$_3$(PMePh$_2$)$_2$]I. To a stirred solution of [ReCl$_2$I(PMePh$_2$)$_3$] (0.20 g, 0.20 mmol) in 25 mL of toluene was added isopropyl isocyanide (0.14 g, 2.0 mmol). After the mixture was allowed to stir for 16 h, the product was filtered out, washed in hexane, and dried in vacuo. Yield: 0.15 g (76%). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.45 (m, P*Ph*, 20 H), 4.17 (spt, C*H*, 3 H), 2.23 (t, PC*H*$_3$, 6 H), 0.98 (d, C(C*H*$_3$)$_2$, 18 H) ppm. IR (Nujol): 2208, 2172, 2145 cm^{-1}. Anal. Calcd for $C_{38}H_{47}Cl_2IN_3P_2Re$: C, 46.02; H, 4.78; Cl, 7.15; I, 12.79; N, 4.24; P, 6.25. Found: C, 45.85; H, 4.70; Cl, 7.94; I, 12.99; N, 4.30; P, 6.35.

[ReCl$_2$(CN-*t*-Bu)$_3$(PMePh$_2$)$_2$]Cl. *tert*-Butyl isocyanide (1.07 g, 12.87 mmol) was added dropwise to a suspension of [ReCl$_3$(PMePh$_2$)$_3$] (1.0 g, 1.1 mmol) in 30 mL of toluene. The orange-yellow solution was allowed to stir for 3 days. The off-white solid was filtered out and washed with hexane. Yield: 1.08 g (96%). Recrystallization of the material was achieved at −30 °C from methylene chloride/diethyl ether to yield a light yellow solid. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.55 (m, P*Ph*, 20 H), 2.30 (t, PC*H*$_3$, 6 H), 1.25 (m, C(C*H*$_3$)$_3$, 27 H) ppm. IR (Nujol): 2180, 2150, 2130 cm^{-1}. Anal. Calcd for [ReCl$_2$(CN-*t*-Bu)$_3$(PMePh$_2$)$_2$]Cl·CH$_2$Cl$_2$, $C_{42}H_{55}Cl_5N_3P_2Re$: C, 49.10; H, 5.40; Cl, 17.25; N, 4.09; P, 6.03. Found: C, 48.68; H, 5.48; Cl, 15.70; N, 4.12; P, 6.03.

[ReCl$_3$(CN-*t*-Bu)$_2$(PMePh$_2$)$_2$]. *tert*-Butyl isocyanide (0.19 g, 2.29 mmol) was added dropwise to a suspension of [ReCl$_3$(PMePh$_2$)$_3$] (1.0 g, 1.1 mmol) in 30 mL of toluene. After the mixture was stirred for 3 days, the yellow solid was filtered out, washed with hexane, and dried in vacuo. Yield: 0.96 g (95%). Recrystallization of the material was achieved at −30 °C from methylene chloride/diethyl ether to yield a yellow solid. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.74, 7.42, 7.20 (br s, P*Ph*, 20 H), 2.43, 1.11 (br s, PC*H*$_3$, 6 H), 1.76, 0.67 (s, C(C*H*$_3$)$_3$, 18 H) ppm. IR (Nujol): 2180, 2130, 2070 cm^{-1}. Anal. Calcd for [ReCl$_3$(CN-*t*-Bu)$_2$(PMePh$_2$)$_2$]·CH$_2$Cl$_2$, $C_{37}H_{46}Cl_5N_2P_2Re$: C, 47.07; H, 4.91; Cl, 18.78; N, 2.97; P, 6.56. Found: C, 47.38; H, 4.92; Cl, 16.1; N, 3.14; P, 6.63.

[ReCl$_3$(CN-2,6-Me$_2$Ph)$_3$(PMePh$_2$)]. To a suspension of [ReCl$_3$(PMePh$_2$)$_3$] (1.0 g, 1.1 mmol) in 50 mL of toluene was added 2,6-dimethylphenyl isocyanide (0.73 g, 5.56 mmol). After 16 h, the yellow solid was filtered out and washed with hexane. Yield: 0.97 g (98%). Recrystallization by methylene chloride/pentane vapor diffusion resulted in a yellow-orange crystalline solid. Anal. Calcd for $C_{40}H_{40}Cl_3N_3PRe$: C, 54.20; H, 4.56; Cl, 12.00; N, 4.74; P, 3.49. Found: C, 54.11; H, 4.51; Cl, 12.28; N, 4.76; P, 3.57.

[ReCl$_2$(CN-*t*-Bu)$_3$(PMePh$_2$)$_2$]SbF$_6$ (1). To a solution of 1.00 g (1.12 mmol) of [ReCl$_3$((PMePh$_2$)$_3$] in 25 mL of methylene chloride was added 0.38 g (1.11 mmol) of silver hexafluoroantimonate. The resulting silver chloride precipitate (0.21 g, 100%) was removed by filtration. *tert*-Butyl isocyanide (1.07 g, 12.87 mmol) was added dropwise, and the reaction mixture was allowed to stir overnight. The volume of the red solution was reduced, and 0.62 g (52%) of a pale orange solid precipitated when diethyl ether was added to the solution. The solid was recrystallized from methylene chloride/diethyl ether at −30 °C. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.38 (br, s, C(C*H*$_3$)$_3$, 27 H), 2.28 (t, J = 4.6 Hz, PC*H*$_3$, 6 H), 7.49–7.52 (m, P*Ph*, 20 H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ −12.3 (s). IR (KBr): 2966 (m), 2176 (sh), 2151 (s), 1437 (m), 1425 (m), 1213 (m), 1192 (s), 1099 (m), 893 (s), 733 (m), 720 (m), 695 (s), 504 (m) cm^{-1}. UV–vis (CH$_2$Cl$_2$, 4.46 × 10^{-4} M): 331 nm (3991 M^{-1} cm^{-1}). Anal. Calcd for $C_{41}H_{53}Cl_2N_3P_2F_6SbRe$: C, 43.10; H, 4.68; Cl, 6.21; N, 3.68. Found: C, 42.95; H, 4.58; Cl, 7.05; N, 3.59.

Alternatively, a 7-fold molar excess of KSbF$_6$ (relative to rhenium) in methanol was added dropwise to a powdered sample of [ReCl$_2$(CN-*t*-Bu)$_3$(PMePh$_2$)$_2$]Cl. The resulting yellow solution was stirred under nitrogen overnight. Methanol was removed under reduced pressure and the residue extracted with dichloromethane, leaving behind KCl and KSbF$_6$. The dichloromethane solution was concentrated, and yellow crystals of **1** were grown by diffusion of diethyl ether into this solution over several days.

Isolation of [ReCl$_2$(O)(OEt)(PMePh$_2$)$_2$] (2) from the Preparation of [ReCl$_3$(PMePh$_2$)$_3$]. A mixture containing 4.073 g (11.37 mmol) of AgReO$_4$, 11.39 g (56.88 mmol) of PMePh$_2$, 4.48 g (43.53 mmol) of 37% HCl, and 200 mL of ethanol was stirred and refluxed for 12 h. The resulting yellow suspension was filtered to leave a yellow solid and a brown ethanolic solution. The yellow solid was then extracted with dichloromethane, and the dichloromethane volume was reduced under vacuum. A yellow powder precipitated upon addition of pentane and was identified as [ReCl$_3$(PMePh$_2$)$_3$] (7.515 g, 8.41 mmol, 74.0%). Nitrogen was bubbled through the brown solution to reduce the solvent volume, during which procedure red crystals formed. These red crystals were isolated by filtration and recrystallized by diffusing pentane into a saturated dichloromethane solution at −30 °C overnight. The red complex was identified as [ReCl$_2$(O)(OEt)(PMePh$_2$)$_2$] (**2**) (2.075 g, 2.89 mmol, 25.4%). ^{1}H NMR (CD$_2$Cl$_2$): δ 0.28 (t, J = 7.0 Hz, OCH$_2$C*H*$_3$, 3 H), 2.29 (t, J = 3.5 Hz, PC*H*$_3$, 6 H), 2.61 (q, J = 7.0 Hz, OC*H*$_2$, 2 H), 7.42–7.48 (m, P–*Ph* *m*- and *p*-H's, 12 H), 7.78–7.98 (m, P–*Ph* *o*-H's, 8 H), 9.37 (br, O*H*, 1 H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ −23.7 (s). IR (KBr): 3053 (m), 2968 (m), 2923 (m), 2859 (m), 1588 (w), 1573 (w), 1484 (m), 1436 (s), 1372 (m), 1340 (m), 1316 (m), 1289 (m), 1191 (w), 1108 (s), 1074 (s), 1028 (w), 999 (w), 954 (s), 917 (s), 895 (s), 886 (s), 747 (s), 740 (s), 695 (s), 568 (m), 516 (s), 507 (m), 480 (m), 451 (w) cm−1. UV–vis (CH$_2$Cl$_2$, 5.43 × 10^{-4} M): 325 (2072), 500 (78), 580 nm (62 M^{-1} cm^{-1}). Mp: 162–164° C dec. Anal. Calcd for $C_{28}H_{31}O_2P_2Cl_2Re$: C, 46.80; H, 4.35. Found: C, 46.94; H, 4.44.

Table I. Experimental Details of the X-ray Diffraction Study of [ReCl$_2$(CN-*t*-Bu)$_3$(PMePh$_2$)$_2$]SbF$_6$ (**1**) and ReCl$_2$(O)(OEt)(PMePh$_2$)$_2$ (**2**)[a]

	1	**2**
formula	$ReSbCl_2P_2F_6N_3C_{41}H_{53}$	$ReCl_2P_2O_2C_{28}H_{31}$
fw	1142.69	718.61
a, Å	10.486 (2)	11.015 (1)
b, Å	13.201 (2)	12.745 (1)
c, Å	17.559 (2)	21.035 (3)
α, deg	76.21 (1)	
β, deg	89.73 (1)	105.19 (1)
γ, deg	87.05 (1)	
V, Å^3	2357.39	2849.86
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
Z	2	4
ρ_{calcd}, g cm^{-3}	1.610	1.675
ρ_{obsd}, g cm^{-3} [b]	1.61 (1)[b]	1.66 (1)[b]
linear abs coeff, cm^{-1} [c]	39.8	103.4
scan range, deg	$3 < 2\theta < 50$	$4 < 2\theta < 130$
no. of unique data colld	6654	5858
R_1 [d,e]	0.037	0.044
R_2 [d,e]	0.049	0.053
no. of observns	5788, $F > 6\sigma(F)$	4634, $F > 4\sigma(F)$
no. of params	498	309

[a] Data were collected by ω(crystal)–2θ(counter) scans at room temperature by using an Enraf-Nonius CAD-4 κ-geometry diffractometer employing Mo K$\bar{\alpha}$ (0.70169 Å) radiation and a graphite monochromator or Cu K$\bar{\alpha}$ (1.5418Å) radiation with a β-filter for **1** and **2**, respectively. For procedures used in our laboratory, see ref 14. [b] By neutral buoyancy in bromoform–carbon tetrachloride. [c] Absorption corrections were performed with the Wehe–Busing–Levy ORABS program. [d] All calculations were performed on a DEC VAX 11/780 computer using SHELX-76.[16] [e] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Physical Measurements. ^{1}H and ^{31}P{^{1}H} (36.6 MHz) NMR spectra were recorded on a JEOL-90X or 360-MHz Bruker Fourier transform instrument in dichloromethane-*d*^{2}. The residual proton resonance of dichloromethane-*d*^{2} (δ 5.28 vs Me$_4$Si) was used as an internal calibrant for proton NMR spectra, and 85% H$_3$PO$_4$ (δ 0.00) was used as an external ^{31}P NMR spectral calibrant. Infrared spectra were recorded in the 4000–400-cm^{-1} range on an IBM IR/32 FTIR spectrometer using samples prepared as KBr pellets and calibrated with polystyrene film or as Nujol mulls with Perkin-Elmer 282B and 983G spectrophotometers. Electronic spectra were measured from 250 to 800 nm on a Perkin-Elmer Lambda 7 UV–visible spectrometer.

Collection and Reduction of X-ray Data. [ReCl$_2$(CN-*t*-Bu)$_3$(PMePh$_2$)$_2$]SbF$_6$ (1). A yellow crystal grown by diffusion of diethyl ether into a dichloromethane solution of **1** was used for the diffraction study. The crystal, a parallelepiped of approximate dimensions 0.38 mm × 0.20 mm × 0.20 mm and bounded by the faces {100}, {010}, and {001}, respectively, was sealed in a glass capillary. Study on the diffractometer revealed only triclinic ($\bar{1}$) symmetry consistent with space group $P1$ (C_1^1, No. 1) or $P\bar{1}$ (C_i^1, No. 2).[12] Open counter ω scans of several strong, low-angle reflections showed no structure ($\Delta\bar{\omega}_{1/2}$ = 0.22°), and the crystal quality was deemed acceptable. Data collection and reduction proceeded by methods standard in our laboratory,[13] the details of which are given in Table I.

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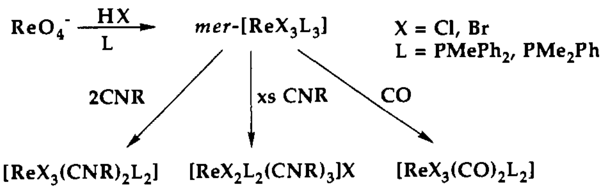
(12) *International Tables for X-ray Crystallography*; D. Reidel: Dordrecht, Holland, 1983; Vol. A, pp 102–105.

(13) Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379.

Scheme I



$[ReCl_2(O)(OEt)(PMePh_2)_2]$ (2). A red crystal grown from the slow evaporation of an ethanol solution of **2** was used for the diffraction study. The crystal was a hexagonal prism of approximate dimensions 0.25 mm × 0.30 mm × 0.29 mm and bound by the faces {101}, $(12\bar{1})$, $(\bar{1}\bar{2}1)$, $(1\bar{1}\bar{1})$, and $(\bar{1}11)$ and was mounted on a glass fiber under epoxy. Study on the diffractometer indicated a monoclinic crystal system with systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) consistent only with space group $P2_1/n$ (C_{2h}^5, No. 14, derived from $P2_1/c$)[14] and acceptable ω scans ($\Delta\bar{\omega}_{1/2} = 0.14°$). Details of the data collection and reduction are given in Table I.

Determination and Refinement of the Structures. $[ReCl_2(CN\text{-}t\text{-}Bu)_3(PMePh_2)_2]SbF_6$ (1). The structure was solved in space group $P\bar{1}$ by using standard Patterson and difference Fourier methods. Difficulties were encountered in the refinement of one of the *tert*-butyl groups (ligand no. 3) and the hexafluoroantimonate anion. Six positions for the methyl carbons could be resolved for the *tert*-butyl group. These were refined as two staggered sets of methyl groups with occupancy factors that refined to 0.58 and 0.42. Similarly, two sets of fluorine atoms could be clearly distinguished and refined with occupancies of 0.61 and 0.39. These disordered carbon (C32–C34A) and fluorine (F1–F6A) atoms were refined isotropically. All other non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms, with the exception of those attached to the disordered carbons, were placed at calculated geometries ($d_{C-H} = 0.95$ Å) and constrained to ride on the carbon atoms to which they were attached. Isotropic thermal parameters were set at $U = 0.10$ and 0.15 Å^2 for the methyl and phenyl hydrogens, respectively.

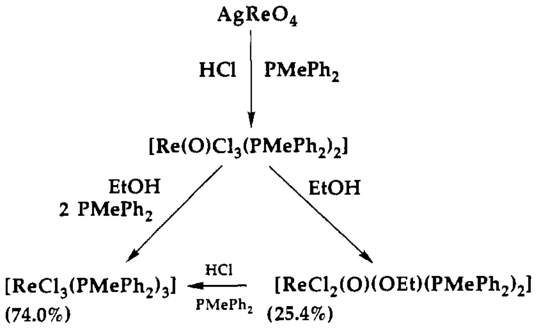
Calculations were performed by using SHELX-76,[15] with neutral atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms obtained from ref 16 and hydrogen atom scattering factors from ref 17. Full-matrix least-squares refinement minimized the function $\sum w(|F_o| - |F_c|)^2$, where weights were set at $w = 1.000[\sigma^2(F_o) + 0.000625(F_o)^2]^{-1}$. This refinement converged to the R factors reported in Table I. A final difference electron density map showed a peak of 1.1 e Å^{-3} located near the disordered *tert*-butyl group. Final non-hydrogen atom positional parameters appear in Table II, and listings of non-hydrogen atom thermal parameters, final hydrogen atom positional and thermal parameters, and observed and calculated structure factors are given in Tables S1–S3, respectively.

$[ReCl_2(O)(OEt)(PMePh_2)_2]$ (2). This structure was solved and refined in space group $P2_1/n$ by methods analogous to those reported for **1**. Anisotropic temperature factors were assigned to all non-hydrogen atoms. Hydrogen atom positions were calculated as for **1** and included in the refinement. Weights were set at $w = 1.00[\sigma^2(F_o) + 0.000625(F_o)^2]^{-1}$, and least-squares refinement converged to the R factors reported in Table I. The final difference Fourier showed a peak of 1.38 e Å^{-3} located 1.13 Å from the rhenium atom. Final non-hydrogen atom positional parameters are given in Table III, and listings of non-hydrogen atom thermal parameters, hydrogen positional and thermal parameters, and observed and calculated structure factors are given as supplementary material in Tables S4–S6, respectively.

Results and Discussion

Synthesis. Addition of excess alkyl isocyanides to neutral six-coordinate rhenium(III) phosphine halide complexes of general formula $[ReX_3(PR_3)_3]$ leads to extrusion of phosphine and halide from the coordination sphere to form the desired seven-coordinate $[ReX_2(CNR)_3(PR_3)_2]^+$ cations in good yields (Scheme I). Recrystallization of the hexafluoroantimonate salt of $[ReCl_2(CN\text{-}t\text{-}Bu)_3(PMePh_2)_2]^+$ (**1**) afforded crystals suitable for structural analysis by X-ray diffraction. Addition of 2 equiv of *tert*-butyl isocyanide to $[ReCl_3(PMePh_2)_3]$ displaced one phosphine ligand from rhenium, yielding $[ReCl_3(CN\text{-}t\text{-}Bu)_2(PMePh_2)_2]$. In the case of the less electron donating the sterically more crowded 2,6-dimethylphenyl isocyanide, the neutral $[ReX_3(CNR)_3(PR_3)]$ complex was obtained. Complex **2**, $[ReCl_2(O)(OEt)(PMePh_2)_2]$, was isolated in 25.4% yield as a red crystalline material that can be recognized as a side product of the well-known chemistry shown in Scheme II.[10,18]

Scheme II



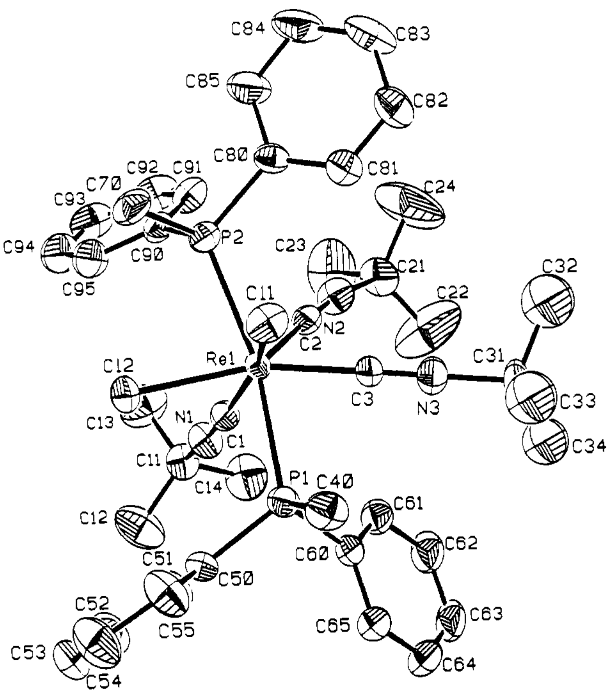


Figure 1. Structure of $[ReCl_2(CN\text{-}t\text{-}Bu)_3(PMePh_2)_2]SbF_6$ (1), showing the 40% probability thermal ellipsoids and atom-labeling scheme and omitting hydrogen atoms.

Crystal Structure of $[ReCl_2(CN\text{-}t\text{-}Bu)_3(PMePh_2)_2]SbF_6$ (1). As shown in Figure 1, the structure of **1** consists of a seven-coordinate rhenium atom with two diphenylmethylphosphine, three *tert*-butyl isocyanide, and two chlorine ligands comprising the coordination sphere. The complex adopts the capped trigonal prismatic geometry, with the Cl2 ligand occupying the capping position, two phosphorus (P1 and P2) and Cl1 and C1 atoms forming the quadrilateral face, and two isocyanide carbon atoms (C2 and C3) filling the unique edge.

Table IV lists the interatomic bond distances and angles for **1**. Comparison of the 21 L–Re–L bond angles with published tables[19,20] for idealized seven-coordinate geometries confirms the C_{2v} capped trigonal prism as the best reference polyhedron. The

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Table II. Final Non-Hydrogen Atom Positional Parameters for $[ReCl_2(CN\text{-}t\text{-}Bu)_3(PMePh_2)_2]SbF_6$ (**1**)[a]

atom	x	y	z
Re1	0.43646 (2)	0.37936 (2)	0.253680 (10)
Cl1	0.59076 (17)	0.43228 (13)	0.14643 (9)
Cl2	0.61309 (16)	0.40035 (12)	0.33828 (9)
P1	0.52565 (16)	0.19467 (11)	0.27399 (8)
P2	0.41998 (16)	0.57243 (11)	0.23385 (8)
N1	0.3174 (5)	0.2951 (4)	0.4229 (3)
N2	0.1426 (7)	0.4369 (5)	0.2439 (4)
N3	0.3233 (6)	0.2927 (4)	0.1181 (3)
C1	0.3626 (6)	0.3234 (5)	0.3600 (4)
C2	0.2543 (8)	0.4178 (5)	0.2469 (4)
C3	0.3619 (6)	0.3246 (4)	0.1669 (3)
C11	0.2555 (7)	0.2701 (5)	0.4985 (4)
C12	0.3459 (9)	0.1977 (8)	0.5573 (5)
C13	0.2234 (11)	0.3690 (7)	0.5225 (6)
C14	0.1329 (9)	0.2131 (8)	0.4892 (5)
C21	0.0012 (7)	0.4435 (6)	0.2366 (5)
C22	−0.0403 (10)	0.3444 (10)	0.2337 (12)
C23	−0.0504 (9)	0.4753 (12)	0.3097 (8)
C24	−0.0341 (12)	0.5304 (12)	0.1663 (10)
C31	0.2811 (7)	0.2518 (6)	0.0504 (4)
C32	0.208 (2)	0.3401 (17)	−0.0041 (12)
C33	0.3968 (19)	0.2324 (15)	0.0039 (11)
C34	0.2095 (20)	0.1559 (13)	0.0853 (10)
C32A	0.133 (3)	0.292 (2)	0.0373 (16)
C33A	0.301 (3)	0.133 (2)	0.0751 (17)
C34A	0.339 (2)	0.3111 (19)	−0.0195 (13)
C40	0.6176 (7)	0.1764 (5)	0.1901 (4)
C50	0.6343 (7)	0.1476 (4)	0.3560 (4)
C51	0.5851 (8)	0.1195 (6)	0.4320 (4)
C52	0.6660 (9)	0.0909 (7)	0.4959 (4)
C53	0.7964 (9)	0.0846 (6)	0.4850 (5)
C54	0.8444 (8)	0.1057 (8)	0.4139 (5)
C55	0.7621 (8)	0.1379 (7)	0.3466 (5)
C60	0.4074 (7)	0.0953 (4)	0.2869 (3)
C61	0.2799 (7)	0.1181 (5)	0.2908 (4)
C62	0.1903 (9)	0.0412 (6)	0.2959 (4)
C63	0.2344 (11)	−0.0586 (6)	0.2973 (5)
C64	0.3617 (11)	−0.0829 (6)	0.2955 (5)
C65	0.4486 (8)	−0.0072 (5)	0.2897 (4)
C70	0.5697 (7)	0.6373 (5)	0.2268 (4)
C80	0.3334 (6)	0.6462 (4)	0.1457 (3)
C81	0.3080 (7)	0.6006 (5)	0.0849 (4)
C82	0.2486 (8)	0.6565 (6)	0.0177 (4)
C83	0.2161 (9)	0.7622 (7)	0.0086 (4)
C84	0.2437 (10)	0.8088 (6)	0.0677 (5)
C85	0.3045 (9)	0.7499 (5)	0.1359 (4)
C90	0.3425 (7)	0.6116 (4)	0.3154 (3)
C91	0.2130 (7)	0.6465 (5)	0.3137 (4)
C92	0.1576 (9)	0.6712 (6)	0.3792 (5)
C93	0.2269 (10)	0.6623 (6)	0.4472 (5)
C94	0.3496 (11)	0.6270 (6)	0.4498 (4)
C95	0.4122 (8)	0.6008 (6)	0.3854 (4)
Sb1	0.13474 (6)	0.11838 (5)	0.80088 (4)
F1	−0.0368 (13)	0.1154 (12)	0.8271 (8)
F2	0.2993 (10)	0.1104 (8)	0.7674 (7)
F3	0.1630 (13)	0.1953 (11)	0.8722 (8)
F4	0.126 (2)	0.0571 (18)	0.7223 (13)
F5	0.1405 (14)	0.2509 (11)	0.7256 (9)
F6	0.133 (3)	0.001 (2)	0.8627 (16)
F1A	0.0756 (18)	0.1187 (15)	0.6923 (10)
F2A	0.178 (3)	0.057 (3)	0.9074 (20)
F3A	−0.0274 (16)	0.1732 (14)	0.7925 (10)
F4A	0.301 (3)	0.065 (3)	0.835 (2)
F5A	0.1082 (17)	−0.0290 (14)	0.8071 (11)
F6A	0.161 (3)	0.245 (2)	0.8203 (17)

[a] Numbers in parentheses are errors in the last significant digit(s). See Figure 1 for atom-labeling scheme.

Table III. Final Non-Hydrogen Atom Positional Parameters for $ReCl_2(O)(OEt)(PMePh_2)_2$ (**2**)[a]

atom	x	y	z
Re1	0.83795 (2)	0.79680 (2)	0.136300 (10)
Cl1	0.95879 (14)	0.12489 (14)	0.82393 (9)
Cl2	1.36741 (17)	0.27440 (19)	0.91688 (12)
P1	1.07367 (16)	0.31985 (12)	0.93548 (8)
P2	1.24391 (14)	0.08373 (12)	0.79006 (8)
O1	1.1384 (5)	0.3027 (4)	0.8081 (2)
O2	1.2031 (4)	0.0984 (3)	0.9295 (2)
C1	1.1527 (4)	0.4466 (3)	0.9465 (2)
C20	1.0808 (6)	0.2689 (5)	1.0166 (3)
C21	1.1360 (8)	0.3241 (7)	1.0732 (4)
C22	1.1400 (10)	0.2823 (9)	1.1344 (4)
C23	1.0826 (9)	0.1854 (8)	1.1389 (4)
C24	1.0281 (8)	0.1308 (7)	1.0835 (4)
C25	1.0274 (8)	0.1709 (6)	1.0225 (4)
C30	0.9093 (7)	0.3560 (5)	0.9015 (3)
C31	0.8175 (7)	0.3407 (6)	0.9352 (4)
C32	0.6949 (7)	0.3761 (7)	0.9088 (4)
C33	0.6626 (8)	0.4237 (7)	0.8492 (4)
C34	0.7523 (9)	0.4388 (7)	0.8151 (4)
C35	0.8735 (5)	0.4062 (4)	0.8393 (3)
C4	1.1717 (5)	−0.0453 (4)	0.7850 (3)
C50	1.1982 (6)	0.1319 (5)	0.7057 (3)
C51	1.0703 (7)	0.1494 (7)	0.6772 (4)
C52	1.0306 (9)	0.1832 (7)	0.6118 (4)
C53	1.1150 (10)	0.2021 (7)	0.5765 (4)
C54	1.2414 (10)	0.1880 (7)	0.6053 (4)
C55	1.2847 (8)	0.1528 (6)	0.6698 (4)
C60	1.4116 (6)	0.0594 (5)	0.8088 (3)
C61	1.4940 (6)	0.1440 (6)	0.8136 (4)
C62	1.6229 (6)	0.1250 (6)	0.8271 (4)
C63	1.6694 (7)	0.0247 (7)	0.8366 (4)
C64	1.5892 (7)	−0.0586 (6)	0.8338 (4)
C65	1.4606 (6)	−0.0415 (6)	0.8190 (3)
C7	1.2883 (8)	0.0623 (6)	0.9888 (3)
C8	1.3276 (8)	−0.0452 (6)	0.9819 (3)

[a] Numbers in parentheses are errors in the last significant digit(s). Atom labels are given in Figure 3.

small distortions from this geometry arise because, instead of seven identical ligands, there are three ligand classes, each with its own steric and electronic preferences. The Re atom lies 0.32 Å out of the best plane through the atoms comprising the quadrilaterial face (P1, P2, Cl1, and C1). These ligand atoms may be regarded as being "tipped" toward the sterically less demanding capping ligand. This effect has been previously noted in complexes of the type $[MX(dmpe)_2(CO)_2]$, where M = Nb, X = Cl, I or M = Ta, X = Me, in which two dmpe ligands occupy the quadrilateral face.[21] The structure of the chloride salt of **1** has also been determined,[22] and although severe unresolved disorder led to poor refinement, the structural parameters are in substantial agreement with those of **1**.

The combination of Re–CNR bond lengths, which range from 1.948 (8) to 2.013 (6) Å, and acute bond angles between C1 and C2 (C1–Re–C2 = 72.6 (2)°) and C2 and C3 (C2–Re–C3 = 72.1 (3)°) lead to close nonbonded contacts between C1 and C2 (2.341 (8) Å) and C2 and C3 (2.330 (9) Å). Close C···C nonbonded contacts along the unique edge of a capped trigonal prism have been previously observed in seven-coordinate molybdenum isocyanide complexes.[19,23] In such cases, extended Hückel calculations reveal the L···L overlap population between the two ligands on the unique edge of a capped trigonal prism to be 0.024 and between two adjacent ligands in the girdle of a pentagonal bipyramid to be 0.020.[24] It is believed that these small positive overlap populations may be indicative of attractive forces, referred to as incipient bonding interactions. Furthermore, reductive coupling of isocyanides has been observed from both the capped trigonal prismatic and pentagonal bipyramidal geometries for molybdenum isocyanide complexes.[2,25]

The refined site occupancy factors for the disordered methyl carbons (0.58/0.42) and the disordered fluorine atoms (0.61/0.39)

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Table IV. Interatomic Distances (Å) and Angles (deg) for [ReCl$_2$(CN-*t*-Bu)$_3$(PMePh$_2$)$_2$]SbF$_6$ (**1**)[a]

Coordination Sphere			
Bond Distances			
Re1–Cl1	2.473 (2)	Re1–Cl2	2.447 (2)
Re1–P1	2.510 (2)	Re1–P2	2.486 (2)
Re1–C1	2.006 (6)	Re1–C2	1.948 (8)
Re1–C3	2.013 (6)		
Bond Angles			
P1–Re1–P2	162.13 (6)	Cl1–Re1–Cl2	84.31 (6)
Cl1–Re1–C1	161.9 (2)	P1–Re1–C1	82.4 (2)
Cl2–Re1–C3	152.5 (2)	P2–Re1–Cl2	80.68 (5)
Cl2–Re1–C2	135.4 (2)	P2–Re1–Cl1	79.12 (5)
Cl1–Re1–C2	125.1 (2)	Cl2–Re1–C1	79.1 (2)
P1–Re1–C2	123.4 (2)	Cl1–Re1–C3	77.5 (2)
P2–Re1–C3	115.3 (2)	P2–Re1–C2	74.5 (2)
C1–Re1–C3	115.0 (3)	P1–Re1–C3	74.3 (2)
P2–Re1–C1	105.1 (2)	C1–Re1–C2	72.6 (2)
P1–Re1–Cl1	88.92 (5)	C2–Re1–C3	72.1 (3)
P1–Re1–Cl1	84.98 (5)		
(i) *tert*-Butyl Isocyanide Groups			
Bond Distances			
C1–N1	1.183 (8)	N1–C11	1.448 (8)
C2–N2	1.18 (1)	N2–C21	1.49 (1)
C3–N3	1.126 (9)	N3–C31	1.495 (9)
C11–C12	1.53 (1)		
mean C–C(methyl)	1.51 (2)	range C–C(methyl)	1.41–1.61
Bond Angles			
Re1–C1–N1	176.9 (5)	C1–N1–C11	174.5 (6)
Re1–C2–N2	177.3 (5)	C2–N2–C21	170.4 (7)
Re1–C3–N3	178.1 (6)	C3–N3–C31	175.9 (7)
mean N–C–C(methyl)	107.6 (8)	range N–C–C(methyl)	104–109
mean C(methyl)–C–C(methyl)	111.4 (10)	range C(methyl)–C–C(methyl)	102–121
(ii) Diphenylmethylphosphine Groups			
Bond Distances			
P1–C40	1.814 (7)	P2–C70	1.817 (7)
P1–C50	1.810 (6)	P2–C80	1.837 (6)
P1–C60	1.826 (7)	P2–C90	1.810 (7)
mean C(ring)–C(ring)	1.380 (10)	range C(ring)–C(ring)	1.32–1.43
Bond Angles			
Re1–P1–C40	111.4 (2)	C40–P1–C50	103.8 (3)
Re1–P1–C50	116.7 (2)	C40–P1–C60	104.1 (3)
Re1–P1–C60	115.4 (2)	C50–P1–C60	104.0 (3)
Re1–P2–C70	116.3 (2)	C70–P2–C80	102.4 (3)
Re1–P2–C80	116.4 (2)	C70–P2–C90	102.6 (3)
Re1–P2–C90	111.9 (2)	C80–P2–C90	105.7 (3)
mean C(ring)–C(ring)–P	120.7 (5)	range C(ring)–C(ring)–P	118.6–123.0
mean C(ring)–C(ring)–C(ring)	120.0 (7)	range C(ring)–C(ring)–C(ring)	118.3–123.0
Anion Geometry of Hexafluoroantimonate			
Bond Distances and Angles			
mean Sb–F	1.85 (2)	range Sb–F	1.67–2.01
mean *cis*-F–Sb–F	89.9 (9)	mean *trans*-F-Sb-F	168 (1)
min *cis*-F-Sb-F	56 (1)	min *trans*-F-Sb-F	155 (1)
max *cis*-F–Sb–F	120 (1)	max *trans*-F–Sb–F	177 (1)

[a] 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.

Table V. Interatomic Distances (Å) and Angles (deg) for ReCl$_2$(O)(OEt)(PMePh$_2$)$_2$ (**2**)[a]

Coordination Sphere			
Bond Distances			
Re1–O1	1.699 (5)	Re1–O2	1.892 (5)
Re1–Cl1	2.393 (8)	Re1–Cl2	2.42 (1)
Re1–P1	2.492 (7)	Re1–P2	2.503 (6)
Bond Angles			
P1–Re1–P2	178.17 (6)	O1–Re1–O2	174.6 (2)
Cl1–Re1–Cl2	173.10 (8)	O1–Re1–Cl1	96.3 (5)
O1–Re1–Cl2	89.7 (5)	O1–Re1–P1	87.6 (2)
O1–Re1–P2	92.5 (2)	O2–Re1–Cl1	89.1 (5)
O2–Re1–Cl2	84.9 (5)	O2–Re1–P1	92.0 (2)
O2–Re1–P2	88.2 (2)	Cl1–Re1–P1	89.0 (3)
Cl1–Re1–P2	89.2 (3)	Cl2–Re1–P1	87.8 (2)
Cl2–Re1–P2	94.0 (3)		
Ligand Geometry			
(i) Ethoxide Group			
Bond Distances and Angles			
O2–C7	1.43 (1)	C7–C8	1.46 (1)
O2–C7–C8	111.2 (5)	C7–O2–Re1	147.6 (4)
(ii) Diphenylmethylphosphine Groups			
Bond Distances			
P1–C1	1.820 (5)	P2–C4	1.818 (5)
P1–C20	1.809 (7)	P2–C50	1.820 (8)
P1–C30	1.82 (1)	P2–C60	1.812 (8)
mean C(ring)–C(ring)	1.38 (1)	range C(ring)–C(ring)	1.35–1.417
Bond Angles			
C1–P1–Re1	110.9 (3)	C4–P2–Re1	111.4 (3)
C20–P1–Re1	115.5 (3)	C50–P2–Re1	110.2 (3)
C30–P1–Re1	114.8 (4)	C60–P2–Re1	118.8 (4)
C1–P1–C20	107.3 (4)	C4–P2–C50	104.1 (4)
C1–P1–C30	102.6 (3)	C4–P2–C60	105.3 (3)
C20–P1–C30	104.7 (6)	C50–P2–C60	106.0 (7)
mean C(ring)–C(ring)–P	120.6 (6)	range C(ring)–C(ring)–P	117.5–122.9
mean C(ring)–C(ring)–C(ring)	119.9 (7)	range C(ring)–C(ring)–C(ring)	118.0–121.8

[a] 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.

are approximately equal, within experimental uncertainty, suggesting that their disorder may be linked. A unit cell packing diagram, shown in Figure 2, reveals that the SbF$_6$- anion of an adjacent unit cell occupies the space near the disordered *tert*-butyl group. This interaction may be the origin of the static (2-fold) disorder observed in this crystal structure.

^{1}H NMR Spectral Properties of [ReCl$_2$(CN-*t*-Bu)$_3$(PMePh$_2$)$_2$]SbF$_6$ (1) and Related Complexes. Both the singlet at −12.3 ppm in the ^{31}P NMR spectrum and the virtual triplet for the phosphine methyl protons at 2.28 ppm (J = 4.6 Hz) in the ^{1}H NMR spectrum confirm that the transoid distribution of phosphine ligands found in the solid-state structure is preserved in solution. In general seven-coordinate complexes are stereochemically nonrigid;[26] thus, the observation of a single broad resonance at 1.38 ppm (≈23 °C) for the *tert*-butyl protons is not surprising. The [ReCl$_2$(CN-*i*-Pr)$_3$(PMePh$_2$)$_2$]$^+$ and [ReCl$_2$(CN-*t*-Bu)$_3$(PMePh$_2$)$_2$]$^+$ cations exhibit virtual triplets for the phosphine methyl ^{1}H NMR resonances, also consistent with a transoid arrangement of phosphine ligands. By contrast, the ^{1}H NMR resonances of both *tert*-butyl isocyanide and phosphine methyl protons of [ReCl$_3$(CN-*t*-Bu)$_2$(PMePh$_2$)$_2$] are split into two singlets. The lower symmetry associated with these spectral features may indicate a cis distribution of phosphine and isocyanide ligands.

X-ray Crystal Structure and Spectroscopic Properties of [ReCl$_2$(O)(OEt)(PMePh$_2$)$_2$] (2). Figure 3 shows an ORTEP illustration of compound **2**. This six-coordinate octahedral Re(V) complex has two phosphine (P1 and P2), two chlorine (Cl1 and Cl2), an oxo (O1), and an ethoxy (O2) group as its ligand set in the all-trans geometry. Table V provides a list of the bond lengths and angles for compound **2**. The Re–P and Re–Cl distances fall within the range reported for similar rhenium(V) oxo complexes.[27-30] The Re–O1 distance of 1.699 (5) Å indicates extensive multiple bonding, best described as a triple bond.[27-29,31-33] Sim-

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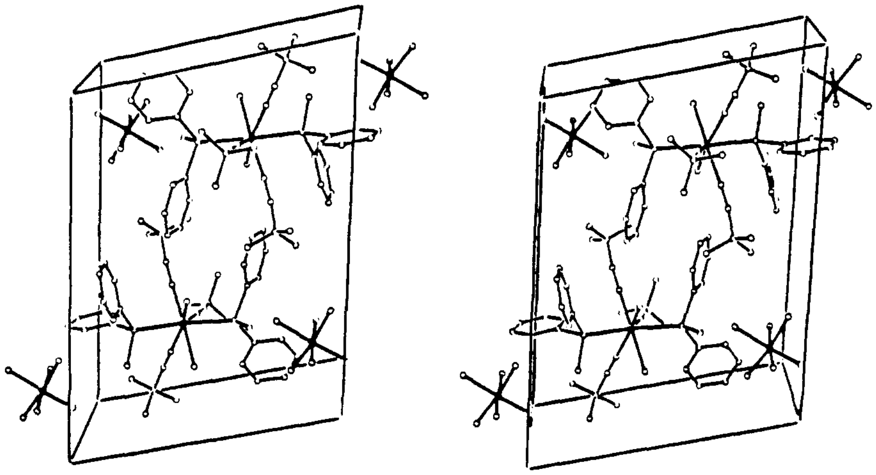

Figure 2. Stereoview of the triclinic unit cell of $[ReCl_2(CN\text{-}t\text{-}Bu)_3(PMePh_2)_2]SbF_6$ (**1**).

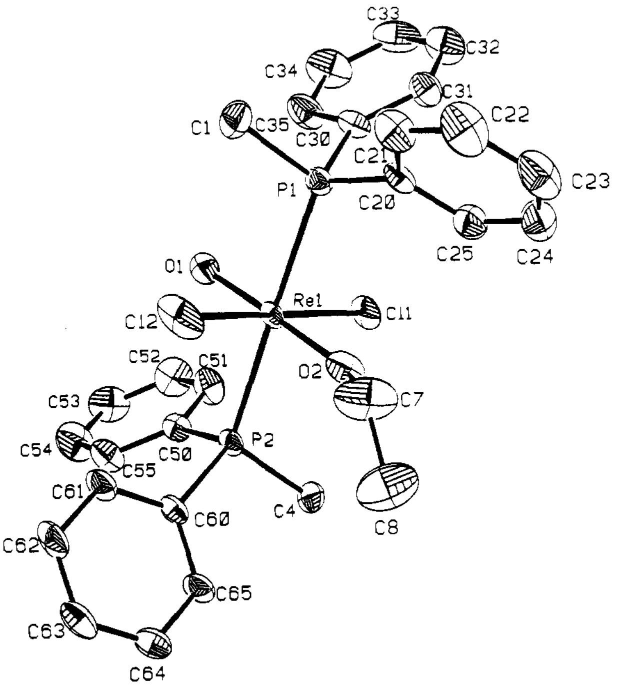

Figure 3. Structure of $ReCl_2(O)(OEt)(PMePh_2)_2$ (**2**), showing the 40% probability thermal ellipsoids and the atom-labeling scheme and omitting hydrogen atoms.

ilarly the Re–O2 ethoxide bond of 1.892 (5) Å implies significant double-bond character.[27,29,33]

A ^{31}P resonance at −23.7 ppm (s) and an unshifted proton NMR spectrum indicate that complex **2** is diamagnetic. The oxo ligand is a strong π donor, well-known to afford diamagnetic d^2 Re(V) complexes. The resulting Re≡O multiple bond gives rise to a strong peak at 954 cm^{-1} in the infrared spectrum; the band at 917 cm^{-1} is similarly characteristic of the bound alkoxide (δ_{OCH_2}) group.[10b] Only irreversible electrochemistry was observed in dichloromethane at a Pt-disk electrode.

Conclusion

In this paper, the last in our series describing mixed rhenium–phosphine–halide–isocyanide chemistry, we have presented a practical synthetic route to seven-coordinate complexes of rhenium(III) that were previously examined as candidates for extending the isocyanide reductive coupling methodology. As described elsewhere, attempts to couple the isocyanide ligands in $[Re(CNR)_6X]^{2+}$ complexes led only to the $[Re(CNR)_5X]^+$ cations.[7] Since phosphines increase the electron density at the Re(III) center with respect to the $[Re(CNR)_6X]^{2+}$ complexes studied earlier, $[ReCl_2(CN\text{-}t\text{-}Bu)_3(PMePh_2)_2]SbF_6$ and its analogues seemed better suited for coupling chemistry.[8,25,34] This possibility has been explored previously and found to afford (alkylamino)carbyne complexes, another intermediate in the generalized isocyanide reductive coupling mechanism.[3,4,9]

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Supplementary Material Available: For **1** and **2**, Tables S1, S2, S4, and S5, containing final non-hydrogen atom thermal parameters and hydrogen atom positional and thermal parameters (5 pages); Tables S3 and S6, listing structure factors (61 pages). Ordering information is given on any current masthead page.

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[34] Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 146.