iodobenzene by HPLC was difficult and we could not accurately quantify the products 2–5.

Synthesis, Structure, and Reactions of Rhenium Aminocarbyne Complexes Formed from [ReCl₂(CNR)₃(PMePh₂)₂]⁺ (R = *t*-Bu or Me) Cations under Reductive Coupling Conditions

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The seven-coordinate [ReCl₂(CNR)₃(PMePh₂)₂]⁺ cations, R = Me or *t*-C₄H₉, react with Zn(s) or Al(s) in refluxing THF containing ~1% H₂O to form (alkylamino)carbyne complexes [ReCl(CNH-*t*-Bu)(CN-*t*-Bu)₂(PMePh₂)₂](SbF₆) (1) and [ReCl(CNHMe)(CNMe)₂(PMePh₂)₂](SbF₆) (2). The structure of 1, determined by X-ray diffraction, contains a chloride ligand, trans pairs of phosphine and isocyanide ligands, and a Re≡CNHR carbyne unit characterized by a Re—C bond length of 1.82 (1) Å, a C—N distance of 1.30 (1) Å, a Re—C—N angle of 175.7 (9)°, and a C—N—C bend angle of 127.6 (9)°, consistent with considerable Re=C=NHR character. Infrared and ¹H, ³¹P, and ¹³C NMR spectroscopic data support the persistence of this structure for both 1 and 2 in solution. Multiple recrystallizations of 2 from THF led to the formation of [ReCl(CNMe)₃(PMePh₂)₂] (3) through formal loss of HSbF₆. Compound 3 was structurally characterized by X-ray diffraction. It contains two trans phosphine ligands and a meridionally disposed set of three isocyanide ligands, all of which have considerable Re=C=NR character, judging by C—N—C bend angles ranging from 144 (2) to 155 (2)°. Addition of excess zinc to 2 in acetonitrile leads to a similar electron-rich isonitrile complex, [Re(NCMe)(CNMe)₃(PMePh₂)₂](SbF₆) (5), in which an acetonitrile solvent molecule replaces the chloride ligand. The structure of 5 is similar to that of 3, but with less back-donation to the isocyanide ligands judging by the C—N—C angles of 160.4 (5)–178.4 (5)°, owing to the positive charge on the complex. Reaction of [ReBr₂(CNMe)₃(PMePh₂)₂]⁺ with Zn in refluxing aqueous THF gave only [ReBr(CNMe)₃(PMePh₂)₂] (4), which was not protonated. Spectral studies of 3–5 established that the solution structures were analogous to those found in the solid state for 3 and 5. These results are consistent with the following reaction pathway for reductive coupling of isocyanide (and analogous CO) complexes:

$$\{M(CNR)_2X\}^{n+} \xrightarrow[-X^-]{+2e^-} \{M(CNR)_2\}^{(n-1)+} \xrightarrow{H^+} \{M(CNHR)(CNR)\}^{n+} \xrightarrow{HX} \{M(RHNC\equiv CNHR)X\}^{n+}$$
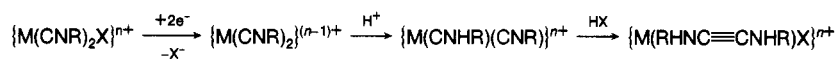
In the present instance, the {Re(CNHR)(CNR)}²⁺ unit is presumably too stable to form the reductively coupled {Re(RHNC≡CNHR)Cl}²⁺ moiety.

Introduction

Previously we studied reductive coupling of isocyanides in seven coordinate group 16 transition metal complexes to form coordinated bis(alkylamino)acetylenes.[1,2] Analogous reactions of group 15 metal carbonyls produced bis(trialkylsiloxy)-[3] and dihydroxyacetylene[4] complexes. Mechanistic studies of the carbonyl reductive coupling reaction revealed the formation of (trialkylsiloxy)carbyne intermediates that react further with coordinated CO to give the bis(trialkylsiloxy)acetylene complexes.[5]

In the interest of extending the isocyanide reductive coupling chemistry to other metal centers, the system [ReX₂(CNR)₃L₂]X (X = Cl, Br; L = PMePh₂, PMe₂Ph; R = Me, *i*-Pr, *t*-Bu, cyclohexyl, benzyl) was investigated. These rhenium(III) cations[6] appeared to be good candidates for reductive coupling. The prototypical compound [ReCl₂(CN-*t*-Bu)₃(PMePh₂)₂]SbF₆ is a seven coordinate d⁴ complex with capped trigonal prismatic geometry in the solid state and close nonbonded C···C contacts of 2.330 (9) and 2.341 (8) Å.[6] These properties are known to contribute to reductive coupling of isocyanides in several seven coordinate molybdenum(II) and tungsten(II) complexes.[1,2]

(1) (a) Lam, C. T.; Corfield, P. W. R.; Lippard, S. J. *J. Am. Chem. Soc.* 1977, 99, 617. (b) Giandomenico, C. M.; Lam, C. T.; Lippard, S. J. *J. Am. Chem. Soc.* 1982, 104, 1263. (c) Caravana, C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* 1982, 21, 1860. (d) Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* 1983, 105, 146.

(2) Warner, S.; Lippard, S. J. *Organometallics* 1986, 5, 1716.

(3) (a) Bianconi, P. A.; Williams, I. D.; Engeler, M. P.; Lippard, S. J. *J. Am. Chem. Soc.* 1986, 108, 311. (b) Bianconi, P. A.; Vrtis, R. N.; Rao, Ch. P.; Williams, I. D.; Engeler, M. P.; Lippard, S. J. *Organometallics* 1987, 6, 1968.

(4) Vrtis, R. N.; Rao, Ch. P.; Bott, S. G.; Lippard, S. J. *J. Am. Chem. Soc.* 1988, 110, 7564.

(5) Vrtis, R. N.; Rao, Ch. P.; Warner, S.; Lippard, S. J. *J. Am. Chem. Soc.* 1988, 110, 2669.

(6) Tulip, T. H.; Calabrese, J. C.; Warner, S.; Williams, I. D.; Lippard, S. J., in preparation. In this synthesis, [ReX₂(CNR)₃L₂] cations are formed by addition of excess RNC to *mer*-ReX₃L₃, where L = PMePh₂ and X = halide.

(7) (a) Chatt, J.; Rowe, G. A. *J. Chem. Soc.* 1962, 4019. (b) Rouschias, G. *Chem. Rev.* 1974, 74, 531.

Moreover, the metal center in the seven coordinate rhenium(III) mixed halo–isocyanide–phosphine complexes was expected to be more electron rich than that of the [M-(CNR)$_6$X]$^{2+}$ cations (M = Tc, Re, R = *t*-Bu, Me, X = Br; M = Tc, R = *t*-Bu, X = Cl) which, as discussed previously,[8] undergo reductive elimination to form [M(CNR)$_6$]$^+$ when subjected to reductive coupling reaction conditions. This difference was thought perhaps to favor reductive coupling of isocyanides over reduction at the metal center. As described in this paper, however, when [ReCl$_2$(CNR)$_3$-(PMePh$_2$)$_2$]$^+$ (R = *t*-Bu or Me) complexes are subjected to the reductive coupling conditions, aminocarbyne ligands are formed. The resulting [ReCl(CNHR)(CNR)$_2$-(PMePh$_2$)$_2$]$^+$ cations are important analogues of the [Ta-(COSiR$_3$)(CO)(dmpe)$_2$] carbyne complexes known to be intermediates in the reductive coupling of carbon monoxide.[5] Reported here are full details of the synthesis, structure, spectroscopic properties, and reactivity of these new rhenium(III) aminocarbyne complexes. Some preliminary results of part of this work have been communicated.[5]

Experimental Section

Materials and Methods. All [ReX$_2$(CNR)$_3$(PMePh$_2$)$_2$]X (R = *t*-Bu, Me, X = Cl or R = Me, X = Br) complexes were either supplied by T.H. Tulip or synthesized as described in ref 6 and 7. Zinc (Fisher), zinc chloride (Matheson, Coleman and Bell, MCB), aluminum (Alfa), and potassium hexafluoroantimonate (Strem) were purchased from commercial sources and used without further purification. Tetrahydrofuran was predried over potassium hydroxide and distilled from potassium benzophenone ketyl under nitrogen. Dichloromethane was predried over calcium chloride and distilled from calcium hydride under nitrogen. Acetonitrile was also distilled from calcium hydride under nitrogen. Diethyl ether and *n*-pentane were distilled from potassium benzophenone ketyl under nitrogen. Reactions and all manipulations were carried out by using standard Schlenk techniques or in a Vacuum Atmospheres drybox, all under nitrogen.

(i) Reaction of [ReX$_2$(CNR)$_3$(PMePh$_2$)$_2$]X with Zn To Form [ReX(CNHR)(CNR)$_2$(PMePh$_2$)$_2$]$^+$ Cations. (a) R = *t*-Bu, X = Cl (1). A mixture containing 3.700 g (3.93 mmol) of [ReCl$_2$(CN-*t*-Bu)$_3$(PMePh$_2$)$_2$]Cl, 0.847 g (12.96 mmol) of Zn, 0.106 g (0.78 mmol) of ZnCl$_2$, 10.79 g (39.26 mmol) of KSbF$_6$, 2.0 mL of H$_2$O, 250 mL of THF, and a magnetic stir bar was placed in a 500-mL three-necked flask under nitrogen. This mixture was stirred and heated at reflux for 6 h. The reaction, monitored by thin-layer chromatography on silica gel using 1:1 diethyl ether/dichloromethane as eluant, was judged to be complete when no starting material remained. The mixture initially turned green, and then the solution gradually became yellow-green over several hours. The major product was yellow, and there seemed to be only a very small amount of highly colored green-blue material, as judged by TLC. This green-blue material was not further purified or isolated. The mixture was filtered and the solvent volume reduced by bubbling N$_2$ through the solution. The remaining residue was extracted with ~10 mL of dichloromethane. This dichloromethane solution was layered with pentane at –30 °C, and the liquids were allowed to diffuse slowly over a period of several days. Yellow crystals of [ReCl(CNH-*t*-Bu)(CN-*t*-Bu)$_2$(PMePh$_2$)$_2$]SbF$_6$ (1) formed and were isolated by filtration followed by several pentane washes.

Complex 1 (3.083 g, 71%) was identified by its spectroscopic properties and by a single-crystal X-ray structure determination: ¹H NMR (CD$_2$Cl$_2$) δ 0.65 (s, 9 H, CNH(CH$_3$)$_3$), 1.14 (s, 18 H, CN(CH$_3$)$_3$), 2.25 (virtual t, $^2J_{PH} \simeq {}^4J_{PH} \simeq$ 3.5 Hz, 6 H, PCH$_3$), 4.52 (br, 1 H, CNH-*t*-Bu), 7.40–7.46 (m, 20 H, PPh); ³¹P{¹H} NMR (CD$_2$Cl$_2$) δ –11.0 (s); ¹³C{¹H} NMR (CD$_2$Cl$_2$) δ 16.58 (virtual t, $^1J_{PC} \simeq {}^3J_{PC} \simeq$ 16.2 Hz, PCH$_3$), 29.57 (s, CNHC(CH$_3$)$_3$), 29.94 (s, CNC(CH$_3$)$_3$), 58.32 (s, CNCMe$_3$ and CNHCMe$_3$), 128.74 (virtual t, $^3J_{PC} \simeq {}^5J_{PC} \simeq$ 6.3 Hz, P-*m*-Ph), 130.34 (s, P-*p*-Ph), 132.58

(virtual t, $^2J_{PC} \simeq {}^4J_{PC} \simeq$ 3.1 Hz, P-*o*-Ph), 136.03 (virtual t, $^1J_{PC} \simeq {}^3J_{PC} \simeq$ 23.9 Hz, P-ipso-Ph), 143.15 (t, $^2J_{PC}$ = 9.1 Hz, CNCMe$_3$), 227.54 (t, $^2J_{PC}$ = 11.3 Hz, CNHCMe$_3$); IR (KBr) 3279 (m), 3054 (w), 2983 (m), 2147 (s), 1588 (s), 1486 (w), 1461 (w), 1436 (s), 1402 (w), 1372 (m), 1315 (m), 1293 (m), 1234 (m), 1187 (s), 1096 (m), 1029 (w), 1000 (w), 885 (s), 757 (m), 747 (m), 698 (s), 684 (m), 660 (s), 579 (m), 538 (m), 509 (s), 483 (w), 450 (w), 417 (w) cm⁻¹. Anal. Calcd for C$_{41}$H$_{54}$N$_3$ReClP$_2$SbF$_6$: C, 44.44; H, 4.91; N, 3.79. Found: C, 43.27, 45.36; H, 4.98, 4.93; N, 3.88, 3.69.

(b) R = Me, X = Cl (2). This procedure was similar to that used for preparing 1. The starting mixture contained 0.904 g (1.10 mmol) of [ReCl$_2$(CNMe)$_3$(PMePh$_2$)$_2$]Cl, 0.247 g (3.78 mmol) of Zn, 0.037 g (0.27 mmol) of ZnCl$_2$, 3.045 g (11.08 mmol) of KSbF$_6$, 0.5 mL of H$_2$O, and 50 mL of THF in a 200-mL three-necked round-bottom flask. This solution was refluxed for 15 min and then stirred for 14 h at 26 °C. The solvent volume was reduced under a stream of nitrogen, and the residue was extracted with ~3 mL of dichloromethane. This solution was put into a drybox and loaded onto a silica gel (2 cm × 18 cm, 15% H$_2$O by weight) column. Elution with diethyl ether and/or 1:1 diethyl ether/dichloromethane gave a yellow product. The solvent was removed under reduced pressure, and the yellow solid was identified spectroscopically as [ReCl(CNHMe)(CNMe)$_2$(PMePh$_2$)$_2$]SbF$_6$ (2): yield, 0.660 g (61%); ¹H NMR (300 MHz, CD$_2$Cl$_2$) δ 2.24 (virtual t, $^2J_{PH} \simeq {}^4J_{PH} \simeq$ 4.0 Hz, 6 H, PCH$_3$), 2.34 (d, $^3J_{HH}$ = 3.8 Hz, 3 H, CNHCH$_3$), 3.14 (s, 6 H, CNCH$_3$), 4.59 (br, 1 H, CNHMe), 7.41–7.50 (m, 12 H, P-*m,p*-Ph), 7.58–7.65 (m, 8 H, P-*o*-Ph); ³¹P{¹H} NMR (CD$_2$Cl$_2$) δ –6.6 (s); ¹³C{¹H} NMR (CD$_2$Cl$_2$) δ 16.16 (virtual t, $^1J_{PC} \simeq {}^3J_{PC} \simeq$ 17.5 Hz, PCH$_3$), 28.11 (s, CNHCH$_3$), 29.75 (s, CNCH$_3$), 128.89 (virtual t, $^3J_{PC} \simeq {}^5J_{PC} \simeq$ 6.4 Hz, P-*m*-Ph), 130.49 (s, P-*p*-Ph), 132.30 (virtual t, $^2J_{PC} \simeq {}^4J_{PC} \simeq$ 7.5 Hz, P-*o*-Ph), 136.15 (virtual t, $^1J_{PC} \simeq {}^3J_{PC} \simeq$ 23.4 Hz, P-ipso-Ph), 145.89 (br, CNMe), 228.46 (t, $^2J_{PC}$ = 11.7 Hz, CNHMe); IR (KBr) 3326 (m, br), 2171 (s), 1594 (s), 1485 (m), 1435 (s), 1411 (m), 1314 (w), 1289 (w), 1098 (m), 889 (s), 748 (m), 734 (m), 696 (s), 660 (s), 505 (s), 485 (m), 451 (m), 421 (w) cm⁻¹. Anal. Calcd for C$_{32}$H$_{36}$ReClP$_2$N$_3$SbF$_6$: C, 39.14; H, 3.70. Found: C, 39.63; H, 4.19.

(ii) Reaction of [ReCl$_2$(CN-*t*-Bu)$_3$(PMePh$_2$)$_2$]SbF$_6$ with Aluminum To Form [ReCl(CNH-*t*-Bu)(CN-*t*-Bu)$_2$-(PMePh$_2$)$_2$]SbF$_6$ (1). This procedure was identical to that of i.a. except that Al was used in place of Zn and no ZnCl$_2$ (or AlCl$_3$) was used in the reaction. The starting mixture contained 0.269 g (0.235 mmol) of [ReCl$_2$(CN-*t*-Bu)$_3$(PMePh$_2$)$_2$]SbF$_6$, 0.037 g (1.37 mmol) of Al, 0.5 mL of H$_2$O, and 35 mL of THF and was stirred and heated at reflux for 31 h. 1 (0.19 g, 73%) was isolated and was identifed on the basis of its infrared, ¹H NMR, and ³¹P NMR spectroscopic properties.

(iii) Decomposition of [ReX(CNHMe)(CNMe)$_2$-(PMePh$_2$)$_2$]SbF$_6$ To Form [ReX(CNMe)$_3$(PMePh$_2$)$_2$]. (a) X = Cl (3). When [ReCl(CNHMe)(CNMe)$_2$(PMePh$_2$)$_2$]SbF$_6$ (2) was recrystallized from THF/pentane several times, the ³¹P NMR spectrum revealed a single new resonance and no ³¹P resonance attributable to starting complex 2. Spectroscopy and a single-crystal X-ray diffraction study showed that 2 had been converted into [ReCl(CNMe)$_3$(PMePh$_2$)$_2$] (3): yield, 95%; ¹H NMR (CD$_2$Cl$_2$) δ 2.12 (virtual t, $^2J_{PH} \simeq {}^4J_{PH} \simeq$ 2.9 Hz, 6 H, PCH$_3$), 2.77 (s, 3 H, CNCH$_3$ trans to chlorine), 2.88 (s, 6 H, trans CNCH$_3$), 7.25–7.33 (m, 12 H, P-*m,p*-Ph), 7.60–7.63 (m, 8 H, P-*o*-Ph); ³¹P{¹H} NMR (CD$_2$Cl$_2$) δ –8.1 (s); IR (KBr) 3055 (w), 2982 (w), 2916 (m), 2845 (m), 2075 (s, br), 1823 (s, br), 1587 (w), 1571 (w), 1483 (m), 1433 (s), 1401 (s), 1311 (w), 1281 (m), 1188 (w), 1093 (s), 997 (w), 878 (s), 747 (m), 724 (m), 698 (s), 682 (m), 509 (s), 483 (m), 444 (m), 417 (m) cm⁻¹. Anal. Calcd for C$_{32}$H$_{35}$N$_3$ReClP$_2$: C, 51.57; H, 4.73; N, 5.64. Found: C, 51.22; H, 5.00; N, 5.32.

(b) X = Br (4). The procedure was identical with that for i.b. except that the chromatography step was followed by recrystallization via vapor diffusion of pentane into a dichloromethane solution at –20 °C. The starting mixture contained 0.456 g (0.48 mmol) of [ReBr$_2$(CNMe)$_3$(PMePh$_2$)$_2$]Br, 0.104 g (1.59 mmol) of Zn, 0.016 g (0.12 mmol) of ZnCl$_2$, 0.643 g (2.34 mmol) of KSbF$_6$, 0.5 mL of H$_2$O, and 40 mL of THF. Recrystallization as above led to the isolation of 0.286 g (75%) of [ReBr(CNMe)$_3$(PMePh$_2$)$_2$] (4): ¹H NMR (CD$_2$Cl$_2$) δ 2.20 (virtual t, $^2J_{PH} \simeq {}^4J_{PH} \simeq$ 3.0 Hz, 6 H, PCH$_3$), 2.72 (s, 3 H, CNCH$_3$ trans to bromine), 2.92 (s, 6 H, trans CNCH$_3$), 7.26–7.33 (m, 12 H, P-*m,p*-Ph), 7.59–7.63 (m, 8 H, P-*o*-Ph); ³¹P{¹H} NMR (CD$_2$Cl$_2$) δ –4.0 (s); IR (KBr) 3050 (w),

(8) Farr, J. P.; Abrams, M. J.; Costello, C. E.; Davison, A.; Lippard, S. J.; Jones, A. G. *Organometallics* **1985**, *4*, 139.

2981 (w), 2918 (m), 2865 (w), 2064 (s, br), 1851 (s, br), 1584 (w), 1567 (w), 1481 (m), 1433 (m), 1401 (s), 1093 (m), 884 (s), 750 (m), 727 (m), 700 (s), 660 (m), 510 (m), 488 (m), 451 (m), 420 (m) cm^{-1}. Anal. Calcd for $C_{32}H_{35}N_3ReBrP_2$: C, 48.67; H, 4.47; N, 5.32. Found: C, 47.86; H, 4.54; N, 5.33.

(iv) Reaction of 2 with Zn in Acetonitrile To Form [Re-(NCMe)(CNMe)$_3$(PMePh$_2$)$_2$]SbF$_6$ (5). A mixture containing 0.0994 g (0.10 mmol) of 2, 0.0331 g (0.51 mmol) of Zn, and 20 mL of acetonitrile was stirred at 23 °C for 22 h under nitrogen in a drybox. The acetonitrile was removed under reduced pressure, and the residue was extracted with dichloromethane. ^{31}P NMR showed complete conversion of 2 to 5. Recrystallization was accomplished by layering pentane onto a dichloromethane solution of 5 at -30 °C and allowing the liquid to mix for several days to afford yellow crystals of [Re(NCMe)(CNMe)$_3$(PMePh$_2$)$_2$]SbF$_6$ (5): yield, 0.0732 g (74%); ^{1}H NMR (CD$_2$Cl$_2$) δ 1.62 (s, 3 H, NCCH_3), 2.17 (br, 6 H, PCH_3), 3.05 (s, 3 H, CNCH_3 trans to acetonitrile), 3.15 (s, 6 H, trans CNCH_3), 7.37–7.44 (m, 20 H, PPh); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ -1.1 (s); IR (KBr) 3072 (w), 2979 (w), 2934 (m), 2877 (w), 2235 (w), 2158 (w, sh), 2082 (s, br), 1962 (s, br), 1587 (w), 1570 (w), 1481 (m), 1438 (s), 1414 (s), 1330 (w), 1313 (w), 1288 (m), 1098 (s), 1077 (w), 888 (s), 760 (s), 731 (s), 702 (s), 661 (s), 518 (m), 498 (w), 457 (w), 429 (m) cm^{-1}. Anal. Calcd for $C_{34}H_{38}N_4ReP_2SbF_6$: C, 41.39; H, 3.88; N, 5.68. Found: C, 40.97; H, 3.93; N, 5.62.

Physical Measurements. ^{31}P{^{1}H} NMR spectra of dichloromethane-d_2 solutions were recorded on a JEOL-90X Fourier transform instrument at 36.6 MHz using 85% H$_3$PO$_4$ as external standard. ^{1}H NMR spectra were also recorded on a JEOL-90X or, in the case of complex 2, on a Varian XL-300 Fourier transform instrument, with the residual proton resonances of dichloromethane-d_2 (δ 5.28 vs TMS) used as internal calibrant. Carbon-13 spectra of dichloromethane-d_2 solutions were recorded on a Varian XL-300 spectrometer at 75.43 MHz with the carbon-13 resonance of dichloromethane-d_2 (δ 53.8 vs TMS) used as the internal calibrant. Infrared spectra were recorded in the 4000–400 cm^{-1} range on an IBM IR/32 FTIR spectrometer or a Beckman Acculab 10 grating spectrometer using samples prepared as KBr pellets and calibrated with polystyrene film. X-ray diffraction measurements were made by using an Enraf-Nonius CAD-4F diffractometer with Mo Kα (λ = 0.7107 Å) radiation.

Collection and Reduction of X-ray Data. [ReCl(CNH-t-Bu)(CN-t-Bu)$_2$(PMePh$_2$)$_2$]SbF$_6$ (1). A lemon yellow crystal grown by the slow diffusion of a layer of pentane into a dichloromethane solution of 1 at -30 °C was used for the diffraction study. The crystal, a parallelepiped of approximate dimensions 0.45 mm × 0.13 mm × 0.08 mm, was mounted on a glass fiber under epoxy. The crystals were not exposed to air during mounting for more than 10 s. Once under the epoxy, it proved impossible to determine accurately the indices of the faces. Study on the diffractometer indicated a monoclinic crystal sytem and systematic absences ($h0l, l \neq 2n$; $0k0, k \neq 2n$) consistent only with the space group $P2_1/c$ (C_{2h}^5, No. 14).[9] A check for higher symmetry space groups using the program TRACER[10] confirmed the choice of the monoclinic crystal system. Open counter ω-scans of several strong low-angle reflections showed no structure ($\Delta\bar{\omega}_{1/2}$ = 0.17°), and the crystal quality was deemed acceptable. Data collection and reduction proceeded by methods standard in our laboratory,[11] the details of which are given in Table I.

[ReCl(CNMe)$_3$(PMePh$_2$)$_2$]·CH$_2$Cl$_2$ (3·CH$_2$Cl$_2$). A yellow crystal grown by diffusion of pentane into a dichloromethane solution of 3 at -40 °C was used for the diffraction study. The crystal was a parallelpiped of approximate dimensions 0.50 mm × 0.50 mm × 0.20 mm. This crystal was mounted, avoiding contact with air, on a glass fiber under epoxy. Once again, it proved impossible to determine accurately the indices of the faces of the crystal. Study on the diffractometer revealed only triclinic (1̄) symmetry consistent with space group $P1$ (C_1^1, No. 1) or $P\bar{1}$ (C_i^1, No. 2)[12] and acceptable ω-scans ($\Delta\bar{\omega}_{1/2}$ = 0.23°). A search

(9) *International Tables for X-ray Crystallography*; D. Reidel: Dordrecht, Holland, 1983; Vol. A, pp 176–181.

(10) Lawton, S. L. TRACER II, *A FORTRAN Lattice Transformation-Cell Reduction Program*; Mobil Oil Corp.: Paulsboro, NJ, 1967.

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

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

Table I. Experimental Details of the X-ray Diffraction Studies of [ReCl(CNH-t-Bu)(CN-t-Bu)$_2$(PMePh$_2$)$_2$]SbF$_6$ (1), [ReCl(CNMe)$_3$(PMePh$_2$)$_2$]•CH$_2$Cl$_2$ (3•CH$_2$Cl$_2$), and [Re(NCMe)(CNMe)$_3$(PMePh$_2$)$_2$]SbF$_6$ (5) at 22–23 °C

formula	ReSbClP$_2$F$_6$N$_3$-C$_{41}$H$_{54}$	ReCl$_3$P$_2$N$_3$-C$_{33}$H$_{37}$	ReSbP$_2$F$_6$N$_4$-C$_{34}$H$_{38}$
fw, g mol^{-1}	1108.2	830.2	986.6
a, Å	15.378 (3)	9.349 (2)	12.974 (3)
b, Å	18.731 (3)	13.205 (2)	22.768 (6)
c, Å	16.225 (3)	8.627 (1)	10.952 (2)
α, deg		93.18 (1)	94.19 (2)
β, deg	95.94 (1)	114.72 (1)	110.21 (2)
γ, deg		108.60 (1)	105.13 (2)
V, Å^3	4648.4	894.50	2882.76
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P1$	$P\bar{1}$
Z	4	1	3
ρ_{obsd}, g cm^{-3}	1.58 (1)^a	1.55 (1)^a	1.69 (1)^b
ρ_{calcd}, g cm^{-3}	1.583	1.541	1.705
linear abs coeff,^{c} cm^{-1}	31.8	35.6	37.8
scan range, deg	$3 \leq 2\theta \leq 50$	$3 \leq 2\theta \leq 56$	$3 \leq 2\theta \leq 52$
no. of unique data colld	8173	5081	11 912
no. of rflns with $F > 4\sigma(F)$	4228	4946	8109
$R_1{}^d$	0.042	0.045	0.032
$R_2{}^d$	0.045	0.057	0.042
no. of observns	4228	4946	8109
no. of parameters	467	318	629

^{a} By neutral buoyancy in carbon tetrachaloride–heptane. ^{b} By neutral buoyancy in bromoform–carbon tetrachloride. ^{c} Absorption corrections were performed empirically on the basis of psi scans of suitable reflections with χ close to 90°. $^d R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

using TRACER[10] failed to reveal any higher symmetry crystal system. Details of the data collection and reduction are given in Table I.

[Re(NCMe)(CNMe)$_3$(PMePh$_2$)$_2$]SbF$_6$ (5). A yellow-orange crystal grown by the slow diffusion of pentane into a dichloromethane solution of 5 at -30 °C was used for the diffraction study. The crystal, an irregular hexagonal prism, was bounded by the faces {010}, separated by 0.19 mm, (11̄0), (1̄10) which were 0.35 mm apart, and {101}, each set separated by 0.28 mm, and was mounted on a glass fiber under epoxy coming in contact with air for less than 10 s. Study on the diffractometer revealed triclinic (1̄) symmetry consistent with $P1$ (C_1^1, No. 1) or $P\bar{1}$ (C_i^1, No. 1)[12] and acceptable ω-scans ($\Delta\bar{\omega}_{1/2}$ = 0.17°). Details of the data collection and reduction are given in Table I.

Determination and Refinement of the Structures. [ReCl(CNH-t-Bu)(CN-t-Bu)$_2$(PMePh$_2$)$_2$]SbF$_6$ (1). The structure was solved by standard Patterson and difference Fourier methods. Anisotropic temperature factors were assigned to all non-hydrogen atoms. Hydrogen atoms of *tert*-butyl groups were placed at calculated positions [d(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 methyl groups, the phosphine phenyl groups, and the amine hydrogen were handled in an analogous manner and refined with separate, but common, isotropic thermal parameters. Calculations were performed by using SHELX-76,[13] with neutral atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms obtained from ref 14 and hydrogen atom scattering factors from ref 15. Least-squares refinement minimized the function $\sum w(|F_o|$

(13) Sheldrick, G. M. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University: Delft, Holland, 1978; pp 34–42. We thank G. M. Sheldrick for kindly providing a version of SHELX-76 extended by D. Rabinowich and K. Reich to handle 400 atoms and 500 parameters.

(14) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(15) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *4*, 3175.

$- |F_c|)^2$ where weights were set at $w = 1.2267[\sigma^2(F_o) + 0.000\,625(F_o)^2]^{-1}$. This refinement converged to the R factors reported in Table I. A final difference electron density map showed a peak of 1.43 e Å^{-3} at 1.02 Å from the rhenium atom and all the other peaks less than 0.85 e Å^{-3}. Final non-hydrogen atom positional and thermal parameters are given in Tables S1 and S2 (supplementary material), respectively. Final hydrogen atom positional and thermal parameters are given in Table S3, and a listing of observed and calculated structure factors are reported in Table S4.

[ReCl(CNMe)$_3$(PMePh$_2$)$_2$]·CH$_2$Cl$_2$ (3·CH$_2$Cl$_2$). The volume of the unit cell (894.50 Å^3) for this compound is such that it could accommodate only one molecule. Spectroscopy had previously identified this complex as **3**. We therefore reasoned that, barring chlorine/isocyanide disorder, the molecule could not have an inversion center and space group *P*1 was our initial choice for solving the structure. A rhenium atom was fixed at 0,0,0 and the R value dropped to ≈37%. Difference Fourier maps revealed the rest of the non-hydrogen atoms. The rhenium and phosphorus atoms, as well as the carbon atoms on the phosphine ligands, were refined with anisotropic thermal parameters. The isocyanide groups were assigned isotropic thermal parameters. A dichloromethane molecule, disordered over two sites, was located in the cell. The site-occupancy factor was refined, leading to the values 0.66/0.34 for this twofold site disorder of the dichloromethane. The hydrogen atoms were handled in a manner analogous to those reported for **1**. A final difference electron density map showed two large (4.8 e Å^{-3}) peaks on either side of, and only ≈0.85 away from, the rhenium atom. These peaks may be due to a poor empirical absorption correction, made using psi scans measured after the crystal had decayed (a 33% decay in the intensity of standard reflections occurred during data collection, for which all data were normalized) and therefore probably not accurate for all the data. This problem, coupled with the dichloromethane disorder, limits the precision of this structure determination. We are confident of the overall structure of **3**, however, which is consistent with IR, ^{1}H NMR, and ^{31}P NMR spectroscopic data.

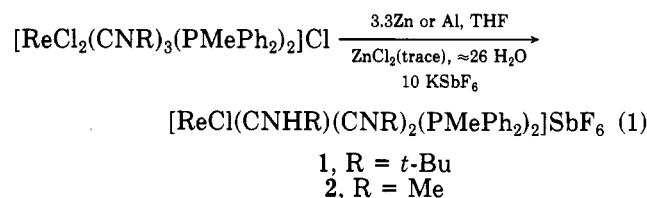Attempts to solve the structure in *P*Ī, assuming a chlorine for isocyanide disorder, led to $R_1 \approx 0.077$ and poor geometry. Moreover, the chlorine atom shows reasonable isotropic, and in later refinements, anisotropic thermal parameters consistent with full occupancy in space group *P*1. No large residual electron density was found near the isocyanide group trans to chlorine. If there were a chlorine-for-isocyanide disorder, some electron density in the region of the isocyanide group would be expected. Although several of the atomic positional parameters (Table S5) seem to be related to one another by a center of inversion, as expected if the space group were *P*Ī, there are atoms which break this center of inversion, e.g., C10 and C40. Space group *P*1 was therefore retained, weights were set at $w = 1.3888\ [\sigma^2(F_o) + 0.000\,625(F_o)^2]^{-1}$, and least-squares refinement converged to the R factors reported in Table I. Refinement of the enantiomorph led to higher R values, thus confirming the initial assignment. Final non-hydrogen atom positional and thermal parameters and a listing of observed and calculated structure factors are given in Tables S5, S6, and S7, respectively. Hydrogen atom positional and thermal parameters are given in Table S8.

[Re(NCMe)(CNMe)$_3$(PMePh$_2$)$_2$]SbF$_6$ (5). This structure was solved in space group *P*Ī by methods analogous to those reported above for **1**. Carbon and nitrogen atoms were distinguished by initially assigning carbon scattering factors to all such atoms and then observing their refined isotropic thermal parameters. The lower values corresponded to nitrogen atoms, the identities of which were confirmed by the reverse procedure of assigning nitrogen scattering factors to all such atoms and then once again inspecting the refined isotropic thermal parameters. Anisotropic thermal parameters were assigned to all non-hydrogen atoms, and hydrogen atoms were placed at calculated positions and refined with isotropic thermal parameters, as described above for **1**. There are three molecules in the unit cell, two of which (molecule 1) are related to one another by a center of inversion. The other molecule (molecule 2) sits on an inversion center at 0,0,0. Molecule 2 shows a fourfold site disorder of acetonitrile over the four positions occupied by three methyl isocyanides and one acetonitrile. Least-squares refinement converged to the R factors reported in
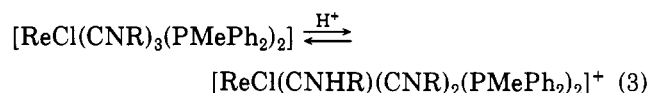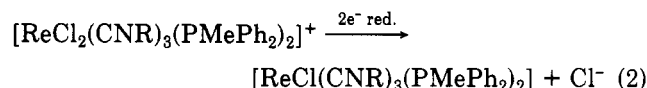
Table I, where weights were set at $w = 1.7275[\sigma^2(F_o) + 0.000\,625(F_o)^2]^{-1}$. The final difference electron density map showed a peak of 1.35 e Å^{-3} located at 0.92 Å from the rhenium atom of molecule 1. Final non-hydrogen atom positional and thermal parameters are given in Tables S9 and S10, respectively. Final hydrogen atom positional and thermal parameters and a listing of observed and calculated structure factors are given in Tables S11 and S12, respectively.

Results and Discussion

Aminocarbyne Complex Chemistry. Although the [ReCl$_2$(CNR)$_3$(PMePh$_2$)$_2$]Cl complexes (R = Me, *t*-Bu) seem to be well suited for reductive coupling of isocyanides, when these compounds were subjected to reductive coupling reaction conditions, no coordinated (*N*,*N*'-dialkyldiamino)acetylenes were formed. Rather, as shown in eq 1, reduction and protonation of the isocyanide ligand occurred to form an aminocarbyne ligand.

$$[ReCl_2(CNR)_3(PMePh_2)_2]Cl \xrightarrow[\substack{ZnCl_2(trace),\ \approx 26\ H_2O \\ 10\ KSbF_6}]{3.3Zn\ or\ Al,\ THF}$$

$$[ReCl(CNHR)(CNR)_2(PMePh_2)_2]SbF_6 \quad (1)$$

$$\textbf{1}, R = \textit{t}\text{-Bu}$$
$$\textbf{2}, R = Me$$

A likely mechanism for this reaction is two-electron reduction of the seven-coordinate Re(III) complex either by Zn(s) or, at longer reaction time, Al(s) to form an octahedral Re(I) intermediate, [ReCl(CNR)$_3$(PMePh$_2$)$_2$], followed by rapid protonation to give the aminocarbyne complexes **1** and **2** (eq 2 and 3). The proton source is

$$[ReCl_2(CNR)_3(PMePh_2)_2]^+ \xrightarrow{2e^-\ red.}$$

$$[ReCl(CNR)_3(PMePh_2)_2] + Cl^- \quad (2)$$

$$[ReCl(CNR)_3(PMePh_2)_2] \xrightleftharpoons{H^+}$$

$$[ReCl(CNHR)(CNR)_2(PMePh_2)_2]^+ \quad (3)$$

water, made slightly acidic owing to coordination to Zn(II) or Al(III). Reaction 2 is analogous to the two-electron reduction of [Tc(CNR)$_6$Cl]$^{2+}$ cations under reductive coupling conditions to form [Tc(CNR)$_6$]$^+$.[8] These latter complexes are apparently less electron rich than [ReCl(CNR)$_3$(PMePh$_2$)$_2$] and do not protonate to form aminocarbynes.

Aminocarbyne complexes have previously been formed by protonation of isocyanides coordinated to electron-rich group 16 metal complexes (eq 4).[16,17] There are also two
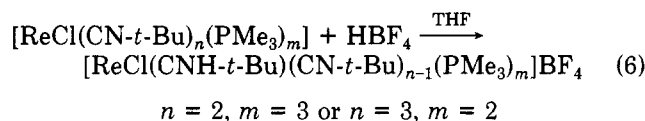
$$\textit{trans-}[M(CNR)_2(dppe)_2] + HX \rightarrow$$

$$[M(CNHR)(CNR)(dppe)_2]X \quad (4)$$
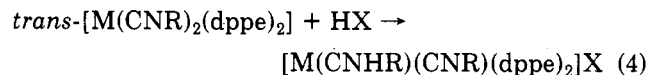
$$M = Mo, X = BF_4;\ M = W,\ X = BF_4,\ HSO_4,\ FSO_3$$

$$R = Me,\ \textit{t}\text{-Bu}$$

(16) (a) Chatt, J.; Pombeiro, A. J. L.; Muir, K. W.; Richards, R. L.; Royston, G. H. D.; Walker, R. *J. Chem. Soc., Chem. Commun.* **1975**, 708. (b) Pombeiro, A. J. L.; Richards, R. L. *Transition Met. Chem. (Weinheim, Ger.)* **1980**, *5*, 55. (c) Chatt, J.; Pombeiro, A. J. L.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1980**, 492; **1979**, 1585. (d) Carvalho, M. F. N. N.; Pombeiro, A. J. L.; Schubert, U.; Orama, O.; Pickett, C. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1985**, 2079. (e) Carvalho, M. F. N. N.; Laranjeira, C. M. C.; Nobre, A. T. Z.; Pombeiro, A. J. L.; Richards, R. L. *Transition Met. Chem. (Weinheim, Ger.)* **1985**, *10*, 427.
(17) Singleton, E.; Oosthivizen, H. E. *Adv. Organomet. Chem.* **1984**, *22*, 292.

examples where Re(I) isocyanide complexes undergo N-protonation to form aminocarbynes (eq 5 and 6).[18,19] In

$$\text{trans-[ReCl(CNR)(dppe)}_2] + \text{HBF}_4 \xrightarrow{C_6H_6}$$
$$\text{trans-[ReCl(CNHR)(dppe)}_2]\text{BF}_4 \quad (5)$$

$$R = Me, \ t\text{-Bu}$$

$$[\text{ReCl(CN-}t\text{-Bu)}_n(\text{PMe}_3)_m] + \text{HBF}_4 \xrightarrow{\text{THF}}$$
$$[\text{ReCl(CNH-}t\text{-Bu)(CN-}t\text{-Bu)}_{n-1}(\text{PMe}_3)_m]\text{BF}_4 \quad (6)$$

$$n = 2, \ m = 3 \ \text{or} \ n = 3, \ m = 2$$
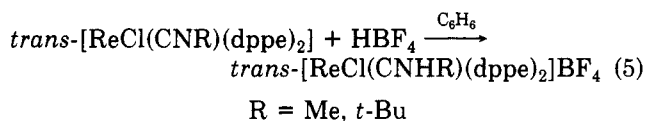
all of the above cases, N-protonation of terminal isocyanide ligands is effected in electron-rich complexes by addition of relatively strong acids. This reaction is favored by electron back-donation from the metal into ligand π-acceptor orbitals which, in turn, creates a basic nitrogen center that can be protonated.
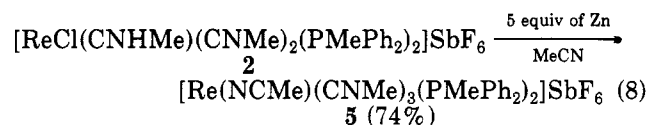
Several CNR₂ (dialkylamino)carbyne groups are known,[20] and bridging (alkylamino)carbyne units have been formed by the action of acid on dinuclear iron,[21] tungsten,[22] platinum,[23] and, more recently, nickel[24] isocyanide complexes. In these examples, the isocyanide ligand is formally reduced and the CN bond order diminished. In one case, the CN bond of the aminocarbyne cleaves to afford the corresponding primary ammonium salt.[16b]

When (ReCl(CNHMe)(CNMe)₂(PMePh₂)₂]SbF₆ (2) is recrystallized from THF several times, deprotonation of the carbyne unit occurs to produce a terminal isocyanide ligand in 95% yield, as shown in eq 7. This reaction is

$$[\text{ReCl(CNHMe)(CNMe)}_2(\text{PMePh}_2)_2]\text{SbF}_6 \xrightarrow[-\text{HSbF}_6]{\text{THF}}$$
$$[\text{ReCl(CNMe)}_3(\text{PMePh}_2)_2] \quad (7)$$
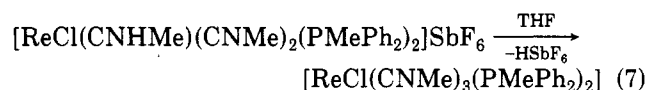
the reverse of eq 3, demonstrating that the protonation/deprotonation chemistry is an equilibrium process. Attempts to prepare the bromide analogue of 2 from [ReBr₂(CNMe)₃(PMePh₂)₂]SbF₆ by the chemistry of eq 1 led only to [ReBr(CNMe)₃(PMePh₂)₂] (4). As discussed above, the chlorotris(isocyanide)bis(phosphine)rhenium(I) complexes are likely precursors in the formation of the aminocarbynes (eq 2). A possible reason for why the bromide analogue of 2 does not form is discussed below with its spectroscopic properties.

The aminocarbyne complex 2 also decomposes to form a terminal isocyanide in the presence of excess Zn in acetonitrile solution (eq 8). In this case, chloride is re-

$$[\text{ReCl(CNHMe)(CNMe)}_2(\text{PMePh}_2)_2]\text{SbF}_6 \xrightarrow[\text{MeCN}]{5 \text{ equiv of Zn}}$$
$$\mathbf{2}$$
$$[\text{Re(NCMe)(CNMe)}_3(\text{PMePh}_2)_2]\text{SbF}_6 \quad (8)$$
$$\mathbf{5} \ (74\%)$$

(18) (a) Pombeiro, A. J. L.; Carvalho, M. F. N. N.; Hitchcock, P. B.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1981**, 1629. (b) Pombeiro, A. J. L.; Hughes, D. L.; Pickett, C. J.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 246.

(19) Chiu, K. W.; Howard, C. G.; Wilkinson, G.; Galas, A. M.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 803.

(20) See, e.g.: (a) Chatt, J.; Pombeiro, A. J. L.; Richards, R. L. *J. Organomet. Chem.* **1980**, *184*, 357. (b) Fischer, E. O.; Huttner, G.; Klein, W.; Frank, A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 760. (c) Fischer, E. O.; Kreiss, G.; Kreissl, F.; Kalbfus, W.; Winkler, E. *J. Organomet. Chem.* **1974**, *65*, C53.

(21) (a) Willis, S.; Manning, A. R.; Stephens, F. S. *J. Chem. Soc., Dalton Trans.* **1981**, 322. (b) Willis, S.; Manning, A. R. *J. Chem. Res., Synop.* **1978**, 390.

(22) Pombeiro, A. J. L.; Richards, R. L. *Transition Met. Chem. (Weinheim, Ger.)* **1980**, *5*, 281.

(23) Grundy, K. R.; Robertson, K. N. *Organometallics* **1983**, *2*, 1736.

(24) DeLaet, D. L.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1986**, *5*, 1807.
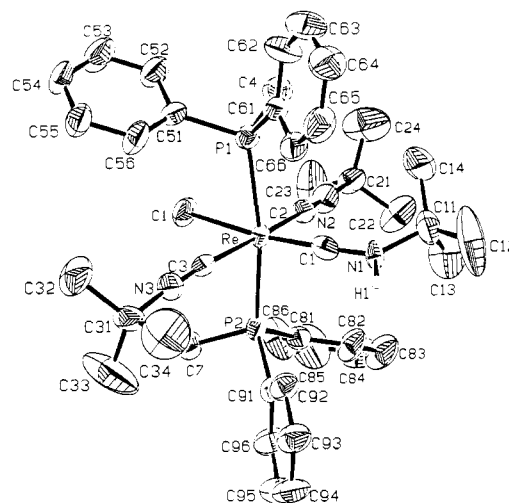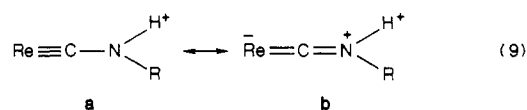

Figure 1. Structure of the [ReCl(CNH-*t*-Bu)(CN-*t*-Bu)₂-(PMePh₂)₂]⁺ (1) cation, showing the 40% probability thermal ellipsoids and atom labeling scheme and omitting hydrogen atoms.

placed by solvent, yielding cationic Re(I) nitrile complex **5**. Possibly zinc promotes this reaction by first reducing H⁺ to hydrogen. The resulting Zn²⁺ cation could bind chloride ion, assisting in its displacement from the rhenium coordination sphere by acetonitrile solvent.

Structure of [ReCl(CNHMe)(CNMe)₂(PMePh₂)₂]-SbF₆ (1). As illustrated in Figure 1, the coordination sphere of rhenium is comprised of two trans phosphines, two trans *tert*-butyl isocyanides, and trans chloride and (*tert*-butylamino)carbyne ligands in pseudooctahedral geometry. Table II reports selected interatomic bond distances and angles. The Re–C(carbyne) bond length of 1.82(1) Å is close to that reported for [ReCl(CNHMe)-(dppe)₂]BF₄,[18a] 1.80 (3) Å. This distance is somewhat longer than the 1.721–1.751 Å range predicted from the sum of the triple-bond radii of C≡C, 0.605 Å,[25] and Re≡Re as derived from [Re₂Cl₄(PEt₃)₄] (1.116 Å)[26] or [Re₂Cl₄(MeSCH₂CH₂SMe)₂] (1.146 Å).[27] Such an elongation is expected on the basis of contribution of canonical form **b** (eq 9) to the structure.

$$\text{Re}\equiv\text{C}-\text{N}\begin{array}{c}{}^{H^+}\\\\{}_{R}\end{array} \longleftrightarrow \overline{\text{Re}}=\text{C}=\overset{+}{\text{N}}\begin{array}{c}{}^{H^+}\\\\{}_{R}\end{array} \quad (9)$$
$$\mathbf{a} \qquad\qquad\qquad \mathbf{b}$$

The C(carbyne)–N–C(*tert*-butyl) angle of 127.6 (9)° and the C(carbyne)–N distance of 1.30 (1) Å are consistent with sp² hybridization at nitrogen. The Re–C(carbyne)–N and Cl–Re–C units are approximately linear, being 175.7 (9)° and 171.4 (3)°, respectively. The Re–C(isocyanide) bond distances of 2.05 (1) and 2.07 (1) Å are slightly longer than the Re–C(isocyanide) bond lengths (1.948 (8), 2.006 (6), 2.013 (6) Å) in the Re(III) seven-coordinate starting complexes.[6] This difference reflects the electron-accepting ability of the aminocarbyne ligand, which diminishes back-bonding to the RNC ligands relative to the RNC ligands in the seven-coordinate Re(III) starting material. The average Re–P bond length of 2.441 (3) Å and the Re–Cl bond length (2.497 (3) Å) have comparable values in the only other structurally characterized rhenium aminocarbyne complex, [ReCl(CNHMe)(dppe)₂],[18a] Re–P(av) = 2.457 (7) Å and Re–Cl = 2.484 (6) Å.

(25) Stoicheff, B. P. *Tetrahedron* **1962**, *17*, 135.

(26) Cotton, F. A.; Frenz, B. A.; Ebner, J. R.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1974**, 4.

(27) Bennett, M. J.; Cotton, F. A.; Walton, R. A. *Proc. R. Soc. London, Ser. A* **1968**, *303*, 175.

Table II. Selected Interatomic Distances (Å) and Angles (deg) for [ReCl(CNH-t-Bu)(CN-t-Bu)₂(PMePh₂)₂]SbF₆ (1)ᵃ

Coordination Sphere

Bond Distances

Re-Cl	2.497 (3)	Re-C1	1.82 (1)
Re-P1	2.453 (3)	Re-C2	2.05 (1)
Re-P2	2.428 (3)	Re-C3	2.07 (1)

Bond Angles

P1-Re-P2	168.8 (1)	P1-Re-Cl	81.7 (1)
P1-Re-C1	95.5 (3)	P1-Re-C2	90.3 (3)
P1-Re-C3	92.4 (3)	P2-Re-Cl	87.17 (9)
P2-Re-C1	95.6 (3)	P2-Re-C2	89.6 (3)
P2-Re-C3	86.2 (3)	Cl-Re-C1	171.4 (3)
Cl-Re-C2	81.2 (3)	Cl-Re-C3	90.6 (3)
C1-Re-C2	90.7 (4)	Cl-Re-C3	97.6 (4)
C2-Re-C3	170.9 (4)		

Ligand Geometry

(i) tert-(Butylamino)carbyne

Bond Distances

N1-C1	1.30 (1)	N1-C11	1.48 (1)
C11-C12	1.50 (1)	C11-C13	1.54 (1)
C11-C14	1.52 (1)		

Bond Angles

Re-C1-N1	175.7 (9)	C1-N1-C11	127.6 (9)
C1-N1-H1	116.2 (6)	C11-N1-H1	116.2 (5)
N1-C11-C12	104.4 (6)	N1-C11-C13	109.2 (7)
N1-C11-C14	109.8 (6)	C12-C11-C13	109.7 (6)
C12-C11-C14	111.9 (7)	C13-C11-C14	111.6 (6)

(ii) tert-Butyl Isocyanide Groups

Bond Distances

N2-C2	1.14 (1)	N2-C21	1.48 (1)
N3-C3	1.14 (1)	N3-C31	1.48 (1)
mean C-C(methyl)	1.53 (1)	range C-C(methyl)	1.51-1.57

Bond Angles

Re-C2-N2	178.1 (9)	Re-C3-N3	174.7 (9)
C2-N2-C21	178 (1)	C3-N3-C31	176 (1)
mean N-C-C(methyl)	107.0 (6)	range N-C-C(methyl)	104.8-109.0
mean C(methyl)-C-C(methyl)	111.8 (6)	range C(methyl)-C-C(methyl)	110.4-112.9

(iii) Diphenylmethylphosphine Groups

Bond Distances

P1-C4	1.835 (7)	P2-C7	1.831 (8)
P1-C51	1.83 (1)	P2-C81	1.83 (1)
P1-C61	1.82 (1)	P2-C91	1.83 (1)
mean C(ring)-C(ring)	1.38 (2)	range C(ring)-C(ring)	1.33-1.41

Bond Angles

Re-P1-C4	112.5 (2)	Re-P2-C7	113.5 (3)
Re-P1-C51	114.5 (4)	Re-P2-C81	116.6 (4)
Re-P1-C61	119.5 (4)	Re-P2-C91	102.0 (5)
C4-P1-C51	103.5 (4)	C7-P2-C81	103.7 (4)
C4-P1-C61	103.1 (4)	C7-P2-C91	100.0 (4)
C51-P1-C61	101.8 (5)	C81-P2-C91	102.1 (5)
mean C(ring)-C(ring)-P	120.6 (8)	range C(ring)-C(ring)-P	118.1-122.6
mean C(ring)-C(ring)-C(ring)	120 (1)	range C(ring)-C(ring)-C(ring)	118-123

Anion Geometry

Hexafluoroantimonate

Bond Distances and Angles

mean Sb-F	1.805 (10)	range Sb-F	1.79-1.83
mean cis F-Sb-F	90.0 (6)	mean trans F-Sb-F	177.4 (6)
min cis F-Sb-F	86.8 (6)	min trans F-Sb-F	176.6 (7)
max cis F-Sb-F	94.3 (6)	max trans F-Sb-F	178.8 (5)

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. See Figure 1 for atom-labeling scheme.
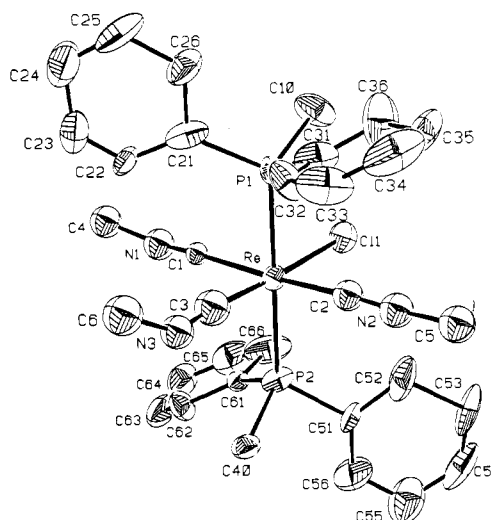

Figure 2. Structure of [ReCl(CNMe)₃(PMePh₂)₂] (3), showing the 40% probability thermal ellipsoids and atom labeling scheme, omitting hydrogen atoms.

Structure of [ReCl(CNMe)₃(PMePh₂)₂] (3). The ligand set for this six-coordinate Re(I) octahedral species is comprised of three methyl isocyanides in meridional positions, two trans phosphines and a chloride. An ORTEP view of this neutral complex is shown in Figure 2, and interatomic bond distances and angles are reported in Table III. The isocyanide ligand trans to chloride has a short Re-C bond length (Re-C3 = 1.85(2) Å), while the other two Re-C bond lengths (Re-C1 = 2.08 (2) Å and Re-C2 = 1.97 (3) Å) are longer. Although crystal decomposition limited the precision of the structure determination, the two longer bond lengths fall in the range for known Re(I) isocyanide complexes.[19] The most interesting feature of 3 is the bend angle at nitrogen for the three isocyanide ligands, 155 (2)° (C1-N1-C4), 158 (2)° (C2—N2-C5), and 144 (2)° (C3-N3-C6). This result implies substantial back-bonding to these isocyanides from the rhenium(I) center, with significant contribution from canonical form b shown in eq 10. The fact that the iso-

$$\overset{-}{Re}-C{\equiv}\overset{+}{N}-R \longleftrightarrow Re{=}C{=}\overset{..}{N}\diagdown_{R} \qquad (10)$$

a   b
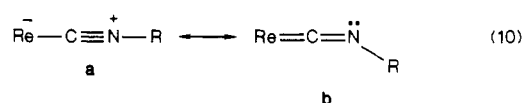
cyanide ligand trans to chloride has the shortest Re-C bond length and smallest C-N-C bend angle implies that it has the greatest contribution from canonical form b (eq 10) among the three isocyanides. This result is expected since this RNC group has no competition for metal π-electron density from its trans chloride ligand compared to the other, mutually trans isocyanide ligands. Similar bend angles in isocyanides coordinated to electron-rich Re(I) and Mo(I) centers have been reported before. trans-[ReCl(CN-t-Bu)₂(PMe₃)₃][19] has bend angles of 175 (1)° and 159 (1)°; trans-[ReCl(CN-t-Bu)₂(PMe₃)₃][19] has bend angles of 175 (5)°, 155 (5)°, and 141 (6)°, with the isocyanide trans to chloride having the smallest bend angle. The bend angle in trans-[Mo(CNMe)₂(dppe)₂] is 156 (1)°.[16a] In all three of these examples, the isocyanide ligands can be N-protonated to form aminocarbynes. As illustrated in eq 10b, the bend angles reflect the Lewis basicity of the isocyanide nitrogen atoms, thus accounting for their reactivity with electrophiles.

The P1-Re-P2, C1-Re-C2, and C3-Re-C11 angles (Table III) are approximately linear, and there are only small deviations from octahedral geometry. The average

Table III. Selected Interatomic Distances (Å) and Angles (deg) for [ReCl(CNMe)$_3$(PMePh$_2$)$_2$]•CH$_2$Cl$_2$ (3•CH$_2$Cl$_2$)^a

Coordination Sphere			
Bond Distances			
Re–P1	2.39 (1)	Re–P2	2.41 (1)
Re–Cl1	2.47 (2)	Re–C1	2.08 (2)
Re–C2	1.97 (3)	Re–C3	1.85 (2)

Bond Angles			
P1–Re–P2	178.7 (2)	P1–Re–Cl1	89.1 (4)
P2–Re–Cl1	89.9 (4)	C1–Re–P1	89.1 (9)
C1–Re–P2	90.1 (9)	C2–Re–P1	86 (1)
C2–Re–P2	95 (1)	C3–Re–P1	90.4 (5)
C3–Re–P2	90.6 (5)	C1–Re–Cl1	90 (1)
C2–Re–Cl1	93 (1)	C3–Re–Cl1	175.3 (3)
C2–Re–C1	174.1 (7)	C3–Re–C1	85 (1)
C3–Re–C2	92 (1)		

Ligand Geometry

(i) Methyl Isocyanide Groups

Bond Distances			
C1–N1	1.24 (3)	N1–C4	1.39 (3)
C2–N2	1.09 (3)	N2–C5	1.61 (3)
C3–N3	1.18 (2)	N3–C6	1.54 (2)

Bond Angles			
N1–C1–Re	170 (1)	C1–N1–C4	155 (2)
N2–C2–Re	165 (2)	C2–N2–C5	158 (2)
N3–C3–Re	171 (1)	C3–N3–C6	144 (2)

(ii) Diphenylmethylphosphine Groups

Bond Distances			
P1–C10	1.89 (1)	P2–C40	1.83 (2)
P1–C21	1.84 (3)	P2–C51	1.85 (3)
P1–C31	1.92 (3)	P2–C61	1.79 (2)
mean C(ring)–C(ring)	1.40 (4)	range C(ring)–C(ring)	1.18–1.63

Bond Angles			
C10–P1–Re	113.5 (6)	C40–P2–Re	113.3 (7)
C21–P1–Re	117 (1)	C51–P2–Re	123 (1)
C31–P1–Re	115 (1)	C61–P2–Re	115 (1)
C21–P1–C10	108 (2)	C40–P2–C51	97 (1)
C10–P1–C31	101 (1)	C61–P2–C40	106 (1)
C21–P1–C31	101 (1)	C61–P2–C51	100 (1)
mean C(ring)–C(ring)–P	119 (2)	range C(ring)–C(ring)–P	109–131
mean C(ring–C(ring)–C(ring)	120 (30)	range C(ring)–C(ring)–C(ring)	101–132

(iii) Disordered Dichloromethane Solvent

Bond Distances and Angles			
mean C(solvent)–Cl	1.91 (6)	range C(solvent)–Cl	1.71–2.13
Cl2–C71–Cl3	77 (3)	Cl4–C81–Cl5	99 (3)

^{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. See Figure 2 for atom-labeling scheme.

Re–P bond distance of 2.40 (1) Å compares well with other Re(I)–P determinations.[28-31] The Re–Cl bond length of 2.47 (2) Å is slightly shorter than other Re(I)–Cl values,[16d,19] but this result is statistically insignificant owing to the large estimated standard deviation.

Structure of [Re(NCMe)(CNMe)$_3$(PMePh$_2$)$_2$]SbF$_6$ (5). This octahedral Re(I) cation has three meridional isocyanides, two trans phosphines, and an acetonitrile. One molecule sits on an inversion center (molecule 2) and the
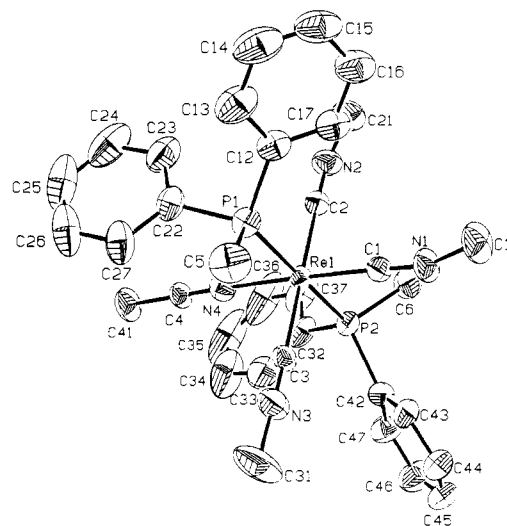
(28) Rossi, R.; Duatti, A.; Magon, L.; Marchi, A.; Medici, A.; Fogagnolo, M.; Casellato, U.; Graziani, R. *Transition Met. Chem. (Weinheim, Ger.)* **1985**, *10*, 413.

(29) Rossi, R.; Duatti, A.; Magon, L.; Casellato, U.; Graziani, R.; Toniolo, L. *Inorg. Chim. Acta* **1983**, *75*, 77.

(30) Graziani, R.; Toniolo, L.; Casellato, U.; Rossi, R.; Magon, L. *Inorg. Chim. Acta* **1981**, *52*, 119.

(31) Forsellini, E.; Casellato, U.; Graziani, R.; Toniolo, L.; Rossi, R.; Magon, L. *Inorg. Chim. Acta* **1982**, *61*, 255.

Figure 3. Structure of the [Re(NCMe)(CNMe)$_3$(PMePh$_2$)$_2$]$^+$ (5) cation, molecule 1, showing the 40% probability thermal ellipsoids and atom labeling scheme and omitting hydrogen atoms.
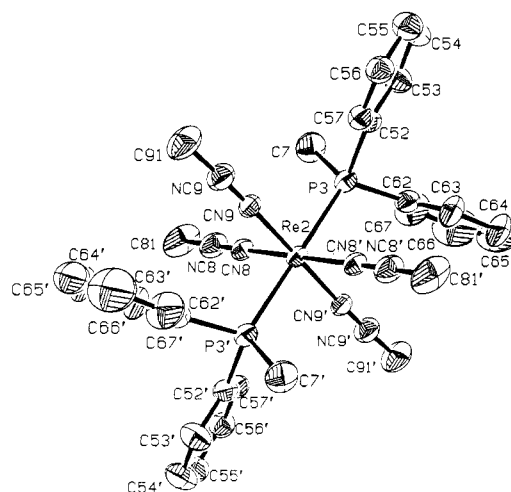

Figure 4. ORTEP view of the [Re(NCMe)(CNMe)$_3$(PMePh$_2$)$_2$]$^+$ (5) cation, molecule 2, showing the 40% probability thermal ellipsoids and atom labeling scheme and omitting hydrogen atoms.

other in a general position in the unit cell. ORTEP views of molecules 1 and 2 are given in Figures 3 and 4, respectively. Table IV lists interatomic bond distances and angles. Inspection of the L–Re–L angles indicates that there is very little distortion from octahedral geometry. The Re1–C bond lengths fall in the range expected for Re(I)–C(isocyanide) bonds.[19] The isocyanide bend angles of C1–N1–C11, 160.4 (5)° (trans to nitrile), C2–N2–C21, 170.6 (4)°, and C3–N3–C31, 178.4 (5)°, also compare well with literature determinations.[19] The bend angle of the isocyanide trans to the acetonitrile ligand is smallest, a result analogous to that found for isocyanide trans to chloride in [ReCl(CNMe)$_3$(PMePh$_2$)$_2$] (3) previously discussed. This isocyanide ligand in 5 is not bent quite as much, nor is the Re1–C1 bond length as short, as the bent isocyanides in 3. This difference is due to the cationic nature of 5, which renders the metal less electron rich and therefore less able to release electron density to the isocyanides than in 3 (eq 10). The Re1–N bond length of 2.086 (4) Å falls in the 2.052 (9)–2.156 (10) Å range found for *cis*-[Re(NCMe)$_4$(CO)$_2$]$^+$.[32] The Re2–C and Re2–N

(32) Cotton, F. A.; Daniels, L. M.; Schmulbach, C. D. *Inorg. Chim. Acta* **1983**, *75*, 163.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for [Re(NCMe)(CNMe)₃(PMePh₂)₂]SbF₆ (5)ᵃ

| Coordination Sphere | | | | (iii) Disordered Methyl Isocyanide/Acetonitrile Groups of Molecule 2 | | |

Bond Distances				Bond Distances and Angles		
Re1-P1	2.396 (1)	Re2-P3	2.397 (1)	CN8-NC8	1.142 (7)	CN9-NC9	1.154 (5)
Re1-P2	2.385 (1)	Re2-P3'	2.397 (1)	NC8-C81	1.434 (7)	NC9-C91	1.433 (4)
Re1-C1	1.981 (4)	Re2-CN8	2.032 (5)	Re2-CN8-NC8	179.2 (4)	Re2-CN9-NC9	178.1 (4)
Re1-C2	2.007 (5)	Re2-CN8'	2.032 (5)	CN8-NC8-C81	176.2 (4)	CN9-NC9-C91	174.3 (5)
Re1-C3	2.047 (6)	Re2-CN9	2.032 (4)				
Re1-N4	2.086 (4)	Re2-CN9'	2.032 (4)				

(iii) Diphenylmethylphosphine Groups

Bond Angles				Bond Distances		
P1-Re1-P2	175.22 (5)	P3-Re2-P3'	180.0	P1-C5	1.862 (2)	P2-C6	1.840 (2)
P1-Re1-C1	92.6 (1)	P3-Re2-CN8	90.2 (1)	P1-C12	1.833 (6)	P2-C32	1.829 (5)
P1-Re1-C2	89.9 (1)	P3-Re2-CN9	91.9 (1)	P1-C22	1.822 (6)	P2-C42	1.836 (6)
P1-Re1-C3	90.9 (1)	P3-Re2-CN8'	89.8 (1)	P3-C7	1.847 (2)	P3-C82	1.841 (6)
P1-Re1-N4	87.4 (2)	P3-Re2-CN9'	88.1 (1)	P3-C92	1.822 (5)		
P2-Re1-C1	90.7 (1)	P3'-Re2-CN8	89.8 (1)	mean C(ring)-C(ring)	1.375 (11)	range C(ring)-C(ring)	1.31-1.42
P2-Re1-C2	86.7 (1)	P3'-Re2-CN9	88.1 (1)				
P2-Re1-C3	92.4 (1)	P3'-Re2-CN8'	90.2 (1)	Bond Angles			
P2-Re1-N4	89.4 (1)	P3'-Re2-CN9'	91.9 (1)	Re1-P1-C5	116.4 (1)	Re1-P1-C12	120.9 (2)
C1-Re1-C2	90.0 (2)	CN8-Re2-CN8'	180.0	Re1-P1-C22	112.2 (1)	Re1-P2-C6	113.4 (1)
C1-Re1-C3	90.7 (2)	CN8-Re2-CN9	90.2 (2)	Re1-P2-C32	113.0 (2)	Re1-P2-C42	121.6 (2)
C1-Re1-N4	178.1 (2)	CN8'-Re2-CN9	89.8 (2)	Re2-P3-C7	114.9 (1)	Re2-P3-C82	121.0 (2)
C2-Re1-C3	178.9 (2)	CN8-Re2-CN9'	89.8 (2)	Re2-P3-C92	112.9 (2)	C5-P1-C12	100.8 (2)
C2-Re1-N4	91.9 (2)	CN8'-Re2-CN9'	90.2 (2)	C5-P1-C22	102.7 (2)	C12-P1-C22	101.4 (3)
C3-Re1-N4	87.4 (2)	CN9-Re2-CN9'	180.0	C6-P2-C32	105.1 (2)	C6-P2-C42	99.0 (2)
				C32-P2-C42	102.6 (2)	C7-P3-C82	101.5 (2)
				C7-P3-C92	103.3 (2)	C82-P3-C92	100.9 (3)

Ligand Geometry

(i) Methyl Isocyanide Groups

				mean C(ring)-C(ring)-P	120.8 (5)	range C(ring)-C(ring)-P	116.7-124.9
Bond Distances				mean C(ring)-C(ring)-C(ring)	120.0 (8)	range C(ring)-C(ring)-C(ring)	116.7-122.4
C1-N1	1.155 (6)	N1-C11	1.417 (5)				
C2-N2	1.159 (7)	N2-C21	1.431 (6)				
C3-N3	1.134 (7)	N3-C31	1.442 (7)				

Anion Geometry

Hexafluoroantimonate

Bond Angles				Bond Distances and Angles		
Re1-C1-N1	178.3 (4)	C1-N1-C11	160.4 (5)	mean Sb-F	1.815 (6)	range Sb-F	1.784-1.844
Re1-C2-N2	177.2 (4)	C2-N2-C21	170.6 (4)	mean cis F-Sb-F	90.0 (4)	mean trans F-Sb-F	179.6 (10)
Re1-C3-N3	178.8 (5)	C3-N3-C31	178.4 (5)	min cis F-Sb-F	85.4 (3)	min trans F-Sb-F	178.6 (3)
				max cis F-Sb-F	95.0 (3)	max trans F-Sb-F	180 (1)

(ii) Acetonitrile Group

Bond Distances and Angles			
N4-C4	1.136 (5)	C4-C41	1.472 (5)
Re1-N4-C4	177.7 (4)	N4-C4-C41	179.8 (5)

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. See Figures 3 and 4 for atom-labeling schemes.

bond length and angle parameters fall between those expected for an isocyanide and a nitrile ligand, as expected considering the disorder present among isocyanide and nitrile. The average Re(1,2)-P bond distance (2.394 (1) Å) compares well with previously determined Re(I)-P bond lengths.[28-31]

Spectroscopic Properties of Aminocarbyne Complexes 1 and 2. The aminocarbyne moiety in 1 and 2 generates absorptions at ~3330 cm⁻¹, due to the N-H stretch, and at ~1590 cm⁻¹, assigned to C≐N stretch of the carbyne unit. This high value for a C-N stretching vibration implies significant weighting of canonical form **b** in eq 9. An absorption arising from the pair of trans isocyanide ligands occurs at 2147 cm⁻¹ for 1 and at 2171 cm⁻¹ for 2.

All of the spectroscopic data for 1 and 2 are consistent with the crystal structure determination of 1. The single ³¹P resonance for 1 and 2 is consistent with a trans disposition of phosphine ligands. The chemical shifts of these ³¹P resonances (see Experimental Section) are 1.3 and 4.5 ppm downfield for 1 and 2, respectively, compared to their seven-coordinate Re(III) precursors, a further indication of the ability of an aminocarbyne ligand to remove electron density from the Re. Proton resonances for the *tert*-butyl group in 1 and the methyl groups in 2 move upfield slightly with respect to their values in the seven-coordinate Re(III) precursors, and the resonances due to the carbyne move

even farther upfield. The methyl protons of the carbyne unit in 2 are coupled to the amino proton to produce a doublet (³*J*HH = 3.8 Hz), an assignment confirmed by decoupling the resonance at δ 4.59. The methyl protons of the phosphine ligands generate a virtual triplet, consistent with a trans stereochemistry.[33] Virtual coupling is also observed in the ¹³C NMR spectra of 1 and 2 for several of the carbons of the methyldiphenylphosphine ligands, once again in accord with a trans disposition of phosphines.[34a] The carbyne carbon atom resonance in 2 occurs at ~228 ppm and is coupled to the two phosphorus atoms (²*J*PC ≈ 11.5 Hz). This value agrees with that reported for [ReCl(CNHMe)(dppe)₂]BF₄ (~223 ppm)[18a] but is far upfield from the resonance of a "normal" carbyne (~300 ppm)[34b] and somewhat upfield from that of a (dialkylamino)carbyne, CNR₂ (~235 ppm).[34c] This upfield shift, once again, is consistent with a large contribution from canonical form **b** in eq 9.
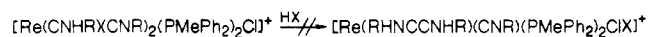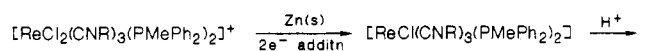
Spectroscopic Properties for Bent Isocyanide Complexes 3-5. Both 3 and 4 have absorptions at ~ 1823-1851 cm⁻¹ assigned as arising from C-N stretching

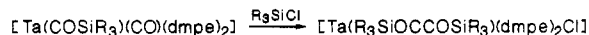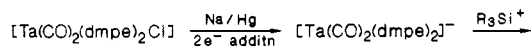(33) Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders: Philadelphia, 1977; p 223.

(34) Mann, B. E.; Taylor, B. F. *¹³C NMR Data for Organometallic Compounds*; Academic: New York, 1981: (a) p 126; (b) pp 144-146; (c) p 146.

Scheme I

Rhenium Isocyanide Reductive Coupling Chemistry

$[ReCl_2(CNR)_3(PMePh_2)_2]^+$ $\xrightarrow[\text{2e}^-\text{ additn}]{\text{Zn(s)}}$ $[ReCl(CNR)_3(PMePh_2)_2]$ $\xrightarrow{\text{H}^+}$

$[Re(CNHRXCNR)_2(PMePh_2)_2Cl]^+$ $\xrightarrow{\text{HX}} \!\!\!\!/\!\!\!\!\!\!\! /\!\!\!-$ $[Re(RHNCCNHR)(CNR)(PMePh_2)_2ClX]^+$

Tantalum Carbonyl Reductive Coupling Chemistry

$[Ta(CO)_2(dmpe)_2Cl]$ $\xrightarrow[\text{2e}^-\text{ additn}]{\text{Na/Hg}}$ $[Ta(CO)_2(dmpe)_2]^-$ $\xrightarrow{\text{R}_3\text{Si}^+}$

$[Ta(COSiR_3)(CO)(dmpe)_2]$ $\xrightarrow{\text{R}_3\text{SiCl}}$ $[Ta(R_3SiOCCOSiR_3)(dmpe)_2Cl]$

of the "bent" isocyanide ligand. Compound 5 also has a rather low C–N stretch at $\sim$1962 cm^{-1}. These values are consistent with the bent structural features and again reflect the importance of resonance form **b** in eq 10.

Single ^{31}P resonances and virtual coupling in the ^{1}H NMR spectra of the methyl protons on the phosphines in 3–5 are consistent with the trans disposition of phosphine ligands. The ^{31}P resonance of 4 is $\sim$4 ppm downfield from that in 3. This result implies that, in this system, chlorine transfers more electron density to the metal than bromine, which is consistent with the infrared data. This trend may also be part of the reason why protonation of 4 to form the bromo analogue of 2 does not occur. Compound 5 has a ^{31}P resonance at −1.1 ppm which is downfield from those of 2 and 3 by more than 5 ppm. This difference is consistent with its cationic nature, which causes the phosphines to experience less electron density at the metal center, and is also in agreement with IR and X-ray structural data. The proton NMR spectra of 3–5 are consistent with meridional isocyanides and trans phosphines.

Relationship to the Reductive Coupling Reaction.
The isolation of aminocarbyne complexes 1 and 2 from the attempted reductive coupling of $[ReCl_2(CNR)_3$-$(PMePh_2)_2]^+$ cations suggests, by analogy, that aminocarbyne species may be important as intermediates in reductive coupling of isocyanide ligands in the related $[Mo(CNR)_6X]^+$ complexes.[1] Scheme I illustrates a possible mechanism for converting 1 or 2 into a hypothetical product containing the N,N'-bis(alkylamino)acetylene unit.

Related carbonyl–carbyne coupling to form C≡C bonds via ligand addition to tungsten carbonyl carbyne complexes is well-known.[35,36] Furthermore, carbonyl–carbyne coupling has also been observed from a proposed W–carbyne–(Lewis acid-activated) carbonyl complex.[37] Finally, and most significantly, the precisely analogous mechanism has been established by isolation and characterization of intermediates in the reductive coupling of carbonyl ligands in $[M(CO)_2(dmpe)_2Cl]$ to form bis(trialkylsiloxy)acetylene complexes $[M(R_3SiOC≡COSiR_3)(dmpe)_2Cl]$ (M = Nb, Ta (Scheme I)).[5] The thermodynamic stability of 1 and 2 relative to that of the putative acetylene complexes $[ReCl_2(RNHCCNHR)(CNR)(PMePh_2)_2]^+$ may account for their failure to complete the reductive coupling reaction.

(35) (a) Uedelhoven, W.; Eberl, K.; Kreissl, F. R. *Chem. Ber.* 1979, *112*, 3376. (b) Kreissl, F. R.; Wolfgruber, M.; Sieber, W. J.; Ackermann, K. *Organometallics* 1984, *3*, 777.

(36) (a) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* 1985, *107*, 4474. (b) Mayr, A.; McDermott, G. A.; Dorries, A. M.; Holder, A. K.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* 1986, *108*, 310.

(37) Churchill, M. R.; Wasserman, H. J.; Holmes, S. J.; Schrock, R. R. *Organometallics* 1982, *1*, 766.