Reaction Chemistry of [M(R₃SiOCCOSiR₃)(dmpe)₂Cl] (M = Ta, Nb): Isolation and Structural Characterization of the First (Dihydroxyacetylene)metal Complexes and Removal of the Disiloxyacetylene Ligand as an Alkene

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The reaction of [M(Me₃SiOCCOSiMe₃)(dmpe)₂Cl] (M = Ta, Nb) with aqueous HCl results in oxidative addition of H⁺ to the metal center and protiolysis of the trimethylsiloxy groups to afford [MH(HOC-COH)(dmpe)₂Cl]Cl complexes, which contain the novel dihydroxyacetylene ligand. Single-crystal X-ray diffraction studies were performed on the tantalum analogue 5. The geometry about the metal center is pentagonal-bipyramidal, with the four phosphorus atoms and the hydride ligand defining the equatorial plane and the axial positions being occupied by the chloride ion and the midpoint of the acetylene ligand. Reaction of [Ta(Me₃SiOCCOSiMe₃)(dmpe)₂Cl] with HBF₄·Me₂O yields the related hydride complex [TaH(Me₃SiOCCOBF₃)(dmpe)₂Cl] (7), which was also structurally characterized. The bis(*tert*-butyldimethylsiloxy)acetylene ligand in [Ta(*t*-BuMe₂SiOCCOSiMe₂-*t*-Bu)(dmpe)₂Cl] was removed with the C–C bond intact by hydrogenation with either pure hydrogen or synthesis gas in the presence of 5% palladium on carbon or [RhCl(PPh₃)₃]. The product of this hydrogenation is bis(*tert*-butyldimethylsiloxy)ethylene, which was characterized by mass spectrometry and by comparison with an authentic sample prepared by an alternate route. Spectroscopic evidence supports a cis geometry for the alkene. Crystal data: compound 5, orthorhombic, *P*2₁2₁2₁, *a* = 8.777 (2) Å, *b* = 14.856 (2) Å, *c* = 18.154 (5) Å, *Z* = 4; compound 7·(toluene), monoclinic, *P*2₁/*c*, *a* = 10.776 (3) Å, *b* = 17.066 (2) Å, *c* = 19.414 (6) Å, *β* = 92.18 (2)°, *Z* = 4.

Introduction

The reductive coupling of carbon monoxide has been known since 1834 when Justus Liebig reported the formation of "potassium carbonyl" upon exposure of carbon monoxide to molten potassium.[1] In 1963 Büchner correctly identified "potassium carbonyl" as the potassium salt of acetylenediolate, K₂(⁻O—C≡C—O⁻),[2] which is the first member in a series of aromatic oxocarbon polyanions,[3] $C_nO_n^{2-}$. While hydroxyacetylene,[4] phenylhydroxyacetylene,[5] and even dihydroxyacetylene[6] have been reported recently in the literature, they are very unstable and have been observed only in the gas phase, by matrix isolation, or by using pulsed laser techniques. These compounds can be stabilized, however, by bonding to one or more metal centers, as evidenced by the isolation and structural characterization of a trinuclear cobalt hydroxyacetylene complex.[7]

Carbon monoxide can be transformed into organic products containing more than one carbon atom by using the Fischer–Tropsch[8] reaction. This process is complicated, however, since a complex mixture of alkanes, olefins, aldehydes, acids, alcohols, and aromatics is obtained from the reaction. The selective conversion of carbon monoxide to ethylene glycol has been achieved with a variety of group 8 or 9 catalysts;[9] however, these transformations require high temperatures and pressures and have slow turnover rates. Alternative routes for reductively coupling carbon monoxide are therefore very desirable. Indeed, reports of the reductive coupling of carbon monoxide with the use of alkali metals and reagents,[1,2,10] by electrochemical techniques,[11] or by employing soluble lanthanide, actinide,

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(6) Terlouw, J. K.; Burgers, P. C.; van Baar, B. L. M.; Weiske, T.; Schwarz, H. *Chim.* **1986**, *40*, 357.

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(10) (a) Joannis, A. C. R. *Hebd. Seances Acad. Sci.* **1893**, *116*, 1518; **1914**, *158*, 874. (b) Pearson, T. G. *Nature* **1933**, *131*, 166. (c) Hackspill, L.; van Altane, L. A. *C. R. Hebd. Seances Acad. Sci.* **1938**, *206*, 1818. (d) Scott, A. F. *Science* **1952**, *115*, 118. (e) Ellis, J. E.; Fjare, K. L.; Hayes, T. G. *J. Am. Chem. Soc.* **1981**, *103*, 6100. (f) Jutzi, P.; Schröder, F. *J. Organomet. Chem.* **1970**, *24*, C43.

or transition-metal complexes[12] have appeared in the literature.

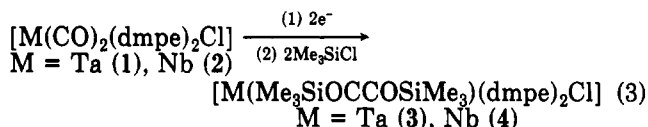Work in our laboratories has shown that it is possible to couple reductively alkyl isocyanides, which are isoelectronic with carbon monoxide, in the seven-coordinate complexes $[M(CNR)_6X]^+$ (M = W, Mo; X = halide, cyanide; R = alkyl), as shown in eq 1.[13] The bis(alkyl-

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

$$[M(RHNCCNHR)(CNR)_4X]^+ \quad (1)$$

$$M = W, Mo$$
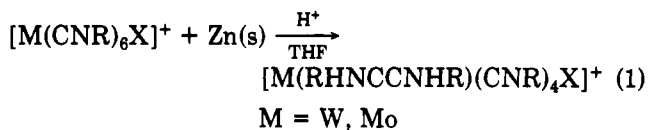
amino)acetylene ligand in these molybdenum complexes can be removed oxidatively with the C–C bond intact by using a variety of oxidizing agents such as H_2O_2, $PhICl_2$, or $AgNO_3$ to yield a N,N'-dialkyloxamide (eq 2).[14] Removal of the coupled ligand in this manner, however, presumably leads to oxidation of the metal center and thus restricts the possibility of evolving a catalytic system.

$$[Mo(RHNCCNHR)(CNR)_4X]^+ \xrightarrow{[Ox]} \underset{RHN}{\overset{O}{\underset{}{\parallel}}} \underset{NHR}{\overset{O}{\underset{}{\parallel}}} \quad (2)$$
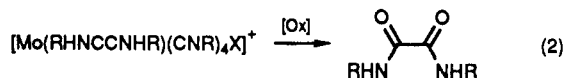
More recently we have discovered the reductive coupling of two carbonyl ligands in the seven-coordinate tantalum and niobium complexes $[M(CO)_2(dmpe)_2Cl]$ (dmpe = bis(dimethylphosphino)ethane; M = Ta (1), Nb (2)).[15] Several key steps in the mechanism of this reaction have been elucidated.[16] As shown in eq 3, the reductively

$$[M(CO)_2(dmpe)_2Cl] \xrightarrow[(2)\ 2Me_3SiCl]{(1)\ 2e^-}$$
$$M = Ta\ (1),\ Nb\ (2)$$

$$[M(Me_3SiOCCOSiMe_3)(dmpe)_2Cl] \quad (3)$$
$$M = Ta\ (3),\ Nb\ (4)$$

coupled product of the reaction is $[M(Me_3SiOCCOSiMe_3)(dmpe)_2Cl]$ [M = Ta (3), Nb (4)], which contains a bound bis(trialkylsiloxy)acetylene ligand. An important goal of this project has been to remove the coupled disiloxyacetylene ligand with the newly formed C–C bond intact. Ideally this objective would be achieved in a manner lending itself to catalytic chemistry. We have therefore been investigating the reactivity of the reductively coupled products 3 and 4 in order to approach this goal. Here we describe details of the reaction of 3 and 4 with inorganic acids to form the first dihydroxyacetylene

complexes, preliminary results of which have been previously communicated.[16b] Also reported is decomplexation of the disiloxyacetylene ligand from the metal center via hydrogenation with use of palladium on carbon or Wilkinson's catalyst, a reaction that affords the corresponding *cis*-1,2-disiloxyethylene.

Experimental Section

Materials. All reactions and manipulations were carried out either in a nitrogen-filled Vacuum Atmospheres drybox or under argon with standard Schlenk-line techniques. Ethers were distilled under nitrogen from sodium benzophenone ketyl and stored over 3-Å molecular sieves. Toluene was distilled from sodium and stored over 3-Å molecular sieves. Deuterated chloroform (Cambridge Isotopes Laboratory) was used without purification. Deuterated THF (Cambridge Isotopes Laboratory) was dried by vacuum transfer from sodium benzophenone ketyl. The starting materials $[Ta(CO)_2(dmpe)_2Cl]$ (1), $[Nb(CO)_2(dmpe)_2Cl]$ (2), $[Ta(Me_3SiOCCOSiMe_3)(dmpe)_2Cl]$ (3), and $[Nb(Me_3SiOCCOSiMe_3)(dmpe)_2Cl]$ (4) were synthesized as previously described.[15] Forty percent sodium amalgam was prepared by a literature method.[17] Concentrated HCl (Mallinckrodt), $HBF_4 \cdot Me_2O$ (Aldrich), chloro-*tert*-butyldimethylsilane (Petrarch), *n*-propyl formate (Aldrich), sodium (Aldrich), 5% palladium on carbon (Aldrich), chlorotris(triphenylphosphine)rhodium(I) (Strem), hydrogen (Airco), and synthesis gas (33.3% CO, 66.7% H_2, Matheson) were obtained from commercial sources and used without further purification.

Preparation of $[TaH(HCOCCOH)(dmpe)_2Cl]Cl$ (5). When 17 μL (0.040 mmol of HCl) of a 7.6% aqueous solution of HCl was added to 0.0282 g (0.039 mmol) of $[Ta(Me_3SiOCCOSiMe_3)(dmpe)_2Cl]$ dissolved in 15 mL of THF, the solution rapidly changed from green to pale yellow. After the reaction mixture was allowed to stand for 30 min, white microcrystals formed, which were isolated by filtration and washed with THF, yielding 0.0226 g (94%) of $[TaH(HOCCOH)(dmpe)_2Cl]Cl$. Spectroscopic data: FTIR (KBr pellet) 3001 (s), 2909 (s), 2806 (s), 2746 (s), 2566 (s), 2387 (m), 1604 (s, ν_{CO} or ν_{CC}), 1421 (m), 1301 (w), 1287 (w), 1183 (s), 1087 (w), 936 (s), 901 (w), 846 (w), 811 (w), 750 (w), 713 (m), 648 (m), 447 (w) cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 10.97 (s, OH), 5.06 (t of t, H, $^2J_{HP_{trans}}$ = 90 Hz, $^2J_{HP_{cis}}$ = 5 Hz), 2.60–1.82 (br m, PCH$_2$), 1.76 (d, PCH$_3$, $^2J_{PH}$ = 9 Hz), 1.58 (d, PCH$_3$, $^2J_{PH}$ = 9 Hz), 1.48 (d, PCH$_3$, $^2J_{PH}$ = 8 Hz), 1.35 (d, PCH$_3$, $^2J_{PH}$ = 8 Hz) ppm (when 2 drops of D_2O were added to the NMR tube and the spectrum was acquired again, the peak at δ 10.97 had disappeared while the rest of the spectrum remained unchanged); $^{31}P\{^1H\}$ NMR (121 MHz, CDCl$_3$, referenced to external 85% H_3PO_4) δ 35.55, 14.55 ppm (the downfield resonance splits into a doublet when not ^1H decoupled, $^2J_{PH}$ = 90 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$) δ 204.6 ppm. Anal. Calcd for $C_{14}H_{35}Cl_2O_2P_4Ta$: C, 27.51; H, 5.77; Cl, 11.60. Found: C, 27.18; H, 5.44; Cl, 11.85. FAB MS: *m/z* = 575.1 (M$^+$).

Reaction of $[Ta(Me_3SiOCCOSiMe_3)(dmpe)_2Cl]$ with 1 Equiv of Distilled Water. When 3 μL (0.167 mmol) of distilled water was added to a solution of 0.1142 g (0.159 mmol) of $[Ta(Me_3SiOCCOSiMe_3)(dmpe)_2Cl]$ in 9 mL of THF, there was a rapid color change from green to yellow followed by the precipitation of colorless crystals. These crystals were isolated by filtration, yielding 0.0262 g (27%) of $[TaH(HOCCOH)(dmpe)_2Cl]Cl$, the spectroscopic properties of which are the same as those described above.

Reaction of $[Ta(Me_3SiOCCOSiMe_3)(dmpe)_2Cl]$ with 2 Equiv of Methanol. When 5 μL (0.1236 mmol) of methanol was added to a solution of 0.0461 g (0.641 mmol) of $[Ta(Me_3SiOCCOSiMe_3)(dmpe)_2Cl]$ in 5 mL of THF, a color change from green to yellow was observed. Colorless crystals of $[TaH(HOCCOH)(dmpe)_2Cl]Cl$ formed upon standing for 20 min, and the nature of this product was confirmed by ^{31}P and ^1H NMR spectroscopy.

Preparation of $[NbH(HOCCOH)(dmpe)_2Cl]Cl$ (6). When 72 μL (0.169 mmol of HCl) of a 7.6% aqueous solution of HCl was added to a solution of 0.1054 g (0.167 mmol) of [Nb-

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(Me$_3$SiOCCOSiMe$_3$)(dmpe)$_2$Cl] in 10 mL of THF, there was a rapid color change from green to yellow, along with the formation of a pale yellow precipitate. The pale yellow precipitate was dissolved in 10 mL of chloroform, to which was added 10 mL of pentane, causing the formation of a white precipitate. The precipitate was isolated by filtration and washed with THF, yielding 0.0664 g (75%) of [NbH(HOCCOH)(dmpe)$_2$Cl]Cl. This product can also be recrystallized from an acetonitrile solution cooled to –30 °F. Spectroscopic data: FTIR (KBr pellet) 3001 (s), 2909 (s), 2806 (s), 2746 (s), 2566 (s), 2387 (m), 1609 (s, ν_{CO} or ν_{CC}), 1422 (m), 1301 (sh), 1287 (m), 1188 (s), 1133 (w), 1090 (w), 949 (s), 936 (s), 900 (m), 856 (w), 845 (w), 820 (m), 751 (m), 712 (m), 645 (m), 485 (m), 447 (m) cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 11.01 (s, OH), 2.40–2.20 (br m, PCH$_2$), 2.20–1.80 (br m, PCH$_2$), 1.67 (d, PCH$_3$, $^2J_{PH}$ = 8.7 Hz), 1.55 (d, PCH$_3$, $^2J_{PH}$ = 8.5 Hz), 1.40 (d, PCH$_3$, $^2J_{PH}$ = 6.9 Hz), 1.31 (d, PCH$_3$, $^2J_{PH}$ = 7.1 Hz) ppm; ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$, referenced to external 85% H$_3$PO$_4$) δ 46.8, 22.4 ppm. Anal. Calcd for C$_{14}$H$_{35}$Cl$_2$O$_2$P$_4$Nb: C, 32.14; H, 6.74; Cl, 13.55. Found: C, 31.82; H, 6.72; Cl, 13.29.

Preparation of [TaH(Me$_3$SiOCCOBF$_3$)(dmpe)$_2$Cl] (7). When 11 μL (0.106 mmol) of HBF$_4$·Me$_2$O was added slowly to a solution containing 0.0726 g (0.101 mmol) of [Ta-(Me$_3$SiOCCOSiMe$_3$)(dmpe)$_2$Cl] in 15 mL of Et$_2$O, there was rapid formation of a white precipitate along with a color change from green to pale yellow. The white precipitate was isolated by filtration, washed several times with Et$_2$O, and then dissolved in a minimal amount of glyme, to which several drops of toluene were added after the precipitate was completely dissolved. After the mixture was cooled to –20 °F for 12 h, 0.0472 g (57%) of [TaH(Me$_3$SiOCCOBF$_3$)(dmpe)$_2$Cl]·C$_6$H$_5$CH$_3$ was isolated as colorless crystals. Spectroscopic data: FTIR (KBr pellet) 2976 (m), 2912 (sh), 1639 (s, ν_{CO} or ν_{CC}), 1423 (s), 1307 (s), 1307 (s), 1289 (s), 1262 (m), 1249 (s), 1207 (s), 1157 (w), 1057 (s), 1002 (m), 952 (s), 938 (s), 900 (m), 872 (s), 847 (s), 799 (m), 763 (w), 741 (m), 719 (m), 710 (m), 700 (m), 651 (m), 572 (w), 558 (w), 448 (w) cm^{-1}; ^{1}H NMR (300 MHz, THF-d_8) δ 5.13 (t, of t, H, $^2J_{HP}$ = 84 Hz, $^2J_{HP}$ = 6 Hz), 2.8–2.3 (br m, PCH$_2$), 2.2–1.9 (br m, PCH$_2$), 1.79 (d, PCH$_3$, J_{PH} = 9 Hz), 1.59 (d, PCH$_3$, J_{PH} = 8 Hz), 1.53 (d, PCH$_3$, J_{PH} = 6 Hz), 1.36 (d, PCH$_3$, J_{PH} = 7 Hz), 0.18 (s, SiCH$_3$) ppm; ^{31}P{^{1}H} NMR (121 MHz, THF-d_8, referenced to external 85% H$_3$PO$_4$) δ 34.9, 14.2 ppm (the downfield resonance splits into a doublet when not ^{1}H decoupled, $^2J_{PH}$ = 79 Hz); ^{19}F NMR (THF-d_8, referenced to internal PhF at –113.1 ppm, with positive values being downfield of CFCl$_3$) δ –147.4 ppm; ^{13}C NMR (75 MHz, THF-d_8) δ 211.1 (d-sext, J_{PC} = 15 MHz, J_{CH} = 5 MHz). Anal. Calcd for C$_{24}$H$_{48}$BClF$_3$O$_2$P$_4$SiTa: C, 28.57; H, 5.92; Cl, 4.96; F, 7.97. Found: C, 28.67; H, 6.00; Cl, 5.13; F, 8.37.

Preparation of [Ta(t-BuMe$_2$SiOCCOSiMe$_2$-t-Bu)-(dmpe)$_2$Cl] (8). A mixture of [Ta(CO)$_2$(dmpe)$_2$Cl] (0.1480 g, 0.258 mmol), excess 40% sodium amalgam, and 10 mL of THF was stirred in a 25-mL flask for 6 h, during which time the color changed from orange to red-brown. To the filtered red-brown solution was added 0.0781 g (0.518 mmol) of t-BuMe$_2$SiCl, after which the color changed to plum red. This mixture was then heated to 65 °C for 10 h, during which time the reaction mixture turned dark green. The THF was removed in vacuo, and the green product was extracted with pentane. When the extracts were cooled to –20 °F, [Ta(t-BuMe$_2$SiOCCOSiMe$_2$-t-Bu)(dmpe)$_2$Cl] formed in 57.7% yield (0.1196 g). Spectroscopic data: FTIR (KBr pellet) 2962 (m), 2946 (m), 2928 (m), 1/$\sigma^2|F_o|$. (m), 2893 (sh), 2854 (m), 2800 (w), 1531 (m, ν_{CO} or ν_{CC}), 1471 (m), 1461 (m), 1418 (m), 1360 (w), 1290 (w), 1278 (m), 1253 (m), 1243 (m), 1124 (s), 1010 (sh), 1003 (m), 934 (s), 893 (s), 838 (s), 799 (m), 772 (m), 711 (m), 696 (w), 692 (m), 661 (w), 615 (m), 455 (w), 416 (w) cm^{-1}; ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 1.70 (v br s, PCH$_2$), 1.50 (br s, PCH$_3$), 1.24 (v br s, PCH$_2$), 1.10 (s, CCH$_3$), 0.24 (s, SiCH$_3$) ppm; ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$, referenced to external 85% H$_3$PO$_4$) δ 24.8 ppm. Anal. Calcd for C$_{26}$H$_{62}$ClO$_2$P$_4$Si$_2$Ta: C, 38.89; H, 7.78; Cl, 4.41. Found: C, 39.24; H, 7.79; Cl, 4.63.

Preparation of (t-BuMe$_2$SiO)CHCH(OSiMe$_2$-t-Bu) (9). The compound (t-BuMe$_2$SiO)CHCH(OSiMe$_2$-t-Bu) (9) was prepared via a modification of a literature preparation.[18] To a stirred mixture of 4.0107 g (26.61 mmol) of t-BuMe$_2$SiCl and 0.6184 g

(26.90 mmol) of sodium sand in 15 mL of Et$_2$O in a 100-mL round-bottomed flask under argon was added dropwise 1.20 g (13.62 mmol) of n-propyl formate in 10 mL of Et$_2$O. After all of the formate ester had been added, the reaction mixture was refluxed for 5 h and the Et$_2$O was removed in vacuo. A mixture of products was obtained that could be separated by column chromatography with silica as the solid phase and pentane as the eluant; the desired product elutes from the column in the second band. Purification in this manner yielded 0.1182 g (3.1% based on HCO$_2$-n-Pr) of (t-BuMe$_2$SiO)CHCH(OSiMe$_2$-t-Bu). Spectroscopic data: FTIR (neat, KBr plates) 3041 (w, $\nu_{=CH}$), 2958 (s), 2930 (s), 2887 (s), 2858 (s), 1663 (m, $\nu_{C=C}$), 1473 (s), 1464 (s), 1389 (m), 1362 (m), 1256 (s), 1146 (s), 1099 (br s), 1006 (s), 939 (w), 895 (m), 837 (s), 719 (w), 683 (w), 662 (w) cm^{-1}; ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 5.51 (s, =CH), 0.99 (s, CCH$_3$), 0.11 (s, SiCH$_3$) ppm; GC/MS m/z 288 (M$^+$).

Reaction of [Ta(t-BuMe$_2$SiOCCOSiMe$_2$-t-Bu)(dmpe)$_2$Cl] (8) with Synthesis Gas in the Presence of 5% Palladium on Carbon. To a solution of 0.1619 g (0.202 mmol) of [Ta(t-BuMe$_2$SiOCCOSiMe$_2$-t-Bu)(dmpe)$_2$Cl] dissolved in 15 mL of glyme in a 50-mL round-bottomed flask was added 0.0298 g of 5% palladium on carbon. The flask was then fitted with a rubber septum, and 1 atm of synthesis gas was introduced. After the mixture was stirred vigorously for 1 h, during which time the color changed from green to red-orange, 3 mL of distilled water was added, followed by extraction with three 5-mL portions of pentane. The combined pentane fractions were then passed through a column of silica, and the pentane was removed in vacuo, yielding 0.0257 g (44.1%, >98% pure by GC) of (t-BuMe$_2$SiO)CHCH-(OSiMe$_2$-t-Bu). Spectroscopic data: FTIR (neat, KBr plates) 3041 (w, $\nu_{=CH}$), 2958 (s), 2930 (s), 2897 (m), 2887 (s), 2859 (s), 1664 (m, $\nu_{C=CH}$), 1473 (s), 1464 (s), 1444 (w), 1389 (m), 1362 (m), 1291 (w), 1255 (s), 1146 (s), 1079 (br s), 1006 (s), 939 (w), 895 (m), 838 (s), 782 (s), 719 (w), 685 (w), 661 (w) cm^{-1}; ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 5.51 (s, =CH), 0.99 (s, CCH$_3$), 0.11 (s, SiCH$_3$) ppm; ^{13}C NMR (300 MHz, C$_6$D$_6$) δ 125.6 ppm; GC/MS m/z 288 (M$^+$).

Reaction of [Ta(t-BuMe$_2$SiOCCOSiMe$_2$-t-Bu)(dmpe)$_2$Cl] (8) with Hydrogen in the Presence of 5% Palladium on Carbon. To a solution of 0.0518 g (0.064 mmol) of [Ta(t-BuMe$_2$SiOCCOSiMe$_2$-t-Bu)(dmpe)$_2$Cl] dissolved in 10 mL of glyme in a pear-shaped flask was added 0.0303 g of 5% Pd on carbon. The flask was then equipped with a rubber septum and 1 atm of hydrogen introduced. After 22 h the reaction was incomplete, as judged by the residual light green color of the reaction mixture. Nevertheless, the product was worked up as before, yielding 0.0024 g (12.9%, >98% pure by GC) of (t-BuMe$_2$SiO)-CHCH(OSiMe$_2$-t-Bu), the spectroscopic properties of which are the same as described above.

Reaction of [Ta(t-BuMe$_2$SiOCCOSiMe$_2$-t-Bu)(dmpe)$_2$Cl] (8) with Synthesis Gas in the Presence of [RhCl(PPh$_3$)$_3$]. To a solution of 0.0518 g (0.064 mmol) of [Ta(t-BuMe$_2$SiOCCOSiMe$_2$-t-Bu)(dmpe)$_2$Cl] dissolved in 10 mL of glyme was added 0.0114 g (0.013 mmol) of [RhCl(PPh$_3$)$_3$]. The flask was then equipped with a rubber septum, and 1 atm of synthesis gas was introduced. The reaction mixture was stirred for 30 min, during which time the color changed from green to red-orange. The reaction mixture was worked up as described previously, yielding 0.0079 g (43%, 98% pure by GC) of (t-BuMe$_2$SiO)CHCH(OSiMe$_2$-t-Bu), which had the expected spectroscopic properties.

Instrumentation. Infrared spectra were recorded on a Mattson Cygnus 100 FTIR instrument. ^{1}H, ^{31}P, ^{19}F, and ^{13}C NMR spectra were recorded on a Varian XL-300 instrument. Spin simulation was accomplished by using an iterative program based on the FORTRAN program LAME, also known as LAOCOON, with magnetic equivalence added. This program is available in the software supplied with the Varian XL-300 instrument. Gas chromatography and gas chromatography/mass spectrometry experiments were performed on a Hewlett-Packard 5890A gas chromatograph with a 5971A mass selective detector using a methyl silicon gum (5 m × 0.53 mm × 2.65 μm film thickness) or TPA modified cross-linked polyethylene glycol (50 m × 0.2 mm × 0.33 μm film thickness) capillary column, respectively.

Collection and Reduction of X-ray Data. [TaH(HOC-COH)(dmpe)$_2$Cl]Cl (5). A colorless crystal was grown by cooling a saturated solution of the compound in chloroform to –30 °F.

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Table I. Experimental Details of the X-ray Diffraction Study of [TaH(HOCCOH)(dmpe)₂Cl]Cl (5) and [TaH(Me₃SiOCCOBF₃)(dmpe)₂Cl]•C₆H₅CH₃ (7•C₆H₅CH₃)[a]

	5	7·C₆H₅CH₃
formula	$C_{14}H_{35}Cl_2O_2P_4Ta$	$C_{24}H_{50}BClF_3O_2P_4SiTa$
fw	611.18	806.85
a, Å	8.777 (2)	10.776 (3)
b, Å	14.856 (2)	17.066 (2)
c, Å	18.154 (5)	19.414 (6)
β, deg		92.18 (2)
V, Å³	2367 (1)	3568 (3)
temp, °C	23	23
Z	4	4
ρcalcd, g cm⁻³	1.71	1.498
space group	$P2_12_12_1$	$P2_1/c$
radiation	Mo Kα	Mo Kα
data limits, deg	3 < 2θ < 55 (+h,+k,+l); 16 < 2θ < 30 (±h,±k,±l)	3 < 2θ < 50 (+h,+k,±l)
cryst dimens, mm		0.2 × 0.25 × 0.38
linear abs coeff, cm⁻¹	50.89	33.64
fudge factor	0.05	0.05
no. of data collected	3093	6892
no. of unique data (F > 6σ(F))[b]	2793	3253
no. of params	218	338
R_1[c]	0.023	0.054
R_2[c]	0.033	0.064

[a] Data were collected on an Enraf-Nonius CAD-4F κ-geometry diffractometer. [b] $\sigma(I) = (C + 1/4(t_c/t_b)^2(b_1 + b_2) + (pI)^2)^{1/2}$, where C is the total number of counts, t_c is the time spent counting peak intensity, t_b is the time spent counting one side of background, b_1 is the high-angle background count, b_2 is the low-angle background count, and p is a factor, set equal to 0.05, to avoid overweighting the strong reflections. [c] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2|F_o|$.

A parallelepiped of this compound was mounted under a nitrogen atmosphere in a Lindemann glass capillary with use of Apiezon grease. Study on the diffractometer revealed *mmm* Laue symmetry with systematic absences *h*00 (*h* ≠ 2*n*), 0*k*0 (*k* ≠ 2*n*), and 00*l* (*l* ≠ 2*n*), consistent with the space group $P2_12_12_1$ (D_2^4, No. 19).[19a] An empirical absorption correction was applied on the basis of azimuthal ψ scans. Monitoring of three intensity standards after every 60 min of exposure showed a linear decay of ~9%, for which the data were accordingly normalized. Data collection proceeded by methods standard in our laboratory,[20] details of which are given in Table I.

[TaH(Me₃SiOCCOBF₃)(dmpe)₂Cl]·C₆H₅CH₃ (7). A clear crystal was grown by cooling a saturated solution of the compound in a mixture of glyme and toluene to −30 °F. An irregularly shaped cube of this compound was mounted under a nitrogen atmosphere in a Lindemann glass capillary with use of Apiezon grease. Study on the diffractometer revealed 2/*m* Laue symmetry with systematic absence 0*k*0 (*k* ≠ 2*n*) and *h*0*l* (*l* ≠ 2*n*), consistent with the space group $P2_1/c$ (C_{2h}^5, No. 14).[19b] An empirical absorption correction was applied on the basis of azimuthal ψ scans. Data collection proceeded by methods standard in our group,[20] details of which are given in Table I.

Structure Determination and Refinement. All calculations were carried out with use of the TEXSAN program package.[21]

[TaH(HOCCOH)(dmpe)₂Cl]Cl (5). The position of the tantalum atom was determined from a Patterson synthesis. All of the remaining non-hydrogen atoms along with the hydroxyl hydrogen atoms were located from a series of difference Fourier maps. The hydroxyl hydrogen atoms were assigned isotropic temperature factors $B(H) = 1.2[B_{eq}(O)]$. The hydride atom was

(19) (a) Hahn, T., Ed. *International Tables for X-ray Crystallography*; D. Reidel: Dordrecht, The Netherlands, 1983; p 196. (b) *Ibid.*, pp 174–176.

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

(21) TEXSAN, a package of crystallographic program supplied by the Molecular Structure Corporation, 1988. All computations were carried out on a DEC MicroVAX II computer. Toward the end of the refinement of 5, the additional absorption correction provided by the program DIFABS was applied (Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158).

Table II. Final Non-Hydrogen Atom[a] Positional and Equivalent Thermal Parameters for [TaH(HOCCOH)(dmpe)₂Cl]Cl (5)[b]

atom	x	y	z	$B(eq)$,[c] Å²
Ta	0.99905 (4)	0.01452 (1)	0.60281 (1)	2.40 (1)
Cl(1)	0.8006 (2)	0.1117 (1)	0.5407 (1)	4.36 (9)
Cl(2)	1.0126 (4)	0.1719 (2)	0.2123 (1)	6.5 (1)
P(1)	0.8632 (3)	0.0611 (1)	0.7214 (1)	4.2 (1)
P(2)	0.8902 (2)	−0.1102 (1)	0.5220 (1)	3.41 (8)
P(3)	1.1327 (2)	0.0370 (1)	0.4736 (1)	3.74 (8)
P(4)	1.1234 (3)	0.1683 (1)	0.6399 (1)	4.5 (1)
O(1)	1.2496 (7)	−0.1526 (5)	0.5932 (4)	6.2 (3)
O(2)	1.2431 (9)	−0.0271 (5)	0.7398 (4)	7.8 (4)
C(1)	1.1668 (7)	−0.0812 (5)	0.6171 (4)	3.1 (3)
C(2)	1.1660 (8)	−0.0324 (5)	0.6747 (4)	3.7 (3)
C(11)	0.943 (1)	0.1634 (9)	0.7619 (6)	7.7 (7)
C(12)	0.872 (1)	−0.0235 (7)	0.7929 (5)	6.4 (5)
C(13)	0.663 (1)	0.0866 (8)	0.7157 (5)	6.7 (6)
C(21)	0.993 (1)	−0.1236 (6)	0.4361 (4)	6.0 (4)
C(22)	0.892 (1)	−0.2214 (6)	0.5621 (5)	5.9 (5)
C(23)	0.6941 (9)	−0.1002 (7)	0.4915 (6)	5.6 (5)
C(31)	1.048 (1)	−0.039 (1)	0.4076 (5)	7.9 (7)
C(32)	1.331 (1)	0.012 (1)	0.4678 (7)	9.5 (8)
C(33)	1.121 (1)	0.1432 (7)	0.4236 (5)	6.5 (5)
C(41)	1.100 (2)	0.184 (1)	0.7357 (7)	11 (1)
C(42)	1.333 (2)	0.177 (1)	0.6274 (9)	11 (1)
C(43)	1.064 (1)	0.2713 (6)	0.5977 (5)	6.4 (6)
H(1)	1.33 (1)	−0.136 (6)	0.633 (5)	7.4
H(2)	1.31 (1)	−0.062 (8)	0.749 (6)	9.3
H(3)	0.88 (2)	−0.07 (1)	0.653 (9)	23 (6)

[a] Also included are the hydroxyl and hydride hydrogen atoms. [b] Numbers in parentheses are errors in the last significant digit(s). See Figure 1 for atom-labeling scheme. [c] $B(eq) = \frac{4}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab \cos \gamma)\beta_{12} + (2ac \cos \beta)\beta_{13} + (2bc \cos \alpha)\beta_{23}]$.

located from difference Fourier maps and refined with an isotropic temperature parameter that indicated fairly large thermal motion. The temperature factor and position of this atom were sensitive to the application of the additional absorption correction by the programs DIFABS.[21] In the final refinement cycles, DIFABS-corrected data were employed, leading to a geometry similar to that for the better behaved hydride ligand in compound 7 (vide infra). Structure refinement proceeded smoothly, and the abundance of data allowed for treatment of all non-hydrogen atoms with anisotropic thermal parameters. High-resolution Fourier maps, in which the grid spacing for the Fourier synthesis was decreased to 0.18 Å, in the vicinity of the methylene groups of the dmpe ligands showed no disorder. All the methyl and methylene hydrogen atoms were placed in calculated positions ($d_{C-H} = 0.95$ Å) and allowed to "ride" on the appropriate carbon atoms to which they were attached. These atoms were assigned isotropic temperature factors $B(H) = 1.2[B_{eq}(C)]$. The function minimized during refinement was $\sum w(|F_o| - |F_c|)^2$. Refinement in this manner yielded the R factors given in Table I. The largest ratio of parameter shift to estimated standard deviation in the final cycle of refinement was less than 0.20, and the largest peak in the difference Fourier map was 0.78 e/Å³, located near the Ta atom. Final non-hydrogen atom positional parameters are given in Table II. Final non-hydrogen atom thermal parameters, hydrogen atom positional and thermal parameters, and observed and calculated structure factors are given in Tables S1–S3 (supplementary material), respectively.

[TaH(Me₃SiOCCOBF₃)(dmpe)₂Cl]·C₆H₅CH₃ (7). The position of the tantalum atom was determined from a Patterson synthesis, and all of the remaining non-hydrogen atoms were located from a series of difference Fourier maps. The hydride was found from a difference map by using data with (sin θ)/λ < 0.3. All non-hydrogen atoms were treated with anisotropic thermal parameters. High-resolution Fourier maps, in which the grid spacing for the Fourier synthesis was decreased to 0.19 Å, in the vicinity of the methylene groups of the dmpe ligands showed some peak splitting; however, a satisfactory disordered model could not be refined. All hydrogen atoms were placed in calculated positions ($d_{C-H} = 0.95$ Å) and allowed to "ride" on the appropriate carbons with $B(H) = 1.2[B_{eq}(C)]$, except for the hydride atom, which was refined independently. The function minimized during refinement

Table III. Final Non-Hydrogen Atom[a] Positional and Equivalent Thermal Parameters for [TaH(Me₃SiOCCOBF₃)(dmpe)₂Cl]•C₆H₅CH₃ (7•C₆H₅CH₃)[b]

atom	x	y	z	$B(eq),^c$ Å²
Ta	0.28995 (5)	0.16256 (4)	0.13038 (3)	3.75 (3)
Cl	0.3939 (4)	0.2649 (3)	0.0582 (2)	6.0 (2)
P(1)	0.0854 (4)	0.2338 (3)	0.0857 (3)	5.6 (2)
P(2)	0.2336 (4)	0.1010 (3)	0.0127 (2)	5.1 (2)
P(3)	0.5049 (4)	0.1497 (3)	0.1890 (3)	6.3 (3)
P(4)	0.2980 (5)	0.2758 (3)	0.2217 (3)	6.5 (3)
Si	0.2547 (5)	0.0187 (4)	0.3443 (3)	6.4 (3)
O(1)	0.263 (1)	0.0847 (8)	0.2826 (6)	6.9 (7)
O(2)	0.051 (1)	0.0444 (8)	0.1492 (6)	7.0 (7)
C(1)	0.237 (1)	0.099 (1)	0.2135 (8)	5.1 (8)
C(2)	0.158 (1)	0.083 (1)	0.1654 (8)	4.8 (8)
C(11)	0.009 (2)	0.174 (2)	0.021 (1)	10 (2)
C(12)	0.091 (2)	0.326 (2)	0.045 (1)	12 (2)
C(13)	−0.042 (2)	0.245 (1)	0.143 (1)	9 (1)
C(21)	0.093 (2)	0.145 (2)	−0.028 (1)	10 (2)
C(22)	0.206 (2)	−0.004 (1)	0.015 (1)	8 (1)
C(23)	0.345 (2)	0.108 (1)	−0.0533 (8)	7 (1)
C(31)	0.517 (3)	0.215 (2)	0.265 (1)	13 (2)
C(32)	0.638 (2)	0.173 (2)	0.139 (1)	13 (2)
C(33)	0.547 (2)	0.052 (1)	0.222 (1)	8 (1)
C(41)	0.443 (3)	0.278 (3)	0.265 (2)	18 (3)
C(42)	0.188 (2)	0.270 (1)	0.290 (1)	8 (1)
C(43)	0.290 (4)	0.376 (1)	0.198 (1)	17 (2)
C(101)	0.107 (2)	0.028 (2)	0.389 (1)	10 (2)
C(102)	0.275 (2)	−0.078 (1)	0.308 (2)	12 (2)
C(103)	0.386 (2)	0.043 (2)	0.404 (1)	16 (2)
B	−0.049 (2)	0.008 (1)	0.1984 (7)	3.3 (7)
F(1)	−0.128 (1)	−0.0091 (9)	0.1651 (6)	9.9 (8)
F(2)	0.014 (1)	−0.097 (9)	0.2273 (8)	12 (1)
F(3)	−0.058 (1)	0.063 (1)	0.2435 (7)	12 (1)
H(1)	0.417 (8)	0.084 (6)	0.104 (4)	1 (2)
C(1S)	0.767 (3)	0.163 (2)	0.408 (2)	11 (2)
C(2S)	0.685 (3)	0.206 (3)	0.446 (2)	12 (2)
C(3S)	0.685 (2)	0.284 (3)	0.429 (2)	11 (2)
C(4S)	0.758 (3)	0.317 (2)	0.379 (1)	10 (2)
C(5S)	0.838 (3)	0.272 (2)	0.347 (2)	10 (2)
C(6S)	0.838 (2)	0.195 (3)	0.360 (2)	10 (2)
C(7S)	0.761 (3)	0.084 (2)	0.418 (2)	16 (3)

[a] The hydride atom is included. [b] Numbers in parentheses are errors in the last significant digit(s). See Figure 2 for atom-labeling scheme. C(1S)–C(7S) are the carbon atoms of the toluene molecule. [c] $B(eq) = \frac{4}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab \cos \gamma)\beta_{12} + (2ac \cos \beta)\beta_{13} + (2bc \cos \alpha)\beta_{23}]$.

was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2|F_o|$. Refinement in this manner yielded the R factors given in Table I. The largest ratio of parameter shift to estimated standard deviation in the final cycle of refinement was less than 0.05, and the largest peak in the difference Fourier map was 0.35 e/Å³, located near the Ta atom. Final non-hydrogen atom positional parameters are given in Table III. Final non-hydrogen atom thermal parameters, hydrogen atom positional and thermal parameters, and observed and calculated structure factors are given in Tables S4–S6 (supplementary material), respectively.

Results

Synthesis of [MH(HOCCOH)(dmpe)₂Cl]Cl Complexes (M = Ta (5), Nb (6)).

The dihydroxyacetylene complexes 5 and 6 are formed from the reaction of the corresponding bis(trimethylsiloxy)acetylene complexes 3 and 4 in THF with dilute aqueous HCl, as shown in eq 4.

$$[M(Me_3SiOCCOSiMe_3)(dmpe)_2Cl] \xrightarrow{HCl}$$
$$M = Ta\ (3),\ Nb\ (4)$$
$$[MH(HOCCOH)(dmpe)_2Cl]Cl\ \ (4)$$
$$M = Ta\ (5),\ Nb\ (6)$$
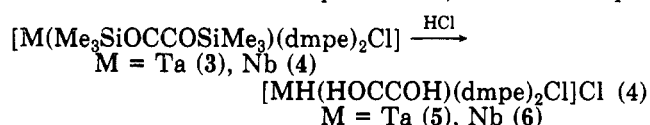
The tantalum dihydroxyacetylene complex 5 can also be obtained by reaction of 3 with either distilled water or methanol. The yields in these latter cases, however, are much lower (<50%) than that seen with aqueous HCl. The reaction of the niobium bis(trimethylsiloxy)acetylene
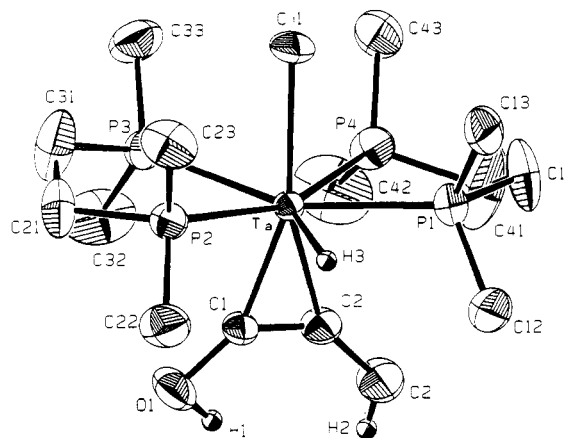
Figure 1. Structure of the [TaH(HOCCOH)(dmpe)₂Cl]⁺ cation (5), showing the atom-labeling scheme. For clarity, the hydrogen atoms are depicted as spheres with $B = 1.0$ Å², and all other atoms show anisotropic thermal ellipsoids at 40% probability.

complex 4 with either distilled water or methanol does not yield the dihydroxyacetylene complex 6; only an intractable mixture of products was obtained.

Crystal Structure of the [TaH(HOCCOH)(dmpe)₂Cl]⁺ Cation.

An ORTEP diagram of the cationic component of 5 is shown in Figure 1. The geometry about the central tantalum atom is pentagonal bipyramidal,[22] with the bound chloride ion and midpoint of the dihydroxyacetylene ligands occupying the axial positions. The equatorial plane, comprised of a hydride, the four phosphorus atoms of two chelating dmpe ligands, and the tantalum, has a mean deviation from planarity of 0.2 (1) Å. Distortion from idealized pentagonal-bipyramidal geometry is mainly due to the constraints of the chelating dmpe ligands. Selected bond lengths and angles are summarized in Table IV.

The geometry of the coordinated dihydroxyacetylene is similar to that of other structurally characterized four-electron-donating alkyne complexes of tantalum (Table V), which have been discussed in more detail elsewhere.[15] The C–C distance of 1.273 (9) Å in the dihydroxyacetylene ligand is shorter than that found in the bis(trimethylsiloxy)acetylene complexes [M(Me₃SiOCCOSiMe₃)(dmpe)₂X] (M = Ta, X = Cl, OTf; M = Nb, X = Cl)[15] and is closer to the value of 1.26 (3) Å measured for the bis(*tert*-butyldimethylsiloxy)acetylene ligand in the carbonyl-bridged complex [(dmpe)₂(CO)Ta(CO)Ta(*t*-BuMe₂SiOCCOSi-*t*-BuMe₂)(dmpe)₂],[23] as indicated in Table V.

The Ta–H distance of 1.9 (2) Å in 5 may be compared to values of 1.80 (1) and 1.774 (3) Å reported from neutron diffraction structural studies of [TaCl(H)₂(PMe₃)₄][24] and [Cp₂Ta(H)₃],[25] respectively, and to the values of 1.94 (11) and 1.85 (11) Å found in the X-ray diffraction structure of [TaCl₂(H)₂(PMe₃)₄].[26] The trans influence[27] of the hydride ligand results in a 0.08-Å lengthening in the av-

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Table IV. Interatomic Distances (Å) and Angles (deg) for [TaH(HOCCOH)(dmpe)₂Cl]⁺ (5)ᵃ

		Bond Lengths		
Ta–C(1)	2.063 (7)		Ta–P(1)	2.556 (2)
Ta–C(2)	2.083 (7)		Ta–P(2)	2.549 (2)
C(1)–O(1)	1.357 (9)		Ta–P(3)	2.645 (2)
C(2)–O(2)	1.363 (9)		Ta–P(4)	2.619 (2)
O(1)–H(1)	1.01 (9)		Ta–Cl(1)	2.528 (2)
O(2)–H(2)	0.8 (1)		Ta–H(3)	1.9 (2)
	C(1)–C(2)		1.273 (9)	

		Bond Angles		
C(1)–Ta–C(2)	35.7 (3)		C(1)–Ta–Cl(1)	160.3 (2)
C(1)–Ta–P(1)	114.4 (2)		C(1)–Ta–P(2)	80.7 (2)
C(1)–Ta–P(3)	83.2		C(1)–Ta–P(4)	105.7 (2)
C(2)–Ta–Cl(1)	162.8 (2)		C(2)–Ta–P(1)	83.7 (2)
C(2)–Ta–P(2)	112.4 (2)		C(2)–Ta–P(3)	106.6 (2)
C(2)–Ta–P(4)	80.6 (2)		Cl(1)–Ta–P(1)	84.23 (7)
Cl(1)–Ta–P(2)	84.30 (7)		Cl(1)–Ta–P(3)	80.67 (7)
Cl(1)–Ta–P(4)	84.45 (7)		P(2)–Ta–P(1)	120.44 (7)
P(2)–Ta–P(3)	75.37 (6)		P(2)–Ta–P(4)	159.70 (7)
P(1)–Ta–P(3)	156.91 (7)		P(1)–Ta–P(4)	75.04 (8)
P(3)–Ta–(4)	86.16 (7)		C(2)–C(1)–O(1)	135.3 (7)
C(2)–C(1)–Ta	73.0 (4)		C(1)–C(2)–O(2)	137.9 (7)
C(1)–C(2)–Ta	71.3 (4)		O(1)–C(1)–Ta	151.7 (5)
O(2)–C(2)–Ta	150.8 (6)		H(1)–O(1)–C(1)	86 (5)
H(2)–O(2)–C(2)	121 (8)		H(3)–Ta–C(1)	85 (5)
H(3)–Ta–C(2)	84 (5)		H(3)–Ta–P(1)	59 (5)
H(3)–Ta–P(2)	66 (5)		H(3)–Ta–P(3)	141 (5)
H(3)–Ta–P(4)	133 (5)		H(3)–Ta–Cl(1)	101 (5)

Intraligand Distances and Angles

bond or angle type	min	max	mean
P–C	1.77 (1)	1.85 (1)	1.81 (2)
(P)C–C(P)			1.47 (4)
Ta–P–C	108.8 (4)	121.7 (3)	115 (4)
C–P–C	100 (1)	106 (1)	103 (2)
P–C–C	112.4 (6)	116.4 (7)	114 (2)

ᵃ Numbers in parentheses are estimated standard deviations in the last digit(s) listed.

Table V. Selected Features of the Coordination Geometry of Various Coordinated Bis(trialkylsiloxy)acetylene Complexes

compd	M–C, Å	(O)C–C(O), Å	C–M–C, deg	ref
[Ta(Me₃SiOCCOSiMe₃)- (dmpe)₂Cl]	2.065 (5)	1.339 (9)	37.8 (3)	15
[Nb(Me₃SiOCCOSiMe₃)- (dmpe)₂Cl]	2.074 (3)	1.310 (6)	36.8 (2)	15
[Ta(Me₃SiOCCOSiMe₃)- (dmpe)₂Cl₀.₈I₀.₂]	2.065 (4)	1.316 (9)	37.2 (2)	15
[Ta(Me₃SiOCCOSiMe₃)- (dmpe)₂OTf]	2.07 (1)	1.36 (1)	38.3 (4)	15
[Ta(i-Pr)₃SiOCCOSiMe₃]- (dmpe)₂Cl]	2.10 (1)	1.40 (2)	35.4 (5)	16c
[(dmpe)₂(CO)Ta(CO)Ta(t- BuMe₂SiOCCOSiMe₂-t- Bu)(dmpe)₂]	2.06 (2)	1.26 (3)	35.5 (7)	23

erage Ta–P bond length of the trans phosphines (P(3) and P(4), 2.632 (2) Å) compared with that for the cis phosphine ligands (P(1) and P(2), 2.553 (5) Å). There is also a chloride ion in the lattice to balance the charge. This ion, which is not bonded to the tantalum center (Ta⋯Cl(2) = 5.477 (3) Å), is hydrogen-bonded to the hydroxy protons on the dihydroxyacetylene ligand, with Cl(2)⋯H(1) and Cl(2)⋯H(2) distances of 2.09 (9) and 2.4 (1) Å, respectively, which can be compared to the range 1.7–2.4 Å that is normally found for such H⋯Cl interactions.[27]

Spectroscopic Properties of 5 and 6. The hydroxyl protons in the ¹H NMR spectrum of 5 appear at 11.0 ppm and exchange with deuterium when D₂O is added to the NMR tube. The hydride ligand resonance, present as a triplet of triplets at 5.1 ppm, does not undergo exchange

under these conditions. The exchangeability of the two hydroxyl protons is also observed in a FAB mass spectrometry experiment in which D₂O was added to the matrix prior to bombardment. The ¹H NMR spectrum of the niobium analogue 6 is nearly identical with that of 5, except that there is no resonance observed for the hydride ligand. The absence of the hydride resonance in 6 is attributed to the large quadrupole moment of niobium (⁹³Nb).

The trans influence of the hydride is also observed in the ³¹P NMR spectrum of 5. When acquired with proton decoupling, the ³¹P NMR spectrum of 5 consists of two resonances at 14.55 and 35.45 ppm. When the spectrum is obtained without proton decoupling, however, the downfield resonance splits into a doublet with $^2J_{PH} = 90$ Hz. Similar behavior is also observed in the ³¹P NMR spectrum of [TaH(CO)₂(dmpe)₂],[28] which has a "capped octahedral" structure with trans carbonyl ligands. The ³¹P NMR spectrum of the niobium dihydroxyacetylene complex 6 shows two very broad resonances at 46.8 and 22.4 ppm with or without proton decoupling. Unlike the Ta complex 5, 6 showed no observable $^2J_{PH}$ value in the downfield resonance when run without proton decoupling. The failure to observe this coupling is attributed to line broadening (width at half-height 140 Hz) caused by the high quadrupole moment of the niobium atom.

The FTIR spectra of 5 and 6 display absorptions at 1604 and 1609 cm⁻¹, respectively, assigned to the dihydroxyacetylene ligands since the former shifts to 1546 cm⁻¹ upon use of ¹³C-enriched [Ta(Me₃SiOCCOSiMe₃)(dmpe)₂Cl]. Stretching bands for the O–H and M–H oscillations could not be identified in the FTIR spectra of either 5 or 6, even with deuterium labeling.[29] The hydroxyl group stretching bands may be lowered in energy because of hydrogen bonding to the chloride counterion and thus be obscured by the methyl and methylene stretching bands. The reason for the failure to observe the metal hydride stretch is unknown, although the presence of hydride is unequivocally established by the ¹H NMR spectrum, FAB mass spectrometry experiment, elemental analysis, and the crystal structure. It is not unusual for metal hydride stretching absorptions to be so weak that they cannot be seen in the infrared spectrum.[30]

Formation and Structure of [TaH(Me₃SiOCCOBF₃)(dmpe)₂Cl]. The hydride complex 7 is formed rapidly when 1 equiv of HBF₄·Me₂O is added to a solution of [Ta(Me₃SiOCCOSiMe₃)(dmpe)₂Cl] (3) in Et₂O, as shown in eq 5. An ORTEP diagram of 7 is shown

$$[Ta(Me_3SiOCCOSiMe_3)(dmpe)_2Cl] \xrightarrow{HBF_4 \cdot Me_2O}$$
$$\mathbf{3}$$
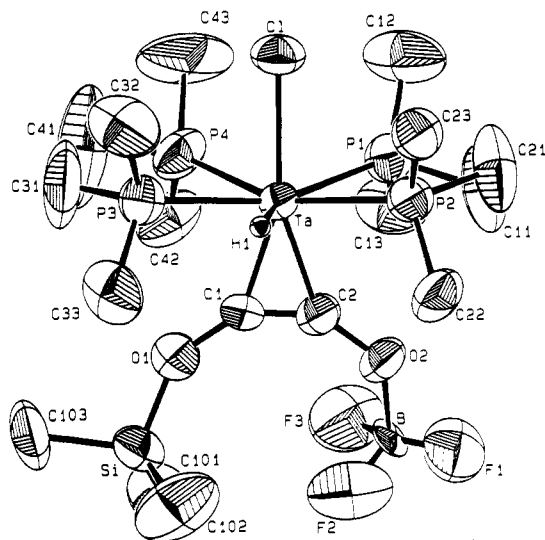$$[TaH(Me_3SiOCCOBF_3)(dmpe)_2Cl] \quad (5)$$
$$\mathbf{7}$$
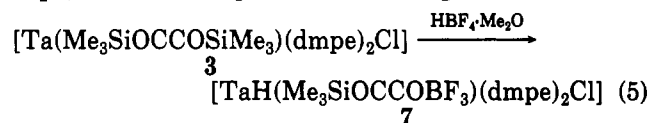
in Figure 2. Complex 7 cocrystallizes with a molecule of toluene in the lattice when the crystals are grown from a mixture of glyme and toluene. The coordination geometry about the tantalum center may be described as pentagonal bipyramidal.[22] The axial positions are occupied by the chloride and the midpoint of the acetylene ligand. The four dmpe phosphorus atoms and the hydride lie in the equatorial plane with a mean deviation from planarity of 0.201 (5) Å. Distortions from idealized pentagonal-bipy-

(28) (a) Tebbe, F. N. *J. Am. Chem. Soc.* **1973**, *95*, 5823. (b) Meakin, P.; Guggenberger, L. J.; Tebbe, F. N.; Jesson, J. P. *Inorg. Chem.* **1974**, *13*, 1025.

(29) The deuterium-labeled [TaD(DOCCOD)(dmpe)₂Cl]Cl was prepared by the reaction of [Ta(Me₃SiOCCOSiMe₃)(dmpe)₂Cl] with D₂O.

(30) Jesson, J. P. In *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Dekker: New York, 1971; p 8.

Figure 2. Structure of [TaH(Me₃SiOCCOBF₃)(dmpe)₂Cl] (7) showing the atom-labeling scheme. For clarity, the hydrogen atom is depicted as a sphere with $B = 1.0$ Å², and all other atoms show anistropic thermal ellipsoids at 40% probability.

Table VI. Interatomic Distances (Å) and Angles (deg) for [TaH(Me₃SiOCCOBF₃)(dmpe)₂Cl]·C₆H₅CH₃ (7·C₆H₅CH₃)[a]

Bond Distances			
Ta–C(1)	2.05 (2)	Ta–P(1)	2.635 (5)
Ta–C(2)	2.10 (2)	Ta–P(2)	2.567 (4)
Ta–Cl	2.527 (4)	Ta–P(3)	2.551 (4)
O(1)–C(1)	1.38 (2)	Ta–P(4)	2.622 (5)
O(2)–C(2)	1.36 (2)	O(2)–B	1.59 (2)
C(1)–C(2)	1.26 (2)	Si–O(1)	1.65 (1)

Bond Angles			
C(1)–Ta–C(2)	35.3 (5)	P(2)–Ta–P(1)	74.3 (2)
C(1)–Ta–Cl	161.5 (5)	P(2)–Ta–P(4)	154.7 (2)
C(1)–Ta–P(3)	83.1 (4)	P(3)–Ta–P(1)	157.0 (2)
C(1)–Ta–P(2)	114.8 (5)	P(3)–Ta–P(2)	122.8 (2)
C(1)–Ta–P(4)	82.2 (5)	P(3)–Ta–P(4)	75.9 (2)
C(1)–Ta–P(1)	104.4 (5)	P(4)–Ta–P(1)	83.6 (2)
C(2)–Ta–Cl	161.2 (4)	Cl–Ta–P(1)	83.2 (2)
C(2)–Ta–P(3)	114.5 (5)	Cl–Ta–P(2)	83.3 (2)
C(2)–Ta–P(2)	83.3 (4)	Cl–Ta–P(3)	83.9 (2)
C(2)–Ta–P(4)	105.2 (5)	Cl–Ta–P(4)	82.0 (2)
C(2)–Ta–P(1)	80.5 (5)	C(2)–C(1)–Ta	74 (1)
C(1)–O(1)–Si	144 (1)	C(1)–C(2)–O(2)	144 (2)
C(2)–O(2)–B	130 (1)	C(1)–C(2)–Ta	70 (1)
O(1)–C(1)–Ta	143 (1)	C(2)–C(1)–O(1)	142 (2)
O(2)–C(2)–Ta	145 (1)		

Intraligand Distances and Angles			
bond or angle type	min	max	mean
P–C	1.75 (3)	1.86 (3)	1.80 (2)
(P)C–C(P)			1.38 (4)
Si–C	1.81 (2)	1.84 (2)	1.83 (2)
B–F	1.09 (2)	1.31 (2)	1.23 (2)
C_solv–C_solv	1.33 (4)	1.39 (4)	1.36 (4)
Ph–Me			1.35 (4)
Ta–P–C	109.1 (7)	123 (1)	115.6 (7)
C–P–C	98 (2)	107 (1)	103 (1)
P–C–C	112 (2)	121 (3)	116 (2)
O–Si–C	104 (1)	111 (1)	108 (1)
C–Si–C	110 (1)	112 (1)	111 (1)
O–B–F	101 (1)	106 (1)	103 (1)
F–B–F	108 (1)	122 (2)	115 (2)
C_solv–C_solv–C_solv	112 (4)	124 (3)	120 (4)
Me–C_solv–C_solv			119 (5)

[a] Numbers in parentheses are estimated standard deviations in the last digit(s) listed. Standard deviations quoted for mean values are the average of the standard deviations for the individual values.

ramidal geometry are caused by the chelating dmpe ligands and the sterically nondemanding nature of the hydride.

Selected bond lengths and angles for compound **7** are reported in Table VI. The geometry about the acetylene ligand in **7** is similar to that of the dihydroxyacetylene complex **5** as well as other known four-electron-donating acetylene complexes of tantalum.[15] As observed for **5**, the acetylenic C–C distance of 1.26 (2) Å is shorter than that found in the bis(trimethylsiloxy)acetylene complexes [M-(Me₃SiOCCOSiMe₃)(dmpe)₂Cl] (M = Ta, X = Cl, OTf; M = Nb, X = Cl)[15] but is identical with that found for the bis(*tert*-butyldimethylsiloxy)acetylene ligand in the carbonyl-bridged complex [(dmpe)₂(CO)Ta(CO)Ta-(Me₃SiOCCOSiMe₃)(dmpe)₂],[23] as shown in Table V. The distance of 2.0 (1) Å for the Ta–H bond is similar to that observed for **5**.

Spectroscopic Properties of 7. The ¹H NMR spectrum of **7** consists of a singlet at 0.18 ppm arising from the trimethylsilyl group, four doublets due to the methyl groups on the phosphines, two very broad signals for the fluxional methylene linkages, and a triplet of triplets for the hydride ligand. The last feature arises because of the larger coupling to the trans ($^2J_{PH}$, 84 Hz) compared with that to the cis ($^2J_{PH}$, 6 Hz) phosphorus atoms. The large trans coupling constant is also observed in the proton-coupled ³¹P NMR spectrum of **7**, which consists of a singlet for the cis phosphines at 14.2 ppm and a doublet for the trans phosphines centered at 34.9 ppm; however, when the spectrum is acquired with proton decoupling, only two resonances, at 34.9 and 14.2 ppm, are seen. The ¹⁹F NMR chemical shift for the BF₃ group in **7** is 2.6 ppm downfield from the shift observed in BF₃·Et₂O.

The FTIR spectrum of **7** reveals a stretching band at 1639 cm⁻¹ assigned to the acetylene ligand. This value is slightly higher than that observed for the dihydroxy-acetylene complexes **5** and **6** and almost 100 cm⁻¹ higher than the stretching frequencies seen for the bis(trimethylsiloxy)acetylene complexes [M-(Me₃SiOCCOSiMe₃)(dmpe)₂X] (M = Ta, X = Cl, OTf; M = Nb, X = Cl).[15] As was the case for complexes **5** and **6**, no Ta–H stretching band was found in the FTIR spectrum of **7**, although deuterium labeling studies were not carried out.

Removal of the Acetylene Ligand in [Ta(*t*-BuMe₂SiOCCOSiMe₂-*t*-Bu)(dmpe)₂Cl] (8) by Hydro-

genation To Form (R₃SiOCH=CHOSiR₃). The bis-(*tert*-butyldimethylsiloxy)acetylene ligand in **8**, which is formed by the reductive coupling of two carbonyl ligands in **1**, can be removed with the C–C bond intact by hydrogenation to form the alkene with the use of synthesis gas in the presence of either 5% palladium on carbon or Wilkinson's catalyst. This conversion can also be accomplished by using pure hydrogen in the presence of 5% palladium on carbon, but hydrogenation occurs at least 20 times slower and with lower yields under these conditions. Although all of the hydrogenations reported here were performed in glyme, THF can also be employed as solvent without appreciably affecting the rate or yield. An authentic sample of the alkene (*t*-BuMe₂SiO)CHCH-(OSiMe₂-*t*-Bu) (9) was prepared by using a variation of a literature method[18] in which *t*-BuMe₂SiCl was substituted for Me₃SiCl, as shown in eq 6. Coinjection of an authentic sample of 9 along with a sample of the hydrogenation product into the gas chromatograph confirmed its identification as the alkene (9).

$$\text{HC(O)O-}n\text{-Pr} \xrightarrow[\text{2 } t\text{-BuMe}_2\text{SiCl}]{\text{2Na}}$$
$$(t\text{-BuMe}_2\text{SiO})\text{HC}{=}\text{CH(OSiMe}_2\text{-}t\text{-Bu)} \quad (6)$$
$$\mathbf{9}$$
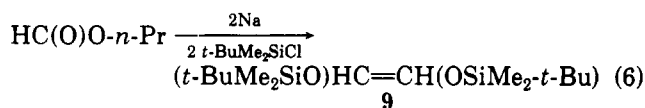
Compound **9** was also identified and characterized by
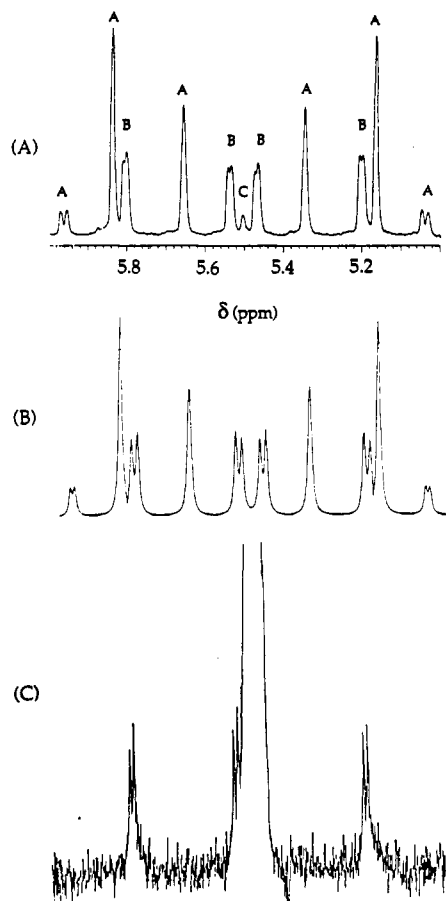
Figure 3. (A) Proton NMR spectrum of (*t*-BuMe$_2$SiO)CHCH-(OSiMe$_2$-*t*-Bu) (9) synthesized from 90% ^{13}C-enriched [Ta(*t*-BuMe$_2$SiOCCOSiMe$_2$-*t*-Bu)(dmpe)$_2$Cl] (8). Peaks labeled A are due to ^{13}C–^{13}C-enriched alkene, peaks labeled B are due to ^{13}C–^{12}C-enriched alkene, and the peak labeled C is due to ^{12}C–^{12}C alkene. (B) Overlay of the computer simulations for the proton NMR spectra of ^{13}C–^{13}C- and ^{13}C–^{12}C-labeled alkenes. (C) Proton NMR spectrum of (*t*-BuMe$_2$SiO)CHCH(OSiMe$_2$-*t*-Bu) showing a mixture of ^{13}C–^{12}C- and ^{12}C–^{12}C-labeled alkenes.

its spectroscopic properties. The ^{1}H NMR spectrum of 9 exhibits three singlets at 5.51 (=CH), 0.99 (CCH$_3$), and 0.11 (SiCH$_3$) ppm in a 1:9:6 ratio, comparable to the chemical shifts of 5.4 (=CH) and 0.25 (SiCH$_3$) ppm reported for (Me$_3$SiO)CHCH(OSiMe$_3$).[18] When the alkene was synthesized with use of 90% ^{13}C-enriched [Ta(CO)$_2$-(dmpe)$_2$Cl] (1), the ^{13}C{^{1}H} NMR spectrum contained a single peak at 125.6 ppm. The ^{1}H NMR spectrum of the ^{13}C-labeled alkene, however, revealed a 17-line pattern for the vinyl protons (Figure 3A). This spectrum arises from the presence of doubly labeled alkene (^{13}C=C^{13}), which appears as an 8-line AA'XX' pattern, along with some singly labeled alkene (^{13}C=C^{12}), which appears as an 8-line AA'X pattern, and a small fraction of unlabeled alkene, which appears as a singlet. To confirm this assignment, the spectra of the AA'XX' and AA'X components were simulated and overlaid, as shown in Figure 3B. The coupling constants used for these simulations are $^3J_{HH}$ = 2.32 Hz, $^1J_{CC}$ = 92.22 Hz, $^1J_{CH}$ = 180.87 Hz, and $^2J_{CH}$ = 19.88 Hz. Further support for this assignment comes from the ^{1}H NMR spectrum of the alkene synthesized from 10% ^{13}C-enriched 1, which has a singlet for the unlabeled alkene and an 8-line AA'X spectrum for the singly labeled alkene, as shown in Figure 3C. The FTIR spectrum of 9 contains peaks at 3041 and 1663 cm^{-1} for the vinyl C—H and C=C double-bond stretches, respectively. These values match those reported in the literature for (Me$_3$SiO)HC=CH-(OSiMe$_3$),[18] namely, 3040 and 1659 cm^{-1}.

Discussion

Formation and Characterization of [MH(HOC-COH)(dmpe)$_2$Cl]$^+$ (M = Ta (5), Nb (6)). The reaction leading to the dihydroxyacetylene complexes 5 and 6 is formally comprised of two steps. One is protiolysis of the trimethylsilyl groups on [M(Me$_3$SiOCCOSiMe$_3$)(dmpe)$_2$Cl] (M = Ta (3), Nb (4)) to yield the dihydroxyacetylene ligand along with bis(trimethylsilyl) ether or trimethylsilanol. The other step involves reaction with protons in an oxidative-addition step. If no HCl is added to the reaction, as in the case when distilled water or methanol is used, chloride ion can be formed in situ by hydrolysis of a Ta–Cl bond. The requirement for chloride as a counterion explains why the yield of 5 is so much lower when distilled water or methanol is added to a solution of 3 than when aqueous HCl is employed. In what may be a similar reaction, the diiron complex [Fe$_2$(Me$_3$SiOC)$_4$(CO)$_6$], which contains a metallacyclopentadiene fragment, reacts with anhydrous HCl, releasing 2 equiv of Me$_3$SiCl.[31] Partial characterization of the product from this reaction revealed the presence of hydroxyl groups, but further details have not been reported.

Spectroscopic data for compounds 5 and 6 are consistent with the solid-state geometry observed in the crystal structure of 5. Although the stretching bands for the hydride and hydroxyl hydrogen atoms are not observed in the FTIR spectrum of either 5 or 6, FAB mass spectrometric experiments support the presence of two hydroxyl protons in the structure of 5 by revealing two exchangeable protons. The existence of the hydride ligand is further confirmed by the observation of a triplet of triplets pattern at 5.06 ppm in the ^{1}H NMR spectrum of 5 that is similar to, although shifted from, the triplet of triplets at -4.17 ppm seen for [TaH(CO)$_2$(dmpe)$_2$].[28]

Formation and Characterization of [TaH-(Me$_3$SiOCCOBF$_3$)(dmpe)$_2$Cl] (7). In an effort to model the oxidative-addition step required to form 5 and 6, 1 equiv of HBF$_4$·Me$_2$O was added to a solution of [Ta-(Me$_3$SiOCCOSiMe$_3$)(dmpe)$_2$Cl] (3). While the expected product [TaH(Me$_3$SiOCCOSiMe$_3$)(dmpe)$_2$Cl]BF$_4$ may be formed initially, this complex is unstable to formal loss of Me$_3$SiF, forming the observed product, as shown in eq 7. Attempts to isolate the postulated initial product by using 1 equiv of anhydrous HCl instead of HBF$_4$·Me$_2$O were unsuccessful.

$$[\text{TaH}(\text{Me}_3\text{SiOCCOSiMe}_3)(\text{dmpe})_2\text{Cl}]\text{BF}_4 \xrightarrow{-\text{Me}_3\text{SiF}}$$
$$[\text{TaH}(\text{Me}_3\text{SiOCCOBF}_3)(\text{dmpe})_2\text{Cl}] \quad (7)$$
$$\mathbf{7}$$
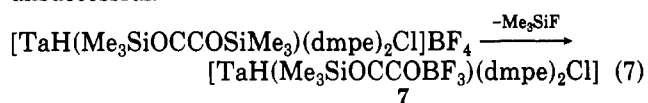
Spectroscopic data for 7 indicate that the geometry observed in the solid state is retained in solution. As observed for compounds 5 and 6, the Ta–H stretching mode is too weak[30] to be located in the FTIR spectrum of 7. Again, however, the presence of a hydride ligand is evidenced by the triplet of triplets pattern observed at 5.13 ppm in the proton NMR spectrum. This type of pattern arises from the greater $^2J_{PH}$ coupling with the two phosphines trans to the hydride versus that of those cis to the hydride. The pattern was also observed for [TaH(CO)$_2$-(dmpe)$_2$],[28] in which the hydride caps an octahedral face and the carbonyls are in a trans orientation.

Efforts to model the protiolysis step involved in the formation of 5 and 6 by addition of 1 equiv of distilled water or 2 equiv of methanol to a solution of [Ta-(Me$_3$SiOCCOSiMe$_3$)(dmpe)$_2$Cl] (3) failed to produce the

(31) (a) Nasta, M. A.; MacDiarmid, A. G.; Saalfeld, F. E. *J. Am. Chem. Soc.* **1972,** 94, 2449. (b) Bennett, M. J.; Graham, W. A. G.; Smith, R. A.; Stewart, R. P., Jr. *J. Am. Chem. Soc.* **1973,** 95, 1684.
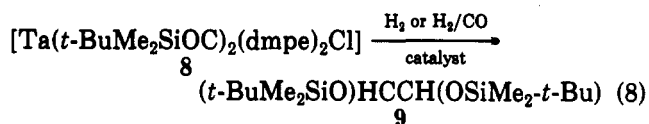
desired dihydroxyacetylene complex [Ta(HOCCOH)-(dmpe)$_2$Cl]. The only products observed from this reaction were [TaH(HOCCOH)(dmpe)$_2$Cl]Cl and a yellow material. The latter may be a metal-containing species in which the Ta–Cl bond has been hydrolyzed. It seems likely, therefore, that the first step in the formation of 5 and 6 is oxidative of 3 or 4 by HCl to form [MH-(Me$_3$SiOCCOSiMe$_3$)(dmpe)$_2$Cl]Cl (M = Ta, Nb), followed by protiolysis of the trimethylsilyl groups to afford the observed product.

Bonding of the Acetylene Ligands in 5–7. If the acetylene ligands in 5–7 are considered to be neutral four-electron-donating alkynes, then the formally d^2 M(III) 18-electron complexes might be expected to exhibit some color arising from d–d transitions. All three hydride complexes are colorless, however. One possible explanation for the lack of color in 5–7 is the contribution of resonance forms II and III to the electronic structures. Significant
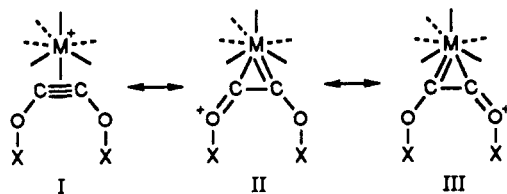
contribution of such canonical forms to the electronic structure of these complexes raises the formal oxidation state to V, conferring a d^0 electronic configuration that would explain the lack of color in these complexes.

Hydrogenation of the Disiloxyacetylene Ligand in 8 To Form Disiloxyethylene. Removal of the disiloxy-acetylene ligand in [Ta(t-BuMe$_2$SiOCCOSiMe$_2$-t-Bu)-(dmpe)$_2$Cl] (8) as an alkene was accomplished via hydrogenation with either pure hydrogen or synthesis gas in the presence of 5% palladium on carbon or [Rh(PPh$_3$)$_3$Cl], Wilkinson's catalyst, as shown in eq 8. Hydrogenation

$$[Ta(t\text{-}BuMe_2SiOC)_2(dmpe)_2Cl] \xrightarrow[\text{catalyst}]{H_2 \text{ or } H_2/CO}$$
$$\mathbf{8}$$
$$(t\text{-}BuMe_2SiO)HCCH(OSiMe_2\text{-}t\text{-}Bu) \quad (8)$$
$$\mathbf{9}$$

of this kind was also observed for the complex [Ta-(Me$_3$SiOCCOSiMe$_3$)(dmpe)$_2$Cl]; however, the resultant bis(trimethylsiloxy)ethylene product is unstable under the reaction conditions. Although not isolated from the reaction mixture, this species was observed by GC/mass spectrometry.

The available evidence suggests that the alkene product (9) has a cis stereochemistry. Spectroscopic data indicate the presence of only one isomer; there is a single C=C bond stretch in the FTIR spectrum and only one vinyl proton resonance in ^{1}H NMR spectrum. Synthesis of bis(trimethylsiloxy)ethylene by the route shown in eq 9,

$$HC(O)O\text{-}n\text{-}Pr \xrightarrow[\text{2Me}_3SiCl]{2Na} (Me_3SiO)HC=CH(OSiMe_3) \quad (9)$$

the same method employed to synthesize an authentic sample of 9 (cf. eq 6), was reported[18] to give pure cis alkene that could be isomerized in the presence of acetophenone by using a mercury lamp. Later, however, it was found[32] that a mixture of cis and trans bis(trimethylsiloxy)ethylene is produced under the same reaction conditions. The low value of 2.32 Hz for $^3J_{HH}$ found from the simulation of the proton NMR spectrum of 9 when the alkene is singly or doubly ^{13}C enriched supports a cis stereochemistry; if the alkene were in the trans configuration, a larger coupling constant would be expected.[33] The cis geometry of 9 is

also consistent with the general observation that most alkyne hydrogenations with palladium or Wilkinson's catalyst yield products with this stereochemistry.[34]

Preliminary attempts to hydrogenate the olefin further to an alkane have thus far been unsuccessful. When a solution of 8 in glyme in the presence of 5% palladium on carbon was placed in a bomb and pressurized to 1400 psi with synthesis gas for 18 h, the only observed product was 9. The failure to hydrogenate 9 to the alkane may be due to poisoning of the palladium catalyst caused by dmpe released from the tantalum center during the reaction. Hydrogenation of purified 9 to the corresponding alkane should be possible once the correct conditions can be found.

It is interesting to note that hydrogenation of 8 in the presence of palladium on carbon is at least 20 times faster when synthesis gas is employed rather than pure hydrogen. One possible explanation for this difference is that CO in synthesis gas displaces the acetylene ligand from the metal center before hydrogenation occurs, thus making the acetylene more accessible to hydrogenation at the palladium. This explanation, however, is not supported by the observation that exposure of a solution of [Ta-(Me$_3$SiOCCOSiMe$_3$)(dmpe)$_2$Cl] (3) to an atmosphere of CO does not displace the acetylene ligand. Instead, it appears that in this reaction some of the phosphines are displaced by carbonyls, as evidenced by the appearance of peaks at −47 and −48 ppm in the phosphorus NMR spectrum of the reaction mixture. The peak at −48 ppm is assigned to free dmpe, while that at −47 ppm may be attributed to a dmpe ligand having one end still bound to the metal center. This type of displacement may account for the enhanced rate seen when 8 is hydrogenated by use of synthesis gas compared with pure hydrogen. Displacement of one or more phosphines by less sterically demanding carbonyl ligands would relieve steric crowding about the metal center, possibly facilitating hydrogenation. The FTIR spectrum of the reaction mixture after hydrogenation of 8 with synthesis gas in the presence of 5% palladium on carbon reveals four major metal–carbonyl stretching bands at 2045, 1968, 1931, and 1884 cm^{-1}. The phosphorus NMR spectrum of this same reaction mixture is quite complicated, suggesting the presence of several metal-containing products. The phosphorus NMR spectrum does, however, contain peaks at −47 and −48 ppm.

Conclusions

The reaction of [M(Me$_3$SiOCCOSiMe$_3$)(dmpe)$_2$Cl] (M = Ta (3), Nb (4)), formed from the reductive coupling of two carbonyl ligands in [M(CO)$_2$(dmpe)$_2$Cl] (M = Ta (1), Nb (2)), with aqueous HCl, yields the novel dihydroxy-acetylene complexes [MH(HOCCOH)(dmpe)$_2$Cl]Cl (M = Ta (5), Nb (6)). This transformation can also be accomplished for the tantalum analogue with the use of other proton sources such as distilled water or methanol, although in much lower yields. Single-crystal X-ray diffraction studies on 5 provide the first structural characterization of a dihydroxyacetylene complex.

Reaction of 3 with HBF$_4$·Me$_2$O yields the hydride complex [TaH(Me$_3$SiOCCOBF$_3$)(dmpe)$_2$Cl] (7), which has also been structurally characterized. Isolation of 7, together with the observation that 3 does not react with 1 equiv of water or 2 equiv of methanol to yield [Ta(HOCCOH)-

(32) Le Goaller, R.; Pierre, J. L. *Can. J. Chem.* 1977, *55*, 757.

(33) See: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 3rd ed.; Wiley: New York, 1974; p 226.

(34) March, J. *Advanced Organic Chemistry*; McGraw-Hill: New York, 1977.

(35) Vrtis, R. N.; Rao, C. P.; Lippard, S. J. Unpublished results.

(dmpe)$_2$Cl], indicates that the first step in the formation of **5** and **6** is oxidative addition of HX. This step would then be followed by protiolysis of the trimethylsilyl groups, yielding the final product.

It has also been discovered in these studies that the disiloxyacetylene ligand in [Ta(*t*-BuMe$_2$SiOCCOSiMe$_2$-*t*-Bu)(dmpe)$_2$Cl] (**8**) can be removed from the metal center with the C–C bond intact via hydrogenation by using hydrogen or synthesis gas in the presence of either 5% palladium on carbon or Wilkinson's catalyst. The resulting alkene, (*t*-BuMe$_2$SiO)CHCH(OSiMe$_2$-*t*-Bu) (**9**), has been characterized by proton and carbon NMR spectroscopy along with comparison to an authentic sample. Compound **9** appears to adopt a cis stereochemistry, which is consistent with this type of hydrogenation reaction. While the chemistry of **9** has not yet been explored further, it may be a potential precursor to useful organic substrates. Investigations of the possibility of catalytic reductive coupling followed by hydrogenation are currently in progress.[36]

Supplementary Material Available: Tables S1, S2, S4, and S5, reporting non-hydrogen atom thermal parameters and hydrogen atom positional and thermal parameters for [TaH(HOCCOH)(dmpe)$_2$Cl]Cl and [TaH(Me$_3$SiOCCOBF$_3$)(dmpe)$_2$Cl]·C$_6$H$_5$CH$_3$ (5 pages); Tables S3 and S6, giving observed and calculated structure factors for the two compounds (65 pages). Ordering information is given on any current masthead page.

(36) Note added in proof: Extension of this work to vanadium has led to the isolation and full characterization of the complexes [V-(Me$_3$SiOC≡COSiMe$_3$)(dmpe)$_2$X] and [V(Me$_3$SiOC≡COSiMe$_3$)-(dmpe)$_2$]X, which react directly with H$_2$ in the absence of an external catalyst to form *cis*-bis(trimethylsilyloxy)ethylene (Protasiewicz, J. D.; Lippard, S. J. Submitted for publication).

(η^5-Cyclopentadienyl)(η^7-cyclooctatrienyl)vanadium: Synthesis via Stereoselective Protonation of the (η^5-Cyclopentadienyl)(cyclooctatetraene)vanadate Anion. NMR and ESR Properties and Evidence for Metal-Assisted H-Migration

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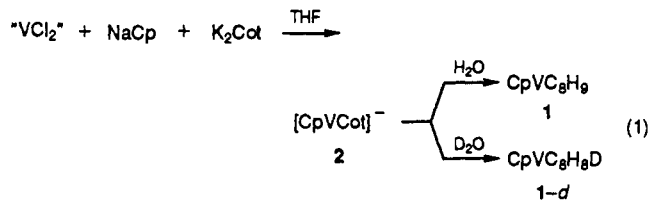
(η^5-Cyclopentadienyl)(η^7-cyclooctatrienyl)vanadium (**1**) can be obtained by a one-pot reaction in THF by starting from VCl$_2$, NaCp (Cp = cyclopentadienyl), and K$_2$Cot (Cot = cyclooctatetraene) as simple educts and with subsequent hydrolysis. The monodeuterated derivative **1-*d*** is obtained on hydrolysis of the reaction mixture with D$_2$O. EPR data for **1** show a paramagnetic V(d^5) mixed sandwich compound with a nondegenerate doublet ground state. By means of ^{1}H and ^{2}H NMR spectroscopy strong evidence is found for a stereoselective exo addition of D$^+$ to the [CpVCot]$^-$ anion and a subsequent metal-assisted H-migration.

Protonation of a metal-coordinated cyclooctatetraene (Cot) can occur stereoselectively via an exo or an endo attack with respect to the metal center. For both pathways some examples have been described previously.[1–3] However, in these examples no migration of hydrogen within the Cot ligand was reported. We wish to give an account of a stereoselective protonation of the anionic Cot complex [CpVCot]$^-$ to CpVC$_8$H$_9$ (**1**) followed by a metal-assisted hydrogen migration.

Results and Discussion

The paramagnetic cyclooctatrienyl complex CpVC$_8$H$_9$ (**1**) was first prepared by the "isopropyl Grignard" method.[4] We found a simpler way to synthesize the highly oxygen sensitive complex **1** in good yield in a one-pot reaction (1). For (**1**) the vanadium(II) chloride, which is obtained by the reduction of VCl$_3$ by Zn, can be used directly without

"VCl$_2$" + NaCp + K$_2$Cot $\xrightarrow{\text{THF}}$

$$[\text{CpVCot}]^- \quad \overset{\text{H}_2\text{O}}{\underset{\text{D}_2\text{O}}{\diagup\diagdown}} \quad \begin{array}{l} \text{CpVC}_8\text{H}_9 \\ \textbf{1} \\ \text{CpVC}_8\text{H}_8\text{D} \\ \textbf{1-}d \end{array} \quad (1)$$

$$\textbf{2}$$

"VCl$_2$" = $^1/_4$[V$_2$(μ-Cl)$_3$(THF)$_6$]$_2$[Zn$_2$Cl$_6$]^5 or $^1/_2$[V$_2$(μ-Cl)$_3$(THF)$_6$][AlCl$_2$Et$_2$]^6

further purification. The advantage of this reaction is the facile one-pot synthesis of **1** from simply prepared starting

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