3504 Organometallics 1991, 10, 3504-3512

Synthesis and Characterization of Chiral (Hydridotris(3,5-dimethylpyrazolyl)borato)tungsten(II) Alkyne Complexes

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Received March 11, 1991

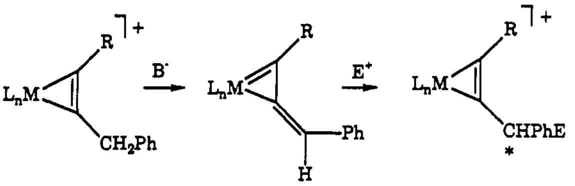
A series of neutral (hydridotris(3,5-dimethylpyrazolyl)borato)tungsten(II) alkyne complexes of the type $\mathrm{Tp'W(CO)(I)(RC{\equiv}CR')}$ (R = R' = Me; R = Ph, R' = H, Me) has been synthesized. Cationic complexes of the form $\mathrm{[Tp'(L)(CO)W(RC{\equiv}CR')][BF_4]}$ (L = CO, $\mathrm{CH_3CN}$; R = R' = Me; R = Ph, R' = Ph, Me, H; R = H, R' = $\mathrm{CMe{=}CH_2}$) and $\mathrm{[Tp'W(CO)(L)(PhC{\equiv}CMe)][BF_4]}$ (L = $\mathrm{P(OMe)_3}$, NCEt) have also been synthesized. These new complexes have been characterized by NMR, IR, and elemental analyses. In addition, single-crystal X-ray diffraction was used to structurally characterize two complexes, $\mathrm{[Tp'W(CO)(MeCN)(PhC{\equiv}CPh)][BF_4]}$ and $\mathrm{Tp'W(CO)(I)(PhC{\equiv}CMe)}$. Crystals of the former are of the orthorhombic space group $P2_12_12_1$, $Z = 4$, with unit cell dimensions of $a = 15.671$ (4) Å, $b = 14.709$ (3) Å, and $c = 15.053$ (6) Å. Refinement of 214 variables led to an R value of 6.0% and $R_w = 4.4\%$ over 2141 reflections. The latter crystallized in the monoclinic space group $P2_1/n$ with unit cell dimensions of $a = 11.368$ (7) Å, $b = 15.241$ (6) Å, $c = 17.300$ (3) Å, and $\beta = 94.24$ (4)°, with $Z = 4$. In this case refinement of 336 variables led to $R = 7.3\%$ and $R_w = 9.5\%$ over 3377 reflections.

Introduction

Cationic metal complexes with four-electron-donor alkyne ligands which are chiral at metal offer a range of potential ligand-based reactions. The number of cationic alkyne monomers with four-electron-donor alkyne ligands is relatively small.[1] The importance of $\pi_\perp$ donation from the alkyne in numerous monomeric group 6 metal complexes such as $\mathrm{M(CO)(RC_2R')L_2X_2}$,[2] $\mathrm{ML(RC_2R')(S_2CNR''_2)_2}$,[3] and $\mathrm{CpM(RC_2R')LX}$[4] has been documented. Stepwise reduction of coordinated acetonitrile in $\mathrm{[Tp'(CO)(MeCN)W(PhC_2Me)]^+}$ (Tp' = hydridotris(3,5-dimethylpyrazolyl)borate) to ethylamine has been communicated.[5] The flexible electron-donating ability of the alkyne ligand, which has been employed to stabilize other reactive transition-metal species,[1] allows isolation of each intermediate during the reduction sequence. We have also succeeded in reducing phenylacetylene in $\mathrm{[Tp'(CO)_2W(PhC_2H)]^+}$ to a β-agostic carbene in $\mathrm{\{Tp'(CO)_2W[{=}C(Me)Ph]\}}$.[6] No analogous Cp compound has been prepared.

Chiral transition-metal complexes are capable of controlling the stereochemical outcome of ligand elaboration reactions. Chiral metal monomers such as $\mathrm{[CpMn(NO)(CO)(PR_3)][PF_6]}$ have provided a rich chemistry of enantioselective transformations.[7] Optically active rhenium complexes of the type $\mathrm{[CpRe(NO)(PR_3)L]^+}$ undergo highly stereoselective ligand-based transformations.[8] Chiral carbene complexes such as $\mathrm{[Cp(CO)(PR_3)Fe{=}CHCH_3]^+}$ have been utilized in carbene-transfer reactions to form optically pure cyclopropanes with high enantioselectivity.[9] Organic transformations of η^2-acyl ligands have been achieved with use of the $\mathrm{Tp'(CO)[P(OPh)_3]Mo[\eta^2\text{-}C(O)CH_2R]}$ system to control stereochemistry.[10]

Similar ligand elaboration reactions have recently been extended to four-electron-donor alkyne chemistry, where deprotonation of cationic η^2-alkyne complexes at C_β generates η^2-allenyl complexes which react with electrophiles to yield substituted alkyne products (eq 1).[11] As mentioned above, the use of Tp'(CO)LW as a chiral auxiliary has produced highly stereoselective reactions for acyl ligands, and stereoselective alkyne elaboration in $\mathrm{Tp'(CO)IW(PhC_2CH_3)}$ has now been achieved.[12]



(1)

Synthetic and theoretical relationships also exist between four-electron-donor alkynes and η^2-vinyl ligands.[13] Indeed, another significant mode of reactivity for cationic four-electron-donor alkyne complexes involves addition of nucleophiles to form η^2-vinyls. Green and co-workers have reported that cationic alkyne complexes of the type $\mathrm{[CpL_2Mo(RC_2R)]^+}$ react with hydride donors or carbon-based nucleophiles to form neutral η^2-vinyl complexes (eq 2).[13] Addition of heteroatom nucleophiles to neutral electron-poor (eq 3)[14] or terminal (eq 4)[15] alkyne complexes to form η^2-vinyl ligands has also been reported. Rearrangement to η^3-allyls has been observed when alkyne ligands which contain β-hydrogens add nucleophiles.[13]

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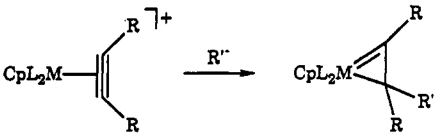
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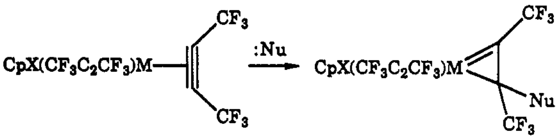
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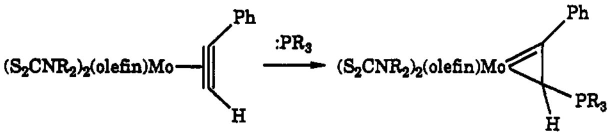
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We now report syntheses and spectral properties of four-electron-donor alkyne complexes of the type [Tp′(CO)LW(RC$_2$R′)$^{n+}$ (L = I, *n* = 0; L = CO, MeCN, EtCN, P(OMe)$_3$, *n* = 1), which provide an array of chiral alkyne complexes for use as reagents. Crystal structures of [Tp′W(CO)(MeCN)(PhC$_2$Ph)][BF$_4$] and Tp′(CO)IW(PhC$_2$Me) are also reported.

Experimental Section

Materials and Procedures. All manipulations were performed under an atmosphere of purified nitrogen gas with use of standard Schlenk techniques. Solvents were purified as follows: CH_2Cl_2 was distilled from P_2O_5; Et_2O, THF, and hexane were distilled from potassium benzophenone ketyl; acetonitrile was distilled from CaH_2; other solvents were purged with nitrogen prior to use. Reagents were obtained from commercial sources and used as received. KTp′,[16] [Et$_4$N][Tp′W(CO)$_3$],[17] Tp′W(CO)$_3^•$,[18] and [Cp$_2$Fe][PF$_6$][19] were prepared according to literature procedures.

Infrared spectra were recorded on a Mattson Polaris FT IR spectrometer as solids in KBr pellets or as solutions in 0.10-mm CaF_2 cells. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-400 (400-MHz) spectrometer. Chemical shifts are reported in ppm downfield relative to TMS. Microanalyses were performed by Oneida Research Services Inc., Whitesboro, NY, or Galbraith Laboratories, Knoxville, TN.

Syntheses. Tp′W(CO)$_3$I (1). To a slurry of [NEt$_4$][Tp′W(CO)$_3$] (5.0 g, 7.2 mmol) in CH_2Cl_2 (100 mL) was added portionwise elemental iodine (1.83 g, 7.2 mmol). The mixture was stirred for 1 h. The resulting red-brown solution was filtered into another flask, and the solvent was evaporated. The oily residue was chromatographed on alumina with toluene as the eluent. The dark solution that was collected was reduced to ca. 10 mL and put in the freezer after 80 mL of MeOH had been added. The dark red-brown crystals which formed were isolated by filtration and dried in vacuo to yield pure Tp′W(CO)$_3$I (4.48 g, 90%). IR (KBr, cm^{-1}): ν_{CO} = 2012, 1915, 1872. (a) At 22 °C: ^{1}H NMR (CD_2Cl_2, δ) 6.03 (broad, 3 H, Tp′C*H*), 2.49, 2.34 (broad, 18 H, Tp′CC*H*$_3$); ^{13}C NMR (CD_2Cl_2, δ) 231.8 (broad, 3 *C*O), 153.9, 146.5 (broad, Tp′*C*CH$_3$), 108.2 (broad, Tp′*C*H), 18.5, 13.0 (broad, Tp′C*C*H$_3$). (b) At −80 °C: ^{1}H NMR (CD_2Cl_2, δ) 6.04, 6.01 (2:1, Tp′C*H*), 2.47, 2.40, 2.31, 2.11 (6:3:6:3, Tp′CC*H*$_3$); ^{13}C NMR (CD_2Cl_2, δ): 242.0 (broad, *C*O), 226.4 (broad, $^1J_{WC}$ = 130 Hz, 2 *C*O), 152.8, 151.1, 147.6, 145.8 (2:1:1:2, Tp′*C*CH$_3$), 107.5, 107.1 (1:2, Tp′*C*H), 17.9, 15.4, 13.1, 12.6 (2:1:1:2, Tp′C*C*H$_3$). (c) The Tp′ protons at 6.04 and 6.01 (2:1) coalesced at −5 °C; ΔG^* = 13.9 kcal/mol. Anal. Calcd for $WC_{18}H_{22}N_6O_3IB$: C, 31.23; H, 3.18; N, 12.15. Found: C, 31.45; H, 3.24; N, 12.08.

Tp′(CO)(PhC$_2$Me)WI (2). A slight excess of 1-phenylpropyne (1.4 mL, 11 mmol) was added to a dark brown toluene solution of Tp′(CO)$_3$WI (7.0 g, 10 mmol). The solution was refluxed for 10 h, and the resulting green solution was passed through an alumina column. A single green band was eluted, toluene was evaporated, and the solid was recrystallized from CH_2Cl_2/Et_2O to form dark green crystals (6.8 g, 90%). Tp′(CO)(PhC$_2$Me)WI. IR (KBr, cm^{-1}): ν_{CO} = 1905. ^{1}H NMR (CD_2Cl_2, δ): 7.25, 6.72 (m, C$_6$*H*$_5$), 5.93, 5.89, 5.73 (1:1:1, Tp′C*H*), 3.58 (PhC$_2$C*H*$_3$), 2.94, 2.65, 2.55, 2.42, 1.76, 1.37 (3:3:3:3:3:3, Tp′CC*H*$_3$). ^{13}C NMR (CD_2Cl_2, δ): 233.3 ($^1J_{WC}$ = 145 Hz, *C*O), 208.9 ($^1J_{WC}$ = 50 Hz, Ph*C*CMe), 206.5 ($^1J_{WC}$ = 12 Hz, $^2J_{HC}$ = 10 Hz, PhC*C*CH$_3$), 155.6, 150.2, 146.1, 145.7, 144.5 (Tp′*C*CH$_3$), 137.7, 129.0, 128.8 (*C*$_6$H$_5$), 108.8, 108.4, 107.2 (Tp′*C*H), 22.8, 18.5, 18.2, 16.3, 13.0, 12.9, 12.8 (PhC$_2$*C*H$_3$ and Tp′C*C*H$_3$). Anal. Calcd for $WC_{25}H_{30}N_6OBI$: C, 39.92; H, 3.99; N, 11.18. Found: C, 39.06; H, 3.94; N, 10.77.

Tp′(CO)(PhC$_2$H)WI (3; Green, 89%). IR (KBr, cm^{-1}): ν_{CO} = 1909, ν_{BH} = 2548, ν_{CN} = 1545. ^{1}H NMR (CD_2Cl_2, δ): major isomer (60%), 13.58 (PhC$_2$*H*), 7.22, 6.72 (m, C$_6$*H*$_5$), 5.94, 5.89, 5.71 (1:1:1, Tp′C*H*), 2.88, 2.61, 2.51, 2.38, 1.79, 1.52 (3:3:3:3:3:3, Tp′CC*H*$_3$); minor isomer (40%) 12.58 (PhC$_2$*H*), 8.00, 7.62, 7.55 (m, C$_6$*H*$_5$), 6.18, 5.90, 5.71 (1:1:1, Tp′C*H*), 2.88, 2.60, 2.58, 2.48, 2.38, 1.59 (3:3:3:3:3:3, Tp′CC*H*$_3$). ^{13}C NMR (CD_2Cl_2, δ): major isomer, 232.9 ($^1J_{WC}$ = 140 Hz, *C*O), 213.3 ($^1J_{WC}$ = 48 Hz, Ph*C*CH), 197.8 (PhC*C*H), 155.6–136.6 (Tp′*C*CH$_3$ and *C*$_{ipso}$), 130.7, 129.1 (Ph), 108.6, 108.4, 107.5 (Tp′*C*H), 18.8, 18.2, 16.8, 13.0, 12.8, 12.7 (Tp′C*C*H$_3$). Anal. Calcd for $WC_{24}H_{28}N_6OBI$: C, 39.05; H, 3.80; N, 11.39. Found: C, 39.12; H, 4.00; N, 11.05.

Tp′(CO)(MeC$_2$Me)WI (4; Blue-Green, 60%). IR (KBr, cm^{-1}): ν_{CO} = 1906, ν_{BH} = 2549, ν_{CN} = 1546. ^{1}H NMR (CD_2Cl_2, δ): 6.19, 5.91, 5.77 (1:1:1, Tp′C*H*), 3.33, 2.91 (C*H*$_3$C$_2$C*H*$_3$), 2.67, 2.63, 2.49, 2.41, 1.49 (3:3:3:6:3, Tp′CC*H*$_3$). ^{13}C NMR (CD_2Cl_2, δ): 233.8 ($^1J_{WC}$ = 146 Hz, *C*O), 212.9 ($^1J_{WC}$ = 49 Hz, Me*C*≡), 202.2 ($^1J_{WC}$ = 13 Hz, ≡*C*Me), 155.4, 154.3, 150.0, 145.5, 144.4 (Tp′*C*CH$_3$), 108.4, 108.2, 107.1 (Tp′*C*H), 21.8, 19.9, 19.2, 18.4, 16.3, 13.0, 12.8, 12.7 (Tp′C*C*H$_3$ and *C*H$_3$C$_2$*C*H$_3$). Anal. Calcd for $WC_{20}H_{28}N_6OBI$: C, 34.80; H, 4.06; N, 12.18. Found: C, 35.47; H, 4.12; N, 11.92.

Tp′W(CO)I(HC$_2$CMe═CH$_2$) (5; Green, 70%). IR (KBr, cm^{-1}): ν_{CO} = 1909, ν_{BH} = 2550, ν_{CN} = 1545. ^{1}H NMR (CD_2Cl_2, δ): major isomer (60%), 13.30 ($^2J_{WH}$ = 4.4 Hz, *H*C$_2$CMe═CH$_2$), 6.07, 5.87, 5.72 (1:1:1, Tp′C*H*), 4.86 (d of q, $^2J_{HH}$ = 2 Hz, $^4J_{HH}$ = 1.2 Hz, HC$_2$CMe═C*H*H), 3.79 (d of q, $^2J_{HH}$ = 2 Hz, $^4J_{HH}$ = 1 Hz, HC$_2$CMe═CH*H*), 1.98 (d of d, $^4J_{HH}$ = 1 Hz, $^4J_{HH}$ = 1.2 Hz, HC$_2$C*Me*═CHH), 2.84, 2.57, 2.45, 2.35, 2.25, 1.52 (3:3:3:3:3:3, Tp′CC*H*$_3$); minor isomer (40%), 12.37 ($^2J_{WH}$ = 2.8 Hz, *H*C$_2$CMe═CH$_2$), 6.16, 5.87, 5.77 (1:1:1, Tp′C*H*), 6.01 (d of q, $^2J_{HH}$ = 1.6 Hz, $^4J_{HH}$ = 0.8 Hz, HC$_2$CMe═C*H*H), 5.81 (d of q, $^2J_{HH}$ = 1.6 Hz, $^4J_{HH}$ = 1.2 Hz, HC$_2$CMe═CH*H*), 2.81, 2.58, 2.46, 2.36, 2.25, 1.66 (3:3:3:3:3:3, Tp′CC*H*$_3$), 2.39 (d of d, $^4J_{HH}$ = 1.2 Hz, $^4J_{HH}$ = 0.8 Hz, HC$_2$C*Me*═CHH). ^{13}C NMR (CD_2Cl_2, δ): major isomer (60%), 232.5 ($^1J_{WC}$ = 142 Hz, *C*O), 214.4 ($^1J_{WC}$ = 50 Hz, H*C*CMe═CH$_2$), 196.2 (HC*C*CMe═CH$_2$), 155.4, 155.2, 148.7, 146.6, 144.2 (Tp′*C*Me), 140.6 (HC$_2$*C*Me═CH$_2$), 120.6 (t of q, $^1J_{HC}$ = 158 Hz, $^3J_{HC}$ = 5.7 Hz, HC$_2$CMe═*C*H$_2$), 108.8, 108.2, 107.0 (Tp′*C*H), 23.5 (q of d of d, $^1J_{HC}$ = 127 Hz, $^3J_{HC}$ = 10.5 Hz, $^3J_{HC}$ = 6 Hz, HC$_2$C*Me*═CHH), 19.1, 18.4, 16.3, 13.0, 12.7, 12.6 (Tp′C*C*H$_3$); minor isomer (40%), 233.2 ($^1J_{WC}$ = 146 Hz, *C*O), 208.2 ($^1J_{WC}$ = 48 Hz, H*C*CMe═CH$_2$), 206.3 (HC*C*CMe═CH$_2$), 155.4, 155.3, 150.7, 146.6, 145.5, 144.3 (Tp′*C*Me), 142.7 (HC$_2$*C*Me═CH$_2$), 122.8 (t of q, $^1J_{HC}$ = 158 Hz, $^3J_{HC}$ = 5.7 Hz, HC$_2$CMe═*C*H$_2$), 108.6, 108.3, 107.4 (Tp′*C*H), 24.7 (q of d of d, $^1J_{HC}$ = 127 Hz, $^3J_{HC}$ = 10.5 Hz, $^3J_{HC}$ = 6 Hz, HC$_2$C*Me*═CHH), 18.7, 18.2, 16.8, 16.3, 13.0, 12.7 (Tp′C*C*H$_3$). Anal. Calcd for $WC_{21}H_{28}N_6OBI$: C, 35.92; H, 3.99; N, 11.97. Found: C, 35.92; H, 3.95; N, 11.91.

[Tp′(CO)$_2$W(RC$_2$R′)]$^+$. These complexes have been prepared by two routes as described below.

(a) In a representative reaction, Tp′(CO)$_3^•$ (0.558 g, 10 mmol), prepared by oxidation of [Et$_4$N][Tp′W(CO)$_3$] with [Cp$_2$Fe][PF$_6$], and 1-phenyl-1-propyne (1.2 equiv) were dissolved in CH_2Cl_2 (25 mL). [Cp$_2$Fe][PF$_6$] was added, with stirring, to the orange-brown solution. The solution fizzed for a few seconds and turned dark green. After 15 min the solvent was stripped under vacuum and the resultant army green solid was washed several times with Et_2O until the supernatant was clear. The remaining forest green powder was purified via recrystallization from CH_2Cl_2/Et_2O. The second recrystallization yielded dark green crystals of [Tp′(CO)$_2$W(MeC$_2$Ph)][PF$_6$].

(b) [Tp′(CO)$_2$W(HC$_2$Ph)][BF$_4$] (6). In a representative synthesis, a stoichiometric amount of AgBF$_4$ (0.58 g, 2.9 mmol) was added to a dark brown CH_2Cl_2 solution containing Tp′W(CO)$_3$I (2.0 g, 2.9 mmol) and phenylacetylene (0.4 mL, 1.2 equiv)

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under a nitrogen atmosphere at 0 °C. After it was stirred at room temperature for 2 h, the solution was green with a gray precipitate. The solution was filtered through fresh Celite twice. The solution volume was reduced to ca. 10 mL and then transferred to Et_2O (100 mL). The green powder that formed was isolated by filtration and washed with Et_2O (2 × 10 mL) and dried in vacuo (1.73 g, 82%). Recrystallization from CH_2Cl_2/Et_2O yielded green crystals. IR (KBr, cm^{-1}): ν_{CO} = 2057, 1970. ^{1}H NMR (CD_2Cl_2, δ): 14.0 ($^2J_{WH}$ = 6 Hz, PhC$_2$*H*), 7.59, 7.40, 7.20 (m, C$_6$*H*$_5$), 6.14, 5.93 (1:2, Tp′C*H*), 2.70, 2.61, 1.29 (3:6:3:6, Tp′CC*H*$_3$). ^{13}C NMR (CD_2Cl_2, δ): 224.6 (HC*C*Ph), 215.7 ($^1J_{WC}$ = 134 Hz, $^3J_{HC}$ = 4 Hz, *C*O), 197.1 ($^1J_{HC}$ = 223 Hz, PhC*C*H), 156.2, 151.6, 150.6, 147.7 (1:2:1:2, Tp′*C*CH$_3$), 135.2, 134.7, 134.4, 130.1 (*C*$_6$H$_5$), 110.2, 108.6 (1:2, Tp′*C*H), 16.5, 15.7, 13.3, 12.7 (1:2:1:2, Tp′C*C*H$_3$). Anal. Calcd for $[Tp'(CO)_2W(HC_2Ph)][BF_4]\cdot CH_2Cl_2$, $WC_{26}H_{30}N_6O_2B_2F_4Cl_2$: C, 38.50; H, 3.70; N, 10.37. Found: C, 38.84; H, 3.82; N, 10.41.

[Tp′(CO)$_2$W(MeC$_2$Ph)][BF$_4$] (7; Green, 85%). IR (KBr, cm^{-1}): ν_{CO} = 2040, 1953. ^{1}H NMR (CD_2Cl_2, δ): 7.65, 7.43, 7.14 (m, C$_6$*H*$_5$), 6.17, 5.95 (1:2, Tp′C*H*), 3.89 (PhC$_2$*Me*), 2.73, 2.65, 2.47, 1.29 (3:6:3:6, Tp′CC*H*$_3$). ^{13}C NMR (CD_2Cl_2, δ): 223.8 ($^1J_{WC}$ = 50 Hz, MeC*C*Ph), 217.3 ($^1J_{WC}$ = 135 Hz, *C*O), 206.8 ($^1J_{WC}$ = 10 Hz, $^2J_{WC}$ = 8 Hz, PhC*C*Me), 156.2, 151.7, 150.6, 147.7 (1:2:1:2, Tp′*C*CH$_3$), 135.8, 135.0, 132.7, 130.2 (*C*$_6$H$_5$), 110.2, 108.7 (1:2, Tp′*C*H), 25.8 (PhC$_2$*Me*), 16.5, 15.6, 13.3, 12.8 (1:2:1:2, Tp′C*C*H$_3$). Anal. Calcd for $[Tp'(CO)_2W(MeC_2Ph)][PF_6]$, $WC_{26}H_{30}N_6O_2BF_6P$: C, 39.06; H, 3.76; N, 10.52. Found: C, 38.63; H, 3.71; N, 10.48.

[Tp′(CO)$_2$W(PhC$_2$Ph)][BF$_4$] (8; Green, 75%). IR (KBr, cm^{-1}): ν_{CO} = 2064, 1971. ^{1}H NMR (CD_2Cl_2, δ): 8.20, 7.86, 7.79, 7.63, 7.41, 7.14 (C$_6$*H*$_5$), 6.21, 5.96 (1:2, Tp′C*H*), 2.82, 2.68, 2.50, 1.31 (3:6:3:6, Tp′CC*H*$_3$). ^{13}C NMR (CD_2Cl_2, δ): 226.4 ($^1J_{WC}$ = 42 Hz, PhC*C*Ph), 217.7 ($^1J_{WC}$ = 136 Hz, *C*O), 200.2 ($^1J_{WC}$ = 12 Hz, Ph*C*CPh), 156.0, 151.8, 150.8, 147.9 (1:2:1:2, Tp′*C*CH$_3$), 136.3, 135.8 (*C*$_{ipso}$), 135.0, 133.9, 131.8, 131.0, 130.6, 130.1 (Ph), 110.2, 108.8 (1:2, Tp′*C*H), 16.8, 15.5, 13.3, 12.7 (1:2:1:2, Tp′C*C*H$_3$). Anal. Calcd for $[Tp'(CO)_2W(PhC_2Ph)][BF_4]$, $WC_{31}H_{32}N_6O_2B_2F_4$: C, 46.42; H, 3.99; N, 10.48. Found: C, 46.34; H, 4.04; N, 10.25.

[Tp′(CO)$_2$W(MeC$_2$Me)][BF$_4$] (9; Blue-Green, 60%). IR (KBr, cm^{-1}): ν_{BH} = 2558, ν_{CO} = 2057, 1971, ν_{CN} = 1541, ν_{BF} = 1069. ^{1}H NMR (CD_2Cl_2, δ): 6.11, 6.06 (1:2, Tp′C*H*), 3.61, 2.85 (*Me*C$_2$*Me*), 2.63, 2.58, 2.43, 1.58 (3:6:3:6, Tp′CC*H*$_3$). ^{13}C NMR (CD_2Cl_2, δ): 217.6 ($^1J_{WC}$ = 136 Hz, *C*O), 236.5, 205.1 (Me*C*$_2$Me), 156.1, 151.4, 150.6, 147.6 (1:2:1:2, Tp′*C*Me), 110.1, 108.7 (1:2, Tp′*C*H), 24.0, 23.6 (*Me*C$_2$*Me*), 16.4, 15.8, 13.3, 12.7 (1:2:1:2, Tp′C*Me*). Anal. Calcd for $[Tp'(CO)_2W(MeC_2Me)][PF_6]$, $WC_{21}H_{28}N_6O_2BF_6P$: C, 34.23; H, 3.80; N, 11.41. Found: C, 33.73; H, 3.72; N, 11.28.

{Tp′(CO)$_2$W[HC$_2$C(Me)═CH$_2$]}[BF$_4$] (10; Green, 60%). IR (KBr, cm^{-1}): ν_{BH} = 2553, ν_{CO} = 2054, 1969, ν_{CN} = 1541, ν_{BF} = 1064. ^{1}H NMR (CD_2Cl_2, δ): 13.6 (*H*C$_2$C(Me)═CH$_2$), 6.13, 6.02 (1:2, Tp′C*H*), 5.63 (broad, HC$_2$C(Me)═C*H*H), 4.78 (broad, HC$_2$C(Me)═CH*H*), 2.67 (HC$_2$C(*Me*)═CH$_2$), 2.59, 2.43, 2.21, 1.49 (6:3:3:6, Tp′C*Me*). ^{13}C NMR (CD_2Cl_2, δ): 226.5 (HC*C*C(Me)═CH$_2$), 216.0 (*C*O), 196.1 (d, $^1J_{HC}$ = 226 Hz, H*C*CCMe═CH$_2$), 156.1, 151.3, 150.7, 147.6 (1:2:1:2, Tp′*C*Me), 141.1 (HC$_2$*C*(Me)═CH$_2$), 135.0 (t, $^1J_{HC}$ = 145 Hz, HC$_2$C(Me)═*C*H$_2$), 110.1, 108.6 (1:2, Tp′*C*H), 23.5 (HC$_2$C(*Me*)═CH$_2$), 16.4, 15.9, 13.3, 12.6 (1:2:1:2, Tp′C*Me*). Anal. Calcd for $[Tp'(CO)_2W(HC_2CMe{=}CH_2)][PF_6]$, $WC_{22}H_{28}N_6O_2BF_6P$: C, 33.13; H, 3.60; N, 10.08. Found: C, 31.64; H, 3.66; N, 11.02.

[Tp′(CO)(RC$_2$R′)W(NCMe)]$^+$. These acetonitrile adducts have been prepared by two general routes as described below.

[Tp′(CO)(PhC$_2$Me)W(NCMe)][BF$_4$] (11). (a) A stoichiometric amount of $AgBF_4$ (0.78 g, 4.0 mmol) was added to a green solution of Tp′(CO)(PhC$_2$Me)WI (3.0 g, 4.0 mmol) in 150 mL of 1:1 $MeCN/CH_2Cl_2$ under a nitrogen atmosphere. After it was stirred at room temperature for 4 h, the solution was light blue and a gray precipitate had formed. The solution was filtered through Celite, and the solvent was evaporated from the filtrate. The solid blue residue that resulted was redissolved in a minimum amount of CH_2Cl_2 and then added to 150 mL of Et_2O. The blue precipitate that formed was isolated by filtration, washed with 30 mL of Et_2O, and dried in vacuo to yield 2.56 g of product (85%). Recrystallization from CH_2Cl_2/Et_2O yields blue crystals. IR (KBr, cm^{-1}): ν_{CO} = 1940. ^{1}H NMR (CD_2Cl_2, δ): 7.34, 6.84 (C$_6$*H*$_5$), 6.07, 5.92, 5.83 (Tp′C*H*), 3.84 (PhC$_2$*Me*), 2.75, 2.69, 2.59, 2.57, 2.45, 1.45, 1.30 (Tp′C*Me* and *Me*CN). ^{13}C NMR (CD_2Cl_2, δ): 225.2 ($^1J_{WC}$ = 142 Hz, *C*O), 214.9 (MeC*C*Ph), 212.8 (q, $^2J_{CH}$ = 9 Hz, $^1J_{WC}$ = 20 Hz, PhC*C*Me), 154.4, 153.4, 150.7, 148.0, 147.7, 145.8 (Tp′*C*Me), 150.4 (q, $^2J_{HC}$ = 11 Hz, $^2J_{WC}$ = 15 Hz, Me*C*N), 136.5, 130.9, 130.0, 129.2 (*C*$_6$H$_5$), 108.8, 108.7, 108.1 (Tp′*C*H), 23.6, 16.1, 15.8, 14.3, 12.9, 12.7 (Tp′C*Me* and PhC$_2$*Me*), 4.8 (q, $^1J_{HC}$ = 140 Hz, *Me*CN). Anal. Calcd for $[Tp'(CO)(PhC_2Me)W(NCMe)][BF_4]$, $WC_{27}H_{33}N_7B_2OF_4$: C, 43.06; H, 4.39; N, 13.02. Found: C, 42.90; H, 4.58; N, 13.41.

[Tp′(CO)(PhC$_2$H)W(NCMe)][BF$_4$] (12; Blue, 89%). IR (KBr, cm^{-1}): ν_{CO} = 1942. ^{1}H NMR (CD_2Cl_2, δ): major isomer (80%), 14.18 (PhC$_2$*H*), 7.31, 6.90 (C$_6$*H*$_5$), 6.05, 5.95, 5.82 (Tp′C*H*), 2.79, 2.64, 2.58, 2.55, 2.41, 1.50, 1.40 (Tp′C*Me* and *Me*CN); minor isomer (20%), 13.16 (PhC$_2$*H*), 8.0, 7.68, 7.57 (C$_6$*H*$_5$), 6.16, 5.95, 5.86 (Tp′C*H*), 2.80, 2.78, 2.65, 2.41, 2.22, 1.44 (Tp′C*Me* and *Me*CN). ^{13}C NMR (CD_2Cl_2, δ): major isomer only, 224.1 ($^1J_{WC}$ = 143 Hz, *C*O), 217.8 ($^1J_{WC}$ = 52 Hz, HC*C*Ph), 203.3 (PhC*C*H), 154.3, 153.7, 149.4, 148.2, 147.8, 146.0 (Tp′*C*Me), 152.0 ($^2J_{WC}$ = 15 Hz, Me*C*N), 135.5 (*C*$_{ipso}$), 131.8, 131.5, 129.2 (Ph), 108.9, 108.8, 108.0 (Tp′*C*H), 16.2, 15.7, 14.4, 12.9, 12.7 (Tp′C*Me*), 4.7 (*Me*CN). Anal. Calcd for $[Tp'(CO)(PhC_2H)W(NCMe)][BF_4]$, $WC_{26}H_{31}N_7B_2OF_4$: C, 42.25; H, 4.20; N, 13.27. Found: C, 42.26; H, 4.28; N, 13.12.

[Tp′(CO)(PhC$_2$Ph)W(MeCN)][BF$_4$] (13). A stoichiometric amount of $AgBF_4$ (0.58 g, 2.9 mmol) was added to a dark red $MeCN/CH_2Cl_2$ (1:1) solution containing Tp′(CO)$_3$WI (2.0 g, 2.9 mmol) and diphenylacetylene (0.52 g, 3 mmol) under a nitrogen atmosphere at 0 °C. After it was stirred at room temperature for 30 min, the solution was brown with a gray precipitate. The filtrate of the solution was refluxed for 1 h. The resulting solution was filtered through fresh Celite twice. The solution volume was reduced to ca. 10 mL and then transferred to Et_2O (100 mL) while it was stirred. The brown powder that formed was isolated by filtration and washed with Et_2O (2 × 10 mL) and dried in vacuo (0.71 g, 30%). Recrystallization from CH_2Cl_2/Et_2O yields brown crystals. IR (KBr, cm^{-1}): ν_{CO} = 1941. ^{1}H NMR (CD_2Cl_2, δ): 7.99, 7.74, 7.63, 7.36, 7.30, 6.82 (C$_6$*H*$_5$), 6.10, 5.90, 5.87 (Tp′C*H*), 2.88, 2.79, 2.65, 2.62, 2.47, 1.38 (Tp′C*Me*) and *Me*CN). ^{13}C NMR (CD_2Cl_2, δ): 226.0 ($^1J_{WC}$ = 147 Hz, *C*O), 216.2 ($^1J_{WC}$ = 48 Hz, PhC*C*Ph), 206.5 ($^1J_{WC}$ = 15 Hz, Ph*C*CPh), 154.5, 152.9, 152.3, 148.2, 148.0, 146.0, 137.9, 136.1 (Tp′*C*Me and *C*$_{ipso}$), 150.9 ($^2J_{WC}$ = 10 Hz, Me*C*N), 131.8, 131.5, 130.9, 130.0, 129.9, 129.2 (Ph), 108.9, 108.7, 108.2 (Tp′*C*H), 16.3, 16.2, 14.2, 13.0, 12.9, 12.7 (Tp′C*Me*), 4.9 (*Me*CN). Anal. Calcd for $[Tp'(CO)(MeCN)W(PhC_2Ph)][BF_4]\cdot CH_2Cl_2$, $WC_{33}H_{37}N_7OB_2F_4Cl_2$: C, 44.92; H, 4.40; N, 11.52. Found: C, 44.03; H, 4.12; N, 10.90.

[Tp′(CO)(MeCN)W(MeC$_2$Me)][BF$_4$] (14). IR (KBr, cm^{-1}): ν_{CO} = 1913, $\nu_{CN(Tp')}$ = 1545, $\nu_{CN(MeCN)}$ = 2282, ν_{BH} = 2552, ν_{BF} = 1070. ^{1}H NMR (CD_2Cl_2, δ): 6.12, 6.00, 5.81 (Tp′C*H*), 3.85, 2.94 (*Me*C$_2$*Me*), 2.70, 2.60, 2.53, 2.46, 2.39, 2.05, 1.37 (Tp′*Me* and *Me*CN). ^{13}C NMR (CD_2Cl_2, δ): 225.6 ($^1J_{WC}$ = 146 Hz, *C*O), 221.0 ($^1J_{WC}$ = 51 Hz, Me*C*≡), 210.6 ($^1J_{WC}$ = 14 Hz, ≡*C*Me), 150.3 (q, $^2J_{HC}$ = 10 Hz, $^2J_{WC}$ = 15 Hz, Me*C*N), 154.1, 152.7, 150.7, 147.7, 147.5, 145.8 (Tp′*C*Me), 108.6, 108.5, 108.0 (Tp′*C*H), 22.6, 20.8 (*Me*C$_2$*Me*), 16.0, 15.7, 14.9, 12.9, 12.8, 12.6 (Tp′C*Me*), 4.7 (q, $^1J_{CH}$ = 138 Hz, *Me*CN). Anal. Calcd for $[Tp'(CO)(MeCN)W(MeC_2Me)][PF_6]$, $WC_{22}H_{30}N_7OBF_6P$: C, 35.32; H, 4.04; N, 13.10. Found: C, 35.38; H, 4.15; N, 12.82.

[Tp′(CO)(EtCN)W(PhC$_2$Me)][BF$_4$] (15). IR (KBr, cm^{-1}): ν_{CO} = 1914, ν_{BH} = 2562, ν_{CN} = 1544, ν_{BF} = 1071. ^{1}H NMR (CD_2Cl_2, δ): 7.35, 6.85 (m, C$_6$*H*$_5$), 6.10, 5.94, 5.85 (Tp′C*H*), 3.86 (PhC$_2$*Me*), 3.10 (q, $^3J_{HH}$ = 8 Hz, MeC*H*$_2$CN), 2.71, 2.62, 2.60, 2.47, 1.50, 1.31 (Tp′C*Me*), 1.26 (t, $^3J_{HH}$ = 8 Hz, *Me*CH$_2$CN). ^{13}C NMR (CD_2Cl_2, δ): 225.3 ($^1J_{WC}$ = 146 Hz, *C*O), 214.8 ($^1J_{WC}$ = 52 Hz, MeC*C*Ph), 212.7 ($^1J_{WC}$ = 14 Hz, PhC*C*Me), 153.7 ($^2J_{WC}$ = 15 Hz, Et*C*N), 154.2, 153.3, 150.6, 147.9, 147.0, 145.8 (Tp′*C*Me), 136.4, 130.8, 129.9, 129.1 (*C*$_6$H$_5$), 108.7, 108.6, 108.0 (Tp′*C*H), 23.5 (PhC$_2$*Me*), 16.0, 15.8, 14.3, 12.9, 12.6, 9.8 (Tp′C*Me* and *Me*CH$_2$CN). Anal. Calcd for $[Tp'(CO)(EtCN)W(PhC_2Me)][BF_4]$, $WC_{28}H_{35}N_7B_2OF_4$: C, 43.84; H, 4.57; N, 12.79. Found: C, 43.88; H, 4.95; N, 12.57.

(b) An alternative way to synthesize the nitrile-substituted complexes is to react free nitrile with the appropriate cationic dicarbonyl complex at room temperature for 24 h or at reflux for 1 h.

[Tp′(CO)[P(OMe)$_3$]W(PhC$_2$Me)][BF$_4$] (16). A green solution of $[Tp'(CO)_2W(PhC_2Me)][BF_4]$ (1.0 g, 1.35 mmol) and P(OMe)$_3$ (1.1 equiv) in 100 mL of THF was refluxed under nitrogen for 3 h. The blue solution that formed was filtered and stripped

Table I. Crystallographic Data Collection Parameters

	Tp′(CO)(PhC≡CMe)-WI·0.2CH$_2$Cl$_2$ (2)	[Tp′(CO)(PhC≡CPh)W(NCMe)]-[BF$_4$]·CH$_2$Cl$_2$ (13)
	Crystal Data	
mol formula	$WC_{25.2}H_{30.4}BIN_6OCl_{0.4}$	$WC_{33}H_{37}B_2F_4N_7OCl_2$
fw	769.1	885.38
cryst dimens, mm	0.20 × 0.20 × 0.40	0.40 × 0.20 × 0.20
space group	$P2_1/n$	$P2_12_12_1$
cell params		
a, Å	11.368 (7)	15.671 (4)
b, Å	15.241 (6)	14.709 (3)
c, Å	17.300 (3)	15.053 (6)
β, deg	94.24 (4)	
V, Å^3	2989 (2)	3470 (3)
Z	4	4
calcd density, g/cm^3	1.709	1.560
	Collection and Refinement Parameters	
radiation (wavelength, Å)	Mo Kα (0.709 30)	Mo Kα (0.710 73)
monochromator	graphite	Zr filter
linear abs coeff, cm^{-1}	33.1	35.9
scan type	$\theta/2\theta$	$\omega/1.33\theta$
2θ limit, deg	50	50
quadrant (2) or octant (13) collected	$\pm h,+k,+l$	$+h,+k,+l$
total no. of rflns	5554	4196
no. of data with $I \geq 2.5\sigma(I)$ (2) or $3.0\sigma(I)$ (13)	3377	2141
R, %	7.3	6.0
R_w, %	9.5	4.4
GOF	4.47	1.65
no. of params	336	214
largest param shift	0.15	0.04

to an oil, which was redissolved in a minimum amount of CH$_2$Cl$_2$ and then transferred to 100 mL of Et$_2$O. The blue powder that formed was isolated and recrystallized from CH$_2$Cl$_2$/Et$_2$O to yield blue crystals (0.9 g, 80%). IR (KBr, cm^{-1}): ν_{CO} = 1947, ν_{BH} = 2567, ν_{CN} = 1545, ν_{BF} = 1055. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.47, 7.35, 6.90 (m, C$_6$*H*$_5$), 6.09, 5.97, 5.79 (Tp′C*H*), 3.72 (PhC$_2$*Me*), 3.40 (d, $^3J_{PH}$ = 11.2 Hz, P(O*Me*)$_3$), 2.76, 2.64, 2.55, 2.46, 1.46, 1.17 (Tp′C*Me*). ^{13}C NMR (CD$_2$Cl$_2$, δ): 225.5 ($^2J_{PC}$ = 7.3 Hz, MeC*C*Ph), 224.8 ($^2J_{PC}$ = 2 Hz, PhC*C*Me), 214.1 ($^2J_{PC}$ = 10 Hz, *C*O), 157.0, 155.1, 149.9, 149.0, 146.9, 146.2 (Tp′*C*Me), 136.9, 132.1, 130.3, 129.5 (*C*$_6$H$_5$), 110.0, 109.5, 107.8 (Tp′*C*H), 53.8 ($^2J_{PC}$ = 7.3 Hz, P(O*Me*)$_3$), 24.2 (PhC$_2$*Me*), 15.8, 15.6, 15.1, 13.5, 13.0, 12.7 (Tp′C*Me*). Anal. Calcd for [Tp′(CO)[P(OMe)$_3$]W(PhC$_2$Me)][BF$_4$], WC$_{28}$H$_{39}$N$_6$B$_2$O$_4$F$_4$P: C, 40.22; H, 4.67; N, 10.05. Found: C, 39.88; H, 4.65; N, 9.79.

X-ray Diffraction Data Collection for Tp′(CO)(PhC≡CMe)WI. A green block of Tp′W(CO)(PhC$_2$Me)I of dimensions 0.20 × 0.20 × 0.40 mm was selected and mounted on a glass wand coated with epoxy. Diffraction data were collected on a Rigaku automated diffractometer. Twenty centered reflections found in the region 30.0° < 2θ < 40.0° and refined by least-squares calculations indicated a monoclinic cell. The cell parameters are listed in Table I. Diffraction data were collected in the quadrant $\pm h,+k,+l$ under the conditions specified in Table I. Only data with $I > 2.5\sigma(I)$ were used in the structure solution and refinement.[20] The data were corrected for Lorentz–polarization effects during the final stages of data reduction.

Solution and Refinement of the Structure. Space group $P2_1/n$ was confirmed, and the position of the tungsten was deduced from the three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were determined through subsequent Fourier and difference Fourier calculations. The large peaks in the final difference map were all close to the W and I atoms. There was 0.2 molecule of CH$_2$Cl$_2$ per asymmetric unit disordered about a center of symmetry. This was modeled with use of C41, C11, and C12. This probably contributes to the relatively high final R and GOF values.

The 37 non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated by using a C–H distance of 0.96 Å and an isotropic thermal parameter calculated from the anisotropic values for the atoms to which they were connected. Final least-squares refinement[21] resulted in the residuals R = 7.3% and R_w = 9.5%.[22] The final difference Fourier map had no peak greater than 4.20 e/Å^3.[23]

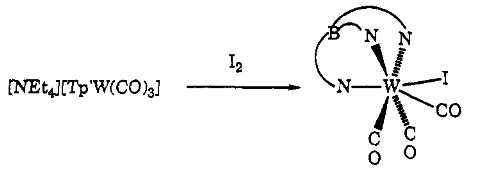
X-ray Diffraction Data Collection for [Tp′(CO)(PhC≡CPh)W(NCMe)][BF$_4$]. A brown block of [Tp′(CO)(PhC≡CPh)W(NCMe)][BF$_4$] was selected and mounted on a glass wand coated with epoxy. Diffraction data were collected on an Enraf-Nonius CAD-4 automated diffractometer.[24] Eighteen centered reflections found in the region 30.0° < 2θ < 35.0° and refined by least-squares calculations indicated an orthorhombic cell. The cell parameters are listed in Table I. Diffraction data were collected in the octant $+h,+k,+l$ under the conditions specified in Table I. Only data with $I > 3.0\sigma(I)$ were used in the structure solution and refinement.[20] The data were corrected for Lorentz–polarization effects during the final stages of data reduction.

Solution and Refinement of the Structure. Space group $P2_12_12_1$ was confirmed, and the position of the tungsten was deduced from the three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were determined through subsequent Fourier and difference Fourier calculations. A molecule of methylene chloride was located in the cell.

The 50 non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated by using a C–H distance of 1.08 Å and an isotropic thermal parameter calculated from the anisotropic values for the atoms to which they were connected. Final least-squares refinement[21] resulted in the residuals R = 6.0% and R_w = 4.4%.[22] The final difference Fourier map had no peak greater than 0.72 e/Å^3.[23]

Results and Discussion

I. Syntheses. Oxidation of the anionic tungsten(0) tricarbonyl reagent Tp′W(CO)$_3^-$ by elemental iodine generates a neutral seven-coordinate tungsten(II) product in high yield (1, 90%; eq 5). This dark brown complex was purified by chromatography on alumina followed by recrystallization from toluene/methanol. This is one of the few seven-coordinate group 6 complexes containing the tridentate Tp′ ligand. The molybdenum analogue Tp′(CO)$_3$MoI[25] has been observed in solution, but it spontaneously loses CO to form a 16-electron dicarbonyl complex, Tp′(CO)$_2$MoI, which may have solvent coordinated. The degree of back-bonding from metal to CO presumably determines the ease of CO loss. Molybdenum generally provides less back-bonding to carbonyl ligands than tungsten, as evidenced by higher CO stretching frequencies for molybdenum complexes. The Tp′(CO)$_3$WI product is slowly oxidized by air in solution or in the solid state over



(5)

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[20] Programs used during solution and refinement were from the NRCVAX structure determination package: Gabe, E. J.; Le Page, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Chem.* **1989**, *22*, 384.

[21] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is based on counter statistics.

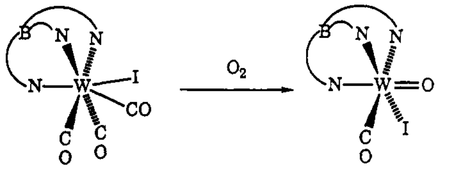
[22] $R_{unweighted} = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $R_{weighted} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

[23] Scattering factors were taken from the following: Cromer, D. T.; Waber, J. T. In *International Tables for X-Ray Crystallography*; Ibers, J. A., Hamilton, J. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.

[24] Programs used during solution and refinement were from the Enraf-Nonius structure determination package.

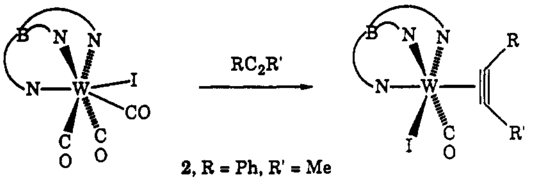
[25] Gamble, A. S.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 693.

a period of weeks to a tungsten(IV) oxo compound, [Tp′W(O)(CO)I] (eq 6).[26]



(6)

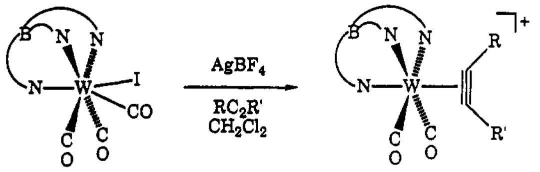
Neutral alkyne complexes Tp′W(CO)(RC_2R')I (**2**–**5**) were prepared by alkyne substitution of two carbonyls in Tp′W$(CO)_3$I in refluxing THF or toluene (eq 7). Purification by chromatography on alumina followed by recrystallization from toluene/hexane produces air-stable green crystals in high yield for high-boiling alkynes (**2**, **3**) and in low yield for low-boiling alkynes (**4**, **5**). These neutral complexes are thermally stable. Upon continued reflux in THF or toluene with excess free alkyne no bis(alkyne) complexes were generated. Two isomers were obtained in a 60:40 ratio for terminal alkyne complexes **3** and **5**. No analogous alkyne complex was formed when diphenylacetylene was used, suggesting bulky ligands are not compatible with the ancillary ligands here.



(7)

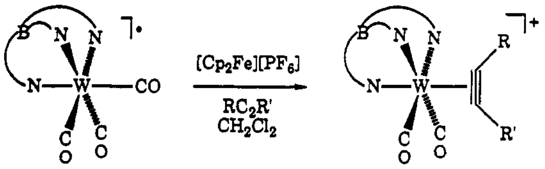
2, R = Ph, R′ = Me
3, R = Ph, R′ = H
4, R = R′ = Me
5, R = H, R′ = CMe=CH_2

Cationic dicarbonyl alkyne complexes **6**–**10** were synthesized by two routes: (a) iodide removal from Tp′W$(CO)_3$I by Ag^+ in the presence of free alkyne (eq 8) and (b) oxidation of the 17-electron radical Tp′W$(CO)_3{}^•$ by ferrocenium in the presence of alkynes (eq 9). Iodide removal from Tp′W$(CO)_3$I or one-electron oxidation of Tp′W$(CO)_3{}^•$ could generate a cationic 16-electron [Tp′W$(CO)_3]^+$ species in solution, perhaps coordinating CH_2Cl_2 as a token ligand. Alkyne substitution of one carbonyl ligand would then lead to formation of the cationic dicarbonyl product (Scheme I). Filtration through Celite and recrystallization from CH_2Cl_2/Et_2O yields the cationic dicarbonyl alkyne complexes as green crystals, which are air- and moisture-sensitive in solution and as solids.



(8)

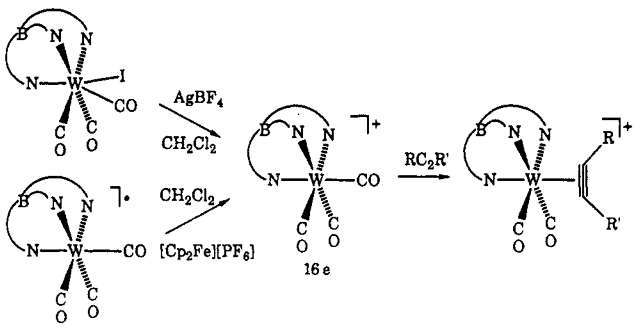
6, R = Ph, R′ = H
7, R = Ph, R′ = Me
8, R = R′ = Ph
9, R = R′ = Me
10, R = H, R′ = CMe=CH_2



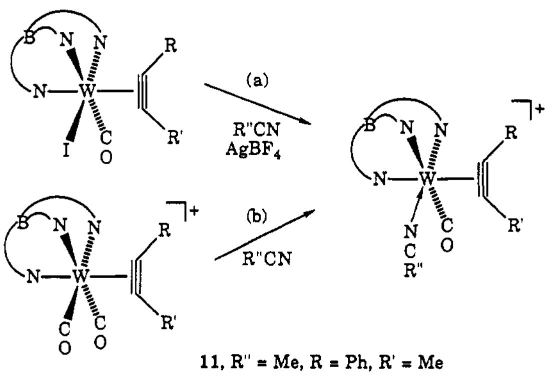
(9)

6, R = Ph, R′ = H
7, R = Ph, R′ = Me
8, R = R′ = Ph
9, R = R′ = Me
10, R = H, R′ = CMe=CH_2

Scheme I



Scheme II

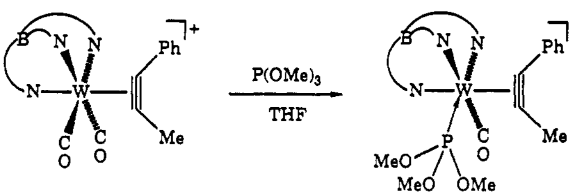


11, R″ = Me, R = Ph, R′ = Me
12, R″ = Me, R = Ph, R′ = H
13, R″ = Me, R = R′ = Ph
14, R″ = Me, R = R′ = Me
15, R″ = Et, R = Ph, R′ = Me

Cationic nitrile complexes **11**–**15** were prepared by two general routes: (a) nitrile substitution for iodide in the neutral iodide complexes and (b) nitrile substitution for one carbonyl ligand in the cationic dicarbonyl complexes (Scheme II). Purification of products from route a by filtration through fresh Celite and recrystallization from CH_2Cl_2/Et_2O yielded blue crystals, which are air- and moisture-sensitive. Reactions via route b went cleanly at room temperature overnight to afford pure products in high yield. Two isomers were formed in a 80:20 ratio for the phenylacetylene complex **12**. Complex **13**, [Tp′W(CO)(MeCN)(PhC_2Ph)$]^+$, was prepared by two routes (route b and Scheme III) as brown crystals in low yield.

Solution IR absorptions (2045, 1955 cm^{-1}) consistent with the generation of [Tp′W$(CO)_3$(MeCN)$]^+$ were observed when Tp′W$(CO)_3$I and Ag[BF_4] were combined in acetonitrile, but this reactive intermediate has not yet been isolated.

Phosphite complex **16** was synthesized in good yield by heating [Tp′$(CO)_2$W(PhC_2Me)][BF_4] with P$(OMe)_3$ in THF for 4 h. Crystallization from CH_2Cl_2/Et_2O yields air-stable blue crystals (eq 10).



(10)

II. X-ray Crystal Structures of Tp′(CO)(PhC≡CMe)WI (2) and [Tp′W(CO)(MeCN)(PhC≡CPh)][BF$_4$] (13).

The coordination sphere of tungsten can be

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(26) Feng, S. G.; Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L.; Young, C. G. *Inorg. Chem.* **1991**, *30*, 2582.

Scheme III

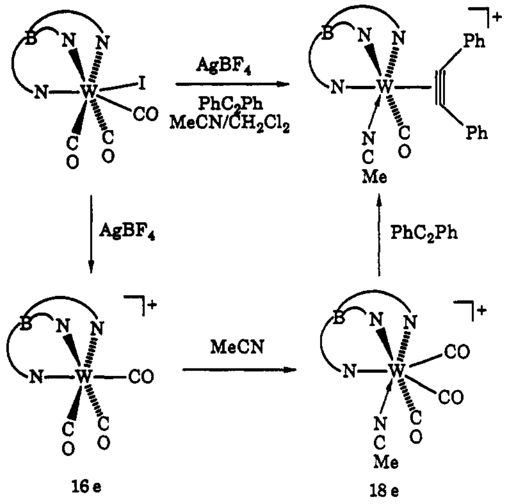

Table II. Atomic Positional Parameters for Tp′W(CO)(PhC≡CMe)I

	x	y	z
W1	0.61297 (8)	0.13911 (6)	0.19516 (5)
I1	0.8563 (1)	0.1088 (1	0.207 (1)
C1	0.677 (3)	0.359 (2)	0.183 (2)
C2	0.627 (2)	0.268 (1)	0.209 (1)
C3	0.586 (2)	0.238 (1)	0.268 (1)
C4	0.535 (2)	0.261 (1)	0.340 (1)
C5	0.577 (2)	0.334 (2)	0.385 (1)
C6	0.528 (3)	0.356 (2)	0.451 (2)
C7	0.443 (3)	0.314 (2)	0.480 (1)
C8	0.395 (2)	0.239 (2)	0.437 (2)
C9	0.444 (2)	0.214 (2)	0.370 (1)
C10	0.635 (3)	0.195 (1)	0.099 (2)
O10	0.655 (1)	0.232 (1)	0.044 (1)
B1	0.444 (3)	–0.033 (2)	0.224 (2)
N11	0.426 (2)	0.125 (1)	0.177 (1)
N12	0.372 (2)	0.044 (1)	0.202 (1)
C13	0.253 (2)	0.051 (2)	0.188 (1)
C14	0.225 (2)	0.134 (2)	0.161 (1)
C15	0.336 (2)	0.175 (2)	0.153 (1)
C16	0.174 (3)	–0.022 (2)	0.202 (2)
C17	0.359 (3)	0.267 (2)	0.129 (2)
N21	0.601 (2)	0.053 (1)	0.301 (1)
N22	0.521 (2)	–0.012 (1)	0.300 (1)
C23	0.523 (2)	–0.046 (2)	0.374 (1)
C24	0.611 (2)	–0.009 (2)	0.419 (1)
C25	0.654 (2)	0.058 (2)	0.373 (1)
C26	0.452 (3)	–0.125 (2)	0.392 (2)
C27	0.746 (3)	0.121 (2)	0.402 (2)
N31	0.601 (2)	0.008 (1)	0.135 (1)
N32	0.527 (2)	–0.054 (1)	0.161 (1)
C33	0.536 (2)	–0.124 (1)	0.122 (1)
C34	0.605 (2)	–0.109 (2)	0.063 (2)
C35	0.638 (2)	–0.025 (2)	0.069 (1)
C36	0.473 (2)	–0.209 (2)	0.139 (1)
C37	0.709 (3)	0.027 (2)	0.013 (2)
C41	0.454 (5)	0.542 (3)	0.013 (3)
Cl1	$^1/_2$	$^1/_2$	0
Cl2	0.389 (4)	0.546 (3)	0.087 (19)

described as roughly octahedral, considering the alkyne as occupying a single coordination site, in both of these complexes. The Tp′ ligand occupies three coordination sites trans to the three remaining ligands: CO, PhC≡CMe, and I for **2** and CO, PhC≡CPh, and NCMe for **13**. Atomic positional parameters are listed in Tables II (**2**) and III (**13**). Selected intramolecular bond distances and angles are listed in Table IV for **2** and in Table V for **13**. Molecular drawings are shown in Figure 1 for **2** and in Figure 2 for **13**. The BF_4^- anion was omitted from the drawing of **13** for clarity; note that eight fluorine locations were found in the structure due to disorder of the anion.

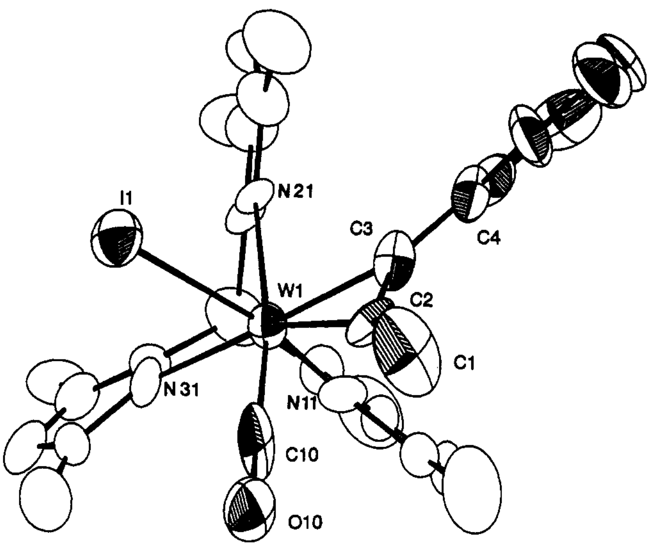

Figure 1. ORTEP drawing of Tp′(CO)(PhC≡CMe)WI.

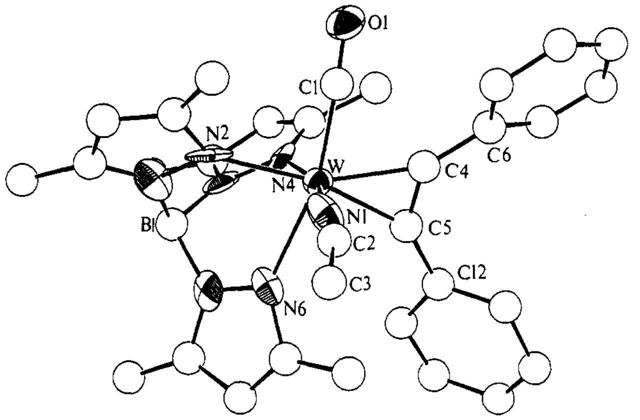

Figure 2. ORTEP drawing of the [Tp′(CO)(PhC≡CPh)W(N≡CMe)][BF_4] complex cation.

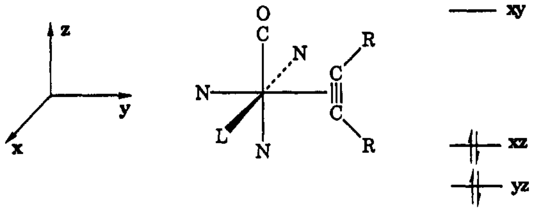

Figure 3. Qualitative molecular orbital scheme for the dπ metal orbitals of a chiral Tp′L(CO)(RC≡CR)W complex.

The salient geometrical features of both alkyne complexes agree with those established by previous structural studies of d^4 alkyne complexes.

(1) The alkyne is parallel to the M–CO axis. This structural feature is common in octahedral d^4 monomeric alkyne complexes and has been found, for example, in CpM(CO)(RC≡CR′)X (M = Mo, W),[4] M(CO)(RC≡CR′)L_2X_2,[2] and M(CO)(RC≡CR′)$(S_2CNR''_2)_2$.[3] This orientation optimizes both the π-acid and π-donor interactions of the alkyne with the dπ orbitals on the tungsten, while the CO ligand can interact with both filled dπ orbitals (Figure 3).[1]

(2) The short $W–C_{alkyne}$ bond distances of 2.01 (2) and 1.98 (2) Å for **2** and 2.02 (1) and 1.98 (1) Å for **13** are consistent with a tightly bound four-electron-donor alkyne. The $W–C_{alkyne}$ bond distance of 1.98 Å is one of the shortest $W–C_{alkyne}$ bonds reported, suggesting substantial metal-to-alkyne back-donation in these electron-rich Tp′ complexes. Most $W–C_{alkyne}$ bonds for four-electron-donor

Table III. Atomic Positional Parameters for [Tp′W(CO)(PhC$_2$Ph)(MeCN)][BF$_4$] (13)

	x	*y*	*z*
W1	0.11633 (5)	0.14935 (5)	0.23579 (5)
O1	0.0582 (8)	0.3383 (8)	0.1727 (7)
N1	0.2459 (9)	0.1816 (9)	0.2439 (10)
N2	0.1083 (10)	0.2089 (8	0.3665 (9)
N3	0.0716 (9)	0.1637 (11)	0.4379 (9)
N4	−0.0112 (9)	0.1151 (7)	0.2664 (9)
N5	−0.0334 (9)	0.0779 (9)	0.3456 (10)
N6	0.1517 (9)	0.0294 (10)	0.3183 (9)
N7	0.1047 (11)	0.0069 (9)	0.3898 (8)
C1	0.084 (1)	0.267 (1)	0.195 (1)
C2	0.318 (1	0.189 (1)	0.244 (2)
C3	0.416 (2)	0.193 (2)	0.266 (2)
C4	0.122 (1)	0.149 (1)	0.102 (1)
C5	0.123 (1)	0.066 (1)	0.132 (1)
C6	0.120 (1)	0.191 (1)	0.014 (1)
C7	0.164 (1)	0.277 (1)	0.007 (1)
C8	0.167 (1)	0.321 (1)	−0.076 (1)
C9	0.124 (1)	0.285 (1)	−0.147 (1)
C10	0.083 (1)	0.201 (1)	−0.138 (1)
C11	0.081 (1)	0.162 (1)	−0.058 (1)
C12	0.123 (1)	−0.029 (1)	0.099 (1)
C13	0.172 (1)	−0.048 (1)	0.024 (1)
C14	0.183 (1)	−0.141 (2)	−0.005 (1)
C15	0.144 (1)	−0.207 (1)	0.040 (1)
C16	0.092 (1)	−0.189 91)	0.113 (1)
C17	0.089 (1)	−0.102 (1)	0.148 (1)
C18	0.082 (1)	0.210 (1)	0.514 (1)
C19	0.116 (1)	0.288 (1)	0.492 (1)
C20	0.136 (1)	0.292 (1)	0.405 (1)
C21	0.047 91)	0.180 (1)	0.600 (1)
C22	0.179 (1)	0.361 (1)	0.356 (1)
C23	−0.119 (1)	0.061 (1)	0.348 (1)
C24	−0.152 (1)	0.085 (1)	0.265 (1)
C25	−0.083 (1)	0.117 (1)	0.219 (1)
C26	−0.163 (1)	0.29 (1)	0.426 (1)
C27	−0.087 (1)	0.150 (1)	0.128 (1)
C28	0.129 (1)	−0.075 (1)	0.427 (1)
C29	0.199 (1)	−0.100 (1)	0.374 (1)
C30	0.213 (1)	−0.043 (1)	0.312 (1)
C31	0.091 (1)	−0.114 (1)	0.505 (1)
C32	0.280 (1)	−0.035 (1)	0.242 (1)
B1	0.031 (1)	0.068 (2)	0.420 (2)

Table IV. Selected Bond Distances (Å) and Angles (deg) for Tp′W(CO)(PhC≡CMe)I (2)

W–I1	2.797 (3)	W–N31	2.26 (2)
W–C2	1.98 (2)	C1–C2	1.58 (3)
W–C3	2.01 (2)	C2–C3	1.24 (3)
W–C10	1.90 (2)	C3–C4	1.45 (3)
W–N11	2.14 (2)	C10–O10	1.15 (3)
W–N21	2.27 (1)		
I–W–C2	95.0 (6)	C3–W–N21	84.7 (8)
I–W–C3	106.0 (6)	C3–W–N31	162.2 (7)
I–W–C10	86.8 (9)	C10–W–N11	97 (1)
I–W–N11	164.0 (5)	C10–W–N21	170.4 (8)
I–W–N21	88.0 (4)	C10–W–N31	89.8 (9)
I–W–N31	85.1 (4)	N11–W–N21	86.4 (7)
C2–W–C3	36.1 (9)	N11–W–N31	79.3 (7)
C2–WC10	70 (1)	N21–W–N31	81.7 (6)
C2–W–N11	100.9 (8)	W–C2–C1	150 (2)
C2–W–N21	119.0 (8)	C1–C2–C3	136 (2)
C2–W–N31	159.2 (8)	W–C3–C4	144 (2)
C3–W–C10	105 (1)	C2–C3–C4	145 (2)
C3–W–N11	88.4 (8)	W–C10–O10	174 (3)

alkynes are slightly greater than 2.00 Å, as in W(CO)(HC≡COAlCl$_3$)(PMe$_3$)$_3$Cl (2.01, 2.03 Å),[27] W(CO)(HC≡CH)(S$_2$CNEt$_2$)$_2$ (2.02, 2.04 Å),[28] and W(CO)(PhC≡COMe)(C$_6$H$_7$N$_2$)$_2$ (2.02, 2.03 Å).[29]

Table V. Selected Bond Distances (Å) and Angles (deg) for [Tp′W(CO)(N≡CMe)(PhC≡CPh)][BF$_4$] (13)

W–N1	2.09 (1)	O1–C1	1.17 (2)
W–N2	2.16 (1)	N1–C2	1.14 (2)
W–N4	2.12 (1)	C2–C3	1.56 (3)
W–N6	2.23 (1)	C4–C5	1.28 (2)
W–C1	1.90 (2)	C4–C6	1.46 (2)
W–C4	2.02 (1)	C5–C12	1.50 (2)
W–C5	1.98 (1)		
N1–W–N2	84.5 (6)	N4–W–C5	93.9 (6)
N1–W–N4	164.5 (5)	N6–W–C1	164.2 (5)
N1–W–N6	84.4 (4)	N6–W–C4	122.9 (7)
N1–W–C1	94.1 (6)	N6–W–C5	86.7 (5)
N1–W–C4	91.3 (7)	C1–W–C4	72.9 (7)
N1–W–C5	97.6 (7)	C1–W–C5	109.1 (6)
N2–W–N4	82.0 (6)	C4–W–C5	37.4 (6)
N2–W–N6	80.2 (5)	W–N1–C2	171 (2)
N2–W–C1	84.0 (6)	N1–C2–C3	168 (3)
N2–W–C4	156.1 (7)	W–C4–C6	154 (1)
N2–W–C5	166.5 (5)	C5–C4–C6	137 (2)
N4–W–N6	86.0 (5)	W–C5–C12	147 (1)
N4–W–C1	92.0 (6)	C4–C5–C12	139 (1)
N4–W–C4	104.1 (7)		

(3) There is a small difference between the two W–C$_{\text{alkyne}}$ distances in each complex. This may be attributable to a constructive interaction between the carbonyl carbon and the proximal alkyne carbon, the one more tightly bound to the metal, in each case. The relatively short distance between the carbonyl carbon and the proximal alkyne carbon (2.24 Å for **2** and 2.30 Å for **13**) is consistent with a three-center–two-electron bond with a filled dπ orbital linking alkyne and carbonyl π orbitals.

(4) The C≡C bond distance of 1.28 (2) Å for **13** is typical for four-electron-donor alkyne ligands, while the neutral iodide complex **2** exhibits a C≡C bond distance of 1.24 (3) Å. Other complexes have shown bond distances between 1.30 and 1.35 Å, for example, W(CO)(HC≡COAlCl$_3$)(PMe$_3$)$_3$Cl[27] (1.32 Å), CpW(CO)(Et$_2$NC≡CMe)[η^1-C(CO)C$_6$H$_4$Me][30] (1.34 Å), and {CpW[(MeO)C≡CC$_6$H$_4$Me)](PMe$_3$)$_2$}[BF$_4$][31] (1.34 Å).

(5) A final feature of [Tp′W(CO)(PhC≡CPh)(MeCN)][BF$_4$] (**13**) and Tp′(CO)(PhC≡CMe)WI (**2**) is the cis bent geometry of the alkyne. For **13** the C4–C5–C12 angle is 139 (1)° and C5–C4–C6 angle is 137 (2)°, while for **2** the internal alkyne angles are 145 (2)° (C2–C3–C4) and 136 (2)° (C1–C2–C3). The alkyne ligand in **2** bisects two of the pyrazole rings with the phenyl group up toward the Tp′ ligand and the methyl away from the bulky Tp′ ligand.

III. Spectral Properties. The seven-coordinate tricarbonyl iodide derivative shows three carbonyl bands (ν_{CO} 2012, 1915, 1872 cm^{-1}) in the solid-state IR spectrum. This suggests that the ground-state geometry resembles a 3:4 structure of C_s symmetry with three normal modes (2a′ + a″) for CO stretching. This observation is consistent with the structures found for Tp′W(CO)$_3$H[32] and TpMo(CO)$_3$Br.[17] In contrast, two ν_{CO} absorptions (a$_1$ + e) were observed for CpW(CO)$_3$X as appropriate for a structure with C_{3v} symmetry with a capping halide in a 1:3:3 geometry.[33] The hypothesis that Tp ligands are able to more effectively polarize metal orbitals into an octahedral array than the delocalized Cp anions has been employed to ex-

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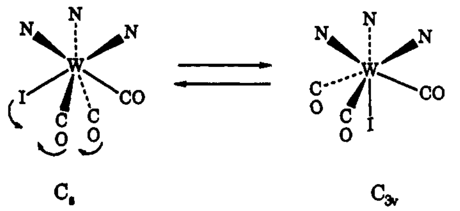
Table VI. Selected IR and NMR Data for Alkyne Complexes

complexes	IR ν_{CO}, cm^{-1}	^1H NMR δ, ppm	^{13}C NMR δ, ppm^a C≡C	^{13}C NMR δ, ppm^a CO
Tp′W(CO)I(RC_2R')				
R = Ph, R′ = Me (2)	1905		207 (12 Hz) 209 (50 Hz)	233 (145 Hz)
R = Ph, R′ = H (3)	1909	13.6	213 (48 Hz), 198	233 (140 Hz)
		isomer 12.6	209, 205	234 (150 Hz)
R = R′ = Me (4)	1906		202 (13 Hz) 213 (49 Hz)	233 (146 Hz)
R = H, R′ = CMe═CH_2 (5)	1909	13.3	214 (50 Hz)	233.5 (142 Hz)
		isomer 12.4	208 (48 Hz)	233 (146 Hz)
[Tp′$(CO)_2$(RC_2R')][BF_4]				
R = Ph, R′ = H (6)	2057, 1970	14.0	225, 197 (223 Hz*)	216 (134 Hz)
R = Ph, R′ = Me (7)	2040, 1953		224 (50 Hz) 207 (10 Hz)	217 (135 Hz)
R = R′ = Ph (8)	2060, 1971		226 (42 Hz) 200 (12 Hz)	218 (136 Hz)
R = R′ = Me (9)	2057, 1971		237, 205	218 (136 Hz)
R = H, R′ = CMe═CH_2 (10)	2054, 1969	13.6	226.5, 196 (226 Hz*)	216
[Tp′W(CO)(MeCN)(RC_2R')][BF_4]				
R = Ph, R′ = Me (11)	1940		215, 213	225 (142)
R = Ph, R′ = H (12)	1942	14.2 isomer 13.2	218 (52), 203	224 (143 Hz)
R = R′ = Ph (13)	1941		216 (48 Hz) 206 (15 Hz)	226 (147 Hz)
R = R′ = Me (14)	1913		221 (51 Hz) 211 (14 Hz)	226 (146 Hz)
[Tp′W(CO)(EtCN)(PhC_2Me)][BF_4] (15)	1914		215 (52 Hz) 213 (14 Hz)	225 (146 Hz)
{Tp′W(CO)[$P(OMe)_3$](PhC_2Me)}[BF_4] (16)	1947		226, 225	214

[a] An asterisk indicates $^1J_{HC}$(≡C—H), while other coupling constants are $^1J_{WC}$.

Scheme IV



Scheme V

plain differences in behavior between Tp and Cp complexes.[17]

At room temperature, equivalent pyrazole rings (C_{3v} symmetry) are observed in both ^1H and ^{13}C NMR spectra for Tp′$(CO)_3$WI, but at −80 °C, two sets of pyrazole rings (2:1) and two carbonyl resonances (242, 226 ppm; 1:2) are observed (C_s symmetry) in ^{13}C NMR spectra. The three pyrazole ring protons coalesce at −5 °C, indicating a $\Delta G^{\ddagger}$ value of 13.9 kcal/mol. This fluxional process exchanges carbonyls, possibly through a 1:3:3 geometry (Scheme IV). Such a rearrangement was proposed by Curtis and coworkers.[17] Other seven-coordinate complexes in the Tp system, Tp$(CO)_3$MoX (X = H, I, Br) and Tp′$(CO)_3$WH, also show fluxionality at room temperature. No dynamic process is observed in the corresponding Cp analogues, Cp$(CO)_3$MoX. As indicated by Curtis and co-workers,[17] the barrier for site exchange of ligands in the basal plane of the 3:4 structure is lower in Tp complexes than in the Cp analogues. Philipp has recently isolated a Tp′$(CO)_3$W$(PR_3)^+$ complex that adopts a 3:3:1 geometry both in the solid state and in solution.[34]

IR and NMR data for the alkyne complexes are summarized in Table VI. Infrared spectra of the neutral alkyne compounds 2–5 exhibit diagnostic Tp′ absorbances near 2550 and 1545 cm^{-1}. The $\nu_{C\equiv C}$ stretch of the alkyne ligands, expected to be weak, was not identified. Donation from both $\pi_{\parallel}$ and $\pi_{\perp}$ as well as acceptance of metal dπ electron density into $\pi_{\parallel}^*$ all contribute to reduction of the acetylenic bond order. The monocarbonyl ν_{CO} absorption at 1907 cm^{-1} is somewhat lower than the value for other monocarbonyl monoalkyne complexes such as $(PR_3)_2X_2$W(CO)(RC_2R'),[2] $(S_2CNR''_2)_2$W(CO)(RC_2R'),[3] and CpXW(CO)(RC_2R').[4] Tp′ complexes generally exhibit ν_{CO} frequencies 10–20 cm^{-1} lower than those of corresponding Cp analogues,[17] indicating that Tp′ is more electron-rich than Cp.

The acetylenic ^1H and ^{13}C NMR chemical shift values here are comparable to literature values for other four-electron-donor alkyne ligands. The ^1H chemical shift range of 12.4–13.6 ppm for the acetylenic protons in Tp′(CO)W(RC_2H)I (R = Ph, CMe═CH_2) complexes falls in the region of four-electron-donor complexes. ^{13}C NMR spectra of 2–5 revealed acetylenic ^{13}C resonances in the range from 196 to 214 ppm, as is typical for four-electron-donor alkynes. One-bond tungsten–carbon coupling constants of approximately 50 and 12 Hz were observed for the distinct ends of the alkynes. The lone metal carbonyl carbon resonates near 233 ppm with one-bond tungsten–carbon coupling close to 145 Hz. Three nonequivalent pyrazole rings in both ^1H and ^{13}C NMR spectra indicate metal chirality. Both ^1H and ^{13}C NMR spectra show pairwise signals of differing intensities to suggest isomeric forms

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(34) Philipp, C.; Templeton, J. L. Unpublished results.

for the terminal alkyne complexes **3** and **5**. This isomerization presumably results from two alkyne orientations (Scheme V).

A variable-temperature NMR study of **3** shows no coalescence up to 373 K (100 °C), suggesting a high rotational barrier for this complex. The two dπ orbitals of the metal directed toward the alkyne are differentiated by their interactions with CO and I$^-$, and indeed studies on CpM(RC$_2$R)LL′ complexes show that the alkyne rotational barrier is sensitive to differences in π acidity of the two cis ligands L and L′.[1] As L and L′ diverge in their π-acid or π-base properties, the energies and extensions of the two dπ orbital combinations available to the alkyne increasingly differ. A large alkyne rotational barrier then characterizes complexes with very different L and L′ ligands, and a small barrier results when L and L′ are similar ligands.

The cationic dicarbonyl alkyne compounds (**6**–**10**) exhibit strong infrared absorptions near 2050 and 1960 cm^{-1}, which are attributed to the two metal carbonyls. The lower energy band is more intense. An intense absorption near 1065 cm^{-1} is due to the B–F stretch of the tetrahedral BF$_4^-$ counterion.

Both ^{1}H and ^{13}C NMR spectra of **6**–**10** display 2:1 patterns for the dimethylpyrazole signals, indicating that the dmpz rings trans to the carbonyl ligands are equivalent on the NMR time scale. Proton NMR spectra of **6** and **10** display resonances assigned to the terminal acetylenic protons at 14.0 and 13.6 ppm, respectively, slightly lower than those of the neutral iodide complexes **3** and **5**. Only one isomer was observed for compounds **6**–**10**. ^{13}C NMR spectra of **6**–**10** display acetylenic ^{13}C resonances in the range of 196–237 ppm; internal alkyne carbons appear downfield of terminal carbon resonances for **6** and **10**. The average chemical shift for each alkyne's acetylenic carbons is downfield of that for the neutral complexes, compatible with greater $\pi_\perp$ donation in the cationic dicarbonyl cases. Gated-decoupled carbon-13 NMR spectra of **6** and **10** served to positively identify the terminal alkyne carbons while furnishing $^1J_{HC}$ coupling constants of 223 and 226 Hz, respectively. The two equivalent carbonyl carbons have $^1J_{WC}$ = 135 Hz and appear near 217 ppm, which is about 15 ppm upfield of the neutral monocarbonyl complexes. Two methyl environments in **9** and two phenyl environments in **8** were observed by both ^{1}H and ^{13}C NMR spectroscopy suggesting that alkyne rotation is slow on the NMR time scale at room temperature.

Substitution of one carbonyl with a nitrile or a phosphite ligand shifts the remaining carbonyl frequency to much lower energies (1913–1947 cm^{-1}) as expected. The infrared frequencies for the 2-butyne acetonitrile adduct and 1-phenyl-1-propyne propionitrile adduct were about 30 cm^{-1} lower in energy than that for the 1-phenyl-1-propyne acetonitrile adduct, indicating that the CO frequencies are sensitive to electronic factors. The nitrile complexes exhibit a weak absorption near 2280 cm^{-1}, indicating some back-bonding from the metal to the nitrile ligands.

Unique sets of resonances for each pyrazole ring of the Tp′ ligands in the NMR spectra of these compounds indicate an unsymmetrical environment for the Tp′ ligands in these chiral molecules. The proton NMR spectrum of **12** displays two downfield acetylenic signals at 14.2 and 13.2 ppm with an intensity ratio of 80:20, suggesting that two isomers exist at room temperature. Again, we believe the isomers result from different alkyne orientations.

Carbon-13 NMR spectra of **11**–**16** revealed acetylenic ^{13}C resonances in the range from 203 to 226 ppm, comparable to other four-electron-donor complexes. The nitrile carbon (N$\equiv$*C*R) appears near 150–154 ppm with two-bond tungsten coupling of 15–20 Hz. The terminal carbonyl carbons resonate near 225 ppm with a one-bond tungsten–carbon coupling constant between 142 and 147 Hz. The spectral properties of the tungsten(II) d^4 alkyne complexes **2**–**16** discussed above and summarized in Table VI fit the classical pattern for alkyne ligands as four-electron donors. The spectral properties of the carbonyl ligands reflect the electron richness of the compounds. Electron-rich metal centers exhibit more back-bonding to the carbonyl ligands, as reflected in lower carbonyl frequencies in infrared spectra and downfield ^{13}C NMR signals.

Summary

Formation of neutral and cationic alkyne complexes has been achieved with Tp′ as an ancillary ligand. The alkyne ligands here exhibit typical four-electron-donor properties in NMR spectra, and the alkyne rotational barriers are high. Crystal structures of [Tp′(CO)(MeCN)W(PhC$_2$Ph)]$^+$ and Tp′(CO)IW(PhC$_2$Me) show a pseudooctahedral geometry with the alkyne roughly parallel to the M–CO axis. The short W–C bond distances and lengthened C$\equiv$C bond distances are consistent with tightly bound four-electron-donor alkynes. The phenyl group in Tp′(CO)IW(PhC$_2$Me) is found to lie near the pyrazole rings, and perhaps ring interactions between the phenyl group and pyrazole rings are important in determining the ground-state geometries. Studies of these alkyne complexes indicate that the pyrazolylborate ligand, while reminiscent of the Cp ligand in many ways, creates a unique chemistry to explore.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE 8907341) and the donors of the Petroleum Research Foundation, administered by the American Chemical Society, for generous support of this research.

Supplementary Material Available: Figures showing the structures and tables of anisotropic temperature factors and bond distances and angles for **2** and **13** (12 pages); tables of calculated and observed structure factors (35 pages). Ordering information is given on any current masthead page.