

Saturated and Unsaturated (Hydrotris(3,5-dimethylpyrazolyl)borato)tungsten(II) Carbene Complexes

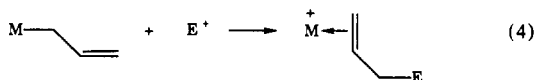
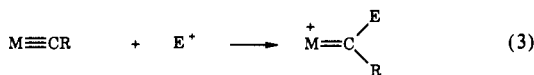
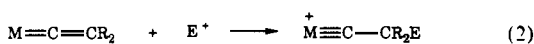
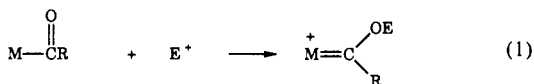
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Abstract: Reaction of $[\text{Tp}'(\text{CO})_2\text{W}(\text{PhC}_2\text{H})][\text{BF}_4]$ ($\text{Tp}' = \text{hydrotris}(3,5\text{-dimethylpyrazolyl})\text{borato}$) with PhC_2H or reaction of $\text{Tp}'(\text{CO})\text{IW}(\text{PhC}_2\text{R})$ ($\text{R} = \text{H}, \text{Me}$) with $\text{PhC}_2\text{H}/\text{AgBF}_4$ generates cationic bisalkyne complexes $[\text{Tp}'(\text{CO})\text{W}(\text{PhC}_2\text{H})\text{-(PhC}_2\text{R})][\text{BF}_4]$. NMR and crystal data suggest that the two alkyne ligands donate a total of six electrons to the metal with phenyl groups distal to each other. Crystals of the bis(phenylacetylene) complex belong to the monoclinic space group $P2_1/n$, $Z = 4$, with unit cell dimensions of $a = 14.868$ (3), $b = 13.085$ (4), $c = 19.835$ (3) Å, $\beta = 109.22$ (1)°. Refinement of 442 variables over 3155 reflections led to $R = 5.2\%$ with $R_w = 7.1\%$. Deprotonation of the cationic bis(phenylacetylene) complex yields an alkyne acetylide product, $\text{Tp}'(\text{CO})(\text{PhC}_2\text{H})\text{W}(\text{C}\equiv\text{CPh})$, which exists as two isomers in solution. Protonation of the acetylide compound with aqueous HCl regenerates the bisalkyne cation. Hydride addition to the bis(phenylacetylene) complex forms an alkyne σ -vinyl complex, $\text{Tp}(\text{CO})(\text{PhC}_2\text{H})\text{W}(\eta^1\text{-CPh}=\text{CH}_2)$, which also exists as two isomers. Protonation of the η^1 -vinyl complex at $\text{C}\beta$ results in the formation of an 18-electron alkyne carbene cation, $[\text{Tp}'(\text{CO})(\text{PhC}_2\text{H})\text{W}=\text{C}(\text{Me})\text{Ph}][\text{BF}_4]$. Protonation of the η^2 -vinyl complexes $\text{Tp}'(\text{CO})_2\text{W}(\eta^2\text{-CPh}=\text{CHR})$ ($\text{R} = \text{Me}, \text{H}$) at $\text{C}\beta$ of the η^2 -vinyl ligand forms β -agostic carbenes $[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{R})\text{Ph}][\text{BF}_4]$ ($\text{R} = \text{Me}, \text{Et}$). The methyl derivative crystallized in the monoclinic space group $P2_1/n$ with unit cell dimensions of $a = 12.87$ (1), $b = 12.376$ (8), $c = 20.93$ (3) Å; $\beta = 103.34$ (7)°, with $Z = 4$. Refinement of 425 variables over 3200 reflections led to $R = 7.0\%$ and $R_w = 8.7\%$. The W-C (methyl) distance is 2.49 Å and the W-C α -C β angle is 91°. Rotation of the methyl group which provides the C-H agostic bond is fast for the methyl derivative. Variable temperature NMR experiments on the ethyl derivative show a barrier of 11.7 kcal/mol for interconversion of agostic enantiomers.

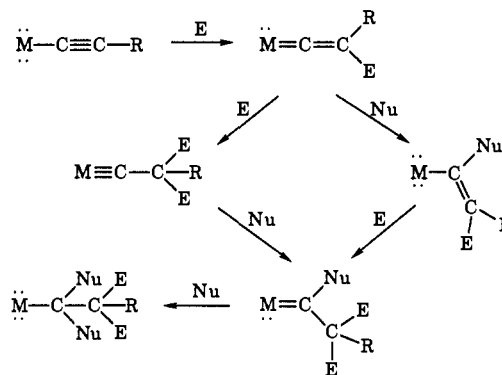
Introduction

Nucleophilic attack on organic ligands has historically been the dominant mode of ligand elaboration;¹ electrophilic additions constitute a smaller but equally fundamental class of ligand transformations.² Addition of an electrophile to a ligand β -position is most common, as illustrated by the conversion of acyls to carbenes (eq 1)³ or vinylidenes to carbynes (eq 2),⁴ but examples of both α (eq 3)⁵ and γ (eq 4)⁶ electrophilic addition are also known.



Proton addition to acetylide ligands is a common way to synthesize vinylidene complexes.⁷ Vinylidene complexes are attractive

Scheme I



reagents for additional transformations since they contain both unsaturated $\text{M}=\text{C}$ and $\text{C}=\text{C}$ bonds, which can serve as reactive sites. The general reactivity pattern of C_2 derived ligands reflects electrophilicity at $\text{C}\alpha$ and nucleophilicity at $\text{C}\beta$ (Scheme I).^{7c} That such selectivity exists for reactions of $\text{M}-\text{C}-\text{C}$ backbones in complexes that adhere to the effective atomic number rule follows directly if one assumes that the metal will happily house lone pairs and that the octet rule will apply for both carbon atoms in the C_2 based ligand. The ability of the metal to serve as an electron reservoir (housing the $\text{M}=\text{C}$ π -electrons as a lone pair upon nucleophile addition to $\text{C}\alpha$ and sharing a lone pair to form a metal carbon multiple bond upon electrophile addition to $\text{C}\beta$) is crucial to these reactions.

Ligand protonation can cause unsaturation at the metal center, and agostic bond formation can result. Numerous agostic complexes have been reported⁸ since the first insightful review by Brookhart and Green⁹ in 1983. Agostic $\text{L}_n\text{M}[(\text{CR}_2)_n(\text{CR})_m\text{CR}_2\text{H}]$ complexes can be classified as (a) agostic alkyls ($m = 0$; $n = 1, 2, 3, \dots$), (b) agostic π -complexes ($n = 1$; $m = 1, 2, 3, \dots$). Olefin insertion and polymerization mechanisms may involve β -agostic

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alkyls.¹⁰ Protonated carbynes, also described as α -agostic carbenes, of both groups V¹¹ and VI¹² have been reported.

Electrophilic addition to vinyl ligands at C β generates carbenes. While electrophilic addition to η^1 -vinyl ligands to form nonagostic carbenes¹³ maintains the electron count at the metal, a similar result from protonation of an η^2 -vinyl ligand would leave the metal unsaturated.

We have utilized nucleophilic addition to a four-electron donor alkyne ligand to form an η^2 -vinyl ligand¹⁴ and nucleophilic attack at a two-electron donor alkyne ligand to form an η^1 -vinyl ligand for use as a reagent. We now report (1) formation of cationic β -agostic carbenes of the type [Tp'(CO)₂W=C(R)Ph][BF₄] (Tp' = hydrotris(3,5-dimethylpyrazolyl)borato; R = Me, Et) from protonation of η^2 -vinyl complexes Tp'(CO)₂W(η^2 -CPh=CHR) (R = H, Me), (2) a single crystal structure of the methylphenylcarbene complex, and (3) detailed NMR studies of the ethyl derivative. For comparison, we also report (1) formation and characterization of a nonagostic carbene from protonation of an η^1 -vinyl complex; (2) formation and reactivity of an alkyne acetylide complex, Tp'(CO)(PhC₂H)W(C \equiv CPh); (3) formation of bisalkyne complexes, Tp'(CO)W(PhC \equiv CH)(PhC \equiv CR)][BF₄] (R = H, Me); and (4) a crystal structure of the bis(phenylacetylene) cation. Formation of the agostic carbene was communicated earlier.^{14a}

Experimental Section

Materials and Methods. Manipulations involving air sensitive reagents were performed under an atmosphere of pure dinitrogen using Schlenk techniques. Solvents were purified as follows: CH₂Cl₂ was distilled from P₂O₅. Et₂O, THF, and hexanes were distilled from potassium benzophenone ketyl. Other solvents were purged with nitrogen prior to use. Literature methods were employed in the synthesis of Tp'(CO)₂W(η^2 -CPh=CHR),¹⁴ Tp'(CO)(PhC \equiv CR)WI,¹⁵ and [Tp'W(CO)₂(PhC \equiv CR)][BF₄]¹⁵ (R = H, Me). All other reagents were purchased from commercial sources and were used without further purification.

Infrared spectra were recorded on a Mattson Polaris FT-IR spectrometer. ¹H and ¹³C NMR spectra were recorded on a Varian XL-400 (400-MHz) spectrometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN, or Oneida Research Services, Whitesboro, NY.

Syntheses. [Tp'(CO)W(PhC₂H)₂][BF₄] (1). This compound was prepared by two routes as described below. (a) A stoichiometric amount of AgBF₄ (0.26 g, 1.36 mmol) was added to a green solution containing Tp'(CO)(PhC₂H)WI (1.0 g, 1.36 mmol) and 1.2 equiv of PhC₂H (0.18 mL, 1.63 mmol) in 100 mL of CH₂Cl₂ under a nitrogen atmosphere, resulting in a color change to orange-brown as a gray precipitate formed. The solution was filtered through Celite. The filtrate volume was reduced to ca. 10 mL and then transferred into 100 mL of Et₂O. The orange precipitate which formed was isolated by filtration, washed with 2 \times 10 mL of Et₂O, and dried in vacuo to yield orange crystals (0.92 g, 85%). (b) A solution of [Tp'(CO)₂W(PhC₂H)][BF₄] (1.0 g, 1.38 mmol) and PhC₂H (0.17 mL, 1.1 equiv) in CH₂Cl₂ was heated to reflux under a nitrogen atmosphere for 5 h, resulting in a color change from green to brown, disappearance of the starting material dicarbonyl stretching frequencies of 2060, 1970 cm⁻¹ in the infrared spectrum, and appearance of a 2080-cm⁻¹ band for the product. The solution volume was reduced to ca. 10 mL and then transferred into 100 mL of Et₂O. The precipitate was isolated and recrystallized from CH₂Cl₂/Et₂O to yield orange crystals (0.55 g, 50%). IR (KBr, cm⁻¹): ν_{BH} = 2566, ν_{CO} = 2073, ν_{CN} = 1546, ν_{BF} = 1071. ¹H NMR (CD₂Cl₂, δ): 13.04 (²J_{WH} = 9.5 Hz, PhC₂H), 10.39 (²J_{WH} = 7.2 Hz, HC₂Ph), 8.25, 7.79, 7.69, 7.23, 7.15, 6.31 (C₆H₅), 6.12, 5.87, 5.85 (Tp'CH), 2.67, 2.47, 2.39, 1.96, 1.89, 1.37

(Tp'CCH₃). ¹³C NMR (CD₂Cl₂, δ): 204.6 (¹J_{WC} = 102 Hz, ³J_{HC} = 6 Hz, CO), 175.3 (d of t, ¹J_{WC} = 37 Hz, ²J_{HC} = 11.6 Hz, ²J_{HC} = 4.8 Hz, HCCPh), 173.6 (d of t, ¹J_{WC} = 11 Hz, ²J_{HC} = 14.9 Hz, ²J_{HC} = 5 Hz, PhCCH), 167.7 (d, ¹J_{WC} = 33 Hz, ¹J_{HC} = 226 Hz, PhCCH), 159.8 (d, ¹J_{HC} = 227 Hz, HCCPh), 155.1, 153.5, 151.9, 147.5, 146.8, 146.3 (Tp'CCH₃), 133.2, 132.7 (C_{ipso}), 133.3, 132.9, 130.4, 130.3, 129.5, 129.0 (Ph), 110.4, 109.1 (Tp'CH), 16.5, 16.4, 15.5, 13.1, 13.0, 12.9 (Tp'CCH₃). Anal. Calcd for [Tp'W(CO)(PhC₂H)₂][BF₄](CH₂Cl₂), W₁C₃₃H₃₆N₆O₁B₂F₄Cl₂: C, 44.77; H, 4.07; N, 9.50. Found: C, 44.68; H, 3.98; N, 9.40.

[Tp'(CO)W(PhC₂Me)(PhC₂H)][BF₄] (2). This compound (orange, 60%) was prepared by route (a) as described above by using Tp'(CO)(PhC₂Me)WI in place of Tp'(CO)(PhC₂H)WI. IR (KBr, cm⁻¹): ν_{BH} = 2565, ν_{CO} = 2065, ν_{CN} = 1546, ν_{BF} = 1057. ¹H NMR (CDCl₃, δ): 10.19 (²J_{WH} = 7.2 Hz, HC₂Ph), 8.22, 7.74, 7.63, 7.24, 7.19, 6.24, (2 C₆H₅), 6.09, 5.87 (3 Tp'CH), 3.74 (PhCCMe), 2.66, 2.49, 2.40, 1.93, 1.81, 1.40 (Tp'CCH₃). ¹³C NMR (CDCl₃, δ): 206.3 (¹J_{WC} = 105 Hz, CO), 175.1 (q, ¹J_{WC} = 10 Hz, ²J_{HC} = 6.8 Hz, PhCCMe), 175.0 (¹J_{WC} = 36 Hz, MeCPh), 167.1 (d of t, ¹J_{WC} = 10.3 Hz, ²J_{HC} = 14.2 Hz, ²J_{HC} = 5 Hz, PhCCH), 164.8 (d, ¹J_{WC} = 33 Hz, ¹J_{HC} = 227 Hz, PhCCH), 154.5, 153.4, 152.1, 146.8, 146.2, 145.5 (Tp'CCH₃), 132.9, 132.7 (C_{ipso}), 132.4, 130.2, 129.8, 128.8, 128.2 (Ph), 110.1, 109.3, 109.2 (Tp'CH), 22.1 (q, ¹J_{HC} = 131 Hz, PhCCMe), 16.4, 16.1, 15.5, 12.9, 12.8, 12.7 (Tp'CCH₃).

Tp'(CO)(PhC₂H)W(η^1 -CPh=CH₂) (3). A stoichiometric amount of Li[Et₂BH] in THF (0.63 mL) was dripped slowly into a cold THF (-78 °C) solution of [Tp'(CO)(PhC₂H)₂][BF₄] (0.5 g, 0.63 mmol), resulting in a color change from brown to green and a decrease in IR CO stretching frequency from 2080 to 1900 cm⁻¹. The solution was allowed to warm to room temperature, and the solvent was removed under vacuum. The solid residue was chromatographed on alumina with toluene as eluent. A green band was collected, and toluene was removed. The solid formed was recrystallized from CH₂Cl₂/hexanes to yield green crystals (0.36 g, 80%). IR (KBr, cm⁻¹): ν_{BH} = 2548, ν_{CO} = 1893, ν_{CN} = 1545. ¹H NMR of major isomer (75%) (CDCl₃, δ): 13.34 (PhC₂H), 7.74-7.02 (10 H, C₆H₅), 6.34, 6.28, 6.04 (Tp'CH), 5.80 (d, ²J_{HH} = 4 Hz, ³J_{WH} = 14.4 Hz, η^1 -CPh=CHH), 4.30 (d, ²J_{HH} = 4 Hz, ³J_{WH} = 8 Hz, η^1 -CPh=CHH), 3.26, 3.01, 2.86, 2.81, 2.06, 1.91 (Tp'CCH₃). ¹H NMR of minor isomer (25%) (CDCl₃, δ): 12.90 (PhC₂H), 7.74-7.02 (C₆H₅), 6.58, 6.27, 6.05 (Tp'CH), 5.84 (d, ²J_{HH} = 4 Hz, ³J_{WH} = 15 Hz, η^1 -CPh=CHH), 4.40 (d, ²J_{HH} = 4 Hz, ³J_{WH} = 8 Hz, η^1 -CPh=CHH), 3.24, 3.03, 3.00, 2.80, 2.01, 1.91 (Tp'CCH₃). ¹³C NMR of major isomer (75%) (CDCl₃, δ): 242.5 (¹J_{WC} = 138 Hz, ³J_{HC} = 8.7 Hz, CO), 213.7 (¹J_{WC} = 51 Hz, HCCPh), 203.5 (¹J_{HC} = 213 Hz, PhCCH), 161.8 (s, η^1 -CPh=CH₂), 153.9, 153.5, 147.9, 144.1, 143.9, 143.4 (Tp'CCH₃), 137.4, 129.4, 128.4, 128.1, 127.0, 125.4, 123.7 (Ph), 119.9 (d of d, ¹J_{HC} = 149 Hz, ¹J_{HC} = 156 Hz, η^1 -CPh=CHH), 107.8, 107.6, 106.6 (Tp'CH), 17.1, 17.0, 15.6, 13.0, 12.8, 12.5 (Tp'CCH₃). Anal. Calcd for W₁C₃₂H₃₅N₆O₁B₁: C, 53.81; H, 4.90; N, 11.77. Found: C, 53.86; H, 4.93; N, 11.70.

[Tp'(CO)(PhC₂H)W=C(Me)Ph][BF₄] (4). A green solution of Tp'(CO)(PhC₂H)W(η^1 -CPh=CH₂) (0.5 g, 0.7 mmol) in 30 mL of CH₂Cl₂/Et₂O (1:5) was cooled to 0 °C. A red-orange precipitate formed when a stoichiometric amount of HBF₄·Me₂O was added dropwise. The flask was put in the freezer (-40 °C) after 20 mL of Et₂O was added. The red-orange powder which formed was isolated by filtration, washed with Et₂O (2 \times 10 mL), and dried in vacuo (0.34 g, 85%). Recrystallization from CH₂Cl₂/Et₂O yields red-orange crystals. IR (KBr, cm⁻¹): ν_{BH} = 2564, ν_{CO} = 2039, ν_{CN} = 1545, ν_{BF} = 1069. ¹H NMR (CD₂Cl₂, δ): 14.20 (²J_{WH} = 6.8 Hz, PhC₂H), 7.50-6.40 (10 H, C₆H₅), 6.15, 5.78, 5.63 (Tp'CH), 4.23 (3 H, =C(Ph)Me), 2.75, 2.47, 2.41, 1.83, 1.35, 1.34 (Tp'CCH₃). ¹³C NMR (CD₂Cl₂, δ): 341.6 (¹J_{WC} = 121 Hz, =C(Ph)Me), 212.3 (¹J_{WC} = 44 Hz, ²J_{HC} = ³J_{HC} = 7 Hz, HCCPh), 211.0 (¹J_{WC} = 115 Hz, ³J_{HC} = 8 Hz, CO), 200.1 (d, ¹J_{HC} = 221 Hz, PhCCH), 156.4, 156.2, 149.9, 149.4, 147.6, 147.0 (Tp'CCH₃), 150.0, 134.0 (C_{ipso}), 132.9, 132.8, 131.7, 129.7, 128.3 (Ph), 110.5, 109.7, 108.8 (Tp'CH), 52.8 [q, ¹J_{HC} = 129 Hz, W=C(Ph)Me], 16.7, 16.2, 14.8, 13.3, 13.1, 12.6 (Tp'CCH₃). Anal. Calcd for [Tp'(CO)(PhC₂H)W=C(Me)Ph][BF₄](CH₂Cl₂), W₁C₃₃H₃₈N₆O₁B₂F₄Cl₂: C, 44.77; H, 4.07; N, 9.50. Found: C, 44.68; H, 3.98; N, 9.40.

Tp'(CO)(PhC₂H)W(η^1 -C \equiv CPh) (5). A stoichiometric amount of lithium diisopropylamide (LDA) in THF/heptane (0.42 mL) was dripped slowly into a cold THF (-78 °C) solution of [Tp'(CO)(PhC₂H)₂][BF₄] (0.5 g, 0.63 mmol), resulting in an immediate color change from brown to green, a shift in IR CO stretching frequency from 2080 to 1896 cm⁻¹, and the appearance of a C \equiv C triple bond stretch at 2075 cm⁻¹. Solvent was removed after the solution had warmed to room temperature. The solid residue was chromatographed on alumina with toluene as eluent. A green band was collected and toluene was removed. The solid that formed was recrystallized from CH₂Cl₂/hexanes to yield green crystals

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(0.36 g, 80%). IR (KBr, cm^{-1}): $\nu_{\text{BH}} = 2548$, $\nu_{\text{CC}} = 2070$, $\nu_{\text{CO}} = 1896$, $\nu_{\text{CN}} = 1544$. ^1H NMR of major isomer (70%) (CD_2Cl_2 , δ): 13.31 ($^2J_{\text{WH}} = 4.4$ Hz, PhC_2H_5), 7.22, 7.16, 7.03, 6.80 (2 C_6H_5), 5.90, 5.88, 5.72 ($\text{Tp}'\text{CH}$), 3.02, 2.56, 2.48, 2.35, 1.91, 1.57 ($\text{Tp}'\text{CCH}_3$). ^1H NMR of minor isomer (30%) (CDCl_3 , δ): 13.38 (PhC_2H_5), 7.84, 7.70, 7.57, 7.46 (2 C_6H_5), 6.11, 5.88, 5.78 ($\text{Tp}'\text{CH}$), 3.02, 2.58, 2.54, 2.44, 1.91, 1.63 ($\text{Tp}'\text{CCH}_3$). ^{13}C NMR of major isomer (70%) (CD_2Cl_2 , δ): 235.7 ($^1J_{\text{WC}} = 136$ Hz, $^3J_{\text{HC}} = 8.4$ Hz, CO), 212.6 ($^1J_{\text{WC}} = 52$ Hz, $^2J_{\text{HC}} = ^3J_{\text{HC}} = 6$ Hz, HCCPh), 197.0 ($^1J_{\text{HC}} = 213$ Hz, PhCCH), 154.7, 154.2, 148.4, 145.4, 145.3, 144.5 ($\text{Tp}'\text{CCH}_3$), 141.7 ($^1J_{\text{WC}} = 152$ Hz, $\text{WC}=\text{CPh}$), 139.2, 136.8, 130.4, 129.9, 129.3, 128.7, 128.2, 126.1 (Ph), 108.2, 107.7, 107.0 ($\text{Tp}'\text{CH}$), 68.4 ($\text{WC}=\text{CPh}$), 16.5, 16.2, 15.7, 13.0, 12.9, 12.7 ($\text{Tp}'\text{CCH}_3$). Anal. Calcd for $\text{W}_1\text{C}_{32}\text{H}_{33}\text{N}_6\text{O}_1\text{B}_1$: C, 53.96; H, 4.64; N, 11.80. Found: C, 53.77; H, 4.60; N, 11.49.

$[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{R})\text{Ph}][\text{BF}_4]$ ($\text{R} = \text{Me}, \text{Et}$). In a representative synthesis, a red-brown solution of $\text{Tp}'(\text{CO})_2\text{W}(\eta^2\text{-CPh}=\text{CH}_2)$ (0.64 g, 1.0 mmol) in 30 mL of $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (1:5) was cooled to 0 °C. A red-orange precipitate formed when a stoichiometric amount of $\text{HBF}_4\cdot\text{Me}_2\text{O}$ was added dropwise. The flask was put in the freezer (-40 °C) after 20 mL of Et_2O was added. The red-orange powder which formed was isolated by filtration, washed with Et_2O (2 \times 10 mL), and dried in vacuo (0.66 g, 90%). Recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ yields red-orange crystals.

$[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{Me})\text{Ph}][\text{BF}_4]$ (6). IR (KBr, cm^{-1}): $\nu_{\text{BH}} = 2571$; $\nu_{\text{CO}} = 2034$, 1941; $\nu_{\text{CN}} = 1542$; $\nu_{\text{BF}} = 1070$. ^1H NMR (CD_2Cl_2 , δ): 7.87, 7.73, 7.60 (C_6H_5), 6.18, 6.15 (1:2, $\text{Tp}'\text{CH}$), 2.66, 2.47, 2.42, 2.14 (3:6:3:6, $\text{Tp}'\text{CCH}_3$), 2.35 ($\text{W}=\text{C}(\text{Ph})\text{CH}_3$). ^{13}C NMR (CD_2Cl_2 , δ): 225.6 ($^1J_{\text{WC}} = 40$ Hz, $\text{W}=\text{C}(\text{Ph})\text{Me}$), 212.3 ($^1J_{\text{WC}} = 140$ Hz, 2 CO), 155.4, 154.0, 149.0, 148.4 (1:2:1:2, $\text{Tp}'\text{CCH}_3$), 140.0 ($^2J_{\text{WC}} = 16$ Hz, C_{ipso}), 135.2, 133.9, 130.1 (Ph), 109.9, 109.1 (1:2, $\text{Tp}'\text{CH}$), 16.5, 14.3, 13.6, 12.6 (1:2:1:2, $\text{Tp}'\text{CCH}_3$), -22.8 (q, $^1J_{\text{HC}} = 132$ Hz, $\text{W}=\text{C}(\text{Ph})\text{CH}_3$). Anal. Calcd for $\text{WC}_{26}\text{H}_{32}\text{N}_6\text{O}_2\text{B}_2\text{F}_4\text{Cl}_2$: C, 38.40; H, 3.94; N, 10.33. Found: C, 38.72; H, 3.97; N, 10.44.

$[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{CH}_2\text{D})\text{Ph}][\text{BF}_4]$ (7). This compound was prepared using $\text{Tp}'(\text{CO})_2\text{W}(\eta^2\text{-CPh}=\text{CHD})$ as a reagent in place of $\text{Tp}'(\text{CO})_2\text{W}(\eta^2\text{-CPh}=\text{CH}_2)$. ^{13}C NMR (CD_2Cl_2 , δ): -22.8 ($^1J_{\text{DC}} = 20$ Hz for $\text{W}=\text{C}(\text{Ph})\text{CH}_2\text{D}$).

$[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{Et})\text{Ph}][\text{BF}_4]$ (8). IR (KBr, cm^{-1}): $\nu_{\text{BH}} = 2570$; $\nu_{\text{CO}} = 2035$, 1945; $\nu_{\text{CN}} = 1544$; $\nu_{\text{BF}} = 1062$. (a) At 22 °C, ^1H NMR (CD_2Cl_2 , δ): 7.80, 7.60 (m, C_6H_5), 6.21, 6.20 (broad, $\text{Tp}'\text{CH}$), 2.65 [broad, $\text{W}=\text{C}(\text{Ph})\text{CH}_2\text{CH}_3$ and 2 $\text{Tp}'\text{CCH}_3$], 2.52, 2.45, 2.25 (broad, 4 $\text{Tp}'\text{CCH}_3$), 1.76 (t, $^3J_{\text{HH}} = 5.7$ Hz, $\text{C}(\text{Ph})\text{CH}_2\text{CH}_3$). ^{13}C NMR (CD_2Cl_2 , δ): 239.5 ($^1J_{\text{WC}} = 41$ Hz, $\text{W}=\text{C}(\text{Ph})\text{Et}$), 213.4 (broad, 2 CO), 155.5, 154.6, 149.5, 148.5 (broad, $\text{Tp}'\text{CCH}_3$), 140.7 ($^2J_{\text{WC}} = 14.5$ Hz, C_{ipso}), 132.8, 132.6, 130.3 (Ph), 109.9, 109.5 ($\text{Tp}'\text{CH}$), 19.7 (broad, $^1J_{\text{HC}} = 131$ Hz, $\text{W}=\text{C}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_3$), 16.6, 14.9, 13.5, 12.8 (broad, $\text{Tp}'\text{CCH}_3$), -11.4 (t, $^1J_{\text{HC}} = 121$ Hz, $\text{W}=\text{C}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_3$). (b) At -60 °C, ^1H NMR (CD_2Cl_2 , δ): 7.75, 7.56 (m, C_6H_5), 6.26, 6.16, 6.07 (1:1:1, $\text{Tp}'\text{CH}$), 3.48 (d of q, $^2J_{\text{HH}} = 17.5$ Hz, $^3J_{\text{HH}} = 5.2$ Hz, 1 H, $\text{W}=\text{C}(\text{Ph})\text{CH}(\text{H})\text{CH}_3$), 2.61, 2.48, 2.44, 2.40, 1.95 (3:3:3:6:3, $\text{Tp}'\text{CCH}_3$), 1.76 (d of q, $^2J_{\text{HH}} = 17.5$ Hz, $^3J_{\text{HH}} = 5.2$ Hz, $\text{W}=\text{C}(\text{Ph})\text{CH}(\text{H})\text{CH}_3$), 1.70 (broad, $\text{W}=\text{C}(\text{Ph})\text{CH}(\text{H})\text{CH}_3$). The two methylene protons $\text{W}=\text{C}(\text{Ph})\text{CH}(\text{H})\text{CH}_3$ coalesced at -5 °C, $\Delta G^\ddagger = 11.7$ kcal/mol. ^{13}C NMR (CD_2Cl_2 , δ): 238.7 ($^1J_{\text{WC}} = 41$ Hz, $\text{W}=\text{C}(\text{Ph})\text{Et}$), 214.9 ($^1J_{\text{WC}} = 134$ Hz, CO), 210.7 ($^1J_{\text{WC}} = 161$ Hz, CO), 154.7, 152.6, 148.6, 148.5, 146.9 (2:1:1:1:1, $\text{Tp}'\text{CCH}_3$), 139.8 ($^2J_{\text{WC}} = 14.5$ Hz, C_{ipso}), 132.2, 132.1, 129.7 (Ph), 109.1, 108.9, 108.4 (1:1:1, $\text{Tp}'\text{CH}$), 19.6 ($^1J_{\text{HC}} = 131$ Hz, $\text{W}=\text{C}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_3$), 16.1, 15.6, 13.2, 12.7, 12.3 (1:1:2:1:1, $\text{Tp}'\text{CCH}_3$), -11.8 (d of d, $^1J_{\text{HC}} = 145$ Hz, $^1J_{\text{HC}} = 96$ Hz, $\text{W}=\text{C}(\text{C}_6\text{H}_5)\text{CH}(\text{H})\text{CH}_3$). Anal. Calcd for $\text{W}_1\text{C}_{27}\text{H}_{34}\text{N}_6\text{O}_2\text{B}_2\text{F}_4\text{Cl}_2$: C, 39.21; H, 4.11; N, 10.16. Found: C, 38.82; H, 4.17; N, 10.22.

X-ray Diffraction Data Collection for $[\text{Tp}'(\text{CO})\text{W}(\text{PhC}=\text{CH})_2][\text{BF}_4]$ (1). A yellow-orange block of $[\text{Tp}'(\text{CO})\text{W}(\text{PhC}=\text{CH})_2][\text{BF}_4]$ of dimensions $0.30 \times 0.30 \times 0.10$ mm was selected and mounted on a glass wand coated with epoxy. Diffraction data were collected on a Rigaku automated diffractometer. A set of 25 centered reflections found in the region $27.17^\circ < 2\theta < 35.14^\circ$ 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 structure solution and refinement.¹⁶ 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

Table I. Crystallographic Data Collection Parameters

	$[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{Me})\text{Ph}][\text{BF}_4] \cdot 0.5\text{CH}_2\text{Cl}_2$ (6)	$[\text{Tp}'(\text{CO})\text{W}(\text{PhC}=\text{CH})_2][\text{BF}_4] \cdot \text{CH}_2\text{Cl}_2$ (1)
molecular formula	$\text{WC}_{25}\text{H}_{31}\text{B}_2\text{F}_4\text{N}_6\text{O}_2\text{Cl}$	$\text{WC}_{33}\text{H}_{36}\text{B}_2\text{F}_4\text{N}_6\text{OCl}_2$
formula weight, g/mol	770.47	885.05
crystal dimens, mm	$0.30 \times 0.40 \times 0.50$	$0.30 \times 0.30 \times 0.10$
space group	$P2_1/n$	$P2_1/n$
cell params		
a, Å	12.87 (1)	14.868 (3)
b, Å	12.378 (8)	13.085 (4)
c, Å	20.93 (3)	19.835 (3)
β , deg	103.34 (7)	109.22 (1)
vol, Å ³	3245 (5)	3644 (2)
Z	4	4
density calcd, g/cm ³	1.577	1.610
Collection and Refinement Parameters		
radiation (wavelength, Å)	Mo K α (0.70930)	Mo K α (0.70930)
monochromator	graphite	graphite
linear abs coeff, cm ⁻¹	38.6	34.4
scan type	$\theta/2\theta$	$\theta/2\theta$
2θ limit, deg	45	50
quadrant collectd	$\pm h+k+l$	$\pm h+k+l$
total no. of reflectns	4266	6411
data with $I \geq 2.5\sigma(I)$	3200	3155
R, %	7.0	5.2
R_w , %	8.7	7.1
GOF	4.81	2.23
no. of params	425	442
largest param shift	0.193	0.34

difference Fourier calculations. The anion was disordered and modeled by two superimposed tetrahedra, each with 50% occupancy. In the final cycles of refinement the entire group was assigned an anisotropic thermal parameter. Methylene chloride was included at 100% occupancy.

The 49 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. The final residuals¹⁷ for 422 variables refined against 3155 data with $I > 2.5\sigma(I)$ were $R = 5.2\%$ and $R_w = 7.1\%$.¹⁸ The final difference Fourier map had no peak greater than $1.72 \text{ e}/\text{Å}^3$.¹⁹

X-ray Diffraction Data Collection for $[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{Me})\text{Ph}][\text{BF}_4]$ (6). A red-orange block of $[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{Me})\text{Ph}][\text{BF}_4]$ of dimensions $0.30 \times 0.40 \times 0.50$ mm was selected and mounted on a glass wand coated with epoxy. Diffraction data were collected on an Enraf-Nonius CAD-4 automated diffractometer. A set of 20 centered reflections found in the region $30.0^\circ < 2\theta < 40.0^\circ$ 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 structure solution and refinement.¹⁶ The data were corrected for Lorentz-polarization effects during the final stages of data reduction. The crystal was checked for orientation every 200 reflections and was recentered if necessary.

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 anion was disordered and modeled by two superimposed groups, each with 50% occupancy. In the final cycles of refinement the entire group was assigned an anisotropic thermal parameter. Methylene chloride was included at 50% occupancy. Both of the above conditions contribute to a higher than normal R factor.

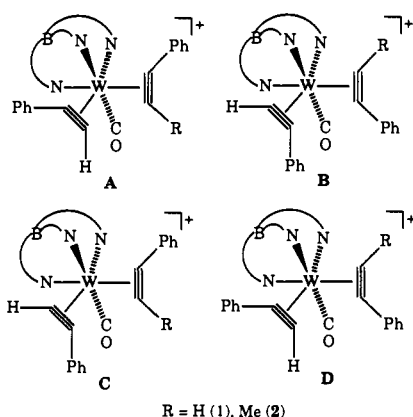
The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated by using a C-H distance of 0.96 Å and an isotropic thermal parameter calculated from the anisotropic values for the atoms to which they were connected. The final residuals¹⁷ for 389 variables refined against 3200 data with $I > 2.5\sigma(I)$ were $R = 7.0\%$ and $R_w = 8.7\%$.¹⁸ The final difference Fourier map had no peak greater than $1.45 \text{ e}/\text{Å}^3$.¹⁹

(17) The function minimized was $\sum \omega(|F_o| - |F_c|)^2$, where ω is based on counter statistics.

(18) $R = \sum (|F_o| - |F_c|) / \sum |F_o|$ and $R_w = [\sum \omega(|F_o| - |F_c|)^2 / \sum \omega F_o^2]^{1/2}$.
 (19) Scattering factors were taken from the following: Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Ibers, J. A., Hamilton, J. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.

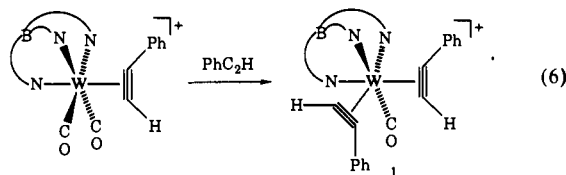
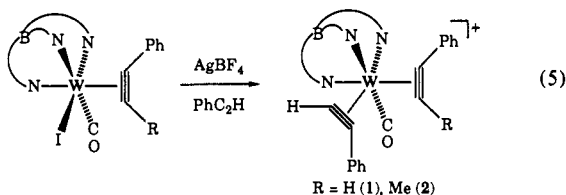
(16) Programs used during solution and refinement were from the NRCVAX structure determination package. Gabe, E. J.; Le Page, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Chem.* 1989, 22, 384.

Chart I



Results and Discussion

Cationic Bisalkyne Complexes. Complex **1**, $[\text{Tp}'(\text{CO})\text{W}(\text{PhC}\equiv\text{CH})_2][\text{BF}_4]$, was prepared by two routes: (a) alkyne substitution for iodide from the neutral iodide complex (eq 5);



(b) alkyne substitution for one carbonyl in the cationic dicarbonyl complex $[\text{Tp}'(\text{CO})_2\text{W}(\text{PhC}\equiv\text{CH})][\text{BF}_4]$ (eq 6). Mixed complex **2** with phenylacetylene and phenylpropyne ligands was synthesized by route a only. Purification of the products by filtration through fresh Celite and recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ yielded yellow-orange crystals.

IR spectra exhibit a Tp' B–H absorbance at 2566 cm^{-1} , which is sufficiently high to be diagnostic for a cationic complex.²⁰ The B–F stretching frequency appears at 1071 cm^{-1} for the BF_4^- counterion. The lone carbonyl absorption at 2073 cm^{-1} is comparable to the 2074 cm^{-1} absorption reported for $[\text{CpMo}(\text{CO})(\text{PhC}_2\text{Ph})_2][\text{BF}_4]$ ²¹ and 60 cm^{-1} higher than the average value (2014 cm^{-1}) for the dicarbonyl monoalkyne complexes $[\text{Tp}'(\text{CO})_2\text{W}(\text{PhC}_2\text{R})][\text{BF}_4]$ ($2057, 1970\text{ cm}^{-1}$).¹⁵ This suggests that the alkyne ligand requires substantial back-bonding from the metal center, and by comparison to the linearly ligating carbonyl ligand the alkyne is a voracious single-faced π -acid ligand. Complex **2** displays similar IR properties with a slightly more electron rich metal center reflected in a lower metal carbonyl stretching frequency.

Three isomers are possible for **1** and four for mixed bisalkyne complex **2**, based solely on alternative orientations of the two alkyne ligands (A, B, and C or D in Chart I). NMR spectra of **1** revealed only an isomer of C_1 symmetry, presumably C (equivalent to D for R = H), present in solution. The solid-state structure is indeed geometry C as well, suggesting that isomers A and B of C_s symmetry are less favored, perhaps since they are more sterically hindered than isomer C. NMR spectra of **2** show only one isomer, and the data is compatible with isomer C according to comparisons of the NMR data with that of **1**.

Detailed NMR studies allowed us to better understand the geometry of the bisalkyne complexes. A chiral metal center, and

hence the absence of a mirror plane, was suggested by the three inequivalent pyrazolyl rings evident in both ^1H and ^{13}C NMR spectra. Observations in the unsymmetrical monoalkyne complexes indicate that¹⁵ the phenyl ring of the alkyne ligand is most likely to be directed toward the pyrazole rings, an alkyne hydrogen exhibits an intermediate propensity, and an alkyl group is least likely to be proximal to the Tp' ligand. Proximity to the pyrazole rings shifts ^1H signals to higher field. For compound **1** the acetylenic proton H_i , which is distal or "trans" to the CO and close to the Tp' , appears at higher field (10.39 ppm) with a smaller two-bond tungsten proton coupling (7.2 Hz) than the H_c proton, proximal or "cis" to the CO and away from Tp' , which appears at 13.04 ppm with a larger two-bond tungsten proton coupling of 9.5 Hz .

The two alkyne carbons which are trans to the CO and close to Tp' exhibit downfield chemical shifts and larger one-bond tungsten–carbon couplings of about 35 Hz (175.3 ppm , $^1J_{\text{WC}} = 37\text{ Hz}$, $\text{PhC}\equiv\text{CH}$; 167.7 ppm , $^1J_{\text{WC}} = 33\text{ Hz}$, $\text{HC}\equiv\text{CPh}$) relative to the alkyne carbons which are cis to the CO and away from Tp' which have upfield chemical shifts and smaller $^1J_{\text{WC}}$ couplings of about 10 Hz (173.6 ppm , $^1J_{\text{WC}} = 11\text{ Hz}$, $\text{HC}\equiv\text{CPh}$; 159.8 ppm , $^1J_{\text{WC}} < 10\text{ Hz}$, $\text{PhC}\equiv\text{CH}$). It is also interesting to note that the terminal alkyne carbons have a higher field chemical shift than the phenyl substituted alkyne carbons. The metal carbonyl carbon resonates at 205 ppm with a relatively small one-bond tungsten–carbon coupling of 102 Hz and a three-bond proton–carbon coupling of 6 Hz from one acetylenic proton. The mixed bisalkyne complex **2** exhibits analogous NMR properties. The chemical shifts and coupling properties of the terminal acetylenic proton (10.19 ppm , $^2J_{\text{WH}} = 7.2\text{ Hz}$), the carbonyl ligand (206 ppm , $^1J_{\text{WC}} = 105\text{ Hz}$), and the alkyne carbons (175.1 ppm , $^1J_{\text{WC}} = 10\text{ Hz}$, $\text{PhC}\equiv\text{CMe}$; 175.0 ppm , $^1J_{\text{WC}} = 36\text{ Hz}$, $\text{PhC}\equiv\text{CMe}$; 167.1 ppm , $^1J_{\text{WC}} = 10.3\text{ Hz}$, $\text{PhC}\equiv\text{CH}$; 164.8 ppm , $^1J_{\text{WC}} = 33\text{ Hz}$, $\text{PhC}\equiv\text{CH}$) support the assignment of isomer C as the only product observed in solution.

A number of bisalkyne complexes are known for group 6 metals,²² and several mixed bisalkyne complexes have been synthesized. Alkyne exchange can occur and often complicates isolation of pure mixed bisalkyne products. Formation of mixed bisalkyne complexes with two unsymmetrical alkyne ligands has been particularly elusive. From the 2 alkyne ligands 6 electrons are required to maintain an 18-electron count at the metal. The chemical shifts of the alkyne carbons here suggest that each alkyne ligand effectively donates three electrons to the metal center in accord with a simple three-center–four-electron molecular orbital scheme for the metal $d\pi$ –alkyne π_{\perp} interactions. Three-electron donor alkyne ligands are known in other complexes involving an alkyne and some other π -donor ligand competing for a single metal $d\pi$ acceptor orbital.²³

Crystal Structure of 1. The coordination sphere of tungsten can be described as roughly octahedral for **1**, if one considers each alkyne ligand as occupying a single coordination site. The Tp' ligand occupies three coordination sites trans to the three remaining ligands: CO and two $\text{PhC}\equiv\text{CH}$ ligands. Atomic positional parameters are listed in Table II. Selected intramolecular bond distances and angles are listed in Table III. An ORTEP drawing is shown in Figure 1. The BF_4^- anion was omitted from the drawing for clarity.

The salient geometrical features of **1** agree with those established by previous structural studies of d^4 bisalkyne complexes.²²

(a) The two cis phenylacetylenes are parallel to each other. The two alkynes are oriented with the two acetylenic protons splayed away from one another rather than adjacent, and of course the same is true for the phenyl substituents.

(b) The $\text{W}-\text{C}_{\text{alkyne}}$ bond distances of $2.17(2)\text{ \AA}$ ($\text{W}-\text{C}_{\text{Ph}}$) and $2.05(2)\text{ \AA}$ ($\text{W}-\text{C}_{\text{H}}$) (for the alkyne with the phenyl group away from the Tp' ligand) and $2.12(2)\text{ \AA}$ ($\text{W}-\text{C}_{\text{Ph}}$) and $2.09(2)\text{ \AA}$ ($\text{W}-\text{C}_{\text{H}}$) (for the alkyne with the phenyl group close to the Tp'

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Table II. Atomic Positional Parameters for $[\text{Tp}'\text{W}(\text{CO})(\text{PhC}\equiv\text{CH})_2][\text{BF}_4]$ (1)

	x	y	z	B_{iso}
W1	0.93146 (5)	0.20584 (5)	0.24475 (4)	2.55 (3)
C1	0.8598 (13)	0.1748 (14)	0.1382 (10)	3.7 (9)
O1	0.8200 (10)	0.1599 (11)	0.0822 (6)	5.5 (8)
C11	0.9321 (13)	0.0467 (13)	0.2394 (9)	3.2 (7)
C12	0.9989 (12)	0.0701 (13)	0.2948 (11)	4.1 (10)
C13	1.0784 (12)	0.0325 (14)	0.3512 (9)	3.2 (8)
C14	1.1644 (13)	0.0846 (14)	0.3718 (11)	4.2 (10)
C15	1.2422 (13)	0.0442 (18)	0.4255 (13)	5.5 (12)
C16	1.2331 (16)	-0.0437 (22)	0.4581 (10)	5.6 (13)
C17	1.1484 (17)	-0.0938 (17)	0.4401 (10)	5.1 (12)
C18	1.0691 (13)	-0.0569 (15)	0.3854 (11)	4.5 (10)
C21	0.8341 (13)	0.2409 (15)	0.2941 (9)	3.8 (10)
C22	0.7834 (12)	0.1933 (16)	0.2387 (9)	3.9 (9)
C23	0.6920 (13)	0.1520 (16)	0.1959 (10)	4.0 (9)
C24	0.6809 (13)	0.0632 (15)	0.1534 (10)	4.1 (10)
C25	0.5915 (17)	0.0313 (18)	0.1143 (12)	5.7 (12)
C26	0.5134 (16)	0.0894 (21)	0.1107 (13)	6.2 (13)
C27	0.5222 (14)	0.1760 (18)	0.1500 (16)	6.7 (15)
C28	0.6126 (13)	0.2111 (18)	0.1949 (11)	5.1 (11)
B1	1.1018 (14)	0.3813 (17)	0.2746 (10)	3.1 (9)
N31	0.9281 (10)	0.3694 (12)	0.2112 (6)	2.8 (7)
N32	1.0046 (10)	0.4254 (11)	0.2258 (6)	3.0 (7)
C33	0.9819 (15)	0.5215 (14)	0.2011 (9)	3.9 (10)
C34	0.8871 (14)	0.5239 (14)	0.1618 (10)	4.2 (10)
C35	0.8502 (14)	0.4288 (14)	0.1656 (9)	3.9 (9)
C36	1.0557 (16)	0.6010 (16)	0.2111 (11)	5.3 (12)
C37	0.7503 (14)	0.3954 (19)	0.1407 (11)	6.0 (12)
N41	1.0266 (9)	0.2725 (8)	0.3450 (6)	2.3 (6)
N42	1.0945 (10)	0.3445 (11)	0.3439 (7)	3.2 (7)
C43	1.1438 (12)	0.3753 (14)	0.4103 (9)	3.2 (8)
C44	1.1095 (12)	0.3201 (13)	0.4565 (9)	3.5 (9)
C45	1.0387 (11)	0.2588 (13)	0.4138 (8)	2.9 (8)
C46	1.2214 (14)	0.4529 (16)	0.4251 (9)	4.6 (10)
C47	0.9831 (14)	0.1846 (16)	0.4440 (9)	4.8 (10)
N51	1.0580 (9)	0.2170 (11)	0.2068 (6)	2.5 (6)
N52	1.1243 (9)	0.2916 (12)	0.2327 (7)	3.2 (7)
C53	1.1984 (13)	0.2871 (16)	0.2101 (9)	4.1 (10)
C54	1.1819 (14)	0.1916 (18)	0.1687 (10)	4.9 (11)
C55	1.0935 (13)	0.1539 (16)	0.1693 (9)	4.0 (9)
C56	1.2829 (14)	0.3458 (17)	0.2292 (11)	5.2 (12)
C57	1.0442 (16)	0.0605 (17)	0.1261 (14)	6.7 (14)
B11	0.7975 (10)	0.8380 (12)	0.0642 (8)	12.2 (13)
F11	0.7072 (12)	0.8443 (18)	0.0651 (14)	7.2 (8)
F12	0.7962 (17)	0.8194 (19)	-0.0031 (10)	8.0 (8)
F13	0.8434 (20)	0.7614 (17)	0.1074 (14)	17.5 (18)
F14	0.8430 (13)	0.9271 (15)	0.0873 (13)	7.2 (8)
F21	0.8243 (23)	0.8817 (20)	0.1295 (6)	15.2 (17)
F22	0.7043 (5)	0.8572 (21)	0.0301 (16)	22.0 (28)
F23	0.8115 (19)	0.7361 (3)	0.0711 (15)	7.2 (9)
F24	0.8497 (20)	0.8772 (18)	0.0261 (16)	11.2 (13)
C61	0.5183 (18)	0.1923 (24)	0.4907 (13)	8.1 (16)
C11	0.4221 (7)	0.2696 (7)	0.4464 (5)	10.5 (6)
C12	0.4950 (5)	0.1193 (6)	0.5558 (3)	8.2 (4)

ligand) are longer than those of most four-electron donor alkyne ligands ($\sim 2.00 \text{ \AA}$),²² and indeed they are consistent with three-electron donor alkyne bond lengths {2.06, 2.08, 2.12, 2.14 \AA for $[\text{CpMo}(\text{CO})(\text{MeC}\equiv\text{CMe})_2][\text{BF}_4]$ ²⁴ and 2.06, 2.07, 2.10, 2.21 \AA for $[\text{Cp}(\text{CO})_3\text{W}(\mu-\eta^1, \eta^2-\text{C}\equiv\text{CPh})\text{W}(\text{CO})(\text{HC}\equiv\text{CPh})\text{Cp}][\text{BF}_4]$.²⁵

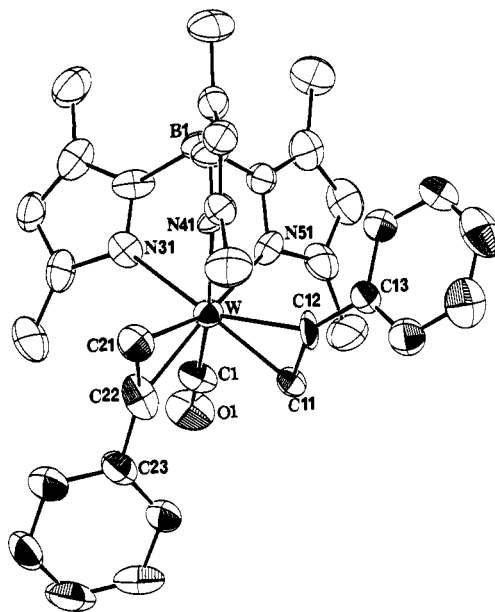
(c) The $\text{C}\equiv\text{C}$ bond distances of 1.25 (3) and 1.27 (3) \AA , only marginally shorter than distances typically reported for four-electron donor alkyne ligands ($\sim 1.30 \text{ \AA}$),²² are typical for three-electron donor alkyne ligands. Other complexes have shown bond distances between 1.23 and 1.30 \AA ,²² for example 1.27, 1.28 \AA for $[\text{CpMo}(\text{CO})(\text{MeC}\equiv\text{CMe})_2][\text{BF}_4]$ ²⁴ and 1.30, 1.30 \AA for $[\text{Cp}(\text{CO})_3\text{W}(\mu-\eta^1, \eta^2-\text{C}\equiv\text{CPh})\text{W}(\text{CO})(\text{HC}\equiv\text{CPh})\text{Cp}][\text{BF}_4]$ ($\text{Cp} = \pi\text{-C}_5\text{H}_5$).²⁵

(24) Mead, K. A.; Morgan, H.; Woodward, P. *J. Chem. Soc., Dalton Trans.* 1983, 271.

(25) Kolobova, N. E.; Skripkin, V. V.; Rozantseva, T. V.; Struchkov, Y. T.; Aleksandrov, G. G.; Andrianov, V. G. *J. Organomet. Chem.* 1981, 218, 351.

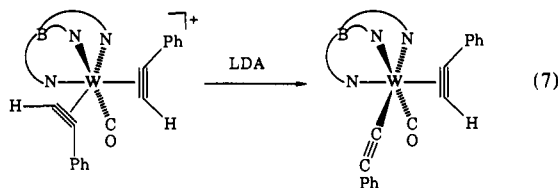
Table III. Selected Bond Distances (\AA) and Angles (deg) for $[\text{Tp}'\text{W}(\text{CO})(\text{PhC}\equiv\text{CH})_2][\text{BF}_4]$ (1)

W-C1	2.07 (2)	W-N51	2.25 (1)
W-C11	2.09 (2)	C11-C12	1.25 (3)
W-C12	2.12 (2)	C12-C13	1.42 (2)
W-C21	2.05 (2)	C21-C22	1.27 (3)
W-C22	2.17 (2)	C22-C23	1.45 (3)
W-N31	2.24 (2)	C1-O1	1.09 (2)
W-N41	2.21 (1)		
C1-W-C11	76.2 (7)	C21-W-N31	88.7 (6)
C1-W-C12	108.6 (8)	C21-W-N41	79.9 (6)
C1-W-C21	108.9 (7)	C21-W-N51	161.0 (6)
C1-W-C22	75.9 (7)	C22-W-N31	97.6 (6)
C1-W-N31	86.0 (6)	C22-W-N41	114.7 (6)
C1-W-N41	163.8 (6)	C22-W-N51	158.6 (5)
C1-W-N51	83.0 (6)	N31-W-N41	80.5 (4)
C11-W-C12	34.7 (7)	N31-W-N51	77.2 (5)
C11-W-C21	105.3 (8)	N41-W-N51	85.3 (5)
C11-W-C22	86.8 (8)	W-C1-O1	178 (2)
C11-W-N31	160.1 (6)	W-C11-C12	74 (1)
C11-W-N41	115.4 (5)	W-C12-C11	71 (1)
C11-W-N51	91.7 (7)	W-C12-C13	143 (1)
C12-W-C21	105.3 (7)	C11-C12-C13	145 (2)
C12-W-C22	106.1 (7)	W-C21-C22	78 (1)
C12-W-N31	154.4 (6)	W-C22-C21	67 (1)
C12-W-N41	81.1 (6)	W-C22-C23	143 (1)
C12-W-N51	83.8 (6)	C21-C22-C23	150 (2)
C21-W-C22	34.9 (7)		

**Figure 1.** ORTEP drawing of $[\text{Tp}'\text{W}(\text{CO})(\text{PhC}\equiv\text{CH})_2][\text{BF}_4]$.

(d) A standard alkyne ligand feature found in $[\text{Tp}'\text{W}(\text{CO})(\text{PhC}\equiv\text{CH})_2][\text{BF}_4]$ is the cis bent geometry of the alkynes. The C11-C12-C13 angle (for the alkyne with the phenyl substituent close to the Tp' ligand) is 145 (2) $^\circ$ and the C21-C22-C23 angle (for the alkyne with the phenyl substituent away from the Tp' ligand) is 150 (2) $^\circ$. Other bisalkyne complexes have shown $\text{R}-\text{C}\equiv\text{C}$ angles between 140 and 147 $^\circ$,²² for example 146 $^\circ$ for $[\text{CpMo}(\text{CO})(\text{MeC}\equiv\text{CMe})_2][\text{BF}_4]$ ²⁴ and 138, 147 $^\circ$ for $[\text{Cp}(\text{CO})_3\text{W}(\mu-\eta^1, \eta^2-\text{C}\equiv\text{CPh})\text{W}(\text{CO})(\text{HC}\equiv\text{CPh})\text{Cp}][\text{BF}_4]$.²⁵ Four-electron donor alkynes normally have 5–10 $^\circ$ larger cis bent $\text{R}-\text{C}\equiv\text{C}$ angles than three-electron donor alkynes.

Neutral Acetylide Alkyne Complex. Addition of a base such as LDA to the cationic bis(phenylacetylene) complex 1 formed a neutral alkyne acetylide tungsten(II) d^4 complex, $\text{Tp}'(\text{CO})(\text{PhC}_2\text{H})\text{W}(\text{C}\equiv\text{CPh})$, reflecting removal of one acetylenic proton (eq 7). The deprotonation reaction appears to be rapid as judged by the sudden color change from yellow-brown to green. The product was purified by chromatography on alumina. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexanes}$ produced green crystals. Two

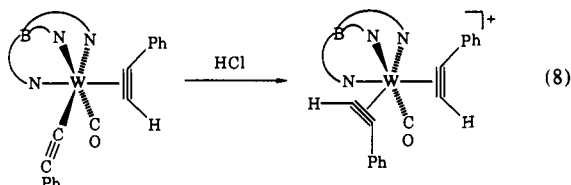


isomers (70:30) were observed by NMR, presumably differing by orientation of the alkyne ligand (Scheme II).

IR spectra display a $\text{Tp}'\text{B-H}$ absorbance at 2548 cm^{-1} which is typical for a neutral compound.²⁰ The carbonyl stretching frequency appears at 1896 cm^{-1} which is 9 cm^{-1} lower than that found in the $\text{Tp}'(\text{CO})(\text{PhC}_2\text{H})\text{W}(\text{C}\equiv\text{CPh})$ complex, suggesting that the acetylide ligand is a slightly better electron donor than iodide. The $\nu_{\text{C}\equiv\text{C}}$ triple bond stretching frequency appears at 2070 cm^{-1} which is lower than that for $\text{Cp}(\text{CO})_3\text{W}(\text{C}\equiv\text{CPh})$ (2105 cm^{-1}),²⁶ possibly suggesting more metal orbital overlap with the $-\text{C}\equiv\text{CPh}$ fragment in $\text{Tp}'(\text{CO})(\text{PhC}_2\text{H})\text{W}(\text{C}\equiv\text{CPh})$.

Both ^1H NMR and ^{13}C NMR spectra exhibit a 1:1:1 pattern for the dimethyl pyrazole ring signals, indicating that the metal center is chiral. Chemical shifts and coupling constants for the acetylenic proton and the alkyne carbons characterize the alkyne as a four-electron donor. The acetylenic proton (major isomer) appears near 13.3 ppm with a two-bond tungsten-proton coupling constant of 4.4 Hz. The phenyl substituted alkyne carbon resonates at 212.6 ppm, with a one-bond tungsten-carbon coupling of 6 Hz. This is downfield from the terminal carbon at 197.0 ppm which has a one-bond proton-carbon coupling constant of 213 Hz. The metal carbonyl carbon resonates at 236 ppm with a one-bond tungsten-carbon coupling of 136 Hz and three-bond proton-carbon coupling of 8.4 Hz to the terminal alkyne hydrogen. The α -carbon of the acetylide ligand appears at 141.7 ppm with a surprisingly large one-bond tungsten-carbon coupling of 152 Hz while C_β appears at 68.4 ppm, also suggesting substantial metal back-donation to the acetylide ligand π^* orbital. These chemical shifts resemble values of 129.3 ppm for C_α and 73.0 ppm for C_β reported for the $\text{Cp}(\text{CO})_3\text{W}(\text{C}\equiv\text{CPh})$ ²⁶ complex.

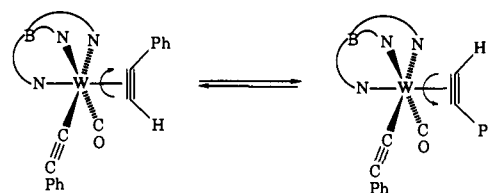
Reaction of this acetylide complex with aqueous hydrochloric acid yields the bis(phenylacetylene) complex (eq 8), while decomposition accompanied by carbon monoxide loss resulted when HBF_4 was used as the proton donor. Protonation of an acetylide ligand to form an alkyne rather than a vinylidene is highly unusual.



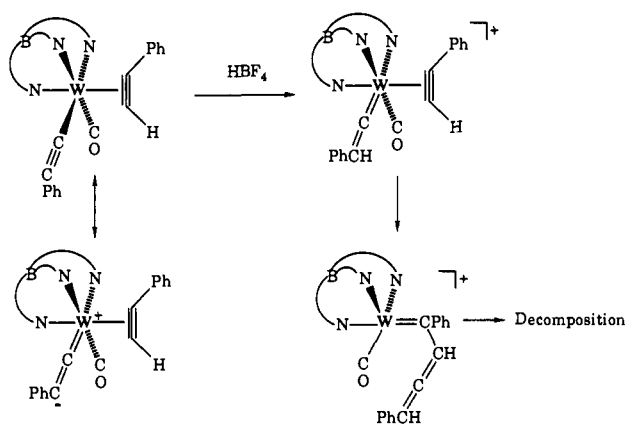
Protonation of acetylide ligands at C_β to make vinylidene ligands is commonly observed^{7a-d} because the β -position of the acetylide ligand is often extremely nucleophilic.^{7c} Indeed, it may be that protonation by HBF_4 leads to the formation of a vinylidene (an IR stretch for ν_{CO} for some intermediate is observed at 2045 cm^{-1}) which rapidly decomposes, possibly by coupling with the alkyne ligand (Scheme III). It may be that protonation by aqueous HCl reflects the relationship between the kinetic and thermodynamic factors in this system. Protonation at C_β is probably kinetically favored. One can imagine that chloride can act as a weak base and deprotonate the vinylidene at C_β to regenerate the starting acetylide complex. Protonation at C_α (maybe via initial metal protonation), although kinetically slow relative to C_β protonation, will then eventually siphon material toward the formation of the thermodynamically favored bisalkyne complex (Scheme IV).

Neutral η^1 -Vinyl Complex. Cationic bis(phenylacetylene)-tungsten(II) d^4 complex **1** reacts with super hydride (LiEt_3H)

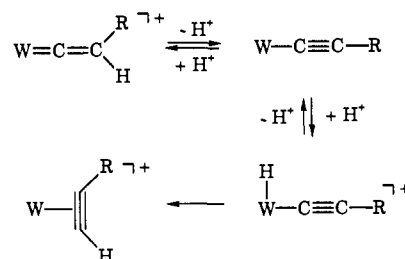
Scheme II



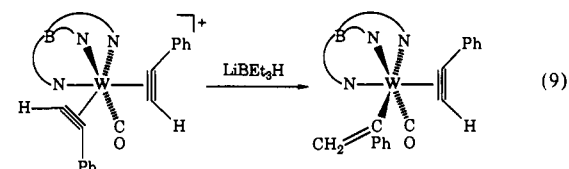
Scheme III



Scheme IV



in THF to form a neutral η^1 -vinyl complex, $\text{Tp}'(\text{CO})(\text{PhC}_2\text{H})\text{W}(\eta^1\text{-CPh}=\text{CH}_2)$, in good yield (eq 9). This neutral air stable



product was purified by chromatography on alumina followed by recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexanes}$. Two isomers (75:25) were identified by NMR, and we believe the isomers result from two distinct alkyne orientations (see Scheme II).

The infrared spectrum of $\text{Tp}'(\text{CO})(\text{PhC}_2\text{H})\text{W}(\eta^1\text{-CPh}=\text{CH}_2)$ displays a medium intensity absorption at 2548 cm^{-1} for ν_{BH} in the Tp' ligand. This value is compatible with formation of a neutral compound.²⁰ The ν_{CO} absorption at 1893 cm^{-1} is comparable to that for the related neutral complex $\text{Tp}'(\text{CO})(\text{PhC}_2\text{H})\text{W}(\text{C}\equiv\text{CPh})$ (1896 cm^{-1}). Both ^1H and ^{13}C NMR spectra reveal the inequivalence of all three pyrazole rings, indicating C_1 symmetry. NMR data suggest that this complex is best described as containing a four-electron donor alkyne and an η^1 -vinyl ligand rather than adopting an η^2 -vinyl coordination with a two-electron donor alkyne. The acetylenic proton appears about 13 ppm. The ^{13}C NMR spectrum displays acetylenic ^{13}C resonances near 214 and 204 ppm with the internal alkyne carbon downfield from the terminal carbon. A gated decoupled ^{13}C NMR spectrum served to identify the terminal alkyne carbon while furnishing a $^1J_{\text{HC}}$ coupling constant of 213 Hz. The two inequivalent vinyl protons appear near 5.80 and 4.30 ppm. Each signal is a doublet with a geminal coupling of 4 Hz while the three-bond W-H coupling is 14.4 Hz for one proton, presumably

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Scheme V

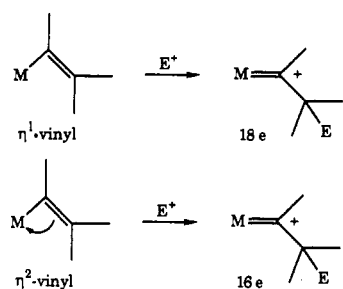
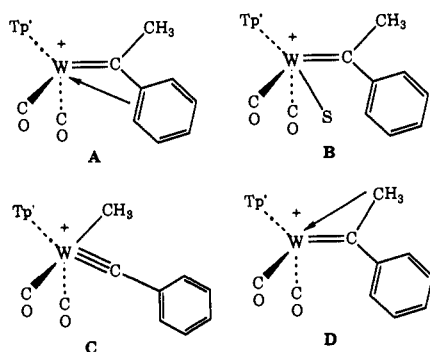
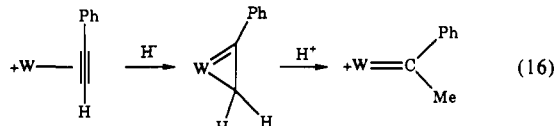


Chart III



If one follows simple counting schemes, these cationic products are formally 16-electron species. Protonation at the metal, $C\alpha$ or $C\beta$ could all lead to feasible cationic products: a saturated η^2 -vinyl hydride from metal protonation (A), a 16-electron olefin adduct from $C\alpha$ protonation (B), or a 16-electron carbene product from $C\beta$ protonation (C) (Chart II). The methylphenylcarbene formulation was suggested by the appearance of the unique new methyl signal at 2.4 ppm in the ^1H NMR spectrum. Thus protonation of the original alkyne terminal carbon results from addition of tetrafluoroboric acid to the neutral η^2 -vinyl monomers. The net result of sequential H^- , H^+ addition to the terminal alkyne carbon is conversion of $\text{PhC}\equiv\text{CH}$ to PhCCH_3 (eq 16). While

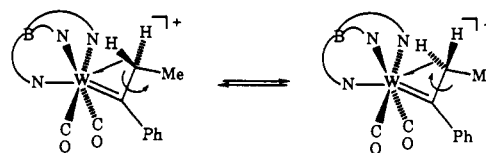


electrophilic addition to the $C\beta$ site of η^1 -vinyl ligands to form saturated carbenes maintains the metal electron count,³¹ a similar result from protonation of an η^2 -vinyl ligand leaves the metal unsaturated (Scheme V).

Several formulations which could produce 18-electron species deserve consideration given that a true 16-electron carbene would be a surprising ground-state geometry for this product (Chart III). The chemical shifts of the phenyl protons and carbons, and their coupling constants, were not indicative of any phenyl interaction with tungsten (A). Coordination of BF_4^- or CH_2Cl_2 was also considered, but no experimental evidence supported these possibilities (B).

The ^1H NMR properties of $[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{CH}_3)\text{Ph}][\text{BF}_4]$ were not indicative of unusual bonding schemes. The Tp' signals indicate that a mirror plane is present on the NMR time scale as the central pyrazole protons appear as two signals in a 2:1 intensity ratio near 6 ppm. The 3,5-dimethyl substituents also reflect equivalence of two of the pyrazole rings in the 6:3:6:3

Scheme VI



pattern observed for the six methyl groups. The unique carbene methyl group appears as a singlet at 2.4 ppm, which does not shift nor broaden appreciably down to -90°C . The only unusual piece of spectral data we obtained for the methylphenylcarbene complex was a high field ^{13}C chemical shift for the methyl carbon (-22.8 ppm). The $^1J_{\text{CH}}$ value of 132 Hz for this group could result either from a normal CH_3 moiety or averaging one agostic C-H coupling constant with two olefin-like C-H coupling constants.⁸ The monodeuterium substituted compound $[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{CH}_2\text{D})\text{Ph}][\text{BF}_4]$ was prepared in order to take advantage of the well-known zero point energy difference for agostic methyls which favors deuterium being in a terminal position. The labeled complex was prepared by protonation of the corresponding η^2 -vinyl complex $\text{Tp}'(\text{CO})_2\text{W}(\eta^2\text{-CPh}=\text{CHD})$ which had in turn been synthesized by D^- addition to the cationic alkyne complex $[\text{Tp}'(\text{CO})_2\text{W}(\text{PhC}_2\text{H})][\text{BF}_4]$. Partial deuterium incorporation did not cause a substantive change in either the methyl ^1H chemical shift or in the methyl $^1J_{\text{CH}}$ coupling constant down to -90°C .³² Facile rotation of agostic methyl groups is known to obscure NMR evidence for agostic bonding in some complexes.³³

Methylation at tungsten by transfer of the carbene methyl group to form a metal alkyl carbyne (C, Chart III) could account for the high field ^{13}C signal, but the presence of two carbonyl π -acid ligands in the coordination sphere of a cationic complex with a carbyne and two monoanionic ligands seemed intuitively unattractive. In other words, if one counts the putative carbyne (or alkylidyne) as a trianion the tungsten has no d electrons left (W^{6+} , d^0) to share with the two carbonyl ligands. The ν_{CO} values of 2033 and 1940 cm^{-1} , though high, are simply not high enough to justify a $[\text{Tp}'(\text{CO})_2\text{MeW}\equiv\text{CPh}]^+$ formulation.

The agostic formulation (D, Chart III) has been confirmed by a single crystal X-ray structure of the phenylmethylcarbene complex and by variable temperature NMR studies of the analogous ethyl derivative.

The ethylphenylcarbene displays an unusually high field shift for the methylene carbon (-11.4 ppm), suggesting a close structural analogy to the methyl derivative. (In contrast, an alkyl scandium example in which agostic spectral properties disappear when methyl is replaced by ethyl, changing from ethyl to propyl, has been reported.³⁴) The methylene $^1J_{\text{CH}}$ value of 121 Hz and several broad room temperature NMR signals for $[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{Ph})\text{CH}_2\text{Me}][\text{BF}_4]$ encouraged us to undertake low temperature NMR studies. Distinct proton signals for the two protons of the methylene group of the ethyl substituent were evident at -60°C (1.76 and 3.48 ppm, $^2J_{\text{HH}} = 17.5$ Hz, $^3J_{\text{HH}} = 5.2$ Hz). The absence of a mirror plane in the solution structure was also evident in the low temperature ^{13}C spectrum as two carbonyl carbon signals were detected (211 ppm, $^1J_{\text{WC}} = 161$ Hz; 215 ppm, $^1J_{\text{WC}} = 134$ Hz).

The keystone which definitively characterizes the cationic ethyl carbene complex as agostic was the doublet of doublets revealed at -60°C for the methylene carbon. The smaller $^1J_{\text{CH}}$ value of 96 Hz is the signature of an agostic bond,⁸ and the larger value of 145 Hz reflects rehybridization from sp^3 toward sp^2 for the methylene carbon. The $^1J_{\text{WC}}$ value of 41 Hz to the carbene carbon is also noteworthy. Coalescence of the methylene protons at -5°C indicates a barrier of 11.7 kcal/mol for enantiomer interconversion (Scheme VI).

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an agostic structure to overcome the metal unsaturation in the simple carbene formulation. The agostic bond present in $[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{Ph})\text{CH}_2\text{R}][\text{BF}_4]$ ($\text{R} = \text{H}, \text{Me}$) complements the range of saturated and unsaturated agostic ligands represented in Chart IV. In a sense the β -agostic carbene resembles both agostic π -complexes with unsaturation in the organic ligand and Schrock α -agostic carbenes with unsaturation in the metal-carbon bond.

Summary

Reaction of $[\text{Tp}'(\text{CO})_2\text{W}(\text{PhC}_2\text{H})][\text{BF}_4]$ with PhC_2H or reaction of $\text{Tp}'(\text{CO})\text{IW}(\text{PhC}_2\text{R})$ ($\text{R} = \text{H}, \text{Me}$) with $\text{PhC}_2\text{H}/\text{AgBF}_4$ generates cationic bisalkyne complexes $[\text{Tp}'(\text{CO})\text{W}(\text{PhC}_2\text{H})(\text{PhC}_2\text{R})][\text{BF}_4]$. A crystal structure of $[\text{Tp}'(\text{CO})\text{W}(\text{PhC}_2\text{H})_2][\text{BF}_4]$ shows a pseudooctahedral geometry with the two cis phenylacetylene ligands parallel to each other. Structural data and NMR data suggest each alkyne adopts a three-electron donor role with phenyl groups distal to one another. Deprotonation of the bis(phenylacetylene) complex yields an alkyne acetylide complex, $\text{Tp}'(\text{CO})_2(\text{PhC}_2\text{H})\text{W}(\text{C}\equiv\text{CPh})$, which exists as two isomers in solution, differing in alkyne orientation. Protonation of the acetylide compound with aqueous HCl yields the bisalkyne cation, but decomposition results when HBF_4 is used as a proton source. Hydride addition to the bis(phenylacetylene) complex forms an alkyne η^1 -vinyl complex, $\text{Tp}(\text{CO})(\text{PhC}_2\text{H})\text{W}(\eta^1\text{-CPh}=\text{CH}_2)$, which also exists as two isomers in solution due to

different alkyne orientations. NMR data support a formulation containing a σ -vinyl and a four-electron alkyne ligand. Protonation of the η^1 -vinyl complex at $\text{C}\beta$ results in the formation of an 18-electron alkyne carbene cation, $\text{Tp}'(\text{CO})(\text{PhC}_2\text{H})\text{W}=\text{C}(\text{Me})\text{Ph}][\text{BF}_4]$, with the alkyne acting as a four-electron donor. Here π donation from the alkyne ligand is observed rather than agostic bond formation from the carbene substituent. Protonation of the η^2 -vinyl complexes $\text{Tp}'(\text{CO})_2\text{W}(\eta^2\text{-CPh}=\text{CHR})$ ($\text{R} = \text{Me}, \text{H}$) at $\text{C}\beta$ of the η^2 -vinyl ligand forms β -agostic carbenes $\{\text{Tp}'(\text{CO})_2\text{W}[\text{C}(\text{R})\text{Ph}][\text{BF}_4]$ ($\text{R} = \text{Me}, \text{Et}$). An X-ray structure of the methyl derivative revealed a W-C (methyl) distance of 2.49 Å with the W-C α -C β angle being 91°. Rotation of the methyl group C-H agostic bonds is fast for the methyl derivative. Variable temperature NMR experiments on the ethyl derivative show a barrier of 11.7 kcal/mol for interconversion of enantiomers.

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Supplementary Material Available: Labeled diagrams of **1** and **6** and tables of anisotropic temperature factors and complete bond distances and angles for **1** and **6** (13 pages); listings of observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

Alcoholysis of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ by Polyethylene Glycols. Comparison with Bismuth(III) Nitrate Crown Ether Complexation

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Abstract: The reactions of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 3:1 $\text{CH}_3\text{CN}:\text{CH}_3\text{OH}$ with 12-crown-4, 18-crown-6, triethylene glycol (EO3), tetraethylene glycol (EO4), pentaethylene glycol (EO5), and hexaethylene glycol (EO6) were studied. The ready isolation of soluble bismuth(III) alkoxides resulted from simple reactions with the inexpensive polyethylene glycols. The EO3^- , EO4^- , and EO6^- complexes are dimeric, bridged by two alkoxide oxygen atoms. Coordination of each Bi^{3+} ion is completed by two NO_3^- anions and the remaining ether donor atoms. The chain length of EO5 is sufficient to allow both terminal alcohols to participate in bridging two Bi^{3+} centers. The net ionization of one is accomplished by a dually ionized EO5 ligand and a neutral EO5 complex producing a rather complicated structure. The neutral crown ether complexes formed are similar to those isolated for the late lanthanides. The structurally characterized complexes include $[\text{Bi}(\text{NO}_3)_2(\text{EO3}^-)]_2$, $[\text{Bi}(\text{NO}_3)_2(\text{EO4}^-)]_2 \cdot 2\text{MeOH}$, $[\text{Bi}(\text{NO}_3)_2(\text{EO5})][\text{Bi}(\text{NO}_3)_2(\text{EO5}^{2-})\text{Bi}(\text{NO}_3)_3] \cdot 2\text{H}_2\text{O}$, $[\text{Bi}(\text{NO}_3)_2(\text{EO6}^-)]_2$, $[\text{Bi}(\text{NO}_3)_3(12\text{-crown-4})]$, and $[\text{Bi}(\text{NO}_3)_3(\text{OH}_2)_3] \cdot 18\text{-crown-6}$. The two covalent Bi-alkoxide interactions activate the Bi^{3+} lone pair resulting in structures with secondary Bi-O contacts surrounding the lone pair site. This results in a very wide range of Bi-O donor contacts. The crown ether complexes do not contain any covalent interactions and do not exhibit lone pair effects. The Bi-O separations have a much narrower range.

Introduction

The chemistry of bismuth has been relatively ignored until recently when the flurry over high T_c oxide-superconducting materials¹⁻⁵ renewed interest in bismuth alkoxides as potential precursors for new superconductor formulations.⁶⁻⁹ Unfortunately, many of the simple alkoxides prepared by alcoholysis have poor solubilities or disproportionate to oxo-centered species.^{10,11} The use of chelating alkoxides for a variety of metals¹¹⁻²¹ has received attention lately as a way to reduce the extent of alkoxide bridging; however, thus far only relatively short chain polyethers with one terminal alkyl group have been examined. Polyethylene

glycol (PEG) and crown ether complexes of bismuth(III) are virtually nonexistent, with two recent reports discussing the

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