(replacing a like R group in R_3Sb with a halogen atom) about the antimony center as well as the inability of $(Me_3CCH_2)_2SbI$ to invert about the antimony center at ambient temperature. However, for **2c**, a room-temperature ^1H spectrum reveals a broadened resonance for the methylene hydrogens ($\nu_{1/2}$ = 7.1 Hz) located midway between where expected diastereotopic resonances for this complex would occur. This anomaly led us to examine **1c** and **2c** by variable-temperature ^1H NMR. For **2c**, as the temperature is lowered from ambient to −70 °C, the methylene resonance continues to broaden ($\nu_{1/2} > 30$ Hz). Even at −70 °C, an AB pattern is not observed. Warming the sample from −70 °C to ambient and continuing to 50 °C produces only a narrowing of the methylene resonance with $\nu_{1/2}$ = 3.1 Hz at 50 °C. This system shows no concentration dependence. Examination of the analogous neopentyl system shows only a slight broadening of the AB pattern at elevated temperatures. We believe the difference in the NMR spectra of these two systems results from $(Me_3CCH_2)_2SbI$ adopting a pyramidal structure and $(Me_3SiCH_2)_2$ SbI one that is intermediate between pyramidal and planar. Because of intramolecular crowding between the Me_3Si groups of the two Me_3SiCH_2 ligands, **2c** could be forced to expand its C–Sb–C angle beyond ca. 95°. The opening of this angle would force a "flattening" of the molecule (a more planar structure). Heating such a system would tend to increase the rate of inversion about the antimony center, thus giving rise to a "time-averaged" (on the NMR time scale) planar geometry and a single, narrow resonance for the methylene hydrogens. If the temperature is lowered in this system, the inversion rate would decrease and a more pyramidal geometry would be favored. However, if internal repulsion forces between the two Me_3SiCH_2 groups were significant, a true pyramidal structure would be energetically unfavorable and a structure intermediate between pyramidal and planar would result. This would account for our observation of only a broadened resonance for the methylene hydrogens, rather than a resolved AB pattern, at low temperatures. Examination of the ^{13}C spectra shows three resonances for **1c** and two resonances for **2c**. The methylene carbon (or α-carbon) exhibits an expected downfield shift of 4.5 ppm for **1c** and 5.4 ppm for **2c** as compared to the parent triorgano compounds **1a** and **2a** due to the presence of the iodine.

A further iteration of the reactions starting with **1c** or **2c** produces the five-coordinate triiodide species (R_2SbI_3 for **1d** or **2d**) and the alkyl(diiodo)stibines ($RSbI_2$ for **1e** or **2e**). The triiodide compounds are dark orange, air-sensitive solids. They also show diminished stability in the presence of light or when stored at ambient temperature. Under either of these conditions, the triiodidies reductively eliminate RI to afford $RSbI_2$ (**1e** or **2e**). However, both **1d** and **2d** are indefinitely stable when stored under an inert atmosphere at −20 °C in the absence of light. The alkyl(diiodo)stibines ($RSbI_2$) are bright yellow, highly viscous, air-sensitive oils. Unlike the monoiodo complexes, these species exhibit simple ^1H NMR spectra (no diastereotopic hydrogens).

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Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms and H-atom coordinates with isotropic parameters for **1a**, **1b**, **2a**, and **2b** and packing diagrams for **1b** and **2a** (6 pages). Ordering information is given on any current masthead page.

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(η^2-Vinyl)- and (η^3-Allyl)tungsten(II) Complexes Containing a Hydridotris(3,5-dimethylpyrazolyl)borate Ligand

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Cationic alkyne complexes react with anionic nucleophiles to generate the η^2-vinyl complexes $Tp'(CO)_2W(\eta^2\text{-}RC{=}CRR')$. Reaction of $[Tp'(CO)_2W(PhC{\equiv}CH)][BF_4]$ with $P(OMe)_3$ produces a $P(O)(OMe)_2$-substituted η^2-vinyl complex, $Tp'(CO)_2W[\eta^2\text{-}CPh{=}CHP(O)(OMe)_2]$, which can be protonated at the oxygen to generate a cationic $P(OH)(OMe)_2$-substituted η^2-vinyl complex, $\{Tp'(CO)_2W[\eta^2\text{-}CPh{=}CHP(OH)(OMe)_2]\}[BF_4]$. Reaction of $[Tp'(CO)_2W(RC{\equiv}CMe)][BF_4]$ (R = Me, Ph) with $LiBEt_3H$ generates η^3-allyl complexes via an η^2-vinyl intermediate. Reaction of $[Tp'(CO)_2W(PhC{\equiv}CMe)][BF_4]$ with $LiCu(Bu^n)_2$ yields an η^1-acyl complex, $Tp'(CO)W(PhC{\equiv}CMe)[\eta^1\text{-}C(O)Bu^n]$, in which the alkyne ligand acts as a four-electron donor.

Introduction

Isolation and characterization of η^2-vinyl complexes have important mechanistic implications since such results imply that vinyl ligands may stabilize unsaturated intermediates. Molecular orbital analyses, which can serve as a guide to synthetic efforts, indicate that four-electron-donor alkyne and η^2-vinyl ligands will bind to similar metal fragments (Chart I); they are isolobal ligands.[1] The three fundamental metal–ligand interactions (σ donation, $\pi_\perp$ donation, and π^* acceptance) identified in monomeric d^4 alkyne complexes have orbital analogies in $\eta^2\text{-}RC{=}CR_2$ ligands. These isolobal relationships are germane to synthetic transformations of alkyne ligands.

Four-electron-donor alkyne ligands have been converted to η^2-vinyl ligands, $RC{=}CR_2$, by addition of nucleophiles. Green and co-workers have reported that reactions of cationic alkyne complexes of the type $[CpL_2M(RC_2R)]^+$ with anionic nucleophiles generate neutral η^2-vinyl complexes, $[CpL_2Mo(\eta^2\text{-}RC{=}CRR')]$ (eq 1).[2] Note that

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[1] Brower, D. C.; Birdwhistell, K. R.; Templeton, J. L. *Organometallics* **1986,** *5,* 94.

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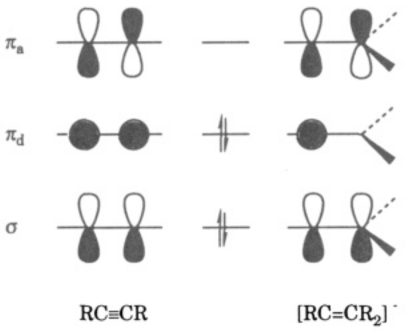
Chart I



two-electron-donor alkyne ligands in stereochemically similar iron compounds form η^1-vinyls when a nucleophile adds to an alkyne carbon (eq 2).[3] Addition of neutral heteroatom nucleophiles to terminal alkynes to form a neutral η^2-vinyl product has also been reported (eq 3).[4]

$$CpL_2Mo(RC{\equiv}CR)^+ \xrightarrow{R'^-} CpL_2Mo(\eta^2\text{-}CR{=}CRR') \quad (1)$$

$$CpL_2Fe(RC{\equiv}CR)^+ \xrightarrow{R'^-} CpL_2Fe(\eta^1\text{-}CR{=}CRR') \quad (2)$$

$$(dtc)_2(olefin)Mo(PhC{\equiv}CH) \xrightarrow{PR_3} (dtc)_2(olefin)Mo(\eta^2\text{-}CPh{=}CHPR_3) \quad (3)$$

Structural features of η^2-vinyl complexes in the Cp system reported[2] by Green and co-workers include the following: (a) the orientation of the two C_β substituents is roughly orthogonal to the $MC_\alpha C_\beta$ plane; (b) short M–C_α distances (1.94–1.96 Å) are appropriate for a Mo–C double bond; (c) M–C_β distances (2.25–2.30 Å) are in the single-bond range; (d) C_α–C_β bond lengths (1.43–1.46 Å) are indicative of some double-bond character.

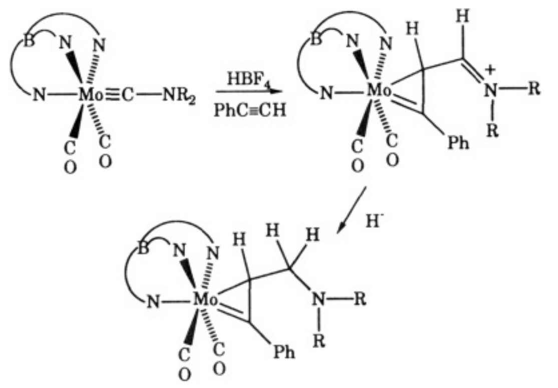
Reactions of bis(alkyne) complexes with nucleophiles have produced both η^2-vinyls and η^1-vinyls. Addition of heteroatom nucleophiles such as phosphines to $CpM(CF_3C_2CF_3)_2X$ monomers formed the η^2-vinyl complexes $CpX(CF_3C_2CF_3)M[\eta^2\text{-}CF_3C{=}C(CF_3)PR_3]$ (eq 4).[5] The electron-poor perfluorinated alkyne ligands promote η^2-vinyl formation, since the CF_3 substituents can increase the electrophilicity of the alkyne carbon and stabilize the remaining alkyne as a two-electron donor. Informative comparisons are provided by the formation of η^1-vinyl ligands upon nucleophilic addition of anionic nucleophiles to the cationic bis(alkyne) complexes $[CpMo(CH_3C{\equiv}CCH_3)_2(CO)]^+$ (eq 5)[6] and $[Tp'W(PhC{\equiv}CH)_2(CO)]^+$ (eq 6; Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate).[7]

$$CpXM(CF_3C{\equiv}CCF_3)_2 \xrightarrow{:Nu} CpX(CF_3C{\equiv}CCF_3)M(\eta^2\text{-}CCF_3{=}CCF_3Nu) \quad (4)$$

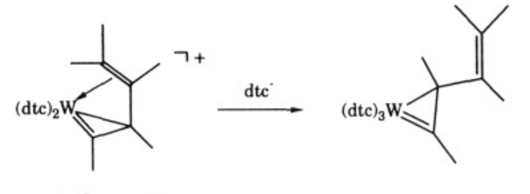
$$Cp(CO)Mo(MeC{\equiv}CMe)_2{}^+ \xrightarrow{R^-} Cp(CO)(MeC{\equiv}CMe)Mo(\eta^1\text{-}CMe{=}CRMe) \quad (5)$$

$$Tp'(CO)W(PhC{\equiv}CH)_2{}^+ \xrightarrow{H^-} Tp'(CO)(PhC{\equiv}CH)W(\eta^1\text{-}CPh{=}CH_2) \quad (6)$$

Formation of η^2-vinyl complexes can be achieved by other, less direct, pathways. Protonation of an aminocarbyne complex in the presence of free alkyne produces a cationic η^2-vinyl complex which can add a hydride to form a neutral η^2-vinyl product (eq 7).[8] A rare tungsten(IV) d^2 vinyl-substituted η^2-vinyl ligand was obtained by ligand addition to an electron-deficient 16-electron cation containing an η^4-butadienyl ligand, $[(S_2CNR_2)_2W(\eta^4\text{-}CPhCPhCPhCPhH)]^+$. Dechelation of the vinyl tail, promoted by the incoming anionic chelating dithiocarbamate ligand, would generate the observed product (eq 8).[9]



(7)



(8)

Several η^2-vinyl isomerization reactions have been reported. Rearrangement to form an η^3-allyl ligand after initial formation of an η^2-vinyl ligand from nucleophilic[10] (eq 9) or electrophilic[11] (eq 10) addition to an alkyne ligand bearing a β-hydrogen has been observed. Rearrangement to a carbyne from an η^2-vinyl has also been reported.[2,10]

$$CpL_2M(RC{\equiv}CMe)^+ \xrightarrow{R'^-} CpL_2M(\eta^3\text{-}CH_2CHCRR') \quad (9)$$

$$CpLRh(MeC{\equiv}CMe) \xrightarrow{H^+} CpLRh(\eta^3\text{-}CH_2CHCHMe)^+ \quad (10)$$

We have undertaken a study of the reactivity of cationic four-electron-donor alkyne complexes with nucleophiles. We report here the formation of (1) η^2-vinyl and η^3-allyl complexes from nucleophilic addition to the alkyne ligand and (2) an alkyne η^1-acyl complex from nucleophilic attack at a carbonyl ligand.

Experimental Section

General Methods. Manipulations involving air-sensitive reagents were performed under a dry nitrogen atmosphere with standard Schlenk techniques. Solvents were purified as follows: methylene chloride was distilled from P_2O_5; Et_2O, THF, and hexanes were distilled from potassium benzophenone ketyl; other solvents were purged with N_2 gas prior to use. Alkyne complexes $[Tp'(CO)_2W(PhC{\equiv}CR)][BF_4]$ (R = H, Me, Ph) were prepared according to literature methods.[12] Other reagents were used as

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obtained from commercial sources.

Infrared spectra were recorded on a Mattson Polaris FT IR spectrometer. NMR spectra were recorded on a Varian XL-400 (400 MHz) spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, or Oneida Research Services Inc., Whitesboro, NY.

Syntheses. Tp′(CO)$_2$W(η^2-CPh=CH$_2$) (1). A stoichiometric amount of Li[BEt$_3$H] in THF (1.5 mL, 1.5 mmol) was dripped slowly into a cold (−78 °C) THF solution of [Tp′(CO)$_2$W(HC$_2$Ph)][BF$_4$] (1.1 g, 1.5 mmol). The solution color changed from green to brown. Solvent was evaporated after the solution had warmed to room temperature. The solid residue was chromatographed on alumina with toluene as the eluent. A brown band was collected, and toluene was removed. The solid which remained was recrystallized from toluene/hexanes to yield brown crystals (0.75 g, 78%). IR (KBr, cm^{-1}): ν_{CO} = 1951, 1863. ^{1}H NMR (CD$_2$Cl$_2$, δ): 8.08, 7.58, 7.43 (C$_6$*H*$_5$), 5.98, 5.92 (1:2, Tp′C*H*), 2.74, 2.49, 2.43, 1.85 (3:6:3:6, Tp′ CC*H*$_3$), 1.32 ($^2J_{WH}$ = 13 Hz, 2 H, η^2-CPh=C*H*$_2$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 234.4 ($^1J_{WC}$ = 28 Hz, η^2-*C*Ph=CH$_2$), 222.5 ($^1J_{WC}$ = 154 Hz, *C*O), 153.8, 151.8, 146.0, 145.0 (1:2:1:2, Tp′ *C*CH$_3$), 143.5, 134.1, 129.2, 129.1 (*Ph*), 107.6, 107.3 (1:2, Tp′ *C*H), 17.3 (t, $^1J_{HC}$ = 158 Hz, $^1J_{WC}$ = 24 Hz, η^2-CPh=*C*H$_2$), 16.0, 14.5, 13.0, 12.8 (1:2:1:2, Tp′ C*C*H$_3$). Anal. Calcd for Tp′(CO)$_2$W(η^2-CPh=CH$_2$)·$^1/_4$C$_7$H$_8$, WC$_{26.75}$H$_{31}$N$_6$O$_2$B: C, 48.44; H, 4.68; N, 12.68. Found: C, 48.38; H, 4.69; N, 12.69.

Tp′(CO)$_2$W(η^2-CPh=CHD) was prepared by using Li[BEt$_3$D] in place of Li[BEt$_3$H].

Tp′(CO)$_2$W(η^2-CPh=CHMe) (2). A stoichiometric amount of MeLi in Et$_2$O (1.0 mL, 1.5 mmol) was dripped slowly into a cold (−78 °C) THF solution of [Tp′(CO)$_2$W(HC$_2$Ph)][BF$_4$] (1.1 g, 1.5 mmol). The solution color changed from green to brown. Solvent was evaporated after the solution had warmed to room temperature. The solid residue was chromatographed on alumina with toluene as the eluent. A red-brown band was collected, and toluene was removed. The solid was recrystallized from CH$_2$Cl$_2$/hexanes to yield red-brown crystals (0.4 g, 41%) of Tp′(CO)$_2$W(η^2-CPh=CHMe). IR (KBr, cm^{-1}): ν_{CO} = 1935, 1838. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.29, 7.11, 6.81 (C$_6$*H*$_5$), 5.91, 5.69 (2:1, Tp′C*H*), 3.50 (q, $^3J_{HH}$ = 5.5 Hz, η^2-CPh=C*H*Me), 2.27 (d, $^3J_{HH}$ = 5.5 Hz, η^2-CPh=CH*Me*), 2.59, 2.57, 2.49, 2.42, 1.80, 1.62 (Tp′ CC*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 264.5 ($^1J_{WC}$ = 80 Hz, η^2-*C*Ph=CHMe), 239.1 ($^1J_{WC}$ = 168 Hz, *C*O), 222.4 ($^1J_{WC}$ = 149 Hz, *C*O), 153.6, 153.1, 146.0, 145.1, 145.0 (Tp′*C*CH$_3$), 144.8, 129.0, 128.8, 127.8 (*Ph*), 107.7, 107.4, 107.2 (Tp′ *C*H), 38.0 (d of q, $^1J_{HC}$ = 156 Hz, $^2J_{HC}$ = 4.8 Hz, η^2-CPh=*C*HMe), 28.8 (q, $^1J_{HC}$ = 126 Hz, η^2-CPh=CH*Me*), 15.8, 15.6, 15.0, 13.0, 12.9, 12.8 (Tp′ C*C*H$_3$). Anal. Calcd for WC$_{26}$H$_{31}$N$_6$O$_2$B: C, 47.73; H, 4.74; N, 12.85. Found: C, 47.63; H, 4.94; N, 12.55.

Tp′(CO)$_2$W(η^2-CPh=CHPh) (3). A stoichiometric amount of LiBEt$_3$H in THF (0.62 mL, 0.62 mmol) was dripped slowly into a cold (−78 °C) THF solution of [Tp′(CO)$_2$W(PhC$_2$Ph)][BF$_4$] (0.5 g, 0.62 mmol). The solution color changed from green to brown. Solvent was evaporated after the solution had warmed to room temperature. The solid residue was chromatographed on alumina with toluene as the eluent. A brown band was collected, and toluene was removed. The solid was recystallized from CH$_2$Cl$_2$/hexanes to yield greenish brown crystals (0.33 g, 75%). IR (KBr, cm^{-1}): ν_{BH} = 2550; ν_{CO} = 1949, 1857; ν_{CN} = 1545. ^{1}H NMR (CD$_2$Cl$_2$, δ): major isomer (55%), 7.90–6.65 (C$_6$*H*$_5$), 5.97, 5.87, 5.74 (Tp′ C*H*), 4.72 ($^2J_{WH}$ = 10 Hz, η^2-CPh=C*H*Ph), 2.67, 2.59, 2.51, 2.41, 1.99, 1.75 (Tp′ CC*H*$_3$); minor isomer (45%), 7.90–6.65 (C$_6$*H*$_5$), 5.97, 5.92, 5.64 (Tp′ C*H*), 4.08 ($^2J_{WH}$ = 10 Hz, η^2-CPh=C*H*Ph), 2.55, 2.46, 2.41, 2.39, 1.72, 1.02 (Tp′ CC*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): both isomers, 255.7, 241.0 (η^2-*C*Ph=CHPh), 237.0, 226.1, 225.4, 224.3, (*C*O), 155.4, 153.8, 153.6, 153.2, 153.0, 150.6, 147.8, 146.1, 145.8, 145.2, 145.0, 144.9, 144.8, 144.6, (Tp′ *C*CH$_3$ and *C*$_{ipso}$), 132.2, 129.8, 127.6, 129.3, 129.0, 128.8, 128.7, 128.5, 128.1, 127.8, 127.6, 127.5, 126.1, 123.9 (Ph), 108.0, 107.9, 107.5, 107.4, 107.3 (Tp′ *C*H), 41.3, 39.8 (η^2-CPh=*C*HPh), 16.2, 16.0, 15.6, 15.3, 14.0, 13.9, 13.2, 13.1, 13.0, 12.8, 12.7 (Tp′ C*C*H$_3$). Anal. Calcd for WC$_{31}$H$_{33}$N$_6$O$_2$B: C, 51.98; H, 4.61; N, 11.74. Found: C, 51.80; H, 4.43; N, 11.54.

Tp′(CO)$_2$W[η^2-CPh=CHPO(OMe)$_2$] (4). Two equivalents of P(OMe)$_3$ was added to a THF (50 mL) solution of [Tp′(CO)$_2$W(HC$_2$Ph)][BF$_4$] (0.5 g, 0.69 mmol), resulting in a color change from green to brown. The solution was stirred for 10 min. Solvent removal left a brown residue. Column chromatography on alumina with toluene as eluent yielded a brown band. Recrystallization from CH$_2$Cl$_2$/hexane yielded brown crystals (0.39 g, 75%). IR (KBr, cm^{-1}): ν_{CO} = 1968, 1880. ^{1}H NMR (CD$_2$Cl$_2$, δ): major isomer (90%), 8.00, 7.56, 7.41 (C$_6$*H*$_5$), 5.94, 5.91, 5.90 (Tp′ C*H*), 3.56 [$^3J_{PH}$ = 10.4 Hz, η^2-CPh=CHP(O)(O*Me*)(OMe)], 2.95 [$^3J_{PH}$ = 10.8 Hz, η^2-CPh=CHP(O)(OMe)(O*Me*)], 2.65, 2.48, 2.46, 2.35, 2.25, 1.80 (Tp′ CC*H*$_3$). The vinyl proton signal for η^2-CPh=C*H*P(O)(OMe)$_2$ was not located. ^{13}C NMR (CD$_2$Cl$_2$, δ): major isomer (90%), 229.6 [$^1J_{WC}$ = 36 Hz, $^2J_{PC}$ = 7.6 Hz, η^2-*C*Ph=CHP(O)(OMe)$_2$], 222.5 ($^1J_{WC}$ = 145 Hz, $^3J_{PC}$ = 5 Hz, *C*O), 221.3 ($^1J_{WC}$ = 160 Hz, $^3J_{PC}$ = 2 Hz, *C*O), 156.7, 153.2, 151.4, 146.4, 146.2, 145.1 (Tp′ *C*CH$_3$), 143.7 (*C*$_{ipso}$), 133.0, 129.6, 129.2 (Ph), 108.0, 107.7, 107.6 (Tp′ *C*H), 51.4 [q of d, $^1J_{HC}$ = 145 Hz, $^2J_{PC}$ = 6.6 Hz, η^2-CPh=CHP(O)(OMe)(O*Me*)], 28.8 [q of d, $^1J_{HC}$ = 126 Hz, $^2J_{PC}$ = 6.5 Hz, η^2-CPh=CHP(O)(O*Me*)(OMe)], 17.3 [d of d, $^1J_{PC}$ = 185 Hz, $^1J_{HC}$ = 151 Hz, $^1J_{WC}$ = 27 Hz, η^2-CPh=*C*HP(O)(OMe)(OMe)], 16.6, 16.0, 14.3, 13.1, 13.0, 12.7 (Tp′ C*C*H$_3$). Anal. Calcd for WC$_{27}$H$_{34}$N$_6$O$_5$BP: C, 43.34; H, 4.55; N, 11.23. Found: C, 43.32; H, 5.08; N, 10.48.

Tp′(CO)$_2$W[η^2-CPh=CHP(OH)(OMe)$_2$][BF$_4$] (5). A brown solution of 4 (0.5 g, 0.67 mmol) in 30 mL of CH$_2$Cl$_2$/Et$_2$O (1:5) was cooled to 0 °C, and a stoichiometric amount of HBF$_4$·Me$_2$O was added dropwise with stirring, resulting in a slight color change and a red precipitate. The flask was put in the freezer (−40 °C) after 20 mL of Et$_2$O was added. The red-orange powder which formed was isolated by filtration, washed with Et$_2$O (2 × 10 mL), and dried in vacuo (0.45 g, 80%). Recrystallization from CH$_2$Cl$_2$/Et$_2$O yielded red crystals. IR (KBr, cm^{-1}): ν_{CO} = 1995, 1897; ν_{BH} = 2557; ν_{CN} = 1544; ν_{BF} = 1043. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.99, 7.58, 7.45 (C$_6$*H*$_5$), 5.99, 5.95, 5.93 (Tp′ C*H*), 5.47 [d, $^3J_{PH}$ = 11 Hz, η^2-CPh=CHP(OH)(O*Me*)(OMe)], 3.24 [d, $^3J_{PH}$ = 11.5 Hz, η^2-CPh=CHP(OH)(OMe)(O*Me*)], 2.64, 2.48, 2.47, 2.34, 2.06, 1.90 (Tp′ CC*H*$_3$). The vinyl proton signal for η^2-CPh=C*H*P(OH)(OMe)$_2$ and the OH proton signal were not located. ^{13}C NMR (CD$_2$Cl$_2$, δ): 225.5 [$^1J_{WC}$ = 29 Hz, $^2J_{PC}$ = 9 Hz, η^2-*C*Ph=CHP(OH)(OMe)$_2$], 221.1 ($^1J_{WC}$ = 153 Hz, $^3J_{PC}$ = 3.5 Hz, *C*O), 220.7 ($^1J_{WC}$ = 147 Hz, $^3J_{PC}$ = 5 Hz, *C*O), 155.4, 153.5, 152.2, 147.0, 146.7, 145.6 (Tp′ *C*CH$_3$), 143.4 (d, $^3J_{PC}$ = 2.4 Hz, *C*$_{ipso}$), 133.1, 130.3, 129.5 (Ph), 108.4, 107.9, 107.8 (Tp′ *C*H), 55.0 [q of d, $^1J_{HC}$ = 149 Hz, $^2J_{PC}$ = 8 Hz, η^2-CPh=CHP(OH)(OMe)(O*Me*)], 53.9 [q of d, $^1J_{HC}$ = 149 Hz, $^2J_{PC}$ = 7.5 Hz, η^2-CPh=CHP(OH)(O*Me*)(OMe)], 13.9 [d of d, $^1J_{PC}$ = 190 Hz, $^1J_{HC}$ = 154 Hz, η^2-CPh=*C*HP(OH)(OMe)(OMe)], 16.1, 16.0, 14.4, 13.2, 12.9, 12.7 (Tp′ C*C*H$_3$). Anal. Calcd for WC$_{27}$H$_{35}$N$_6$O$_5$B$_2$F$_4$P: C, 38.78; H, 4.19; N, 10.05. Found: C, 38.46; H, 3.86; N, 9.70.

Tp′(CO)$_2$W(η^3-CH$_2$CHCHR) (R = Me, Ph). In a representive synthesis, a green solution of [Tp′(CO)$_2$W(PhC$_2$Me)][BF$_4$] (0.5 g, 0.68 mmol) in 100 mL of THF was cooled to −78 °C and Li[BEt$_3$H] in THF (0.68 mL, 0.68 mmol) was added slowly with stirring, resulting in a color change to brown and a shift in infrared carbonyl stretching frequencies to lower energies (1949 and 1858 cm^{-1}). The solution was warmed to room temperature and stirred for an additional 5 h, resulting in a further shift in the CO absorptions to 1925 and 1826 cm^{-1}. Solvent was removed. The product was extracted with 20 mL of Et$_2$O/toluene (1:1) and chromatographed on alumina with toluene as the eluent. Solvent removal and recrystallization from CH$_2$Cl$_2$/hexanes yielded red-orange crystals of 6 (0.34 g, 78%).

Tp′(CO)$_2$W(η^3-CH$_2$CHCHPh) (6). IR (KBr, cm^{-1}): ν_{BH} = 2549; ν_{CO} = 1922, 1822; ν_{CN} = 1546. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.15 (m, C$_6$*H*$_5$), 5.90, 5.85, 5.65 (Tp′ C*H*), 5.26 (m, CH$_a$H$_s$C*H*$_c$CH$_{a'}$Ph), 3.93 (d, $^3J_{H_cH_{a'}}$ = 8 Hz, CH$_a$H$_s$CH$_c$C*H*$_{a'}$Ph), 2.85 (d of d, $^3J_{H_cH_s}$ = 6 Hz, $^2J_{H_aH_s}$ = 1 Hz, CH$_a$*H*$_s$CH$_c$CH$_{a'}$Ph), 1.88 ($^3J_{H_cH_a}$ = 8 Hz, $^2J_{H_sH_a}$ = 1 Hz, C*H*$_a$H$_s$CH$_c$CH$_{a'}$Ph), 2.46, 2.37, 2.36, 2.32, 2.29, 2.28 (Tp′ CC*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 230.3 ($^1J_{WC}$ = 150 Hz, *C*O), 225.0 ($^1J_{WC}$ = 180 Hz, *C*O), 153.6, 153.0, 152.3, 145.6, 145.4, 145.2 (Tp′ *C*CH$_3$), 140.5 (*C*$_{ipso}$), 128.0, 127.9, 126.3 (Ph), 108.4, 107.9, 107.8 (Tp′ *C*H), 81.5 (d, $^1J_{HC}$ = 170 Hz, CH$_a$H$_s$*C*H$_c$CH$_{a'}$Ph), 69.3 (d, $^1J_{HC}$ = 160 Hz, CH$_a$H$_s$CH$_c$*C*H$_{a'}$Ph), 50.5 (t, $^1J_{HC}$ = 158 Hz, *C*H$_a$H$_s$CH$_c$CH$_{a'}$Ph), 16.1, 15.8, 15.5, 13.1, 12.9, 12.8 (Tp′ C*C*H$_3$). Anal. Calcd for WC$_{26}$H$_{31}$N$_6$O$_2$B: C, 47.73; H, 4.74; N, 12.85.

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(12) (a) Feng, S. G.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 8192. (b) Feng, S. G.; Philipp, C. C.; Gamble, A. S.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 3504.

Found: C, 47.69; H, 4.70; N, 12.90.

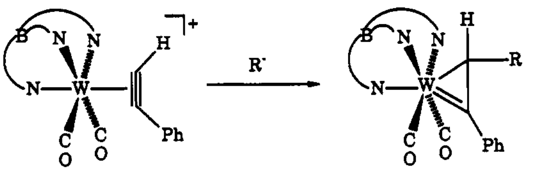
Tp′(CO)$_2$W(η^3-CH$_2$CHCDPh) was prepared by using Li[BEt$_3$D] in place of Li[BEt$_3$H].

Tp′(CO)$_2$W(η^3-CH$_2$CHCHMe) (7; Yellow-Orange, 75%). IR (KBr, cm^{-1}): ν_{BH} = 2548; ν_{CO} = 1910, 1815; ν_{CN} = 1545. ^{1}H NMR (CD$_2$Cl$_2$, δ): 5.84, 5.81, 5.74 (Tp′ C*H*), 4.13 ($^3J_{H_cH_{s'}}$ = 7.2 Hz, $^3J_{H_{Me}H_{s'}}$ = 6.4 Hz, $^4J_{H_sH_{s'}}$ = 2 Hz, CH$_a$H$_s$CH$_c$C*H*$_{s'}$Me), 3.25 ($^3J_{H_aH_c}$ = 10 Hz, $^3J_{H_sH_c}$ = 7.2 Hz, $^3J_{H_{s'}H_c}$ = 7.2 Hz, CH$_a$H$_s$C*H*$_c$CH$_{s'}$Me), 3.18 ($^3J_{H_cH_s}$ = 7.2 Hz, $^4J_{H_{s'}H_s}$ = 2 Hz, $^2J_{H_aH_s}$ = 1 Hz, CH$_a$*H*$_s$CH$_c$CH$_{s'}$Me), 2.50 ($^3J_{H_cH_a}$ = 10 Hz, $^2J_{H_sH_a}$ = 1 Hz, C*H*$_a$H$_s$CH$_c$CH$_{s'}$Me), 2.85, 2.52, 2.41, 2.32, 2.09 (Tp′ CC*H*$_3$), 1.37 (d, $^3J_{H_{s'}H_{Me}}$ = 6.4 Hz, CH$_a$H$_s$CH$_c$CH$_{s'}$*Me*). ^{13}C NMR (CD$_2$Cl$_2$, δ): 224.2 ($^1J_{WC}$ = 158 Hz, *C*O), 220.3 ($^1J_{WC}$ = 165 Hz, *C*O), 155.5, 154.3, 154.2, 146.5, 146.4, 144.3 (Tp′ *C*CH$_3$), 108.8, 108.6, 106.7 (Tp′ *C*H), 71.4 (d, $^1J_{HC}$ = 167 Hz, CH$_a$H$_s$*C*H$_c$CH$_{s'}$Me), 65.4 (d of q, $^1J_{HC}$ = 153 Hz, $^2J_{HC}$ = 5 Hz, CH$_a$H$_s$CH$_c$*C*H$_{s'}$Me), 55.1 (t, $^1J_{HC}$ = 159 Hz, *C*H$_a$H$_s$CH$_c$CH$_{s'}$Me), 14.7 (q of d, $^1J_{HC}$ = 126 Hz, $^2J_{HC}$ = 6 Hz, CH$_a$H$_s$CH$_c$CH$_{s'}$*Me*), 16.9, 16.6, 16.1, 12.9, 12.8, 12.7 (Tp′ C*C*H$_3$). Anal. Calcd for WC$_{21}$H$_{29}$N$_6$O$_2$B: C, 42.59; H, 4.90; N, 14.20. Found: C, 42.86; H, 4.94; N, 13.92.

Tp′(CO)(PhC$_2$Me)W[η^1-C(O)CH$_2$CH$_2$CH$_2$CH$_3$] (8). A stoichiometric amount of LiCu(Bu^n)$_2$, freshly prepared from reaction of CuI (0.4 g, 2.1 mmol) and Bu^{n}Li (2.5 M in hexanes, 1.68 mL, 4.2 mmol) at 0 °C in 20 mL of THF, was cannulated into a cold THF (−78 °C) solution of [Tp′W(CO)$_2$(PhC$_2$Me)][BF$_4$] (1.55 g, 2.1 mmol) resulting in an immediate color change from green to red-brown. The solution was warmed to room temperature and stirred for an additional 20 min. The solvent was removed, and the solid residue was chromatographed on alumina with CH$_2$Cl$_2$/THF as the eluent. A band was collected, and the solvents were removed. The solid which remained was recrystallized from toluene/hexanes to yield wine red crystals (1.15 g, 77%). IR (KBr, cm^{-1}): ν_{BH} = 2542, ν_{CO} = 1902, $\nu_{C=O}$ = 1568, ν_{CN} = 1545. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.28, 6.85 (m, C$_6$*H*$_5$), 5.91, 5.86, 5.66 (Tp′ C*H*), 3.58 (3 H, PhC$_2$C*H*$_3$), 2.56, 2.49, 2.44, 2.38, 1.36, 1.35 (3 H each, Tp′ CC*H*$_3$), 1.92 (m, 2 H, C*H*$_2$CH$_2$CH$_2$CH$_3$) 1.58 (m, 2 H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.22 (m, 2 H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.87 (t, $^3J_{HH}$ = 8 Hz, 3 H, CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 293.9 ($^1J_{WC}$ = 120 Hz, –*C*O–CH$_2$CH$_2$CH$_2$CH$_3$), 237.2 ($^1J_{WC}$ = 136.5 Hz, *C*O), 213.3 ($^1J_{WC}$ = 54 Hz, MeC*C*Ph), 208.1 ($^1J_{WC}$ = 14 Hz, $^2J_{HC}$ = 7 Hz, PhC*C*Me), 154.0, 153.6, 149.3, 145.3, 145.2, 144.7 (Tp′ *C*CH$_3$), 138.1, 129.1, 129.0, 128.9 (Ph), 108.2, 107.9, 106.8 (Tp′ *C*H), 69.2 (t, $^1J_{HC}$ = 125 Hz, *C*H$_2$CH$_2$CH$_2$CH$_3$), 27.6 (t, $^1J_{HC}$ = 126 Hz, CH$_2$*C*H$_2$CH$_2$CH$_3$), 23.6 (t, $^1J_{HC}$ = 126 Hz, CH$_2$CH$_2$*C*H$_2$CH$_3$), 21.7 (q, $^1J_{HC}$ = 129 Hz, CH$_2$CH$_2$CH$_2$*C*H$_3$), 16.7 (PhC$_2$*C*H$_3$), 15.8, 15.7, 14.5, 13.2, 13.1, 12.5 (Tp′ C*C*H$_3$). Anal. Calcd for Tp′(CO)(PhC$_2$Me)W(η^1-C(O)CH$_2$CH$_2$CH$_2$CH$_3$)·$^1/_4$C$_7$H$_8$, WC$_{31.75}$H$_{41}$N$_6$O$_2$B: C, 52.00; H, 5.60; N, 11.47. Found: C, 51.83; H, 5.65; N, 11.67.

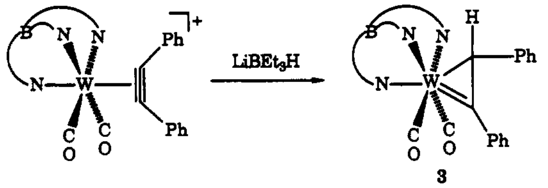
Results and Discussion

η^2-Vinyl Complexes. Low-temperature nucleophilic addition of Li[Et$_3$BH] or MeLi to [Tp′(CO)$_2$W(PhC$_2$H)][BF$_4$] and of Li[Et$_3$BH] to [Tp′(CO)$_2$W(PhC$_2$Ph)][BF$_4$] in THF yields neutral η^2-vinyl complexes, Tp′(CO)$_2$W(η^2-CPh=CHR) (R = H (1), Me (2), Ph (3); eqs 11 and 12). Addition of the nucleophile to the solution was accompanied by a rapid color change from green to brown and a shift in IR (CO) stretching frequencies to lower energy. The neutral η^2-vinyl products are air-stable and can be purified by chromatography on alumina followed by recrystallization from methylene chloride and hexanes. These neutral dicarbonyl η^2-vinyl complexes exhibit strong infrared absorptions near 1950 and 1860 cm^{-1} due to the two metal carbonyls. The methyl addition product 2 displays CO stretching frequencies (1935 and 1838 cm^{-1}) lower than those of the hydride addition product (1951, 1863 cm^{-1}), indicating that the methyl group provides more electron density to the metal than does the hydrogen.



(11)

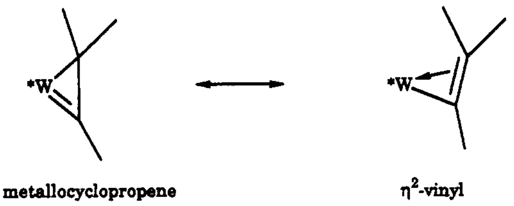
R = H (1), Me (2)



(12)

3

Scheme I



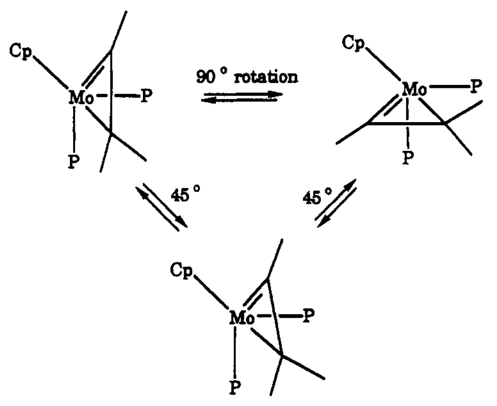
Both ^{1}H and ^{13}C NMR spectra of 1 display 2:1 patterns for the dimethylpyrazole signals, indicating that the dmpz rings trans to the carbonyl ligands are equivalent on the NMR time scale. Unique sets of resonances for each pyrazole ring of the Tp′ ligand in the NMR spectra of 2 and 3 indicate an unsymmetrical environment in these molecules. The two unique vinyl protons of 1 appear upfield at 1.32 ppm with a two-bond W–H coupling constant of 13 Hz. The vinyl proton of 2 resonates downfield at 3.50 ppm as a quartet ($^3J_{HH}$ = 5.5 Hz). Compound 3 displays two vinyl proton signals at 4.72 and 4.08 ppm with nearly equal intensities (each with a two-bond W–H coupling of 10 Hz), indicating that two isomers are present.

^{13}C NMR spectra are crucial for identifying η^2-vinyl ligands or metallocyclopropenes (Scheme I). The carbenoid character of C$_\alpha$ in these complexes is reflected in the downfield chemical shifts, which range from 234 to 265 ppm. Specific chemical shifts for C$_\alpha$ are as follows: 234 ppm, W–C coupling constant of 28 Hz for 1; 265 ppm, W–C coupling constant of 80 Hz for 2; 256 and 241 ppm for the two isomers of 3. The four-coordinate C$_\beta$ signal appears at much higher field: 17.3 ppm ($^1J_{WC}$ = 24 Hz) as a triplet with H–C coupling of 158 Hz for 1; 38.0 ppm as a doublet of quartets with one-bond H–C coupling of 156 Hz and two-bond H–C coupling of 4.8 Hz for 2; 41.3 and 39.8 ppm for the two isomers of 3.

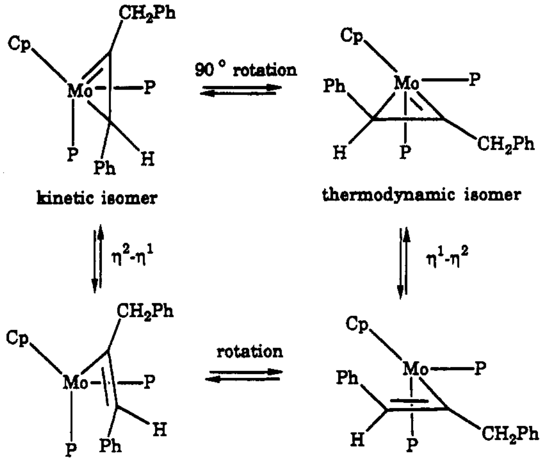
Complex 1 displays only one carbonyl signal at 223 ppm with a one-bond W–C coupling constant of 154 Hz, again indicating that a mirror plane is present in the molecule on the NMR time scale. Distinct carbonyl signals were observed at 239 ($^1J_{WC}$ = 168 Hz) and 222 ($^1J_{WC}$ = 149 Hz) ppm for 2 and at 237, 226, 225, and 224 ppm for the two isomers of 3. Thus, the NMR data indicate mirror symmetry for 1, but if C$_\alpha$ and C$_\beta$ do not lie in the mirror plane of the Tp′(CO)$_2$W fragment, then the two carbonyl groups should be inequivalent. Rotation or oscillation of the η^2-vinyl ligand can place both C$_\alpha$ and C$_\beta$ in the mirror plane, and this will equilibrate the two carbonyls. EHMO calculations on an η^2-vinyl model complex, CpMo[P(OH)$_3$]$_2$(η^2-CH=CH$_2$), suggested[2] a barrier of less than 5 kcal/mol for the vinyl ligand to rotate 90°, while a much higher barrier (about 20 kcal/mol) was calculated for a complete rotation (360°) of the η^2-vinyl ligand. These theoretical results are consistent with the observed fluxional process on the NMR time scale, which is compatible with a windshield wiper motion (less than 90° vinyl rotation through the mirror plane) (Scheme II).

Formation of η^2-vinyl ligands with different C$_\beta$ substituents creates diastereotopic carbonyl ligands due to chirality at carbon. This causes NMR-inequivalent car-

Scheme II

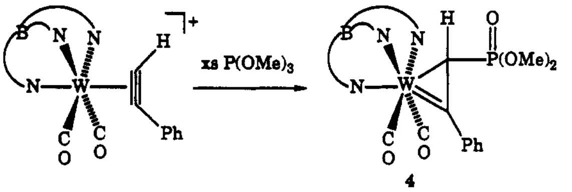


Scheme III



bonyl carbons regardless of the time scale of η^2-vinyl rotation. Two isomers in about a 1:1 ratio have been observed for 3, while only one isomer is observed for 2. Green reported[2] isolation of two isomers for η^2-vinyl complexes of the type $CpL_2Mo[\eta^2\text{-}C(CH_2Ph){=}CHPh]$. He described the isomerization as due to a 90° rotation of the η^2-vinyl ligand (Scheme III).

An unusual η^2-vinyl complex (4) was synthesized from the reaction of $[Tp'(CO)_2W(PhC_2H)][BF_4]$ with excess $P(OMe)_3$ in THF at room temperature (eq 13). A rapid

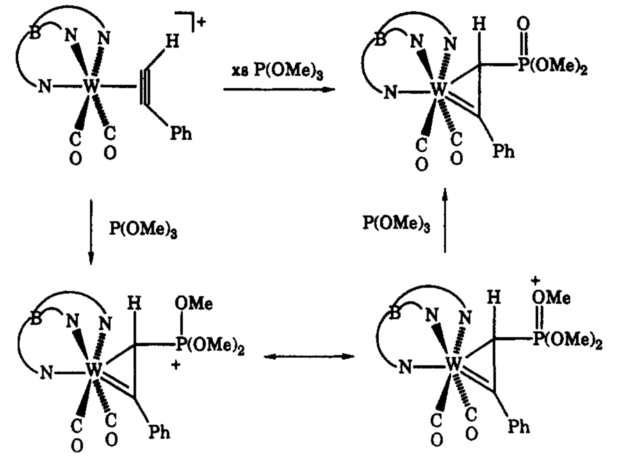


(13)

reaction occurred as $P(OMe)_3$ was added, and the color of the THF solution changed from green to brown. The product was purified by column chromatography on alumina followed by recrystallization from CH_2Cl_2/hexanes. This neutral compound is moderately air- and moisture-sensitive. Excess $P(OMe)_3$ was necessary, presumably serving to remove Me^+ from the coordinated phosphite entity (Scheme IV). Apparently the second step is faster than the first one, since use of 1 equiv of $P(OMe)_3$ did not stop at the first step.

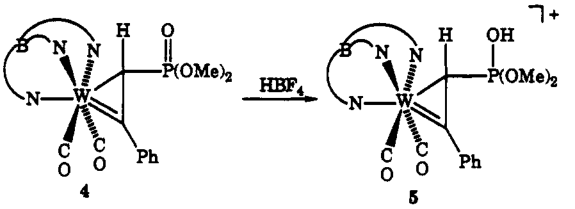
Infrared spectra of 4 exhibit strong dicarbonyl absorptions at 1968 and 1880 cm^{-1} which are consistent with formation of a neutral complex. NMR spectra show a unique set of resonances for each pyrazole ring of the Tp′ ligand, suggesting a chiral molecule with C_1 symmetry. Both ^{1}H and ^{13}C NMR spectra show pairwise signals of differing intensities (9:1) which suggest isomeric forms, perhaps due to different orientations of the vinyl ligand. The vinyl proton was not located; probably it is buried under the methyls of the dmpz rings. Note that its presence is evident in the proton-coupled ^{13}C NMR spectrum. ^{13}C NMR spectra reveal a low-field signal at 230 ppm ($^1J_{WC} = 36$ Hz) as a doublet with two-bond phosphorus coupling of 7.6 Hz for C_α and an upfield signal at 17.3 pm ($^1J_{WC} = 27$ Hz) as a doublet of doublets with one-bond P–C coupling of 185 Hz and H–C coupling of 151 Hz for C_β of the major isomer. One of the metal carbonyl carbons resonates at 223 ppm ($^1J_{WC} = 145$ Hz) as a doublet with a three-bond P–C coupling constant of 5 Hz, and the other appears at 221 ppm ($^1J_{WC} = 160$ Hz) as a doublet with a three-bond P–C coupling of 2 Hz.

Scheme IV

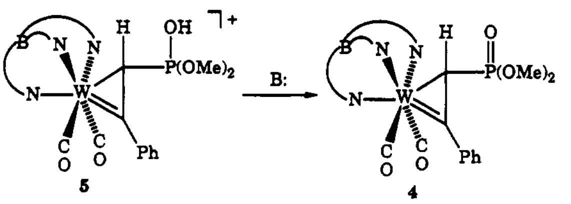


This product is reminiscent of an earlier result where addition of a phosphorus nucleophile to a terminal alkyne carbon in the neutral $W(MA)(PhC_2H)(S_2CNEt_2)_2$ (MA = maleic anhydride) complex was reported to produce an η^2-vinyl $PhC{=}CH(PR_3)$ fragment.[4] The vinyl proton was found upfield at 2.97 ppm as a doublet with a two-bond P–H coupling of 29 Hz. The C_α carbon resonated downfield at 222 ppm, which is indicative of W–C double-bond character. The C_β carbon appeared upfield at 11.6 ppm with $^1J_{HC} = 158$ Hz and $^1J_{PC} = 164$ Hz.

A cationic η^2-vinyl complex (5; eq 14) was prepared by protonation of the neutral complex 4 in CH_2Cl_2/Et_2O.



(14)



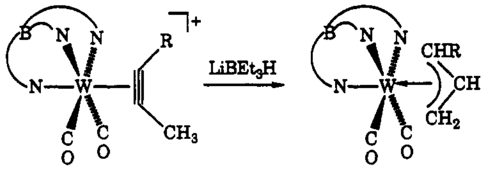
(15)

The protonation reaction is rapid at 0 °C, as judged by the instantaneous formation of the product as a red precipitate. Recrystallization from CH_2Cl_2/Et_2O yields red crystals of the simple proton addition product in 80% yield. This compound decomposed slowly in solution. The cationic η^2-vinyl complex 5 is analogous to the intermediate postulated in the formation of the neutral η^2-vinyl complex 4, with H^+ in place of Me^+. Indeed, addition of base to

5 regenerated the neutral complex 4 (eq 15).

The η^2-vinyl complex 5 displays a Tp′ B–H absorption at 2557 cm^{-1}, which is characteristic of a cationic compound.[13] Strong infrared absorptions at 1995 and 1897 cm^{-1} are attributed to the two metal carbonyls. An intense absorption at 1043 cm^{-1} is due to the B–F stretch of the tetrahedral BF_4^- counterion. Only a small shift (~25 cm^{-1}) to higher energy in IR CO stretching frequencies resulted when 4 was converted to 5, suggesting that protonation at oxygen has minimal impact on the ability of the phosphorus ligand to contribute electron density to the metal. Unique sets of resonances for each pyrazole ring of the Tp′ ligand in the NMR spectrum indicate an unsymmetrical environment for the Tp′ ligand, consistent with chirality at C_β. The vinyl and the OH protons were not located; they may be buried under the methyl region of the Tp′ ligand. ^{13}C NMR spectra exhibit a downfield signal at 226 ppm ($^1J_{PC}$ = 190 Hz) as a doublet with a two-bond P–C coupling of 9 Hz and an upfield signal at 14 ppm as a doublet of doublets ($^1J_{PC}$ = 190 Hz, $^1J_{HC}$ = 154 Hz). The carbonyl carbons appear at 221 ($^1J_{WC}$ = 153 Hz) ppm with $^3J_{PC}$ = 3.5 Hz and 220 ppm ($^1J_{WC}$ = 147 Hz, $^3J_{PC}$ = 5 Hz).

η^3-Allyl Complexes. Addition of a hydride reagent ($LiBEt_3H$) to cationic dicarbonyl complexes containing an alkyne with a β-hydrogen yielded η^3-allyl complexes (eq 16). The stable red-orange products were purified by column chromatography on alumina followed by recrystallization from CH_2Cl_2/hexanes.



(16)

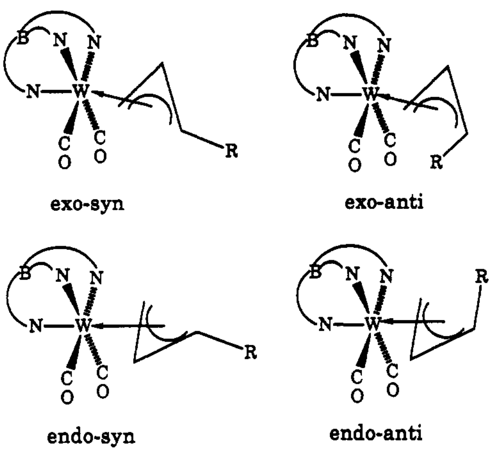
R = Ph (6), Me (7)

These η^3-allyl complexes exhibit carbonyl absorptions 30–40 cm^{-1} lower than those of the corresponding η^2-vinyl complexes, indicating that the allyl groups push more electron density to the metal than do the isomeric vinyl groups. The methyl derivative displays lower frequencies (1910 and 1815 cm^{-1}) than the phenyl derivative (1922 and 1822 cm^{-1}), which is consistent with the fact that a methyl group is a better electron donor than the phenyl group.

Four isomers are possible for these dicarbonyl η^3-allyl complexes (Chart II). An X-ray structure of [(indenyl)Mo(CO)(PEt_3)(η^3-$CH_2CHCHMe$)] reported by Green has confirmed an anti, exo allyl geometry.[2] Both ^{1}H and ^{13}C NMR data for 6 and 7 unambiguously dictate an η^3-allyl formulation. Coupling between the anti protons and the central proton ($^3J_{H_aH_c}$ and $^3J_{H_{a'}H_c}$) tends to be large (8–10 Hz), while syn couplings ($^3J_{H_sH_c}$ and $^3J_{H_{s'}H_c}$) are slightly smaller (6–8 Hz). Two J_{HH} couplings near 10 Hz for 6 suggest that protons occupy both anti positions in the π-allyl ligand, while one J_{HH} coupling near 10 Hz was found for 7, suggesting the methyl group occupies the anti position. The long-range W-shaped coupling ($^4J_{H_sH_{s'}}$ = 2 Hz) was observed for 7, but not for 6, also suggesting a syn geometry for the phenyl derivative and an anti geometry for the methyl derivative (Table I).

^{13}C NMR spectra of 6 and 7 reveal downfield chemical shifts for the central carbons of the allyl fragments and upfield chemical shifts for the allyl carbons bearing two protons with the carbons bearing one proton in between (Table II). All allyl carbons exhibit $^1J_{HC}$ values of 150–170 Hz.

Chart II



A reaction mechanism which accounts for allyl formation following initial η^2-vinyl formation via nucleophilic attack at an alkyne carbon has been suggested by Green.[2] Rearrangement of an η^2-vinyl product to an unsaturated η^1-vinyl complex would allow β-hydrogen transfer to generate a metal hydride allene intermediate. Rotation of the allene ligand followed by hydrogen migration to the central carbon of the allene would funnel the η^2-vinyl to the thermodynamically favored η^3-allyl complex (Scheme V).

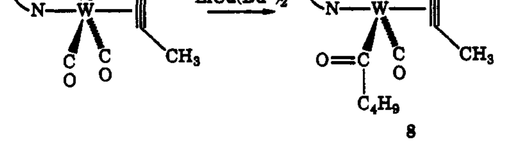
Deuterium labeling studies in our system are also consistent with a net 1,2-hydrogen shift: reaction of [Tp′(CO)$_2$W(PhC_2Me)][BF_4] with $LiBEt_3D$ forms η^3-*syn*-$CH_2CHCDPh$ with deuterium in the anti position. Initial η^2-vinyl formation was suggested by low-temperature solution IR spectroscopy, which revealed an intermediate with bands at 1969 and 1858 cm^{-1}. Our rearrangement appears to be rapid as monitored by solution IR spectra; in contrast, the rearrangement[2] of $CpL_2Mo(\eta^2\text{-}CMe{=}CPh_2)$ to $CpL_2Mo(\eta^3\text{-}CH_2CHCPh_2)$ requires 3 days.

Reaction of methyllithium with Tp′(CO)$_2$W(PhC_2H)$^+$ gives an η^2-vinyl product, Tp′(CO)$_2$W(η^2-CPh=CHMe). This slowly rearranges, over a period of months, to form an η^3-allyl complex, Tp′(CO)$_2$W(η^3-CHPhCHCH$_2$). In contrast, reaction of $LiCuMe_2$ with [$CpL_2Mo(Bu^tC_2H)$]$^+$ produces only an η^3-allyl product, $CpL_2Mo(\eta^3\text{-}CHBu^tCHCH_2)$ (eq 17).[2] These results imply that the

$$[CpL_2Mo(HC{\equiv}CBu^t)][BF_4] \xrightarrow{LiCuMe_2} CpL_2Mo(\eta^3\text{-}CH_2CHCHBu^t) \quad (17)$$

interconversion of isomeric species A and B, perhaps by hydrogen transfer to the metal (Scheme VI), is fast in the Cp system but slow in our Tp′ system.

η^1-Acyl Alkyne Complex. Addition of LiCu(Bu^n)$_2$ did not deprotonate the alkyne at C_β of the phenylpropyne ligand in [Tp′(CO)$_2$W(PhC≡CMe)]$^+$, nor did it add to an alkyne carbon. Instead, LiCu(Bu^n)$_2$ attacked a carbonyl ligand; hence, nucleophiles are not restricted to attack at the alkyne ligand. That the carbonyls are susceptible to nucleophilic attack is not surprising, given the high ν_{CO} stretching frequencies for this dicarbonyl cation (2060, 1970 cm^{-1}). This nucleophilic addition of LiCu(Bu^n)$_2$ to one of the carbonyls in Tp′(CO)$_2$W(PhC≡CMe)]$^+$ produces a neutral η^1-acyl alkyne complex in good yield (eq 18).



(18)

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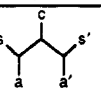
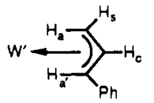
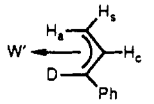
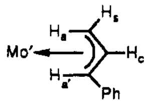
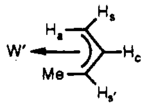
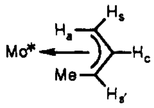
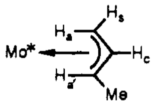
[13] Curtis, M. D.; Shiu, K.-B. *Inorg. Chem.* **1985**, *24*, 1214.

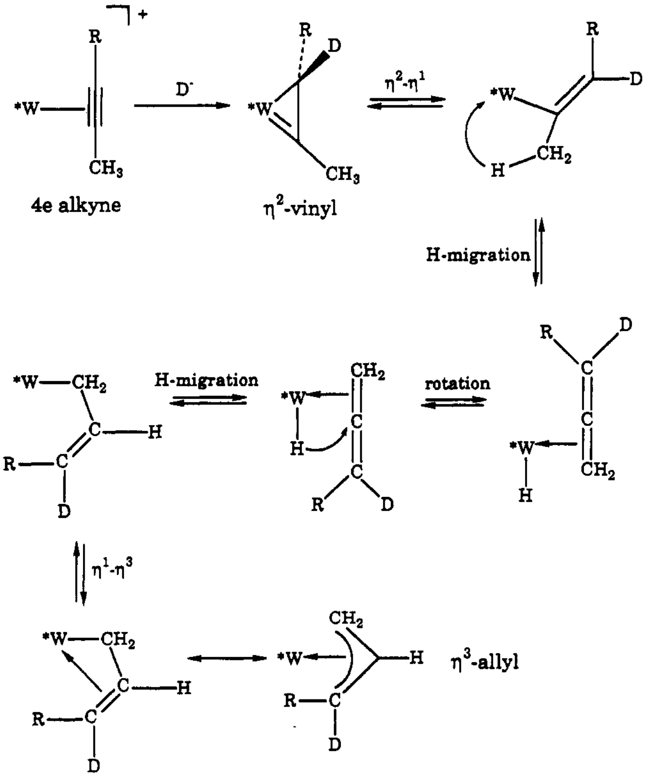
Table I. ^{1}H NMR Data for η^3-Allyl Complexes of W(II) and Mo(II)^a



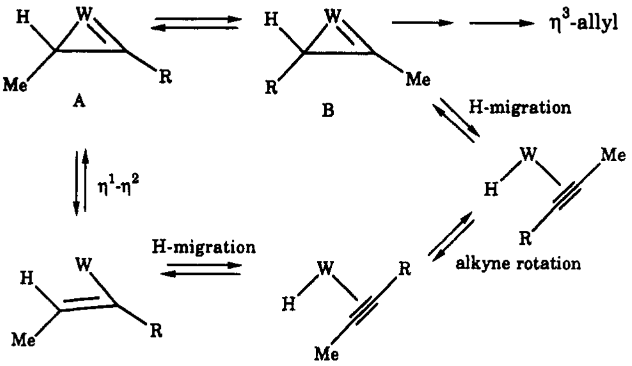
complex	H_a	$H_{a'}$	H_s	$H_{s'}$	H_c	ref
	1.88 $^3J_{ca} = 8$ $^2J_{sa} = 1$	3.93 $^3J_{ca'} = 8$	2.85 $^3J_{cs} = 6$ $^2J_{as} = 1$		5.26 $^3J_{ac} = 8$ $^3J_{a'c} = 8$ $^3J_{sc} = 6$	this work
	1.88 $^3J_{ca} = 8$ $^2J_{sa} = 1$	X	2.85 $^3J_{cs} = 6$ $^2J_{as} = 1$		5.26 $^3J_{ac} = 8$ $^3J_{sc} = 6$	this work
	2.06 $^3J_{ca} = 10.3$ $^2J_{sa} = 1$	4.22 $^3J_{a'c} = 9.8$	3.67 $^3J_{cs} = 6.8$ $^2J_{as} = 1$		5.37 (m)	15
	2.49 $^3J_{ca} = 10$ $^2J_{sa} = 1$		3.18 $^3J_{cs} = 7.2$ $^2J_{as} = 1$ $^4J_{s's} = 2$	4.13 $^3J_{Mes'} = 6.4$ $^3J_{cs'} = 7.2$ $^4J_{ss'} = 2$	3.24 $^3J_{ac} = 10$ $^3J_{s'c} = 7.2$ $^3J_{sc} = 7.2$	this work
	1.32 $^3J_{ca} = 10.2$ $^2J_{sa} = 2.6$		2.80 $^3J_{cs} = 7$ $^2J_{as} = 2.6$ $^4J_{s's} = 1.9$	3.83 $^3J_{cs'} = 7.9$ $^4J_{ss'} = 1.9$	4.0 (m)	16
	1.26 $^3J_{ca} = 10.2$ $^2J_{sa} = 2.2$	1.75 $^3J_{ca'} = 7.9$ $^2J_{sa'} = 0.3$	2.54 $^3J_{cs} = 6.8$ $^2J_{as} = 2.2$		3.90 (m)	16

^{a} M′ = Tp′(CO)$_2$M, Mo* = Cp(CO)$_2$Mo. δ values are in ppm and *J* values in Hz.

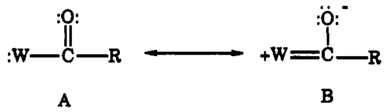
Scheme V



Scheme VI

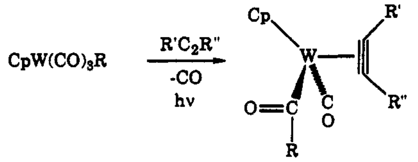


Scheme VII

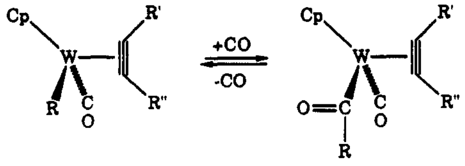


Purification by chromatography on alumina and recrystallization from CH$_2$Cl$_2$/MeOH gave stable wine red crystals. The acyl product exhibits a single strong infrared absorption at 1902 cm^{-1}, which is assigned as the lone metal carbonyl stretching frequency.

Alt and co-workers[14] prepared a series of alkyne acyl complexes of the type Cp(CO)(RC$_2$R′)W[C(O)R], as indicated in eqs 19 and 20. ν_{CO} stretching frequencies higher

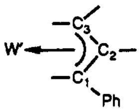
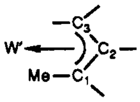


(19)



(20)

Table II. IR and ^{13}C NMR Data for η^3-Allyl Complexes $Tp'(CO)_2W(\eta^3\text{-}CH_2CHCHR)$

complex[a]	IR ν_{CO} (cm^{-1})	^{13}C NMR[b]		
		C_1	C_2	C_3
	1922 1822	69.3 (d) $^1J_{HC}$ = 160	81.5 (d) $^1J_{HC}$ = 170	50.5 (t) $^1J_{HC}$ = 158
	1910 1815	65.4 (d of q) $^1J_{HC}$ = 153 $^2J_{HC}$ = 5	71.4 (d) $^1J_{HC}$ = 167	55.1 (t) $^1J_{HC}$ = 159

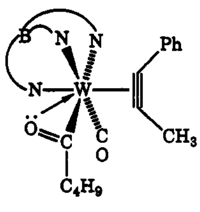
[a] W′ = Tp′(CO)$_2$W. [b] δ values are in ppm and J values in Hz.

than those we observe with Tp′ characterized the terminal carbonyls in Alt's Cp derivatives (1938–1959 cm^{-1}), consistent with the fact that the Tp′ ligand is more electron-rich than the Cp ligand. While $\nu_{C=O}$ for the acyl carbonyl absorption was reported between 1588 and 1607 cm^{-1} in the Cp system, the acyl carbonyl absorption was observed at 1568 cm^{-1} in our complex. Two resonance structures, A and B, can contribute to the metal acyl fragment (Scheme VII). An electron-rich metal center would favor resonance form B and shift the acyl $\nu_{C=O}$ absorptions to lower energy. Complexes of the type Cp(CO)(RC$_2$R′)WR were also reported by Alt,[14] and they exhibit terminal ν_{CO} stretching frequencies between 1905 (Cp*) and 1925 cm^{-1} (Cp). These are substantially lower than the ν_{CO} values observed for Cp(CO)(RC$_2$R′)W[C(O)R], and this frequency difference perhaps reflects metal to acyl back-bonding in addition to the normal electron-withdrawing properties of acyl units.

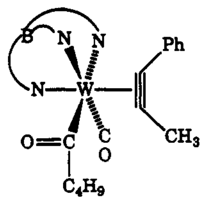
Formation of a complex containing a four-electron-donor alkyne and an η^1-acyl ligand was evidenced here by carbon-13 NMR data for the acetylenic carbons. As we have shown earlier,[7,12b] the alkyne ligand (PhC≡CMe) in Tp′W(CO)L(PhC≡CMe)$^{n+}$ (n = 0, 1) complexes lies parallel to the cis carbonyl ligand with the phenyl group adjacent to the Tp′ ligand and the acetylenic carbon which is adjacent to the Tp′ ligand tends to have a lower chemical shift and a larger one-bond tungsten–carbon coupling than those of the acetylenic carbon away from the Tp′. These carbons appear at 213 ppm ($^1J_{WC}$ = 54 Hz, MeC≡CPh) and 208 ppm ($^1J_{WC}$ = 14 Hz, MeC≡CPh) in 8, well downfield of signals observed for the Cp analogues, where alkyne carbon signals range from 185 to 200 ppm. The lone terminal metal carbonyl carbon resonates at 237 ppm with a one-bond tungsten–carbon coupling of 137 Hz in Tp′(CO)(PhC≡CMe)WC(=O)Bu^n, comparable to the range of 231–237 ppm for the carbonyl in the Cp complexes. The acyl carbon is located further downfield at 294 ppm ($^1J_{WC}$ = 120 Hz), which is substantially lower than the 261–265 ppm range observed for Cp(CO)(R″C$_2$R′)WC(O)R complexes. An electron-rich metal center favoring resonance form B in Scheme VII would be expected to shift the acyl carbon to lower field. A similar pattern was observed[14] for the acyl carbon in complexes of the type CpL(R″C$_2$R′)W[C(O)R], where the acyl carbon moved downfield as L changed to a more electron-rich donor ligand: 261 ppm (L = CO), 270 ppm (L = P(OMe)$_3$), and 276 ppm (L = PMe$_3$).

An alkyne acyl complex has been postulated as an intermediate in the formation of an alkyne insertion product, Tp′(CO)$_2$Mo[η^2-CRCRC(O)Et].[15] Note that η^2-acyl complexes are observed for group 6 metals when the electron pair on the oxygen is needed to achieve an 18-electron count at the metal.[15] In the product here 5 electrons from the alkyne and the acyl ligand are required in the neutral counting formalism to produce an 18-electron compound. Both ligands are known as flexible electron-donor ligands: 2, 3, or 4 electrons for alkyne ligands; 1 or 3 electrons for acyl ligands. Possible combinations then could be either an η^2-acyl (3 e$^-$) and a 2-electron-donor alkyne or an η^1-acyl (1 e$^-$) and a 4-electron-donor alkyne. The ground-state properties clearly depend on which ligand wins this competition between $\pi_\perp$ of the alkyne and the lone pair on the oxygen of the acyl for electron donation into the lone vacant dπ orbital. In the product isolated here, $\pi_\perp$ donation dominates and the acyl acts as an η^1 ligand (Chart III).

Chart III



η^2-acyl/2e alkyne



η^1-acyl/4e alkyne

Summary

The dual donor and acceptor properties of η^2-RC=CR$_2^-$ ligands toward orthogonal dπ orbitals resemble those of η^2-RC≡CR′ ligands. Reactions of cationic dicarbonyl alkyne complexes of the type Tp′(CO)$_2$W(RC≡CR′)$^+$ with anionic nucleophiles generate stable neutral η^2-vinyl complexes, Tp′(CO)$_2$W(η^2-RC=CRR′). We believe that the two isomers observed for Tp′(CO)$_2$W(η^2-CPh=CHPh) result from 180° rotation of the vinyl ligand; only one isomer is observed for Tp′(CO)$_2$W(η^2-CPh=CHMe). Reaction of the phenylacetylene complex [Tp′(CO)$_2$W(PhC$_2$H)][BF$_4$] with excess P(OMe)$_3$ results in the formation of an unusual P(O)(OMe)$_2$-substituted η^2-vinyl complex, Tp′(CO)$_2$W[η^2-CPh=CHP(O)(OMe)$_2$]. Protonation of this compound at oxygen generates a cationic P(OH)(OMe)$_2$-substituted η^2-vinyl complex, Tp′(CO)$_2$W[η^2-CPh=CHP(OH)(OMe)$_2$][BF$_4$]. Reaction of cationic dicarbonyl alkyne complexes of the type [Tp′(CO)$_2$W(RC$_2$Me)][BF$_4$] (R = Me, Ph) with LiBEt$_3$H generates η^3-allyl complexes, Tp′(CO)$_2$W(η^3-CH$_2$CHCHR), via initial η^2-vinyl formation. Nucleophilic addition to the terminal carbon of a phenylacetylene ligand is favored both sterically and electronically. With an internal alkyne bearing β-hydrogens as the target, nucleophilic attack at the alkyne carbon without a β-hydrogen can lead to the formation of a thermodynamically favored η^3-allyl complex. Reaction of [Tp′(CO)$_2$W(PhC$_2$Me)][BF$_4$] with LiCu(Bu^n)$_2$ yields a neutral alkyne η^1-acyl complex, Tp′(CO)W(PhC$_2$Me)[η^1-C(O)Bu^n], with the alkyne ligand acting as a four-electron donor.

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