Electrophilic Addition Reactions of Tungsten η^2-Allenyl Complexes Formed by Deprotonation of Four-Electron Alkyne Ligands

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Abstract: Deprotonation of a series of cationic tungsten alkyne complexes, $[(dppe)(dtc)(OC)W(\eta^2\text{-}MeOC{\equiv}CCH_2Ph)][X]$, generates the corresponding neutral η^2-allenyl complexes, $(dppe)(dtc)(OC)W(\eta^2\text{-}MeOC{=}C{=}CHPh)$ (dppe = $Ph_2PCH_2CH_2PPh_2$; dtc = $R_2NCS_2^-$, R_2 = Me_2, $i\text{-}Pr_2$, C_4H_4; X = $CF_3SO_3^-$, BF_4^-). These allenyl complexes exist as a mixture of two isomers in solution at 25 °C. We attribute the isomerism to the orientation of the allenyl fragment with respect to the S-W-CO axis. Since these allenyl complexes readily add electrophiles (H^+ and Me^+) at C_γ, they offer a route to systematically substitute cationic alkyne complexes at the alkyne C_γ position. A series of NMR experiments was performed to examine the relative reactivities of each pair of allenyl isomers. Extended Hückel calculations have been conducted on a model allenyl complex, $H_4(OC)W(HOC{=}C{=}CH_2)^{3-}$, to probe the electronic barrier to rotation of the allenyl relative to the metal fragment and to probe the barrier to rotation of the terminal CH_2 unit of the η^2-allenyl ligand.

The chemistry of tungsten η^2-allenyl complexes offers an analogy to the chemistry of η^2-enolates. Metal η^2-acyls can be deprotonated at C_β to generate η^2-enolates, which add electrophiles to yield substituted products.[1] Similar reactivity may be observed for η^2-alkyne complexes: deprotonation to yield η^2-allenyl complexes, followed by reaction with electrophiles to form substituted η^2-alkyne products (Scheme I).

Evidence that such a pathway is accessible was provided by Watson and Bergman in 1980.[2] They observed the conversion of $Cp(OC)Mo(\eta^2\text{-}H_3CC{\equiv}CCH_3)_2^+$ to $Cp(OC)Mo(\eta^2\text{-}D_3CC{\equiv}CCD_3)_2^+$ in the presence of NEt_3 in acetone-d_6 solution. An η^2-allenyl complex has been reported by Green et al.[3] Deprotonation of $Cp[(MeO)_3P]_2Mo(\eta^2\text{-}PhC{\equiv}CCH_2Ph)^+$ yields a 7:3 ratio (trans to cis) of allenyl isomers (Ph trans or cis to tungsten across the C_β-C_γ double bond) (Scheme II).

Reactions of electrophiles with "organic allenyls" (lithium or potassium salts of allenyl anions) to afford substituted allenes and alkyne products have proven to be a useful synthetic route to carbon-carbon bond formation.[4] Incorporation of a transition-metal center, generating η^1-allenyl complexes, allows for some stereoselective reactivity, depending on the nature of the electrophile.[5] Yamamoto et al. have produced exclusively *threo*-$Me_3SiC{\equiv}CC(H)(Me)C(H)(R')NHR$ (R = CH_2Ph, *i*-Pr, Pr; R' = Et, *i*-Pr, Pr) from the addition of $R'HC{=}NR$ to $(i\text{-}PrO)_3TiC(SiMe_3){=}C{=}CHMe$.[6]

We have undertaken a study of $(dppe)(dtc)(OC)W(\eta^2\text{-}MeOC{=}C{=}CHPh)$ (dppe = $Ph_2PCH_2CH_2PPh_2$; dtc = $R_2NCS_2^-$, R_2 = Me_2, $i\text{-}Pr_2$, C_4H_4) η^2-allenyl complexes that are generated by deprotonation of cationic tungsten alkyne complexes, $[(dppe)(dtc)(OC)W(\eta^2\text{-}MeOC{\equiv}CCH_2Ph)][X]$. Addition of electrophiles to the η^2-allenyl complexes yields substituted η^2-alkyne products. We report here characterization of η^2-allenyl isomer pairs, electrophilic addition chemistry at the η^2-allenyl C_γ site, and an MO study of a model η^2-allenyl complex.

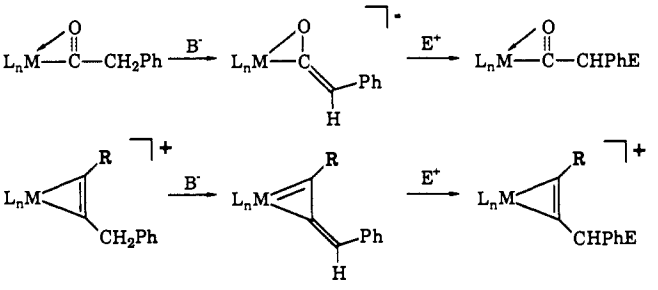
Experimental Section

Materials and Methods. Reactions were performed under a dry nitrogen atmosphere with standard Schlenk techniques. Tetrahydrofuran (THF), diethyl ether (Et_2O), and hexanes were distilled from sodium benzophenone ketyl; methylene chloride (CH_2Cl_2) was distilled from P_2O_5; all other solvents were purged with nitrogen and used without further purification. Iodomethane (MeI) was dried over alumina before use. $W(CO)_3(dppe)(acetone)$,[7] $[W(CO)_3(dppe)(\equiv CCH_2Ph)][BF_4]$,[8] $KS_2CN(C_4H_4)(K^+pyrdtc^-)$,[9] $NaS_2CN(CHMe_2)_2(Na^+diprtc^-)$,[10] $(dppe)(dmtc)(OC)W(C,C\text{-}\eta^2\text{-}OC{=}CH_2Ph)$ (**13**),[8] and $[(dppe)(dmtc)(OC)W(MeOC{\equiv}CH_2Ph)][BF_4]$ (**1b**)[8] were prepared according to literature methods.

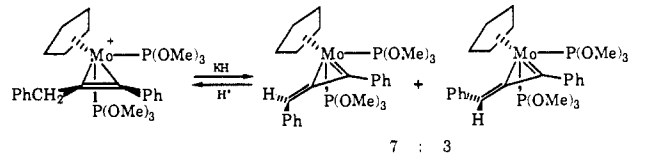
Infrared spectra were collected on a Beckman IR 4250 spectrometer and calibrated with a polystyrene standard or on a Mattson Polaris FTIR spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 (200-MHz) or a Varian XL 400 (400-MHz) spectrometer. Analyses are by Galbraith Laboratories of Knoxville, TN.

(dppe)(diprtc)(OC)W(*C,C*-η^2-OC=CCH_2Ph) (14). A solution of $[W(CO)_3(dppe)(\equiv CCH_2Ph)][BF_4]$ (4.8 g, 5.8 mmol) in 40 mL of CH_2Cl_2 was heated to reflux for 12 h (the IR ν_{CO} band pattern shifted from 2080 and 2005 cm^{-1} to 2020 and 1955 cm^{-1}, indicating loss of CO). The solution was cooled to −23 °C, and 2.2 equiv (2.50 g, 12.5 mmol) of $NaS_2CN(CHMe_2)_2$ was added. The mixture was warmed to 0 °C after 1 h and then to room temperature after an additional 1 h and stirred for 12 h. The reaction was monitored by IR. After filtration and solvent removal, the red brown tar was taken up in a minimum of THF and passed through an alumina column. A deep burgundy band was eluted

Scheme I



Scheme II



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0002-7863/90/1512-1818$02.50/0

with THF. Solvent removal and trituration with hexanes gave 1.57 g (29%) of a burgundy powder: IR (KBr, cm^{-1}) ν_{CO} 1880 s, $\nu_{C=O}$ 1745 m; ^1H NMR (CD_2Cl_2) δ 8.06–6.96 (m, 25 H, Ph), 4.71 (AB q, $^2J_{HH}$ = 14.4 Hz; H_A, d, $^4J_{HP}$ = 1.5 Hz; H_B, dd, $^4J_{HP}$ = 5, 2 Hz; CH_2Ph), 3.20–2.25 (m, 6 H, PCH_2CH_2P, $N(CHMe_2)_2$), 1.21, 1.06 (d, $^3J_{HH}$ = 7.2 Hz, 6 H each, $N(CHMe_2)_2$). Anal. Calcd: C, 56.27; H, 4.94; N, 1.52. Found: C, 55.63; H, 5.28; N, 1.47.

(dppe)(pyrdtc)(OC)W(*C,C*-η^2-OC=CCH$_2$Ph) (15). The preparation of **15** was analogous to that of **14** (pyrdtc = $S_2CN(C_4H_4)$), with the exception of a 4-h reaction time rather than 12 h following addition of the dithiocarbamate. The product was isolated as a dark brown solid in 40% yield: IR (KBr, cm^{-1}) ν_{CO} 1878 s, $\nu_{C=O}$ 1728 m; ^1H NMR ($CDCl_3$) δ 8.07–6.78 (m, 27 H, Ph, H_α of pyrrole), 6.15 (pseudo t, $^3J_{HH}$ = 2 Hz, 2 H, H_β of pyrrole), 4.79 (AB q, $^2J_{HH}$ = 15 Hz; H_A, d, $^4J_{HP}$ = 3 Hz; H_B, pseudo t, $^4J_{HP}$ = 2 Hz; CH_2Ph), 3.29–2.30 (m, 4 H, PCH_2CH_2P). Anal. Calcd: C, 55.72; H, 3.99; N, 1.59. Found: C, 55.73; H, 4.13; N, 1.37.

(dppe)(pyrdtc)(OC)W(*C,C*-η^2-OC=CCHMe$_2$) (19). To a solution of $W(CO)_3$(dppe)(acetone) (5.2 g, 7.5 mmol) in 50 mL of THF was added 2 equiv (0.98 g, 16 mmol) of $NaC{\equiv}CCH_3$. After 6 h, the solution was a bright yellow slurry. Three equiv (3.05 g, 21.5 mmol) of CH_3I was added, and the mixture was allowed to stir overnight. Filtration and solvent removal left a dark green tar, which was taken up in a minimum of toluene and loaded onto an alumina column. A dark green band was eluted with toluene. Solvent removal and trituration with hexanes gave *mer*-(dppe)$(OC)_3W{=}C{=}C(CH_3)_2$ (**17**) as a green powder in 89% yield. Recrystallization from toluene/hexanes gave dark green crystals.

A solution of **17** (4.83 g, 6.70 mmol) in 40 mL of CH_2Cl_2 was cooled to −78 °C, and 1.2 equiv (1.07 g, 8.00 mmol) of $HBF_4{\cdot}OMe_2$ was added with stirring. After 25 min, the solution was warmed to 0 °C, resulting in a color change to gold. After an additional 10 min, the solution was warmed to room temperature and the volume was reduced to 10 mL. The solution was transferred into 250 mL of Et_2O and 50 mL of 2-methylbutane, resulting in a bright yellow precipitate. Trituration, followed by washing with Et_2O, gave [*mer*-(dppe)$(OC)_3W(\equiv CCH(CH_3)_2)$][$BF_4$] (**18**) as a yellow solid in 79% yield.

The preparation of **19** from **18** is analogous to that of **15**. The product was isolated as a dark brown solid in 68% yield: IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1880 s, $\nu_{C=O}$ 1728 m; ^1H NMR (CD_2Cl_2) δ 8.00–6.79 (m, 22 H, Ph, H_α of pyrrole), 6.13 (pseudo t, $^3J_{HH}$ = 2.1 Hz, 2 H, H_β of pyrrole), 4.42 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, $CHMe_2$), 3.20–2.35 (m, 4 H, PCH_2CH_2P), 0.95, 0.91 (d, $^3J_{HH}$ = 6.8 Hz, 3 H each, $CHMe_2$). Anal. Calcd: C, 53.18; H, 4.22; N, 1.68. Found: C, 52.91; H, 4.29; N, 1.56.

[(dppe)(dmtc)(OC)W(MeOC=CCH$_2$Ph)][CF$_3$SO$_3$] (1a). A solution of **13** (1.66 g, 1.93 mmol) in 40 mL of CH_2Cl_2 was cooled to −78 °C, and 1.5 equiv (0.50 g, 3.0 mmol) of $CH_3SO_3CF_3$ was added with stirring. The solution was warmed to room temperature after 45 min, resulting in a color change from burgundy to red. After 2 h the solution volume was reduced to 10 mL, and the solution was transferred into 250 mL of Et_2O, resulting in a pink precipitate. Washing with Et_2O gave the product as a pink powder in 92% yield. Recrystallization from CH_2Cl_2/Et_2O gave red crystals: IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1955 s, $\nu_{C=C}$ 1688 m; ^1H NMR (CD_2Cl_2) δ 8.12–6.83 (m, 25 H, Ph), 4.56 (AB q, $^2J_{HH}$ = 16 Hz; H_A, dd, $^4J_{HP}$ = 2 Hz, 1 Hz; H_B, s; CH_2Ph), 3.53 (s, 3 H, OMe), 3.35–2.45 (m, 4 H, PCH_2CH_2P), 2.83, 2.65 (s, 3 H each, NMe_2).

[(dppe)(dmtc)(OC)W(MeOC=CCD$_2$Ph)][CF$_3$SO$_3$] (1c). To a solution of **1a** (2.0 g, 1.9 mmol) in 60 mL of THF was added 10 mL of D_2O and 0.1 mL of NEt_3. The solution was stirred for 72 h. Addition of Et_2O gave the product as a pink powder: ^1H NMR (CD_2Cl_2) δ 8.06–6.84 (m, 25 H, Ph), 3.52 (s, 3 H, OMe), 3.30–2.50 (m, 4 H, PCH_2CH_2P), 2.82, 2.65 (s, 3 H, NMe_2).

[(dppe)(diprtc)(OC)W(MeOC=CCH$_2$Ph)][CF$_3$SO$_3$] (4a). Preparation of **4a** from **14** was analogous to that of **1a**. The product was isolated as a pink powder in 90% yield: IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1952 s, $\nu_{C=C}$ 1687 m; ^1H NMR ($CDCl_3$) δ 8.15–6.92 (m, 25 H, Ph), 4.85 (AB q, $^2J_{HH}$ = 15 Hz; H_A, d, $^4J_{HP}$ = 5 Hz; H_B, s; CH_2Ph), 3.85–2.40 (m, 6 H, PCH_2CH_2P, $N(CHMe_2)_2$), 3.63 (s, 3 H, OMe), 1.34, 1.18 (d, $^3J_{HH}$ = 6.8 Hz, 6 H each, $N(CHMe_2)_2$).

[(dppe)(diprtc)(OC)W(MeOC=CCH$_2$Ph)][BF$_4$] (4b). Preparation of **4b** from **14** was analogous to that of **1a**, with the substitution of Me_3OBF_4 for MeO_3SCF_3 and a 4-h reaction time. The product was isolated as a pink powder in 90% yield: IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1955 s, $\nu_{C=C}$ 1687 m; ^1H NMR ($CDCl_3$) δ 8.06–6.82 (m, 25 H, Ph), 4.70 (AB q, $^2J_{HH}$ = 15 Hz; H_A, dd, $^4J_{HP}$ = 5 Hz, 1 Hz; H_B, s; CH_2Ph), 3.82–2.50 (m, 6 H, PCH_2CH_2P, $N(CHMe_2)_2$), 3.57 (s, 3 H, OMe), 1.22, 1.08 (d, $^3J_{HH}$ = 6.8 Hz, 6 H each, $N(CHMe_2)_2$). Anal. Calcd: C, 51.83; H, 4.74; N, 1.37. Found: C, 50.81; H, 4.86; N, 1.20.

[(dppe)(pyrdtc)(OC)W(MeOC=CCH$_2$Ph)][CF$_3$SO$_3$] (7a). Preparation of **7a** from **15** was analogous to that of **1a**. The product was isolated as an orange powder in 90% yield: IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1964 s, $\nu_{C=C}$ 1677 m; ^1H NMR ($CDCl_3$) δ 7.98–6.79 (m, 27 H, Ph, H_α of pyrrole), 6.24 (pseudo t, $^3J_{HH}$ = 2 Hz, 2 H, H_β of pyrrole), 4.48 (AB q, $^2J_{HH}$ = 16 Hz; H_A, br s; H_B, s; CH_2Ph), 3.30–2.60 (m, 4 H, PCH_2CH_2P), 3.58 (s, 3 H, OMe).

[(dppe)(pyrdtc)(OC)W(MeOC=CCH$_2$Ph)][BF$_4$] (7b). Preparation of **7b** from **15** was analogous to that of **4b**. The product was isolated as an orange powder in 95% yield: IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1955 s, $\nu_{C=C}$ 1682 m; ^1H NMR ($CDCl_3$) δ 8.05–6.80 (m, 27 H, Ph, H_α of pyrrole), 6.25 (pseudo t, $^3J_{HH}$ = 2 Hz, 2 H, H_β of pyrrole), 4.49 (AB q, $^2J_{HH}$ = 16 Hz; H_A, br s; H_B, s; CH_2Ph), 3.40–2.70 (m, 4 H, PCH_2CH_2P), 3.59 (s, 3 H, OMe). Anal. Calcd: C, 51.19; H, 3.89; N, 1.42. Found: C, 50.67; H, 4.16; N, 1.33.

[(dppe)(pyrdtc)(OC)W(MeOC=CCHMe$_2$)][BF$_4$] (16). Preparation of **16** from **19** was analogous to that of **1**. The product was isolated as an orange powder in 90% yield: IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1955 s, $\nu_{C=C}$ 1672 m; ^1H NMR (CD_2Cl_2) δ 8.00–7.01 (m, 22 H, Ph, H_α of pyrrole), 6.26 (pseudo t, $^3J_{HH}$ = 2 Hz, 2 H, H_β of pyrrole), 4.21 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, $CHMe_2$), 3.79 (s, 3 H, OMe), 3.58–2.72 (m, 4 H, PCH_2CH_2P), 1.05, 0.92 (d, $^3J_{HH}$ = 6.8 Hz, 3 H each, $CHMe_2$). Anal. Calcd: C, 46.85; H, 3.83; N, 1.40. Found: C, 46.43; H, 3.79; N, 1.30.

NMR Studies of (dppe)(dmtc)(OC)W(η^2-MeOC=C=CHPh) (2, 3). A solution of **1a** (0.07 g, 0.07 mmol) in 1 mL of THF-d_8 at −78 °C was added to an NMR tube containing $NaN(SiMe_3)_2$ (0.03 g, 0.16 mmol) at −78 °C, resulting in a color change to dark red. Low-temperature ^1H NMR of this material indicated formation of a kinetically favored isomer (**2**). Upon being warmed above −40 °C, the material converted to an equilibrium mixture with a final 3:2 ratio of isomers, favoring the second isomer (**3**). ^{13}C NMR spectra were collected at ambient temperature: IR (THF cm^{-1}) ν_{CO} 1860 m.

Kinetically favored isomer (**2**): ^1H NMR (THF-d_8) δ 8.09–6.52 (m, 25 H, Ph), 5.23 (s, $^3J_{HW}$ = 9.6 Hz, 1 H, C=C*H*Ph), 4.19 (s, 3 H, OMe), 3.5–2.2 (m, 4 H, PCH_2CH_2P), 2.73, 2.50 (s, 3 H each, NMe_2); ^{13}C NMR (THF-d_8) δ 250.8 (ddd, $^2J_{CP}$ = 9, 5 Hz, $^3J_{CH}$ = 5 Hz, MeOC=C=CHPh), 227.0 (dd, $^2J_{CP}$ = 12, 4 Hz, CO), 215.6 (br s, S_2CNMe_2), 146.0–120.0 (m, Ph, MeOC=*C*=CHPh), 112.1 (br d, $^1J_{CH}$ = 156 Hz, MeOC=C=*C*HPh), 64.8 (q, $^1J_{CH}$ = 144 Hz, OMe), 39.0, 38.6 (q, $^1J_{CH}$ = 137 Hz, NMe_2), 34.0–27.5 (m, PCH_2CH_2P).

Thermodynamically favored isomer (**3**): ^1H NMR (THF-d_8 δ 8.09–6.52 (m, 25 H, Ph), 4.69 (s, 3 H, OMe), 4.06 (br s, $^3J_{HW}$ = 9.6 Hz, 1 H, C=C*H*Ph), 3.5–2.2 (m, 4 H, PCH_2CH_2P), 2.61, 2.43 (s, 3 H each, NMe_2); ^{13}C NMR (THF-d_8) δ 235.3 (dd, $^2J_{CP}$ = 52, 7 Hz, MeOC=C=CHPh), 213.4 (br s, S_2CNMe_2), 204.0 (dd, $^2J_{CP}$ = 7, 4 Hz, CO), 146.0–120.0 (m, Ph), 139.6 (br dd, $^2J_{CP}$ = 8, 7 Hz, MeOC=*C*=CHPh), 116.5 (ddt, $^1J_{CH}$ = 152 Hz, $^3J_{CP}$ = 6 Hz, $^3J_{CH}$ = 6 Hz, MeOC=C=*C*HPh), 64.9 (q, $^1J_{CH}$ = 144 Hz, OMe), 38.2, 37.3 (q, $^1J_{CH}$ = 137 Hz, NMe_2), 34.0–27.5 (m, PCH_2CH_2P).

In a separate experiment, a solution of **1b** (0.25 g, 0.26 mmol) in THF was deprotonated with KH, stripped to an oily paste, and extracted with C_6D_5Br into an NMR tube, which was then sealed. Variable-temperature ^1H NMR showed broadening of the C=CHPh, OMe, and dmtc protons at 67 °C. Coalescence was approached at approximately 120 °C.

(dppe)(diprtc)(OC)W(η^2-MeOC=C=CHPh) (5, 6). To an NMR tube containing **4a** (0.30 g, 0.28 mmol) and $NaN(SiMe_3)_2$ (0.06g, 0.33 mmol) at room temperature was added 1 mL of THF-d_8, resulting in a dark orange solution. The tube was sealed, and NMR data were collected at room temperature. A 3:2 ratio of isomers was observed.

Minor isomer (**5**): ^1H NMR (THF-d_8) δ 8.04–6.48 (m, 25 H, Ph), 5.20 (s, $^3J_{HW}$ = 9.0 Hz, 1 H, C=C*H*Ph), 4.19 (s, 3 H, OMe), 3.95–2.30 (m, 6 H, PCH_2CH_2P and $CHMe_2$), 1.31–0.98 (m, 12 H, $CHMe_2$); ^{13}C NMR (THF-d_8) δ 251.6 (ddd, $^2J_{CP}$ = 8, 5 Hz, $^3J_{CH}$ = 5 Hz, MeOC=C=CHPh), 226.3 (dd, $^2J_{CP}$ = 14, 4 Hz, CO), 214.4 (br s, S_2CNMe_2), 146.0–120.0 (m, Ph, MeOC=*C*=CHPh), 110.8 (br d, $^1J_{CH}$ = 152 Hz, MeOC=C=*C*HPh), 64.6 (q, $^1J_{CH}$ = 144 Hz, OMe), 50.8, 48.3 (d, $^1J_{CH}$ = 141 Hz, $N(CHMe_2)_2$), 33.0–26.0 (m, PCH_2CH_2P), 24.0–19.0 (q, $^1J_{CH}$ = 126 Hz, $N(CHMe_2)_2$).

Major isomer (**6**): ^1H NMR (THF-d_8) δ 8.04–6.48 (m, 25 H, Ph), 4.66 (s, 3 H, OMe), 4.05 (br s, $^3J_{HW}$ = 9.0 Hz, 1 H, C=C*H*Ph), 3.95–2.30 (m, 6 H, PCH_2CH_2P and $CHMe_2$), 1.31–0.98 (m, 12 H, $CHMe_2$); ^{13}C NMR (THF-d_8) δ 235.3 (dd, $^2J_{CP}$ = 55, 6 Hz, MeOC=C=CHPh), 214.8 (br s, S_2CNMe_2), 203.1 (dd, $^2J_{CP}$ = 7, 4 Hz, CO), 146.0–120.0 (m, Ph), 139.6 (br dd, $^2J_{CP}$ = 8, 7 Hz, MeOC=*C*=CHPh), 116.5 (ddt, $^1J_{CH}$ = 154 Hz, $^3J_{CP}$ = 6 Hz, $^3J_{CH}$ = 6 Hz, MeOC=C=*C*HPh), 65.0 (q, $^1J_{CH}$ = 144 Hz, OMe), 50.1, 49.3 (d, $^1J_{CH}$ = 141 Hz, $N(CHMe_2)_2$), 33.0–26.0 (m, PCH_2CH_2P), 24.0–19.0 (q, $^1J_{CH}$ = 126 Hz, $N(CHMe_2)_2$).

(dppe)(pyrdtc)(OC)W(η^2-MeOC=C=CHPh) (8, 9). A solution of **7b** (0.30 g, 0.30 mmol) in 30 mL of THF was transferred to a flask containing KH (washed with hexanes), resulting in a color change from orange to dark green and evolution of H_2 over a 5-min period. After 30 min, the solution was filtered and reduced in volume to 5 mL and 30 mL of hexanes was layered on top. After 2 days at −25 °C, a dark green

precipitate had formed. Washing with hexanes and Et_2O gave the product as a dark green solid. ^1H NMR data were collected at room temperature. A 7:2 ratio of isomers was observed.

Minor isomer (**8**): ^1H NMR (CD_2Cl_2) δ 8.98–6.56 (m, 27 H, Ph, H_α of pyrrole), 6.08 (pseudo t, $^3J_{HH}$ = 2 Hz, 2 H, H_β of pyrrole), 5.27 (s, $^3J_{HW}$ = 9.0 Hz, 1 H, C=C*H*Ph), 4.29 (s, 3 H, OMe), 3.30–2.20 (m, 4 H, PCH_2CH_2P).

Major isomer (**9**): ^1H NMR (CD_2Cl_2) δ 8.98–6.56 (m, 27 H, Ph, H_α of pyrrole), 6.04 (pseudo t, $^3J_{HH}$ = 2 Hz, 2 H, H_β of pyrrole), 4.78 (s, 3 H, OMe), 4.21 (t, $^4J_{HP}$ = 1.8 Hz, $^3J_{HW}$ = 9.0 Hz, 1 H, C=C*H*Ph), 3.30–2.20 (m, 4 H, PCH_2CH_2P).

[(dppe)(dmtc)(OC)W(MeOC≡CCHMePh)][CF_3SO_3] (10a). A solution of **1a** (0.40 g, 0.39 mmol) in 20 mL of CH_2Cl_2 was cooled to −78 °C and transferred into a solution of *n*-BuLi (0.78 mmol, 2 equiv) in 10 mL of CH_2Cl_2 at −78 °C, resulting in a color change from pink to dark red. After 10 min, MeO_3SCF_3 (1.0 g, 6.1 mmol) was added, resulting in a slow color change from dark red to pink over a 1-h period. After the solution was warmed to room temperature, the volume was reduced to 5 mL and the solution was transferred into 100 mL of Et_2O and 100 mL of 2-methylbutane, resulting in a pink precipitate. Washing with Et_2O gave the product as a pink solid. Only one isomer was observed in the ^1H NMR: ^1H NMR ($CDCl_3$) δ 8.03–6.79 (m, 25 H, Ph), 5.31 (q, $^3J_{HH}$ = 7.0 Hz, 1 H, C*H*MePh), 3.55 (s, 3 H, OMe), 3.30–2.40 (m, 4 H, PCH_2CH_2P), 2.81, 2.63 (s, 3 H, NMe_2), 1.35 (d, $^3J_{HH}$ = 7.0 Hz, 3 H, CH*Me*Ph).

[(dppe)(dmtc)(OC)W(MeOC≡CCHMePh)][BF_4] (10b). The dmtc allenyl (**2**) was generated as in a **10a** and transferred into a mixture of excess Me_3OBF_4 and 10 mL of CH_2Cl_2 at −78 °C. After 3 h, no color change was observed and the solution was warmed to −43 °C, resulting in a slow color change from dark red to pink over a 1-h period. After the solution was warmed to room temperature, the volume was reduced to 5 mL and the solution was transferred into 100 mL of Et_2O and 100 mL of 2-methylbutane, resulting in a pink precipitate. Washing with Et_2O gave the product as a pink solid. Only one isomer was observed in the ^1H NMR: ^1H NMR ($CDCl_3$) δ 8.01–6.77 (m, 25 H, Ph), 5.27 (q, $^3J_{HH}$ = 7.0 Hz, 1 H, C*H*MePh), 3.51 (s, 3 H, OMe), 3.30–2.40 (m, 4 H, PCH_2CH_2P), 2.78, 2.59 (s, 3 H, NMe_2), 1.35 (d, $^3J_{HH}$ = 7.0 Hz, 3 H, CH*Me*Ph).

[(dppe)(dmtc)(OC)W(MeOC≡CCHMePh)][I] (10c). A solution of **1b** (0.20 g, 0.21 mmol) in 20 mL of THF was transferred to a flask containing KH (washed with hexanes), resulting in a color change from pink to dark orange and evolution of H_2. After 10 min, the solution was filtered into a flask containing CH_3I in 10 mL of THF. After being stirred for 30 min, the solution was again pink. The volume was reduced to 10 mL and transferred into 200 mL of Et_2O, resulting in a pink precipitate. The product was isolated as a pink powder with a 3:1 ratio of diastereomers: ^1H NMR ($CDCl_3$) δ 8.05–6.73 (m, 25 H, Ph), 5.23 (q, $^3J_{HH}$ = 7.0 Hz, 1 H, C*H*MePh of major isomer), 5.14 (q, $^3J_{HH}$ = 7.0 Hz, 1 H, C*H*MePh of minor isomer), 3.59 (s, 3 H, OMe of minor isomer), 3.48 (s, 3 H, OMe of major isomer), 3.30–2.50 (m, 4 H, PCH_2CH_2P), 2.79, 2.64 (s, 3 H, NMe_2 of minor isomer), 2.76, 2.58 (s, 3 H, NMe_2 of major isomer), 1.30 (d, $^3J_{HH}$ = 7.0 Hz, 3 H, CH*Me*Ph of major isomer), 1.16 (d, $^3J_{HH}$ = 7.0 Hz, 3 H, CH*Me*Ph of minor isomer).

[(dppe)(diprtc)(OC)W(MeOC≡CCHMePh)][I] (11). Preparation of **11** from **4** was analogous to that of **10**. The product was isolated as a pink powder with a 4.5:1 ratio of diastereomers: ^1H NMR ($CDCl_3$) δ 8.20–6.92 (m, 25 H, Ph), 5.86 (q, $^3J_{HH}$ = 7.0 Hz, 1 H, C*H*MePh of major isomer), 5.45 (q, $^3J_{HH}$ = 7.0 Hz, 1 H, C*H*MePh of minor isomer) 3.85–2.50 (m, 6 H, PCH_2CH_2P, $N(CHMe_2)_2$), 3.53 (s, 3 H, OMe of major isomer), 3.47 (s, 3 H, OMe of minor isomer) 1.29, 1.04 (d, $^3J_{HH}$ = 7.0 Hz, 6 H each, $N(CHMe_2)_2$ of major isomer), 1.19 (d, $^3J_{HH}$ = 7.0 Hz, 3 H, CH*Me*Ph of major isomer). $N(CHMe_2)_2$, and CH*Me*Ph peaks of the minor isomer were unassignable.

[(dppe)(pyrdtc)(OC)W(MeOC≡CCHMePh)][I] (12). Preparation of **12** from **7** was analogous to that of **10**. The product was isolated as an orange powder with a 2.5:1 ratio of diastereomers: ^1H NMR ($CDCl_3$) δ 8.18–6.70 (m, 27 H, Ph, H_α of pyrrole), 6.33 (pseudo t, $^3J_{HH}$ = 2 Hz, 2 H, H_β of pyrrole, minor isomer), 6.29 (pseudo t, $^3J_{HH}$ = 2 Hz, 2 H, H_β of pyrrole, major isomer), 5.23 (q, $^3J_{HH}$ = 7.0 Hz, 1 H, C*H*MePh of minor isomer), 5.10 (q, $^3J_{HH}$ = 7.0 Hz, 1 H, C*H*MePh of major isomer), 4.00 (s, 3 H, OMe of minor isomer), 3.92 (s, 3 H, OMe of major isomer), 3.30–2.60 (m, 4 H, PCH_2CH_2P), 1.45 (d, $^3J_{HH}$ = 7.0 Hz, 3 H, CH*Me*Ph of minor isomer), 1.11 (d, $^3J_{HH}$ = 7.0 Hz, 3 H, CH*Me*Ph of major isomer).

Protonation of (dppe)(dmtc)(OC)W(η^2-MeOC=C=CDPh). A series of three protonation reactions was performed.

(A) A solution of **1c** (0.30 g, 0.29 mmol) in 5 mL of THF was added to a Schlenk tube containing a solution of LDA (0.38 mmol) in 5 mL of THF at −78 °C, resulting in a color change to dark red. After 10 min, 1.1 equiv of *n*-BuLi (with respect to LDA)[11] was added to the solution. After an additional 10 min, the solution was transferred into a solution of CF_3COOH (3 mmol) in 10 mL of THF at −78 °C, resulting in a color change to light orange. After the solution was warmed to room temperature, the volume was reduced to 10 mL and the solution was transferred into 200 mL of Et_2O, resulting in a pink precipitate. Washing with Et_2O gave the product as a pink powder with a 15:1 ratio of diastereomers: ^1H NMR (CD_2Cl_2) δ 8.05–6.85 (m, 25 H, Ph), 4.74 (br s, 1 H, CHDPh of minor isomer), 4.31 (br d, $^4J_{HP}$ = 2 Hz, 1 H, CDHPh of major isomer), 3.52 (s, 3 H, OMe), 3.30–2.40 (m, 4 H, PCH_2CH_2P), 2.82, 2.66 (s, 3 H, NMe_2).

(B) The allenyl complex was generated as in A and then allowed to warm to room temperature after addition of *n*-BuLi, resulting in a color change to dark orange. After 20 min at room temperature, the solution was transferred into a solution of CF_3COOH (3 mmol) in 10 mL of THF, resulting in a color change to light orange. The solution volume was reduced to 10 mL, and the solution was transferred into 200 mL of Et_2O, resulting in a pink precipitate. Washing with Et_2O gave the product as a pink powder with a 2.4:1 ratio of diastereomers: ^1H NMR (CD_2Cl_2) δ 8.06–6.86 (m, 25 H, Ph), 4.75 (br s, 1 H, CHDPh of minor isomer), 4.31 (br s, 1 H, CDHPh of major isomer), 3.52 (s, 3 H, OMe), 3.30–2.40 (m, 4 H, PCH_2CH_2P), 2.81, 2.65 (s, 3 H, NMe_2).

(C) The allenyl complex was generated and warmed to room temperature as in B, then cooled to −78 °C, and transferred into a solution of CF_3COOH (3 mmol) in 10 mL of THF at −78 °C, resulting in a color change to dark green. After being warmed to room temperature, the solution became light orange. The solution volume was reduced to 10 mL, and the solution was transferred into 200 mL of Et_2O, resulting in a pink precipitate. Washing with Et_2O gave the product as a pink powder with a 2.4:1 ratio of diastereomers: ^1H NMR (CD_2Cl_2) δ 8.05–6.84 (m, 25 H, Ph), 4.75 (br s, 1 H, CHDPh of minor isomer), 4.31 (br s, 1 H, CDHPh of major isomer), 3.52 (s, 3 H, OMe), 3.30–2.40 (m, 4 H, PCH_2CH_2P), 2.82, 2.66 (s, 3 H, NMe_2).

NMR Protonation Study. A solution of **1a** (0.15 g, 0.15 mmol) in 1 mL of THF-d_8 was transferred into an NMR tube containing 2 equiv (0.05 g, 0.27 mmol) of $NaN(SiMe_3)_2$ at −78 °C, resulting in a color change from pink to dark red. The sample was warmed to 25 °C for 30 min, resulting in a color change to dark orange, and then cooled to −78 °C. The sample was protonated at low temperature with 6 M CF_3COOH (0.05 mL, 0.30 mmol), and the tube was sealed. The sample was warmed slowly to ambient temperature (22 °C), in increments of 10 °C/h. Spectra were recorded every 10 min.

MO Calculations. A series of extended Hückel calculations[12] were undertaken to assess the relative barriers to isomerization for the rotation of the allenyl fragment with respect to the metal center versus rotation about the C_β–C_γ double bond of the allenyl. Calculations were performed on a simplified model complex, $H_4(OC)W(\eta^2\text{-}HOC{=}C{=}CH_2)^{3-}$. Parameters[13] and bond distances and angles are summarized in Tables I and II. W–C_α, W–C_β, and C_α–C_β bond distances were approximated on the basis of the molecular structure of (dppe)(dmtc)(OC)W(η^2-OC≡CCH$_2$Ph), and the C_α–C_β–C_γ angle was taken to be 151°, that of C_α–C_β–O of the ketenyl.[8] C_α–O and O–H bond distances were taken from the molecular structure of [$(PMe_3)(OC)(Cp)W(\eta^2\text{-}HOC{\equiv}C\text{-}p\text{-}C_6H_4Me)$][$BF_4$],[14] with O–$C_\alpha$–$C_\beta$ and H–O–C_α angles taken from the X-ray crystal structure of [(dppe)(dmtc)(OC)W(η^2-MeOC≡CCH$_2$Ph)][CF_3SO_3][15] by analogy to MeOC≡CCH$_2$Ph. C_β–$C_\gamma H_2$ dis-

Table I. Extended Hückel Parameters

orbital	$H(i,i)$, eV	exponents ζ_1	exponents ζ_2
H	−13.6	1.3	
C 2s	−21.4	1.625	
C 2p	−11.4	1.625	
O 2s	−32.3	2.275	
O 2p	−14.8	2.275	
W 5d	−10.37	4.982 (0.6685)	2.068 (0.5424)
W 6s	−8.26	2.341	
W 6p	−5.17	2.309	

(11) Addition of *n*-BuLi removes deuterium from diisopropylamine-d_1, preventing redeuteration of the allenyl due to complexation of the allenyl with the conjugate acid. In the absence of *n*-BuLi, approximately 60% protonation was observed. Laube, T.; Dunitz, J. D.; Seebach, D. *Helv. Chim. Acta* **1985**, *68*, 1373.

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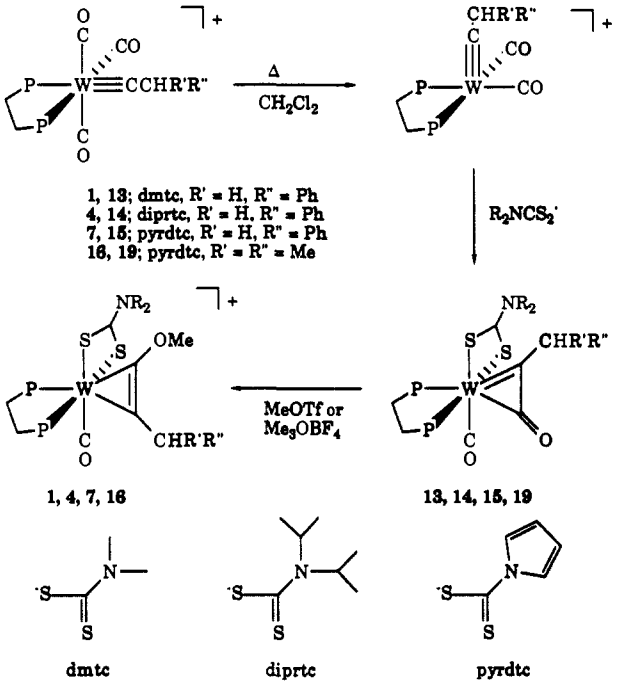
Table II. Bond Distances and Angles

linkage	dist, Å	ref	linkage	angle, deg	ref
W–C_α	2.00	8	C_α–C_β–C_γ	151	14
W–C_β	2.18	8	C_β–C_α–O	135	15
W–C_{co}	1.91	8	C_α–O–H	130	15
W–H	1.80	19	C_β–C_γ–H	121	17
C_α–C_β	1.30	8	H–C_γ–H	118	17
C_β–C_γ	1.34	16			
C_α–O	1.32	14			
C_{co}–O	1.18	8			
O–H	1.00	14			
C–H	1.09	16			

Scheme III

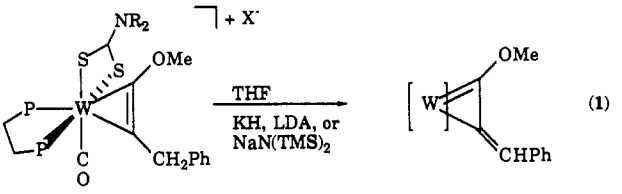


tances[16] and angles[17] were idealized on the basis of sp^2 hybridization at the C_γ carbon.[18] All atoms of the allenyl fragment lie in the *xz* plane. The $H_4(OC)W$ fragment was idealized octahedral, with all cis angles 90°, and the CO lying along the +*x* axis. The +*z* axis bisected the C_α–C_β bond. For 0° rotation, C_γ was proximal to CO.[19]

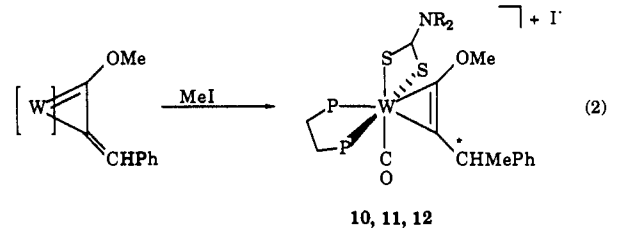
Results

Syntheses. Vinylidene complexes[20] were prepared either by alkylation of anionic acetylide complexes[21] or by rearrangement of neutral alkyne complexes.[8,22] Cationic carbyne complexes were prepared by electrophilic addition[23] to neutral vinylidene complexes.[8,24] Loss of CO results from heating a CH_2Cl_2 solution of the tricarbonyl carbyne complex. Addition of a dithiocarbamate salt results in coupling of CO and carbyne to form an η^2-ketenyl complex, as previously reported for dmtc.[8] Addition of either $MeSO_3CF_3$ or Me_3OBF_4 results in methylation at the ketenyl oxygen, yielding a cationic alkyne complex (Sceme III).[8] Of the two Me^+ sources, $MeSO_3CF_3$ more rapidly methylates the oxygen. The triflate salt crystallizes readily.

Cationic alkyne complexes of the type [(dppe)(dtc)(OC)W-(MeOC≡CCH_2Ph)][X] (X = $CF_3SO_3^-$, BF_4^-; dtc = dmtc (**1**), diprtc (**4**), and pyrdtc (**7**)) are readily deprotonated by strong base to yield neutral η^2-allenyl complexes, (dppe)(dtc)(OC)W-(MeOC=C=CHPh) (eq 1). The reaction is accompanied by



a shift in the carbonyl IR pattern to lower wavenumber and by a color change to dark red (low temperature) or dark orange (room temperature) for dtc = dmtc or diprtc or to dark green for dtc = pyrdtc. These allenyl complexes are highly reactive and sensitive to air or moisture. They react readily with electrophiles to give C_γ-substituted alkyne complexes (eq 2).



Though not isolated as a solid, the allenyl complex with dtc = dmtc has been studied by NMR. A kinetically favored isomer (**2**) of the allenyl is generated exclusively when the alkyne complex (**1**) is deprotonated at low temperature with a hindered base such as LDA or $NaN(SiMe_3)_2$. As the sample warms above −40 °C, the kinetically favored product isomerizes to a 3:2 equilibrium ratio of isomers, favoring a second allenyl isomer (**3**). Heating an allenyl ^1H NMR sample in C_6D_5Br results in a broadening of the vinyl H signals, with the two isomer signals approaching coalescence near 120 °C. This NMR data allowed us to estimate an energy barrier for conversion of the kinetically favored isomer to the thermodynamically favored isomer of 18.5 kcal/mol. The allenyl isomer ratios vary slightly with different dtc substituents, with dmtc and diprtc allenyl complexes having approximately 3:2 ratios and pyrdtc allenyl complexes having a 7:2 ratio.

Methylation of the neutral allenyl complexes with CH_3I yields the respective C_γ-methyl-substituted cationic tungsten alkyne complexes as pairs of diastereomers. The diastereomeric ratios range from 2.5:1 for pyrdtc (**12**) to 3:1 for dmtc (**10**) to 4.5:1 for diprtc (**11**). The allenyl complexes react with MeI more slowly than they react with acid or water. Complexes with larger dtc ligands react more slowly.

The cationic alkyne complex **1** is deuterated at the C_γ carbon by stirring in a THF/D_2O solution with a catalytic amount of NEt_3. The high-field proton signal (4.30 ppm) disappears faster than the low-field signal (4.75 ppm). The deuterated product (**1c**) has been used in a series of dedeuteration/protonation experiments to assess the relative protonation selectivities of the kinetically

(15) Unpublished structure of [(dppe)(dmtc)(OC)W(η^2-MeOC≡CCH_2Ph)][CF_3SO_3]. Final *R* and R_w values were 5.0% and 7.4%, respectively.

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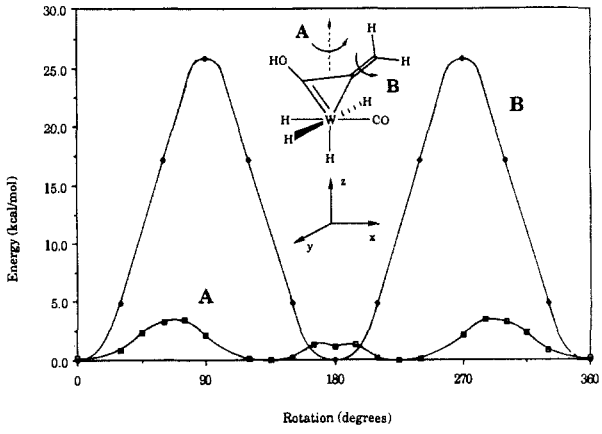


Figure 1. Rotational profiles for the model allenyl complex: (A) rotation of the entire allenyl ligand; (B) rotation about the uncoordinated double bond.

favored and thermodynamically favored isomers. In the first experiment, a sample of **1c** was dedeuterated at −78 °C with LDA and *n*-BuLi, giving exclusively the kinetically favored isomer. The complex was then rapidly protonated at low temperature with excess CF_3COOH. The product showed an isomer ratio of 15:1, favoring the high-field diastereomer (4.3 ppm).

In the second experiment, the monodeuterated allenyl complex was allowed to warm to ambient temperature (25 °C), resulting in conversion of the kinetically favored isomer to the 3:2 equilibrium ratio. Protonation at 25 °C gave an alkyne complex with an isomer ratio of 2.4:1 favoring the high-field diastereomer.

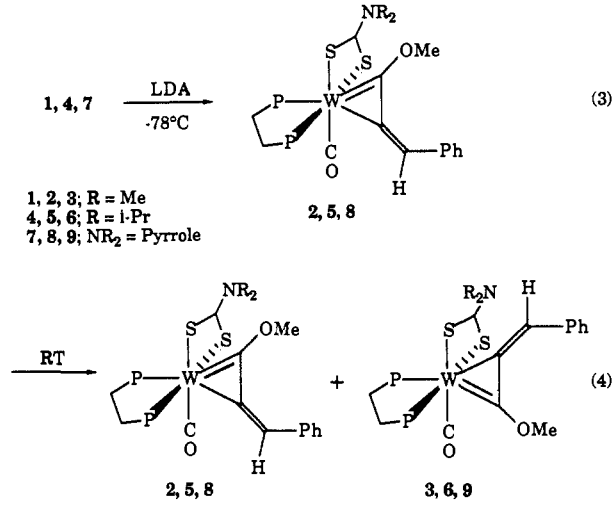
In the last experiment, the 3:2 allenyl isomer mix was cooled to −78 °C, thereby preventing interconversion of isomers. Immediately upon protonation, the color of the solution turned from dark orange to dark green as the kinetically favored isomer was protonated, leaving the thermodynamically favored isomer. Warming resulted in slow conversion to the characteristic pink color of the alkyne complex. The isomer ratio was again 2.4:1 favoring the high-field diastereomer.

In order to better understand the dynamics of low-temperature protonation of the second allenyl isomer, an NMR sample of the proteoallenyl isomer mix was generated, cooled to −78 °C, and protonated with 1 equiv of CF_3COOH. At −60 °C, the sample consisted of 52% alkyne (**1**), 33% thermodynamically favored isomer (**3**), and 15% kinetically favored isomer (**2**). By −40 °C, **2** had reacted almost completely to form the alkyne complex, with approximately 1% still visible in the NMR. At −30 °C, **3** began to disappear, with a concomitant increase in the amount of alkyne complex. Trace amounts of **2** were always detectable at −30 °C. With about 10% **3** remaining, the solution was warmed to −20 °C. At this temperature, no **2** was observed, and **3** disappeared virtually completely.

MO Results. The rotational profiles for rotation of the allenyl fragment about the *z* axis and rotation about the C_β–C_γ double bond, for the model complex $H_4(OC)W(\eta^2\text{-}HOC{=}C{=}CH_2)^{3-}$, are shown in Figure 1. Rotation about the double bond shows a significantly higher barrier, ~26 kcal/mol, than rotation of the allenyl fragment, ~3.5 kcal/mol. The profile for rotation of the allenyl fragment shows local maxima and a local minimum in the vicinity of 180° rotation. The global minima lie at 130° and 230°, about 0.3 kcal/mol lower in energy than at 0° rotation.

Discussion

Formation of a neutral η^2-allenyl complex has been accomplished by deprotonation of a cationic η^2-alkyne complex. An X-ray crystal structure of the tungsten alkyne starting material shows C_γ proximal to CO.[15] Only one isomer of the alkyne complex is observed in THF solution. We postulate that the isomer formed by low-temperature deprotonation with LDA and *n*-BuLi has C_γ proximal to CO with phenyl trans to tungsten across the C_β–C_γ double bond and the allenyl fragment roughly parallel to the carbonyl C–O vector (**2**) (eq 3). Warming a solution of **2**



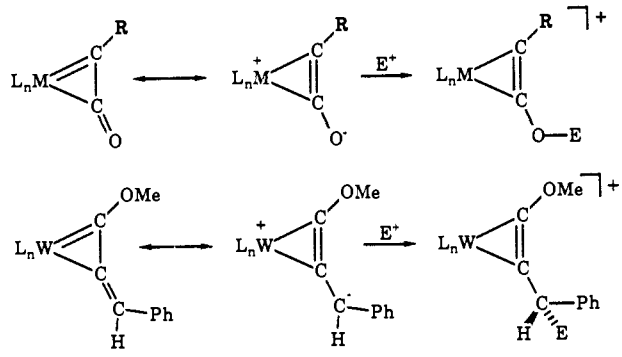
allows rotation of the allenyl by 180° to give a rotamer with the methoxy group proximal to CO (**3**) and a final equilibrium ratio of 3:2 favoring **3** (eq 4). Identical $^3J_{HW}$ values for the two isomers (9.6 Hz) suggest that the substituents on the C_γ carbons have the same conformation with respect to tungsten. Similar chemical shift values for the C_γ and OMe protons for the diprtc allenyls and pyrdtc allenyls, as well as similar $^3J_{HW}$ values (9.0 Hz for both isomers of each), suggest that they form analogous isomers. Rotation of the allenyl fragment may also account for the large chemical shift differences between rotamers observed for the C_α and carbonyl carbons of the allenyl complexes, as their environments are altered most by rotation. The large $^2J_{CP}$ values observed for the C_α carbon of the thermodynamically favored isomers may reflect a more closely trans P–W–C_α configuration than in the kinetically favored isomers. Green observes rapid rotation of the allenyl fragment of $Cp((OMe)_3P)_2Mo(\eta^2\text{-}PhC{=}C{=}CHPh)$ on the NMR time scale. Rotation occurs between the two equivalent conformations having the allenyl aligned with one or the other phosphorus ligands with C_α proximal to phosphorus.[3]

Green reports ^{13}C NMR data for the major isomer of $Cp((OMe)_3P)_2Mo(\eta^2\text{-}PhC{=}C{=}CHPh)$ (Ph trans to tungsten across the C_β–C_γ double bond). The shift values for the carbons of the allenyl fragment agree well with the corresponding carbons for **2** and **5**, the minor isomers of the dmtc and diprtc allenyls. The C_α carbon in Green's system resonates at 235.5 ppm, in the range for carbons multiply bonded to a metal,[25] with C_β and C_γ coming at 151.6 and 109.0 ppm, respectively.[3] For **2** and **5**, the C_α carbons resonate at 250.8 and 251.6 ppm and C_γ carbons at 112.1 and 110.8 ppm. The C_β signals for both **2** and **5** are lost in the phenyl region (~146–120 ppm). The C_β carbons are assignable for both of the major isomers at 139.6 ppm.

The C^2-allenyl ligand is structurally similar to and isolobal with η^2-vinyl and η^2-ketenyl ligands. Both η^2-vinyl and η^2-allenyl complexes are derivatives of η^2-alkyne complexes, with addition of nucleophiles to η^2-alkynes yielding η^2-vinyls[26] and deprotonation of η^2-alkynes producing η^2-allenyls.[3] Further, both η^2-ketenyl and η^2-allenyl complexes add electrophiles to form η^2-alkyne complexes. The nucleophilicity observed at C_γ of the η^2-allenyl, analogous to η^2-ketenyl reactivity,[8,14,27] is consistent with the resonance form shown in Scheme IV, where electron density is localized on the C_γ carbon in a zwitterionic configuration with positive charge at the metal center. The nucleophilicity at C_γ can be affected

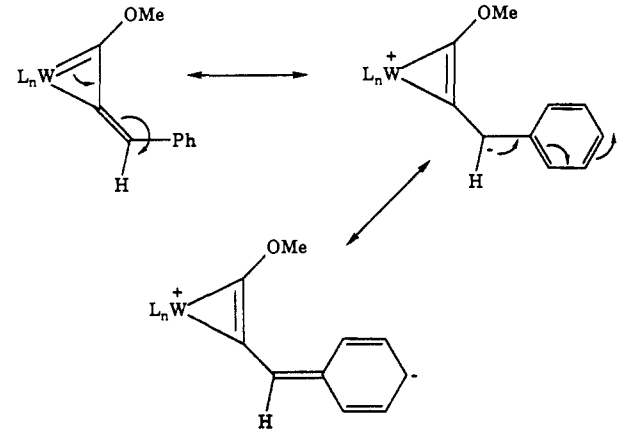
(25) Chisholm, M. H.; Godleski, S. *Prog. Inorg. Chem.* **1976**, *20*, 299.
(26) (a) Davidson, J. L.; Murray, I. E. P.; Preston, P. N.; Russo, M. V.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1981**, 1059. (b) Davidson, J. L.; Vasapollo, G.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1982**, 1025. (c) Allen, S. R.; Beevor, R. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton, Trans.* **1985**, 435. (d) Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 6956.
(27) (a) Fischer, E. O.; Friedrich, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 327. (b) Churchill, M. R.; Wasserman, H. J.; Holmes, S. J.; Schrock, R. R. *Organometallics* **1982**, *1*, 766.

Scheme IV



somewhat by varying the ancillary ligands at the metal. The pyrdtc allenyl complex, with the nitrogen lone pair involved in an aromatic ring and contributing less electron density to the metal, is less reactive toward MeI than the corresponding dmtc or diprtc complexes.

Attempts to make the allenyl of $[(dppe)(pyrdtc)(OC)W(MeOC{\equiv}CHMe_2)]^+$ at low temperature failed. Resonance forms shown below with negative charge distributed about the phenyl ring presumably contribute to the stability of the allenyl complexes prepared from benzyl precursors.

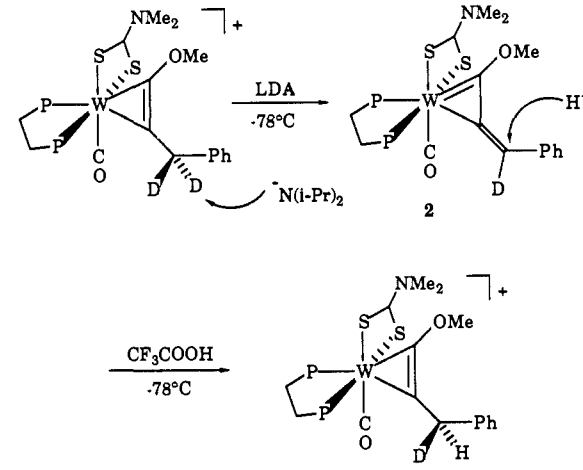


The selectivity toward protonation of the deuterated allenyl isomers helps to elucidate the structures and reactivities of the isomers. Protonation at low temperature yields a large excess of the HD diastereomer with the proton signal at 4.30 ppm. The 15:1 experimental ratio is probably a lower limit for the selectivity of the kinetically favored allenyl isomer, with some of the minor isomer likely due to slight warming of the sample during transfer. Protonation occurs at a specific face of the C=CHPh fragment, which is surely the same site as deprotonation.[28] The mechanism in Scheme V is suggested, where dedeuteration from the backside (away from the dppe phenyls) gives the kinetically favored isomer. Protonation occurs at the same site, to yield the major diastereomer as shown.

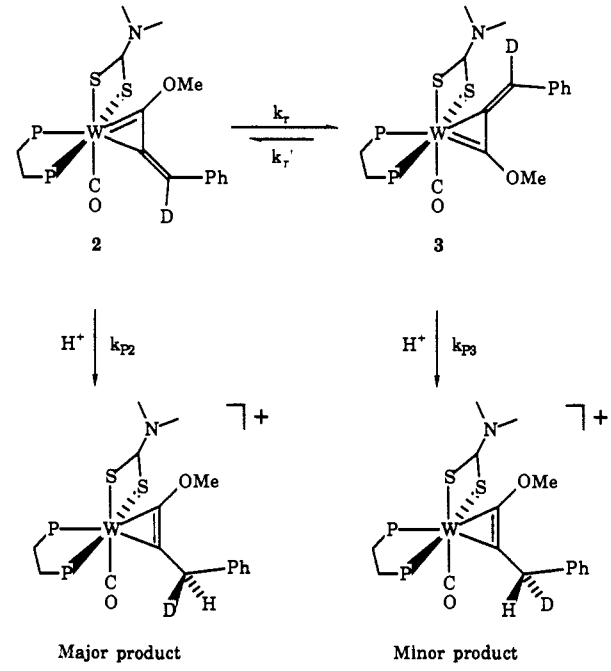
Room-temperature protonation of the 3:2 isomer mix also favors the product with the high-field proton resonance (2.4:1). Assuming the kinetically favored isomer reacts predominately to give the high-field product, this indicates that the thermodynamically favored allenyl isomer exhibits no significant selectivity (1.2:1). Low-temperature protonation of the 3:2 allenyl mix also results in a 2.4:1 product ratio favoring the high-field signal, suggesting that, as observed, the minor isomer (**2**) reacts at low temperature and the major isomer (**3**) either reacts or isomerizes as the sample warms, with the same net selectivity as observed for room-temperature protonation. A variable-temperature ^1H NMR study

(28) Though microscopic reversibility does not apply for dedeuteration–protonation reactions, it is a reasonable generalization taking steric considerations into account. March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; p 195.

Scheme V



Scheme VI



Major product Minor product

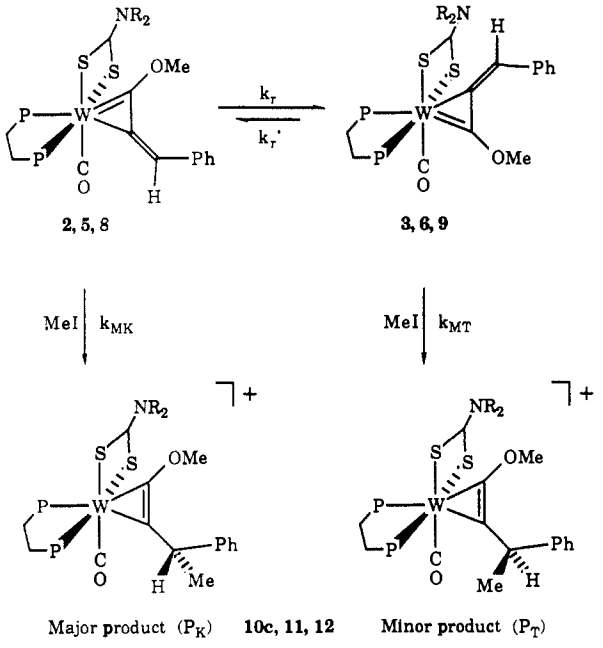
$$k_{P2} >> k_r - k_r' - k_{P3}$$

of the reaction was enlightening. As the sample was warmed to −30 °C, a constant trace of **2** was observed as **3** was depleted, indicating that isomerization of **3** to **2** competes with protonation. As **3** warmed and the barrier to protonation was overcome, so too was the barrier to isomerization. The proposed mechanism for room-temperature protonation is shown in Scheme VI.

The rate of protonation of **2** is much faster than the rate of isomerization to **3**, as evidenced by exclusive low-temperature protonation of **2**. Isomerization of **3** to **2** followed by protonation is a competitive pathway to protonation of **3**. In the presence of acid, **2** reacts rapidly to give the major diastereomeric product, with **3** protonating more slowly to give the minor diastereomer or funneling over to **2** and protonating. Assuming preferential protonation of both **2** and **3** by backside attack (away from the dppe phenyls), the rate of rotation of **3** to **2** is approximately equal to the rate of protonation of **3** in our experiments.

Results of methylation are similar to that of protonation (Scheme VII). Low-temperature methylation of **2** with $MeSO_3CF_3$ or Me_3OBF_4 yields only one diastereomer, whereas room-temperature methylation with MeI gives a 3:1 diastereomeric ratio favoring the low-temperature methylation product. The enhanced product ratio for methylation over protonation indicates only slightly greater selectivity for methylation of **2** over **3**, relative

Scheme VII



$$k_r - k_r' >> k_{MK} > k_{MT}$$

	Allenyl isomer ratios	Alkyne ratios
dmtc	3/2 - 3:2	10c - 3:1
diprtc	6/5 - 3:2	11 - 4.5:1
pyrdtc	9/8 - 7:2	12 - 2.5:1

to protonation. The relative rates for methylation of **2** and **3** can be approximated as follows:

$$2 + MeI \xrightarrow{k_{MK}} P_K$$

$$3 + MeI \xrightarrow{k_{MT}} P_T$$

For a large excess of MeI:

$$d[P_T]/dt = k_{MT}[3] \qquad d[P_K]/dt = k_{MK}[2]$$

On the basis of the observed product ratio and assuming methylation is selective for each isomer and is much slower than isomerization, we have the following relationships:

$$d[P_K]/dt = 3d[P_T]/dt \qquad [2] = \tfrac{2}{3}[3]$$

So that

$$k_{MK}/k_{MT} = 4.5$$

The diastereomeric ratio of products (4.5:1) observed for room-temperature methylation of the diprtc allenyl isomers (**5** and **6**) with MeI correlates to an isomer rate ratio (k_{MK}/k_{MT}) of 6.8. This suggests that the larger dithiocarbamate ligand slows methylation of **6** relative to **5**. The product ratio observed for methylation of the pyrdtc allenyl isomers (**8** and **9**; 2.5:1 ratio) is attributed to the allenyl isomer ratio (7:2 as opposed to 3:2 for dmtc and diprtc), which increases the amount of product due to methylation of the thermodynamically favored isomer (**9**). The calculated rate ratio for methylation of **8** and **9** is 8.8. The greater selectivity is attributed to a decrease in the rate of methylation

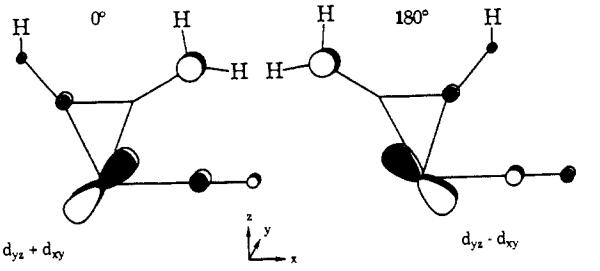


Figure 2.

for the pyrdtc allenyls relative to dmtc or diprtc as described above.

MO Calculations. The rotational profiles shown in Figure 1 indicate a lower barrier to rotation of the allenyl fragment with respect to the metal fragment (~3.5 kcal/mol) than for rotation about the C_β–C_γ double bond (~26 kcal/mol). The profile for rotation of the allenyl fragment has minima at 130° and 230°, but the calculated energy barriers are small. We expect that the conformation of the allenyl fragment relative to the metal moiety will be controlled by steric rather than electronic effects. Steric factors will presumably increase the barriers for both modes of isomerization. We believe the weight of the NMR data and these MO calculations are more compatible with isomerization due to restricted rotation of the allenyl fragment than to rotation about the C_β–C_γ double bond.

A description of the HOMOs for 0° and 180° rotation is worthwhile (Figure 2). At 0°, the tungsten orbital involved is a $d_{yz} + d_{xy}$ hybrid, with additional contribution from the P_y orbitals of C and O of the carbonyl and O, C_α, and C_γ of the allenyl. The results are virtually the same for 180° rotation, with the exception of a $d_{yz} - d_{xy}$ hybrid contribution at tungsten. The coefficients for the p_y orbitals of the C_γ carbons for the 0° and 180° rotamers are each 0.53. These significant contributions at C_γ are illustrative of the nucleophilicity that we have observed.

Summary

Molecular orbital considerations indicate that four-electron donor alkynes[29] and anionic η^2-allenyl ligands will bind to similar d^4 ML_5 fragments.[19] Accordingly, we have synthesized tungsten η^2-allenyl complexes, (dppe)(dtc)(OC)W(η^2-MeOC=C=CHPh), through the deprotonation of cationic tungsten η^2-alkyne complexes, [(dppe)(dtc)(OC)W(η^2-MeOC≡CCH$_2$Ph)][X]. The η^2-allenyl complexes exist as pairs of kinetically favored and thermodynamically favored isomers at room temperature, which interconvert through rotation of the allenyl fragment with respect to the metal center. The kinetically favored isomer is generated exclusively through low-temperature deprotonation. The chiral metal center results in stereoselective addition of Me^+ (MeI) to the C_γ carbon of these η^2-allenyl complexes, yielding diastereomers of substituted cationic tungsten η^2-alkyne products. The proximity of the dithiocarbamate group to the site of addition shows the reaction rate of the thermodynamically favored isomer with respect to the kinetically favored isomer. Low-temperature methylation of the kinetically favored isomer of (dppe)(dmtc)(OC)W(η^2-MeOC=C=CHPh) with MeO_3SCF_3 or Me_3OBF_4 yields only one diastereomer.

Acknowledgment. We thank the National Science Foundation for support of this work (Grant CHE8907341).

(29) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.