

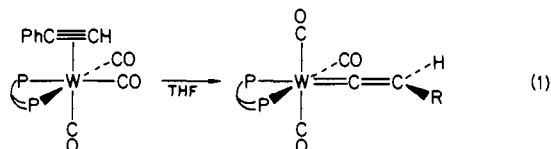
Transformation of a Tungsten(0) Alkyne to a Tungsten(II) Alkyne via Vinylidene, Carbyne, and Ketenyl Ligands

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Abstract: Rearrangement of the W(0) d^6 η^2 -alkyne complex *fac*-(dppe)(OC)₃W(η^2 -PhC≡CH) (dppe = Ph₂PCH₂CH₂PPh₂) yields a meridional tricarbonyl tungsten vinylidene complex, *mer*-(dppe)(OC)₃W=C=CHPh, which provides an M-C-C framework for further ligand-based transformations. Electrophilic addition at the β -carbon of the vinylidene ligand generates a cationic tungsten carbyne, [*mer*-(dppe)(OC)₃W≡CCH₂Ph][BF₄]. This carbyne cation undergoes carbon monoxide substitution by Cl⁻, Br⁻, and I⁻ and in the absence of added ligand thermal dissociation of CO allows isolation of the highly electrophilic [(dppe)(OC)₂W≡CCH₂Ph][BF₄] complex. This reagent adds F⁻ to form a *trans*-FW≡CCH₂Ph unit in (dppe)(OC)₂FW≡CCH₂Ph and also adds neutral ligands to form cationic dicarbonyl derivatives, [(dppe)(OC)₂LW≡CCH₂Ph][BF₄], with L = PMe₃, MeCOMe, and H₂O. Addition of dithiocarbamate salts (S₂CNR₂, R = Me or Et) to the electrophilic dicarbonyl cation initially forms an η^1 -S₂CNR₂ adduct which leads to a coupling of carbyne and carbon monoxide ligands to form an η^2 -ketenyl complex upon chelation of the dithiocarbamate ligand. Addition of H⁺ or Me⁺ to the electron-rich ketenyl oxygen of (S₂CNMe₂)(dppe)(OC)W(C,C- η^2 -OC=CCH₂Ph) yields cationic tungsten(II) alkyne complexes of the type [(S₂CNMe₂)(dppe)(OC)W(η^2 -ROC=CCH₂Ph)][BF₄] (R = H, Me). The conversion from a d^6 alkyne complex to a d^4 alkoxyalkyne complex presented here combines electrophilic addition at ligand β -positions, effectively oxidizing the metal, with known carbyne-carbonyl coupling reactions. The (S₂CNEt₂)(dppe)(OC)W(C,C- η^2 -OC=CCH₂Ph) complex has been structurally characterized: $a = 10.910$ (6) Å, $b = 19.303$ (9) Å, $c = 9.513$ (10) Å, $\alpha = 91.38$ (7)°, $\beta = 103.69$ (7)°, $\gamma = 100.51$ (4)°, $Z = 2$, $d_{\text{calcd}} = 1.55$ g cm⁻³, space group P1̄.

The facile conversion of *fac*-(dppe)(OC)₃W(η^2 -HC₂Ph) (dppe = Ph₂PCH₂CH₂PPh₂) to *mer*-(dppe)(OC)₃W=C=CHPh (eq 1)¹ serves as a point of departure for the C₂-based ligand transformations reported here. Molecular orbital studies indicate substantial charge localization at the β carbon of metal acetylides and metal vinylidenes² and thus rationalize electrophilic addition reactions at the β position of these metal σ -bound unsaturated organic moieties.^{3,4}



Protonation of *mer*-(dppe)(OC)₃W=C=CHPh yields [*mer*-(dppe)(OC)₃W≡CCH₂Ph][BF₄] which provides access to *trans*-LW≡CCH₂Ph⁺ and *trans*-XW≡CCH₂Ph fragments through CO substitution reactions. Carbyne plus carbon monoxide coupling reactions produce η^2 -ketenyl ligands which can be converted to coordinated alkoxyalkynes by addition of electrophiles to the electron-rich ketenyl oxygen. Generation of the cationic alkoxyalkyne complexes completes a cycle which converts W(0) d^6 alkyne reagents to W(II) d^4 alkyne products by successive electrophilic addition to the β -position of C₂-derived fragments.

Experimental Section

Materials and Methods. All manipulations were performed under a dry nitrogen atmosphere with standard Schlenk techniques. Methylene chloride was distilled from CaH₂; diethyl ether was distilled from sodium benzophenone ketyl and purged with nitrogen; all other solvents were purged with nitrogen and used without further purification. Tungsten hexacarbonyl, sodium dialkyldithiocarbamates, phosphines, and other reagents were used as obtained from commercial sources. W(CO)₄-(dppe)⁵ and *fac*-W(CO)(dppe)(acetone)⁶ were prepared by literature methods.

Infrared spectra were recorded on a Beckman IR 4250 spectrometer and calibrated with a polystyrene standard. ¹H NMR spectra were recorded on a Varian XL-100 (100 MHz) or a Bruker WM (250 MHz) spectrometer. Carbon-13 NMR (62.89 MHz) and ³¹P NMR (101.25 MHz) were obtained on a Bruker (250 MHz) spectrometer. Electronic spectra were recorded on a Hewlett Packard model 8450A UV/vis spectrophotometer. Electrochemical measurements were made at room temperature with a Bioanalytical Systems Inc. Model CV-27 instrument with dichloromethane solutions containing 0.2 M tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte. $E_{1/2}$ values [(E_{pa} + E_{pc})/2] were recorded against a saturated sodium chloride calomel electrode (SSCE) and were uncorrected for junction potentials.

***mer*-(dppe)(OC)₃W=C=CHPh (1a).** A solution of PhC₂H (8 mmol, 0.83 g) in 20 mL of tetrahydrofuran (THF) was added to 3.0 g (4 mmol) of W(CO)₃(dppe)(acetone), resulting in a deep red slurry. The slurry was diluted to 100 mL with THF after 5 min. To this mixture was added approximately 0.2 mL of H₂O. (We found that the alkyne to vinylidene isomerization is catalyzed by H₂O, producing a much better yield of vinylidene.) After stirring for 8 h at room temperature the mixture is a deep green color. The extent of reaction can be easily monitored by IR. The solvent was removed, leaving a green tar. Chromatography of the green tar on alumina gave one green band. Removal of the solvent and washing with hexane gave 2.94 g (96% yield) of a green powder. The spectroscopic properties of *mer*-(dppe)(OC)₃W=C=CHPh have been reported.¹

Isotopic Enrichment of *mer*-(dppe)(OC)₃W=C=CHPh with ¹³CO. A 50-mL Schlenk flask was charged with a yellow solution of [*mer*-(dppe)(OC)₃W≡CCH₂Ph][BF₄] (0.64 mmol, 0.55 g) in 20 mL of CH₂Cl₂. This solution was heated at reflux for 24 h or until reaction had gone completely (by IR) to [(dppe)(OC)₂W≡CCH₂Ph][BF₄]. The yellow solution was frozen in a liquid N₂ bath, and the flask was evacuated and back filled with 1 atm of 90% carbon-13 CO. The mixture was warmed to room temperature and stirred under enriched ¹³CO for

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6 h. The yellow mixture of $[mer-(dppe)(OC)_3W\equiv CCH_2Ph][BF_4]$ appeared to be 50% enriched with ^{13}CO . The solution was cooled to 0 °C, and 0.5 g of Al_2O_3 was added. After 5 min of stirring at 0 °C the solution turned green. Completion of the reaction was checked by IR. The solution was extracted away from the Al_2O_3 and the solvent removed in vacuo. The green solid was extracted with 2 × 15 mL of toluene. The toluene extracts were combined and the solvent removed to give a green powder after trituration with pentanes. ^{13}C NMR indicated the label was randomly incorporated in the carbonyls of the $mer-(dppe)(OC)_3W\equiv C=CHPh$ product.

$[mer-(dppe)(OC)_3W\equiv CCH_2Ph][BF_4]$ (2a). A green solution of 2.1 g of **1a** (2.7 mmol) in 25 mL of CH_2Cl_2 was cooled to -78 °C and 3 mmol of $HBF_4 \cdot Me_2O$ was added by syringe. The mixture was stirred at -78 °C for 15 min and then allowed to warm to 0 °C. The yellow solution was reduced to 5 mL and filtered into 80 mL of a 3:1 diethyl ether:2-methylbutane mixture, resulting in a yellow powder. The powder was washed with 40 mL of the diethyl ether:2-methylbutane mixture and 2 × 30 mL of hexane to yield 2.25 g (97%) of a yellow air-stable solid. IR (CH_2Cl_2) ν_{CO} (cm^{-1}) 2080 (m), 2005 (vs), ν_{BF_4} (KBr) (cm^{-1}) 1050 (br s); 1H NMR (CD_2Cl_2) δ 7.63–7.16 (m, 25 H, Ph), 3.83 (dd, $^4J_{HP} = 5$ Hz, 2 H, CH_2Ph), 3.0 (m, 4 H, PCH_2CH_2P); ^{13}C NMR (CD_2Cl_2) δ 317.4 (dd, $^2J_{C-P} = 20$ Hz, 10 Hz; $M\equiv C-R$), 203.4 (dd, $^2J_{C-P} = 23$ Hz, 9 Hz, CO trans to P, ^{183}W satellites $^1J_{CW} = 142$ Hz), 199.6 (t, $^2J_{CP} = 18$ Hz, 2 trans CO, ^{183}W satellites $^1J_{CW} = 126$ Hz), 125.0–136.0 (m, Ph), 53.6 (td, $^1J_{CH} = 135$ Hz, $^3J_{C-P} = 15$ Hz, CH_2Ph), 28.6 (m, $PCHHCHHP$), 27.1 (m, $PCHHCHHP$); ^{31}P { 1H } NMR (CD_2Cl_2) δ 21.6 (s, ^{183}W satellites $^1J_{PW} = 93$ Hz, P trans to carbyne), 38.4 (s, ^{183}W satellites $^1J_{PW} = 242$ Hz, P cis to carbyne).

Isotopic Enrichment of $[mer-(dppe)(OC)_3W\equiv CCH_2Ph][BF_4]$ (2a). The ^{13}CO enriched sample of **2a** was obtained by protonation of the ^{13}C NMR sample of ^{13}CO enriched $mer-(dppe)(OC)_3W\equiv C=CHPh$. IR (CH_2Cl_2) ν_{CO} 2065 (m), 2000 (s), 1980 (s) cm^{-1} .

$[mer-(dppe)(OC)_3W\equiv CCHMePh][BF_4]$ (2b). The 2-phenylpropylidene complex (**2b**) was prepared as described above for **2a** except that $[Me_3O][BF_4]$ was used as the alkylating agent. IR (CH_2Cl_2) ν_{CO} (cm^{-1}) 2078 (w), 2000 (s); IR (KBr) ν_{BF_4} (cm^{-1}) 1050 (br s); 1H NMR (CD_2Cl_2) δ 7.83–6.63 (m, 25 H, Ph), 3.00 (m, 5 H, $PCH_2CH_2P + CHMePh$), 1.68 (d, $^3J_{HH} = 8$ Hz, 3H, Me).

$mer-(dppe)(OC)_3W\equiv C=CMePh$ (1b). A yellow CH_2Cl_2 solution of **2b** at 0 °C was treated with 0.5 g of alumina and stirred for 5 min. This process was repeated until reaction was complete as judged by IR. The mixture was filtered and the alumina was extracted with 30 mL of CH_2Cl_2 . The CH_2Cl_2 extracts were combined and the solvent removed. The resulting green tar was triturated with a 1:3 diethyl ether:hexane mixture to give a green powder. IR (CH_2Cl_2) ν_{CO} (cm^{-1}) 2000 (w), 1927 (m) 1890 (s); 1H NMR (CD_2Cl_2) δ 7.75–6.90 (m, 25 H, Ph), 2.73 (m, 4 H, PCH_2CH_2P) 2.08 (s, 3 H, Me).

$[(dppe)(OC)_2W\equiv CCH_2Ph][BF_4]$ (4a). A yellow solution of 2.43 g (2.84 mmol) of **2a** in 20 mL of CH_2Cl_2 was heated at reflux for 24 h. This yellow solution was reduced to 5 mL and filtered into 80 mL of 4:1 diethyl ether:2-methylbutane, resulting initially in a yellow powder which subsequently oils. Trituration of this oil for several hours gave 1.99 g (85%) of a yellow powder. IR (CH_2Cl_2) ν_{CO} (cm^{-1}) 2020 (s), 1955 (s); ν_{BF_4} (KBr) (cm^{-1}) 1090 (br s); 1H NMR (CD_2Cl_2) δ 7.83–6.61 (m, 25 H, Ph), 2.83 (m, 4 H, PCH_2CH_2P), 2.59 (pseudo t, $^4J_{H-P} = 3$ Hz, 2 H, CH_2Ph); ^{31}P { 1H } NMR (CD_2Cl_2) δ 49.71 (br s, fwhm = 19 Hz, $^1J_{PW} = 244$ Hz).

Isotopic Enrichment of $[(dppe)(OC)_2W\equiv CCH_2Ph][BF_4]$ (4a) with ^{13}CO . A ^{13}CO enriched sample of **2a** was dissolved in CH_2Cl_2 (see preparation of ^{13}CO enriched $[mer-(dppe)(OC)_3W\equiv CCH_2Ph][BF_4]$) and heated to reflux for 24 h. The $[(dppe)(OC)_2W\equiv CCH_2Ph][BF_4]$ showed 50% enrichment by IR. IR (CH_2Cl_2) ν_{CO} (cm^{-1}) 2020 (s), 2005 (s), 1958 (s), 1928 (s).

$trans-(dppe)(OC)_2FW\equiv CCH_2Ph$ (3d). A yellow solution of 0.91 g (1.10 mmol) of $[(dppe)(OC)_2W\equiv CCH_2Ph][BF_4]$ was cooled to -78 °C and 1 equiv of $[Et_4N]F \cdot 2H_2O$ (0.20 g, 1.1 mmol) was added. The solution was stirred at -78 °C for 1 h and then allowed to warm to room temperature and stirred for an additional hour. After solvent removal the green oil was extracted with 50 mL of toluene. Solvent removal and subsequent hexane washing gave 0.72 g (86%) of a yellow powder. IR ν_{CO} (KBr) (cm^{-1}) 1985 (s), 1912 (s), (CH_2Cl_2) (cm^{-1}) 2000 (s), 1925 (s); 1H NMR (acetone- d_6) δ 7.97–6.66 (m, 25 H, Ph), 2.80 (m, 4 H, PCH_2CH_2P), 2.59 (pseudo q, $^4J_{PH} \approx ^4J_{FH} \approx 4$ Hz, 2 H, CH_2Ph); ^{13}C NMR ($CDCl_3$) δ 279.0 (dt, $^2J_{C-F} = 104$ Hz, $^2J_{C-P} = 9$ Hz, $M\equiv C-CH_2Ph$), 213.6 (dt, $^2J_{C-Prans} = 51$ Hz, $^2J_{C-Pcis} = ^2J_{C-Fcis} = 8$ Hz, 2 cis CO, $^1J_{CW} = 151$ Hz), 124.4–135.6 (m, Ph), 55.1 (td, $^1J_{CH} = 127$ Hz, $^3J_{C-F} = 9$ Hz, $M\equiv C-CH_2Ph$), 27.8 (t m, $^1J_{CH} = 129$ Hz, PCH_2CH_2P); ^{31}P { 1H } NMR ($CDCl_3$) δ 37.7 (d, $^2J_{P-F} = 46$ Hz, $^1J_{PW} = 234$ Hz).

$trans-(dppe)(OC)_2ClW\equiv CCH_2Ph$ (3a). A solution of 0.42 g (0.49 mmol) of **2a** and 1 equiv of $[Et_4N]Cl \cdot 2H_2O$ in 20 mL of CH_2Cl_2 was

heated at reflux for 2 h. The mixture was worked up as described for isolation of **3d** to yield a yellow powder in 80–90% yield. Yellow crystals were isolated by recrystallization from CH_2Cl_2 /cyclohexane. IR ν_{CO} (KBr) (cm^{-1}) 2000 (s), 1927 (s); 1H NMR (CD_2Cl_2) δ 7.79–6.97 (m, 25 H, Ph), 2.71 (m, 2 H, $PCHH-CHHP$), 2.84 (t, $^4J_{HP} = 5$ Hz, 2 H, CH_2Ph), 2.63 (m, 2 H, $PCHH-CHHP$); ^{13}C NMR ($CDCl_3$) δ 276.3 (t, $^2J_{C-P} = 9$ Hz, $M\equiv C-CH_2Ph$), 212.1 (dd, $^2J_{C-P} = 48$ Hz, $^2J_{C-P} = 6$ Hz, 2 cis CO), 125.0–136.0 (m, Ph), 55.1 (t, $^1J_{CH} = 126$ Hz, $M\equiv C-CH_2Ph$), 27.3 (m, PCH_2CH_2P); ^{31}P { 1H } NMR ($CDCl_3$) δ 39.1 (s, $^1J_{PW} = 231$ Hz). Anal. Calcd: C, 55.66; H, 4.02; Cl, 4.56. Found: C, 55.53; H, 4.08; Cl, 4.45.

$trans-(dppe)(OC)_2BrW\equiv CCH_2Ph$ (3b). The preparation of yellow $trans-(dppe)(OC)_2BrW\equiv CCH_2Ph$ in 80–90% yield is analogous to that of **3a**. IR (KBr) ν_{CO} (cm^{-1}) 2000 (s), 1932 (s); 1H NMR (CD_2Cl_2) δ 7.0–7.76 (m, Ph, 25 H), 3.0 (m, 2 H, $PCHH-CHHP$) 2.78 (t, $^4J_{H-P} = 4$ Hz, 2 H, CH_2Ph), 2.65 (m, 2 H, $PCHH-CHHP$).

$trans-(dppe)(OC)_2IW\equiv CCH_2Ph$ (3c). The preparation of $trans-(dppe)(OC)_2IW\equiv CCH_2Ph$ is analogous to that of **3a**. IR ν_{CO} (KBr) (cm^{-1}) 2008 (s), 1940 (s); 1H NMR (CD_2Cl_2) δ 7.05–7.76 (m, 25 H, Ph), 3.03 (m, 2 H, $PCHH-CHHP$), 2.66 (t, $^4J_{H-P} = 4$ Hz, 2 H, CH_2Ph), 2.66 (m, 2 H, $PCHH-CHHP$).

$[(trans-(dppe)(CO)_2(Me_2P)W\equiv CCH_2Ph)[BF_4]$ (5a). A yellow solution of 0.80 g (0.96 mmol) of **4a** in 50 mL of CH_2Cl_2 was cooled to -78 °C and 1 equiv of PMe_3 was added by syringe. The mixture was stirred at -78 °C for 15 min and then allowed to warm to room temperature. The solution was stirred for an additional hour and reduced to 4 mL and a 3:1 diethyl ether:hexane mixture was added to induce crystallization. After cooling to -20 °C yellow crystals were isolated and washed with 2 × 30 mL of hexane. The yellow crystals were isolated in 49% yield. IR ν_{CO} (KBr) (cm^{-1}) 1993 (s), 1928 (s), ν_{BF_4} (KBr) (cm^{-1}) 1050; 1H NMR (acetone- d_6) δ 7.18–8.00 (m, 25 H, Ph), 3.44 (m, 2 H, $PCHH-CHHP$), 3.44 (q, $^4J_{H-Prans} = ^4J_{H-Pcis} = 3$ Hz, 2 H, CH_2Ph), 3.00 (m, 2 H, $PCHH-CHHP$), 0.66 (d, $^2J_{H-P} = 8$ Hz, 9 H, PMe_3); ^{31}P { 1H } NMR (acetone- d_6) δ 45.1 (d, $^2J_{PP} = 24$ Hz, $^1J_{W-P} = 232$ Hz, dppe P cis to carbyne), -51.4 (t, $^2J_{PP} = 24$ Hz, $^1J_{PW} = 43$ Hz, PMe_3 trans to carbyne); ^{13}C NMR (1H decoupled in acetone- d_6) δ 310.0 (br, $M\equiv C-R$), 212.3 (dt, $^2J_{C-Prans} = 32$ Hz, $^2J_{C-Pcis} = 7$ Hz, 2 cis CO), 137.2–127.3 (m, Ph), 58.6 (d, $^2J_{C-P} = 15$ Hz, $C-CH_2Ph$), 27.2 (dd, $J_{C-P} = 30$ Hz, $J_{C-P} = 10$ Hz, PCH_2CH_2P), 15.0 (d, $^1J_{C-P} = 23$ Hz, PMe_3).

$[(trans-(dppe)(OC)_2(Me_2CO)W\equiv CCH_2Ph)[BF_4]$ (5b). Addition of acetone to $[(dppe)(OC)_2W\equiv CCH_2Ph][BF_4]$ gave the acetone adduct immediately according to IR and 1H NMR spectroscopy. (Not isolated.) IR ν_{CO} (cm^{-1}), (acetone) 2000 (s), 1932 (s); 1H NMR (acetone d_6) δ 6.88–8.10 (m, Ph) 3.24 (t, $^4J_{HP} = 4$ Hz, CH_2Ph), 2.80 (m, PCH_2CH_2P).

$[(trans-(dppe)(OC)_2(H_2O)W\equiv CCH_2Ph)[BF_4]$ (5c). A few drops of H_2O were added to a yellow CH_2Cl_2 solution of $[(dppe)(OC)_2W\equiv CCH_2Ph][BF_4]$. Within 15 min the **4a** reagent completely converted to $[(trans-(dppe)(OC)_2(H_2O)W\equiv CCH_2Ph)[BF_4]$ as judged by IR. This complex was not isolated. IR (CH_2Cl_2) ν_{CO} (cm^{-1}) 2000 (s), 1935 (s); 1H NMR (CD_2Cl_2) δ 6.66–7.90 (m, 25 H, Ph), 5.00 (br s, OH_2), 2.88 (m, PCH_2CH_2P), 2.82 (t, $^4J_{H-P} = 3$ Hz, CH_2Ph); ^{13}C NMR (CD_2Cl_2) δ 299.1 (br m, $M\equiv C-CH_2Ph$), 215.4 (dd, $^2J_{C-P} = 41$ Hz, 6 Hz, 2 cis CO), 135.9–125.5 (m, Ph), 56.8 (t, $^1J_{CH} = 130$ Hz, $M\equiv C-CH_2Ph$), 28.5 (tm, $^1J_{CH} = 134$ Hz, PCH_2CH_2P); ^{31}P { 1H } NMR (CD_2Cl_2) δ 48.9 (s, $^1J_{P-W} = 244$ Hz).

$(dmtc)(dppe)(OC)W(C,C-\eta^2-OC\equiv CCH_2Ph)$ (7a). A solution of 0.63 mmol (0.53 g) of $[(dppe)(OC)_2W\equiv CCH_2Ph][BF_4]$ in 25 mL of CH_2Cl_2 was cooled to -23 °C and 1 equiv of $Na(dmtc) \cdot 2H_2O$ ($dmtc = S_2CNMe_2$) was added. This mixture was stirred at -23 °C for 0.5 h, warmed to 0 °C and stirred another 1.5 h, and then warmed to ambient temperature and left for 2 h. (Note: If the mixture is warmed to room temperature too quickly the yield of the ketylenyl product is decreased.) The reddish-purple mixture was filtered and 10 mL of ethanol was added. Slow evaporation of the solvent produces a burgundy solid in 98% yield. Recrystallization from CH_2Cl_2 /Et₂O gives deep red crystals. IR ν_{CO} (KBr) (cm^{-1}) 1860 (s), $\nu_{C=O} = 1730$ (m); 1H NMR (CD_2Cl_2) δ 7.26–8.05 (m, 25 H, Ph), 4.69 [AB_q , $J_{HAHB} = 15$ Hz, (H_A , t, $^4J_{H-P} = 2.5$ Hz) (H_B , d, $^4J_{HP} = 2$ Hz), CH_2H_2Ph], 2.96 (m, 2 H, PCH_2CH_2P), 2.77 (s, 3 H, NMe), 2.61 (s, 3 H, NMe), 2.43 (m, 2 H, PCH_2CH_2P); ^{13}C NMR (CD_2Cl_2) δ 222.2 (d, $^2J_{C-P} = 10$ Hz, $^1J_{C-W} = 163$ Hz, $M-CO$), 212.9 (s, S_2CNMe_2), 198.7 (dd, $^2J_{C-P} = 20$, 10 Hz, $O=C-C-R$), 195.6 (br s, $C=C=O$), 141.3–125.7 (m, Ph), 42.4 (t, $^1J_{CH} = 132$ Hz, $OC=C-CH_2Ph$), 40.1 (q, $^1J_{C-H} = 140$ Hz, NMe), 38.9 (q, $^1J_{C-H} = 140$ Hz, NMe), 30.4 (t m, $^1J_{CH} = 132$ Hz, PCH_2-), 24.6 (t m, $^1J_{CH} = 132$ Hz, PCH_2-); ^{31}P { 1H } NMR (CD_2Cl_2) δ 47.8 (d, $^2J_{P-P} = 19$ Hz, $^1J_{PW} = 327$ Hz, P cis to ketylenyl), 23.3 (d, $^2J_{P-P} = 19$ Hz, $^1J_{PW} = 70$ Hz, P trans to ketylenyl).

$(detc)(dppe)(OC)W(C,C-\eta^2-OC\equiv CCH_2Ph)$ (7b). The preparation of **7b** was analogous to that of **7a** ($detc = S_2CNEt_2$). Complex **7b** can be purified by chromatography on alumina using CH_2Cl_2 :THF (1:1). IR

Table I. Crystallographic Data for (detc)(dppe)(OC)W(C,C- η^2 -OC=CCH₂Ph)

molecular formula	WS ₂ P ₂ O ₂ NC ₄₁ H ₄₁
formula weight, g/mol	889.72
space group	<i>P</i> $\bar{1}$
cell parameters	
<i>a</i> , Å	10.910 (6)
<i>b</i> , Å	19.303 (9)
<i>c</i> , Å	9.513 (10)
α , deg	91.38 (7)
β , deg	103.69 (7)
γ , deg	100.51 (4)
vol, Å ³	1909.1
ρ_{calcd} , g/cm ³	1.55
<i>Z</i>	2
Collection and Refinement Parameters	
radiation (wavelength, Å)	Mo K α (0.71073)
linear abs. coeff, cm ⁻¹	34.32
scan type	$\omega/1.67\theta$
scan width	1.1 + 0.35 tan θ
background	25% of full scan width on both sides
θ limits	1° < θ < 25°
hemisphere collected	+ <i>h</i> ± <i>k</i> ± <i>l</i>
unique data	7024
data with <i>I</i> ≥ 3 σ (<i>I</i>)	5364
<i>R</i>	0.060
<i>R</i> _w	0.065
largest parameter shift	0.43
no. of parameters	292
error in an observation of unit wt.	2.42

ν_{CO} (CH₂Cl₂) (cm⁻¹) 1870 (s), $\nu_{\text{C}=\text{O}}$ 1732 (m), IR ν_{CO} (KBr) (cm⁻¹) 1860 (s), $\nu_{\text{C}=\text{O}}$ 1730 (m); ¹H NMR (CDCl₃) δ 8.09–7.10 (m, 25 H, Ph), 4.72 [AB_q, *J*_{H_AH_B} = 15 Hz, (H_A, dd, ⁴*J*_{HP} = 4, 2 Hz) (H_B, d, ⁴*J*_{HP} = 3 Hz), CH₂H_BPh], 3.20 (m, 6 H, NCH₂CH₃ and PCH₂CH₂P), 2.50 (m, 2 H, PCH₂CH₂P), 0.94 (t, ³*J*_{HH} = 8 Hz, 3 H, NCH₂CH₃), 0.92 (t, ³*J*_{HH} = 8 Hz, 3 H, NCH₂CH₃).

Isotopic Enrichment of (dmtc)(dppe)(OC)W(C,C- η^2 -OC=CCH₂Ph) (7a). A ¹³CO enriched sample of [*mer*-(dppe)(OC)₃W=CCH₂Ph][BF₄] was dissolved in CH₂Cl₂ and refluxed for 24 h to form ¹³CO enriched [(dppe)(OC)₂W=CCH₂Ph][BF₄]. The procedure for the synthesis of (dmtc)(dppe)(OC)W(C,C- η^2 -OC=CCH₂Ph) was then followed to give a sample 40% enriched with ¹³CO. IR (CH₂Cl₂) ν_{CO} (cm⁻¹) 1868 (s), 1838 (s), $\nu_{\text{C}=\text{O}}$ 1720 (br).

[(dmtc)(dppe)(OC)W(MeOC=CCH₂Ph)][BF₄] (8a). A burgundy solution of (dmtc)(dppe)(OC)W(C,C- η^2 -OC=CCH₂Ph) (0.59 g, 0.71 mmol) in 25 mL of CH₂Cl₂ was cooled to -78 °C. One equivalent of [Me₃O][BF₄] was added and the solution stirred for 0.5 h at -78 °C. As the mixture was warmed to room temperature the color changed to a deeper red. The mixture was stirred for 2 h. After reducing the volume to 5 mL, the mixture was filtered into 60 mL of diethyl ether, resulting in a fluffy pink solid. The pink solid was isolated and washed with 2 × 40 mL of hexane to give 0.64 g (96%) of (8a). IR (KBr) ν_{CO} (cm⁻¹) 1948 (s), $\nu_{\text{C}=\text{C}}$ 1678 m, ν_{BF_4} 1050 (br s); ¹H NMR (CD₂Cl₂) δ 8.08–6.83 (m, 25 H, Ph), 4.66 [AB_q, ²*J*_{H_AH_B} = 15 Hz, (H_A, dd, ⁴*J*_{HP} = 2 Hz, 1 Hz) (H_B, s)], 3.55 (s, 3 H, OMe), 3.12 (m, 2 H, PCH₂CH₂P), 2.84 (s, 3 H, NMe), 2.65 (m, 2 H, PCH₂CH₂P), 2.67 (s, 3 H, NMe); ¹³C NMR (CDCl₃) δ 221.8 (d, ²*J*_{C-P} = 13 Hz, ¹*J*_{CW} = 129 Hz, CO), 220 (d, ²*J*_{CP} = 7 Hz, ¹*J*_{C-W} = 43 Hz, PhCH₂-C=C-OMe), 209.0 (S₂CNMe₂), 193.7 (dd, ²*J*_{C-P} = 14 Hz, 6 Hz, PhCH₂-C=C-OMe), 138.2–126.5 (m, Ph), 65.8 (q, ¹*J*_{CH} = 150 Hz, OMe), 40.1 (q, ¹*J*_{CH} = 144 Hz, NMe), 39.3 (t, ¹*J*_{CH} = 134 Hz, CH₂Ph), 38.9 (q, ¹*J*_{CH} = 144 Hz, NMe), 29.0 (t m, ¹*J*_{CH} = 138 Hz, PCH₂-), 20.2 (t m, ¹*J*_{CH} = 138 Hz, PCH₂-); ³¹P{¹H} NMR (CDCl₃) δ 38.9 (d, ²*J*_{PP} = 10 Hz, ¹*J*_{PW} = 289 Hz, P cis to alkyne), 13.3 (d, ²*J*_{PP} = 10 Hz, ¹*J*_{WP} = 64 Hz, P trans to alkyne).

Collection of Diffraction Data. Red crystals of (detc)(dppe)(OC)W(C,C- η^2 -OC=CCH₂Ph) were grown by layering a diethyl ether-hexanes mixture on top of a methylene chloride solution of the material. A rhombohedral prism having approximate dimensions 1.5 × 0.30 × 0.20 mm was selected, mounted on a glass wand, and coated with epoxy cement. Diffraction data were collected on an Enraf-Nonius CAD-4 automated diffractometer.⁷ A triclinic cell was indicated from 25 centered reflections found in the region 30° < 2 θ < 35° and refined by least-squares calculations. The cell parameters are listed in Table I.

(7) Programs utilized during solution and refinement were from the Enraf-Nonius structure determination package.

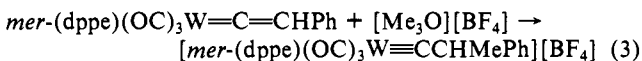
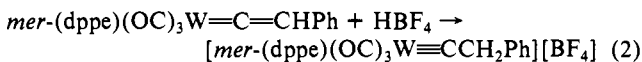
Diffraction data were collected in the hemisphere +*h* ± *k* ± *l* under the conditions specified in Table I. Three reflections chosen as intensity standards were monitored every 5 h and showed no significant (<1.5%) decay. The crystal was checked for orientation after every 300 reflections, and recentering was performed if the scattering vectors varied by more than 0.15°. ψ scans with nine reflections having 80° < χ < 90° were performed to provide an empirical correction for absorption. Only the 5364 reflections having *I* > 3 σ (*I*)⁸ were used in the structure solution and refinement. The data were corrected for Lorentz-polarization effects and absorption during the final stages of refinement.

Solution and Refinement of the Structure. The structure solution was straightforward from the application of the heavy-atom method. The space group *P* $\bar{1}$ was deduced from the presence of two molecules per unit cell which were related by an inversion center. The tungsten atom was located in a three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were obtained from subsequent Fourier and difference Fourier calculations.

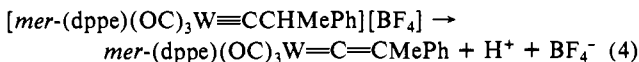
Least-squares refinement⁹ of the 49 non-hydrogen atoms allowing all except the phenyl carbons to vary anisotropically produced unweighted and weighted residuals of 0.084 and 0.128, respectively.¹⁰ The positions of the hydrogen atoms were calculated by using a C-H distance of 0.95 Å and the isothermal parameter set at 8.0. Further full-matrix least-squares refinement with isotropic thermal parameters for the phenyl carbons and the hydrogens and anisotropic thermal parameters for the rest of the atoms converged with *R* = 0.060 and *R*_w = 0.065.¹¹ The final difference Fourier map contained four peaks with intensities near 1.0 e/Å³, all of which were determined to be residual electron density around the tungsten.

Results

Syntheses. Cationic carbyne complexes of the type [*mer*-(dppe)(OC)₃W=CCHPh][BF₄] are formed when electrophiles react with the neutral vinylidene complex *mer*-(dppe)(OC)₃W=C=CHPh (1a). Addition of a slight excess of HBF₄Me₂O (eq 2) or [Me₃O][BF₄] (eq 3) to a green CH₂Cl₂ solution of 1a results in nearly quantitative conversion to the respective carbyne cation (R = H, 2a; R = CH₃, 2b). The reaction can be monitored by infrared spectroscopy in the carbonyl region. The solution is kept cold (0 °C) during reaction and isolation of the yellow solid to optimize the yield.



The cationic carbyne complexes are quite acidic and readily undergo deprotonation to regenerate the vinylidene reagent. Even weakly basic solvents such as tetrahydrofuran, acetone, and alcohols cause partial deprotonation of the cations upon dissolution. The acidity of 2b provides access to alkyl phenyl vinylidene-complexes (eq 4), and thus overcomes the limitation inherent in the initial synthesis of these vinylidene complexes by 1,2-hydrogen migration of a terminal acetylene proton. Addition of alumina to a yellow CH₂Cl₂ solution of [*mer*-(dppe)(OC)₃W=CCHMePh][BF₄] (2b) at 0 °C produces the green vinylidene complex *mer*-(dppe)(OC)₃W=C=CMePh (1b). The reaction was easily monitored by observing the intensity of the carbonyl vibration at 2080 cm⁻¹ of the carbyne reagent. The [*mer*-(dppe)(OC)₃W=CCHPh]⁺ cations can also be deprotonated by 1,8-bis(dimethylamino)naphthalene, but alumina is the reagent of choice due to simplification of the isolation procedure.



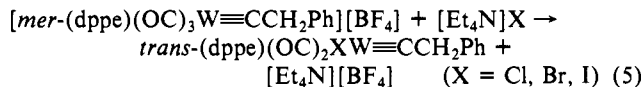
(8) $I = S(C + RB)$ and $\sigma(I) = [2S^2(C + R^2B) + (\rho I)^2]^{1/2}$, where *S* = scan rate, *C* = total integrated peak count, *R* = ratio of scan count time to background count time, *B* = total background count, and $\rho = 0.01$ is a correction factor.

(9) The function minimized was $\sum w(|F_o| - |F_c|)^2$.

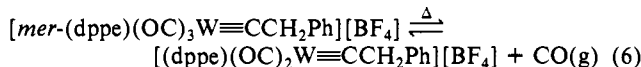
(10) $R_{\text{unweighted}} = \sum (|F_o| - |F_c|) / \sum |F_o|$ and $R_{\text{weighted}} = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$.

(11) Scattering factors were taken from the following: Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.

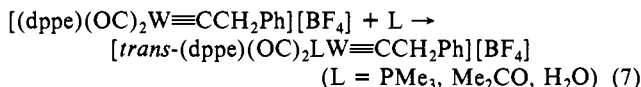
Heating a CH_2Cl_2 solution of $[\text{mer}(\text{dppe})(\text{OC})_3\text{W}\equiv\text{CCH}_2\text{Ph}][\text{BF}_4]$ (**2a**) with 1 equiv of $[\text{Et}_4\text{N}]\text{X}$ ($\text{X} = \text{Cl, Br, or I}$) leads to halide substitution for one carbon monoxide ligand and isomerization to form neutral Fischer-type *trans*-halocarbyne complexes, *trans*-(dppe)(OC) $_2$ XW $\equiv\text{CCH}_2\text{Ph}$ ($\text{X} = \text{Cl}$, **3a**; Br , **3b**; I , **3c**) (eq 5). The *trans*-iodocarbyne complex **3c** has also been prepared directly from *mer*-(dppe)(OC) $_3$ W $\equiv\text{C}\equiv\text{CHPh}$ and hydroiodic acid in CH_2Cl_2 . Heating a CHCl_3 solution of *mer*-(dppe)(OC) $_3$ W $\equiv\text{C}\equiv\text{CHPh}$ generates the *trans*-chlorocarbyne derivative **3a** in good yield. Addition of $[\text{Et}_4\text{N}]\text{F}$ to $[\text{mer}(\text{dppe})(\text{OC})_3\text{W}\equiv\text{CCH}_2\text{Ph}][\text{BF}_4]$ does not yield the *trans*-fluorocarbyne complex, but this compound has been prepared by a different route (vide infra).



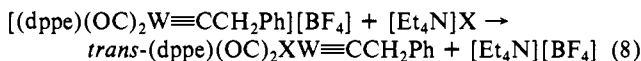
Heating a CH_2Cl_2 solution of $[\text{mer}(\text{dppe})(\text{OC})_3\text{W}\equiv\text{CCH}_2\text{Ph}][\text{BF}_4]$ at reflux for 24 h leads to CO loss and isomerization to form $[(\text{dppe})(\text{OC})_2\text{W}\equiv\text{CCH}_2\text{Ph}][\text{BF}_4]$ (**4a**) (eq 6) which has both dppe donor atoms and the two carbonyls cis to the carbyne ligand. We believe the coordination site *trans* to the carbyne is vacant, although it is possible that the $[\text{BF}_4]^-$ counterion is weakly bound. This tricarbonyl to dicarbonyl conversion was monitored by solution infrared techniques. Exposure of a CH_2Cl_2 solution of **4a** to 1 atm of CO gas regenerates $[\text{mer}(\text{dppe})(\text{OC})_3\text{W}\equiv\text{CCH}_2\text{Ph}][\text{BF}_4]$ within hours.



The neutral ligands trimethylphosphine, acetone, and water readily form cationic *trans*-(dppe)(OC) $_2$ LW $\equiv\text{CCH}_2\text{Ph}][\text{BF}_4]$ complexes (eq 7: L = PMe_3 , **5a**; MeCOMe , **5b**; H_2O , **5c**). These adducts of **4a** have been characterized by IR and NMR spectroscopy. Removal of H_2O from *trans*-(dppe)(OC) $_2$ (H_2O)W $\equiv\text{CCH}_2\text{Ph}][\text{BF}_4]$ to regenerate $[(\text{dppe})(\text{OC})_2\text{W}\equiv\text{CCH}_2\text{Ph}][\text{BF}_4]$ is accomplished by heating a CH_2Cl_2 solution of **5c** for 1 day. Note that $[(\text{dppe})(\text{OC})_2\text{W}\equiv\text{CCH}_2\text{Ph}][\text{BF}_4]$ does not react with alkynes or $\text{P}(\text{OMe})_3$.



trans-(dppe)(OC) $_2$ FW $\equiv\text{CCH}_2\text{Ph}$. Addition of $[\text{Et}_4\text{N}]\text{X}$ to $[(\text{dppe})(\text{OC})_2\text{W}\equiv\text{CCH}_2\text{Ph}][\text{BF}_4]$ in CH_2Cl_2 yields a *trans*-halocarbyne complex of fluoride (**3d**) as well as for $\text{X} = \text{Cl, Br, and I}$ (eq 8). The tetraalkylammonium fluoride salt was added to a solution of $[(\text{dppe})(\text{OC})_2\text{W}\equiv\text{CCH}_2\text{Ph}][\text{BF}_4]$ at -78°C and slowly warmed to room temperature while stirring. The *trans*-(dppe)(OC) $_2$ FW $\equiv\text{CCH}_2\text{Ph}$ product was then isolated in the same manner as the other halo analogues.



$(\text{S}_2\text{CNR}_2)(\text{dppe})(\text{OC})\text{W}(\text{C,C-}\eta^2\text{-OC}\equiv\text{CCH}_2\text{Ph})$. The facile addition of halide ion to $[(\text{dppe})(\text{OC})_2\text{W}\equiv\text{CCH}_2\text{Ph}][\text{BF}_4]$ encouraged us to investigate the reactivity of this cationic carbyne complex with a chelating monoanionic ligand such as diethyldithiocarbamate. Addition of 1 equiv of sodium diethyldithiocarbamate (detc) to a CH_2Cl_2 solution of **4a** at low temperature produces a yellow solution which we believe contains $(\eta^1\text{-S}_2\text{CNEt}_2)(\text{dppe})(\text{OC})_2\text{W}\equiv\text{CCH}_2\text{Ph}$. This species was observed in solution infrared spectra and exhibited carbonyl vibrational frequencies (2000, 1940 cm^{-1}) similar to those of the neutral *trans*-(dppe)(OC) $_2$ XW $\equiv\text{CCH}_2\text{Ph}$ derivatives (**5a-d**). Slow warming of this solution to room temperature followed by stirring for 2 h yields a deep burgundy solution with a single terminal CO absorption at 1860 cm^{-1} and a second CO stretch at 1730 cm^{-1} assigned to the $(\eta^2\text{-S}_2\text{CNET}_2)(\text{dppe})(\text{OC})\text{W}(\eta^2\text{-O}\equiv\text{C}\equiv\text{CCH}_2\text{Ph})$ (**7a**) product. We believe that chelation of the dithiocarbamate ligand promotes coupling of the carbyne ligand and carbon monoxide to form the η^2 -ketenyl ligand present in **7a** (eq 9).

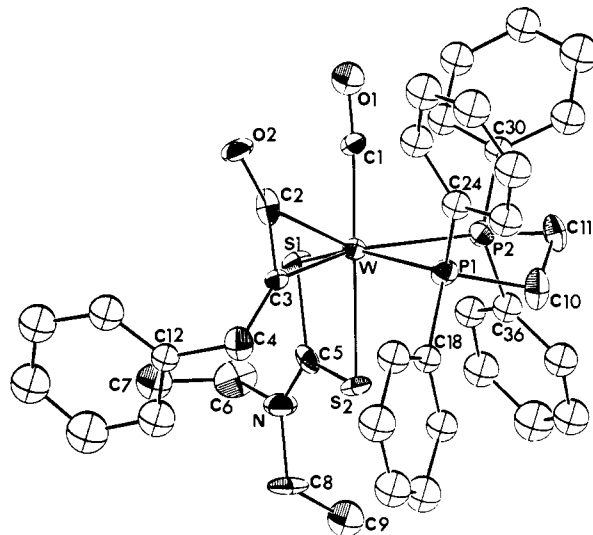
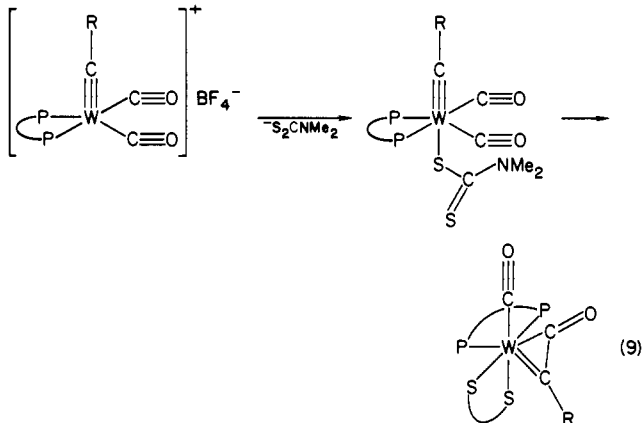
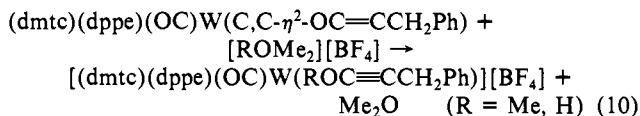


Figure 1. An ORTEP of $(\text{detc})(\text{dppe})(\text{OC})\text{W}(\text{C,C-}\eta^2\text{-OC}\equiv\text{CCH}_2\text{Ph})$ illustrating the atomic numbering scheme.

Exposure of the ketenyl complex to 1 atm of ^{13}CO at room temperature results in ^{13}CO incorporation into both the terminal carbonyl and the ketenyl CO positions within a few hours.



$[(\text{dmtc})(\text{dppe})(\text{OC})\text{W}(\text{ROC}\equiv\text{CCH}_2\text{Ph})][\text{BF}_4]$. The nucleophilic character of the ketenyl oxygen in $(\text{dmtc})(\text{dppe})(\text{OC})\text{W}(\text{C,C-}\eta^2\text{-OC}\equiv\text{CCH}_2\text{Ph})$ was confirmed by addition of $[\text{Me}_3\text{O}][\text{BF}_4]$ or $\text{HBF}_4\cdot\text{Me}_2\text{O}$ to a CH_2Cl_2 solution of **7b** at -78°C . Infrared solution spectra indicated formation of cationic alkyne complexes, $[(\eta^2\text{-S}_2\text{CNMe}_2)(\text{dppe})(\text{OC})\text{W}(\eta^2\text{-ROC}_2\text{CH}_2\text{Ph})][\text{BF}_4]$ (eq 10: $\text{R} = \text{CH}_3$, **8a**; $\text{R} = \text{H}$, **8b**). The hydroxyalkyne complex decomposed at room temperature and was not isolated, but it could be deprotonated with 1,8-bis(dimethylamino)naphthalene to regenerate the η^2 -ketenyl complex $(\text{dmtc})(\text{dppe})(\text{OC})\text{W}(\text{C,C-}\eta^2\text{-OC}\equiv\text{CCH}_2\text{Ph})$. The methoxyalkyne derivative **8a** was isolated as an air-stable pink solid.



Molecular Structure of $(\text{detc})(\text{dppe})(\text{OC})\text{W}(\text{C,C-}\eta^2\text{-OC}\equiv\text{CCH}_2\text{Ph})$. The solid-state molecular structure of $(\eta^2\text{-benzylketenyl})(\text{diethyldithiocarbamate})[\text{bis}(\text{diphenylphosphino})\text{ethane}]$ carbonyltungsten(II) is shown in Figure 1 where the atomic numbering scheme is defined. If one considers the two bound carbon atoms of the η^2 -ketenyl ligand as occupying a single site the geometry can be described as roughly octahedral. The ketenyl ligand is then *trans* to a dppe phosphorus donor atom with the carbonyl *trans* to a dithiocarbamate sulfur. The remaining ends of the chelating ligands are approximately *trans* to one another to complete the inner coordination sphere. The $\text{OC}\equiv\text{CC}$ back-

Table II. Final Atomic Positional Parameters for (detc)(dppe)(OC)W(C,C- η^2 -OC=CCH₂Ph)^a

atom	X	Y	Z
W	0.35522 (5)	0.24346 (2)	0.06975 (5)
S(1)	0.1777 (3)	0.1435 (1)	-0.0240 (3)
S(2)	0.1539 (3)	0.2603 (1)	0.1526 (3)
P(1)	0.4950 (3)	0.3377 (1)	0.2473 (3)
P(2)	0.4163 (3)	0.1754 (1)	0.3049 (3)
O(1)	0.5569 (7)	0.1779 (4)	-0.0387 (9)
O(2)	0.4675 (8)	0.2904 (4)	-0.2128 (7)
N(1)	-0.0479 (9)	0.1603 (5)	0.027 (1)
C(1)	0.482 (1)	0.2024 (6)	0.008 (1)
C(2)	0.401 (1)	0.2912 (5)	-0.121 (1)
C(3)	0.321 (1)	0.3200 (5)	-0.063 (1)
C(4)	0.247 (1)	0.3773 (5)	-0.100 (1)
C(5)	0.076 (1)	0.1857 (5)	0.050 (1)
C(6)	-0.113 (1)	0.0960 (7)	-0.069 (1)
C(7)	-0.167 (2)	0.1146 (8)	-0.222 (2)
C(8)	-0.132 (1)	0.1983 (7)	0.086 (1)
C(9)	-0.171 (1)	0.1644 (9)	0.216 (2)
C(10)	0.519 (1)	0.3115 (6)	0.432 (2)
C(11)	0.541 (1)	0.2332 (5)	0.438 (1)
C(12)	0.136 (1)	0.3535 (5)	-0.230 (1)
C(13)	0.015 (1)	0.3387 (7)	-0.210 (1)
C(14)	-0.092 (2)	0.3152 (8)	-0.331 (2)
C(15)	-0.069 (1)	0.3082 (7)	-0.466 (2)
C(16)	0.050 (1)	0.3238 (7)	-0.490 (1)
C(17)	0.152 (1)	0.3476 (7)	-0.367 (1)
C(18)	0.425 (1)	0.4161 (5)	0.261 (1)
C(19)	0.463 (1)	0.4762 (6)	0.193 (1)
C(20)	0.403 (1)	0.5333 (7)	0.197 (1)
C(21)	0.305 (1)	0.5278 (7)	0.265 (1)
C(22)	0.261 (1)	0.4702 (7)	0.329 (1)
C(23)	0.326 (1)	0.4130 (6)	0.328 (1)
C(24)	0.654 (1)	0.3749 (5)	0.228 (1)
C(25)	0.702 (1)	0.3538 (6)	0.116 (1)
C(26)	0.824 (1)	0.3882 (7)	0.099 (1)
C(27)	0.896 (1)	0.4426 (7)	0.196 (1)
C(28)	0.854 (1)	0.4633 (7)	0.308 (1)
C(29)	0.732 (1)	0.4314 (6)	0.326 (1)
C(30)	0.480 (1)	0.0947 (5)	0.292 (1)
C(31)	0.434 (1)	0.0481 (6)	0.172 (1)
C(32)	0.476 (1)	-0.0151 (6)	0.167 (1)
C(33)	0.571 (1)	-0.0298 (6)	0.273 (1)
C(34)	0.621 (1)	0.0157 (7)	0.392 (1)
C(35)	0.576 (1)	0.0790 (6)	0.404 (1)
C(36)	0.288 (1)	0.1458 (5)	0.398 (1)
C(37)	0.192 (1)	0.0920 (6)	0.334 (1)
C(38)	0.085 (1)	0.0696 (7)	0.390 (1)
C(39)	0.083 (2)	0.1036 (8)	0.517 (2)
C(40)	0.177 (1)	0.1558 (7)	0.581 (1)
C(41)	0.287 (1)	0.1812 (6)	0.527 (1)

^aNumbers in parentheses are the estimated standard deviations of the coordinates and refer to the last significant digit of the preceding numbers.

Table III. Selected Bond Distances (Å) in (detc)(dppe)(OC)W(C,C- η^2 -OC=CCH₂Ph)

W-S(1)	2.451 (2)	C(2)-C(3)	1.323 (9)
W-S(2)	2.572 (2)	C(2)-O(2)	1.262 (8)
W-P(1)	2.471 (2)	C(3)-C(4)	1.485 (9)
W-P(2)	2.633 (2)	C(4)-C(12)	1.506 (10)
W-C(1)	1.909 (8)	S(1)-C(5)	1.750 (7)
W-C(2)	2.176 (7)	S(2)-C(5)	1.686 (7)
W-C(3)	1.997 (7)	C(5)-N(1)	1.314 (9)
C(1)-O(1)	1.181 (8)		

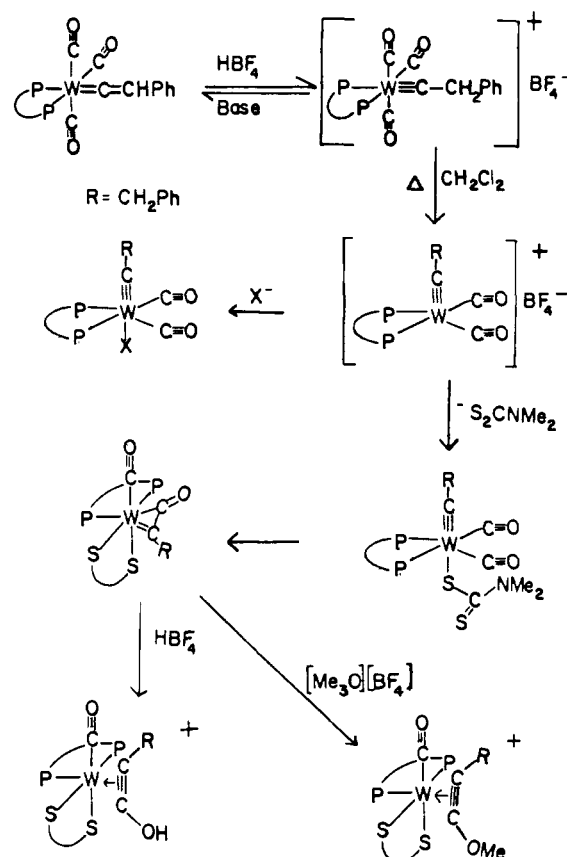
bone of the ketyl ligand is planar with the O and CH₂Ph wings swept back 151° and 136° from the C2-C3 linkage. The cis carbon monoxide also lies in the plane defined by the metal-ketyl moiety. Atomic positional parameters are listed in Table II, and intramolecular bond distances and angles are listed in Tables III and IV, respectively.

Discussion

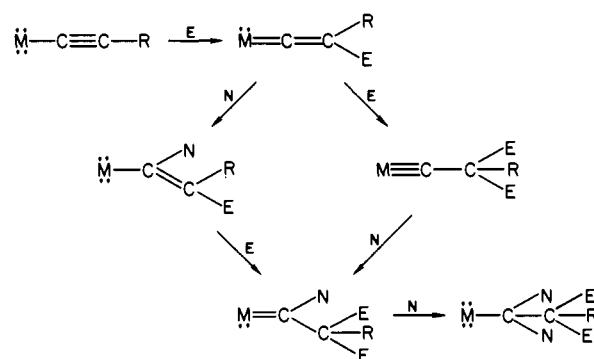
Syntheses and Spectral Properties. The scheme presented in Figure 2 summarizes the reactions reported in this work. Vi-

Table IV. Selected Bond Angles (deg) in (detc)(dppe)(OC)W(C,C- η^2 -OC=CCH₂Ph)

S(1)-W-P(1)	157.03 (6)	C(3)-C(2)-O(2)	150.75 (65)
S(1)-W-P(2)	87.67 (6)	C(2)-C(3)-C(4)	135.64 (66)
S(2)-W-C(1)	163.07 (23)	W-C(1)-O(1)	175.62 (63)
P(2)-W-C(3)	162.41 (19)	C(2)-W-C(3)	36.64 (25)
P(2)-W-C(2)	151.19 (20)	P(1)-W-P(2)	77.27 (6)
C(1)-W-C(3)	105.37 (30)	S(1)-W-C(3)	105.36 (21)

**Figure 2.** Scheme summarizing C₂ ligand transformations as described in the Discussion Section.

Scheme I



nylidene complexes are attractive reagents since they contain both unsaturated M=C and C=C bonds which can serve as reactive sites. Nucleophilic attack at the α -carbon of vinylidene ligands has been exploited to prepare η^1 -vinyl derivatives; cationic vinylidene complexes are particularly prone to such reactions.¹² More recently electrophilic addition to the β -carbon of vinylidene ligands has been reported.^{4,13} Note that the ability of the metal

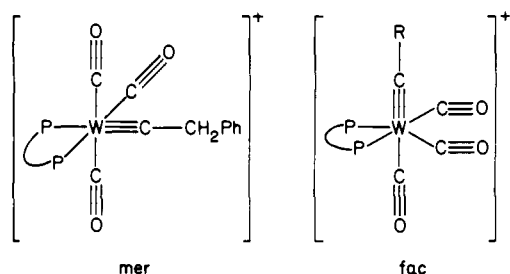
(12) (a) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 2455. (b) Boland-Lussier, B. E.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1982**, *1*, 628. (c) Bottrill, M.; Green, M. *J. Am. Chem. Soc.* **1977**, *99*, 5795.

to serve as an electron reservoir (housing the $M=C$ π electrons as a lone pair upon α -nucleophilic addition and sharing a lone pair to form $M=C$ upon β -electrophilic addition) is crucial to the observed reactions.

The general pattern of nucleophilic addition at the α -carbon and electrophilic addition at the β -carbon of C_2 ligands is well established and examples of each transformation in Scheme I are known.¹⁴ That such selectivity exists for reactions of $M-C-C$ backbones in complexes that adhere to the effective atomic number rule follows directly if one assumes that only the metal will happily house lone pairs and that the octet rule will apply for both carbon atoms in the C_2 -derived ligand.

[mer-(dppe)(OC)₃W=CCH₂Ph][BF₄] (2a). Protonation of the vinylidene complex **1a** produces an increase of about 100 cm^{-1} in the average CO stretching frequency. The intensity pattern in the γ_{CO} region is consistent with retention of the meridional geometry of the vinylidene precursor. The higher ν_{CO} values in **[mer-(dppe)(OC)₃W=CCH₂Ph][BF₄]** compared to the **1a** reagent reflect formation of both a cationic complex and a cylindrically symmetrical carbyne ligand which utilizes two $d\pi$ orbitals in contrast to the single-faced π -acid vinylidene ligand of **1a**. Solution infrared spectra of **1a** and **2a** in the carbonyl region (2200–1600 cm^{-1}) are reproduced in Figure 3 along with spectra of the facial tricarbonyl complexes *fac*-(dppe)(OC)₃W(THF) and *fac*-(dppe)(OC)₃W(η^2 -HC₂Ph) for comparison.

The benzylcarbyne ligand in **2a** was identified by the characteristic low-field ¹³C NMR chemical shift of the α -carbon¹⁵ (317.4 ppm; dd, ² J_{C-P} = 20, 10 Hz). Formation of only the *mer* isomer as suggested by the infrared data is supported by the difference in ² J_{C-P} values for the carbyne carbon and confirmed by ³¹P{¹H} NMR data. Singlets at 21.6 and 38.4 ppm in the ³¹P NMR



spectrum of **2a** exhibit one-bond ¹⁸³W–P coupling constants of 93 and 242 Hz, respectively (¹⁸³W, $I = 1/2$, 14% abundant). The ¹ J_{PW} coupling constant of the low-field signal is typical of phosphines trans to carbonyls.¹⁶ The unusually small ¹ J_{PW} value exhibited by the high-field signal is assigned to the phosphorus nucleus trans to the carbyne and reflects the high trans influence associated with a carbyne ligand.¹⁷ A correlation between increasing trans influence of L, which produces weaker Pd–P bonds, and a shift to higher magnetic fields for ³¹P δ values has been reported for *trans*-Cl₂LPdPEt₃ compounds.¹⁸ The same correlation holds individually for each of the compounds reported here in that the ¹ J_{PW} value of the high-field ³¹P signal is invariably smaller than that of the low-field resonance. The ³¹P data for

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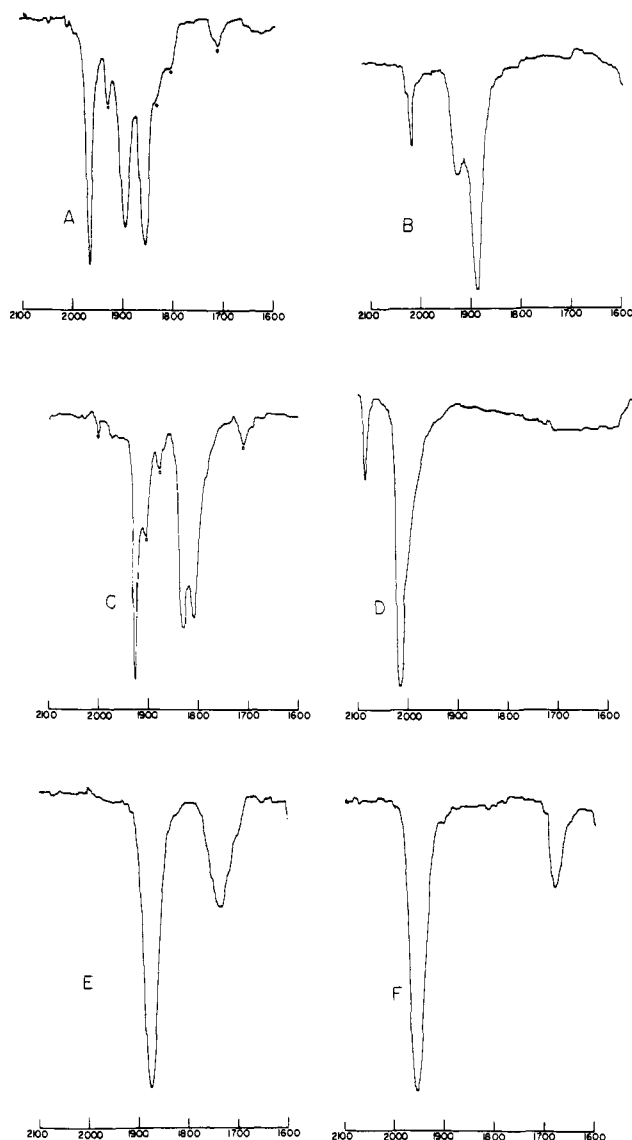


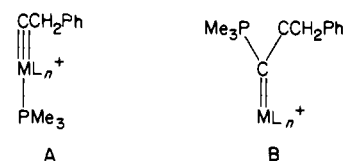
Figure 3. Solution infrared spectra of carbonyl absorptions for (A) *fac*-(dppe)(OC)₃W(η^2 -HC=CPh) in THF with dots designating absorptions due to a small amount of *fac*-(dppe)(OC)₃W(THF) remaining, (B) *mer*-(dppe)(OC)₃W=C=CHPh, (C) *fac*-(dppe)(OC)₃W(THF) in THF with dots designating absorptions due to a small amount of (dppe)(OC)₃W remaining and free acetone, (D) [*mer*-(dppe)(OC)₃W=C=CHPh][BF₄] in CH₂Cl₂, (E) (detc)(dppe)(OC)W(C,C- η^2 -OC=CCH₂Ph) in CH₂Cl₂, and (F) [(detc)(dppe)(OC)W(MeOC=CCH₂Ph)][BF₄] in CH₂Cl₂.

mer-(dppe)(OC)₃W=C=CHPh resembles that of **2a** with the vinylidene trans influence intermediate to that of CO and \equiv CCH₂Ph [45.4 ppm, ¹ J_{PW} = 242 Hz (trans to CO); 35.6 ppm, ¹ J_{PW} = 155 Hz (trans to =C=CHPh)] as probed by coupling constants. The methylated product, [*mer*-(dppe)(OC)₃W=C=CHMePh][BF₄], was characterized by IR and ¹H NMR spectroscopy with the methyl group appearing as a doublet (³ J_{HH} = 8 Hz) at 1.68 ppm (see Experimental Section). The methylphenylvinylidene complex formed by deprotonation of **2b** exhibited infrared γ_{CO} absorptions nearly identical with those of *mer*-(dppe)(OC)₃W=C=CHPh, and the CH₃ group appeared as a singlet at 2.08 ppm in ¹H NMR spectra.

trans-(dppe)(OC)₂XW=CCH₂Ph [X = Cl (**3a**), Br (**3b**), I (**3c**)]. Substitution of a halide for one carbonyl in [*mer*-(dppe)(OC)₃W=CCH₂Ph][BF₄] is easily achieved and yields neutral *trans*-(dppe)(OC)₂XW=CCH₂Ph compounds analogous to Fischer's series of *trans*-(OC)₄XW=CR complexes.¹⁹ We believe

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Scheme II



that the substitution proceeds by dissociation of CO followed by X⁻ addition (vide infra). This carbon monoxide lability is no doubt enhanced by the carbyne ligand consuming dπ electron density as well as the positive charge of the reagent, both effecting a decrease in the multiple bond character of the metal-carbonyl linkages. The carbyne carbon ¹³C resonance of *trans*-(dppe)-(OC)₂ClW≡CCH₂Ph at 276.3 ppm (t, *J*_{CP} = 9 Hz) is close to the 288.8 ppm signal reported for *trans*-(OC)₄ClW≡CMe.²⁰ The ³¹P spectrum of **3a** exhibits only a singlet with the ¹*J*_{PW} value of 231 Hz in the normal range for phosphorus nuclei *trans* to carbonyl ligands.¹⁶ The methylene protons of the carbyne benzyl substituent appear as a triplet (⁴*J*_{HP} = 5 Hz) at 2.84 ppm in the ¹H spectrum of *trans*-(dppe)(OC)₂ClW≡CCH₂Ph. Both proton NMR spectra and IR spectra of the bromo and iodo analogues of **3a** are nearly identical with those of *trans*-(dppe)(OC)₂ClW≡CCH₂Ph.

[(dppe)(OC)₂W≡CCH₂Ph][BF₄]⁻ (**4a**). Loss of carbon monoxide from [*mer*-(dppe)(OC)₃W≡CCH₂Ph][BF₄]⁻ occurs in refluxing CH₂Cl₂ to form [(dppe)(OC)₂W≡CCH₂Ph][BF₄]⁻. The resulting ν_{CO} pattern is compatible with a *cis*-L_nM(CO)₂ formulation exhibiting two strong bands at 2020 and 1955 cm⁻¹.²¹ Complex **4a** can be isolated as a yellow powder. The disposition of the [BF₄]⁻ anion remains unresolved. Solid-state infrared spectra of **4a** do not display the B-F stretching vibrations characteristic of metal-bound [BF₄]⁻ ligands,²² but the ³¹P NMR of [(dppe)(OC)₂W≡CCH₂Ph][BF₄]⁻ consists of a single resonance which is unusually broad (δ = 49.7 ppm, ¹*J*_{PW} = 244 Hz). The signal width of 19 Hz at half-height may be due to ¹⁹F coupling averaged over the four fluorine nuclei of the [BF₄]⁻ to produce an unresolved quintet (²*J*_{PF} < 4 Hz). Fischer has reported a bound tetrafluoroborate anion in *mer*-(PMe₃)(OC)₃(BF₄)Cr≡CMe which displays the four B-F vibrational modes characteristic of coordinated [BF₄]⁻. The PMe₃ phosphorus appears as a quintet in the ³¹P NMR with ²*J*_{PF} = 9 Hz in this chromium complex.²² The reactivity of [(dppe)(OC)₂W≡CCH₂Ph][BF₄]⁻ mimics that of Fischer's *trans*-(OC)₄(BF₄)W≡CR carbyne derivatives²³ in that it is an excellent electrophile. The question of ligated BF₄⁻ vs. ion pairs in the solid state or in solvents such as CH₂Cl₂ has been addressed in other systems.²⁴ The previous conclusion that nucleophilic addition reactions dominate the chemistry of such compounds holds equally well for [(dppe)(OC)₂W≡CCH₂Ph][BF₄]⁻. It may be that the solution and solid-state molecular structure of **4a** differ in the occupancy of the site *trans* to the carbyne ligand.

[*trans*-(dppe)(OC)₂LW≡CCH₂Ph][BF₄]⁻ [L = PMe₃ (**5a**), Me₂CO (**5b**), H₂O (**5c**)]. Trimethylphosphine adds to **4a** to form [*trans*-(dppe)(OC)₂(Me₃P)W≡CCH₂Ph][BF₄]⁻ which was identified by ³¹P NMR signals at 45.1 ppm (2 P, d, ²*J*_{PP} = 24 Hz) assigned to the two equivalent dppe phosphorus nuclei and at -51.4 ppm (1 P, t, ²*J*_{PP} = 24 Hz) assigned to the PMe₃ ligand. The extraordinarily small ¹*J*_{PW} coupling constant of 43 Hz associated with the PMe₃ ligand underscores the *trans* influence of the carbyne ligand in these cationic derivatives. This coupling constant was sufficiently small that we considered an alternative structure resulting from phosphine attack at the carbyne α-carbon to form

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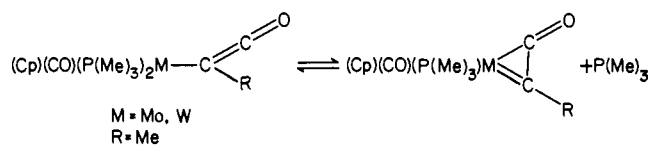
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Scheme III



a metal-substituted ylide. We believe this isomer is incompatible with details of ¹H and ¹³C NMR spectra of **5a**. The phosphine methyl groups appear as a doublet with ²*J*_{PH} = 8 Hz in the ¹H spectrum while four coordinate phosphonium salts of the type [PR₄]⁺ typically display ²*J*_{PH} values of 12–14 Hz.²⁵ Furthermore, the ¹*J*_{CP} coupling constant of 23 Hz to the phosphine methyl substituents observed in the ¹³C NMR of **5a**, normal for metal-bound PMe₃, contrasts with the larger value near 50 Hz reported for transition-metal-substituted ylides.²⁶ Further support for a weakly bound PMe₃ ligand *trans* to the benzyl carbyne can be gleaned from considering the structure of *trans*-(OC)₄(PMe₃)Cr≡CMe where the Cr-P distance of 2.47 Å is exceptionally long.¹⁹

Water and acetone adducts of [(dppe)(OC)₂W≡CCH₂Ph][BF₄]⁻ were characterized by ¹H NMR and solution IR techniques. The methylene protons of the benzyl carbyne appear as a triplet for both adducts (L = Me₂CO, δ 3.24, ⁴*J*_{HP} = 4 Hz; L = H₂O, δ = 2.84, ⁴*J*_{HP} = 3 Hz). Heating a CH₂Cl₂ solution of [(dppe)(OC)₂(H₂O)W≡CCH₂Ph][BF₄]⁻ appears to regenerate [(dppe)(OC)₂W≡CCH₂Ph][BF₄]⁻, but we cannot rule out the formation of [F₃BOH]⁻ with loss of HF in analogy to results reported by Beck for [Re(CO)₅(H₂O)][BF₄]⁻.²⁷

trans-(dppe)(OC)₂FW≡CCH₂Ph (**3d**). Addition of fluoride ion to [(dppe)(OC)₂W≡CCH₂Ph][BF₄]⁻ yields the *trans*-fluorocarbyne complex **3d**, a unique molecule. We are not aware of any other carbyne fluoro derivatives, and even fluorocarbonyl complexes are rare compared to the vast number of halocarbonyls known for the other halides.²⁸ As noted in the Results section the fluorocarbyne complex is not accessible directly from [*mer*-(dppe)(OC)₃W≡CCH₂Ph][BF₄]⁻ as are the other carbyne halo complexes. Fischer has also noted that fluoride is unique in reactions with the cationic carbyne complex [(CO)₅Cr≡CNEt₂]⁺.²⁹ While all four halides initially attack the carbyne α-carbon to form carbene derivatives, (OC)₅Cr=C(X)NEt₂, rearrangement with CO loss yields *trans*-(OC)₄XCr≡CNEt₂ for X = Cl, Br, and I upon heating. The fluorocarbene complex decomposes when heated rather than forming the *trans*-fluorocarbyne.

The presence of ¹⁸³W nuclei in addition to ¹H, ¹³C, ³¹P, and ¹⁹F in *trans*-(dppe)(OC)₂FW≡CCH₂Ph provides a wealth of NMR data. The carbyne ¹³C signal is a doublet of triplets (²*J*_{CF_{trans}} = 104 Hz, ²*J*_{CP_{cis}} = 9 Hz) as is the ¹³C signal at 213.6 ppm which we assign to the two carbonyl ligands. The largest coupling constant to each CO carbon (51 Hz) is assigned to the *trans* phosphorus nucleus while the triplet appearance is ascribed to coincidental similarity of the *cis* coupling constants to P and F (²*J*_{CP} = ²*J*_{CF} = 8 Hz).

(dte)(dppe)(OC)W(C,C-η²-OC≡CCH₂Ph) (dte = S₂CNMe₂, dmte (**7a**); dte = S₂CNEt₂, detc (**7b**)). Kreissel and co-workers have established ligand addition to tungsten carbonyl carbyne

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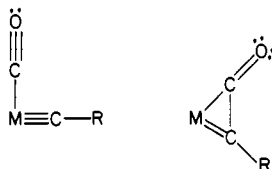
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complexes as a general route to ketylenyl complexes via carbonyl-carbyne coupling to form the C=C bond of the O=C=C-R moiety.³⁰ Both η^1 ³¹ and η^2 ³² ketylenyl complexes have been prepared; interconversions can be effected as a function of added phosphine (See Scheme III).

In our system addition of a dithiocarbamate salt to **4a** at low temperature initially generates a species with two ν_{CO} frequencies which are roughly 20 cm^{-1} lower than those of the **4a** reagent. The similarity of the IR absorptions to those of *trans*-(dppe)-(OC)₂XW=CCH₂Ph halide compounds suggests that this first product is a neutral complex with a monodentate dithiocarbamate trans to the carbyne ligand. The solution color and infrared pattern change at room temperature to those of the (dtc)(dppe)(OC)W-(C,C- η^2 -OC=CCH₂Ph) product. In effect the first sulfur donor completes the coordination sphere of the tungsten and the second sulfur donor atom provides the additional electron pair needed to maintain an 18-electron count at the metal following carbon-carbon bond formation between the carbyne ligand and a carbonyl ligand. If a neutral ligand formalism is used one can consider



the carbyne and the η^2 -ketylenyl ligand as providing 3 electrons each, so the coupling reaction depletes the total electron count at the metal by two prior to ligand addition.

The spectral data recorded for **7a** and **7b** are compatible with the structure determined for (dtc)(dppe)(OC)W(C,C- η^2 -OC=CCH₂Ph). The ketylenyl ν_{CO} vibration is a valuable diagnostic for the ketylenyl ligand (see Figure 3). Furthermore, while this stretch falls in the 1670 to 1750 cm^{-1} range for η^2 -ketylenyl ligands,³² it is much higher in energy for η^1 -ketylenyl complexes (1980 to 2100 cm^{-1}).³¹ An unambiguous ¹³C NMR differentiation of the terminal CO and the ketylenyl CO was achieved by incorporating ¹³C into the precursor complex. The large ¹J_{CW} coupling constant of 163 Hz exhibited by the 222.2-ppm signal is appropriate for a W-CO carbon nucleus. The other prominent signal in ¹³C enriched (dmtc)(dppe)(OC)W(C,C- η^2 -OC=CCH₂Ph) at 195.6 ppm was assigned to the ketylenyl carbon derived from carbon monoxide, W(C,C- η^2 -O=C=CCH₂Ph), while the less intense ¹³C signal at 198.7 ppm (dd, ²J_{CP} = 20, 10 Hz) was assigned to the α -carbon of the ketylenyl ligand W(C,C- η^2 -O=C=CCH₂Ph). A weak singlet at 212.9 ppm with no observable coupling to ³¹P or ¹⁸³W lies in the normal chemical shift range for dithiocarbamate central carbon nuclei.³³ The ³¹P spectrum of (dmtc)(dppe)-(OC)W(C,C- η^2 -OC=CCH₂Ph) consists of two doublets (²J_{PP} = 19 Hz) with ¹⁸³W satellites which illustrate the high trans influence of the η^2 -ketylenyl ligand (δ 47.8, ¹J_{PW} = 327 Hz, P trans to S; δ 23.3, ¹J_{PW} = 70 Hz, P trans to η^2 -ketylenyl). The one-bond tungsten-phosphorus coupling constant reflecting the ketylenyl trans influence is less than those observed for corresponding vinylidene (155 Hz) and carbyne cation values (93 Hz) of *mer*-(dppe)-(OC)₃W=C=CHPh and [*mer*-(dppe)(OC)₃W=CCH₂Ph][BF₄], respectively.

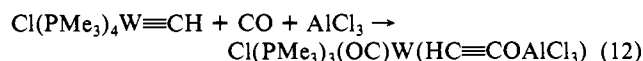
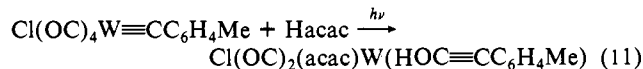
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[(dmtc)(dppe)(OC)W(ROC=CCH₂Ph)][BF₄] (R = CH₃ (**8a**); R = H (**8b**)). Addition of Lewis acids to η^2 -ketylenyl complexes is a facile route to alkoxyalkyne derivatives.^{32d,e} Fischer³⁴ and Schrock³⁵ have both reported carbonyl-carbyne coupling reactions which yielded η^2 -alkoxyalkyne complexes (eq 11 and 12, respectively). Given the nucleophilic character of η^2 -ketylenyl oxygen



atoms and the presence of H⁺ or AlCl₃ sources in the reactions above, one can write an attractive mechanism with an η^2 -ketylenyl complex as an intermediate which rapidly adds acid to form the observed product. Note that both coupling reactions 11 and 12 occur in the presence of added ligand, either acac (acetylacetonate) or CO, in analogy with chelation of the second dithiocarbamate sulfur donor in our system.

Either protonation or methylation of the η^2 -ketylenyl complex **7a** causes the 1730 cm^{-1} ν_{CO} stretch to be replaced by a weaker IR absorption at 1678 cm^{-1} (see Figure 3)³⁰ which we assign to the vibrational mode dominated by the alkyne C≡C stretch. Although π -bound alkynes normally exhibit only very weak C≡C absorptions, the presence of a single heteroatom substituent enhances the intensity of this vibrational mode. The terminal carbonyl ν_{CO} frequency moves up to 1948 from 1860 cm^{-1} in **7a** as expected for formation of a cationic complex. Numerous d⁴ *cis*-L₄M(CO)(η^2 -alkyne) (M = Mo, W) complexes provide a comparative spectral data base.³⁶

NMR spectra of [(dmtc)(dppe)(OC)W(MeOC=CCH₂Ph)][BF₄] exhibit many features common to the η^2 -ketylenyl precursor molecule **7a**. As in **7a** the ³¹P spectrum consists of a downfield doublet (²J_{PP} = 10 Hz with a normal ¹J_{PW} of 289 Hz) and an upfield doublet assigned to a more weakly bound dppe phosphorus (²J_{PP} = 10 Hz, ¹J_{PW} = 64 Hz) which we assign as the P trans to the alkyne ligand. A sample of (dmtc)(dppe)-(OC)W(C,C- η^2 -OC=CCH₂Ph) enriched in ¹³C was converted to **8a** to aid in ¹³C NMR interpretation. The terminal carbonyl resonates at 221.8 ppm (d, ²J_{CP} = 13 Hz, ¹J_{CW} = 129 Hz), and the methoxy-substituted alkyne carbon (C=COME) appears as a doublet, ²J_{CP} = 7 Hz, at 220.0 ppm with a much smaller ¹J_{CW} value (43 Hz) than the carbonyl carbon. Related tungsten(II) alkyne complexes exhibit similar ¹³C coupling constants and chemical shifts.³⁷ The naturally abundant alkyne carbon (CCH₂Ph) is a doublet of doublets (²J_{CP} = 14, 6 Hz) at 193.7 ppm. The diastereotopic methylene protons of the benzyl alkyne substituent appear as an AB quartet centered at 4.66 ppm (²J_{HH} = 15 Hz) with additional coupling to phosphorus evident: H_A-dd, ⁴J_{HP} = 2, 1 Hz; H_B-m, unresolved. The benzylic protons of (dmtc)(dppe)(OC)W(C,C- η^2 -OC=CCH₂Ph) displayed a similar ¹H NMR pattern built from an AB quartet at 4.69 ppm (²J_{HH} = 15 Hz): H_A-t, ⁴J_{HP} = 2.5 Hz; H_B-d, ⁴J_{HP} = 2 Hz.

Molecular Structure of (dtc)(dppe)(OC)W(C,C- η^2 -OC=CCH₂Ph). The η^2 -ketylenyl ligand formed from the benzyl carbyne and a carbonyl ligand exhibits structural parameters which are informative relative to other structural reports of η^2 -ketylenyl, η^1 -ketylenyl, and η^2 -alkyne ligands bound to tungsten or molybdenum. The C2-O2 and C2-C3 distances of 1.26 Å and 1.32 Å are similar to those found in (π -C₅H₅)(PMe₃)(OC)W(η^2 -O=C

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Table V. Structural Features of η^2 -Ketenyl, η^1 -Ketenyl, and η^2 -Alkyne Complexes of Mo(II) and W(II)

complex	bond distances (Å)					bond angles (deg)		ref
	W-C _B	W-C _A	C _A -C _B	C _A -O	C _B -C _C	C _B -C _A -O	C _A -C _B -C _C	
(π -C ₅ H ₅)(PMe ₃)(OC)W(η^2 -OC=CC ₆ H ₄ Me)	1.97	2.07	1.32	1.30	1.52			32a
[(π -C ₅ H ₅)(PMe ₃)(OC)W(η^2 -HOC=CC ₆ H ₄ Me)] ⁺	2.06	2.00	1.37	1.33	1.44	133	135	32d
(detc)(dppe)(OC)W(η^2 -OC=CCH ₂ Ph)	2.00	2.18	1.32	1.26	1.48	151	136	this work
(Et ₃ P) ₂ Br ₂ (OC)Mo(η^2 -HC=CPh)	1.98	1.99	1.27		1.54	139	134	40
[(NC) ₂ (phen)(OC)W(η^2 -OC=CPh)] ^{-a}	1.97	2.14	1.41	1.25		145		32b
(π -C ₅ H ₅)(PMe ₃) ₂ (OC)W(η^1 -OC=CC ₆ H ₄ Me)	2.27		1.24	1.21				31b
Cl(OC) ₂ (acac)W(η^2 -HOC=CC ₆ H ₄ Me) ^b	2.04	2.04	1.30	1.30		138	141	34
free R ₂ C=C=O			1.31	1.16		180		c

^a phen = 1,10-phenanthroline. ^b acac = acetylacetonate. ^c Cox, A. P.; Thomas, L. F.; Sheridan, J. *Spectrochim. Acta* 1959, 15, 542.

C=CC₆H₄Me),³² as well as other η^2 -ketenyl complexes listed in Table V. The W-C3 bond length of 2.00 Å is 0.27 Å shorter than the tungsten-carbon bond in a related η^1 -ketenyl complex, (π -C₅H₅)(PMe₃)₂(OC)W(η^1 -C(C₆H₄Me)=C=O),³¹ and indicates multiple bond character. Even the W-C2 distance of 2.18 Å is less than the simple M-C single-bond distances in (π -C₅H₅)(OC)₃W-C₂H₅³⁸ and (π -C₅H₅)(OC)₃Mo-C₂H₅³⁹ (2.32 and 2.38 Å, respectively).

The cis-bent coordination mode of the η^2 -ketenyl (C2-C3-C4, 151°; C3-C2-O2, 136°) is reminiscent of η^2 alkynes. The cis carbonyl ligand in the plane of the ketenyl backbone is a geometry common to d⁴-L₄M(CO)(η^2 -alkyne) complexes. A closer comparison of the W(Cl-01)(η^2 -C2-C3) fragment with the Mo(CO)(η^2 -C-C) fragment from (PEt₃)₂Br₂Mo(CO)(η^2 -HC₂Ph)⁴⁰ reinforces the bonding kinship between η^2 -ketenyl ligands and 4-electron donor alkyne ligands. Even the short nonbonded contact between the carbonyl carbon and the proximate alkyne carbon found in (PEt₃)₂Br₂Mo(CO)(HC₂Ph) (2.29 Å) is reproduced in the *cis*-CO, ketenyl moiety of (detc)(dppe)(OC)W(C,C- η^2 -OC=CCH₂Ph) (C1...C2, 2.32 Å). The three-center 2-electron molecular orbital scheme suggested earlier to account for the constructive ligand overlap involved one d π , a CO π^* , and an alkyne π_{\perp}^* .⁴¹ Here the ketenyl carbonyl carbon provides an orbital to mix with the d π and CO π^* as in Figure 4. A simple depiction of the η^2 -ketenyl/ η^2 -alkyne relationship is available in resonance form ii shown below. The C2-O2 distance of 1.26 Å

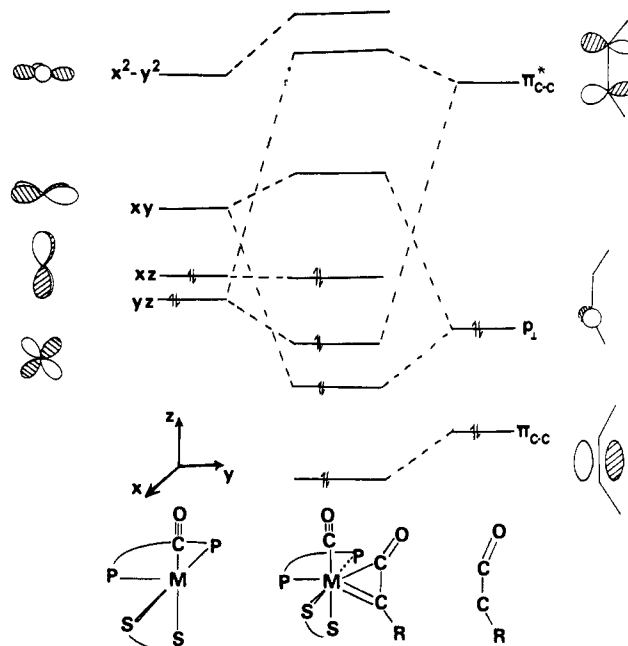
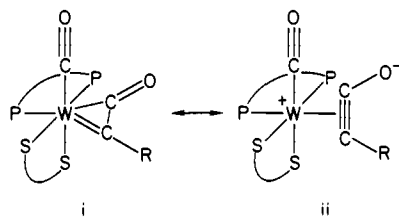


Figure 4. A qualitative molecular orbital scheme for d⁴ L₄(OC)M(η^2 -OC=CR) complexes.

Another influential factor in W-S dithiocarbamate bond distances is the extent of π -donation from the ligand π -system to the metal. In a d⁴ formalism the S2 trans to CO encounters the two filled d π orbitals derived from the octahedral t_{2g} set while S1 encounters the lone vacant d π orbital and is correctly oriented to provide π -electron density from the delocalized chelate π -system.⁴³

Visible Spectroscopy and Electrochemistry of [(detc)(dppe)-(OC)W(MeOC=CCH₂Ph)][BF₄]. Electronic absorption spectra and cyclic voltammograms have been reported for a series of 20 M(CO)(η^2 -alkyne)(S₂CNR₂)₂ complexes (M = Mo, W).⁴⁴ A relationship between the energy of the visible absorption, assigned as a HOMO \rightarrow LUMO transition between d π dominated molecular orbitals, and the reduction potential of the complex was evident as a function of the π -donor ability of the alkyne substituents. As the π -donor character of the alkyne substituents decreased, the visible transition moved to lower energies and the complex could be reduced more easily.

The cationic methoxyalkyne complex **8a** has a visible absorption at 504 nm ($\epsilon = 330 \text{ M}^{-1} \text{ cm}^{-1}$) and a reversible reduction at -1.20 V. The reduction for **8a** is easier than that for any of the W-(CO)(alkyne)(detc)₂ complexes, presumably reflecting the net charge difference and the presence of an additional electron rich

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Table VI. Phosphorus–Tungsten Coupling Constants ($^1J_{P-W}$, Hz) and Bond Lengths (W–P, Å) in $W(dppe)L_3X$ Complexes

complex	trans ligand	$^1J_{PW}$ (Hz)	W–P (Å)	ref
$W(CO)(dppe)(detc)(C,C-\eta^2-OC=CCH_2Ph)$	$O=C=C-CH_2Ph$	70	2.63	this work
$[mer-W(CO)_3(dppe)(\equiv CCH_2Ph)]^+$	$C-CH_2Ph$	93		this work
$mer-W(CO)_3(dppe)(=C=CHCO_2Me)$	$C=CHCO_2Me$	146	2.58	1a
$mer-W(CO)_3(dppe)(trans-EtO_2CCH=CHCO_2Et)$	CO	219	2.54	a
$mer-W(CO)_3(dppe)(=C=CHCO_2Me)$	CO	245	2.53	1a
$[mer-W(CO)_3(dppe)(\equiv C-CH_2Ph)]^+$	CO	242		this work
$mer-W(CO)_3(dppe)(trans-EtO_2CCH=CHCO_2Et)$	$EtO_2CCH=CHCO_2Et$	219	2.50	a
$W(CO)(dppe)(detc)(C,C-\eta^2-OC=CCH_2Ph)$	S_2CNR_2	327	2.47	this work

^a Personal communication, Dr. J. W. Faller.

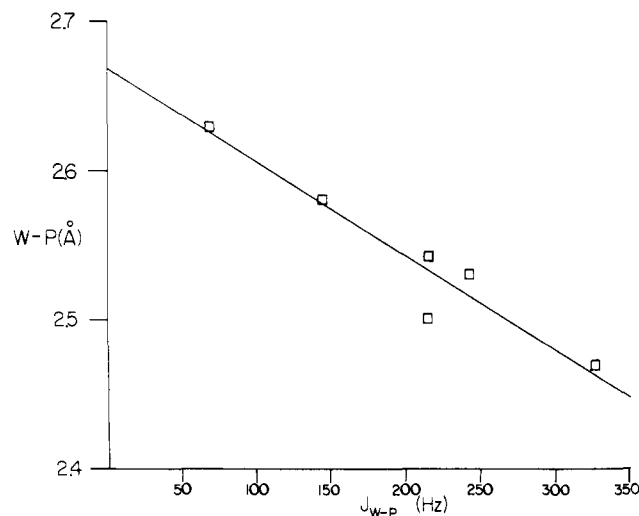


Figure 5. A plot of W–P bond distances vs. W–P coupling constants.

dtc vs. dppe in the coordination sphere. The η^2 -ketenyl precursor complex also displays an electronic absorption in the visible region ($\lambda = 494$ nm, $\epsilon = 200$ M⁻¹ cm⁻¹). The similarity of the electronic transitions in **7a** and **8a** supports the premise that the η^2 -ketenyl fragment interacts with the $d\pi$ metal orbitals in much the same way as the alkyne ligand.

Tungsten–Phosphorus Coupling Constants. ³¹P NMR provides abundant information regarding transition-metal phosphine complexes. Both the ³¹P chemical shift and the one-bond W–P coupling constant are sensitive to the coordination environment of the phosphine ligand. The trans influence of numerous ligands has been probed by monitoring one-bond metal–phosphorus coupling constants in a series of related compounds with retention of a single coordination geometry.

A compilation of W–P bond lengths and $^1J_{W-P}$ values for a series of $W(dppe)L_3X$ complexes is presented in Table VI. Figure 5 presents these same data graphically with W–P distances along

the ordinate and W–P coupling constants plotted on the abscissa. The approximate linearity of the correlation was unexpected. The $^1J_{W-P}$ value is probably dominated by the Fermi contact term which is a function of the s character in the W–P bond. A linear relationship between s orbital overlap and distance is not expected, and our results may simply reflect the limited range of distances and coupling constants accumulated to date. Note that an exponential correlation of Pt–P bond length vs. Pt–P coupling constant has been reported.⁴⁵ Regardless of the mathematical formulation the $^1J_{M-P}$ value is a good indicator of the M–P distance variation and provides insight into the bonding characteristics of the trans ligand.

Once again the data guide one to compare the η^2 -ketenyl ligand of **7a** and the methoxyalkyne ligand of **8a**. The $^1J_{W-P}$ values indicate that both are strong trans influence ligands. The structure of (detc)(dppe)(OC)W(C,C- η^2 -OC=CCH₂Ph) reinforces this conclusion.

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Registry No. **1a**, 88035-90-9; **1a** (¹³Co enriched), 96481-29-7; **1b**, 96454-56-7; **2a**, 96454-51-2; **2a** (¹³CO enriched), 96454-53-4; **2b**, 96454-55-6; **3a**, 88035-91-0; **3b**, 96454-57-8; **3c**, 96454-58-9; **3d**, 96454-59-0; **4a**, 96454-61-4; **4a** (¹³CO enriched), 96454-63-6; **5a**, 96454-65-8; **5b**, 96454-67-0; **5c**, 96481-31-1; **7a**, 96454-68-1; **7a** (¹³CO enriched), 96454-69-2; **7b**, 96454-70-5; **8a**, 96454-72-7; W(CO)₃-(dppe)(B) (B = acetone), 87900-84-3; PhC₂H, 536-74-3; Na(dmtc), 128-04-1; Na(detc), 148-18-5.

Supplementary Material Available: Tables of thermal parameters, calculated hydrogen positions, complete bond distances and angles, least-squares-planes analysis, and observed and calculated structure factors are available as Tables VII–XV, respectively (34 pages). Ordering information is given on any current masthead page.

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