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Reactions of tungsten phosphonium carbyne complexes with aryloxide nucleophiles to form aryloxycarbyne and η^2-ketenyl complexes

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Dedicated to the memory of Professor Luigi Venanzi

Abstract

Tungsten phosphoranylideneketene complexes of the type $Tp'(CO)(p\text{-}OC_6H_4R)W(\eta^2\text{-}(C,C)\text{–}O{=}CC\text{–}PR'_2Ph)$ ($R = NO_2$, $R' = Me$ (**6a**); $R = NO_2$, $R' = Ph$ (**6b**); $R = CN$, $R' = Me$ (**7a**); $R = CN$, $R' = Ph$ (**7b**); $R = Cl$, $R' = Ph$ (**8b**)) have been synthesized from phosphonium carbyne precursors in a reaction that reflects coupling of carbonyl and carbyne ligands. In addition to these products, aryloxycarbyne complexes $Tp'(CO)_2W{\equiv}CO(p\text{-}C_6H_4NO_2)$ (**9a**), $Tp'(CO)_2W{\equiv}CO(p\text{-}C_6H_4CN)$ (**9b**), and $Tp'(CO)_2W{\equiv}CO(p\text{-}C_6H_4Cl)$ (**9c**)) have been prepared via substitution of the phosphonium carbyne phosphine with an aryloxide nucleophile. The product ratio of substitution at the carbyne carbon to carbonyl–carbyne coupling can be tuned by variation of the aryloxide *para*-substituent. Aryloxy carbyne complexes are the favored products with stronger nucleophiles, while weaker nucleophiles result in a mixture of aryloxy carbyne complexes and η^2-ketenyl coupled complexes. Formation of η^2-ketenyl complexes is favored for the least nucleophilic aryloxides. Ketenyl complexes **6a** and **6b** were methylated at the ketenyl oxygen to form cationic alkyne complexes $[Tp'(CO)(p\text{-}OC_6H_4NO_2)W(\eta^2\text{-}(C,C)\text{–}CH_3OC{\equiv}CPR_2Ph)][OTf]$ ($R = Me$ (**10a**), $R = Ph$ (**10b**)). The structures of η^2-ketenyl complexes **6a** and **7b** and the structure of cationic alkyne complex **10a** were determined by X-ray crystallography. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Phosphoranylideneketene; Tungsten; Phosphonium carbyne; Ligand coupling; Phosphonium carbyne complexes; Aryloxycarbyne

1. Introduction

Fischer founded a new class of complexes containing transition metal–carbon triple bonds in 1973 [1]. Reactivity patterns of carbyne complexes have been thoroughly reviewed by Kim and Angelici [2]. Cationic carbyne complexes generally react with nucleophiles at the carbyne carbon, while neutral carbyne complexes can react at either the metal center or the carbyne carbon. The reactivity of cationic carbyne complexes is compatible with the predictions of frontier molecular orbital theory. Molecular orbital calculations identify the LUMO of cationic carbyne complexes as a metal–carbon π^* orbital [3]. Similar molecular orbital calculations on neutral carbyne complexes reveal that the vacant metal–carbon π^* orbital is close in energy to both metal and ligand based orbitals [4]. As a result of this orbital energy proximity, strong nucleophiles can access both carbon-centered and metal-centered orbitals. Weak nucleophiles tend to favor attack at the vacant orbital centered on the metal [5].

Angelici has reported an exception to the general reactivity pattern of cationic carbyne complexes. Treatment of the cationic carbyne complex $[(HC(pz)_3)(CO)_2W{\equiv}C\text{–}SMe][PF_6]$ (pz = pyrazolyl) (**1**) with phosphine nucleophiles (PR_3) provides η^2-ketenyl products, $(HC(pz)_3)(CO)(PR_3)W(\eta^2\text{-}(C,C)\text{–}O{=}CC\text{–}SMe)$ (**2**), reflecting net nucleophilic addition to tungsten rather than nucleophilic attack at C_α (Scheme 1) [6]. The neutral analog of **2**, $(HB(pz)_3)(CO)_2W{\equiv}C\text{–}SMe$ (**3**), undergoes an analogous carbyne–carbonyl coupling reaction when treated with phosphines [7].

Cationic phosphonium carbyne complexes, $[Tp'(CO)_2W{\equiv}CPR_3][PF_6]$ (**5**), have been synthesized by

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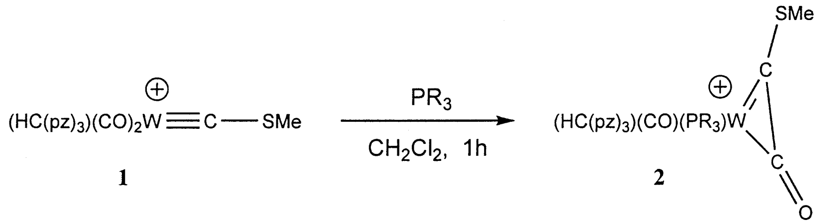
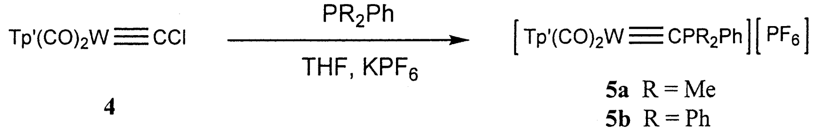
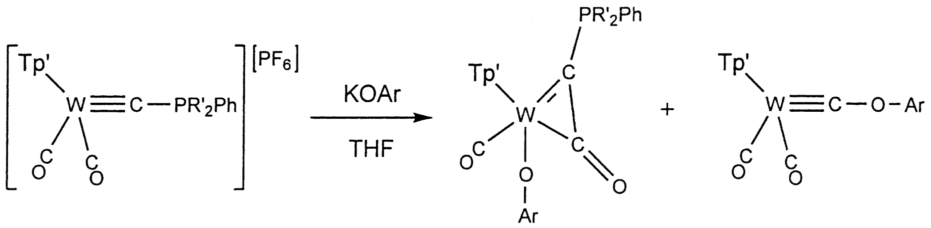


Scheme 1.



Scheme 2.



Scheme 3.

treating Tp′(CO)$_2$W≡CCl (**4**) [8] (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) with PR$_3$ in the presence of KPF$_6$ (Scheme 2) [9]. These phosphonium carbyne complexes undergo nucleophilic displacement of phosphine at C$_\alpha$ with anionic nucleophiles to provide neutral Tp′(CO)$_2$W≡C–R (R = H, aryloxide) [9–11] compounds in high yields. Treatment of [Tp′(CO)$_2$W≡CPMe$_2$Ph][PF$_6$] (**5a**) with the electron-rich aryloxide [*p*-OC$_6$H$_4$OCH$_3$]$^-$ provides exclusively the aryloxycarbyne product Tp′(CO)$_2$W≡CO(*p*-C$_6$H$_4$OMe). Here we report that this same cationic phosphonium carbyne reagent, **5a**, forms an η^2-ketenyl complex when treated with an electron-poor aryloxide nucleophile like [*p*-OC$_6$H$_4$NO$_2$]$^-$.

The ratio of aryloxycarbyne product to η^2-phosphoranylideneketene (η^2-ketenyl) product obtained by treating phosphonium carbyne complexes with different *para*-substituted aryloxide nucleophiles has now been probed (Scheme 3). Variation of the electron donating and electron withdrawing properties of *para*-substituents on the aryloxide reagent alters the electronic properties of the nucleophile and influences the product distribution.

Tungsten phosphoranylideneketene complexes of the type Tp′(CO)(*p*-OC$_6$H$_4$R)W(η^2-(C,C)–O=CC–PR′$_2$Ph) (R = NO$_2$, R′ = Me (**6a**); R = NO$_2$, R′ = Ph (**6b**); R = CN, R′ = Me (**7a**); R = CN, R′ = Ph (**7b**); R = Cl, R′ = Ph (**8b**)) have been synthesized (Fig. 1). Complexes **6a** and **6b** were methylated to form alkyne complexes [Tp′(CO)(*p*-OC$_6$H$_4$NO$_2$)W(η^2-(C,C)–CH$_3$OC≡CPR$_2$Ph)][OTf] (R = Me (**10a**), R = Ph (**10b**)). Data for the new carbyne complexes Tp′(CO)$_2$W≡CO(*p*-C$_6$H$_4$NO$_2$) (**9a**), Tp′(CO)$_2$W≡CO(*p*-C$_6$H$_4$Cl) (**9c**), and Tp′(CO)$_2$W≡CPh (**11**) are also included. The structures

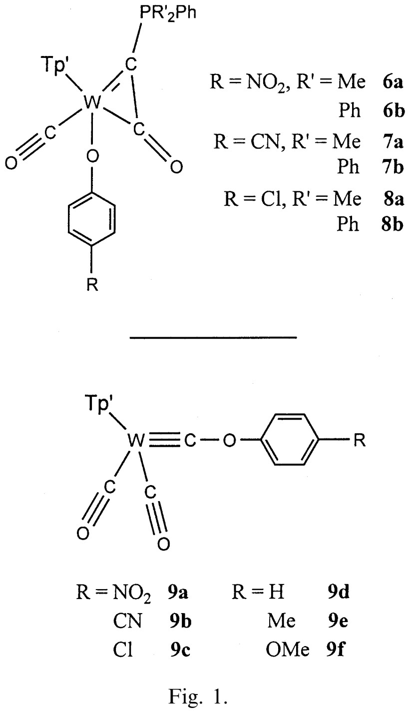


Fig. 1.

of **6a**, **7b**, and **10a** have been determined by X-ray crystallography.

2. Experimental

Reactions were carried out under an inert atmosphere of nitrogen or argon using standard Schlenk techniques. Tetrahydrofuran (THF) was dried by distillation from sodium and benzophenone. Other solvents were dried with activated alumina [12]. The complexes [Tp′(CO)$_2$W≡CPMe$_2$Ph][PF$_6$] (**5a**) and [Tp′(CO)$_2$W≡CPPh$_3$][PF$_6$] (**5b**) were prepared according to literature methods [9]. The potassium salts of the aryloxides were synthesized in dry THF in one of three ways: (i) by reaction of the alcohol with solid potassium, (ii) by deprotonation of the alcohol with potassium hydride in the presence of 18-crown-6, or (iii) by deprotonation of the alcohol with potassium *tert*-butoxide. Other reagents were used as obtained from commercial sources.

IR spectra were obtained on an ASI React IR 1000 spectrometer. NMR spectra were obtained on a Bruker Avance 400 or a Bruker AMX-300 spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. Products were isolated analytically pure after recrystallization or chromatography unless otherwise stated.

Spectroscopic data for aryloxide substituted carbyne complexes **9a**–**f** are in agreement with data for other aryloxycarbyne complexes [9].

2.1. Synthesis of Tp′(CO)(p-OC$_6$H$_4$NO$_2$)W(η^2-(C,C)–OCCPMe$_2$Ph) (6a)

An oven-dried Schlenk flask was charged with an excess of KH in mineral oil, which was washed with THF. The KH was suspended in 75 ml THF, and 0.40 g (2.90 mmol) of HO(p-C$_6$H$_4$NO$_2$) was added, generating immediate gas evolution. Addition of 0.75 g (2.90 mmol) of 18-crown-6 to the bright yellow solution initiated further gas evolution. The mixture was allowed to stir at 25 °C for 30 min, then filtered via cannula to a Schlenk flask containing a cooled (−78 °C) solution of 2.00 g (2.40 mmol) of [Tp′(CO)$_2$W≡C–PMe$_2$Ph][PF$_6$] in 150 ml THF. After warming to room temperature, the solution turned dark green, and a new infrared band appeared at 1875 cm^{-1}. The solvent was removed in vacuo and the residue was chromatographed (alumina; eluted first with hexanes, then changed to 2:1 THF:hexanes). Dark green crystals of **6a** (0.62 g, 31% yield) were isolated following recrystallization from CH$_2$Cl$_2$/MeOH at −35 °C. IR (THF, cm^{-1}): ν_{CO} 1875, 1720. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.42 (m, 5H, CPMe$_2$*Ph*), 7.26 (AA′BB′, 4H, p-C$_6$*H*$_4$NO$_2$), 5.84, 5.81, 5.71 (s, 1:1:1H, Tp′ C*H*), 2.48, 2.45, 2.31, 2.26, 2.06, 1.56 (s, 3:3:3:3:3:3H, Tp′ CC*H*$_3$), 1.68, 1.28 (d, 3:3H $^2J_{\mathrm{P-H}} = 14$ Hz, CP*Me*$_2$Ph). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): 229.0 (d, $^3J_{\mathrm{P-C}} = 3$ Hz, $^1J_{\mathrm{W-C}} = 181$ Hz, W*C*O), 201.2 (s, O*C*CPMe$_2$Ph), 177.2, 151.8, 125.9, 125.0 (s, p-*C*$_6$H$_4$NO$_2$), 154.6, 153.6, 152.0, 146.3, 145.2, 144.6 (s, 1:1:1:1:1:1C, Tp′ *C*CH$_3$), 133.2, 130.4, 129.7, 125.6 (d, CPMe$_2$*Ph*), 117.6 (d, $^1J_{\mathrm{P-C}} = 88$ Hz, $^1J_{\mathrm{W-C}} = 53$ Hz, OC*C*PMe$_2$Ph), 107.9, 107.5, 107.4 (s, 1:1:1C, Tp′ *C*H), 16.2, 15.4, 14.2, 13.0, 12.9, 12.5 (s, 1:1:1:1:1:1C, Tp′ C*C*H$_3$), 11.5, 10.1 (d, $^1J_{\mathrm{P-C}} = 60$ Hz, P*Me*$_2$Ph). ^{31}P NMR (CD$_2$Cl$_2$, δ): 15.5. *Anal.* Found: C, 43.15; H, 4.24; N, 10.73. Calc. for C$_{32}$H$_{37}$BN$_7$O$_5$PW·CH$_2$Cl$_2$: C, 43.54; H, 4.32; N, 10.77%.

2.2. Tp′(CO)(p-OC$_6$H$_4$NO$_2$)W(η^2-(C,C)–OCCPPh$_3$) (6b)

A solution of 0.093 g K[p-OC$_6$H$_4$NO$_2$] in 30 ml of THF and a solution of 0.50 g **5b** in 30 ml of THF were prepared and the latter was cooled to −78 °C. The yellow aryloxide solution was added drop-wise into the cooled solution causing a color change from purple to red. After 10 min there was no further color change, and the solution was allowed to warm to ambient temperature. After stirring for 4 h, little product was observed by IR (ν_{CO} 1872 cm^{-1}) and the reaction solution was refluxed overnight before the dark yellow–green solution was stripped in vacuo. Chromatography (alumina, THF) afforded a single green band. The solid remaining after rotary evaporation was an amorphous brown solid, but recrystallization from dichloromethane and hexanes afforded green needles. The needles were washed with hexanes and dried in vacuo. Yield: 68%. Complexes **7a** and **7b** were prepared by a similar method. **6b**: IR (KBr, cm^{-1}): ν_{CO} 1872, 1710. ^{1}H NMR (CD$_2$Cl$_2$, δ): 8.16, 6.90 (AA′BB′, 2:2H, p-C$_6$*H*$_4$NO$_2$), 7.56, 7.34, 7.24 (m, 3:6:6H, CP*Ph*$_3$), 5.79, 5.71, 5.01 (s, 1:1:1H, Tp′C*H*), 2.58, 2.34, 2.31, 2.25, 1.58, 1.51 (s, 3:3:3:3:3:3H, Tp′C*H*$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): 229.4 (d, $^3J_{\mathrm{P-C}} = 3$ Hz, W*C*O), 203.7 (d, $^2J_{\mathrm{P-C}} = 3$ Hz, C*C*O), 177.4, 139.3, 126.1, 120.0 (s, 1:1:2:2C, p-*C*$_6$H$_4$NO$_2$), 154.1, 153.6, 151.6, 146.2, 144.9, 143.7 (s, 1:1:1:1:1:1C, Tp′*C*CH$_3$), 133.4, 133.2, 129.3, 123.8 (d, 6:3:6:3C, CP*Ph*$_3$), 119.5 (d, $^1J_{\mathrm{P-C}} = 85$ Hz, C*C*PPh$_3$), 107.7, 107.5 (s, 2:1C, Tp′*C*H) 15.49, 15.48, 14.2, 13.0, 12.8, 12.5 (s, 1:1:1:1:1:1C, Tp′C*H*$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): 20.7 (s, C*P*Ph$_3$). *Anal.* Found: C, 52.96; H, 4.42; N, 10.19. Calc. for C$_{42}$H$_{41}$BN$_7$O$_5$PW: C, 53.13; H, 4.35; N, 10.33%.

2.3. Tp′(CO)(p-OC$_6$H$_4$CN)W(η^2-(C,C)–OCCPMe$_2$Ph) (7a)

Yield: 25%. IR (KBr, cm^{-1}): ν_{CN} 2212, ν_{CO} 1849, 1722. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.55, 7.43, 7.31 (m, 1:2:2H, PMe$_2$*Ph*), 7.44, 6.68 (AA′BB′, 2:2H, p-

C_6H_4CN), 5.83, 5.79, 5.71 (s, 1:1:1H, Tp′C*H*), 2.47, 2.45, 2.31, 2.25, 2.06, 1.57 (s, 3:3:3:3:3:3H, Tp′CH_3), 1.66, 1.26 (d, 3:3H, $^2J_{P-H} = 13$ Hz, CPMe_2Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 229.4 (d, $^3J_{P-C} = 3$ Hz, W*C*O), 201.1 (s, C*C*O), 174.7, 133.6, 121.0, 100.1 (s, 1:2:2:1C, *p*-C_6H_4CN), 154.5, 153.6, 152.0, 146.2, 145.1, 144.5 (s, 1:1:1:1:1:1C, Tp′*C*CH_3), 133.1, 130.4, 129.7, 125.7 (d, 1:2:2:1C, CPMe_2*Ph*), 121.0 (s, *p*-C_6H_4*C*N), 115.0 (d, $^1J_{P-C} = 89$ Hz, OC*C*PMe_2Ph), 107.8, 107.5, 107.3 (s, 1:1:1C, Tp′*C*H), 16.2, 15.4, 14.1, 12.93, 12.87, 12.5 (s, 1:1:1:1:1:1C, Tp′CH_3), 11.6, 10.1 (d, $^1J_{P-C} = 61$ Hz, CPMe_2Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 15.0 (s, CPMe_2Ph). *Anal.* Found: C, 46.52; H, 4.54; N, 11.19. Calc. for $C_{33}H_{37}BN_7O_3PW{\cdot}CH_2Cl_2$: C, 46.59; H, 4.36; N, 10.87%.

2.4. $Tp'(CO)(p\text{-}OC_6H_4CN)W(\eta^2\text{-}(C,C)\text{–}OCCPPh_3)$ (**7b**)

Yield: 52%. IR (KBr, cm^{-1}): ν_{CN} 2216, ν_{CO} 1868, 1714. ^1H NMR (CD_2Cl_2, δ): 7.56, 7.34, 7.23 (m, 3:6:6H, CPPh_3), 7.54, 6.93 (AA′BB′, 2:2H, *p*-C_6H_4CN), 5.78, 5.71, 5.01 (s, 1:1:1H, Tp′C*H*), 2.57, 2.34, 2.30, 2.23, 1.58, 1.52 (s, 3:3:3:3:3:3H, Tp′CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 229.8 (d, $^3J_{P-C} = 3$ Hz, W*C*O), 203.5 (d, $^2J_{P-C} = 3$ Hz, O*C*CPPh_3), 175.0, 133.9, 121.0, 100.1 (s, 1:2:2:1C, *p*-C_6H_4CN), 154.0, 153.6, 151.6, 146.1, 144.8, 143.6 (s, 1:1:1:1:1:1C, Tp′*C*CH_3), 133.3, 133.2, 129.2, 123.9 (d, 6:3:6:3C, CPPh_3), 121.1 (s, *p*-C_6H_4*C*N), 117.0 (d, $^1J_{P-C} = 84$ Hz, OC*C*PPh_3), 107.64, 107.63, 107.5 (s, 1:1:1C, Tp′*C*H), 15.5, 14.2, 13.0, 12.8, 12.5 (s, 2:1:1:1:1C, Tp′CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 19.9 (s, C*P*Ph_3). *Anal.* Found: C, 55.25; H, 4.44; N, 10.35. Calc. for $C_{43}H_{41}BN_7O_3PW$: C, 55.57; H, 4.45; N, 10.55%.

2.5. $Tp'(CO)(p\text{-}OC_6H_4Cl)W(\eta^2\text{-}(C,C)\text{–}OCCPPh_3)$ (**8b**)

A dry, N_2 purged, flask was charged with 0.30 g of **5b** and 0.080 g of K[*p*-OC_6H_4Cl] before 20 ml of THF was added. The solution soon turned from purple to green and another 20 ml of THF was added. The solution was allowed to stir overnight. Solvent was then removed by rotatory evaporation, and the remaining green solid was chromatographed on silica. A solution of 1:4 hexanes:THF was the initial eluent, and then the proportion of THF was increased gradually until neat THF was used. The last band was eluted with 4:1 THF:acetonitrile. Five discrete bands came off the column: an uncolored substance (*p*-chlorophenol), a yellow band (identified as pure **9c**, vide infra), a brown band (unidentifiable mixture), a dark green band (also an unidentifiable mixture), and finally a light green band. Proton NMR showed that the light green band was impure, so a second column was performed as before (silica, 1:3 hexanes:THF ramping to neat acetonitrile). Recrystallization from CH_2Cl_2:hexanes produced a mixture of dark green rods and green starbursts (30 mg). The two types of crystals consisted of the same material by IR and NMR. Proton NMR showed a 10:1 mixture of **8b** and an uncharacterized ketenyl product that was not separable. Yield: 12%. IR (KBr, cm^{-1}): ν_{CO} 1861, 1706. ^1H NMR (CD_2Cl_2, δ): 7.54, 7.33, 7.24 (m, 3:6:6H, CPPh_3), 7.19, 6.82 (AA′BB′, 2:2H, *p*-C_6H_4Cl), 5.76, 5.68, 4.99 (s, 1:1:1H, Tp′C*H*), 2.55, 2.32, 2.29, 2.25, 1.62, 1.54 (s, 3:3:3:3:3:3H, Tp′CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 230.7 (d, $^3J_{P-C} = 3$ Hz, W*C*O), 203.0 (d, $^2J_{P-C} = 2$ Hz, O*C*CPPh_3), 170.4, 128.8, 122.9, 121.4 (s, 1:2:1:2C, *p*-C_6H_4Cl), 154.0, 153.7, 151.7, 145.8, 144.6, 143.5 (s, 1:1:1:1:1:1C, Tp′*C*CH_3), 133.4, 133.0, 129.2, 124.5 (d, 6:3:6:3C, CPPh_3), 110.7 (d, $^1J_{P-C} = 85$ Hz, OC*C*PPh_3), 107.6, 107.5, 107.4 (s, 1:1:1C, Tp′*C*H), 15.50, 15.47, 14.2, 13.0, 12.8, 12.5 (s, 1:1:1:1:1:1C, Tp′CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 19.6 (s, C*P*Ph_3).

2.6. $Tp'(CO)_2W{\equiv}CO(p\text{-}C_6H_4NO_2)$ (**9a**)

In the manner described above (see **6a**), excess KH, 0.83 g (6.0 mmol) of HO(*p*-$C_6H_4NO_2$) and 1.60 g (6.0 mmol) of 18-crown-6 were used to generate a THF solution of the phenoxide, which was cannulated into a Schlenk flask containing 3.20 g (5.5 mmol) $Tp'(CO)_2W{\equiv}C\text{–}Cl$ in 200 ml of acetonitrile. Refluxing the mixture for 7 days affected slow conversion of the chlorocarbyne complex to aryloxycarbyne complex **9a**; infrared intensities diminished after prolonged reflux, and the reaction was stopped at 50% conversion (by IR). Solvent removal and alumina chromatography (first with hexanes, then changed to 2:1 hexanes:THF) permitted separation of starting material (first yellow band) from 0.50 g (13% yield) of **9a**, which was isolated as a light-sensitive yellow powder after solvent removal. IR (THF, cm^{-1}): ν_{CO} 1977, 1877. ^1H NMR (CD_2Cl_2, δ): 7.89 (AA′BB′, 4H, $C_6H_4NO_2$), 5.91, 5.87 (s, 2:1H, Tp′–C*H*), 2.48, 2.39, 2.38, 2.36 (s, 3:6:6:3H, Tp′ CCH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 222.5 (s, $^1J_{W-C} = 161$ Hz, W*C*O), 214.5 (s, $^1J_{W-C} = 247$ Hz, W≡*C*OAr), 159.0, 145.0, 126.4, 117.4 (s, *p*-$C_6H_4NO_2$), 152.7, 152.0, 145.9, 145.3 (s, 1:2:1:2C, Tp′ *C*CH_3), 107.0, 106.7 (s, 1:2C, Tp′ *C*H), 16.6, 15.5, 12.8 (s, 2:1:3H, Tp′ CCH_3). *Anal.* Found: C, 41.64; H, 3.87; N, 13.89. Calc. for $C_{24}H_{26}BN_7O_5W$: C, 41.95; H, 3.81; N, 14.27%.

2.7. $Tp'(CO)_2W{\equiv}CO(p\text{-}C_6H_4Cl)$ (**9c**) (continued from the synthesis of **8b**)

The yellow aryloxy carbyne product (0.039 g, 18% yield) slowly turned black upon exposure to light. IR (KBr, cm^{-1}): ν_{CO} 1969, 1864. ^1H NMR (CD_2Cl_2, δ): 7.34 (AA′BB′, 4H, *p*-C_6H_4Cl), 5.89, 5.85 (s, 2:1H, Tp′C*H*), 2.47, 2.37, 2.36, 2.35 (s, 3:6:6:3H, Tp′CH_3).

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 222.7 (s, W*C*O), 218.0 (s, W≡*C*OAr), 153.1, 130.6, 130.2, 118.7 (s, 1:1:2:2C, *p*-C_6H_4Cl), 152.7, 152.1, 145.7, 145.1 (s, 1:2:1:2C, Tp′*C*CH_3), 106.9, 106.6 (s, 2:1C, Tp′*C*H) 16.6, 15.5, 12.7 (s, 2:1:3C, Tp′*C*H_3). *Anal.* Found: C, 43.22; H, 3.95; N, 12.96. Calc. for $C_{24}H_{26}BClN_6O_3W$: C, 42.60; H, 3.87; N, 12.42%.

2.8. Synthesis of [Tp′(CO)(p-$OC_6H_4NO_2$)-W(η^2-MeOC≡CPMe$_2$Ph)][OTf] (**10a**)

An oven-dried Schlenk flask was charged with 0.62 g (0.75 mmol) **6a** and 50 ml dry CH_2Cl_2, and cooled to −78 °C with stirring. Methyl triflate (0.25 ml, 2.20 mmol) was added drop-wise to the cold solution, and the resulting mixture was slowly warmed to 25 °C. Upon warming, the solution changed from dark green to bright green, and a shift in the terminal carbonyl stretching frequency from 1869 to 1942 cm^{-1} accompanied the color change. Solvent removal followed by washing with 2 × 20 ml Et_2O and recrystallization (CH_2Cl_2/Et_2O, 25 °C) resulted in isolation of 0.53 g (71% yield) of green crystals of **10a**. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1942. ^1H NMR (CD_2Cl_2, δ): 7.57 (m, 5H, W(η^2-MeOC≡CPMe$_2$*Ph*)), 7.36 (AA′BB′, 4H, W(*p*-OC_6*H*$_4NO_2$)), 6.06, 6.04, 5.81 (s, Tp′C*H*), 4.40 (s, 3H, W(η^2-*Me*OC≡CPMe$_2$Ph)), 2.56, 2.54, 2.32, 2.08, 1.96, 1.83 (s, Tp′C*H*$_3$), 1.81, 1.64 (d, $^2J_{P-H}$ = 14 Hz, 3:3 H, W(η^2-MeOC≡CP*Me*$_2$Ph)). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 228.7 (d, $^3J_{P-C}$ = 3 Hz, $^1J_{W-C}$ = 150 Hz, W(*C*O)), 226.2 (d, $^2J_{P-C}$ = 16 Hz, W(η^2-MeO*C*≡CPMe$_2$Ph)), 153.7, 153.6, 153.5, 148.6, 146.7, 146.4 (s, Tp′*C*CH_3), 175.2, 141.2, 125.9, 119.4 (s, W(*p*-O*C*$_6H_4NO_2$)), 135.0, 131.0, 130.6, 123.8 (d, W(η^2-MeOC≡CPMe$_2$*Ph*)), 116.6 (d, $^1J_{P-C}$ = 112 Hz, W(η^2-MeOC≡*C*PMe$_2$Ph)), 109.2, 109.1, 108.0 (s, Tp′*C*H), 69.9 (s, W(η^2-*Me*OC≡CPMe$_2$Ph)), 16.0, 15.4, 15.0, 13.0, 12.9, 12.7 (s, Tp′*C*H_3), 12.8, 11.3 (d, $^1J_{P-C}$ = 61 Hz, W(η^2-MeOC≡CP*Me*$_2$Ph)).

2.9. Synthesis of [Tp′(CO)(p-$OC_6H_4NO_2$)-W(η^2-MeOC≡CPPh$_3$)][OTf] (**10b**)

Complex **10b** was prepared in the same manner as **10a**, except that chromatography (alumina; eluted with methylene chloride, then changed to acetonitrile) was employed before recrystallization. Yield: 48%. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1945. ^1H NMR (CD_2Cl_2, δ): 8.22, 6.68 (AA′BB′, 2:2H, W(*p*-OC_6*H*$_4NO_2$)), 7.45 (m, 15H, W(η^2-MeOC≡CP*Ph*$_3$)), 6.17, 5.81, 5.16 (s, 1:1:1H, Tp′C*H*), 4.17 (s, 3H, W(η^2-*Me*OC≡CPPh$_3$)), 2.70, 2.37, 2.32, 2.06, 1.88, 1.55 (s, 3:3:3:3:3:3H, Tp′C*H*$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 231.1 (d, $^2J_{P-C}$ = 17 Hz, W(η^2-MeO*C*≡CPPh$_3$)), 229.3 (d, $^3J_{P-C}$ = 3 Hz, W(*C*O)), 175.0, 141.6, 126.3, 119.0 (s, 1:1:2:2C, W(*p*-O*C*$_6H_4NO_2$)), 153.84, 153.76, 152.9, 149.1, 146.4, 145.6 (s, 1:1:1:1:1:1C, Tp′*C*CH_3), 135.2, 133.2, 130.5, 120.6 (d, 3:6:6:3C W(η^2-MeOC≡CP*Ph*$_3$)), 121.4 (d, $^1J_{P-C}$ = 321 Hz, W(η^2-MeOC≡*C*PPh$_3$)), 109.5, 109.0, 108.2 (s, Tp′*C*H), 68.5 (s, W(η^2-*Me*OC≡CPPh$_3$)), 16.0, 15.6, 14.8, 13.2, 12.9, 12.7 (s, Tp′*C*H_3). *Anal.* Found: C, 47.62; H, 4.13; N, 8.77. Calc. for $C_{44}H_{44}BF_3N_7O_8PSW$: C, 47.46; H, 3.98; N, 8.80%.

2.10. Tp′(CO)$_2$W≡CPh (**11**)

IR (KBr, cm^{-1}): ν_{CO} 1969, 1876. ^1H NMR (CD_2Cl_2, δ): 7.47, 7.33 (m, 2:3H, WC*Ph*), 5.97, 5.87 (s, 2:1H, Tp′C*H*), 2.53, 2.48, 2.42, 2.39 (s, 6:3:6:3H, Tp′C*H*$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 277.9 (s, $^1J_{W-C}$ = 187 Hz, W≡*C*Ph), 224.2 (s, $^1J_{W-C}$ = 166 Hz W*C*O), 152.8, 152.4, 146.1, 145.4 (s, 1:2:1:2C, Tp′*C*CH_3), 150.5 (d, 1C, $^2J_{W-C}$ = 43 Hz, W≡C–C_{ipso}), 129.5, 128.4, 127.9 (s, 2:2:1C, W≡C*Ph*), 107.0, 106.7 (s, 1:2C, Tp′*C*H), 16.6, 15.3, 12.8, 12.7 (s, 2:1:2:1C, Tp′*C*H_3). *Anal.* Found: C, 45.57; H, 4.48; N, 12.64. Calc. for $C_{24}H_{27}BN_6O_2W$: C, 46.04; H, 4.35; N, 13.42%.

2.11. Collection of diffraction data for Tp′(CO)(p-$OC_6H_4NO_2$)W(η^2-C(PMe$_2$Ph)CO) (**6a**) and Tp′(CO)(p-$OC_6H_4NO_2$)W(η^2-C(PPh$_3$)CO) (**7b**) and [Tp′(CO)(p-$OC_6H_4NO_2$)W(η^2-(C,C)–MeOC≡CPMe$_2$Ph)][OTf] (**10a**)

A dark green crystal of **6a** of dimensions 0.40 × 0.25 × 0.15 mm, a dark green crystal of **7b** of dimensions 0.40 × 0.20 × 0.20, and a green crystal of **10a** of dimensions 0.35 × 0.30 × 0.18 mm were selected, mounted on a glass fiber and coated with epoxy. Diffraction data were collected on a Rigaku automated diffractometer for **6a** and **10a**, and a Bruker SMART diffractometer for **7b**. Cell parameters, listed in Table 1, were refined by least-squares from the positions of 74 well-centered reflections found in the region $30.0 < 2\theta < 33.0°$ and indicated a monoclinic cell for **6a**, from 6610 reflections found in the region $5.00 < 2\theta < 60.00°$ and indicated a triclinic cell for **7b**, and from 50 well-centered reflections found in the region $40.0 < 2\theta < 45.0°$ and indicated a triclinic cell for **10a**.

Intensity data were collected in the quadrant $\pm h$, k, l for **6a**, the hemisphere $\pm h$, k, $\pm l$ for **7b**, and hemisphere $\pm h$, k, $\pm l$ for **10a** under the conditions specified in Table 1. Only data with $I > 2.5\sigma(I)$ were used in the structure solution and refinement [13].

2.12. Solution and refinement of structures **6a**, **7b** and **10a**

The space group $P2_1/n$ was confirmed for **6a** by the successful structure solution as was $P\bar{1}$ for **7b** and **10a**. The asymmetric unit for **7b** contains two non-equivalent conformations of **7b**. The bond angles and dis-

Table 1
Crystallographic data collection and refinement parameters for **6a**, **7b**, and **10a**

	6a	**7b**	**10a**
Empirical formula	$C_{32}H_{37}BN_7O_5PW\cdot(22/25)CH_2Cl_2$	$C_{43}H_{41}BN_7O_3PW\cdot(3/4)CH_2Cl_2$	$C_{34}H_{40}BF_3N_7O_8PSW$
Formula weight	900.1	993.17	989.41
Crystal size (mm)	0.40 × 0.25 × 0.15	0.40 × 0.20 × 0.20	0.35 × 0.30 × 0.18
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	11.405(2)	10.9514(4)	10.574(1)
b (Å)	23.85(1)	21.0989(8)	12.711(2)
c (Å)	13.948(2)	22.0823(8)	15.394(2)
α (°)		115.416(1)	82.36(1)
β (°)	90.73	100.906(1)	80.70(1)
γ (°)		95.896(1)	81.718(9)
V (Å^3)	3793(2)	4426.9(3)	2007.8(4)
Z	4	4	2
D_{calc} (g cm^{-3})	1.576	1.490	1.637
Radiation (λ, Å)	Mo Kα (0.70930)	Mo Kα (0.70930)	Mo Kα (0.70930)
Monochromator	graphite	graphite	graphite
Linear absorption coefficient (mm^{-1})	3.19	2.79	3.09
Scan mode	$\theta/2\theta$	ω	$\theta/2\theta$
Background	25% of full scan width on both sides	SMART CCD	25% of full scan with on both sides
2θ limits (°)	$2<2\theta<45$	$5<2\theta<60$	$2<2\theta<45$
Quadrant collected	$\pm h, k, l$	$\pm h, k, \pm l$	$\pm h, k, \pm l$
Total number of reflections	4939	46099	5236
Data with $I\geq 2.5\sigma(I)$	3655	20 561	4756
R (including unobserveds)	0.047 (0.069)	0.065 (0.085)	0.041 (0.045)
R_W (including unobserveds)	0.061 (0.063)	0.066 (0.071)	0.059 (0.060)
Goodness-of-fit	1.91	2.1287	2.17
Number of parameters	451	1059	500
Largest parameter shift	0.002	0.045	0.160

tances for each molecule are close in value, therefore only one was selected for discussion (see supporting information). The position of the tungsten atom was deduced from the three-dimensional Patterson function for each structure. In each case, the positions of the remaining non-hydrogen atoms were determined through subsequent Fourier and difference Fourier calculations.

The non-hydrogen atoms were refined using anisotropic thermal parameters.[1] Hydrogen atom positions were calculated with use of a C–H distance of 0.96 Å and an isotropic thermal parameter calculated from the anisotropic values for the atoms to which they were connected. Final least-squares refinement resulted in residuals of $R = 4.7\%$ and $R_W = 6.1\%$ for **6a**, $R = 6.5\%$ and $R_W = 6.6\%$ for **7b**, and $R = 4.1\%$ and $R_W = 5.9\%$ for **10a**.[2] The final difference Fourier map had no peak greater than 2.00 e Å^{-3} for **6a**, 3.680 e Å^{-3} for **7b**, and 1.35 e Å^{-3} for **10a** [14].

3. Results and discussion

3.1. Synthesis of $Tp'(CO)(p\text{-}OC_6H_4R)W(\eta^2\text{-}(C,C)\text{–}O{=}CC\text{–}PR'_2Ph)$ ($R = NO_2$, $R' = Me$ (**6a**), $R' = Ph$ (**6b**); $R = CN$, $R' = Me$ (**7a**); $R' = Ph$(**7b**); $R = Cl$, $R' = Ph$ (**8b**))

After a THF solution of $[Tp'(CO)_2W{\equiv}CPMe_2Ph][PF_6]$ (**5a**) and potassium *para*-nitrophenoxide was stirred overnight a monocarbonyl product with ν_{CO} at 1875 cm^{-1} was observed by IR. Chromatography on alumina afforded the η^2-ketenyl product $Tp'(CO)(p\text{-}OC_6H_4NO_2)W(\eta^2\text{-}(C,C)\text{–}O{=}CC\text{–}PMe_2Ph)$ (**6a**) in 68% yield. Similar reactions of phosphonium carbyne complexes **5a** and **5b** with $K[p\text{-}OC_6H_4NO_2]$, $K[p\text{-}OC_6H_4CN]$, and $K[p\text{-}OC_6H_4Cl]$ formed the *p*-nitro adduct **6b**, *para*-cyano complexes **7a** and **7b**, and the *para*-chloro complex **8b**, although in poorer yields. Concomitant formation of the aryloxycarbyne complex product resulting from phosphine substitution was also observed in the reaction mixtures (vide infra).

The dimethylphenylphosphine (**6a**, **7a**, **8a**) and triphenylphosphine (**6b**, **7b**, **8b**) η^2-ketenyl products have similar spectroscopic characteristics. Both groups of complexes contain a stereogenic center at tungsten

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[1] The function minimized was $\Sigma\omega(|F_C|)^2$, where ω is based on counter statistics.

[2] $R_{unweighted} = \Sigma(|F_O| - |F_C|)/\Sigma|F_O|$ and $R_{weighted} = [\Sigma\omega(|F_O| - |F_C|)^2/\Sigma\omega F_O{}^2]^{1/2}$.

and display 1:1:1 patterns for the Tp′ methine signals in the ^{1}H spectrum. Neglecting coincidental overlap there are six resonances of equal intensity for the six methyl groups of the Tp′ ligand located between 2.5 and 1.5 ppm in the ^{1}H spectra with the associated carbons somewhere between 16.0 and 12.0 ppm in the ^{13}C spectra. The range of carbon chemical shifts for the ketenyl carbon attached to oxygen is narrow (201–204 ppm), and lies close to reported chemical shift values for other η^2-ketenyl complexes [15].

Closer inspection of the spectroscopic data reveals some differences between the dimethylphenylphosphonium and triphenylphosphonium derivatives. The 1:1:1 patterns in the ^{1}H NMR spectra of the methine protons on the Tp′ ligand are significantly more dispersed in spectra of the triphenylphosphonium derivatives (**6b**, **7b**, **8b**). One of the Tp′ methine protons resonates unusually far upfield, near 5.0 ppm, probably due to shielding by the phenyl rings of the triphenylphosphine substituent (c.f. crystal structures, vide infra). The two signals from the diastereotopic phosphine methyl groups of PMe_2Ph complex **6a** are differentiated from Tp′ methyl signals by phosphorus coupling. Ketenyl products generated from dimethylphenylphosphonium carbyne complex **5a** resonate near 15 ppm in ^{31}P NMR spectra, while those generated from triphenylphosphonium complex **5b** resonate near 20 ppm. Crystal structures of η^2-ketenyl *p*-nitrophenoxide/dimethylphenylphosphine adduct **6a** and η^2-ketenyl *p*-cyanophenoxide/triphenylphosphine adduct **7b** reveal that the ketenyl orientation positions the phosphine substituents proximal to the Tp′ ligand. A single rotomer of the phosphoranylideneketene is observed in solution for all ketenyl products.

3.2. Product ratios of aryloxy substituted carbyne complexes and η^2-ketenyl coupled products generated from phosphonium carbyne complexes

While monitoring the formation of ketenyl product **6b** (absorptions at 1872 and 1710 cm^{-1}) from $[Tp'(CO)_2W{\equiv}CPPh_3]^+$ and $K[p\text{-}OC_6H_4NO_2]$ by IR spectroscopy, an absorption consistent with the presence of $Tp'(CO)_2W{\equiv}CO(p\text{-}C_6H_4NO_2)$ (**9a**) was observed at 1972 cm^{-1}. (The companion dicarbonyl asymmetric stretch from the aryloxycarbyne complex at 1880 cm^{-1} is obscured by the 1872 cm^{-1} absorption of the ketenyl product.) Observation of the 1972 cm^{-1} IR signal of the carbyne complex prompted a control experiment where phosphonium carbyne complex **5b** and *p*-nitrophenoxide were stirred for 20 h in THF, and then a ^{1}H NMR spectrum was obtained of the residue remaining after solvent removal. The spectrum revealed a product ratio of approximately 60:1 η^2-ketenyl complex:aryloxycarbyne product (**6b** to **9a**), based on integration of the methine and methyl proton signals. The syntheses of the η^2-ketenyl complexes **6a**, **7a**, **7b**, and **8b** were reproduced under the same standardized conditions. The ratio of the starting materials (1.5:1 aryloxide nucleophile:cationic carbyne complex) was held constant, and all of the reactions were stirred in THF for 20–24 h before solvent removal. The product ratios determined by NMR are listed in Table 2.

Table 2
Product ratios from phosphine substitution and carbonyl–carbyne ligand coupling in phosphonium carbyne complexes

K[*p*-OC_6H_4R] R =	$[Tp'(CO)_2WCPMe_2Ph]$-$[PF_6]$ (carbyne:η^2-ketenyl)	$[Tp'(CO)_2WCPPh_3]$-$[PF_6]$ (carbyne:η^2-ketenyl)
OCH_3	carbyne only	carbyne only
CH_3	carbyne only	carbyne only
H	carbyne only	carbyne only
Cl	carbyne only	6:1
CN	1:2	1:5
NO_2	1:3	1:60

In contrast to the results with electron poor aryloxide reagents, the reaction of *p*-methoxyphenoxide with phosphonium carbyne complex **5a** produced only *para*-methoxyphenoxycarbyne complex **9f**. The *p*-nitro substituent on an aryloxide reduces the nucleophilicity of the oxide oxygen while the *p*-methoxy substituent increases the nucleophilicity of the oxide oxygen. Likewise, only aryloxycarbyne product was observed from the reactions of **5a** with phenoxide and *p*-chlorophenoxide. No η^2-ketenyl coupled complexes were detected in reactions of **5b** with phenoxide or *p*-chlorophenoxide or *p*-methoxyphenoxide.

Formation of η^2-ketenyl coupled products (P_1) and aryloxycarbyne products (P_2) was not reversible, so the product distribution reflects the ratio of the rates of formation of the two products. This linear free energy relationship can be probed by plotting $\log([P_1]/[P_2])$ versus σ_{para} for the three aryloxide reagents where both products (P_1 and P_2) could be detected from the reaction with $Tp'(CO)_2W{\equiv}CPPh_3][PF_6]$ (**5b**). The plot reveals a general trend toward less ketenyl product as the electron donating power of the *para*-substituent increases (Fig. 2). Even from a qualitative perspective it is predictable that no ketenyl product was detected for the reaction of **5b** with potassium phenoxide, and indeed the plot extrapolates to roughly 100:1 favoring the aryloxycarbyne at $\sigma_{para} = 0$. The points representing the reactions of **5a** with *p*-cyanophenoxide and *p*-nitrophenoxide are below the points for the reactions of **5b** with potassium aryloxides. Therefore, it is not surprising that no ketenyl product was detected from the reaction of *p*-chlorophenoxide with **5a**. These results are consistent with the mechanism in Scheme 4.

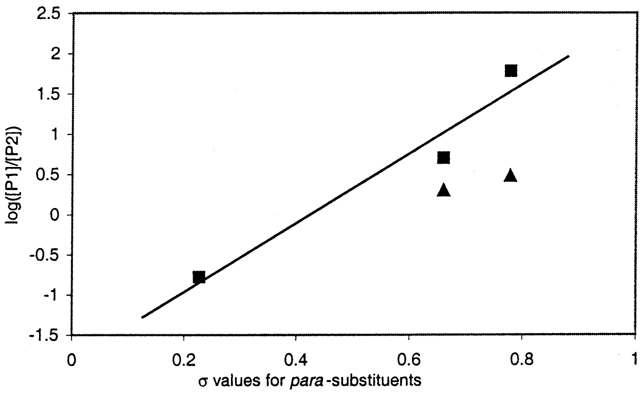
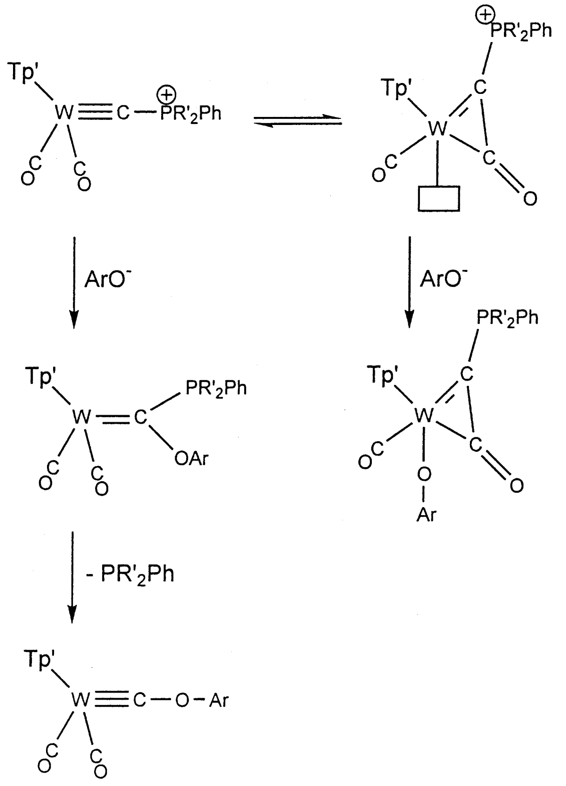


Fig. 2. Plot of log([ketene]/[carbyne]) versus σ_{para}. Reactions with **5a** are represented by triangles (▲) and reactions of **5b** are represented by squares (■).



Scheme 4.

3.3. *Reactivity trends between the dimethylphenylphosphonium carbyne (5a) and triphenylphosphonium carbyne (5b) complexes*

A larger proportion of substituted carbyne product is formed in reactions with **5a** ($[W]\equiv CPMe_2Ph^+$) ($[W]=Tp'(CO)_2W$) than with **5b** ($[W]\equiv CPPh_3{}^+$). The difference in product ratios may be due to the greater steric bulk of the $[W]\equiv CPPh_3{}^+$ reagent, with the bulky PPh_3 substituent inhibiting nucleophilic attack at the carbyne carbon. Electronic factors, such as electron density at the carbyne carbon or the ability of the phosphine to act as a leaving group, seem incompatible with the observed product ratios. Greater electron density at the carbyne carbon of **5a** ($[W]\equiv CPMe_2Ph^+$) would reduce the electrophilicity of that site and more η^2-ketenyl coupled product would be expected. This is not observed. Dimethylphenylphosphine is expected to be a poorer leaving group than triphenylphosphine, but more carbyne product forms in reactions with **5a**. Although steric factors are compatible with more substitution at the carbyne carbon with PMe_2Ph in the reagent and more coupling product formation with PPh_3 in the reagent, the determinants of product distribution remain debatable.

3.4. *Attempts to detect η^2-ketenyl coupled product in reactions of phosphonium carbyne complex **5** with phenoxide, p-methylphenoxide, and p-methoxyphenoxide*

The η^2-ketenyl coupled products (**6**–**8**) each have one strong IR carbonyl stretching absorption for the W–CO unit located somewhere between 1861 and 1875 cm^{-1}. The less intense ketenyl CO absorption occurs at lower energy, between 1706 and 1722 cm^{-1}. The aryloxy carbyne products (**9**) have symmetric and antisymmetric CO vibrations near 1970 and 1870 cm^{-1}. Because the antisymmetric carbonyl stretch is strongly absorbing in the IR region, attempting to determine the presence of η^2-ketenyl product by IR spectroscopy is difficult due to overlap in the 1870 cm^{-1} region. The IR spectrum of the reaction products is further complicated by aryl C–H stretching overtones [16] that absorb in the same region as the ketenyl carbonyl (e.g. an absorption is observed at 1714 cm^{-1} for free PPh_3). When complex **5** was reacted with the phenoxides with hydrogen, methyl, and methoxy in the *para*-position, the major products were **9d**, **9e**, and **9f**, respectively, and no η^2-ketenyl coupled product was observed. The aryloxy carbyne products were isolated in low yields and identified by NMR based on literature values [9].

3.5. *Molecular structures of $Tp'(CO)(p\text{-}OC_6H_4NO_2)W(\eta^2\text{-}(C,C)\text{-}O{=}CC\text{-}PMe_2Ph)$ (6a) and $Tp'(CO)(p\text{-}OC_6H_4CN)W(\eta^2\text{-}(C,C)\text{-}O{=}CC\text{-}PPh_3)$ (7b)*

ORTEP drawings of the solid-state molecular structures of **6a** and **7b** are shown in Figs. 3 and 4, respectively; selected bond distances and angles are shown in Tables 3 and 4. Each complex can be described as a distorted octahedron if the η^2-ketenyl ligand is considered to occupy a single coordination site.

The bonding parameters of the phosphoranylideneketene ligands in **6a** and **7b** are congruent with the ligand geometry in $Cl_2(PMePh_2)_2(CO)W(\eta^2\text{-}C(PMePh_2)CO)$ reported by Hillhouse [17,18]. Short W(1)–C(3) bond lengths (1.998(11) Å (**6a**), 2.031(6) Å

(**7b**)) suggest a multiple bond. Typical η^2-ketenyl W=C bond distances (where C is the carbon adjacent to the carbonyl) are on the order of 1.97–2.0 Å, whereas η^1-ketenyls have M–C bond lengths in the range of 2.2–2.3 Å [15,19]. Even the W(1)–C(2) interatomic distances of 2.212(11) Å (**6a**) and 2.185(6) Å (**7b**) are shorter than W–C$_{\text{benzyl}}$ single bonds (i.e. $r_{\text{W–C}} = 2.28(7)$ Å (avg.) in $Cp_2W(CH_2Ph)_2$ [20]). C(2)–C(3) distances of 1.285(16) Å (**6a**) and 1.362(9) Å (**7b**) are comparable to other η^2-ketenyl C–C bonds (1.323(9) Å in (dppe)(detc)(CO)W(η^2-C(CH$_2$Ph)CO) [21], 1.37(1) Å in Cl$_2$(PMePh$_2$)$_2$(CO)W(η^2-C(PMePh$_2$)CO) [15,19], 1.32(4) Å in Cp(CO)(PMe$_3$)W(η^2-C(p-tol)CO) [22]. The C(3)–P(1) distances of 1.743(11) Å (**6a**) and 1.721(6) Å (**7b**) reflect bonding of a formal phosphonium substituent to a carbon nucleus [9], and the C(2)–O(2) bond lengths (1.211(15) Å (**6a**) and 1.226(8) Å (**7b**)) are typical of η^2-ketenyl C=O distances [15,19].

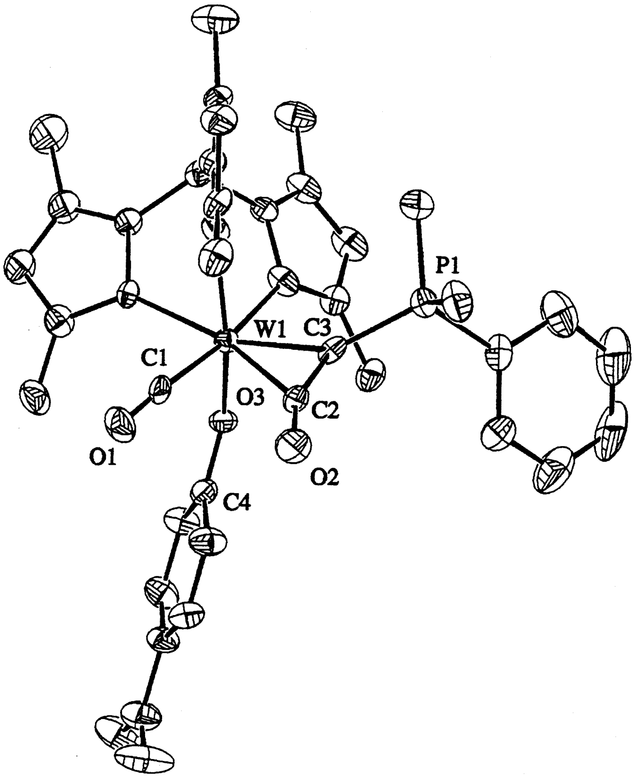


Fig. 3. Thermal ellipsoid representation of **6a**.

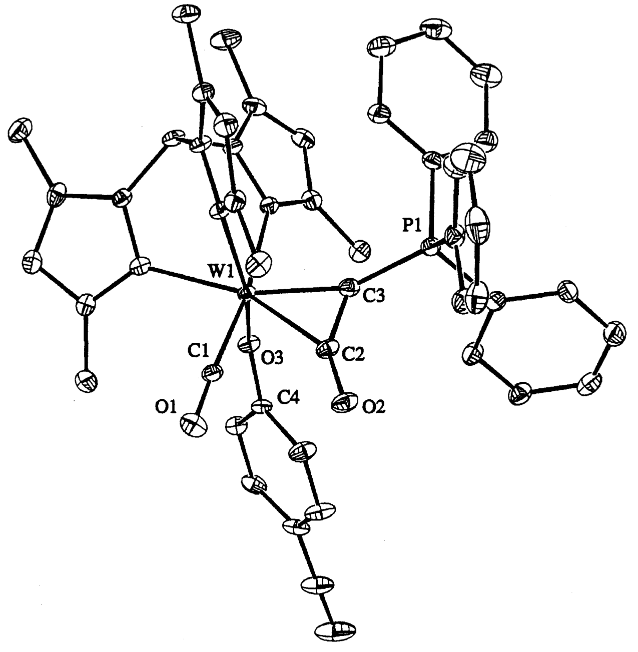


Fig. 4. Thermal ellipsoid representation of **7b**.

Table 3
Selected bond distances (Å), angles (°), and torsion angles for **6a**

Bond distances			
W(1)–C(1)	1.872(13)	C(2)–C(3)	1.285(16)
W(1)–O(3)	2.016(7)	C(2)–O(2)	1.211(15)
W(1)–C(2)	2.212(11)	C(3)–P(1)	1.743(11)
W(1)–C(3)	1.998(11)	O(3)–C(4)	1.317(13)
Bond angles			
C(1)–W(1)–O(3)	97.0(4)	O(2)–C(2)–C(3)	152.1(11)
W(1)–O(3)–C(4)	134.4(7)	W(1)–C(3)–C(2)	81.6(7)
W(1)–C(2)–O(2)	144.5(8)	W(1)–C(3)–P(1)	143.5(7)
W(1)–C(2)–C(3)	63.3(7)	C(2)–C(3)–P(1)	132.0(9)
Torsion angles			
O(2)–C(2)–C(3)–P(1)		+13.5(5)	
C(1)–W(1)–C(2)–C(3)		+12.7(11)	

Table 4
Selected bond distances (Å), angles (°), and torsion angles for **7b**

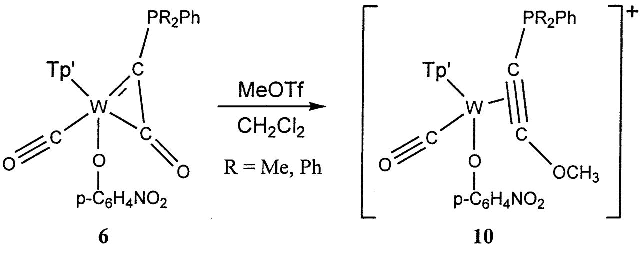
Bond distances			
W(1)–C(1)	1.927(6)	C(2)–C(3)	1.362(9)
W(1)–O(3)	2.021(4)	C(2)–O(2)	1.226(8)
W(1)–C(2)	2.185(6)	C(3)–P(1)	1.721(6)
W(1)–C(3)	2.031(6)	C(4)–O(3)	1.333(7)
Bond angles			
C(1)–W(1)–O(3)	94.96(22)	O(2)–C(2)–C(3)	147.0(6)
W(1)–O(3)–C(4)	135.1(4)	W(1)–C(3)–C(2)	77.4(4)
W(1)–C(2)–O(2)	147.8(5)	W(1)–C(3)–P(1)	155.5(4)
W(1)–C(2)–C(3)	65.1(4)	C(2)–C(3)–P(1)	126.1(5)
Torsion angles			
O(2)–C(2)–C(3)–P(1)		−11.5(4)	
C(1)–W(1)–C(2)–C(3)		+6.6(5)	

A slight twisting of the η^2-ketenyl (or metallacyclopropanone) moiety from a parallel alignment with the terminal tungsten–carbonyl axis is seen (C(1)–W(1)–C(3)–C(2) = 12.7(11)° (**6a**), 6.6(5)° (**7b**)). The four-atom ketenyl O–C–C–P linkage is slightly distorted from planarity (O(2)–C(2)–C(3)–P(1) = 13.5(5)° (**6a**), − 11.5(4)° (**7b**)). A rationale for the preferential orientation of the ketenyl CO proximal to the terminal carbonyl ligand in d^4 L$_n$(CO)M complexes has been published [23], and the donor properties of ketenyl ligands bound to d^4 metal fragments have been described [21]. The orientation of the η^2-ketenyl ligand in both **6a** and **7b** reflects the ability of this unsaturated ligand to interact constructively with the d orbitals of the d^4 W(II) center [24].

The four metal based electrons reside in two d_π orbitals directed toward the π-acid CO ligand. One aryloxide lone pair residing in an orbital of largely oxygen p character is aligned to interact with the lone empty d_π orbital of tungsten. The W–O–C bond angle at O(3) is 134.4(7)° for **6a** and 135.1(4)° for **7b**; hybridization at O(3) is between sp^2 and sp. The torsion angles (absolute values) defined by C(1)–W(1)–O(3)–C(4) (18.3(6)° (**6a**) and 34.5(5)° (**7b**)) position the oxygen lone pair with more p character so that donation to the vacant d_π orbital is possible. Bond lengths of 2.016(7) Å (**6a**) and 2.021(4) Å (**7b**) for the tungsten–alkoxide bonds are in the typical range for W(VI) d^0 complexes, suggesting that some π-donation from the aryloxide ligand to tungsten is present [25,26].

*3.6. Nucleophilicity of the neutral η²-ketenyl complexes: formation of [Tp′(CO)(p-OC₆H₄NO₂)-W(η²-MeOCCPMe₂Ph)][OTf] (**10a**) and [Tp′(CO)(p-OC₆H₄NO₂)W(η²-MeOCCPPh₃)][OTf] (**10b**)*

Electrophilic addition to the oxygen of η^2-ketenyl ligands is a well-established route to alkoxyalkyne complexes [15,19,24]. Addition of methyl triflate to an olive-green CH_2Cl_2 solution of either neutral η^2-ketenyl complex **6a** or **6b** at −78 °C followed by warming to 25 °C generated bright green cationic methoxyalkyne complexes **10a** and **10b**, respectively, affirming the nucleophilic character of the ketenyl oxygen (Scheme 5). A shift in the frequency of the lone terminal metal carbonyl stretch of the η^2-ketenyl complexes (ν_{CO} **6a**, 1869 cm^{-1}; **6b**, 1872 cm^{-1}) to a higher frequency in the monocarbonyl alkyne complex (ν_{CO} **10a**, 1942 cm^{-1}; **10b**, 1945 cm^{-1}) accompanies the transformation, and the η^2-ketenyl CO stretch of the reagents (**6a**, 1718 cm^{-1}; **6b**, 1710 cm^{-1}) disappears. Recrystallization of the reaction mixture from CH_2Cl_2/Et_2O provided a 71% isolated yield of the cationic alkyne complex **10a**. The reaction product containing **10b** required chromatography on alumina prior to recrystallization from CH_2Cl_2/Et_2O, which provided light green crystals of **10b** in 48% yield.



Scheme 5.

^1H NMR analysis of the crude reaction residue of **10a** indicated the presence of two isomers of the cationic alkyne product in a 5:2 ratio. Following recrystallization, however, only those signals corresponding to the major isomer were observed. We believe the two isomers reflect two possible orientations of the alkyne ligand, one in which the phosphonium substituent resides close to the Tp′ pyrazole rings, and the other in which the methoxy group is proximal to the Tp′ ligand. The triphenylphosphine substituent in **10b** is larger than the PMe_2Ph moiety of **10a** and only one isomer of **10b** is observed. In addition to aromatic signals due to the phosphorus-bound phenyl group and aryloxide ligands, distinct signals for each Tp′ pyrazole indicate C_1 symmetry for **10a** and **10b**. Diastereotopic phosphine methyl doublets (δ 1.81 ppm, $^2J_{P-H} = 15$ Hz; 1.64 ppm, $^2J_{P-H} = 14$ Hz) are observed for **10a**. The methoxy group on the alkyne ligand appears as a singlet at 4.40 ppm for **10a** and as a singlet at 4.17 ppm for **10b**.

Phosphorus coupled doublets at 226 ppm ($^2J_{P-C} = 16$ Hz) and 117 ppm ($^1J_{P-C} = 112$ Hz) in the ^{13}C NMR spectrum are assigned to the methoxy-bearing and phosphonium-bearing alkyne carbons of **10a**, respectively (231 ppm ($^2J_{P-C} = 17$ Hz) and 121 ppm ($^1J_{P-C} = 321$ Hz) for **10b**). The coupling between the phosphorus and the directly connected alkyne carbon in **10b** is unusually large, however phosphorus–carbon single-bond coupling is known to approach 450 Hz [27]. Two compounds that are similar in P–C linkage structure to the alkyne ligand are ketenylidenetriphenylphosphorane ($Ph_3P{=}C{=}C{=}O$), which has a $^1J_{P-C} = 190$ Hz [28] and the carbodiphosphorane $(Me_2N)_3P{=}C{=}P(NMe_2)_3$, which has a $^1J_{P-C} = 304.7$ Hz [29]. As in the case of ketenyl complexes **6a** and **6b**, the phosphonium-bearing alkyne carbon resonance occurs at unusually high field for a coordinated four-electron donor alkyne complex [24]. The terminal carbonyl resonates at 229 ppm ($^1J_{W-C} = 150$ Hz, $^3J_{P-C} = 3$ Hz) for **10a** and at 229 ppm ($^3J_{P-C} = 3$ Hz) for **10b**. The methoxide substituent on the alkyne gives rise to a ^{13}C NMR singlet at 70 ppm for **10a** and at 68.5 ppm for **10b**, and diastereotopic methyl doublets from the phosphonium group of **10a** appear at 12.8 and 11.3 ppm ($^1J_{P-C} = 61$ Hz).

*3.7. Molecular structure of [Tp′(CO)(p-OC₆H₄NO₂)-W(η²-MeOC≡CPMe₂Ph)][OTf] (**10a**)*

An ORTEP drawing of the solid-state molecular structure of **10a** is shown in Fig. 5; selected bond distances and angles are shown in Table 5. The complex is pseudo-octahedral if the alkyne ligand is considered to occupy only a single coordination site.

The orientation and geometry of the alkyne ligand are consistent with expectations for η^2-alkyne coordina-

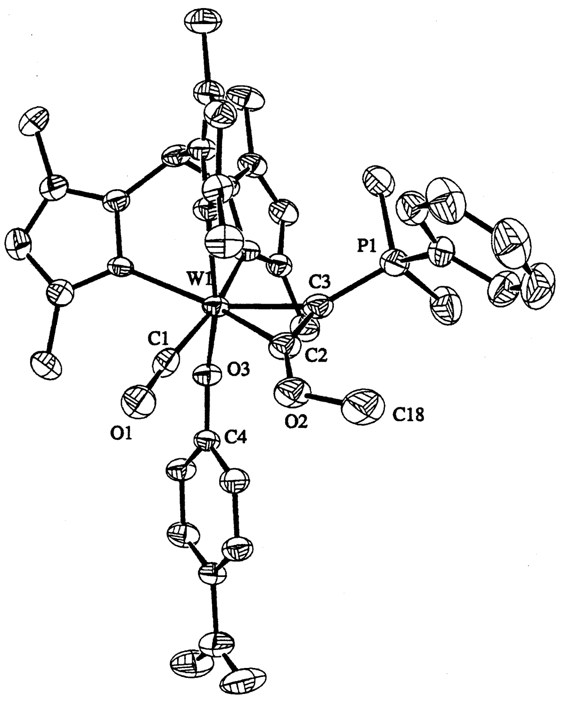


Fig. 5. Thermal ellipsoid representation of **10a**.

Table 5
Selected bond distances (Å) and angles (°) for **10a**

Bond distances			
W(1)–C(1)	1.960(8)	C(2)–O(2)	1.335(9)
W(1)–O(3)	2.009(5)	C(3)–P(1)	1.748(8)
W(1)–C(2)	2.042(8)	P(1)–C(10)	1.774(10)
W(1)–C(3)	2.077(8)	P(1)–C(11)	1.777(10)
C(2)–C(3)	1.320(11)	P(1)–C(12)	1.799(8)
Bond angles			
C(1)–W(1)–O(3)	92.7(3)	C(3)–C(2)–O(2)	144.3(8)
W(1)–O(3)–C(4)	133.7(4)	W(1)–C(3)–C(2)	69.8(5)
W(1)–C(2)–O(2)	142.7(6)	W(1)–C(3)–P(1)	145.2(4)
W(1)–C(2)–C(3)	72.8(5)	C(2)–C(3)–P(1)	141.5(7)

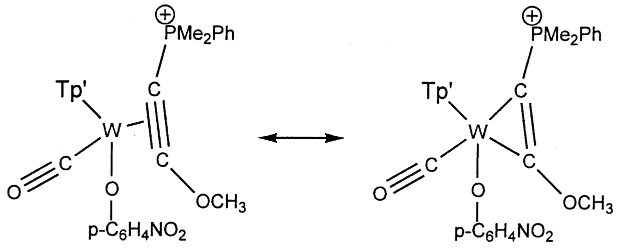
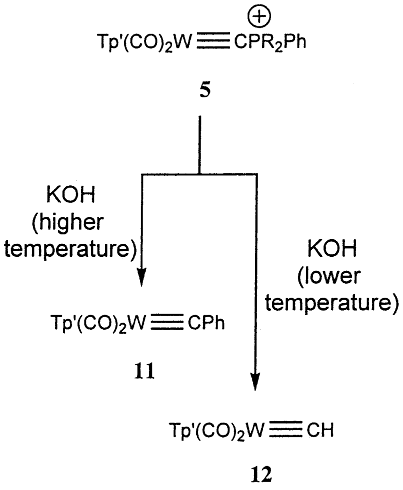


Fig. 6.

tion in d^4 L(CO)M(η^2-alkyne)X complexes [22–24]. The unusual alkyne ligand is bound to the tungsten nucleus with tungsten–carbon distances typical of η^2-alkyne coordination (W(1)–C(2) = 2.042(8) Å; W(1)–C(3) = 2.077(8) Å) [30]. The four electron-donor alkyne ligand displays an elongated C(2)–C(3) bond distance (1.320(11) Å) relative to free alkynes [31]. Bond angle summations of 360° about C(2) and 357° about C(3) indicate essentially planar geometries at the alkyne carbons, consistent with the bonding scenario for d^4 L(CO)M(η^2-RC≡CR′)X complexes [24]. The two most significant resonance contributors are shown Fig. 6.

3.8. Related reactions: formation of Tp′(CO)$_2$W≡CPh (**11**), and Tp′(CO)$_2$W≡CH (**12**)

Two additional tungsten carbyne byproducts deserve mention. An orange side product, Tp′(CO)$_2$W≡CPh (**11**), is commonly observed during reactions of phosphonium carbyne complex **5** with nucleophiles [32,33].[3] A methylidyne complex, Tp′(CO)$_2$W≡CH (**12**), definitively identified based on comparison with literature data, was also isolated from some aryloxide addition reactions [11]. Both side products probably result from similar intermediates. Quaternary phosphonium salts are known to react with hydroxide in organic solvents to give a dissociated alkyl anion or a product resulting from a 1,2-phenyl migration (Scheme 6) [34]. The most stable carbanion typically dissociates [35], and for triphenyl phosphonium carbyne complex **5b** one possible dissociating carbanion could be the anionic carbide complex. At low temperature (−78 °C), phenyl migration seems to be inhibited and only the protonated carbide dissociation product, **12**, was observed for the reaction with *p*-cresolate (K[*p*-OC$_6$H$_4$CH$_3$]). Solid potassium hydroxide was combined with a solution of [Tp′(CO)$_2$W≡CPPh$_3$][PF$_6$] in THF at −78 °C and no reaction occurred until the solution was warmed (sodium hydroxide is virtually insoluble in THF) and



Scheme 6.

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[3] Tp′(CO)$_2$WCPh is the tungsten analog of the molybdenum complex Tp′(CO)$_2$MoCPh which has been reported in Refs. [32,33].

then the reaction proceeded slowly. At room temperature, $Tp'(CO)_2W{\equiv}CPh$ and $Tp'(CO)_2W{\equiv}CH$ carbyne complexes were formed in approximately equal amounts. Rigorous exclusion of water during the preparation of potassium aryloxide and drying the phosphonium carbyne complex in vacuo reduced the amount of phenyl and C–H carbyne products to undetectable levels.

4. Summary

Tungsten η^2-phosphoranylideneketene and aryloxy carbyne complexes have been synthesized from phosphonium carbyne precursors. The product ratio of phosphine replacement by aryloxide at the carbyne carbon to carbonyl coupling products can be tuned by variation of the aryloxy *para*-substituent in order to tune the aryloxide nucleophilicity. Aryloxy carbyne complexes are the favored products with stronger nucleophiles. Weaker nucleophiles result in a mixture of aryloxy carbyne complexes and η^2-ketenyl coupled complexes. Formation of η^2-ketenyl complexes is favored for the least nucleophilic aryloxides. Methylation of two neutral η^2-ketenyl complexes to form cationic methoxy alkyne complexes was accomplished, in accord with the anticipated nucleophilicity of the ketenyl oxygen.

5. Supplementary material

Complete tables of atomic parameters, anisotropic temperature factors, bond distances, and bond angles for **6a**, **7b**, and **10a** as well as drawings with numbering schemes are available (37 pages). Torsion angles are also provided for **6a** and **7b**. Ordering information is available on any current masthead page.

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