Protonation and Alkylation Reactions at Phosphaalkenyl Carbyne Complexes $Tp'(CO)_2M{\equiv}C{-}P{=}C(NR'_2)_2$ [$Tp' = HB(3,5\text{-}Me_2C_3HN_2)_3$; M = Mo, W; R = Me, Et][†,1]

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Reaction of the carbyne complexes $Tp'(CO)_2M{\equiv}C{-}P{=}C(NR_2)_2$ (**1**, **2**) [$Tp' = HB(3,5\text{-}Me_2C_3\text{-}HN_2)_3$; M = Mo (**1**, **3**); W (**2**, **4**); R = Me (a); Et (b)] with methyl trifluoromethanesulfonate afforded the orange-red salts $[Tp'(CO)_2M{\equiv}C{-}P(Me)C(NR_2)_2]SO_3CF_3$ (**3**, **4**), the cations of which can be considered as methylphosphines featuring additional bisaminocarbenium- and metallaalkynyl substituents. Analogously, complex $Tp'(CO)_2W{\equiv}C{-}P{=}C(NEt_2)_2$ (**2b**) was protonated with ethereal HBF_4 in ether at the phosphorus atom to give $[Tp'W{\equiv}C{-}P(H){-}C(NEt_2)_2]BF_4$ (**5**), which in CH_2Cl_2 solution experienced a clean rearrangement to the metallaphosphirene $[Tp'(CO)_2\overline{W{=}C(H)P}C(NEt_2)_2]BF_4$ (**6**). Treatment of **2b** with F_3CSO_3H led directly to $[Tp'(CO)_2\underline{W{=}C(H){-}P}C(NEt_2)_2]SO_3CF_3$ (**6′**). The molecular structures of **4b** and **6′** were established by X-ray structure analysis.

Introduction

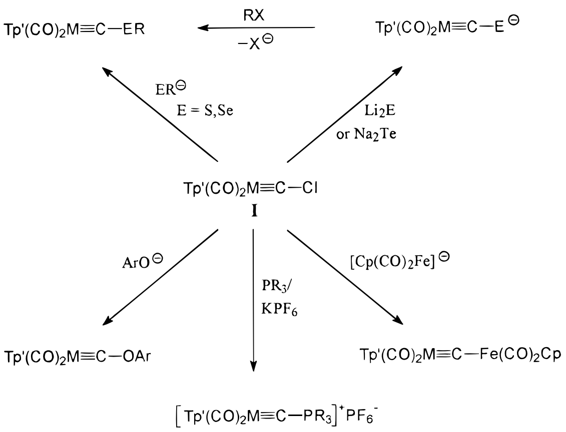
A general and powerful approach to heteroatom-substituted molybdenum and tungsten carbyne complexes is based upon chloride displacement in Lalor's chlorocarbyne complexes **I**[2] by a variety of anionic as well as neutral nucleophiles. Alkyl and aryl sulfides,[3] phenylselenide,[3] aryloxides,[4] $[Cp(CO)_2Fe]^-$,[5] and phosphines[4] have all been shown to displace chloride in $Tp'(CO)_2M{\equiv}CCl$ (M = Mo, W) with the formation of new carbyne complexes (Scheme 1).

Methylthiocarbyne, methylselenocarbyne, and methyltellurocarbyne complexes are also available by reacting **I** with Li_2S, Li_2Se, or Na_2Te and subsequent methylation of the anionic carbon monochalcogenide complexes.[3]

Recently we reported the synthesis of phosphaalkenyl-functionalized carbyne complexes by condensation of **I** with P-silylated phosphaalkenes $Me_3SiP{=}C(NR_2)_2$ (R = Me, Et) (Scheme 2).[6]

Complexes **1a**,**b** and **2a**,**b** exhibit a remarkable nucleophilicity at the phosphorus atom as evidenced by the facile oxidation with dioxygen to afford the first carbyne complexes functionalized by a zwitterionic α-carbenium phosphinate group $[Tp'(CO)_2M{\equiv}C{-}P(O)_2{-}C(NR_2)_2]$.[1]

Scheme 1



Angelici et al. investigated the protonation of methylthiocarbyne complexes which occurred at the carbyne carbon atom with formation of η^2-methylthiocarbene complexes[7,8] (Scheme 3).

Herein we describe our results on the protonation and alkylation of the phosphaalkenyl carbyne complexes **1** and **2** (M = Mo, W; R = Me, Et).

Experimental Section

All operations were performed with standard Schlenk techniques in an oxygen-free Ar atmosphere. Solvents were

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[†] Dedicated to Professor Edgar Niecke, University of Bonn, on the occasion of his 60th birthday.

(1) Part 36: Weber, L.; Dembeck, G.; Stammler, H. G.; Neumann, B. *Eur. J. Inorg. Chem.* **1998**, 579−582.

(2) Desmond, T.; Lalor, F. J.; Ferguson, G.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1983**, 457−459.

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(5) Etienne, M.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1991,** *113*, 2324−2325.

(6) Weber, L.; Dembeck, G.; Boese, R.; Bläser, D. *Chem. Ber./Recueil* **1997**, *130*, 1305−1308.

(7) Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1984**, *3*, 1124−1126.

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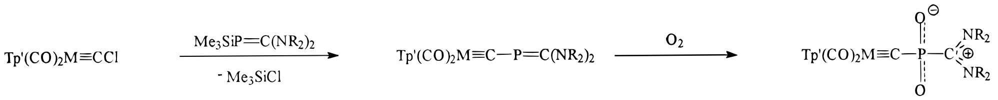
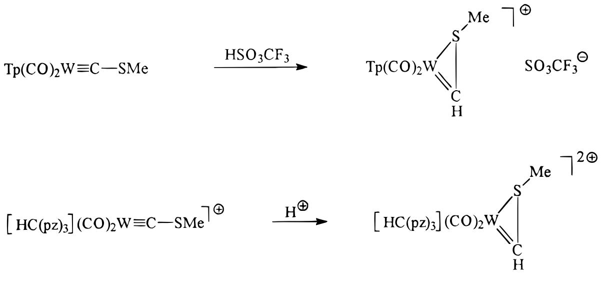
Scheme 2



	M	R
1a	Mo	Me
2a	W	Me
1b	Mo	Et
2b	W	Et

Scheme 3



pz = pyrazolyl

Tp = $HB(C_3H_3N_2)_3$

dried by standard methods and freshly distilled under argon. Infrared spectra were recorded on a Bruker FT-IR IFS66 spectrometer, and the ^1H, ^{13}C, and ^{31}P NMR spectra were taken in CD_2Cl_2 on Bruker AM Avance DRX 500, Bruker AC 250P, and Bruker AC 100 instruments, standards: $SiMe_4$ (^1H, ^{13}C) and external 85% H_3PO_4 (^{31}P). Elemental analyses were performed in the microanalytical laboratory of the University of Bielefeld. Mass spectra were obtained with a VG Autospec sector-field mass spectrometer (micromass). Literature methods were used to prepare $Tp'(CO)_2M{\equiv}C{-}P{=}C(NR_2)_2$ (Mo, W; R = Me, Et).[6] Ethereal HBF_4, trifluormethanesulfonic acid, and methyl triflate were purchased commercially.

Preparation of Compounds. [$Tp'(CO)_2Mo{\equiv}C{-}P(Me){-}C(NMe_2)_2$]$SO_3CF_3$ (3a). A solution of methyl triflate (0.14 g, 0.84 mmol) in diethyl ether (30 mL) was added dropwise to a chilled solution (−78 °C) of $Tp'(CO)_2Mo{\equiv}C{-}P{=}C(NMe_2)_2$ (**1a**) (0.50 g, 0.84 mmol) in 1250 mL of diethyl ether, whereupon the color of the solution changed from crimson to light orange. The reaction mixture was allowed to warm to ambient temperature. A light red precipitate separated, which was filtered off after 90 min of stirring. After washing with diethyl ether (3 × 20 mL) the product was dried in vacuo (10^{-3} Torr) overnight. Crude **3a** was dissolved in 10 mL of CH_2Cl_2. Diethyl ether (10 mL) was added to induce crystallization. After 24 h pure **3a** was obtained as orange crystals (0.53 g, 84% yield). IR (KBr): 2553 w [ν(BH)], 1997 vs [ν(CO)], 1915 vs [ν(CO)] cm^{-1}. ^1H NMR: δ 1.89 (d, $^2J_{PH}$ = 4.3 Hz, PCH_3), 2.34 (s, 3H, $Tp'CH_3$), 2.35 (s, 3H, $Tp'CH_3$), 2.41 (s, 6H, $Tp'CH_3$), 2.51 (s, 6H, $Tp'CH_3$), 3.44 (s, 12H, NCH_3), 5.80 (s, Tp′CH), 5.98 (s, 2H, Tp′CH). $^{13}C\{^1H\}$ NMR: δ 9.54 (d, $^1J_{PC}$ = 17.7 Hz, PCH_3), 12.81 (s, $Tp'CCH_3$), 14.66 (s, $Tp'CCH_3$), 16.27 (s, $Tp'CCH_3$), 45.1 (s, NCH_3), 106.80 (s, Tp′CH), 121.30 (q, $^1J_{FC}$ = 320.0 Hz, CF_3), 146.05 (s, $Tp'CCH_3$), 146.53 (s, $Tp'CCH_3$), 150.82 (s, $Tp'CCH_3$), 152.07 (s, $Tp'CCH_3$), 177.65 (d, $^1J_{PC}$ = 45.9 Hz, PCN_2), 226.93 (s, CO), 287.68 (d, $^1J_{PC}$ = 94.2 Hz, Mo≡C). $^{31}P\{^1H\}$ NMR: δ 18.32 s. MS (LSIMS, *p*-nitrobenzyl alcohol matrix): 607 (M − SO_3CF_3). Anal. Calcd for $C_{25}H_{37}BF_3MoN_8O_5PS$ (756.41): C, 39.69; H, 4.93; N, 14.81. Found: C, 38.94; H, 4.92; N, 14.37.

[$Tp'(CO)_2Mo{\equiv}C{-}P(Me){-}C(NEt_2)_2$]$SO_3CF_3$ (3b). Analogously, a solution of $Tp'(CO)_2Mo{\equiv}C{-}P{=}C(NEt_2)_2$ (**1b**) (0.38 g, 0.59 mmol) in diethyl ether (400 mL) at −78 °C was reacted with a solution of methyl triflate (0.09 g, 0.59 mmol) in diethyl ether (50 mL). A light yellow precipitate was separated by filtration and washed with ether (2 × 10 mL) and *n*-pentane (2 × 10 mL). After drying overnight in vacuo (10^{-3}) Torr), the precipitate was dissolved in CH_2Cl_2 (10 mL). Crystallization was effected by adding 10 mL of diethyl ether and storing overnight. Product **3b** was isolated as orange crystals (0.33 g, 70% yield). IR (KBr): 2558 w [ν(BH)], 1994 vs [ν(CO)], 1903 vs [ν(CO)] cm^{-1}. ^1H NMR: δ 1.31 (t, $^3J_{HH}$ = 7.1 Hz, 12H, CH_2CH_3), 1.82 (d, $^2J_{PH}$ = 4.6 Hz, PCH_3), 2.33 (s, 3H, $Tp'CH_3$), 2.34 (s, 3H, $Tp'CH_3$), 2.40 (s, 6H, $Tp'CH_3$), 2.52 (s, 6H, $Tp'CH_3$), 3.82 (q, $^3J_{HH}$ = 7.1 Hz, 8H, CH_2CH_3), 5.79 (s, 1H, Tp′CH), 5.97 (s, 1H, Tp′CH). $^{13}C\{^1H\}$ NMR: δ 10.35 (d, $^1J_{PC}$ = 17.5 Hz, PCH_3), 12.84 (s, $Tp'CH_3$), 13.69 (s, CH_2CH_3), 14.64 (s, $Tp'CH_3$), 16.65 (s, $Tp'CH_3$), 48.67 (s, CH_2CH_3), 106.78 (s, Tp′CH), 107.05 (s, Tp′CH), 121.34 (q, $^1J_{FC}$ = 321.7 Hz, CF_3), 146.03 (s, $Tp'CCH_3$), 146.58 (s, $Tp'CCH_3$), 150.70 (s, $Tp'CCH_3$), 152.04 (s, $Tp'CCH_3$), 178.72 (d, $^1J_{PC}$ = 46.9 Hz, PCN_2), 227.15 (s, CO), 286.67 (d, $^1J_{PC}$ = 97.0 Hz, Mo≡C). $^{31}P\{^1H\}$ NMR: δ 18.74 s. MS/CI: 664 (M − $SO_3CF_3^-$). Anal. Calcd for $C_{29}H_{45}BF_3MoN_8O_5PS$ (812.50): C, 42.87; H, 5.58; N, 13.79. Found: C, 42.76; H, 5.77; N, 15.50.

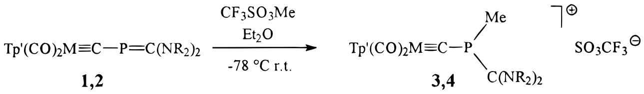
[$Tp'(CO)_2W{\equiv}C{-}P(Me){-}C(NMe_2)_2$]$SO_3CF_3$ (4a). A solution of 0.12 g, (0.74 mmol) of methyl triflate in 50 mL of diethyl ether was added dropwise to a chilled solution (−78 °C) of $Tp'(CO)_2W{\equiv}C{-}P{=}C(NMe_2)_2$ (**2a**) (0.50 g, 0.74 mmol) in 200 mL of a 3:1 mixture of diethyl ether and CH_2Cl_2, whereupon a color change from red to light orange was observed. The reaction mixture was allowed to warm to ambient temperature, and was then concentrated to ca. 100 mL. A light red solid was precipitated by slow addition of *n*-hexane (100 mL). It was filtered, and the filter cake was washed (3 × 10 mL of diethyl ether and 3 × 10 mL of *n*-pentane). After drying overnight at 10^{-3} Torr the crude product was crystallized from a 1:1 mixture of diethyl ether and CH_2Cl_2 (50 mL). Yield: 0.54 g, (87%) of orange crystalline **4a**. IR (KBr): 2555 w [ν(BH)], 1982 vs [ν(CO)], 1893 vs [ν(CO)] cm^{-1}. ^1H NMR: δ 1.83 (d, $^2J_{PH}$ = 4.3 Hz, 3H, PCH_3), 2.34 (s, 3H, $Tp'CH_3$), 2.38 (s, 3H, $Tp'CH_3$), 2.41 (s, 6H, $Tp'CH_3$), 2.54 (s, 6H, $Tp'CH_3$), 3.43 (s, 12H, NCH_3), 5.84 (s, 1H, Tp′CH), 6.03 (s, 2H, Tp′CH). $^{13}C\{^1H\}$ NMR: δ 9.18 (d, $^1J_{PC}$ = 17.6 Hz, PCH_3), 12.78 (s, $Tp'CH_3$), 15.28 (s, $Tp'CH_3$), 17.03 (s, $Tp'CH_3$), 45.00 (s, NCH_3), 107.10 (s, Tp′CH), 107.39 (s, Tp′CH), 121.28 (q, $^1J_{FC}$ = 320.9 Hz, CF_3), 146.08 (s, $Tp'CCH_3$), 146.76 (s, $Tp'CCH_3$), 151.69 (s, $Tp'CCH_3$), 153.14 (s, $Tp'CCH_3$), 178.25 (d, $^1J_{PC}$ = 45.9 Hz, PCN_2), 225.48 (s, CO), 273.04 (d, $^1J_{PC}$ = 83.0 Hz, W≡C).$^{31}P\{^1H\}$ NMR: δ 17.2 (s, $^2J_{WP}$ = 43.0 Hz). MS/EI: 694 (M − $CF_3SO_3^-$). Anal. Calcd for $C_{25}H_{37}BF_3N_8O_5PSW$ (844.31): C, 35.56; H, 4.42; N, 13.27. Found: C, 35.05; H, 4.57; N, 12.92.

[$Tp'(CO)_2W{\equiv}C{-}P(Me){-}C(NEt_2)_2$]$SO_3CF_3$ (4b). Compound $Tp'(CO)_2W{\equiv}C{-}P{=}C(NEt_2)$ (**2b**) (0.45 g, 0.61 mmol) was alkylated with an equimolar amount of methyl triflate (0.10 g, 0.61 mmol) in 200 mL of diethyl ether at −78 °C. Workup as described above afforded crude orange **4b**, which was crystallized from a 1:2 mixture of CH_2Cl_2 and diethyl ether (100 mL). Yield: 0.36 g (67%). IR(KBr): 2560 w [ν(BH)], 1981 vs [ν(CO)], 1884 vs [ν(CO)] cm^{-1}. ^{1}H NMR: δ 1.32 (t, $^3J_{\mathrm{HH}}$ = 7.1 Hz, 12H, CH$_2$CH_3), 1.75 (d, $^2J_{\mathrm{PH}}$ = 4.6 Hz, 3H, PCH$_3$), 2.33 (s, 3H, Tp′CH$_3$), 2.37 (s, 3H, Tp′CH$_3$), 2.41 (s, 6H, Tp′CH$_3$), 2.54 (s, 6H, Tp′CH$_3$), 3.81 (q, $^3J_{\mathrm{HH}}$ = 7.1 Hz, 8H, CH_2CH$_3$), 5.83 (s, 1H, Tp′CH), 6.02 (s, 2H, Tp′CH). ^{13}C{^{1}H} NMR: δ 10.04 (d, $^1J_{\mathrm{PC}}$ = 16.3 Hz, PCH$_3$), 12.77 (s, Tp′CH$_3$), 13.75 (s, CH$_2$CH$_3$), 15.26 (s, Tp′CH$_3$), 17.38 (s, Tp′CH$_3$), 48.60 (s, CH$_2$-CH$_3$), 107.11 (s, Tp′CH), 107.43 (s, Tp′CH), 121.39 (q, $^1J_{\mathrm{FC}}$ = 320.7 Hz, CF$_3$). 146.11 (s, Tp′CCH$_3$), 146.81 (s, Tp′CCH$_3$), 151.65 (s, Tp′CCH$_3$), 153.17 (s, Tp′CCH$_3$), 179.53 (d, $^1J_{\mathrm{PC}}$ = 48.4 Hz, PCN$_2$), 225.72 (s, CO), 271.90 (d, $^1J_{\mathrm{PC}}$ = 85.6 Hz, W≡C). ^{31}P{^{1}H} NMR: δ 18.12 (s, $^2J_{\mathrm{WP}}$ = 44.7 Hz). MS/EI: 844 (M$^+$ −2CO), 751 (M − CF$_3$SO$_3^-$). Anal. Calcd for C$_{29}$H$_{45}$BF$_3$N$_8$O$_5$PSW (900.00): C, 38.68; H, 5.04; N, 12.44. Found: C, 38.60; H, 4.87; N, 12.07.

[Tp′(CO)$_2$W≡C−P(H)−C(NEt$_2$)$_2$]BF$_4$ (5). A solution of 0.68 mmol of HBF$_4$ in 50 mL of diethyl ether was added dropwise over a period of 3 h to the chilled solution (−100 °C) of Tp′(CO)$_2$W≡C−P═C(NEt$_2$)$_2$ (**2b**) (0.45 g, 0.61 mmol) in diethyl ether (200 mL), whereupon the color of the mixture changed from dark-red to light orange. Warming up to room temperature led to the separation of an orange precipitate, which was filtered off after 1 h of stirring at 20 °C. The filtercake was washed (3 × 10 mL of diethyl ether and 3 × 10 mL of *n*-pentane) and dried overnight in vacuo (10^{-3} Torr) to afford 0.40 g (80%) of orange powdery **5**. IR (KBr): 2558 w [ν(BH)], 2336 w [ν(PH)], 1986 vs [ν(CO)], 1897 vs [ν(CO)], 1070 s [ν(BF)] cm^{-1}. ^{1}H NMR:δ 1.39 (s, br, $W_{1/2} \approx$ 20 Hz, 12H, CH$_2$CH_3), 2.35 (s, 3H, Tp′CH$_3$), 2.38 (s, 3H, Tp′CH$_3$), 2.41 (s, 6H, Tp′CH$_3$), 2.54 (s, 6H, Tp′CH$_3$), 3.78 (s, br, $W_{1/2} \approx$ 32 Hz, 4H, CH_2CH$_3$), 3.89 (s, br, $W_{1/2} \approx$ 32 Hz, 4H CH_2CH$_3$), 5.72 (d, $^1J_{\mathrm{PH}}$ = 255.8 Hz, 1H, PH), 5.85 (s, 2H, Tp′CH), 6.03 (s, 1H, Tp′CH). ^{13}C-{^{1}H} NMR: δ 12.68 (s, Tp′CH$_3$), 13.54 (s, CH$_2$CH$_3$), 15.24 (s, Tp′CH$_3$), 16.83 (s, Tp′CH$_3$), 49.23 (s, CH$_2$CH$_3$), 107.01 (s, Tp′CH), 107.44 (s, Tp′CH), 146.01 (s, Tp′CCH$_3$), 146.81 (s, Tp′CCH$_3$), 151.66 (s, Tp′CCH$_3$), 153.01 (s, Tp′CCH$_3$), 176.33 (d, $^1J_{\mathrm{PC}}$ = 42.0 Hz, PCN$_2$), 225.23 (s, CO), 261.8 (d, $^1J_{\mathrm{PC}}$ = 80.9 Hz, W≡C). ^{31}P{^{1}H} NMR: −22.9 s. MS/LSIMS (*p*-nitrobenzyl alcohol matrix): 743 (M − BF$_4^-$). Anal. Calcd for C$_{27}$H$_{43}$B$_2$F$_4$N$_8$O$_2$PW (824.13): C, 39.34; H, 5.25; N, 13.59. Found: C, 39.02; H, 5.16; N, 13.41.

[Tp′(CO)$_2\overline{\mathrm{W{=}C(H){-}P}}$−C(NEt$_2$)$_2$]SO$_3CF_3$ (6′). A solution of Tp′(CO)′$_2$W≡C−P═C(NEt$_2$)$_2$ (**2b**) (0.45 g, 0.61 mmol) in 200 mL of diethyl ether was chilled to −120 °C, and a solution of 0.11 g, (0.72 mmol) of CF$_3$SO$_3$H in diethyl ether (100 mL) was added dropwise within a period of 4 h. The resulting orange solution was warmed to 20 °C, whereupon an orange precipitate was separated. Stirring was continued for 90 min. It was filtered, and the filter cake was washed with diethyl ether (1 × 10 mL and *n*-pentane 2 × 10 mL) and dried in vacuo (10^{-3} Torr). Compound **6′** was obtained as a light red powder (0.32 g, 58% yield). IR(KBr): 2553 w [ν(BH)], 2019 vs [ν(CO)], 1921 vs [ν(CO)] cm^{-1}. ^{1}H NMR: δ 0.82 (s, br, $W_{1/2} \approx$ 45 Hz, 6H CH$_2$CH_3), 1.37 (s, br, $W_{1/2} \approx$ 45 Hz, 6H CH$_2$CH_3), 1.74 (s, 3H, Tp′CH$_3$), 2.35 (s, 3H, Tp′CH$_3$), 2.47 (s, 6H, Tp′CH$_3$), 2.49 (s, 3H, Tp′CH$_3$), 2.52 (s, 3H, Tp′CH$_3$), 2.89 (s, br, $W_{1/2} \approx$ 45 Hz, 2H, CH_2CH$_3$), 3.02 (s, br, $W_{1/2} \approx$ 45 Hz, 2H, CH_2CH$_3$), 3.67 (s, br, $W_{1/2} \approx$ 45 Hz, 2H, CH_2CH$_3$), 4.00 (s, br, $W_{1/2} \approx$ 45 Hz, 2H, CH_2CH$_3$), 5.97 (s, 2H, Tp′CH), 6.09 (s, 1H, Tp′CH), 14.24 (d, $^2J_{\mathrm{PH}}$ = 16.9 Hz, 1H, W═CH). ^{13}C{^{1}H} NMR: δ 12.74 (s, Tp′CH$_3$), 13.16 (s, CH$_2$CH$_3$), 15.50 (s, Tp′CH$_3$), 15.86 (s, Tp′CH$_3$), 16.83 (s, Tp′CH$_3$), 17.04 (s, Tp′CH$_3$), 46.77 (s, CH$_2$-CH$_3$), 48.44 (s, CH$_2$CH$_3$), 108.09 (s, Tp′CH), 108.46 (s, Tp′CH), 109.09 (s, Tp′CH), 121.4 (q, $^1J_{\mathrm{FC}}$ = 316.9 Hz, CF$_3$), 145.97 (s, Tp′CCH$_3$), 147.15 (s, Tp′CCH$_3$), 153.93 (s, Tp′CCH$_3$), 156.08 (s, Tp′CCH$_3$), 198.65 (d, $^1J_{\mathrm{PC}}$ = 150.3 Hz, PCN$_2$), 218.12 (s, CO), 219.55 (s, CO), 242.00 (d, $^1J_{\mathrm{PC}}$ = 119.0 Hz, W═C). ^{31}P-{^{1}H} NMR: δ = −148.86. ^{31}P NMR: δ = −148.86, d, $^2J_{\mathrm{PH}}$ = 17.1 Hz. MS/LSIMS (*p*-nitrobenzyl alcohol matrix): 737 (M − CF$_3$SO$_3^-$). Anal. Calcd for C$_{28}$H$_{43}$BF$_3$N$_8$O$_5$PSW (886.36): C, 37.94; H, 4.88; N, 12.64. Found: C, 37.80; H, 4.85; N, 12.56.

Scheme 4



Comp.	M	R
1a, 3a	Mo	Me
1b, 3b	Mo	Et
2a, 4a	W	Me
2b, 4b	W	Et

Tp' = HB(3,5-Me$_2$HC$_3$N$_2$)$_3$

X-ray Crystal Structure Determination of 4b. Single crystals of **4b** were grown from a 1:2 mixture of CH$_2$Cl$_2$ and diethyl ether. An orange crystal with the approximate dimensions of 0.28 × 0.16 × 0.06 mm^3 was measured on a Bruker-AXS SMART CCD area detector system with a three axis goniometer and with Mo Kα radiation at 183K. Crystal data and refinement details: space group $P2_1/c$, cell dimensions a = 8.0801(4) Å, b = 30.339(2) Å, c = 15.1757(9) Å, β = 94.849(1)°, V = 3706.9(4) Å^3 (refined from all reflections with $F > 20\sigma(F)$, Z = 4, d_{calcd} = 1.613 g cm^{-3}, μ = 3.279 mm^{-1}, hemisphere data collection in ω at 0.3° scan width in three runs with 606, 435, and 230 frames (φ = 0, 88 and 180°) at a detector distance of 5 cm ($2\theta_{\max}$ = 54°), data reduction with the SAINT programm (V4.050 Bruker AXS), semiempirical absorption correction with redundant data (SADABS programm) max/min transmission 0.694/0.523, R(merge) before/after correction 5.43/2.97. Structure solution and refinement on F^2 with SHELXS-97 and SHELXL-93, 21 396 intensities read, 7952 unique (R_{int} = 0.0329) and 6468 observed [$I > 2\sigma(I)$], 446 parameters, hydrogen atoms treated as riding groups with U = 0.08 Å^2. R1 = 0.0282; wR2 = 0.0820, GooF(F^2) = 0.697, $w^{-1} = \sigma^2 (F_0{}^2) + (0.1P)^2$, where $P = (F_o{}^2 + 2F_c{}^2)/3$ maximum/minimum residual electron densities 0.854 and −0.733 e Å^{-3}.

X-ray Crystal Structure Determination of 6′. Single crystals of **6′** were grown from diethyl ether. A red crystal of the approximate dimensions 0.50 × 0.50 × 0.25 mm^3 was examined on a Siemens $R3m$V diffractometer using Mo Kα radiation at 173 K. Crystal data and refinement details: space group *Pbca*, orthorhombic. Cell dimensions: a = 17.860(10) Å, b = 18.167(8) Å, c = 22.304(11) Å, V = 7237(6) Å^3, Z = 8, d_{calcd} = 1.627 g cm^{-3}, μ = 3.357 mm^{-1}, empirical absorption correction from ψ scans, max/min transmission 0.4874/0.2846, 10 901 reflections collected, 10 544 unique (R_{int} = 0.0114). Structure solution and refinement on F^2 with SHELXTL-PLUS and SHELXL-97. 443 parameters, anisotropic refinement for all non-hydrogen atoms, hydrogen atoms treated as riding groups with a 1.2-fold (1.5-fold for methyl groups) isotropic U value of the equivalent U value of the corresponding C atom. R indices for 6503 reflections with $I > 2\sigma(I)$: R_F = 0.0529, wR_{F^2} = 0.1195 for all data, $w^{-1} = \sigma^2 (F_0{}^2) + (0.0495P)^2 + 0.4888P$, where $P = (F_0{}^2 + 2F_c{}^2)/3$, max/min residual electron densities 1.759 and −1.166 e Å^{-3}, 0.97 Å from W(1).

Results and Discussion

Reaction of the phosphaalkenyl carbyne complexes **1a**,**b** and **2a**,**b** with one molar equivalent of methyl triflate in diethyl ether at temperatures ranging from −78 to 20 °C led to a color change from crimson to orange and to the precipitation of the orange salts **3a**,**b** and **4a**,**b** in good yields (67−87%) (Scheme 4). Purification of the products was effected by recrystallization from CH$_2$Cl$_2$/diethyl ether.

The cations in **3** and **4** can be considered as tertiary phosphines ligated by a methyl group, a carbenium unit and a metal carbynyl substituent. Compared to the resonances of the starting materials (**1a**, δ 62.3 s; **1b**, 65.9 s; **2a**, 49.0 s, $^2J_{PW} = 51.4$ Hz; **2b**, 54.8s, $^2J_{PW} = 61.6$ Hz),[6] the ^{31}P NMR resonances of products **3** and **4a**,**b** (δ 17.20−18.74) are markedly shielded. The tungsten−phosphorus coupling constants in **4a** (43.0 Hz) and **4b** (44.7 Hz) decreased during methylation of the precursors **2a** and **2b**. The ^{13}C{^{1}H} NMR spectra of **3a**,**b** and **4a**,**b** are especially interesting in the low-field region, where doublets at $\delta = 271.90-287.68$ are seen for the metal-bound carbon atoms of the organophosphorus ligand. Coupling constants $^1J_{PC}$ range from 83.0 to 97.0 Hz. The alkylation of **1a**,**b** and **2a**,**b** is obviously accompanied by a strong shielding of the carbyne carbon atom (**1a**, δ 337.5, d $^1J_{PC} = 111.3$ Hz; **1b**, 338.6, d, 115.6 Hz; **2a**, 318.3, d, 101.2 Hz; **2b**, 319.0, d, 108.3 Hz) as well as by a significant decrease of the coupling constants. Obviously the s-orbital contribution from the tricoordinate phosphorus atom to the P−C(M) bond is less pronounced in **3a**,**b** and **4a**,**b** in comparison to that of the dicoordinate P atom in **1a**,**b** and **2a**,**b**. A similar situation is encountered for the doublet resonances of the amino-substituted tricoordinate carbon atom (δ^{13}C = 177.65−179.53; $^1J_{PC} = 45.9-48.4$ Hz) which are shifted to higher field, when compared with the respective doublets in the starting materials (**1a**, δ 202.7, d, 89 Hz; **1b**, 201.3, d, 91.6 Hz; **2a**, 201.3, d, 88.3 Hz; **2b**, 199.6, d, 89.7 Hz). A decrease of the coupling constants to about 50% of the values in the precursors is observed. The methyl carbon atoms at phosphorus give rise to doublets at δ 9.18−10.35 (d, $^1J_{PC} = 16.3-17.7$ Hz).

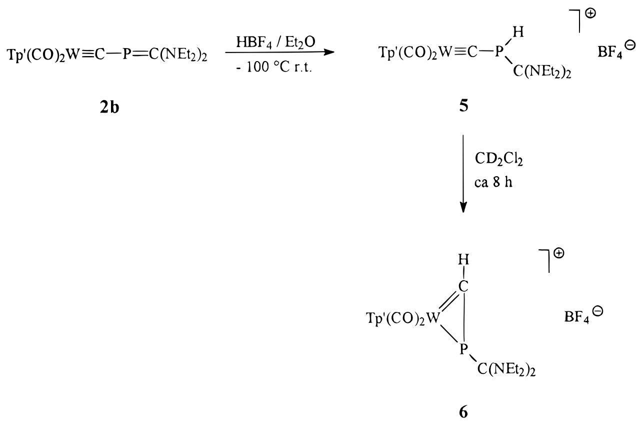
The ^{13}C NMR resonances for the carbonyl ligands in **1a**,**b** and **2a**,**b** were observed as singlets in the region δ 228.1−230.7. The high field shifts to δ 225.48−227.15 in **3a**,**b** and **4a**,**b** agree with a decreased transfer of electron density from the organophosphorus ligand in the cations onto the carbonyls. Accordingly, the ν(CO) bands in the alkylation products **3a**,**b** and **4a**,**b** are registered at higher wavenumbers (1981−1997 and 1884−1915 cm^{-1}) than in the IR spectra of **1a** (1946, 1864 cm^{-1}), **1b** (1943, 1859 cm^{-1}), **2a** (1935, 1848 cm^{-1}), and **2b** (1933, 1845 cm^{-1}).

In the following the tungsten carbyne complex **2b** was treated with a slight excess of ethereal HBF$_4$ in diethyl ether at −100 °C, whereupon a color change from dark-red to light orange occurred. Warming up to ambient temperature led to the precipitation of the orange carbyne complex **5** (80% yield) (Scheme 5).

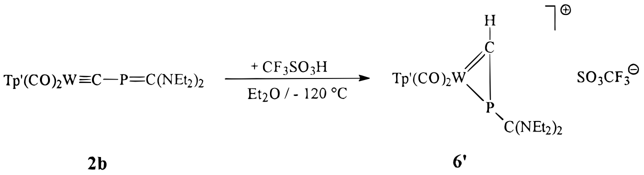
This observation clearly contrasts the behavior of Tp(CO)$_2$W≡CSMe, which was directly converted into a η^2-methylthiocarbene complex when treated with ethereal HBF$_4$.[7,8] At room temperature, however, solutions of **5** in CD$_2$Cl$_2$ rearranged to the cyclic η^2-carbene complex **6** within a period of 8h. In the ^{31}P{^{1}H} NMR spectrum of the product the singlet at δ −22.9 for **5** was replaced by a resonance at δ −148.9, which falls in the high-field region typical for phosphorus-containing three-membered rings.[9]

In line with Angelici's results[7,8] protonation of **2b** with trifluoromethane sulfonic acid in diethyl ether at −120 °C directly afforded the heterocyclic product **6′** (58% yield). Intermediates of the type **5** could not be detected by ^{31}P{^{1}H} NMR spectroscopy (Scheme 6).

Scheme 5



Scheme 6



The presence of a PH group in the cation of **5** is evident from a sharp band at 2336 cm^{-1} [ν(PH)] in the IR spectrum and from a doublet at δ 5.72 with a characteristic coupling constant $^1J_{PH} = 255.8$ Hz in the ^{1}H NMR spectrum. Accordingly, the proton-coupled ^{31}P NMR spectrum displays a doublet at δ −22.5 ($^1J_{PH} = 255.8$ Hz).

Again the ^{13}C{^{1}H}NMR spectrum is especially informative in the low-field region, where a doublet at δ 261.80 ($^1J_{PC} = 80.9$ Hz) is attributed to the carbyne carbon atom. This resonance is markedly shielded in going from **2b** (δ 319.0; d, $^1J_{PC} = 108.3$ Hz) to **5**. The tricoordinate carbon atom of the C(NEt$_2$)$_2$ function in α-position to the phosphorus atom gives rise to a doublet at δ 176.33 ($^1J_{PC} = 42.0$ Hz).

Formally, the cation of salt **5** may be regarded as the result of a metallaalkynylation of the phosphaalkene HP=C(NEt$_2$)$_2$ (**7**)[10] by the chlorocarbyne complex Tp′-(CO)$_2$W≡CCl.

Two intense bands at ν 1986 and 1897 cm^{-1} in the IR spectrum of **5** are assigned to the stretching frequencies of the two CO ligands. They are significantly shifted to lower wavenumbers when compared with the corresponding ν (CO) absorptions in the cyclic isomer **6′** (ν 2016, 1921 cm^{-1}). Obviously the η^2-phosphido carbene ligand in **6′** has an inferior σ donor/π acceptor capability toward the [Tp′(CO)$_2$W] fragment than the organophosphorus ligand in **5**. In keeping with this, the ^{13}C NMR signal of the carbonyls of **5** ($\delta = 225.23$ s) is shifted to high-field in **6′**, and due to the diastereotopic character of the carbonyls observed as two discrete singlets at δ 218.12 ($^1J_{WC} = 136$ Hz) and 219.55 ($^1J_{WC} = 136$ Hz). The carbon atom within the three-membered ring was observed as a doublet at δ 242.00 ($^1J_{PC} = 119.0$ Hz). In the related metallaphosphirenium salts

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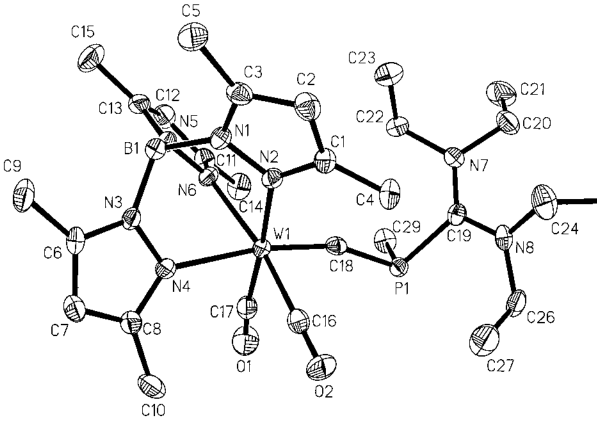

Figure 1. Molecular structure of the cation of **4b** in the crystal with ellipsoids drawn at 50% probability (hydrogen atoms are omitted for clarity).

Table 1. Selected Bond Lengths [Å] and Angles [deg] for 4b

W(1)C–(18)	1.840(4)	W(1)–N(4)	2.281(3)
W(1)–C(16)	1.990(4)	P(1)–C(18)	1.778(4)
W(1)–C(17)	2.002(4)	P(1)–C(29)	1.828(4)
W(1)–N(6)	2.206(3)	P(1)–C(19)	1.879(4)
W(1)–N(2)	2.208(3)	N(8)–C(26)	1.475(5)
N(7)–C(19)	1.342(5)	N(8)–C(24)	1.486(5)
N(7)–C(22)	1.481(5)	O(1)–C(17)	1.153(6)
N(7)–C(20)	1.488(5)	O(2)–C(16)	1.151(5)
N(8)–C(19)	1.333(5)		

C(18)–W(1)–C(16)	83.9(2)	C(18)–P(1)–C(29)	105.7(2)
C(18)–W(1)–C(17)	81.0(2)	C(18)–P(1)–C(19)	100.8(2)
C(16)–W(1)–C(17)	84.2(2)	C(29)–P(1)–C(19)	102.6(2)
C(18)–W(1)–N(6)	106.46(14)	C(19)–N(7)–C(22)	122.4(3)
C(16)–W(1)–N(6)	169.57(14)	C(19)–N(7)–C(20)	121.8(3)
C(17)–W(1)–N(6)	96.32(15)	C(22)–N(7)–C(20)	115.7(3)
C(18)–W(1)–N(2)	102.95(13)	C(19)–N(8)–C(26)	121.9(3)
C(16)–W(1)–N(2)	96.02(14)	C(19)–N(8)–C(24)	123.6(4)
C(17)–W(1)–N(2)	176.01(14)	C(26)–N(8)–C(24)	113.9(3)
N(6)–W(1)–N(2)	82.75(11)	P(1)–C(18)–W(1)	162.1(2)
C(18)–W(1)–N(4)	170.85(13)	N(8)–C(19)–N(7)	122.0(3)
C(16)–W(1)–N(4)	89.06(13)	N(8)–C(19)–P(1)	116.1(3)
C(17)–W(1)–N(4)	92.44(14)	N(7)–C(19)–P(1)	121.8(3)
N(6)–W(1)–N(4)	80.51(11)	O(1)–C(17)–W(1)	172.6(3)
N(2)–W(1)–N(4)	83.57(11)	O(2)–C(16)–W(1)	176.6(3)

[Tp′(CO)$_2$W=C(Ph)–PPh$_2$](PF$_6$)[11] and Tp′(CO)$_2$W=C-(Tol)–P(Me)Cl](BPh$_4$)[12] [Tp′ = HB(C$_3$H$_3$N$_2$)$_3$] the ^{13}C NMR resonances were observed as doublets at δ 243.7 ($^1J_{PC}$ = 38.6 Hz) and δ 244.1 ($^1J_{PC}$ = 62.5 Hz), respectively.

X-ray Structural Analysis of 4b. A thermal ellipsoid drawing of **4b** is shown in Figure 1; selected bond lengths and angles are given in Table 1. The complex contains a monomeric cation with distorted octahedral geometry. Three facial position are occupied by the nitrogen atoms of the tripod ligand. The bond angles between the organophosphorus ligand and the two carbonyl ligands are markedly less than 90° (81.0(2) – 84.2(2)°), as are those between the nitrogen donor atoms N(2), N(4), and N(6) of the Tp′ ligand. The most interesting structural feature of the cation is the geometry of the organophosphorus ligand. The bond length W(1)–C(18) of 1.840(4) Å compares well with the corresponding bond lengths in **2b** [1.838(6) Å] or [Tp′(CO)$_2$W≡CPMe$_2$Ph]PF$_6$ [1.821(9) Å][4] and, thus, has to be considered as a metal–carbon triple bond. The valence angle P(1)–C(18)–W(1) of 162.1(2)° deviates stronger from than the corresponding angles W–C–P in **2b** [167.9(4)°] or [Tp′(CO)$_2$W≡CPMe$_2$Ph]$^+$ [168.1(5)°]. Upon methylation the bond length between the sp-hybridized carbon atom and phosphorus in **2b** [1.759(7) Å] did not change significantly [in **4b**: C(18)–P(1) = 1.778(4) Å]. In contrast to this, the atomic distance between P(1) and the carbon atom of the CN$_2$ unit [in **2b**: 1.759(9) Å] is elongated to 1.879(4) Å and clearly becomes a P–C single bond. A typical range of 1.70–1.76 Å is accepted for P=C-double bond lengths in aminosubstituted phosphaalkenes [cf. 1.740(1) Å in HP=C(NMe$_2$)$_2$].[13] Atom C(19) has a trigonal-planar environment [sum of angles = 359.9(3)°]. Accordingly, the carbon–nitrogen bond lengths C(19)–N(7) [1.342(4) Å] and C(19)–N(8) [1.333(5) Å] are shorter than the calculated value of a C$_{sp^2}$–N$_{sp^2}$ single bond of 1.450 Å.[13]

Table 2. Selected Bond Lengths [Å] and Angles [deg] for 6′

W(1)–C(18)	1.980(6)	O(1)–C(16)	1.140(7)
W(1)–C(16)	2.005(6)	O(2)–C(17)	1.149(8)
W(1)–C(17)	2.010(7)	N(7)–C(19)	1.330(8)
W(1)–N(4)	2.203(5)	N(7)–C(22)	1.462(8)
W(1)–N(2)	2.206(5)	N(7)–C(20)	1.481(8)
W(1)–N(6)	2.246(5)	N(8)–C(19)	1.344(8)
W(1)–P(1)	2.5309(18)	N(8)–C(24)	1.470(9)
P(1)–C(18)	1.764(6)	N(8)–C(26)	1.474(8)
P(1)–C(19)	1.922(7)		

C(18)–W(1)–C(16)	73.0(3)	N(4)–W(1)–P(1)	163.55(13)
C(18)–W(1)–C(17)	81.0(3)	N(2)–W(1)–P(1)	96.17(13)
C(16)–W(1)–C(17)	92.0(3)	N(6)–W(1)–P(1)	86.44(13)
C(18)–W(1)–N(4)	151.8(2)	C(18)–P(1)–C(19)	104.9(3)
C(16)–W(1)–N(4)	80.8(2)	C(18)–P(1)–W(1)	51.2(2)
C(17)–W(1)–N(4)	89.7(2)	C(19)–P(1)–W(1)	113.29(18)
C(18)–W(1)–N(2)	105.1(2)	C(19)–N(7)–C(22)	121.9(5)
C(16)–W(1)–N(2)	87.3(2)	C(19)–N(7)–C(20)	124.6(6)
C(17)–W(1)–N(2)	173.3(2)	C(22)–N(7)–C(20)	112.6(5)
N(4)–W(1)–N(2)	83.67(18)	C(19)–N(8)–C(24)	124.0(6)
C(18)–W(1)–N(6)	129.1(2)	C(19)–N(8)–C(26)	121.4(6)
C(16)–W(1)–N(6)	157.8(2)	C(24)–N(8)–C(26)	114.0(6)
C(17)–W(1)–N(6)	90.4(2)	O(1)–C(16)–W(1)	179.1(6)
N(4)–W(1)–N(6)	77.12(18)	O(2)–C(17)–W(1)	178.1(6)
N(2)–W(1)–N(6)	87.71(18)	P(1)–C(18)–W(1)	84.8(3)
C(18)–W(1)–P(1)	43.97(18)	N(7)–C(19)–N(8)	123.0(6)
C(16)–W(1)–P(1)	115.6(2)	N(7)–C(19)–P(1)	116.7(5)
C(17)–W(1)–P(1)	90.1(2)	N(8)–C(19)–P(1)	119.7(5)

X-ray Structural Analysis of 6′. A thermal ellipsoid drawing of the cation of **6′** is shown in Figure 2; selected bond lengths and angles are given in Table **2**. The cation of **6′** displays the structural features of a metallaphosphirene and, thus, is closely related to compound Cp(CO)$_2$W=C(Ph)–P(Ph)[W(CO)$_5$] (**9**), where an additional [W(CO)$_5$] is attached to the phosphorus atom via its lone-pair of electrons.[14] The W(1)–C(18) bond length 1.980(6) Å in **6′** is well comparable with the respective atomic distances in **9** [1.954(8) Å][14] and [Tp(CO)$_2$W=CHSMe]$^+$ **8** [1.93(2) Å].[7] Thus, the W(1)–C(18) bond length is between the W–C(sp^2) single bond distance in Cp(CO)$_3$W–Ph [2.32(2) Å][15] and the W≡C

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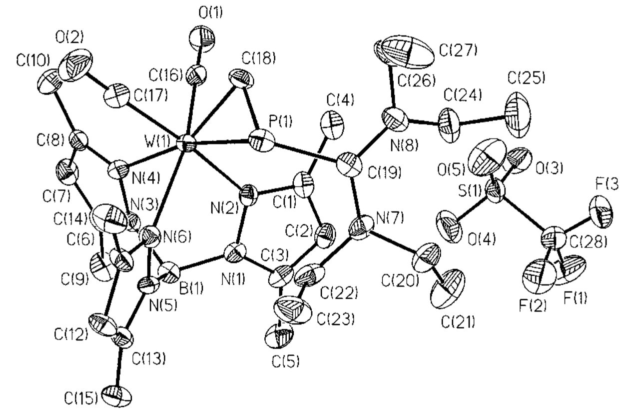

Figure 2. Molecular structure of **6′** in the crystal with ellipsoids drawn at 50% probability (hydrogen atoms are omitted for clarity).

triple bond distance in **4b** [1.840(4) Å] and related complexes. The W=C double bond lengths in **6′**, **8**, and **9** are comparable to those in the carbene complexes $Cp(CO)_2W{=}C(CF_3)C(CF_3)C(O)SMe$ [1.962(8) Å],[16] $tBuCH_2(tBuC)(Me_2PCH_2CH_2PMe_2)W{=}CHtBu$ [1.942(9) Å[17] and $Cl_2(O)(PMe_3)_2W{=}CHtBu$ [1.986(21) Å].[18] They are about 0.20 Å shorter than the corresponding distances in Fischer-carbene complexes of the type pentacarbonyl[alkyl(alkoxy)carbene]tungsten [2.161 Å].[19] The P−C(ring) bond length in **6′** [1.764(6) Å] is very similar to the corresponding bond distances in **9** [1.775(8) Å][14] and in the phosphirene complex $(CO)_5W\overline{P(Ph)C(Ph){=}C}(Ph)$ [1.709(4); 1.787(4) Å].[20] Comparable observations were made concerning the W−P atomic distances in **6′** [2.5309(18) Å] and **9** [2.511(3) Å] and the endocyclic angles C(18)−W(1)−P(1) [43.97(18)°], W(1)−P(1)−C(18) [51.2(2)°], and W(1)−C(18)−P(1) [84.8(3)°] in **6′** and **9** [44.7(2), 50.7(2), and 84.6(3)°], respectively. The planar carbon atom C(19) is attached to the phosphorus atom P(1) by a long single bond of 1.992(7) Å. The carbon nitrogen distances within the diaminocarbenium unit C(19)−N(7) [1.330(8) Å] and C(19)−N(8) [1.344(8) Å] indicate multiple bond character.

The coordination geometry about the tungsten atom is that of a pentagonal bipyramid. The atoms P(1), C(18), C(16), N(4), and N(6) constitute a slightly puckered five-membered ring, whereas the atoms C(17) and N(2) are located in axial positions. The angle N(2)−W(1)−C(17) [173.3(2)°] is close to linearity.

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Supporting Information Available: Tables of X-ray data, atomic coordinates, thermal parameters, and complete bond distances and angles and thermal ellipsoid plots for compounds **4b** and **6′** (18 pages). Ordering information is given on any current masthead page.

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