

Reactions of a tungsten phosphonium ion complex with carbenoid reagents

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Abstract

The reactions of diazomethane, the silylene fragments Me_2Si and Ph_2Si , and stannylene fragment Me_2Sn with the metallophosphonium ion complex $\text{CpW}(\text{CO})_2\{\text{P}(\text{Ph})[\text{N}(\text{SiMe}_3)_2]\}$ were examined and the new species $\text{Cp}(\text{CO})_2\overline{\text{W}}(\text{ER}_2)\overline{\text{P}}(\text{Ph})[\text{N}(\text{SiMe}_3)_2]$ ($\text{ER}_2 = \text{CH}_2$, SiMe_2 and SiPh_2) were isolated and characterized. The molecular structures for the compounds with $\text{R}_2\text{E} = \text{CH}_2$ and SiMe_2 were determined by single crystal X-ray diffraction techniques. © 1997 Elsevier Science S.A.

Keywords: Tungsten; Phosphorus; Phosphonium ion; Carbenoid; Cyclopentadienyls

1. Introduction

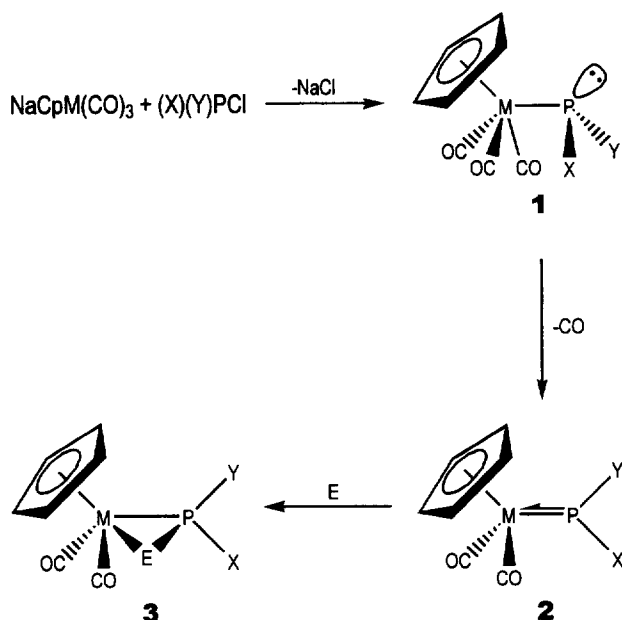
Monochlorophosphanes $(\text{X})(\text{Y})\text{PCl}$ combine with metal carbonyl anions $\text{NaCpM}(\text{CO})_3$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) to give neutral metallophosphane complexes $\text{CpM}(\text{CO})_3[\text{P}(\text{X})(\text{Y})]$ **1** as described below. These complexes contain a pyramidal phosphorus atom, and the phosphorus lone pair promotes facile intramolecular base displacement through loss of one CO ligand. The resulting metallophosphonium complexes **2** contain a planar phosphorus atom environment and a short $\text{M}=\text{P}$ multiple bond [1–13]. See Scheme 1.

The chemistry of **1** and **2** has been partially developed [1–13]. For example, the reactivity of examples of **1** is dominated by the nucleophilicity of the phosphorus lone pair. Additions of $\text{H}_3\text{B} \cdot \text{THF}$, CH_3I and $\text{Ni}(\text{CO})_4$ to $\text{CpW}(\text{CO})_2(\text{Me}_3\text{P})(\text{Ph}_2\text{P})$ produce adducts $\text{CpW}(\text{CO})_2(\text{Me}_3\text{P})[\text{P}(\text{A})(\text{Ph})_2]$ ($\text{A} = \text{H}_3\text{B}$, CH_3^+ , $\text{Ni}(\text{CO})_3$), and oxidations with S_8 and Br_2 also take place at the phosphorus center [4]. Similarly, the metallophosphaalkene $\text{CpW}(\text{CO})_3[\text{P}=\text{C}(\text{SiMe}_3)_2]$ undergoes protonation, methylation and oxidation at the phosphorus atom when combined with $\text{CF}_3\text{SO}_3\text{H}$, $\text{CF}_3\text{SO}_3\text{CH}_3$, and S_8 respectively [5]. Since the phosphorus lone pair in **2** is tied up in $\text{M}=\text{P}$ multiple bonding, the reactivity

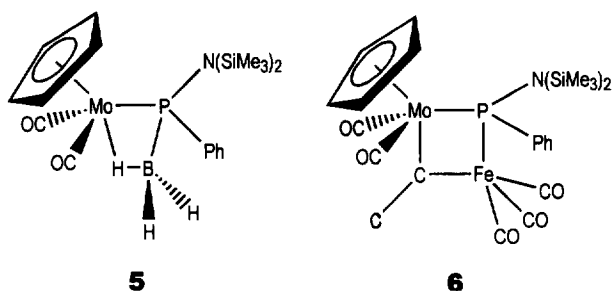
patterns for these molecules are expected to be somewhat different. For example, Malisch et al. [3] reported that some examples of **2**, e.g. $\text{CpM}(\text{CO})_2[\text{POCMe}_2\text{CMe}_2\text{O}]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) [4] and $\text{Cp}(\text{CO})_2\text{Mo}[\text{P}(\text{NMe}_2)_2]$ [2], combine with S_8 to give thio-bridged species **3a** ($\text{E} = \text{S}$). Similarly, reaction of CH_2N_2 with the former compound produces a [2 + 1] cycloaddition species **3b** ($\text{E} = \text{CH}_2$), and addition of $\text{Fe}_2(\text{CO})_9$ results in **3c** ($\text{E} = \text{Fe}(\text{CO})_4$). Malisch et al. [3] have also reported that another compound, $\text{CpW}(\text{CO})_2[\text{P}(\text{tBu})_2]$, reacts with S_8 , Se , CH_2N_2 , $(\text{MeP})_5$, Me_2P , $\text{Fe}_2(\text{CO})_9$, and $\text{Ru}_3(\text{CO})_{10}$, each forming [2 + 1] cycloaddition products **3**. With $\text{M} = \text{Mo}$, and W and $\text{X} = \text{Y} = \text{alkyl}$ and aryl , it was reported that alkenes, alkynes and dienes give [2 + 2] and [2 + 4] cycloaddition products, and metal halides CuCl , AgCl , $\text{Au}(\text{Cl})\text{PPh}_3$ and $\text{Rh}(\text{CO})_2\text{Cl}$ produce [2 + 1] cycloaddition products [3]. Finally, Lang and associates [7,8] have recently reported reactivity studies on bifunctional σ^3, λ^4 -phosphanediyl phosphonium complexes $\text{CpM}(\text{CO})_2[\text{P}(\text{R})\text{C} \equiv \text{C}\text{R}]$, $\text{CpM}(\text{CO})_2[\text{P}(\text{R})\text{C}(\text{H}) = \text{C}(\text{H})\text{R}]$, and $\text{CpM}(\text{CO})_2[\text{P}(\text{R})\text{CH}_2\text{C} \equiv \text{CH}]$. These species undergo [2 + 1] cycloadditions with CH_2N_2 , $\text{Fe}(\text{CO})_5$, PhN_3 , and $(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}_3$.

Despite the multiple bond character in the metallophosphonium ion interaction, these observations suggest that the phosphorus atom in **2** retains some nucleophilic

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activity at the phosphorus atom. In our studies, we have observed that $\text{H}_3\text{B} \cdot \text{THF}$ adds across the $\text{M}=\text{P}$ double bond in $\text{CpMo}(\text{CO})_2\{\text{P}(\text{Ph})[\text{N}(\text{SiMe}_3)_2]\}$ **4a** giving the complex **5**, whose novel structure was deduced by single crystal X-ray diffraction analysis [10]. In addition, we have found that **4a** reacts with $\text{Fe}_2(\text{CO})_9$ to give a complex **6** of the general type illustrated by **3** ($\text{E} = \text{Fe}(\text{CO})_4$, $\text{X} = \text{Ph}$, $\text{Y} = \text{N}(\text{SiMe}_3)_2$) [11]. However, single crystal X-ray diffraction analysis of **6** showed that its molecular structure does not feature a three-membered ring core, but instead displays a bridging CO interaction between the Mo and Fe centers. In the present report, studies of the addition of carbenoid fragments CH_2 , SiMe_2 , SnMe_2 , and SiPh_2 to **4a** are described.



2. Experimental

Standard inert atmosphere techniques were employed for the synthesis and manipulation of all compounds.

Solvents were dried, deoxygenated and distilled prior to use. Mass spectra were obtained by using a Finnegan GC/MS spectrometer and samples were introduced via the solids probe. Infrared spectra were measured on a Nicolet model 6000 FT-IR spectrometer by using solution cells. NMR spectra were recorded on Varian FT-80A and GE NT-360 spectrometers. Spectral standards were Me_4Si (^{13}C , ^1H) and H_3PO_4 (^{31}P). Downfield shifts from the standard were given a positive sign. The complex $\text{CpW}(\text{CO})_2\{\text{P}(\text{Ph})[\text{N}(\text{SiMe}_3)_2]\}$ **4b** [12] was prepared from $\text{NaWCp}(\text{CO})_3$ [14] and $\text{Ph}(\text{Cl})\text{P}[\text{N}(\text{SiMe}_3)_2]$ [15]. Solutions of diazomethane in Et_2O were prepared and analyzed as described in the literature [16]. Me_2SiCl_2 , Ph_2SiCl_2 and Me_2SnCl_2 were purchased from Alfa Ventron. Active Mg was made from the reaction of $\text{MgCl}_2 + \text{K}$ in THF, and it was prepared and used immediately. Elemental analyses were performed at the UNM microanalytical facility.

2.1. Formation of $\text{Cp}(\text{CO})_2\overline{\text{W}(\text{CH}_2)\text{P}(\text{Ph})[\text{N}(\text{SiMe}_3)_2]}$, **7**

To 1.0 g (1.75 mmol) of **4b** in 30 ml of THF was added an approximately 30% excess of diazomethane/diethylether solution at -78°C . The mixture was stirred briefly at -78°C and then slowly (2 h) warmed to 23°C and stirred for 4 h, during which time the reaction solution turned from purple to red-brown in color. The solvent was vacuum evaporated and the residue redissolved in benzene and filtered. The filtrate was concentrated, and addition of cyclohexane produced a yellow-brown crystalline solid **7**: yield 0.80 g, 72%. Anal. Found: C, 40.25; H, 5.22; N, 2.73. $\text{C}_{20}\text{H}_{30}\text{NO}_2\text{Si}_2\text{PW}$ (587.46): C, 40.89; H, 5.15; N, 2.38. Mass spectrum (m/e , rel. intensity): 589–585 (M^+ , 51%), 561–557 ($\text{M} - \text{CO}^+$, 9%), 533–529 ($\text{M} - 2\text{CO}^+$, 94%). Infrared spectrum (cyclohexane, cm^{-1}) (carbonyl region): 1935, 1848. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 9.9 ($J_{\text{PW}} = 222.6$ Hz). ^1H NMR (C_6D_6): δ 7.6–7.0 (Ph), 4.99 (Cp), 1.32 (CH_2), 0.27 (SiMe_3), 0.13 (SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ (C_6D_6): δ 136.13 (d, $J_{\text{CP}} = 54.0$ Hz, $\text{Ph}(\text{C}_1)$), 130.65 (d, $J_{\text{CP}} = 4.99$ Hz, $\text{Ph}(\text{C}_3)$), 129.20 ($\text{Ph}(\text{C}_4)$), 128.07 (d, $J_{\text{CP}} = 11.2$ Hz, $\text{Ph}(\text{C}_2)$), 92.75 (Cp), 4.17 (SiMe_3), 3.49 (SiMe_3), 2.55 (CH_2).

2.2. Formation of $\text{Cp}(\text{CO})_2\overline{\text{W}(\text{SiR}_2)\text{P}(\text{Ph})[\text{N}(\text{SiMe}_3)_2]}$: $\text{R} = \text{Me}$, **8a**; $\text{R} = \text{Ph}$, **8b**

To a suspension of active Mg (0.1 g, 4 mmol) in 30 ml of THF was added 1.0 g (1.75 mmol) of **4b** in 20 ml of THF. This mixture was cooled to -78°C and Me_2SiCl_2 (0.23 g, 1.8 mmol) was added via a syringe. The color changed immediately to red-brown and the mixture was stirred for 1 h at -78°C and then warmed to 23°C and stirred for another hour. The solvent was

Table 1
Summary of X-ray diffraction data for
Cp(CO)₂W(CH₂)P(Ph)[N(SiMe₃)₂] **7** and
Cp(CO)₂WSi(CH₃)₂P(Ph)[N(SiMe₃)₂] **8a**

	7	8a
Formula	C ₂₀ H ₃₀ NO ₂ Si ₂ PW	C ₂₁ H ₃₄ NO ₂ Si ₃ PW
Crystal dimensions	0.12 × 0.21 × 0.28	0.09 × 0.14 × 0.21
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /n	P2 ₁ /n
a (Å)	11.515(3)	11.444(2)
b (Å)	16.946(3)	15.634(3)
c (Å)	12.270(3)	15.702(3)
α (°)	90.0	90.0
β (°)	92.52	105.99(1)
γ (°)	90.0	90.0
V (Å ³)	2391.7(9)	2700.7(8)
Z	4	4
Formula weight	587.5	631.6
D _{calc} (g cm ⁻³)	1.63	1.55
Absorption coefficient (mm ⁻¹)	52.6	47.2
F(000)	1160	1256
Temperature (K)	20	20
2θ limit	2–50°	2–55°
No. collected reflections	9532	13830
No. observed reflections	3404 (F > 3σ(F))	4267 (F > 3σ(F))
R (%) ^a	5.56	9.12
R _w (%) ^b	4.66	4.53

^a R = Σ(|F_o| - |F_c|) / Σ|F_o|; R_w = {Σw(|F_o| - |F_c|)² / Σw|F_o|²}^{1/2}.

^b GOF = [Σw(|F_o| - |F_c|)² / (N_o - N_v)]^{1/2}.

N_o = number of observations and N_v = number of variables.

removed by vacuum evaporation and the residue extracted with benzene. The extract was filtered and the product recovered by evaporation, leaving a red crystalline solid **8a**: yield 0.75 g, 68%. Mass spectrum (*m/e*, rel. intensity): 633–629 (M⁺, 2%), 575–571 (M - 2CO⁺, 7%). Infrared spectrum (cyclohexane, cm⁻¹): 1925, 1851. ³¹P{¹H} NMR (C₆D₆): δ -42.5, ¹J_{PW} = 266.4 Hz. ¹H NMR (C₆D₆): δ 7.6–7.0 (Ph), 4.7 (Cp), 1.05 (d, J_{PH} = 5.9 Hz, SiMe₂), 0.70 (d, J_{PH} = 4.9 Hz, SiMe₂), 0.35 (SiMe₃), 0.22 (SiMe₃). ¹³C{¹H} NMR (C₆D₆): δ 130.6 (Ph), 128.6 (Ph), 128.3 (Ph), 127.8 (Ph), 89.0 (Cp), 4.9 (SiMe₃), 4.3 (SiMe₃), 1.3 (SiMe₂). An identical procedure was used to prepare **8b**: yield 1.02 g, 77%. Anal. Found: C, 49.13; H, 5.05; N, 1.42. C₃₁H₃₈NO₂PSi₃W (755.73) Calc.: C, 49.27; H, 5.07; N, 1.85%. Mass spectrum (*m/e*, rel. intensity): 761–755 (M⁺, 8%), 704–699 (M - 2CO⁺, 1%). Infrared spectrum (cyclohexane, cm⁻¹): 1929, 1853. ³¹P{¹H} NMR (C₆D₆): δ -49.97 (¹J_{PW} = 219.8 Hz). ¹H NMR (C₆D₆): δ 9.8–7.1 (m, Ph), 4.76 (Cp), 0.27 (SiMe₃), 0.20 (SiMe₃).

2.3. Formation of Cp(CO)₂W(SnMe₂)P(Ph)[N(SiMe₃)₂] **9**

Compound **9** was prepared in an identical fashion to **8a**; however, it was not obtained in pure form. The

following spectroscopic data provide evidence for its formation. Infrared spectrum (cyclohexane, cm⁻¹): 1929, 1852. ³¹P{¹H} NMR (C₆D₆): δ 39.4 (¹J_{PW} = 339.4 Hz, ¹J_{PSn} = 104 Hz).

2.4. Structure determinations

Suitable crystals of **7** and **8a** were obtained by slow crystallization from cyclohexane solutions at -10 °C. Crystals were placed in glass capillaries under nitrogen and sealed. The crystals were centered on a Siemens R3m/V four circle diffractometer, and determinations of the crystal class, orientation matrix, and accurate unit cell parameters were made at 20 °C. The crystal parameters and data collection parameters are summarized in Table 1. The intensity data were collected with Mo Kα (λ = 0.71069 Å) monochromated radiation, a scintillation counter, and pulse height analyzer. Intensities of three standard reflections were measured at the beginning and end of each ω (**7**) or 2θ (**8a**) scan. No crystal decay was noted. All calculations were performed on the Siemens P3 structure solution system using SHELXTL. Neutral atom scattering factors and anomalous dispersion terms were used for all non-hydrogen atoms during the refinements. A small empirical adsorption correction was applied in each case based upon Ψ scans. The structures were solved by direct methods (**7**) and stan-

Table 2
Atomic positional parameters for
Cp(CO)₂W(CH₂)P(Ph)[N(SiMe₃)₂] **7**

Atom	x/a	y/b	z/c
W	0.01857(3)	0.92862(2)	0.23274(3)
C(1)	0.1435(10)	0.9805(5)	0.1662(8)
O(1)	0.2223(7)	1.0129(4)	0.1246(7)
C(2)	0.1173(9)	0.9526(6)	0.3607(9)
O(2)	0.1785(8)	0.9694(5)	0.4361(7)
C(3)	0.0720(8)	0.8308(5)	0.1185(7)
C(4)	-0.1632(9)	0.9320(7)	0.1335(10)
C(5)	-0.1252(10)	1.0097(7)	0.1495(12)
C(6)	-0.1195(11)	1.0240(7)	0.2586(12)
C(7)	-0.1537(10)	0.9586(7)	0.3132(10)
C(8)	-0.1798(9)	0.8976(7)	0.2384(11)
P	0.09759(19)	0.79910(13)	0.25328(19)
C(9)	0.2511(7)	0.7799(5)	0.2838(7)
C(10)	0.3344(8)	0.8387(5)	0.2701(8)
C(11)	0.4507(9)	0.8238(6)	0.2895(9)
C(12)	0.4860(8)	0.7492(6)	0.3264(9)
C(13)	0.4063(8)	0.6918(5)	0.3419(9)
C(14)	0.2893(8)	0.7057(5)	0.3177(8)
N	0.0258(6)	0.7169(4)	0.2871(6)
Si(1)	-0.01972(25)	0.70690(18)	0.42281(26)
C(15)	-0.1781(10)	0.6974(8)	0.4208(12)
C(16)	0.0218(14)	0.7935(7)	0.5054(10)
C(17)	0.0475(12)	0.6214(8)	0.4931(12)
Si(2)	-0.00868(26)	0.64573(16)	0.18437(27)
C(18)	0.1126(10)	0.6331(7)	0.0921(10)
C(19)	-0.0344(12)	0.5473(7)	0.2454(12)
C(20)	-0.1466(10)	0.6752(6)	0.1089(10)

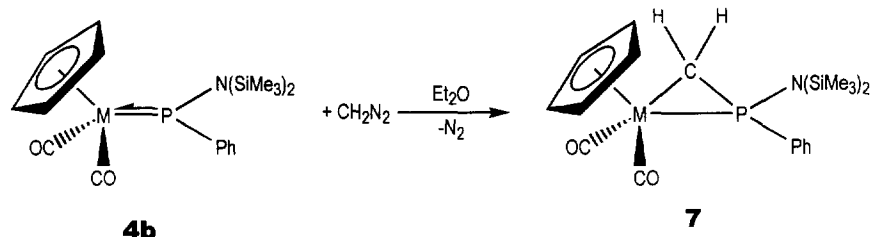
Table 3
Atomic positional parameters for
 $\text{Cp}(\text{CO})_2\text{W}(\text{SiMe}_2)\text{P}(\text{Ph})[\text{N}(\text{SiMe}_3)_2]$ **8a**

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
W	0.26759(3)	0.39591(3)	0.78415(2)
C(1)	0.2391(10)	0.5048(8)	0.7274(7)
O(1)	0.2233(8)	0.5737(5)	0.6923(5)
C(2)	0.3192(8)	0.3617(7)	0.6812(5)
O(2)	0.3613(6)	0.3432(6)	0.6245(4)
C(3)	0.4544(8)	0.4220(7)	0.8846(6)
C(4)	0.4481(9)	0.3349(9)	0.8671(7)
C(5)	0.3537(8)	0.3016(7)	0.9005(5)
C(6)	0.3045(8)	0.3690(7)	0.9384(5)
C(7)	0.3648(8)	0.4426(7)	0.9281(6)
P	0.05213(18)	0.36933(13)	0.76389(12)
Si(1)	0.11664(21)	0.32443(17)	0.65223(14)
C(14)	0.1192(8)	0.2090(5)	0.6223(5)
C(15)	0.0584(7)	0.3866(6)	0.5504(4)
C(8)	0.0187(6)	0.2875(5)	0.8360(4)
C(9)	0.0608(7)	0.2049(5)	0.8355(5)
C(10)	0.0356(7)	0.1438(5)	0.8913(5)
C(11)	-0.0289(7)	0.1642(6)	0.9503(5)
C(12)	-0.0687(8)	0.2454(7)	0.9513(6)
C(13)	-0.0468(7)	0.3071(6)	0.8949(5)
N	-0.0692(5)	0.4370(4)	0.7469(4)
Si(2)	-0.20961(21)	0.39968(20)	0.67698(17)
C(16)	-0.1993(7)	0.2980(5)	0.6216(5)
C(17)	-0.3224(8)	0.3780(9)	0.7405(7)
C(18)	-0.2710(9)	0.4806(7)	0.5923(7)
Si(3)	-0.05939(25)	0.53869(17)	0.79521(17)
C(19)	0.0693(8)	0.5458(5)	0.8954(5)
C(20)	-0.1950(8)	0.5620(6)	0.8353(6)
C(21)	-0.0469(9)	0.6250(6)	0.7186(5)

standard heavy atom methods (**8a**). Full-matrix least-squares methods were utilized in the refinements and the function minimized was $\sum \omega(|F_o| - |F_c|)^2$. Tables 2 and 3 contain listings of the atom positional parameters, and selected bond distances and angles are summarized in Table 4.

3. Results and discussion

The combination of $\text{CpW}(\text{CO})_2[\text{P}(\text{Ph})[\text{N}(\text{SiMe}_3)_2]]$ **4b** with excess diazomethane, $\text{CH}_2\text{N}_2/\text{Et}_2\text{O}$ solution results in a rapid discharge of the purple solution color characteristic of **4b**. This is accompanied by gas evolution and formation of a red-brown solution. Following



Scheme 2.

Table 4
Selected geometric data for $\text{Cp}(\text{CO})_2\text{W}(\text{CH}_2)\text{P}(\text{Ph})[\text{N}(\text{SiMe}_3)_2]$ **7**
and $\text{Cp}(\text{CO})_2\text{W}(\text{SiMe}_2)\text{P}(\text{Ph})[\text{N}(\text{SiMe}_3)_2]$ **8a**

Distances (Å)				
M–P	W–P	2.385(2)	W–P	2.434(2)
M–CO	W–C(1)	1.900(11)	W–C(1)	1.908(12)
	W–C(2)	1.940(11)	W–C(2)	1.942(9)
C=O	C(1)–O(1)	1.195(13)	C(1)–O(1)	1.201(14)
	C(2)–O(2)	1.174(14)	C(1)–O(2)	1.160(12)
M–C	W–C(3)	2.272(9)		
M–Si			W–Si(1)	2.560(2)
P–C	P–C(3)	1.752(9)		
	P–C(9)	1.820(8)	P–C(8)	1.818(8)
P–N	P–N	1.681(8)	P–N	1.707(6)
P–Si			P–Si(1)	2.197(3)
Si–N	Si(1)–N	1.776(8)	Si(3)–N	1.751(6)
	Si(2)–N	1.777(8)	Si(2)–N	1.777(6)
Angles (°)				
OC–M–CO	C(1)–W–C(2)	79.4(4)	C(1)–W–C(2)	84.8(5)
E–M–P	C(3)–W–P	44.1(2)	Si(1)–W–P	52.1(1)
M–E–P	W–C(3)–P	71.4(3)	W–Si(1)–P	61.0(1)
M–P–E	W–P–C(3)	64.5(3)	W–P–Si(1)	66.9(1)
E–P–N	C(3)–P–N	115.0(4)	Si(1)–P–N	120.7(2)
M–P–N	W–P–N	126.8(3)	W–P–N	131.7(2)
M–P–C	W–P–C(9)	123.3(3)	W–P–C(8)	114.7(8)
N–P–C	N–P–C(9)	106.6(4)	N–P–C(8)	103.4(3)
P–N–Si	P–N–Si(1)	118.6(4)	P–N–Si(2)	116.8(3)
	P–N–Si(2)	119.0(5)	P–N–Si(3)	122.9(3)
Si–N–Si	Si(1)–N–Si(2)	122.3(4)	Si(2)–N–Si(3)	120.3(4)

work-up and recrystallization, a yellow-brown crystalline solid **7** was isolated in good yield. See Scheme 2.

The compound is air- and moisture-sensitive, but it has indefinite stability in an inert atmosphere at 23 °C. Elemental analyses (CHN) gave satisfactory agreement with the proposed composition, and electron impact mass spectra show a parent ion envelope, as well as envelopes corresponding to $[\text{M} - \text{CO}^+]$ and $[\text{M} - 2\text{CO}^+]$ ions. The infrared spectrum from a cyclohexane solution shows two bands in the terminal CO stretch region at 1935 and 1848 cm^{-1} . These values are shifted slightly down-frequency from the values for **4b** [12]: 1941 and 1869 cm^{-1} . Compound **7** shows a single ^{31}P NMR resonance at δ 9.9 that displays tungsten-183 satellite coupling ($^1J_{\text{PW}} = 222.6$ Hz). This chemical shift is significantly upfield of the value for the starting material **4b**, δ 267 [12], and the coupling constant is significantly reduced (**4b**, $^1J_{\text{PW}} = 702$ Hz). These data

are consistent with disruption of the W=P multiple bonding in **4b** and adoption of a pyramidal geometry about the phosphorus atom in **7**. Similar upfield shifts and W–P coupling constant reductions have appeared upon formation of the tungsten derivatives of **5** [17], **6** [11] and S and Se cycloaddition products [12]. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show resonances that can be unambiguously assigned to the bridging methylene group and inequivalent silyl methyl groups on the silylamine fragment. Expected $^1J_{\text{PC}}$ and $^2J_{\text{PH}}$ couplings for the methylene resonance in the ^{13}C and ^1H NMR spectra were not resolved.

The molecular structure of **7** was determined by single crystal X-ray diffraction techniques and a view of the molecule is shown in Fig. 1. Selected bond distances are summarized in Table 4. The molecule displays a pseudo-four-legged piano stool structure with the W atom bonded to a $^5\eta\text{-Cp}$ ring, two terminal CO groups, the bridging methylene carbon atom, and the phosphorus atom of the phosphonium ion fragment. The CO groups are *cis* to each other, and there is no evidence in the solid state or solution for a *trans* isomer. As proposed by Malisch et al. [3,4] for related systems, the CH_2 group in **7** adds across the W=P bond and bridges these two atoms, forming a $\text{W}-\text{C}(\text{H}_2)-\text{P}$ three-membered ring.

The average bond lengths W–CO, 1.92 Å and C≡O, 1.18 Å and the OC–W–CO angle, 79.8(4)° in **7** are comparable to the values found for the starting material **4b**, 1.94 Å, 1.27 Å and 78(2)°, although the accuracy of the parameters for **4b** is reduced by a disorder problem involving the phenyl ring [17]. The parameters are also

similar to the average values in $\text{CpMo}(\text{CO})_2\{\text{P}(\text{Ph})[\text{N}(\text{SiMe}_3)_2]\}$ **4a**, 1.950 Å, 1.152 Å and 81.7(1)°, which have been refined more accurately [12]. The average value of the W–C bond lengths involving the Cp ring, 2.337 Å (range 2.299(12)–2.376(10) Å) is also similar to the values in **4b**, 2.39 Å, and **4a**, 2.348 Å. These parameters indicate that the $\text{CpW}(\text{CO})_2$ fragment does not undergo any large distortions as a result of the methylene addition to the W=P bond.

The phosphorus atom, on the other hand, converts from a trigonal planar geometry in **4b** to a distorted tetrahedral geometry in **7**. Newman projections down the W–P bond in both compounds show that the relative orientations of the W atom and P atom substituent groups are little affected by the methylene addition (Figs. 2 and 3). It is interesting to note that the W–P bond vector approximately bisects the OC–W–CO bond angle and the W–C(3)–P plane makes an angle of 96.0° with the OC–W–CO plane. The $\text{W}-\text{C}(\text{H}_2)-\text{P}$ ring is irregular, with distances W–P 2.385(2) Å, W–C(3) 2.272(9) Å and P–C(3) 1.752(9) Å, and internal angles C(3)–W–P 44.1(2)°, P–C(3)–W 71.4(3)° and W–P–C(3) 64.5(3)°. The W–P bond length, 2.385(2) Å, is significantly longer than the distance in the starting material **4b**, 2.252(6) Å [12], which is consistent with a change in formal hybridization at the phosphorus atom ($\text{sp}^2 \rightarrow \text{sp}^3$). The P–N bond length, 1.681(8) Å, is comparable to the value in **4b**, 1.68(2) Å. The nitrogen atom is trigonal planar and the average Si–N bond length in **7**, 1.777 Å, is identical to the average value in **4b**, 1.77 Å.

In an effort to prepare heavier E-element congeners of **7**, we examined the reactions of **4b** with the transient carbenoid fragments Me_2Si , Ph_2Si and Me_2Sn . Each was prepared in a similar fashion by combining the appropriate precursor R_2ECl_2 with a mixture of **4b** and active Mg, which are otherwise unreactive. The two silicon derivatives, **8a**, **8b**, were isolated in good yields as red crystalline, moisture-sensitive solids. The tin compound, **8c**, was obtained in smaller, impure amounts.

Characterization data for **8a–c** are similar and related to data obtained for **7**. Compounds **8a** and **8b** each display a parent ion envelope, as well as an $[\text{M} - 2\text{CO}^+]$ fragment ion, in the mass spectra. All three compounds display a two band ν_{CO} pattern in the IR: **8a** 1925, 1851 cm^{-1} ; **8b** 1929, 1853 cm^{-1} ; and **8c** 1929, 1852 cm^{-1} . Each compound shows a single resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra with clearly resolved $^{183}\text{W}-^{31}\text{P}$ coupling, and in the case of **8c**, $^{117/119}\text{Sn}-^{31}\text{P}$ coupling: **8a** $\delta -42.5$, $^1J_{\text{PW}} = 266.4$ Hz; **8b** $\delta -49.97$, $^1J_{\text{PW}} = 219.8$ Hz; and **8c** $\delta 32.9$, $^1J_{\text{PW}} = 339.4$ Hz, $^1J_{\text{PSn}} = 104$ Hz. It is interesting that the ^{31}P chemical shift for **7** falls between the values for **8a/8b** and **8c**. A full explanation for this trend is not yet apparent. As in **7**, the reductions of $^1J_{\text{PW}}$ in **8a–c** indicate that the planar P

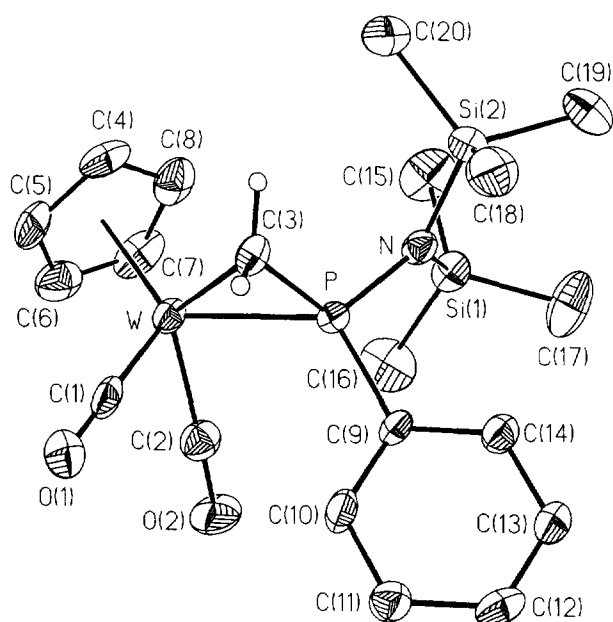


Fig. 1. Molecular structure and atom numbering scheme for $\text{Cp}(\text{CO})_2\text{W}(\text{CH}_2)\text{P}(\text{Ph})[\text{N}(\text{SiMe}_3)_2]$ **7** with H atoms, except on C(3), omitted. Thermal ellipsoids shown at 30%.

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