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Reactions of protic reagents with a tungsten phosphenium ion complex

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Abstract

The reactions of metallophosphenium ion complex $CpW(CO)_2\{P(Ph)[N(SiMe_3)_2]\}$ with protic reagents HBF_4, HCl, and CF_3COOH have been studied. The 1:1 reactions result in protonation of the W=P bond, while the 1:2 reactions display cleavage of the P–N bond. The molecular structure of one product, $Cp(CO)_2(Cl)WP(H)(Ph)[N(SiMe_3)_2]$, was determined by single crystal X-ray diffraction techniques: triclinic space group $P\bar{1}$ with $a = 9.6732(14)$ Å, $b = 11.3419(15)$ Å, $c = 11.5930(14)$ Å, $\alpha = 87.724(11)°$, $\beta = 77.647(11)°$, $\gamma = 82.989(11)°$, $V = 1233.0(3)$ Å^3, $Z = 2$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Tungsten; Phosphorus; Phosphenium ion; Acid reactivity

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1. Introduction

Some metal carbonyl anions react with monochlorophosphanes of the general type (X)(Y)PCl to initially give metallophosphane complexes **1** containing a terminal, pyramidal P(X)(Y) fragment. Many of these compounds undergo intramolecular CO displacement reactions that produce metallophosphenium ion complexes **2** which possess a planar MP(X)(Y) fragment, and short M=P bond. This process is summarized in Scheme 1 specifically for metal carbonyl fragments $CpM(CO)_3^-$ (M = Cr, Mo, W) [1–4].

The reactivity of **1** and **2** is of interest as a probe of the electronic properties of these molecules. For example, additions of $H_3B\cdot THF$, CH_3I, and $Ni(CO)_4$ to **1**, e.g. $CpW(CO)_2(Me_3P)(Ph_2P)$, produce phosphane adducts $CpW(CO)_2(Me_3P)[P(A)(Ph)_2]$ ($A = H_3B, CH_3^+$, $Ni(CO)_3$), and oxidations with S_8, and Br_2 occur at the phosphorus atom ([2]d). Similarly, the metallophosphaalkene $CpW(CO)_3[P{=}C(SiMe_3)_2]$ undergoes protonation, methylation, and oxidation at the phosphorus atom when combined with CF_3SO_3H, $CF_3SO_3CH_3$, and S_8, respectively ([2]f). Unlike **1**, the phosphorus lone pair in **2** is involved in M=P multiple bonding; therefore it is expected that the P atom reactivity might be somewhat different. Malisch ([2]c) reported that **2**, e.g. $CpM(CO)_2[\overline{POCMe_2CMe_2O}]$ (M = Cr, Mo, W) ([2]d), and $CpMo[P(NMe_2)_2])$ ([2]a), react with S_8 to give thio-bridged species **3a** (E = S). Reaction of CH_2N_2 with the former compound produces a [2 + 1] cycloaddition species **3b** ($E = CH_2$), and addition of $Fe_2(CO)_9$ results in **3c** ($E = Fe(CO)_4$). Malisch et al. ([2]c) have also reported that $CpW(CO)_2[P(^tBu)_2]$ reacts with S_8, Se, CH_2N_2, $(MeP)_5$, Me_2P, $Fe_2(CO)_9$, and $Ru_3(CO)_{10}$, each forming [2 + 1] cycloaddition products **3**. With M = Mo, and W and X = Y = alkyl and aryl, it was reported that alkenes, alkynes, and dienes give [2 + 2] and [2 + 4] cycloadditions and metal halides CuCl, AgCl, $Au(Cl)PPh_3$, and $Rh(CO)_2Cl$ produce [2 + 1] cycloadditions ([2]c). Lang and associates ([3]b,f) have recently reported reactivity studies on bifunctional σ^3, λ^4-phosphanediyl phosphenium complexes $CpM(CO)_2$ $[P(R)C{\equiv}CR]$, $CpM(CO)_2[P(R)C(H){=}C(H)R]$, and $CpM(CO)_2[P(R)CH_2C{\equiv}CH]$, and these species also undergo [2 + 1] cycloadditions with CH_2N_2, $Fe(CO)_5$, PhN_3, and $(2,4,6\text{-}Me_3C_6H_2)N_3$.

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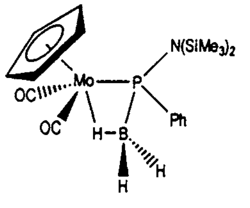
It is apparent from these results that the reactivity of **1** is dominated by the phosphorus lone pair nucleophilicity, while the reactivity in **2** seems centered on the electron rich M=P bond. Still, it appears that the P atom in **2** retains a good deal of nucleophilic character. For example, we observe that $H_3B \cdot THF$ adds across the M=P double bond in $CpMo(CO)_2\{P(Ph)[N(SiMe_3)_2]\}$ **4a** giving the complex **5**, whose unique structure was deduced by single crystal X-ray diffraction analysis ([4]f). Identical chemistry occurs with $CpW(CO)_2\{P(Ph)[N(SiMe_3)_2]\}$ **4b** [5]. Reactions with other classical Lewis acids, e.g. BCl_3, BBr_3, BH_2Cl and $AlCl_3$, have been studied; however, pure products are not obtained [6]. Compound **4a** also reacts with $Fe_2(CO)_9$ to give **6**. This compound is of the general type illustrated by **3** (E=$Fe(CO)_4$, X = Ph, Y = $N(SiMe_3)_2$) ([4]h); however, single crystal X-ray diffraction analysis shows that the molecular structure does not feature a three-membered ring core, but instead displays a bridging CO interaction between the Mo and Fe centers.



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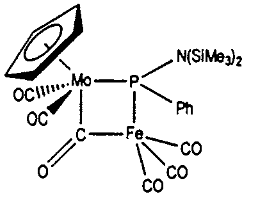

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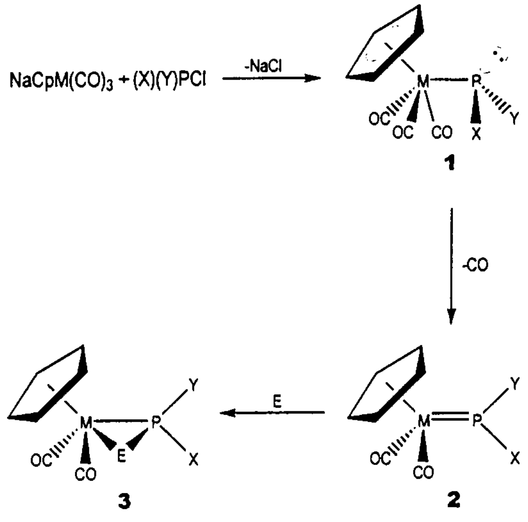
We have also recently reported on the outcome of oxidations of **4a** and **4b** with S_8 and Se ([4]i), and here we report reactions with protic sources HBF_4, HCl, and CF_3COOH.



Scheme 1.

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. IR 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, ^{1}H) and H_3PO_4 (^{31}P). Downfield shifts from the standard were given a positive sign. The complex $CpW(CO)_2\{P(Ph)[N(SiMe_3)_2]$ **4b** ([4]i) was prepared from $NaWCp(CO)_3$ [7] and $Ph(Cl)P[N(SiMe_3)_2]$ [8]. Samples of the acids were obtained from Aldrich Chemical Co. Microanalyses were obtained from the UNM microanalytical facility.

2.1. Reaction of $Cp(CO)_2W\{P(Ph)[N(SiMe_3)_2]\}$ with HCl; 1:1 ratio

To 1.0 g (1.75 mmol) of **4b** in 30 ml of THF held at − 78°C was added 0.3 ml (2.0 mmol) of a HCl solution (pre-titrated) in Et_2O. The mixture was stirred for 1 h and then warmed to 23°C and stirred for 1 h. The purple color of **4b** changed rapidly to red upon warming. The volatiles were vacuum evaporated, the residue dissolved in benzene, filtered and the filtrate evaporated. The red residue was recrystallized from cold benzene, leaving red crystals of **7**: yield 0.87 g, 82%; m.p.: 196–198°C. Anal. Calc. for $C_{19}H_{29}NO_2PSi_2ClW$: C, 37.42; H, 4.79; N, 2.30. Found: C, 35.80; H, 4.88; N, 2.41. Mass spectrum (*m/e*, relative intensity): 613–607 (M^+, 1.5%), 585–579 ($M\text{–}CO^+$, 3.5%), 576–572 ($M\text{–}Cl^+$, 45%), 557–553 ($M\text{–}2CO^+$, 10%). IR spectrum (cyclohexane, cm^{-1}) (carbonyl region): 1928, 1859. $^{31}P\{^{1}H\}$-NMR (C_6D_6): δ 27.0 ($^{1}J_{PW} = 308$ Hz, $^{1}J_{PH} = 408$ Hz). ^{1}H-NMR (C_6D_6): δ 8.0–7.2 (m, Ph), 7.39 ($^{1}J_{PH} = 410$ Hz), 5.48 (Cp), 0.26 ($SiMe_3$). $^{13}C\{^{1}H\}$-NMR (C_6D_6): δ 135.3 (d, $^{1}J_{CP} = 32$ Hz, Ph (C_1)), 133.0 (Ph(C_6)), 132.9 (Ph ($C_{3,5}$), 130.5 (Ph, $C_{2,4}$), 92.7 (Cp), 3.1 ($SiMe_3$).

2.2. Reaction of $Cp(CO)_2W\{P(Ph)[N(SiMe_3)_2]\}$ with excess HCl

To 1.0 g (1.75 mmol) of **4b** in 30 ml of benzene was added 0.9 ml (9.0 mmol) of an HCl solution (pre-titrated) in Et_2O. The mixture was heated to 50°C and the solution color changed from purple to orange. After stirring at 50°C for 30 min, the mixture was cooled to 23°C, filtered and solvent evaporated to dryness leaving an orange solid **8**: yield 0.51g, 60%. IR spectrum (cyclohexane, cm^{-1}) (carbonyl region): 1963 and 1884. $^{31}P\{^{1}H\}$-NMR (C_6D_6): δ 41.7 ($^{1}J_{PW} = 313$ Hz, $^{1}J_{PH} =$

421 Hz). ^{1}H-NMR (C_6D_6): δ 8.0–7.6 (Ph), 5.18 (Cp). ^{13}C{^{1}H}-NMR (C_6D_6): δ 135.2 (Ph(C$_1$)), 133.2 (Ph(C$_6$)), 132.7 (Ph (C$_{3,5}$)), 129.9 (Ph(C$_{2,4}$)), 93.2 (Cp).

2.3. Reaction of Cp(CO)$_2$W{P(Ph)[N(SiMe$_3$)$_2$]} with HBF$_4$; 1:1 ratio

To 1.0 g (1.75 mmol) of **4b** in 20 ml of toluene held at −78°C was added 0.29 g (1.79 mmol) of HBF$_4$·OEt$_2$. The mixture was stirred and warmed to 23°C, during which time the solution color changed to red–brown and a brown solid formed. The mixture was filtered and the filtrate evaporated, producing a larger quantity of brown solid (**9a**): yield 0.74 g (64%); m.p.: 148–150°C (dec.). Anal. Calc. For $C_{19}H_{29}BNO_2F_4Si_2PW$: C, 34.51; H, 4.42; N, 2.12. Found: C, 34.95; H, 4.51; N, 2.11. IR spectrum (benzene, cm^{-1}): 1971, 1872. ^{31}P{^{1}H}-NMR (C_6D_6): δ 205.9 ($^1J_{PW}$ = 361 Hz, J_{PH} = 76 Hz), 178.2 ($^1J_{PW}$ = 390 Hz, J_{PH} = 76 Hz). ^{1}H-NMR (C_6D_6): δ 7.8–7.1 (Ph), 5.29 (Cp) 4.97 (Cp), 0.35 (SiMe$_3$), 0.33 (SiMe$_3$), 0.27 (SiMe$_3$).

Attempts were made to recrystallize **9a** from several solvents. During the course of these attempts, crystals of **9b** deposited from Et$_2$O/toluene solutions held at −30°C. Mass spectrum (*m*/*e*, relative intensity): 669–662 (M$^+$, 30%), 642–635 (M–CO$^+$, 20%), 614–605 (M–2CO$^+$, 40%), 586–577 (40%), 558–549 (30%), 530–521 (20%). IR spectrum (cyclohexane, cm^{-1}): 1945, 1864. ^{31}P{^{1}H}-NMR (C_6D_6): δ 27.6 ($^1J_{PW}$ = 307 Hz, $^1J_{PH}$ = 392 Hz).

*2.4. Reaction of **9a** with Ph$_3$P*

A sample of **9a** (0.5 g, 0.8 mmol) was combined with Ph$_3$P (0.21 g, 0.8 mmol) in benzene and stirred at 23°C for 2 h. The solvent was evaporated and the residue recrystallized from benzene leaving a reddish solid **9c**: yield 0.6 g (65%); m.p.: 94–96°C. Anal. Calc. for $C_{37}H_{45}BO_2NF_4Si_2P_2W$: C, 48.07; H, 4.91; N, 1.52. Found: C, 49.04; H, 5.18; N, 1.39. Mass spectrum (*m*/*e*, relative intensity): 855–845 (M–SiMe$_3^+$, 0.1%), 776–767 (M–Ph–SiMe$_3$H$^+$, 0.2%), 745–739 (M–Ph–SiMe$_3$H–CO, 0.1%), 715–709 (M–Ph–SiMe$_3$H–2CO$^+$, 0.1%), 639–631 (M–PPh$_3$–CO, 0.3%), 610–601 (M–PPh$_3$–2CO, 1%). IR spectrum (cyclohexane, cm$^-$ 1): 1969, 1932, 1885. ^{31}P{^{1}H}-NMR (C_6D_6): δ 22.5 ($^1J_{PH}$ = 410 Hz), 20.3 ($^2J_{PP}$ = 12 Hz). ^{13}C{^{1}H}-NMR (C_6D_6): δ 7.7–7.1 (Ph), 7.6 ($^1J_{PH}$ = 395 Hz), 5.50 (Cp), 0.26 (SiMe$_3$).

2.5. Reaction of Cp(CO)$_2$W{P(Ph)[N(SiMe$_3$)$_2$]} with CF$_3$COOH; 1:1 ratio

To 1.0 g (1.75 mmol) of **4b** in 20 ml of THF was added 0.20 g (1.75 mmol) of CF$_3$COOH at −78°C. The mixture was stirred and warmed over 2 h, during which time the color changed to red–brown and a small amount of brown solid formed. The solution was filtered and the filtrate evaporated leaving a red–brown solid **10**, which was washed with two 10 ml portions of cyclohexane: yield 0.69 g (61%); m.p.: 115–118°C. Anal. Calc. For $C_{21}H_{29}NO_4F_3Si_2PW$: C, 36.69; H, 4.25; N, 2.04. Found: C, 38.14; H, 4.44; N, 1.86. IR spectrum (benzene, cm^{-1}): 1930, 1852, 1721. ^{31}P{^{1}H}-NMR (C_6D_6): δ 35.6 ($^1J_{PW}$ = 379 Hz, $^1J_{PH}$ = 339 Hz), 29.2 ($^1J_{PW}$ = 331, $^1J_{PH}$ = 372 Hz). ^{1}H-NMR (C_6D_6): δ 8.17 ($^1J_{PH}$ = 360 Hz), 8.02 ($^1J_{PH}$ = 382 Hz), 7.8–7.4 (Ph), 5.18 (Cp), 5.10 (Cp), 0.27 (SiMe$_3$).

2.6. Structure determination

Suitable crystals of **7** were obtained by slow crystallization from saturated benzene solution. A crystal was placed in a glass capillary under nitrogen and sealed. The crystal was 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–K$_\alpha$ (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 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 based upon Ψ scans. The structure was solved by standard heavy atom methods. Full matrix least squares methods were utilized in the refinements and the function minimized was $\Sigma\omega(|F_o|-|F_c|)^2$. Table 2 contains a listing of the atom positional parameters, and selected bond distances and angles are summarized in Table 3.

3. Results and discussion

The reactions of protic reagents with metallophosphenium and metallophosphane complexes appear to have been little studied. Malisch and coworkers ([4]b) reported that reactions of Cp(CO)$_2$WP(^{t}Bu)$_2$ with H$_2$O, MeOH and EtOH produce addition across the formal W=P bond, giving Cp(CO)$_2$(H)W[P(X)^{t}Bu$_2$] X = OH, MeO and EtO. Spectroscopic characterization data were provided only for the product having X = OH. Cowley and coworkers ([1]e) reported that the phosphavinylidene complex Cp(CO)$_2$Mo [P=C(SiMe$_3$)$_2$] combines with EtOH, CD$_3$OH, ^{i}Pr$_2$NH and C$_6$F$_5$SH to give $Cp(CO)_2MoP(H)[C(X)(SiMe_3)_2]$ X = EtO, CD_3O, $^iPr_2N$ and C_6F_5S. The phosphaalkene, $Cp(CO)_3WP{=}C(SiMe_3)_2$, on the other hand, reacts with CF_3SO_3H to give $Cp(CO)_3W[P(H)C(SiMe_3)_2]^+(F_3CSO_3^-)$. The last reaction, of course, can be considered a protonation of the lone pair on the 'bent' phosphaalkene phosphorus atom.

In the present study, we have examined the reactions of the metallophosphenium complex $Cp(CO)_2W[P(Ph)[N(SiMe_3)_2]$ **4b** with the proton donors $HCl\cdot OEt_2$, $HBF_4\cdot OEt_2$, and CF_3COOH. The reactions are sensitive to reagent stoichiometry and solvent. The 1:1 reaction of **4b** and $HCl\cdot OEt_2$ in THF solution leads to isolation of $Cp(CO)_2W(Cl)\{P(H)(Ph)[N(SiMe_3)_2]\}$ **7** in high yield as a red crystalline solid. NMR tube reactions of **7** with equimolar amounts of the proton acceptors ^{t}BuLi or DBU result in reversal of the protonation process and quantitative reformation of **4b** as indicated by its ^{31}P chemical shift. Compound **7** is also obtained in an NMR tube scale reaction from the combination of $Cp(CO)_3WCl$ and $P(H)(Ph)[N(SiMe_3)_2]$ in benzene at 60°C. This chemistry is summarized in Scheme 2.

The mass spectrum of compound **7** displays a parent ion envelope m/e 613–607, and fragment ion envelopes corresponding to $[M-CO^+]$, $[M-Cl^+]$ and $[M-2CO^+]$. The compound shows two IR bands in the terminal CO stretch region at 1928 and 1859 cm^{-1}, both shifted slightly down frequency from the frequencies of **4b**: 1941 and 1869 cm^{-1} [6]. The $^{31}P\{^1H\}$-NMR spectrum shows a resonance centered at δ 27.0 with $^{183}W-^{31}P$ coupling, $^1J_{PW} = 308$ Hz. The ^1H-coupled ^{31}P-NMR spectrum displays a doublet with $^1J_{PH} = 408$ Hz. As expected, the chemical shift and $^1J_{PW}$ are predictably different from the values in **4b**: δ 267; $^1J_{PW} = 702$ Hz. The ^1H-NMR spectrum contains a complex multiplet, δ 8.0–7.2, a singlet, δ 5.48, and a singlet, δ 0.26, that may be assigned to the Ph, Cp and $N(SiMe_3)_2$ groups, respectively. These data are comparable to data for **4b**:

Table 1
Summary of X-ray diffraction data for $Cp{-}W(CO)_2Cl\{P(H)(Ph)[N(SiMe_3)_2]\}$ 7

Formula	$C_{19}H_{28}O_2Si_2PClW$
Crystal dimensions (mm)	0.18 × 0.21 × 0.29
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a, Å	9.6732(14)
b, Å	11.3419(15)
c, Å	11.5930(16)
α, °	87.724(11)
β, °	77.647(11)
γ, °	82.989(11)
V, Å^3	1233.0(3)
Z	2
Formula weight	608.95
$D_{calc.}$ (g cm^{-3})	1.64
Absorption coefficient (mm^{-1})	52.2
$F(000)$	598
Temperature (K)	293
2θ limit	2–55°
No. collected reflections	12.321
No. observed reflections	4851 ($F > 3\sigma(F)$)
R (%)[a]	4.84
R_w (%)[b]	3.37

NO, number of observations; NV, number of variables.

[a] $R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; $R_w = \{\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2\}^{\frac{1}{2}}$.

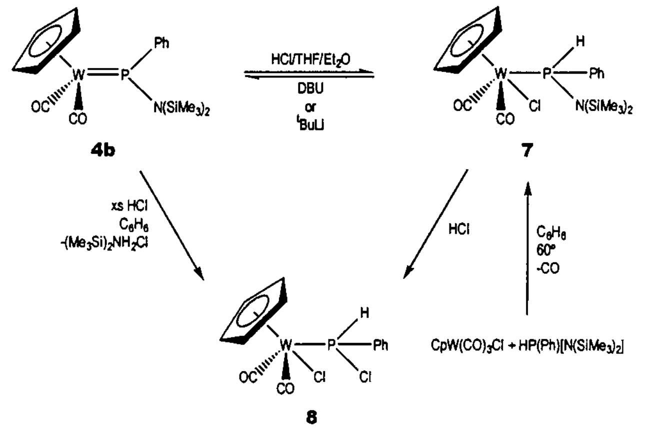
[b] GOF, $[w(|F_o|-|F_c|)^2/(NO-NV)]^{\frac{1}{2}}$.

Table 2
Atomic positional parameters for $CpW(CO)_2Cl\{P(H)(Ph)[N(SiMe_3)_2]$ **7**

Atom	x/a	y/b	z/c
W	0.18654(3)	0.22263(2)	0.08439(2)
Cl	−0.04374(15)	0.35260(13)	0.14684(14)
C(1)	0.2944(7)	0.1022(5)	0.1643(6)
O(1)	0.3560(6)	0.0256(4)	0.2091(5)
C(2)	0.0594(7)	0.1015(5)	0.1385(6)
O(2)	−0.0127(5)	0.0263(4)	0.1682(6)
C(9)	0.1948(7)	0.3267(5)	−0.0999(5)
C(10)	0.3243(7)	0.3288(5)	−0.0723(5)
C(11)	0.3843(7)	0.2094(5)	−0.0659(5)
C(12)	0.2917(7)	0.1354(6)	−0.0917(6)
C(13)	0.1695(8)	0.2087(5)	−0.1111(5)
P	0.21442(15)	0.33836(11)	0.25668(12)
N	0.3314(4)	0.2900(3)	0.3435(4)
Si(1)	0.2517(2)	0.2397(2)	0.4867(2)
C(14)	0.3969(9)	0.1815(7)	0.5680(7)
C(15)	0.1429(7)	0.3627(6)	0.5759(5)
C(16)	0.1393(11)	0.1219(7)	0.4776(7)
Si(2)	0.5160(2)	0.2941(1)	0.2931(2)
C(17)	0.5874(7)	0.3924(7)	0.3814(7)
C(18)	0.6185(8)	0.1477(6)	0.2862(8)
C(19)	0.5523(7)	0.3566(7)	0.1422(6)
C(3)	0.2211(5)	0.5001(4)	0.2395(5)
C(4)	0.1886(6)	0.5606(4)	0.1416(5)
C(5)	0.1901(6)	0.6836(5)	0.1312(6)
C(6)	0.2259(7)	0.7435(5)	0.2182(7)
C(7)	0.2580(7)	0.6833(5)	0.3162(7)
C(8)	0.2572(6)	0.5625(4)	0.3261(5)

Table 3
Selected geometric data for $CpW(CO)_2Cl\{P(H)(Ph)[N(SiMe_3)_2]$ **7**

Distances (Å)			
W–Cl	2.501(1)	C(1)–O(1)	1.162(8)
W–P	2.513(1)	C(2)–O(2)	1.161(8)
W–C(1)	1.942(6)	P–N	1.699(5)
W–C(2)	1.952(6)	P–C(3)	1.846(5)
W–C(Cp)avg	2.334	N–Si(1)	1.779(4)
		N–Si(2)	1.762(4)
Angles (°)			
C(1)–W–C(2)	74.6(3)	W–C(1)–O(1)	176.3(6)
Cl–W–C(1)	134.0(2)	W–C(2)–O(2)	177.4(5)
Cl–W–C(2)	80.2(2)	W–P–N	122.8(1)
Cl–W–P	74.1(1)	W–P–C(3)	119.0(2)
C(1)–W–P	79.4(2)	N–P–C(3)	105.4(2)
C(2)–W–P	110.2(2)	P–N–Si(1)	114.6(2)
		P–N–Si(2)	121.3(2)
		Si(1)–N–Si(2)	124.0(3)



Scheme 2.

7.8–7.3, 5.73, 0.37. In addition, **7** displays a doublet centered at δ 7.39 with J_{PH} ca. 410 Hz which is assigned to the terminal P–H group. These spectroscopic data are clearly consistent with addition of the HCl molecule across the W=P bond, and the large value of the P–H coupling constant is indicative of proton addition to the P atom as opposed to the W atom.

The proposed molecular structure of **7** is confirmed by the results of single crystal X-ray diffraction analysis. The compound has a four-legged piano stool structure formed by the Cp ring, two CO ligands, the phosphorus atom, and the Cl atom bonded to the central W atom. The CO ligands are in *cis* positions. There is no evidence in the solid state or in solution for the *trans* isomer. The average W–CO, 1.947 Å and C≡O, 1.162 Å bond lengths, and OC–W–CO bond angle, 74.6(3)°, are similar to values displayed by **4b**, 1.94 , 1.27 Å and 78(2)°, although the parameters for **4b** are less reliable due to a disorder problem in the phenyl group bound to the P atom [6]. The data are also comparable to parameters for the Mo compound **4a**: 1.949(3), 1.151(5) Å and 81.7(1)°, which have been refined more accurately ([4]i). The average value of the W–C(Cp) distances, 2.334AAA, is similar to the average values of M–C distances in **4a**, 2.348 Å, and **4b**, 2.39 Å.

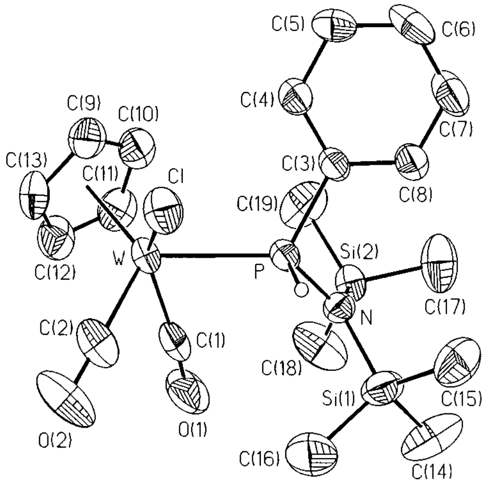


Fig. 1. Molecular structure and atom labeling scheme for CpW(CO)$_2$Cl{P(H)(Ph)[N(SiMe$_3$)$_2$] **7**. Thermal ellipsoids shown at 30%.

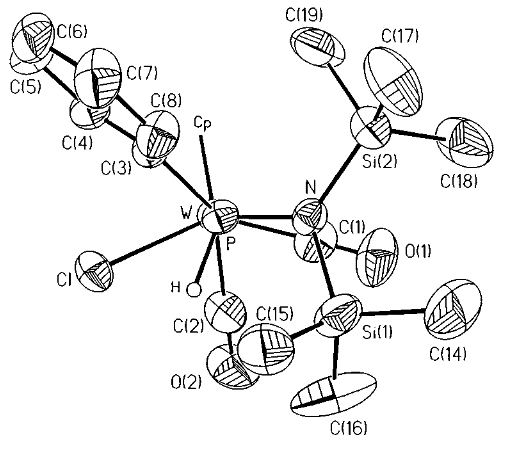
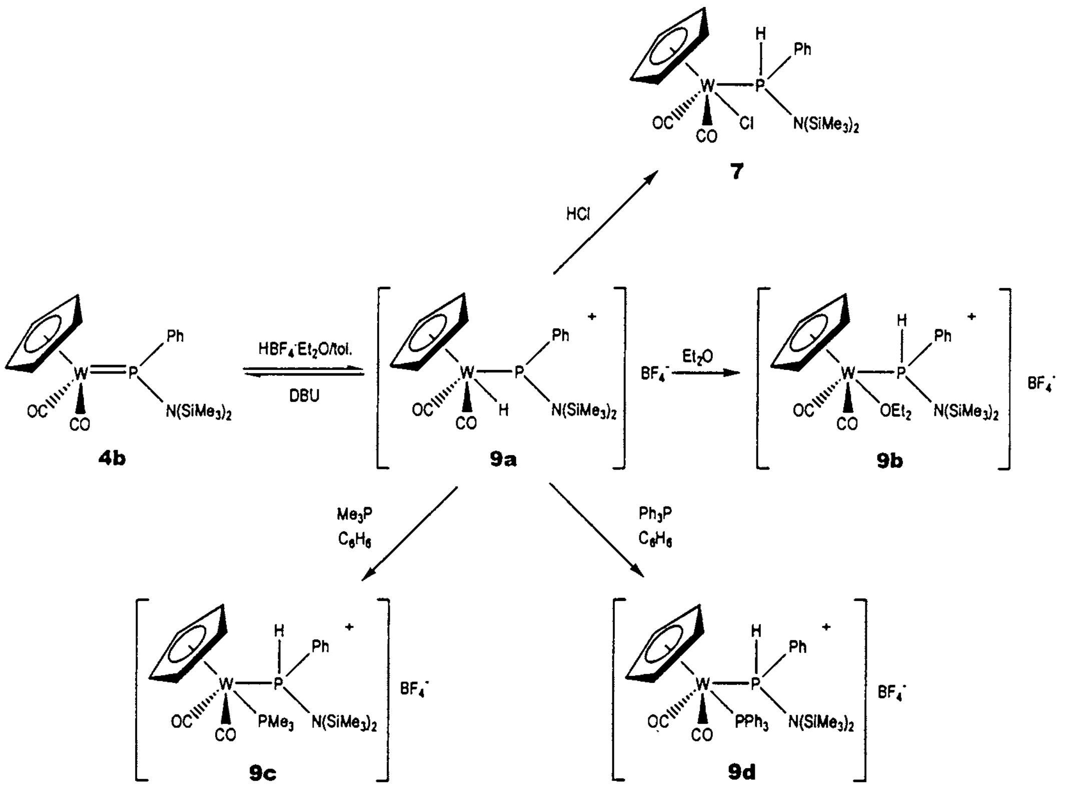


Fig. 2. Newman projection down the W–P bond vector for **7**.

The chiral phosphorus atom is bonded to the W atom, the H atom, the phenyl ring and the (Me$_3$Si)$_2$N group, and it has a distorted tetrahedral geometry. The molecular structure and a view of the arrangement of substituents relative to the CpW(CO)$_2$Cl fragment are shown in Figs. 1 and 2, respectively. The W–P bond length, 2.513(1) Å, is significantly longer than the W–P distance in **4b**, 2.252(6) Å [6], and the Mo–P distance in **4a**, 2.248(1) Å. This distance and the geometry about the P atom are consistent with disruption of the W=P multiple bonding and modification of the P atom hybridization from sp^2 to sp^3. The P–N bond distance, 1.699(5) Å is similar to the distances in **4a** and **4b**.

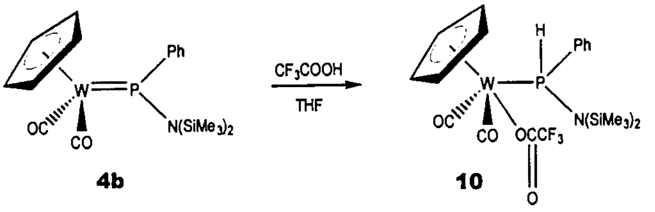
The 1:2 reaction of **4b** and HCl in benzene/Et$_2$O solution at 50°C results in the formation of an orange solid **8**, which was not obtained in analytically pure form. An IR spectrum shows two bands in the ν_{CO} region at 1963 and 1884 cm^{-1} that are upfrequency from the bands for **4b** or **7**. The ^{31}P{^{1}H}-NMR spectrum shows a single peak at δ 41.7, which is downfield from **7** but still significantly upfield of **4b**. This resonance displays W–P coupling, $^1J_{PW} = 313$ Hz, and the proton coupled spectrum shows a doublet structure with $^1J_{PH} = 421$ Hz. The ^{1}H and ^{13}C{^{1}H}-NMR spectra are also informative, as neither shows the presence of the (Me$_3$Si)$_2$N group. Based upon this data it is proposed that the first equivalent of HCl produces **7**, which, with additional HCl, undergoes reaction at the P–N bond, resulting in cleavage and formation of a Cl–P bond and (Me$_3$Si)$_2$N(H)$_2$Cl. This is a common reaction of aminophosphanes [9]. Unfortunately, since the phosphane Ph(Cl)PH is unavailable, **8** was not independently prepared from base displacement on CpW(CO)$_3$Cl.



Scheme 3.

The reaction of **4b** with $HBF_4 \cdot OEt_2$ in a 1:1 ratio in toluene appears to take a different course, as summarized in Scheme 3. Initially at 23°C a brown solid is formed whose CHN analysis is consistent with the suggested composition of **9a**. Reaction of this compound in an NMR tube with DBU regenerates **4b**. Compound **9a** does not show a parent ion in the EI-mass spectrum, but it does show weak fragment envelopes corresponding to [**4b**$^+$] (*m*/*e* 575–571) and [**4b** + HF$^+$], (*m*/*e* 595–591).]. The IR spectrum obtained from benzene solution shows two strong bands in the ν_{CO} region at 1971 and 1872 cm^{-1}, as well as a band at 1946 cm^{-1}. The last band is likely to belong to unreacted **4b**, whose second ν_{CO} band at 1869 cm^{-1} is obscured by the 1872 cm^{-1} band of **9a**. The $^{31}P\{^1H\}$-NMR spectrum shows two resonances of nearly equal intensity centered at δ 205.9 and 178.2, and both display $^{183}W-^{31}P$ satellites, $^1J_{PW} = 361$ Hz and 390 Hz, respectively. These coupling constants fall in the upper end of the range associated with phosphane metal complexes, and they are consistent with sp^3 hybridization for the P atom in **9a**. The proton coupled ^{31}P-NMR spectrum shows both of these resonances split into a doublet with $J_{PH} = 76$ Hz. The small value suggests that it does not originate from one bond coupling but instead from two bond coupling, as would occur in the proposed structure. The presence of two peaks in the $^{31}P\{^1H\}$-NMR spectrum is consistent with the formation of *cis* and *trans* isomers of **9a** with a four-legged piano stool structure. The ^1H-NMR spectrum in fact shows two Cp resonances, δ 5.29 and 4.97, of equal intensity, and three Me_3Si resonances, δ 0.35, 0.33 and 0.27 with 1:1:2 ratios. The integrated intensities of all five peaks are 5:5:9:9:18. Unfortunately, a resonance that could be unambiguously assigned to a proton bound to W is not detected.

During attempts to recrystallize **9a**, a red microcrystalline compound **9b** was obtained in modest yield. The compound displays a different, more intense mass spectrum than **9a**. The highest mass envelope at *m*/*e* 669–662 corresponds to the ion ($M-BF_3^-$), and envelopes corresponding to ($M-BF_3-CO^+$) and ($M-BF_3-2CO^+$) are also observed. The IR spectrum contains two ν_{CO} bands at 1945 and 1864 cm^{-1}, which are essentially unshifted from bands in **4b**. The $^{31}P\{^1H\}$-NMR spectrum shows a single resonance at δ 27.6 with $^1J_{PW} = 307$ Hz. The proton coupled ^{31}P-NMR spectrum contains a doublet with $J_{PH} = 392$ Hz. This value is fully consistent with one-bond P–H coupling. These data suggest that, in the presence of Et_2O from the reaction medium, **9a** rearranges by coordination of Et_2O at the W atom and transfer of the H atom from the W atom to the P atom. Similarly, addition of Ph_3P or Me_3P to fresh solutions of **9a** in benzene gives **9c** and **9d**, respectively. Compound **9c** does not display a parent ion in the mass spectrum, but fragment ion en-



(1)

velopes for ($M-SiMe_3^+$) as well as ($M-PPh_3-CO^+$) and ($M-PPh_3-2CO^+$) are observed. The IR spectrum shows three bands in the ν_{CO} region at 1969, 1932 and 1885 cm^{-1}. One of the first two may be due to an impurity, as the NMR spectra show no evidence for isomers. The $^{31}P\{^1H\}$-NMR spectrum for **9c** displays two doublet resonances of equal intensity at δ 22.5 and 20.3 with $^2J_{PP} = 12$ Hz. Neither resonance reveals P–W satellite coupling, although the low solubility of the compound limits the signal-to-noise achieved in the spectrum. The proton coupled spectrum shows the downfield doublet split into a doublet of doublets with $^1J_{PH} = 410$ Hz.

The synthesis of **9d** was followed only through NMR analysis. In this case the $^{31}P\{^1H\}$-NMR data clearly indicate the formation of two isomers with isomer 1/isomer 2 = 3/1. The following ^{31}P-NMR data were obtained: isomer 1, δ_A 21.6, δ_B -18.9, $^2J'_{PP} = 15.8$ Hz, $^1J_{PW} = 180$ Hz, and isomer 2, δ_A 20.05, δ_B -19.47, $^2J'_{PP} = 23.1$ Hz, $^1J_{PW} = 240$ Hz. These coupling constant values are similar to those reported for $CpW(CO)_2(PMe_3)[P(H)(Mes)]$ ([4]h).

The 1:2 reaction of **4b** with $HBF_4 \cdot OEt_2$ in THF or benzene produced a complex mixture which appears to include a bimetallic product (based upon M.S. analysis); however, full characterization was hampered by separation and purification problems.

The 1:1 reaction of **4b** with CF_3COOH in THF solution was also studied. The resulting red–brown solid **10** (Eq. 1) was not obtained in analytically pure form. Nonetheless, the following data were obtained. The IR spectrum from benzene solution shows three bands in the carbonyl region: 1930, 1852 and 1721 cm^{-1}. The first two bands can be assigned to terminal ν_{CO} stretches, while the last, most likely, is a carboxylate band. The $^{31}P\{^1H\}$-NMR spectrum consists of two resonances centered at δ 35.6, $^1J_{PW} = 339$ Hz and δ 29.2, $^1J_{PW} = 331$ Hz with ca. 1:1 area ratios. These are considered to result from *cis* and *trans* isomers of **10**. In the proton coupled spectrum each resonance is split into a doublet with $^1J_{PH} = 379$ and 372 Hz, respectively. Consistent with this model, the ^1H-NMR spectrum shows two Cp resonances, δ 5.18 and 5.10, and two P–H resonances, δ 8.17, $^1J_{PH} = 360$ Hz and δ 8.02, $^1J_{PH} = 382$ Hz. Only a single $(Me_3Si)_2N$ resonance at δ 0.27 is resolved. No evidence for coordinated THF is found in the ^1H-NMR spectrum and this supports the O-bonded trifluoroacetate linkage shown in Eq. 1.

4. Conclusion

The reactions of the proton donors HCl, $HBF_4 \cdot OEt_2$, and CF_3COOH with the metallophosphenium ion complex **4b** reveal additional interesting features about the nature of the W=P bond. Most importantly, there appears to exist a delicate balance between the acceptor properties of the $CpW(CO)_2$ fragment and H^+ toward the lone pair of electrons on the phosphenium ion fragment in **4b**. With proton donors (e.g. HCl and CF_3COOH) that provide a basic, coordinating anion, protonation occurs at the phosphorus atom and the anion binds to the tungsten atom, thereby accommodating for some of the loss of σ electron density from the phosphorus lone pair. For proton donors that do not provide a strongly coordinating anion, e.g. BF_4^-, protonation appears to take place initially at the tungsten atom, suggesting that the HOMO in **4b** may reside in a metal centered orbital. However, if a secondary neutral base is provided, e.g. Et_2O, Ph_3P, Me_3P, the proton migrates to the P atom and the neutral base coordinates to the W atom. These interesting results should stimulate further reactivity studies of this electronically interesting class of metal complexes.

5. Supplementary material available

Tables of crystal structure analysis data, atomic coordinates, anisotropic thermal parameters, H-atom coordinates, and full listings of bond distances and angles (13 pages) and calculated and observed structure factors (16 pages) for **7**. Ordering information is given on any current masthead page.

Acknowledgements

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