Formation of Metallophosphenium Cluster Complexes: Synthesis and Structure of $\mathrm{Cp\overline{W(CO)_2(\mu\text{-}CO)Fe(CO)_3P}(Ph)[N(SiMe_3)_2]}$[☆]

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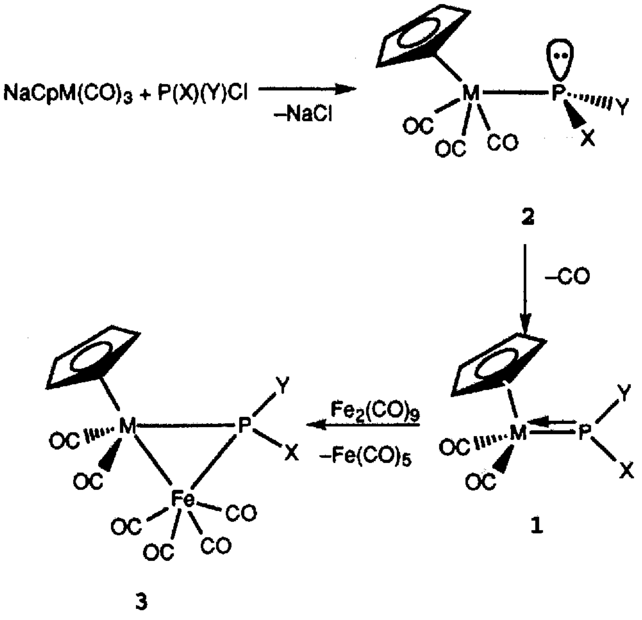
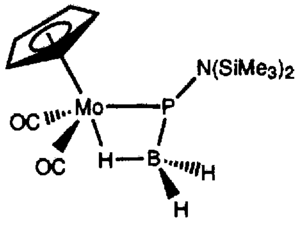
The reaction of $[(Me_3Si)_2N](Ph)PW(CO)_2Cp$ with $Fe_2(CO)_9$ produces in good yield the bimetallic compound $\mathrm{Cp\overline{W(CO)_2(\mu\text{-}CO)Fe(CO)_3P}(Ph)[N(SiMe_3)_2]}$ that was characterized by mass spectrometry, IR, ^{1}H-, and ^{31}P-NMR spectroscopy, and single crystal X-ray diffraction analysis. The molecular structure consists of $Fe(CO)_3$ and $CpW(CO)_2$ fragments joined by a bridging CO ligand and a phosphenium ion fragment which comprise a $\overline{\mathrm{Fe-C-W-P}}$ four-membered bicyclic structure.

It is well-known that reactions of many monochlorophosphanes, P(X)(Y)Cl, with Group 6 metal carborylates $NaMCp(CO)_3$ (M = Cr, Mo, W) produce metallophosphenium ion complexes, $CpM(CO)_2[P(X)(Y)]$ **1**, and metallophosphane complexes, $CpM(CO)_3[P(X)(Y)]$ **2**[1–4]. The former features a trigonal planar phosphorus atom environment and a formal M = P, σ/π multiple bond, while the latter has a pyramidal phosphorus atom and a formal M−P σ bond. Examples of **2** are often unstable; they undergo decarbonylation quantitatively forming the respective complexes **1**. Several examples of **2** have been spectroscopically detected[2], and the molecular structures of two compounds, $CpMo(CO)_3[P{=}C(SiMe_3)_2]$[2f] and $CpMo(CO)_3[P(Cl)(t\mathrm{Bu}_3C_6H_2O)]$[3e] have been determined by single crystal X-ray diffraction methods.

The chemical reactivity of these species is of interest[1–4] because the patterns that evolve may help elucidate additional details of the electronic structures of **1** and **2**. In particular, Malisch and coworkers[2] have observed that several examples of **1** combine with $Fe_2(CO)_9$. They proposed that the resulting complexes **3** have three-membered heterocyclic structures, although characterization details have not yet appeared in the literature. Such behavior suggests that the phosphorus atom in **1** retains considerable nucleophilic activity consistent with our observation[4f] that $CpMo(CO)_2P(Ph)[N(SiMe_3)_2]$ **1a** reacts smoothly with $H_3B \cdot THF$ and forms the novel complex **4**. This structure was crystallographically confirmed, and extended Hückel calculations for a model compound revealed a rational justification for the unique Mo−H−B bridging interaction. These results also suggest that perhaps a related M−C(O)−Fe bridging interaction might take place in complexes such as **3**. We report here the synthesis of $\mathrm{Cp\overline{W(CO)_2(\mu\text{-}CO)Fe(CO)_3P}(Ph)[N(SiMe_3)_2]}$ **5** and its molecular structure determination, which confirms the formation of a four-membered $\overline{\mathrm{W-C(O)-Fe-P}}$ bicycle.

The reaction of $CpW(CO)_2P(Ph)[N(SiMe_3)_2]$ **1a** and $Fe_2(CO)_9$ in a 1 : 1 ratio results in addition of an $Fe(CO)_4$ fragment to the metallophosphenium complex, as shown in the equation. Compound **5** is a dark red crystalline solid that melts in the range 122−125 °C and is indefinitely stable in the absence of air and moisture. The composition was confirmed by elemental analysis and mass spectrometry. The EI-MS of **5** in the high mass region is complicated by the presence of four abundant W isotopes; however, a weak parent ion envelope (*m/e* 745−740) is detected as are envelopes for $(M-CO^+)$, $(M-2\,CO^+)$, $(M-3\,CO^+)$, $(M-4\,CO^+)$, and $(M-2\,SiMe_3^+)$. The fragment ions below *m/e* 573 closely resemble those observed for the starting material **1a**[5].





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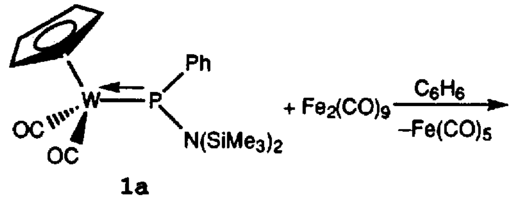
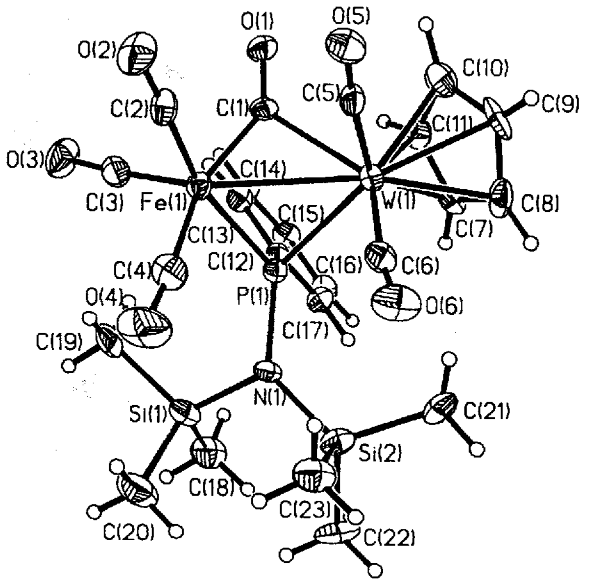


$CpW(CO)_2P(Ph)[N(SiMe_3)_2]\cdot Fe(CO)_4$

5

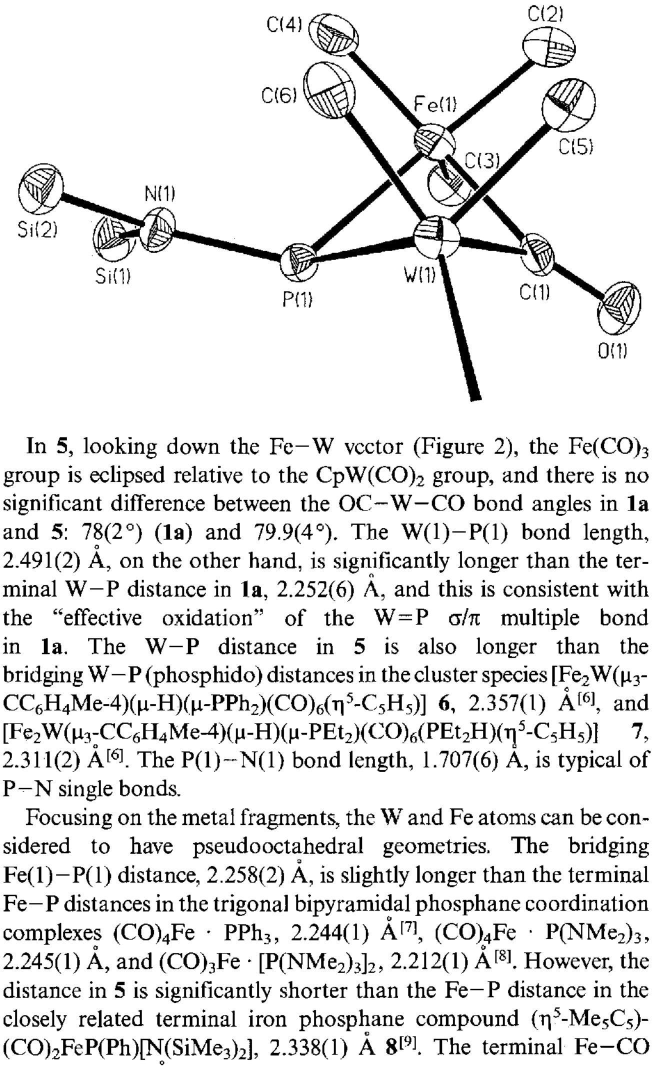
Figure 1. ORTEP-type representation of the molecular structure of **5**. Thermal ellipsoids are represented at the 25% probability level. Selected bond lengths [Å] for molecule 1 [molecule 2]: W(1)–Fe(1) 2.856(1) [2.847(1)], W(1)–P(1) 2.491(2) [2.484(2)], W(1)–C(1) 2.256(9) [2.237(7)], Fe(1)–P(1) 2.258(2) [2.258(3)], Fe(1)–C(1) 1.901(8) [1.877(10)], P(1)–C(12) 1.827(10) [1.812(7)] P(1)–N(1) 1.707(6)° [1.701(8)]



X-Ray Analysis

The single crystal X-ray diffraction analysis reveals the structural framework and metrical parameters of **5**. There are two independent molecules in the unit cell and a view of molecule 1 is shown in Figure 1. The structure consists of $CpW(CO)_2$ and $Fe(CO)_3$ fragments bonded through a W–Fe bond asymmetrically bridged by a CO ligand and a $[(Me_3Si)_2N](Ph)P$ group. The resulting $\overline{W-C-Fe-P}$ bicycle is folded along the W–Fe vector, with a fold angles of 108.7°. It is instructive to compare the structural parameters in **5** with corresponding data from the starting material **1a**[5]. In the latter, the phosphorus and nitrogen atoms are trigonal planar, and the plane defined by the W, P, and C_{ipso} atoms approximately bisects the OC–W–CO angle. In addition, the N–Si–N plane is approximately perpendicular to the plane defined by the phenyl ring and the P and W atoms. The W–P and P–N bond lengths are 2.252(6) Å and 1.68(2) Å, respectively. In compound **5**, the nitrogen atom N(1) is trigonal planar, but the phosphorus atom P(1) is four-coordinate and forms a distorted tetrahedral geometry, as indicated in part by the sum of the angle about the P atoms (e.g., involving W, Fe, and N atoms): 322.4°.

Figure 2. Heavy atom core of **5**



In **5**, looking down the Fe–W vector (Figure 2), the $Fe(CO)_3$ group is eclipsed relative to the $CpW(CO)_2$ group, and there is no significant difference between the OC–W–CO bond angles in **1a** and **5**: 78(2°) (**1a**) and 79.9(4°). The W(1)–P(1) bond length, 2.491(2) Å, on the other hand, is significantly longer than the terminal W–P distance in **1a**, 2.252(6) Å, and this is consistent with the "effective oxidation" of the W=P σ/π multiple bond in **1a**. The W–P distance in **5** is also longer than the bridging W–P (phosphido) distances in the cluster species $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(\eta^5\text{-}C_5H_5)]$ **6**, 2.357(1) Å[6], and $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}H)(\mu\text{-}PEt_2)(CO)_6(PEt_2H)(\eta^5\text{-}C_5H_5)]$ **7**, 2.311(2) Å[6]. The P(1)–N(1) bond length, 1.707(6) Å, is typical of P–N single bonds.

Focusing on the metal fragments, the W and Fe atoms can be considered to have pseudooctahedral geometries. The bridging Fe(1)–P(1) distance, 2.258(2) Å, is slightly longer than the terminal Fe–P distances in the trigonal bipyramidal phosphane coordination complexes $(CO)_4Fe\cdot PPh_3$, 2.244(1) Å[7], $(CO)_4Fe\cdot P(NMe_2)_3$, 2.245(1) Å, and $(CO)_3Fe\cdot[P(NMe_2)_3]_2$, 2.212(1) Å[8]. However, the distance in **5** is significantly shorter than the Fe–P distance in the closely related terminal iron phosphane compound $(\eta^5\text{-}Me_5C_5)(CO)_2FeP(Ph)[N(SiMe_3)_2]$, 2.338(1) Å **8**[9]. The terminal Fe–CO distance, 1.792 Å (average) is slightly longer than the Fe–CO distance in **8**, 1.750(7) Å[9], but it is comparable to the distances in several Mo–Fe and W–Fe cluster species: $[FeMo[\mu\text{-}CC_6H_4Me\text{-}4](CO)_6(\eta^5\text{-}C_5H_5)]$ 1.814 Å (average)[10]; $[FeMo_2(\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2)(CO)_6(\eta^5\text{-}C_5H_5)]$ 1.792 Å (average)[10]. As described above, one of the four original terminal carbonyl groups from the $Fe(CO)_4$ fragment takes up a bridging position in **5** between the Fe and W atoms with Fe–(μ-CO) distance of 1.901(8) Å and W–(μ-CO) distance of 2.256(9) Å.

Finally, the metal-metal distance Fe(1)–W(1) 2.856(1) Å is at the upper end of the single-bond range found in a series of clusters: **6** W–Fe(1) 2.817(1) Å, W–Fe(2) 2.523(1) Å[6]; **7** W–Fe(1) 2.763(1) Å, W–Fe(2) 2.830(1) Å[6]; $[Fe_2W(\mu_3\text{-}OCCH_2R)(\mu\text{-}PPh_2)(CO)_5(\eta^5\text{-}C_5H_5)]$ W–Fe(1) 2.723(1) Å, W–Fe(2) 2.712(1) Å[11]; $[Fe_2W(\mu_2\text{-}OCCH_2R)(\mu\text{-}PPh_2)(CO)_6(PPh_2H)(\eta^5\text{-}C_5H_5)]$ W–Fe(2) 2.940(1) Å[11]. The last compound features a single phosphido-bridged W–Fe bond.

In summary, the isolation and characterization of **5** show that, at least in **1a**, addition of an $Fe(CO)_4$ fragment across the W=P bond results in the formation of a complex with an $Fe(CO)_3$ unit bonded to the phosphorus atom through a direct Fe–P bond and linked to the W atom through a *carbonyl-supported* Fe–W bond. This contrasts with structure **3** previously proposed for several other related complexes.

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Experimental

Standard inert atmosphere techniques were used for the manipulation of all reagents and products. Solvents were dried, deoxygenated, and distilled prior to use. Infrared spectra were recorded on a Nicolet Model 6000 FT-IR spectrometer, and samples were contained in NaCl solution cells. NMR spectra were recorded on GE NT-360 and JEOL GSX-400 NMR spectrometers. Spectral standards were Me_4Si (^1H) and 85% H_3PO_4 (^{31}P). The $NaWCp(CO)_3$ was prepared from NaCp and $W(CO)_6$[14], and the solutions were used immediately. $PhP(Cl)[N(SiMe_3)_2]$ and the complex **1** were prepared as described by McNamara[5].

5: A mixture of **1a** (1.0 g, 1.74 mmol) and $Fe_2(CO)_9$ (0.65 g, 1.79 mmol) in dry benzene (20 ml) was stirred at 23° for 12 h. The resulting mixture was filtered, and the filtrate was evaporated to dryness, leaving a red crystalline product (1.2 g, 93%). The solid was recrystallized from benzene or benzene/hexane mixtures at −10 °C (melting point, 122−125 °C). – IR (cyclohexane): $\tilde{\nu}$ = 2047, 1987, 1975, 1960, 1917, 1757. – MS (EI, 70 eV), *m/z* (%): 745−740 (0.1) [M^+], 685−681 (0.7) [$M\text{-}2CO^+$], 659−654 (2.2) [$M\text{-}3CO^+$], 630−626 (4.8) [$M\text{-}2SiMe_3^+$], 575−571 (50) [$M\text{-}Fe(CO)_4^+$]. – ^1H NMR (C_6D_6): δ = 0.37 [$N(SiMe_3)_2$], 4.31 (Cp), 7.0−7.7 (Ph). – ^{31}P NMR (C_6D_6): δ = 117.0, $^1J_{P,W}$ = 208.1 Hz. – $C_{23}H_{28}FeNO_6PSi_2W$ (741.33): Calcd.: C 37.26, H 3.81; found: C 37.85, H 4.26.

Crystal Structure Analysis: A red single crystal of **5** was placed in a glass capillary under nitrogen and centered on a Syntex P3/F four circle-automated diffractometer with a graphite monochromator and $Mo_{K\alpha}$ radiation (λ = 0.71069 Å). Determinations of the crystal class, orientation matrix, and unit cell parameters were performed in a standard manner. The data were collected at 20 °C in the ω-scan mode. A small empirical absorption correction based on ψ scans (laminar model) was applied, and the agreement factors were 9.28% before and 2.16% after. Data were corrected for Lorentz and polarization effects, and redundant and equivalent data were averaged. All calculations were performed by using SHELXTL. *Crystallographic Data:* Size of crystal: $0.02 \cdot 0.41 \cdot 0.51$ mm, $[C_{23}H_{28}FeNO_6PSi_2W]_2$, M_r = 1482.642; a = 9.985(2), b = 17.001(2), c = 17.441(3) Å, α = 93.20(1), β = 105.67(1), γ = 97.70(1)°; V = 2812.1(7) $Å^3$, triclinic crystal system, space group $P\bar{1}$; d_{calcd} = 1.75 g cm^{-3}, μ = 50.12 cm^{-1}, F(000) = 1456. *Data Collection:* 2θ range = 1−55° measured in $\pm h$, $\pm k$, $\pm l$; scan speed = 3−30° min^{-1}; reflections measured: 25,593 independent reflections; 12,630 reflections observed: 9259 with $F \geq 3\sigma(F)$. *Structure Solution and Refinement:* The structure was solved by standard heavy atom techniques and refined with all heavy atoms, anisotropic, and H atoms in fixed positions with U_{iso} = 1.2 U_{equiv} of the parent atom. The 001 reflection was removed since it suffers from strong absorption (f_{calc} = 251, f_{obs} = 47). The final agreement factors were R = 7.00% and R_{WF} = 4.72%. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$.

☆ Dedicated to Prof. Dr. *Max Herberhold* on the occasion of his 60th birthday.

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[15] Details of the crystal structure determination are deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, and may be obtained by quoting the depository number CSD-59183.

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