

Synthesis of a Phosphavinyl Complex via Shift of a Pentamethylcyclopentadienyl from Phosphorus to Iron

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Summary: The reaction of the phosphalkene (η^1 -Me₅C₅)P=C(SiMe₃)₂ with Fe₂(CO)₉ affords the η^1 (P-bonded) complex (η^1 -Me₅C₅)[(CO)₄Fe]P=C(SiMe₃)₂ (**4**). Photolysis of **4** produces the phosphavinyl complex [Fe{ η^1 -P=C(SiMe₃)₂}(η^5 -Me₅C₅)(CO)₂] (**5**). Compound **5** can also be prepared via the metathetical reaction of (Me₃Si)₂C=P-Cl with K[Fe(η^5 -Me₅C₅)(CO)₂]. The structure of **5** has been determined by X-ray crystallography.

Phosphaalkenes, RP=CR₂,¹ are proving to be remarkably versatile ligands. As intact units, they can coordinate

(1) (a) Klebach, T. C.; Lourens, R.; Bickelhaupt, F.; Stam, C. H.; Van Herk, A. J. *Organomet. Chem.* 1981, 210, 211. (b) Kroto, H. W.; Nixon, J. F.; Taylor, M. J.; Frew, A. A.; Muir, K. W. *Polyhedron* 1982, 1, 89. (c) Neilson, R. H.; Thoma, R. J.; Vickovic, I.; Watson, W. A. *Organometallics* 1984, 3, 1132.

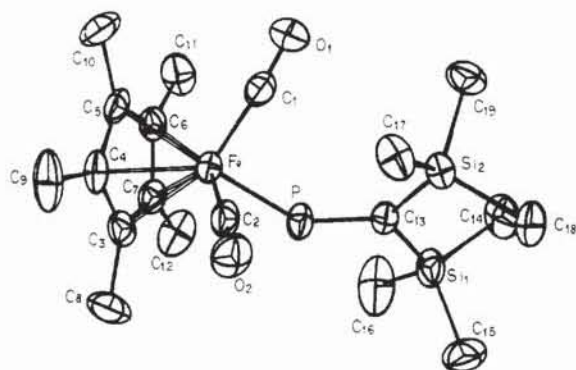
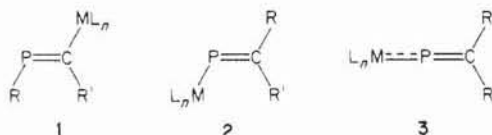


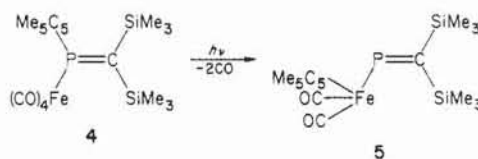
Figure 1. ORTEP drawing of $[\text{Fe}(\eta^1\text{-P}=\text{C}(\text{SiMe}_3)_2)(\eta^5\text{-Me}_5\text{C}_5)(\text{CO})_2]$ (**5**) showing the atom numbering scheme. Important structural parameters: P-Fe = 2.256 (2) and P-C(13) = 1.680 (9) Å; Fe-P-C(13) = 126.2 (3), P-C(13)-Si(1) = 107.1 (5), P-C(13)-Si(2) = 134.4 (5), and Si(1)-C(13)-Si(2) = 118.4 (5)°.

in an η^1 (P donor)¹ or an η^2 (P=C donor)² fashion. Combinations of η^1 and η^2 ligation have also been observed³ as has equilibration between these bonding modes.⁴ Further elaboration of this chemistry has become possible by the incorporation of organometallic substituents. Thus, monometalation at carbon produces **1**⁵ while P-metalation results in either phosphavinyl (**2**)⁶ or phosphavinylidene (**3**)⁷ complexes depending on whether the phosphorus atom functions as a one- or three-electron donor. We report a novel synthesis of a phosphavinyl complex via migration of a C_5Me_5 group from phosphorus to iron.



Treatment of 3.24 g (10 mmol) of $(\eta^1\text{-Me}_5\text{C}_5)\text{P}=\text{C}(\text{SiMe}_3)_2$ ⁸ with an equimolar quantity of $\text{Fe}_2(\text{CO})_9$ for 3 days at 25 °C produced a dark red solution. After filtration and removal of the solvent and volatiles, the resulting red oil was recrystallized from 20 mL of (2:3) toluene/acetonitrile at -30 °C. The red-black crystals (mp 79 °C), which were isolated in 41% yield, were identified as the η^1 -phosphaalkene complex **4** on the basis of analytical and spectroscopic data.⁹ Of particular significance is the ³¹P

chemical shift (371.5 ppm) which falls in the region typical of P-bonded phosphaalkene complexes.¹



Photolysis of a *n*-hexane solution of **4** with a Hanau TQ-718 mercury lamp caused immediate gas evolution. After 3 h the carbonyl bands of **4** (2055, 1975, and 1959 cm^{-1}) disappeared and were replaced with absorptions at 1942 and 1988 cm^{-1} which are attributable to **5**. ³¹P NMR spectroscopic assay indicated that the reaction mixture contained **5** (s, 641.5 ppm) and traces of $(\eta^1\text{-Me}_5\text{C}_5)\text{P}=\text{C}(\text{SiMe}_3)_2$ (s, 374.5 ppm).⁸ Compound **5** can also be prepared by treatment of $(\text{Me}_3\text{Si})_2\text{C}=\text{P}(\text{Cl})_2$ ¹⁰ with $\text{K}[\text{Fe}(\eta^5\text{-Me}_5\text{C}_5)(\text{CO})_2]$ in THF solution (-20 °C) and purified by recrystallization from *n*-hexane solution at -20 °C (yield 57.7%). The composition of brown, crystalline **5** (mp 117–123 °C) was established on the basis of analytical and spectroscopic data,¹¹ and its structure (Figure 1) was elucidated by single-crystal X-ray diffraction methods.¹² The phosphorus-carbon bond length (1.680 (9) Å) is similar to those of unmetalated phosphaalkenes;^{2d,13} moreover, the sum of bond angles at C(13) is 360° within experimental error. The phosphorus-iron bond length (2.256 (2) Å) and the Fe-P-C bond angle (126.2 (3)°) indicate that the phosphorus lone pair is not involved in bonding to the metal. The fact that the Fe-P-C angle is ~15° larger than those of unmetalated phosphaalkenes seems to be a consequence of steric effects because the P-C(13)-Si(2) angle (134.4 (5)°) is considerably larger than the P-C(13)-Si(1) angle (107.1(5)°).

The scope of the Me_5C_5 (and C_5H_5) main-group/transition-metal shift reaction is presently being studied as is the reactivity of **5**.

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Registry No. **4**, 100082-33-5; **5**, 100082-34-6; $\text{K}[\text{Fe}(\eta^5\text{-Me}_5\text{C}_5)(\text{CO})_2]$, 59654-59-0; $\text{Fe}_2(\text{CO})_9$, 15321-51-4; $(\eta^1\text{-Me}_5\text{C}_5)\text{P}=\text{C}(\text{SiMe}_3)_2$, 100082-32-4; $(\text{Me}_3\text{Si})_2\text{C}=\text{P}(\text{Cl})_2$, 79454-85-6.

(2) (a) Cowley, A. H.; Jones, R. A.; Stewart, C. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Zhang, H.-M. *J. Am. Chem. Soc.* **1983**, *105*, 3737. (b) Al-Resayes, A. I.; Klein, S. I.; Kroto, H. W.; Meidine, M. F.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 930. (c) Van der Knaap, Th. A.; Jenneskens, L. W.; Meerwisen, H. J.; Bickelhaupt, F.; Walther, D.; Dinjus, E.; Uhlig, E.; Spek, A. L. *J. Organomet. Chem.* **1983**, *254*, C33. (d) Cowley, A. H.; Jones, R. A.; Lasch, J. G.; Norman, N. C.; Stewart, C. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Zhang, H.-M. *J. Am. Chem. Soc.* **1984**, *106*, 7015. (e) Werner, H.; Paul, W.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 626.

(3) (a) Knoll, K.; Huttner, G.; Wasiucionek, M.; Zsolnai, L. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 739. (b) Holland, S.; Charrier, C.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1984**, *106*, 826. (c) Appel, R.; Casser, C.; Knoch, F. *J. Organomet. Chem.* **1985**, *293*, 213.

(4) (a) Van der Knaap, Th. A.; Bickelhaupt, F.; van der Poel, H.; van Koten, G.; Stam, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 1756. Kroto, H. W.; Klein, S. I.; Meidine, M. F.; Nixon, J. F.; Harris, R. K.; Packer, K. J.; Reams, P. *J. Organomet. Chem.* **1985**, *280*, 281.

(5) Weber, L.; Reizig, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 53.

(6) Weber, L.; Reizig, K.; Boese, R.; Polk, M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 604.

(7) Cowley, A. H.; Norman, N. C.; Quashie, S. *J. Am. Chem. Soc.* **1984**, *106*, 5007.

(8) Gudat, D.; Niecke, E.; Krebs, B.; Dartmann, M. *Chimia* **1985**, *39*, 277.

(9) Anal. Calcd for $\text{C}_{21}\text{H}_{33}\text{FePO}_4\text{Si}_2$: C, 51.22; H, 6.75. Found: C, 51.06; H, 6.97. MS (EI, 70 eV): *m/e* (relative intensity) 492 (M^+ , 0.4), 477 ($\text{M}^+ - \text{CH}_3$, 0.4), 436 ($\text{M}^+ - 2\text{CO}$, 2.7), 408 ($\text{M}^+ - 3\text{CO}$, 27.1), 380 ($\text{M}^+ - 4\text{CO}$, 76.2), 73 (SiMe_3^+ , 100). ¹³C{¹H} NMR: (C_6D_6 , 28 °C): 4.2 (d, *J* = 8.2 Hz, SiC₃), 5.1 (d, *J* = 4.8 Hz, SiC₃), 11.8 (broad, CCH₃), 136.5 and 142.8 (very broad, CCH₃), 187.8 (d, *J* = 24.5 Hz, P=C), 216.1 (d, *J* = 15 Hz, CO).

(10) Appel, R.; Westerhaus, A. *Tetrahedron Lett.* **1984**, *22*, 2159.

(11) Anal. Calcd for $\text{C}_{19}\text{H}_{33}\text{FePO}_2\text{Si}_2$: C, 52.29; H, 7.62. Found: C, 50.84; H, 7.72. MS (EI, 70 eV): *m/e* (relative intensity) 436 (M^+ , 2.9), 408 ($\text{M}^+ - \text{CO}$, 44.0), 380 ($\text{M}^+ - 2\text{CO}$, 100), 73 (SiMe_3^+ , 72.5). ¹³C{¹H} NMR (CD_2Cl_2 , 28 °C): 3.5 (s, SiC₃), 3.9 (d, *J* = 15.6 Hz, SiC₃), 9.3 (d, *J* = 9.2 Hz, CCH₃), 98.9 (s, CCH₃), 208.9 (d, *J* = 106.1 Hz, P=C), 217.6 ppm (s, CO).

(12) A single crystal of **5** with dimensions 0.35 × 0.35 × 0.20 mm was sealed under dry nitrogen in a Lindemann capillary. Some crystal data for **5** are as follows: $\text{C}_{21}\text{H}_{33}\text{FePO}_2\text{Si}_2$, *M* = 436.47, monoclinic, space group *P2*₁/*n* (No. 14); *a* = 12.807 (2) Å, *b* = 9.364 (3) Å, *c* = 20.328 (3) Å, β = 103.55 (1)°; *V* = 2370 Å³; *Z* = 4; *D*(calcd) = 1.223 g cm⁻³, and μ = 8.1 cm⁻¹. A total of 3720 symmetry-independent reflections were recorded by using ω - 2θ scans in the range 3.0 < 2θ < 48.0° using graphite-monochromated Mo K α X-radiation with λ = 0.71069 Å. Of these, 2339 reflections (*I* > 3.0 σ (*I*)) were used to solve (SIMPEL) and refine (full matrix, least squares) the structure of **5**. Final least-squares refinement gave *R* = 0.0572 and *R*_w = 0.0746.

(13) For a review, see: Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1984**, *20*, 731.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, thermal parameters, and structure factors for **5** (17 pages). Ordering information is given on any current masthead page.