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

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Summary: The reaction of the phosphaalkene \( \eta^1-Me_5C_5P=CSiMe_3 \) with \( \text{Fe}_2\text{(CO)}_9 \) affords the \( \eta^1 \) (P-bonded) complex \( \eta^1-Me_5C_5P=CSiMe_3\text{(CO)}_2\text{Fe} \) \( \left( \text{Fe} \right) \) \( \text{(4)} \). Photolysis of 4 produces the phosphovinyli complex \( \text{Fe} \left( \eta^1-P=CSiMe_3\text{(CO)}_2\text{Cl} \right) \) \( \left( \text{Fe} \right) \) \( \text{(5)} \). Compound 5 also can be prepared via the metathetical reaction of \( \text{(Me}_2\text{Si)}\text{Cl} \) \( \left( \text{Fe} \right) \text{(5)} \) \( \left( \text{Fe} \right) \text{Cl} \) with \( \text{K}[\text{Fe}(\eta^1-Me_5C_5\text{CO}_2)] \). The structure of 5 has been determined by X-ray crystallography.

Phosphaalkenes, \( \text{RP}=\text{CR}_2 \), are proving to be remarkably versatile ligands. As intact units, they can coordinate

in an $n^1$ (P donor) or an $n^2$ (P=C donor) fashion. Combinations of $n^1$ and $n^2$ ligation have also been observed as has equilibration between these bonding modes. Further elaboration of this chemistry has become possible by the incorporation of organometallic substituents. Thus, monometalation at carbon produces while P-metalation results in either phosphinyl (23) or phosphavinylidene (3') complexes depending on whether the phosphorus atom functions as a one- or three-electron donor. We report a novel synthesis of a phosphinyl complex via migration of a C$_2$H$_5$ group from phosphorus to iron.

![Diagram](image-url)

Treatment of 3.24 g (10 mol) of $\text{(P=CSiMe}_3\text{)}$P=C-(SiMe$_3$)$_2$ with an equimolar quantity of Fe$_2$(CO)$_4$ 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 $\text{Me}_2\text{C}_5\text{P}=(\text{Me}_3\text{Si})\text{C}=\text{P}=(\text{SiMe}_3)$ on the basis of analytical and spectroscopic data. Of particular significance is the $^31$P chemical shift (371.5 ppm) which falls in the region typical of P-bonded phosphalkene complexes.

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, 1775, and 1659 cm$^{-1}$) disappeared and were replaced with absorptions at 1942 and 1988 cm$^{-1}$ which are attributable to 5. $^3$P NMR spectroscopic assay indicated that the reaction mixture contained 5 (6, 641.5 ppm) and traces of $\text{Fe}_{11}-\text{P}=(\text{SiMe}_3)$ (6, 374.5 ppm). Compound 5 can also be prepared by treatment of Me$_2\text{C}_5\text{C}=\text{P}=(\text{SiMe}_3)$ with K[Fe$_{11}-\text{P}=(\text{SiMe}_3)$] in THF solution (−20 °C), and purified by redissolution from $n$-hexane solution at −20 °C using 2-propanol (57.7%). The composition of brown, crystalline 5 (mp 117–123 °C) was established on the basis of analytical and spectroscopic data, and its structure (Figure 1) was elucidated by single-crystal X-ray diffraction methods. The phosphorus–carbon bond length (1.680 (9) Å) is similar to those of unmetallated phosphalkenes; 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 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 unmetallated phosphalkenes 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(6°)).

The scope of the Me$_2\text{C}_5\text{P}=\text{C}(\text{SiMe}_3)$ main-group/migration 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; K[Fe$_{11}-\text{P}=(\text{SiMe}_3)$], 59654-59-0; Fe$_2$(CO)$_4$, 15321-54-1; $\text{Me}_2\text{C}_5\text{P}=(\text{SiMe}_3)$, 100082-32-4; (Me$_3$Si)$_2\text{C}=\text{P}=(\text{SiMe}_3)$, 79454-85-6.

(9) Anal. Caled for C$_2$H$_5$FePOSi$_3$: C, 51.22; H, 6.75. Found: C, 51.06; H, 0.59. MS (EI, 70 eV), $m/e$ (relative intensity) 492 (M$^+$, 0.4), 477 (M$^+$–CH$_3$, 0.4), 438 (M$^+$–CO, 2.7), 408 (M$^+$–CO, 27.1), 380 (M$^+$–CO, 75.2), 73 (SiMe$_3^+$, 100). $^3$P NMR. DC$_6$(28°C): 4.2 d, $J = 8.2$ Hz, Si(C$_5$), 3.1 (d, $J = 4.8$ Hz, Si(C$_5$)), 1.18 (broad, C(H$_3$)), 128.5 and 142.8 (very broad, C(H$_3$)), 187.8 (d, $J = 24.5$ Hz, P=F), 216.2 (d, $J = 15$ Hz, CO).


(11) Anal. Caled for C$_2$H$_5$FePOSi$_3$: C, 52.98; H, 7.62. Found: C, 52.84; H, 7.73. MS (EI, 70 eV), $m/e$ (relative intensity) 436 (M$^+$, 2.9), 408 (M$^+$–CO, 44.0), 380 (M$^+$–CO, 19.0), 73 (SiMe$_3^+$, 72.5). $^3$P NMR. DC$_6$(28°C): 3.5 (s, Si(C$_5$)), 3.9 (d, $J = 15.8$ Hz, Si(C$_5$)), 9.3 (d, $J = 9.2$ Hz, C(H$_3$)), 98.9 (s, C(H$_3$)), 208.9 (d, $J = 106.1$ Hz, P=F), 217.8 ppm (s, CO).

(12) A single crystal of 5 with dimensions 0.33 × 0.63 × 0.20 mm was sealed under dry nitrogen in a Lindemann capillary. Some crystal data for 5 are as follows: C$_2$H$_5$FePO$_4$P$_2$, M = 436.47, monoclinic space group $P2_1/n$ (No. 14); $a = 12.807$ (2) Å, $b = 3.942$ (3) Å, $c = 20.328$ (3) Å, $\beta = 105.55$ (1°), $V = 2070$ Å$^3$; $Z = 4$; D(calcd) = 1.222 g cm$^{-3}$ and $\alpha = 8.1$ cm$^{-1}$. A total of 5720 symmetry-independent reflections were recorded by using $\omega$-scan in the range $0<\theta<48.5^\circ$ using graphite-monochromated Mo Kα radiation with $\lambda = 0.71069$ Å. Of these, 2359 reflections ($\theta > 3.0$) were used to solve (SHELXTL) and refine (full matrix, least squares) the structure of 5. Final least-squares refinement gave $R = 0.0572$ and $R_w = 0.0764$.

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.