

Phosphasilaferracyclopropane: An Activator of Small Molecules Having Polarized Single, Double, and Aromatic Unsaturated Bonds

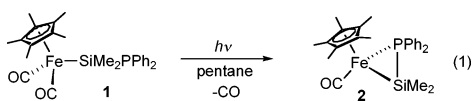
Masaaki Okazaki,* Kyeong A Jung, Kazuyuki Satoh, Hiroshi Okada, Junpei Naito, Tadahiro Akagi, Hiromi Tobita,* and Hiroshi Ogino†

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

Received November 20, 2003; E-mail: mokazaki@mail.tains.tohoku.ac.jp

The synthesis of small membered silametallacycles, particularly three-membered ring compounds, has attracted considerable interest because of their strained molecular structures, peculiar bonding modes, and novel reactivities.¹ To date, π -complexes containing silene,² disilene,³ and silanimine⁴ ligands have been synthesized and well characterized by X-ray diffraction studies, and their fundamental reactivities have been investigated. However, little is known about those complexes having $\kappa^2(\text{Si},E)$ - $\text{SiR}_2\text{ER}'_n$ ligands ($\text{ER}'_n = \text{SR}'$,⁵ TeR' ,⁶ and PR'_2),⁷ which work as three-electron donors. Our previous work revealed that irradiation of $\text{Cp}(\text{CO})_2\text{FeSiMe}_2\text{PPh}_2$ led to the intermediate formation of $\text{Cp}(\text{CO})\text{Fe}\{\kappa^2(\text{Si},P)\text{-Me}_2\text{SiPPh}_2\}$.^{7b} This three-membered ring complex gradually dimerized to give an $\text{Fe}_2\text{Si}_2\text{P}_2$ six-membered metallacycle $\text{Cp}_2\text{Fe}_2(\text{CO})_2[\mu_2\text{-}\{\kappa^2(\text{Si},P)\text{-Me}_2\text{SiPPh}_2\}]_2$. The high reactivity of this silametallacycle is in sharp contrast to the thermally stable carbon analogue, $\text{Cp}(\text{CO})\text{Fe}\{\kappa^2(\text{C},P)\text{-CH}_2\text{PEt}_2\}$.⁸ This paper reports the successful isolation of $\text{Cp}^*(\text{CO})\text{Fe}\{\kappa^2(\text{Si},P)\text{-Me}_2\text{SiPPh}_2\}$ (**2**) by introduction of the bulkier and more electron-releasing Cp^* ligand. The reactivity of **2** toward small molecules with polarized bonds is also discussed.

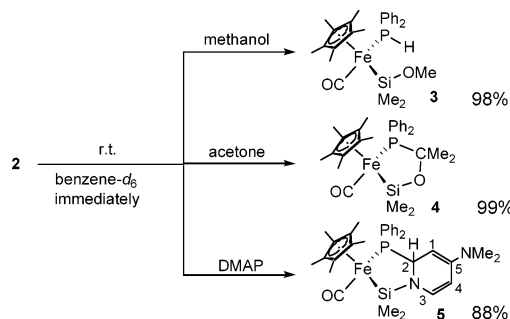
$\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{PPh}_2$ (**1**) was synthesized by treatment of $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{Cl}$ with LiPPh_2 in 44% yield. A pentane solution of **1** was irradiated using a 450 W medium-pressure Hg lamp for 70 min (eq 1). Recrystallization of the residue from pentane at -75 °C gave highly air-sensitive orange crystals of **2** in 79% yield. A dimerization reaction such as that observed in the cyclopentadienyl analogue of **2**, that is, $\text{Cp}(\text{CO})\text{Fe}\{\kappa^2(\text{Si},P)\text{-Me}_2\text{SiPPh}_2\}$,^{7b} did not occur in the case of **2**.



The monomeric structure of **2** was confirmed from the ³¹P NMR data. The ³¹P NMR signal of **2** at $\delta -48.3$ is shifted considerably upfield as compared to those of the usual PPh_2R -coordinated complexes and the dimerized form of the Cp analogue $\text{Cp}_2\text{Fe}_2(\text{CO})_2[\mu_2\text{-}\{\kappa^2(\text{Si},P)\text{-Me}_2\text{SiPPh}_2\}]_2$ [δ 19.9 (trans form) and 10.9 (cis form)]. This upfield shift of the ³¹P NMR signal is typically observed in phosphorus-containing three-membered ring compounds.⁹ Such a tendency was also observed in the ³¹P NMR signal of the first reported phosphasilametallacyclopropane.^{7a}

The ²⁹Si NMR spectrum exhibits a doublet signal at δ 25.4 with $J_{\text{PSi}} = 125.5$ Hz. The large coupling constant clearly supports the existence of a direct Si–P bond. The IR spectrum shows only one strong band assigned to ν_{CO} at 1894 cm^{-1} , indicating the dissociation of one carbonyl ligand from **1** followed by intramolecular coordination of the PPh_2 part.

Scheme 1



Our studies revealed that **2** was extremely reactive toward organic molecules having polarized bonds (Scheme 1). In contrast, the dimerized form of the Cp analogue, $\text{Cp}_2\text{Fe}_2(\text{CO})_2[\mu_2\text{-}\{\kappa^2(\text{Si},P)\text{-Me}_2\text{SiPPh}_2\}]_2$, did not react with methanol, acetone, and 4-(dimethylamino)pyridine (DMAP) even at 100 °C. The difference in the reactivity strongly supports the monomeric structure of **2**. All reactions of **2** proceeded immediately at room temperature to give products in high yields.

Treatment of **2** with methanol resulted in opening of the three-membered ring to give a methoxysilyl(hydrophosphine) complex **3**. ¹H NMR signals assignable to the PH and SiOMe moieties were observed at δ 6.67 (d, $^1J_{\text{PH}} = 347.0$ Hz) and 3.48 (s), respectively. The crystal structure was unequivocally determined by X-ray diffraction analysis (Figure 1). The hydrogen atom on the phosphine ligand was located by the difference Fourier map and refined isotropically. Structural parameters fall into the range expected for the typical three-legged piano stool geometry, except for the Cp^* ligand and CO ligand, and the iron center possesses the SiMe_2OME and PPh_2H ligands formed through addition of MeOH across the silicon–phosphorus bond.

Complex **2** reacted with acetone to give the insertion product **4**. Cooling of the pentane solution at -75 °C allowed the growth of yellow crystals suitable for X-ray diffraction analysis. As shown in Figure 2, the O=C double bond is inserted into the silicon–phosphorus bond, in which the silicon atom is bonded to the oxygen and the phosphorus atom is bonded to the carbon. The C26–O2 bond distance ($1.419(4)$ Å) lies in the normal range expected for a single bond (1.42 – 1.43 Å).

The formation of a five-membered phosphametallacycle is supported by the ³¹P NMR chemical shift of δ 123.1, which is shifted considerably downfield as compared to the values for iron phosphine complexes of the $\text{L}_n\text{Fe-PPh}_2\text{R}$ (R = alkyl) type. This tendency is typical for phosphorus-containing five-membered metallacycles.⁹ The ¹H NMR signals of the methyl groups of the inserted acetone appear at δ 1.01 (d, $^3J_{\text{HP}} = 12.7$ Hz) and 1.56 (d, $^3J_{\text{HP}} = 9.0$ Hz). A doublet signal in the ²⁹Si NMR spectrum is observed at δ 93.2 ($^2J_{\text{PSi}} = 42.0$ Hz).

* Present address: Miyagi Study Center, The University of the Air, Sendai 980-8577, Japan.

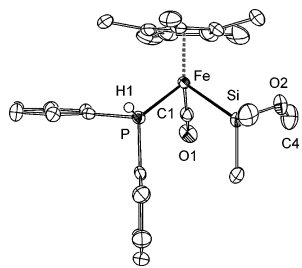


Figure 1. Molecular structure of **3** showing the atom label scheme.

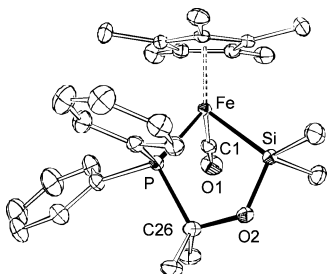


Figure 2. Molecular structure of **4** showing the atom label scheme.

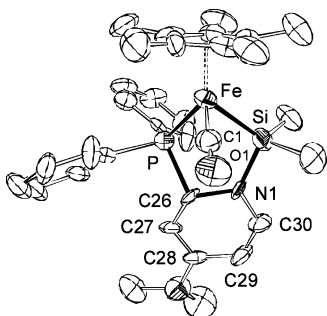
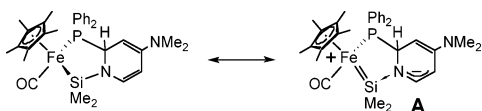


Figure 3. Molecular structure of **5** showing the atom label scheme.

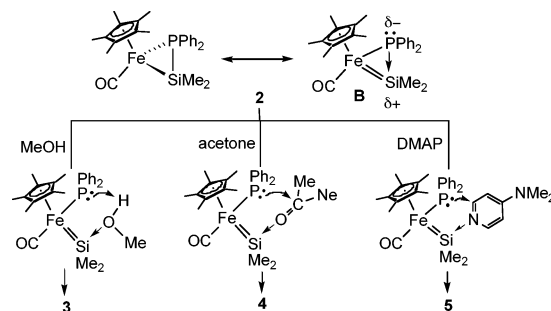
Scheme 2



An aromatic compound, DMAP, also reacted with **2** to give the insertion product **5**. Recrystallization of **5** from toluene–hexane at $-30\text{ }^{\circ}\text{C}$ gave orange crystals that were suitable for X-ray diffraction study (Figure 3). Complex **5** was shown to be a five-membered metallacycle, in which the aromatic N–C bond is inserted into the silicon–phosphorus bond of **2**. The bond lengths of Fe–Si (2.290(2) Å) and Fe–P (2.176(2) Å) are both shorter than the normal range of the corresponding single bonds.^{1,10} These data are in good agreement with a significant contribution of the cationic phosphine(silylene) complex **A** shown in Scheme 2. The inserted pyridine ring in **5** has lost its aromaticity: the bond lengths N1–C30 (1.380(8) Å), C29–C30 (1.343(9) Å), and C27–C28 (1.337(9) Å) are definitely shorter than the other three bonds in the ring (1.47–1.51 Å). Interestingly, the atoms Si, N1, C26, C29, and C30 are nearly coplanar, in accordance with the structural contribution of **A**. The formation of **5** is a rare type of reaction in which the aromatic compound is inserted between the two main-group elements.

The ^1H and ^{13}C NMR signals of the inserted pyridine ring have been successfully assigned in reference to ^1H – ^1H and ^{13}C – ^1H two-dimensional NMR data. These signals were observed at $\delta(^1\text{H})$ 3.58 (1), 4.34 (d, $J_{\text{PH}} = 8.0$ Hz, 2), 4.80 (d, $^3J_{\text{HH}} = 7.5$ Hz, 4), 6.37 (d, $^3J_{\text{HH}} = 7.5$ Hz, 3) and $\delta(^{13}\text{C})$ 68.1 (d, $J_{\text{PC}} = 49.0$ Hz, 2), 84.5 (1),

Scheme 3



96.2 (4), 138.4 (3), 148.9 (5), respectively, where the numbers in parentheses denote the positions (see Scheme 1).

It should be noted that the phosphinosilyl complex **1** does not react with MeOH, acetone, or pyridine at room temperature. Thus, it is reasonable to consider that the high reactivity of **2** is attributable to ring strain and/or a significant contribution of an internally base-stabilized phosphido(silylene) complex **B** as a canonical structure (Scheme 3).¹¹ In a plausible mechanism for the formation of **3**–**5**, the first step is considered to be the attack of nucleophiles toward the electron-deficient silicon atom of **2** to generate base-stabilized phosphido(silylene) complexes. Subsequently, the lone pair of the phosphido ligand attacks the proton in the case of MeOH and the α -carbon in the case of acetone and pyridine to give the final products **3**–**5**.

In conclusion, the present study revealed that phosphasilaferracyclopropane is a good activator of small organic molecules having polarized bonds, in which the silicon and phosphorus atoms work cooperatively as a Lewis acid and Lewis base, respectively.

Supporting Information Available: Text providing the experimental details of the synthesis and characterization of all compounds (PDF), and full details of the X-ray analysis in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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