

## Recombination of an Fe–Si–P Linkage to an Fe–P–Si Linkage through an Isolable Intermediate Phosphasilaferracyclopropane

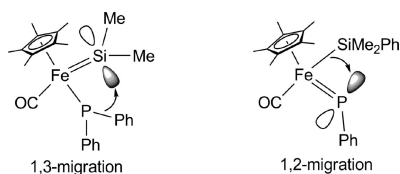
Masaaki Okazaki,<sup>†</sup> Takahiko Yoshitomi, Junpei Naito, Akira Sato, Takashi Komuro, and Hiromi Tobita\*

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

Received October 28, 2008; E-mail: tobita@m.tains.tohoku.ac.jp

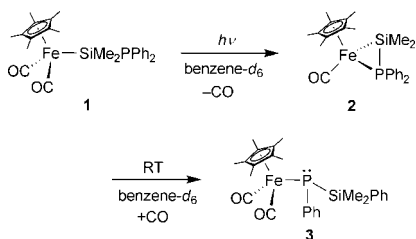
Silyl(silylene) complexes have attracted considerable interest as key intermediates in the metal-catalyzed oligomerization/deoligomerization and redistribution of organosilicon compounds.<sup>1</sup> Both Pannell's group and we have shown, through the generation of silyl(silylene) complexes and synthesis of their base-stabilized forms, that 1,2- and 1,3-group migration reactions of these systems occur fairly easily under mild conditions.<sup>2</sup> In a study of the reactions of an isolable base-free silyl(silylene)iron complex, we recently proved that these migration reactions proceed through silyl(silylene) complexes.<sup>3</sup> In the migration process, the low-lying p-orbital on the silylene silicon atom plays a crucial role, providing a low activation barrier. We report here extremely facile 1,2- and 1,3-group migrations in an FeSiP system, in which readily accessible empty p-orbitals on the silylene and phosphinidene ligands are thought to play a crucial role (Scheme 1).

### Scheme 1

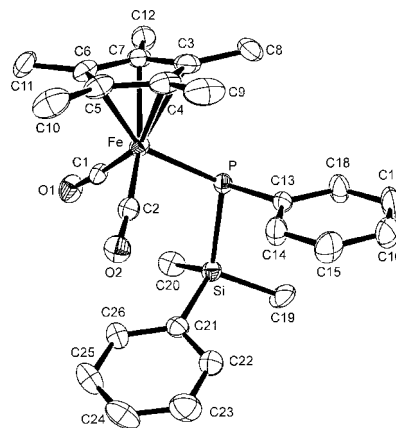


In a recent study, we examined the photochemistry of  $[\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{PPh}_2]$  (**1**).<sup>4</sup> A Pyrex NMR tube was charged with **1** and  $\text{C}_6\text{Me}_6$  (internal standard), and benzene- $d_6$  was introduced into the tube under vacuum by a trap-to-trap transfer technique. After 20 min irradiation,  $[\text{Cp}^*(\text{CO})\text{Fe}\{\kappa^2\text{Si},\text{P}-\text{SiMe}_2\text{PPh}_2\}]$  (**2**) was formed exclusively through dissociation of one carbonyl ligand. During this work, we found that **2** is not a thermodynamically stable form in the presence of CO. By keeping the irradiated sample tube in the dark at room temperature, we observed the conversion of **2** to  $[\text{Cp}^*(\text{CO})_2\text{FeP}(\text{Ph})\text{SiMe}_2\text{Ph}]$  (**3**) in 87% NMR yield within 1 day (Scheme 2).

### Scheme 2



A large-scale reaction in pentane and cooling of the concentrated solution at  $-80\text{ }^\circ\text{C}$  resulted in the growth of reddish purple crystals



**Figure 1.** ORTEP drawing of **3** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe–C1 = 1.759(4), Fe–C2 = 1.754(4), Fe–P = 2.3284(11), P–Si = 2.2672(15), C13–P–Si = 96.71(14), C13–P–Fe = 111.55(14), Si–P–Fe = 113.68(5).

of **3**, suitable for X-ray diffraction study, in 94% yield. The molecular structure of **3** (Figure 1) shows that complex **3** adopts a typical three-legged piano-stool geometry, and carries a silylphosphido ligand. Thus, the phosphinosilyl ligand in **1** is converted to the silylphosphido ligand in **3** via phosphasilaferracycle **2**. The Fe–P bond distance (2.3284(11) Å) is near the shorter limit previously reported for phosphidoiron complexes (2.32–2.36 Å).<sup>5</sup> This shortening is attributable to back-donation from the iron  $d\pi$  orbital to the  $\sigma^*$  orbital of the phosphorus–silicon bond.<sup>6</sup> Accordingly, the P–Si bond distance (2.2672(15) Å) is near the longer limit for typical silicon–phosphorus bonds (2.20–2.29 Å).<sup>5</sup> The sum of the bond angles around P is  $321.9^\circ$ , indicating the pyramidalized geometry of the phosphido ligand.

The  $^{29}\text{Si}$  and  $^{31}\text{P}$  NMR signals of **2** were observed at  $\delta(^{29}\text{Si})$  25.4 (d,  $^1J_{\text{PSi}} = 125.5$  Hz) and  $\delta(^{31}\text{P})$   $-48.3$ ,<sup>4a</sup> whereas those of **3** were observed at  $\delta(^{29}\text{Si})$   $-3.1$  (d,  $^1J_{\text{PSi}} = 43.3$  Hz) and  $\delta(^{31}\text{P})$   $-72.2$ . The  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectroscopic data is helpful in confirming the structure. The upfield shift of the  $^{29}\text{Si}$  NMR signal in **3** supports the contention that cleavage of the iron–silicon bond occurred. The coupling constant  $J_{\text{PSi}}$  indicates the existence of a silicon–phosphorus bond in **3**, although the value is considerably smaller than that of **2**. In the  $^1\text{H}$  NMR spectrum of **3**, the signals of the two methyl groups on the silicon appear equivalently as a doublet coupled with the  $^{31}\text{P}$  nucleus ( $\delta$  0.67, d,  $^3J_{\text{PH}} = 3.2$  Hz) due to rapid inversion at the phosphido phosphorus atom.

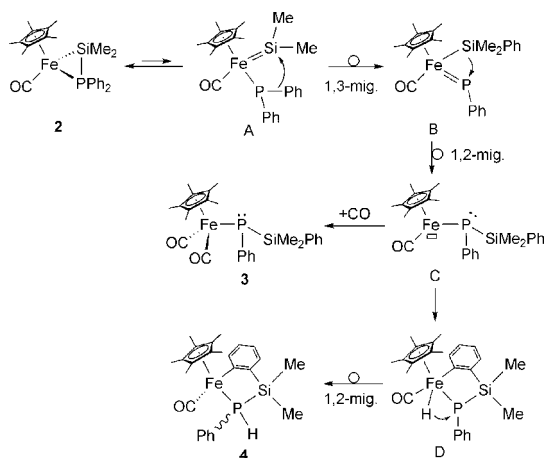
Orange crystals of **2** were dissolved in toluene- $d_8$ , and the reaction of **2** in the absence of CO was monitored at  $3\text{ }^\circ\text{C}$  by NMR spectroscopy. After one week, the solution turned green in color, and an NMR spectrum demonstrated the formation of  $[\text{Cp}^*(\text{CO})\text{Fe}\{\kappa^2\text{P},\text{C}-\text{PH}(\text{Ph})\text{SiMe}_2(o\text{-C}_6\text{H}_4)\}]$  (**4**) in 70% yield.<sup>7</sup> The structure of **4** can reasonably be explained by the mechanism mentioned

<sup>†</sup> Present address: International Research Center for Elements Science, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan.

below. In complex **4**, there are two geometric isomers, attributable to the five-membered metallacycle. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shows two singlet signals at  $\delta -54.4$  and  $-54.3$  with an intensity ratio of 1.7:1. In the  $^1\text{H}$  NMR spectrum, there are two doublets at  $\delta 7.31$  ( $J_{\text{PH}} = 370$  Hz) and  $7.38$  ( $J_{\text{PH}} = 370$  Hz), which are assigned to the PH moieties.

A possible mechanism for the conversion of **2** to **3** and **4** is shown in Scheme 3. Phosphasilaferracycle **2** is considered to be in equilibrium with the open-form, phosphido(silylene) complex **A** through scission of the P–Si bond.<sup>4</sup> 1,3-Migration of the phenyl group on **A** gives silyl(phosphinidene) complex **B**, and 1,2-migration of the silyl group followed by ligation of CO results in the formation of **3**. In the absence of CO, ortho metalation of one of the phenyl groups on the phosphorus atom in **C** leads to **D**, and finally, 1,2-migration of the hydrido ligand to the phosphido phosphorus atom affords **4**.

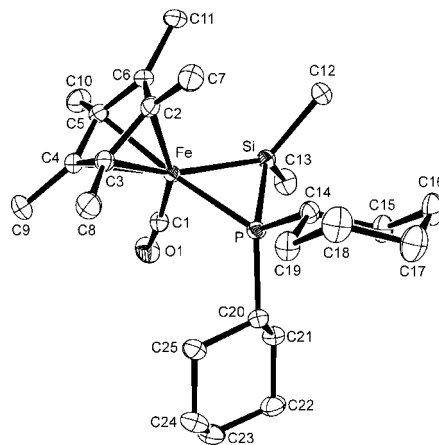
### Scheme 3. Possible Formation Mechanism for **3** and **4**



Interestingly, the introduction of cyclohexyl (Cy) groups onto the phosphorus atom resulted in the suppression of 1,2- and 1,3-migration in the FeSiP system. A pentane solution of  $[\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{PCy}_2]$  was irradiated for 100 min. Cooling of the concentrated solution at  $-80$  °C gave orange crystals of  $[\text{Cp}^*(\text{CO})\text{Fe}\{\kappa^2\text{Si},\text{P}-\text{SiMe}_2\text{PCy}_2\}]$  (**5**) in 81% yield. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shows a signal at  $\delta -48.8$ . In the  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum, a doublet signal was observed at  $\delta 14.1$  coupled with the  $^{31}\text{P}$  nucleus ( $^1J_{\text{PSi}} = 106.7$  Hz). This spectroscopic feature is very similar to that observed for **2**.<sup>4a</sup>

The molecular structure of **5** is depicted in Figure 2. Complex **5** adopts a novel three-membered metallacycle structure composed of Fe, Si, and P atoms. The Fe–Si bond distance (2.2569(5) Å) is significantly shorter than the normal range expected for silyliron complexes [2.32–2.37 Å] and lies in the range observed for base-stabilized silyleneiron complexes [2.20–2.29 Å].<sup>5</sup> In addition, the  $\text{SiMe}_2$  fragment is almost planar (the sum of the angles C12–Si–C13, C12–Si–Fe, and C13–Si–Fe is  $355.1^\circ$ ). These structural features suggest a considerable contribution from an internally base-stabilized phosphido(silylene) complex as a canonical structure.

In sharp contrast with **2**, complex **5** is thermally stable even at 80 °C regardless of the presence of CO. The difference in the thermal stabilities of **2** and **5** can be explained as being due to steric and electronic factors: the introduction of the bulkier cyclohexyl group onto the P atom suppresses the 1,3-migration from phosphorus to silicon for steric reasons. Meanwhile, the high nucleophilicity of the phenyl  $\pi$ -electrons in **2** can be considered as an electronic factor in lowering the activation barrier for 1,3-migration of the phenyl group in this complex.



**Figure 2.** ORTEP drawing of **5** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe–Si = 2.2569(5), Fe–P = 2.2392(5), Si–P = 2.2048(6), Si–Fe–P = 58.730(17), Fe–P–Si = 61.036(17), P–Si–Fe = 60.234(17), Fe–Si–C12 = 123.73(6), Fe–Si–C13 = 125.15(7), C12–Si–C13 = 106.19(9).

Braunstein reported the photoreaction of  $[\text{Fe}(\text{CO})_4\{\text{P}(\text{OEt})_3\}]$  with  $\text{HSi}(\text{NMe}_2)_3$  to give a base-stabilized silylene complex,  $[\text{Fe}(\text{CO})_3\{\text{P}(\text{OEt})(\text{NMe}_2)_2\}\{\text{Si}(\text{OEt})_2\cdot\text{NHEt}_2\}]$ .<sup>8</sup> This reaction can be rationalized by assuming 1,3-migration of the OEt group from the phosphite to the silylene ligand. Our reaction provides evidence for unprecedented 1,3-group migration from a phosphido to a silylene ligand to give silyl(phosphinidene) complex **B**, and 1,2-migration of the silyl group from iron to a phosphinidene ligand to give silylphosphido complex **C**. Thus, we have demonstrated the generality of these processes for systems composed of transition-metal and main group elements other than the silyl(silylene) complex. This elementary reaction should also be useful for metal-mediated synthesis and transformation of inorganic polymers composed of typical elements.

**Acknowledgment.** This work was supported by the Ministry of Education, Culture, Sports, Science, and Technology of Japan (Grants-in-Aid for Scientific Research Nos. 18064003 and 18350027).

**Supporting Information Available:** Experimental procedures, spectroscopic data, and CIF files for **3** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

### References

- (a) Okazaki, M.; Tobita, H.; Ogino, H. *Dalton Trans.* **2003**, 493–506. (b) Waterman, R.; Hayes, P. G.; Tilley, T. D. *Acc. Chem. Res.* **2007**, *40*, 712–719.
- (a) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351. (b) Ogino, H. *Chem. Rec.* **2002**, *2*, 291.
- Tobita, H.; Matsuda, A.; Hashimoto, H.; Ueno, K.; Ogino, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 221.
- (a) Okazaki, M.; Jung, K. A.; Satoh, K.; Okada, H.; Naito, J.; Akagi, T.; Tobita, H.; Ogino, H. *J. Am. Chem. Soc.* **2004**, *126*, 5060–5061. (b) Okazaki, M.; Satoh, K.; Jung, K. A.; Tobita, H.; Ogino, H. *Organometallics* **2004**, *23*, 1971–1973.
- Based on a survey of the Cambridge Structural Database, CSD version 5.29; The Cambridge Crystallographic Data Centre: Cambridge, U.K., November 2007.
- Hübler, K.; Hunt, P. A.; Maddock, S. M.; Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Schwerdtfeger, P.; Wright, L. J. *Organometallics* **1997**, *16*, 5076.
- An alternative structure,  $[\text{Cp}^*(\text{CO})\text{Fe}\{\kappa^2\text{Si},\text{P}-\text{SiMe}_2(o\text{-C}_6\text{H}_4\text{PPh})\}]$ , cannot be ruled out from the spectroscopic data. However, it seems difficult to conceive of a reasonable pathway to this complex.
- (a) Bodensieck, U.; Braunstein, P.; Deck, W.; Faure, T.; Knorr, M.; Stern, C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2440. (b) Braunstein, P.; Knorr, M.; Stern, C. *Coord. Chem. Rev.* **1998**, *178–180*, 903.

JA808443V