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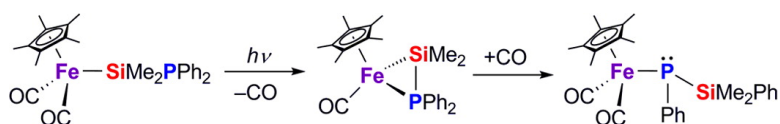
Communication

Recombination of an Fe#Si#P Linkage to an Fe#P#Si Linkage through an Isolable Intermediate Phospha-sila-ferracyclopropane

Masaaki Okazaki, Takahiko Yoshitomi, Junpei Naito, Akira Sato, Takashi Komuro, and Hiromi Tobita

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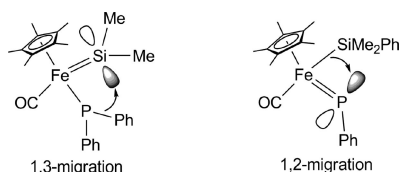
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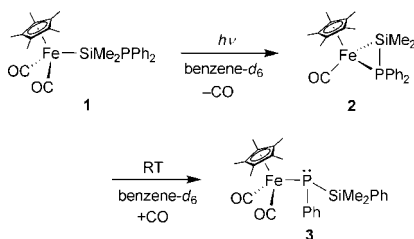
Silyl(silylene) complexes have attracted considerable interest as key intermediates in the metal-catalyzed oligomerization/deoligomerization and redistribution of organosilicon compounds.¹ Both Pannell's group and we have shown, through the generation of silyl(silylene) complexes and synthesis of their base-stabilized forms, that 1,2- and 1,3-group migration reactions of these systems occur fairly easily under mild conditions.² 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.³ 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**).⁴ A Pyrex NMR tube was charged with **1** and C_6Me_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°C resulted in the growth of reddish purple crystals

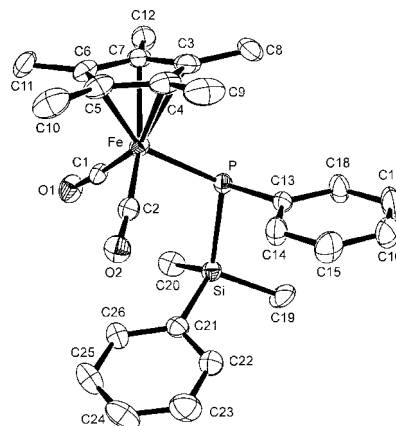


Figure 1. ORTEP drawing of **3** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe–C1 = 1.759(4), Fe–C2 = 1.754(4), Fe–P = 2.3284(11), P–Si = 2.2672(15), C13–P–Si = 96.71(14), C13–P–Fe = 111.55(14), Si–P–Fe = 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 phosphasilaferrocyclopropane **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).⁵ This shortening is attributable to back-donation from the iron $d\pi$ orbital to the σ^* orbital of the phosphorus–silicon bond.⁶ 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).⁵ The sum of the bond angles around P is 321.9° , indicating the pyramidalized geometry of the phosphido ligand.

The ^{29}Si and ^{31}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 ,^{4a} 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}Si NMR signal in **3** supports the contention that cleavage of the iron–silicon bond occurred. The coupling constant J_{PSi} indicates the existence of a silicon–phosphorus bond in **3**, although the value is considerably smaller than that of **2**. In the ^1H NMR spectrum of **3**, the signals of the two methyl groups on the silicon appear equivalently as a doublet coupled with the ^{31}P nucleus (δ 0.67, d, $^3J_{\text{PH}} = 3.2$ Hz) due to rapid inversion at the phosphido phosphorus atom.

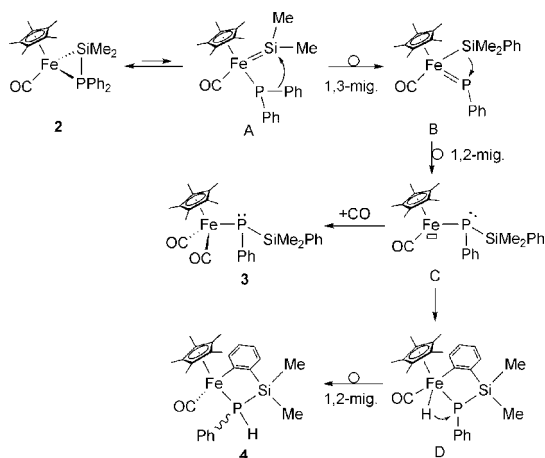
Orange crystals of **2** were dissolved in toluene- d_8 , and the reaction of **2** in the absence of CO was monitored at 3°C by NMR spectroscopy. After one week, the solution turned green in color, and an NMR spectrum demonstrated the formation of $[\text{Cp}^*(\text{CO})\text{Fe}\{\kappa^2\text{P},\text{C}-\text{PH}(\text{Ph})\text{SiMe}_2(o\text{-C}_6\text{H}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

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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 δ -54.4 and -54.3 with an intensity ratio of 1.7:1. In the ^1H NMR spectrum, there are two doublets at δ 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.⁴ 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 δ -48.8. In the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum, a doublet signal was observed at δ 14.1 coupled with the ^{31}P nucleus ($^1J_{\text{PSi}} = 106.7$ Hz). This spectroscopic feature is very similar to that observed for **2**.^{4a}

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].⁵ In addition, the SiMe_2 fragment is almost planar (the sum of the angles C12–Si–C13, C12–Si–Fe, and C13–Si–Fe is 355.1°). 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 π -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.

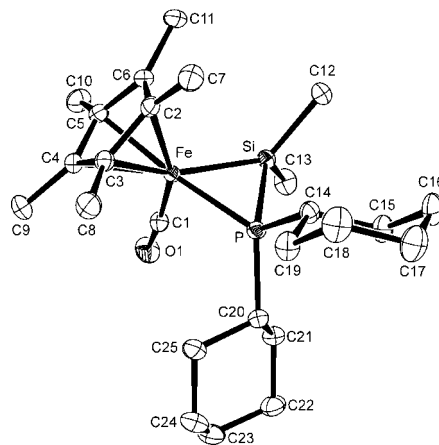


Figure 2. ORTEP drawing of **5** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe–Si = 2.2569(5), Fe–P = 2.2392(5), Si–P = 2.2048(6), Si–Fe–P = $58.730(17)$, Fe–P–Si = $61.036(17)$, P–Si–Fe = $60.234(17)$, 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, $[\text{Fe}(\text{CO})_3\{\text{P}(\text{OEt})(\text{NMe}_2)_2\}\{\text{Si}(\text{OEt})_2\cdot\text{NHEt}_2\}]$.⁸ 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.

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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>.

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