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Dimerization of Phosphasilaferracycles: Formation and Structures of Isomeric $Fe_2Si_2P_2$ Six-Membered Metallacylcles

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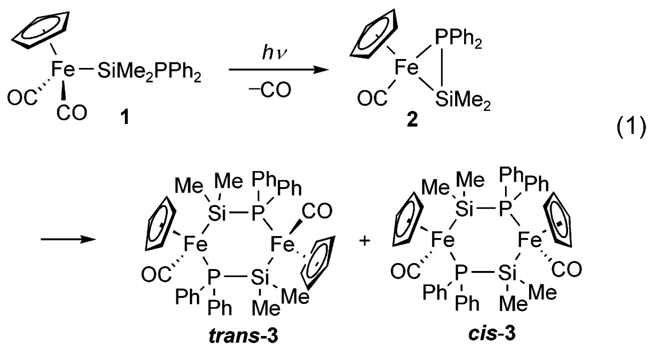
Summary: Irradiation of $Cp(CO)_2FeSiMe_2PPh_2$ led to formation of an isomeric mixture of $Cp_2Fe_2(CO)_2[\mu_2$-$\{\kappa^2(Si,P)$-$Me_2SiPPh_2\}]_2$ through generation of $Cp(CO)Fe\{\kappa^2(Si,P)$-$Me_2SiPPh_2\}$ and its successive dimerization. The three-membered-ring complex reacted smoothly with acetone to give the insertion product $Cp(CO)Fe\{\kappa^2(Si,P)$-$Me_2SiOCMe_2PPh_2\}$.

Numerous examples of transition-metal complexes containing a η^2-CH_2PR_2 ligand have been reported, and most have been synthesized through either cyclometalation of methylphosphine[1] or coordination of a phosphine part in a coordinatively unsaturated phosphinomethyl complex.[1] The present study is concerned with the silicon analogue, which is expected to be highly reactive due to the polarized Si−P bond. The first and only example of such a phosphasilametallacycle was reported by Paine et al., who utilized the reaction of a tungsten phosphenium complex with silylenoid reagents for the synthesis.[2] However, no reactivity studies have been explored as yet. We report here the generation and dimerization of the phosphasilaferracycle $Cp(CO)Fe\{\kappa^2(Si,P)$-$Me_2SiPPh_2\}$ as well as the structures of two isomeric dimers.

$Cp(CO)_2FeSiMe_2PPh_2$ (**1**) was synthesized by the reaction of $Cp(CO)_2FeSiMe_2Cl$ with $LiPPh_2$ in Et_2O. Molecular distillation of the mixture at 100 °C/3.6 × 10^{-3} mmHg gave analytically pure **1** in 30% yield. Successful introduction of the PPh_2 moiety onto silicon was confirmed by ^{29}Si NMR spectroscopy, which revealed a doublet signal at δ 43.9 coupled with the ^{31}P nuclei ($^1J_{PSi} = 61.1$ Hz).

In an attempt to synthesize a phosphasilaferracycle, a solution of **1** (3.0 mg) in benzene-d_6 (0.5 mL) was irradiated using a 450 W medium-pressure Hg lamp, and the reaction was monitored by NMR spectroscopy (eq 1).[3] In the initial stage, the growth of ^1H and ^{31}P NMR signals assigned to $Cp(CO)Fe\{\kappa^2(Si,P)$-$Me_2SiPPh_2\}$ (**2**) was observed (vide infra). Upon prolonged photolysis, **2** was converted to an isomeric mixture of $Cp_2Fe_2(CO)_2$-$[\mu_2$-$\{\kappa^2(Si,P)$-$Me_2SiPPh_2\}]_2$ (**3**), in which *trans*-**3** gradually diminished. After photolysis for 50 min, the NMR yields of *cis*-**3** and *trans*-**3** were 38% and 5%, respectively.



(1)

trans-**3** and *cis*-**3** were isolated as follows: a toluene solution of **1** was irradiated in a sealed Pyrex tube for 15 min. After removal of the volatiles, recrystallization of the residue from dichloromethane−hexane (1:3) at −30 °C gave orange crystals of *trans*-**3** in 19% yield. Prolonged photolysis of **1** in toluene for 2 h led to the formation of *cis*-**3** as a major product, although there were many other weak peaks in the ^1H NMR spectrum. The reaction mixture was concentrated in vacuo, and recrystallization of the residue from dichloromethane at −30 °C gave orange crystals of *cis*-**3** in 37% yield. Complexes **3** are the first metallacycles containing an $M_2Si_2P_2$ six-membered ring, whose structures were determined by X-ray diffraction studies.

The molecular structure of *trans*-**3** is depicted in Figure 1. The asymmetric unit consists of two independent half-molecules of the dimer, with no major differences between the two. The molecule contains an $Fe_2Si_2P_2$ six-membered ring, in which two iron centers adopt a three-legged piano-stool geometry and the ring is in a chair configuration.[4] The two cyclopentadienyl ligands are in a mutually trans relationship.

Compound *cis*-**3** crystallized with one molecule of dichloromethane per asymmetric unit. The molecular

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[3] The time-dependent distribution of products is illustrated in the Supporting Information.

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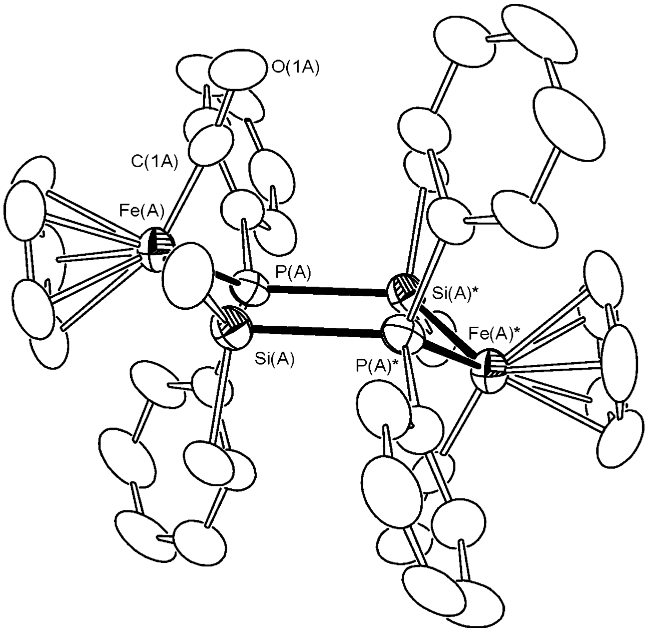

Figure 1. Molecular structure of *trans*-**3** (half-molecule A). Selected bond distances (Å) and angles (deg): Fe(A)−P(A) = 2.234(3), Fe(A)−Si(A) = 2.317(3), P(A)−Si(A)* = 2.380(4); P(A)−Fe(A)−Si(A) = 98.4(1), Fe(A)−P(A)−Si(A)* = 122.5(1), Fe(A)−Si(A)−P(A)* = 124.6(1). Asterisks indicate atoms generated by the symmetry operation $-x + 2$, $-y$, $-z + 1$.

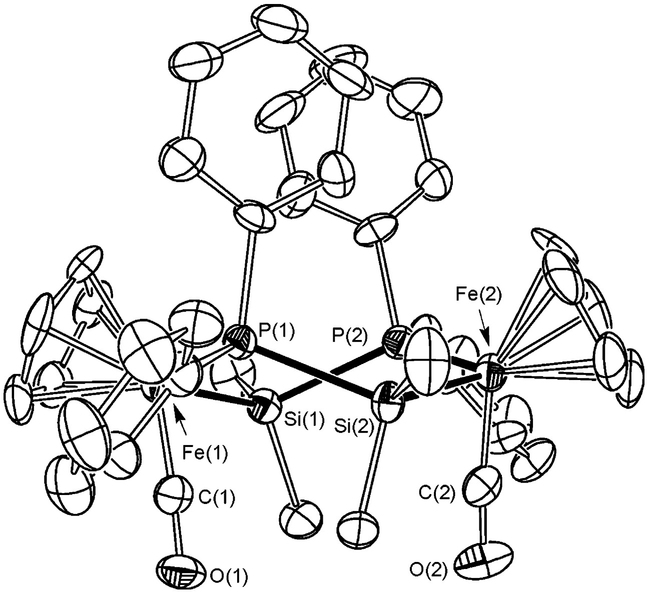

Figure 2. Molecular structure of *cis*-**3**. Selected bond distances (Å) and angles (deg): Fe(1)−P(1) = 2.247(3), Fe(2)−P(2) = 2.250(3), Fe(1)−Si(1) = 2.329(3), Fe(2)−Si(2) = 2.346(3), P(1)−Si(2) = 2.343(3), P(2)−Si(1) = 2.348(3); P(1)−Fe(1)−Si(1) = 100.46(9), Fe(1)−Si(1)−P(2) = 120.6(1), Si(1)−P(2)−Fe(2) = 120.1(1), Fe(2)−Si(2)−P(1) = 119.5(1).

structure of *cis*-**3** is illustrated in Figure 2. The conformation of the $Fe_2Si_2P_2$ six-membered ring is best described as a twisted boat,[5] on which the two cyclopentadienyl ligands are located at mutually cis positions.

The ^{31}P NMR signals of **3** are observed at δ 19.9 (*trans*-**3**) and 10.9 (*cis*-**3**). The $^{29}Si\{^1H\}$ NMR spectrum of **3** exhibits a virtual triplet at δ 54.5 (*trans*-**3**) and δ 31.2 (*cis*-**3**), coupled with two magnetically inequivalent phosphorus atoms.

Irradiation of **1** in a *dilute* benzene-d_6 solution for 1 min led to the formation of **2** as a major product (55%). Under the present conditions, the subsequent dimerization of **2** proceeded slowly. The structure of **2** was uniquely determined by spectroscopic analysis. In the ^1H NMR spectrum of **2**, the methyl groups on the silicon atom are inequivalent and are observed as two doublets, at δ 0.58 ($^3J_{PH}$ = 8.4 Hz) and 0.74 ($^3J_{PH}$ = 7.2 Hz). The ^1H NMR signal of the Cp ligand appears at δ 4.23 as a doublet coupled with the ^{31}P nuclei ($^3J_{PH}$ = 1.2 Hz), indicating coordination of the phosphine part to the iron center. The ^{31}P NMR signal of **2**, observed at δ −46.0, exhibits an upfield shift characteristic of three-membered phosphametallacycles.[6] The infrared spectrum exhibits only one intense band in the terminal CO region (1909 cm^{-1}). The presence of a single ν_{CO} band and its wavenumber indicate that dissociation of one carbonyl ligand in **1** occurred and was followed by coordination of the PPh_2 moiety.

Complex **2** was light-sensitive, and prolonged photolysis of the dilute solution led to decomposition, accompanied by the formation of **3** in low yields. When a solution of **2** was allowed to stand at room temperature, **2** was slowly converted to *trans*-**3** in 79% yield.[3] This observation clearly shows that the dimerization of **2** to give *trans*-**3** is a nonphotochemical process. Furthermore, photolysis of the isolated *trans*-**3** in benzene-d_6 for 5 min caused isomerization to give *cis*-**3** in 75% yield. Thus, the isomerization of **3** is expected to proceed via photochemical dissociation of a carbonyl ligand followed by recoordination from the opposite side of the iron (Scheme 1).

In the presence of CO or PMe_3, **2** did not give the adducts $Cp(L)(CO)FeSiMe_2PPh_2$ (L = CO, PMe_3) but gave only the dimerization products. Interestingly, introduction of PMe_3 accelerated the dimerization of **2** to give *trans*-**3** instantaneously at room temperature. These experimental results seem to disfavor a mechanism involving the dimerization of the coordinatively unsaturated phosphinosilyliron(II) complex Cp(CO)-$FeSiMe_2PPh_2$, formed via reversible dissociation of the phosphine moiety in **2**.

Instead, we propose two plausible mechanisms involving the dimerization of phosphasilaferracycle **2** via cleavage of the Si−P bond (Scheme 1). Hester and Yang reported the photoreaction of $Cp(CO)_2FeCH_2PEt_2$ to give Cp(CO)Fe(η^2-CH_2PEt_2), in which no dimer formation was observed.[7] The unique reactivity of the silicon analogue **2** is attributable to a significant contribution of a canonical structure corresponding to an internally base-stabilized silylene complex **A**.[8,9] In path A, the two molecules of **2** interact with each other to give a head-to-tail dimerization product.[9] In an alternative explanation (path B), complex **1** catalyzes the dimerization

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[5] Metallacycles with a twisted boat form: (a) Hoehne, S.; Lindner, E.; Schilling, B. *J. Organomet. Chem.* **1977**, *139*, 315. (b) Schore, N. E.; Young, S. J.; Olmstead, M.; Hofmann, P. *Organometallics* **1983**, *2*, 1769. (c) Forniés, J.; Martínez, F.; Navarro, R.; Urriolabeitia, E. P.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1993**, 2147.

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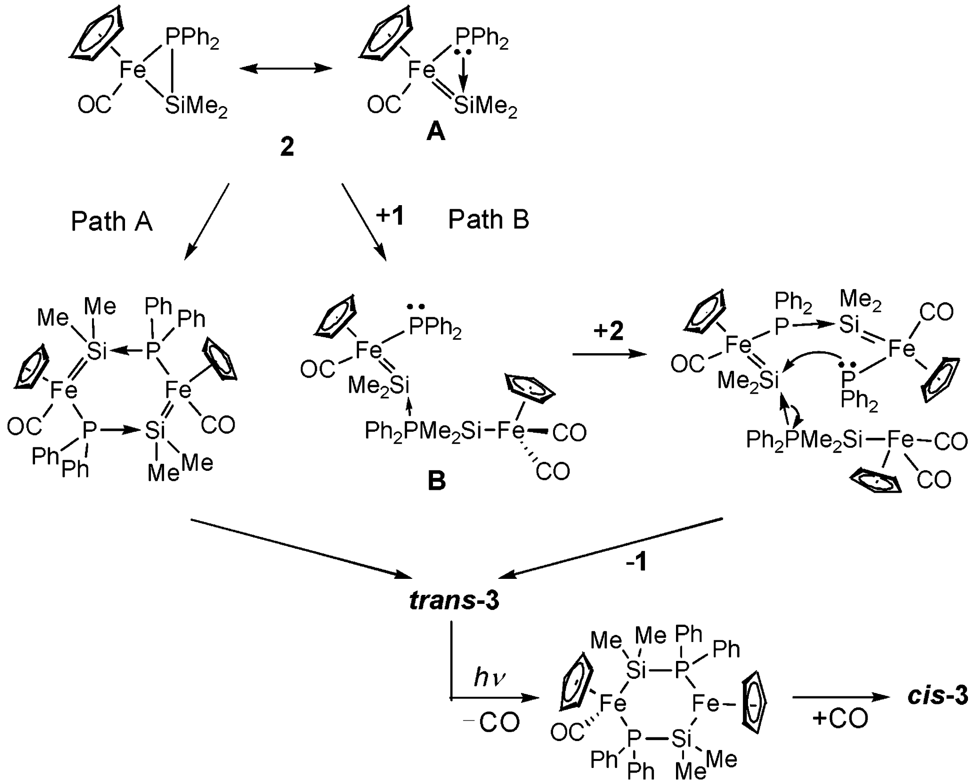
[7] Hester, D. M.; Yang, G. K. *Orgnometallics* **1991**, *10*, 369.

[8] For a review concerning reactivity of silylene complexes: Okazaki, M.; Tobita, H.; Ogino, H. *Dalton Trans.* **2003**, 493.

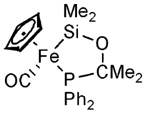
Scheme 1. Plausible Formation Mechanism for 3



process: nucleophilic attack of **1** toward the silicon atom in **2** cleaves the Si−P bond and generates the base-stabilized phosphido(silylene) intermediate **B**. The phosphido ligand of **B** then attacks the silicon atom in another **2** to cleave the Si−P bond and induces the formation of six-membered ring. Both mechanisms can explain the PMe_3-accelerated dimerization of **2**. In path A, PMe_3 facilitates the ring opening of **2**, probably through the transient formation of the PMe_3-stabilized phosphido(silylene) complex $Cp(CO)(PPh_2)Fe({=}SiMe_2{\cdot}PMe_3)$,[9] and thus accelerates the formation of *trans*-**3**. In path B, PMe_3 can work as an efficient catalyst instead of **1**. At this time there is no direct evidence available to distinguish between the two mechanisms.

Facile cleavage of the Si−P bond in phosphasilaferracycle **2** was demonstrated by the reaction of **2** with acetone, which occurred instantaneously at ambient temperature to give the insertion product **4** in 68% yield (eq 2). The ^1H and $^{13}C\{^1H\}$ NMR spectra of **4** each

$$\mathbf{2} + (CH_3)_2CO \xrightarrow[\text{instantaneously}]{\text{r.t.}}$$



4 (2)

exhibit four peaks assignable to chemically inequivalent methyl groups on the silicon and carbon atoms, supporting the formation of the five-membered metallacycle. The chemical shift of the ^{31}P NMR signal, δ 126.1, is shifted considerably downfield compared to the values for common iron phosphine complexes of the type L_n-$Fe{-}PPh_2R$ (R = alkyl). This downfield shift is characteristic of the phosphorus-containing five-membered metallacycles.[6] As the precursor does not react with acetone at ambient temperature, it is likely that the highly enhanced reactivity of **2** is consistent with the significant contribution of **A** in **2**, on which acetone is coordinated to the electron-deficient silicon atom to generate the acetone-stabilized phosphido(silylene) intermediate. Intramolecular nucleophilic attack of the PPh_2 part to the carbonyl carbon of the coordinated acetone then occurs to yield **4**.

In conclusion, the highly reactive phosphasilametallacycle **2** was successfully synthesized and was shown to dimerize gradually to produce **3**. Acetone insertion into the Si−P bond of **2** proceeded instantaneously at room temperature to give **4**. These results are consistent with the significant contribution of the canonical structure corresponding to phosphido(silylene) complex **A** in **2**.

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Supporting Information Available: Text giving experimental details for the synthesis and characterization of all compounds and full details of the crystal structure analysis as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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