

# Synthesis and Thermal Rearrangement of Tetramethyldisilane-bridged Bis(cyclopentadienyl) Diiron Complexes with Bis(phosphine) Substitution

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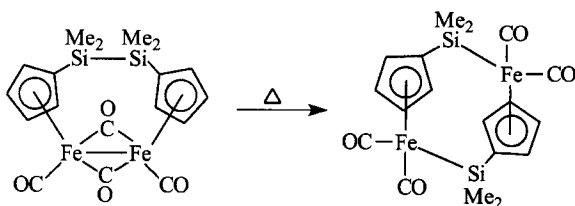
Photolysis of  $(\text{Me}_2\text{SiSiMe}_2)[\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$  with a series of bis(phosphine) ligands  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 1-4$ ) leads to the formation of the corresponding diiron complexes with intramolecular and intermolecular bis(phosphine) substitution. When these complexes were heated in refluxing xylene, only in the complexes with intermolecular bis(phosphine) substitution the thermal rearrangement reaction occurred.

**Keywords** thermal rearrangement, bis(phosphine), photolysis

## Introduction

We have recently reported a novel thermal rearrangement reaction between Si—Si and Fe—Fe bonds in the diiron complex  $(\text{Me}_2\text{SiSiMe}_2)[\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$  (Scheme 1).<sup>1</sup> A detailed investigation of the reaction mechanism indicated that it is a stereospecific intramolecular reaction via the iron radical intermediate.<sup>2,3</sup> Later, we further studied the scope of the reaction and found that not only the thermal rearrangement reaction could still occur but also the rearrangement rate increased significantly, when a carbonyl ligand was substituted by a phosphite or phosphine and isocyanide ligand.<sup>4-6</sup>

### Scheme 1



In order to examine the effect of bis(phosphine) substitution on the rearrangement reaction, in this paper a series of

tetramethyldisilane-bridged bis(cyclopentadienyl) diiron complexes with bis(phosphine) substitution was synthesized and their thermal rearrangement reaction was studied.

## Experimental

### General

All manipulations and reactions were carried out under argon using standard Schlenk and vacuum line techniques. Reaction solvents were distilled from appropriate drying agents under argon before use. <sup>1</sup>H NMR spectra were obtained on a Bruker AC-P 200 spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C instrument. Infrared spectra were obtained as KBr disks and recorded on a Nicolet 5DX FT-IR spectrometer.  $(\text{Me}_2\text{SiSiMe}_2)[\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$ <sup>1</sup> and  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 1$ , dppm;  $n = 2$ , dppe;  $n = 3$ , dppp;  $n = 4$ , dppb)<sup>7</sup> were prepared according to the reported method.

### Preparation of $(\text{Me}_2\text{SiSiMe}_2)[\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2[\text{dppm}]$ (1)

A solution of  $(\text{Me}_2\text{SiSiMe}_2)[\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$  (0.56 g, 1.2 mmol) and dppm (0.50 g, 1.3 mmol) in benzene (250 mL) was irradiated with a 500 W high-pressure mercury lamp until the substrate disappeared (*ca.* 8 h). After filtration, the solvent was removed under vacuum and the residue was placed in an  $\text{Al}_2\text{O}_3$  column. Elution with benzene developed a green band firstly and a blue green band secondly. The first green band was collected and, after solvent removal, recrystallization from acetonitrile yielded complex 1 as green needles (0.20 g, 22%). The second blue band only gave trace amount of complex 5 as blue solid, which was not further

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Received August 2, 2002; revised November 20, 2002; accepted November 20, 2002.

Project supported by the National Natural Science Foundation of China (Nos. 29972023 and 20202004), Specialized Research Fund for the Doctoral Program of Higher Education (No. 2000005504) and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (No. 2001-345).

characterized. **1**, m.p. 113 °C (dec.),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 0.32 (s, 12H, SiMe), 1.80—1.70 (m, 2H,  $\text{CH}_2$ ), 4.17—4.07 (m, 4H,  $\text{C}_5\text{H}_4$ ), 4.60—4.50 (m, 4H,  $\text{C}_5\text{H}_4$ ), 7.45—7.35 (m, 20H,  $\text{C}_6\text{H}_5$ ); IR (KBr)  $\nu_{\text{CO}}$ : 1676, 1670  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{41}\text{H}_{42}\text{Fe}_2\text{O}_2\text{P}_2\text{Si}_2$ : C 61.82, H 5.31; found C 61.80, H 5.52.

#### Preparation of $(\text{Me}_2\text{SiSiMe}_2)[\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2[\text{dppe}]$ (**2**)

**2** was prepared by the reaction of  $(\text{Me}_2\text{SiSiMe}_2)-[\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$  (0.97 g, 2.07 mmol) and dppe (1.82 g, 4.56 mmol) in benzene (450 mL) under irradiation for 23 h using the similar method described for **1**. After recrystallization from THF, complex **2** was obtained as green crystals (0.30 g, 18%). M.p. 191 °C (dec.),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 0.40 (s, 12H, SiMe), 2.10—2.00 (m, 4H,  $\text{CH}_2$ ), 3.90—3.80 (m, 4H,  $\text{C}_5\text{H}_4$ ), 5.35—5.25 (m, 4H,  $\text{C}_5\text{H}_4$ ), 7.47—7.37 (m, 10H,  $\text{C}_6\text{H}_5$ ), 7.70—7.60 (m, 10H,  $\text{C}_6\text{H}_5$ ); IR (KBr)  $\nu_{\text{CO}}$ : 1670  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{42}\text{H}_{44}\text{Fe}_2\text{O}_2\text{P}_2\text{Si}_2$ : C 62.23, H 5.47; found C 62.14, H 5.54.

#### Preparation of $(\text{Me}_2\text{SiSiMe}_2)[\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2[\text{dppp}]$ (**3**) and $[(\text{Me}_2\text{SiSiMe}_2)(\text{C}_5\text{H}_4)_2\text{Fe}_2(\text{CO})_3]_2[\text{dppp}]$ (**7**)

A solution of  $(\text{Me}_2\text{SiSiMe}_2)[\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$  (0.40 g, 0.96 mmol) and dppp (0.80 g, 2.0 mmol) in benzene (200 mL) was irradiated with a 500 W high-pressure mercury lamp until the substrate disappeared (ca. 60 h). After filtration, the solvent was removed under vacuum and the residue was placed in an  $\text{Al}_2\text{O}_3$  column. Elution with benzene/petroleum ether (9:1,  $V:V$ ) developed a green band firstly and a blue green band secondly. The first green band afforded complex **3** as green solid (43 mg, 5%), which decomposed during further purification and no satisfied  $^1\text{H}$  NMR spectra and elemental analysis were given. The second blue green band yielded complex **7** as dark green solid (0.22 g, 13%). **3**, IR (KBr)  $\nu_{\text{CO}}$ : 1915, 1719  $\text{cm}^{-1}$ . **7**, m.p. 102—103 °C,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 0.13 (s, 12H, SiMe), 0.31 (s, 12H, SiMe), 1.07—1.24 (m, 6H,  $\text{CH}_2$ ), 3.47 (s, 4H,  $\text{C}_5\text{H}_4$ ), 4.31 (s, 4H,  $\text{C}_5\text{H}_4$ ), 4.67 (s, 4H,  $\text{C}_5\text{H}_4$ ), 5.18 (s, 4H,  $\text{C}_5\text{H}_4$ ), 7.29 (s, 20H,  $\text{C}_6\text{H}_5$ ); IR (KBr)  $\nu_{\text{CO}}$ : 1927, 1724  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{61}\text{H}_{66}\text{Fe}_4\text{O}_6\text{P}_2\text{Si}_4$ : C 56.67, H 5.15; found C 56.71, H 5.04.

#### Preparation of $[(\text{Me}_2\text{SiSiMe}_2)(\text{C}_5\text{H}_4)_2\text{Fe}_2(\text{CO})_3]_2[\text{dppe}]$ (**6**) and **2**

Similarly as described above, reaction of  $(\text{Me}_2\text{SiSiMe}_2)-[\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$  (1.50 g, 3.90 mmol) and dppe (0.60 g, 1.65 mmol) in benzene (100 mL) under irradiation for 15 h afforded complex **6** as blue green solid (0.18 g, 7%) and complex **2** (40 mg, 1%). **6**, m.p. 167 °C (dec.),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 0.17 (s, 12H, SiMe), 0.30 (s, 12H, SiMe), 1.45—1.35 (m, 4H,  $\text{CH}_2$ ), 3.58

(s, 4H,  $\text{C}_5\text{H}_4$ ), 4.28 (s, 4H,  $\text{C}_5\text{H}_4$ ), 4.69 (s, 4H,  $\text{C}_5\text{H}_4$ ), 5.12 (s, 4H,  $\text{C}_5\text{H}_4$ ), 7.35 (s, 20H,  $\text{C}_6\text{H}_5$ );  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 57.52 (s); IR (KBr)  $\nu_{\text{CO}}$ : 1932, 1724  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{60}\text{H}_{64}\text{Fe}_4\text{O}_6\text{P}_2\text{Si}_4$ : C 56.35, H 5.04; found C 56.20, H 5.19.

#### Preparation of $[(\text{Me}_2\text{SiSiMe}_2)(\text{C}_5\text{H}_4)_2\text{Fe}_2(\text{CO})_3]_2[\text{dppb}]$ (**8**) and **4**

Similarly as described above, reaction of  $(\text{Me}_2\text{SiSiMe}_2)-[\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$  (1.50 g, 3.90 mmol) and dppb (0.70 g, 1.65 mmol) in benzene (200 mL) under irradiation for 11 h afforded complex **8** as blue green solid (0.63 g, 24%) and complex **4** as green solid (trace). **8**, m.p. 137 °C (dec.),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 0.16 (s, 12H, SiMe), 0.33 (s, 12H, SiMe), 1.05—0.95 (m, 4H,  $\text{CH}_2$ ), 1.30—1.20 (m, 4H,  $\text{CH}_2$ ), 3.51 (s, 4H,  $\text{C}_5\text{H}_4$ ), 4.36 (s, 4H,  $\text{C}_5\text{H}_4$ ), 4.76 (s, 4H,  $\text{C}_5\text{H}_4$ ), 5.23 (s, 4H,  $\text{C}_5\text{H}_4$ ), 7.40—7.30 (m, 20H,  $\text{C}_6\text{H}_5$ ); IR (KBr)  $\nu_{\text{CO}}$ : 1927, 1728  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{62}\text{H}_{68}\text{Fe}_4\text{O}_6\text{P}_2\text{Si}_4$ : C 56.98, H 5.24; found C 56.85, H 5.41.

#### Rearrangement reaction

Complex **6** (0.11 g) was refluxed in xylene (50 mL) for 20 min. The blue green color changed light rapidly. After removal of solvent, the residue was resolved in  $\text{CH}_2\text{Cl}_2$ , filtered through an  $\text{Al}_2\text{O}_3$  column and eluted with petroleum ether/ $\text{CH}_2\text{Cl}_2$  (5:1,  $V:V$ ). The yellow band was collected, which afforded complex **9** as yellow crystals (42 mg, 38%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : -0.33 (s), 0.20 (s), 0.30 (s), 0.55 (s, total 24H, SiMe), 1.30—1.20 (m, 4H,  $\text{CH}_2$ ), 3.40—3.30 (m), 3.70—3.60 (m), 4.15—4.05 (m), 5.10—4.30 (m, total 16H,  $\text{C}_5\text{H}_4$ ), 6.98—7.25 (m, 20H,  $\text{C}_6\text{H}_5$ ); IR (KBr)  $\nu_{\text{CO}}$ : 1984, 1937, 1891  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{60}\text{H}_{64}\text{Fe}_4\text{O}_6\text{P}_2\text{Si}_4$ : C 56.35, H 5.04; found C 56.02, H 5.06.

The rearrangement reaction of **8** (0.40 g) was carried out under similar conditions. The reactions were completed after about 20 min and the corresponding rearrangement product **10** was obtained as yellow crystals (0.11 g, 29%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 0.04 (s), 0.15 (s), 0.34 (s), 0.60 (s, total 24H, SiMe), 0.95—0.85 (m, 4H,  $\text{CH}_2$ ), 1.30—1.20 (m, 4H,  $\text{CH}_2$ ), 3.43—3.33 (m), 4.25—4.15 (m), 5.10—4.50 (m, total 16H,  $\text{C}_5\text{H}_4$ ), 7.24—7.35 (m, 20H,  $\text{C}_6\text{H}_5$ ); IR (KBr)  $\nu_{\text{CO}}$ : 1985, 1930, 1891  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{62}\text{H}_{68}\text{Fe}_4\text{O}_6\text{P}_2\text{Si}_4$ : C 56.98, H 5.24; found C 56.30, H 5.22.

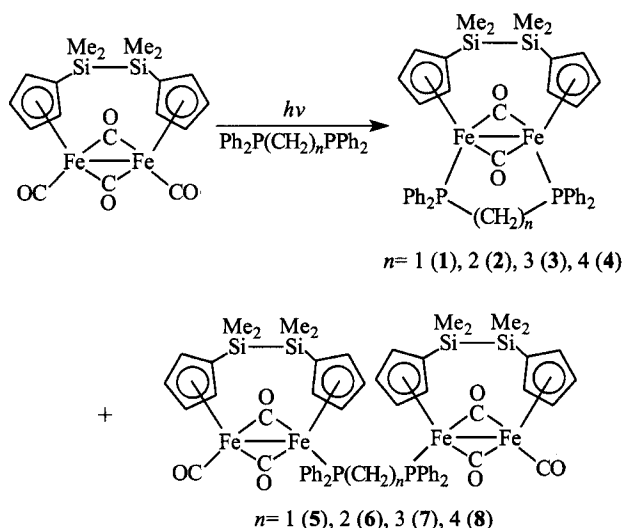
## Results and discussion

### Preparation of complexes **1**—**8**

Irradiation of a benzene solution of  $(\text{Me}_2\text{SiSiMe}_2)-[\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$  in the presence of the appropriate bis-

(phosphine) ligand results in the formation of the corresponding intramolecular and intermolecular bis(phosphine) substitution products (Scheme 2):

Scheme 2



Similar to the bis(phosphine) substitution of  $(\text{Me}_2\text{Si})\text{-}[\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$ <sup>8,9</sup> and  $[\text{CpFe}(\text{CO})_2]_2$ ,<sup>10</sup> the distribution of the intramolecular and intermolecular substitution products strongly depends on the choice of ligand, the concentration and stoichiometry of the reactants employed. When *dppm* was used, only trace amounts of the intermolecular substitution product **5** were monitored by TLC. As the number of methylene units increases, the intermolecular substitution product increases. This can be attributed to the increase of ring strain for intramolecular substitution product with the increasing of the number of methylene units. For  $n = 1, 2$ , the intramolecular substitution product is the main product in all cases. But for  $n = 4$ , even if the molar ratio of bis(phosphine) ligand to  $(\text{Me}_2\text{SiSiMe}_2)[\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$  is 3:1, the intermolecular substitution product is still much more than the intramolecular substitution product, due to the larger ring strain.

The bis(phosphine) substitution complexes **1–8** are thermally unstable. In solid, they can stand for a long time, but in solution, especially in  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$ , they are very sensitive to air. However, in benzene they can be kept at low temperature or under Ar for some time.

### Spectroscopy

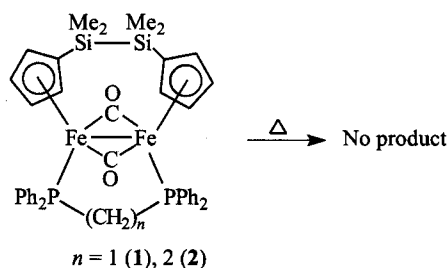
Complexes **1, 2** and **6–8** were characterized by IR, <sup>1</sup>H NMR spectra and elemental analysis. The cyclopentadienyl ring protons display two <sup>1</sup>H NMR resonances in an AA'BB' pattern for the intramolecular substitution complexes **1** and **2** and four resonances for the intermolecular substitution complexes **6–8**. For the intramolecular bis(phosphine) substitution products **1** and **2**, the protons of silicon methyl group showed only one peak, indicating these molecules have symmetry. Due to the shielding effect by aromatic ring current of

a bis(phosphine) ligand, the four protons of cyclopentadienyl group in the intermolecular bis(phosphine) substitution complexes **2, 6, 7** and **8** appeared at a much higher field ( $\delta$  3.84, 3.58, 3.47, 3.51) than other cyclopentadienyl protons. The IR spectra of **1** and **2** only showed the bridging carbonyl absorption, indicating that the bis(phosphine) ligands replaced the two terminal carbonyls. The IR spectra of **3** showed both the bridging and terminal carbonyl absorptions, indicating that the bis(phosphine) ligand probably replaced one terminal and one bridging carbonyls. The poor stability of **3** may be as an indirect support for this.

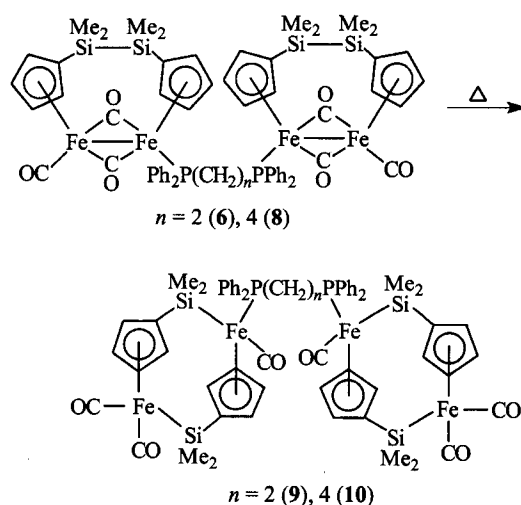
### Rearrangement reaction

When the intramolecular bis(phosphine) substitution complexes **1** and **2** were heated in refluxing xylene for 30 h, or even in refluxing decahydronaphthalene for 10 h, no rearrangement reaction was observed except the decomposition of the starting materials by TLC monitoring (Scheme 3). This indicated that complexes **1** and **2** can not undergo the thermal rearrangement reaction between the Si—Si and Fe—Fe bonds. When the intermolecular bis(phosphine) substitution complexes **6** and **8** were heated in refluxing xylene, they were rearranged to the corresponding rearrangement products **9** and **10** in 20 min (Scheme 4). This is agreed with the rearrangement reaction of the monophosphine or phosphite substituted analogues.

Scheme 3



Scheme 4



Based on the mechanism of the rearrangement reaction

suggested by us,<sup>2,3</sup> iron radicals are formed through the thermal homolysis of Fe—Fe bond upon heating at first, followed by a suitable rotation along the Si—Si bond and concerted (or stepwise) attack of iron radicals at the Si—Si bond to complete the rearrangement reaction. The suitable rotation along the Si—Si single bond was assumed to be an essential condition for the rearrangement. For the intramolecular bis(phosphine) substitution complexes **1** and **2**, even if iron radicals could be formed during heating, they cannot be rotated along the Si—Si bond owing to the bridge linking of the bis(phosphine) ligands. So the iron radicals cannot attack at the Si—Si bond to lead to the rearrangement reaction. For the intermolecular bis(phosphine) substitution complexes **6** and **8**, there is no limit for the rotation of Si—Si bond, so they can perform the thermal rearrangement reaction smoothly. This result further supported the mechanism suggested by us from another aspect. The rearrangement of **6** and **8** afforded only one product respectively, further indicating the rearrangement is an intramolecular reaction.

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(E0208023 ZHAO, X. J.; FAN, Y. Y.)