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Synthesis, structure and thermal rearrangement of tetramethyldisilanebridged bis(cyclopentadienyl) diiron complexes with a phosphite or phosphine ligand substitution

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Abstract

Photolysis of tetramethyldisilane-bridged bis(cyclopentadienyl) tetracarbonyl di-iron in the presence of phosphite or phosphine ligand afforded the corresponding Fe–Fe bond complexes with one carbonyl replaced by a phosphite or phosphine ligand: $[(Me_2SiSiMe_2)Cp_2Fe_2(CO)(PR_3)(\mu-CO)_2]$ (R=OPh, 1; OEt, 2; Ph, 3). When these complexes were heated in refluxing xylene, they become rearranged to the corresponding products $[(Me_2SiCpFe)_2(CO)_3(PR_3)]$ (R=OPh, 4; OEt, 5; Ph, 6). It was found that, after phosphite or phosphine ligand substitution, the rearrangement became facile. The molecular structures of 1–6 were characterized by IR, ¹H NMR spectra and elemental analyses. The crystal structures of 1 and 4 were determined by X-ray diffraction analysis. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Rearrangement; Sila-bridged; Fe-Fe bond

1. Introduction

The chemistry of transition metal-silicon complexes has become a significant facet of the general chemistry of silicon [1]. Another important and in many ways a more fundamental feature of silicon chemistry that has attracted researchers is the nature of the Si-Si bond. Since transition metal complexes either activating or containing a Si-Si bond were reported in 1965 and 1969 [2,3], a significant amount of work followed these seminal studies in the literature [4]. We have recently reported a novel thermal rearrangement reaction involving Si-Si and Fe-Fe bonds in the tetramethyldisilane-bridged diiron complex $(Me_2SiSiMe_2)[(\eta^5-C_5H_4)Fe(CO)_2]_2(\mu-CO)_2$ [5]. A detailed investigation of the reaction mechanism indicated that it is a stereospecific intramolecular reaction via the iron radical intermediate [6]. Later, we further studied the scope of the reaction and found that when the hydrogen

atoms of the cyclopentadienyl rings were substituted, or the cyclopentadienyl replaced by indenyl, or the silyl bridge replaced by germyl bridge, or using ruthenium instead of iron, the thermal rearrangement reaction could still occur [7–13] (Scheme 1).

In order to examine the effect of replacement of the carbonyl ligand on the rearrangement reaction, we report here the synthesis of tetramethyldisilane-bridged bis(cyclopentadienyl) Fe–Fe bond complexes with a phosphite or phosphine ligand substitution and the effect on their thermal rearrangement reaction.

2. Experimental

Solvents were distilled from appropriate drying agents under argon before use. All manipulations were under argon using standard Schlenk and vacuum-line techniques. ¹H NMR spectra were obtained on a BRUKER AC-P200 or JEOL FX-90Q spectrometer, while IR spectra were obtained on a Nicolet 5DX FT-IR spectrometer. Elemental analyses were performed with a CHN CORDER MF-3 analyzer.

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E = Si, Ge; M = Fe, RuRn = H, 3-Me, 3-*t*-Bu, Me₄, 2, 3-CH=CHCH=CH, 2,3-(CH₂)₄

Scheme 1.

2.1. Preparation of complex 1

solution of А of 1.1g (2.3)mmol) $(Me_2SiSiMe_2)[CpFe(CO)]_2(\mu-CO)_2$ [5] and 1.21 g (3.8) mmol) of P(OPh)₃ in 50 ml of benzene was irradiated with a 300 W high-pressure mercury lamp until disappearance of the substrate (ca. 15 h). Then the solvent was removed under vacuum and the residue was extracted with CH₂Cl₂. The extraction was concentrated and recrystallized from benzene/pentane to give 1.05 g (60%) of **1** as dark red crystals, m.p. 242°C (dec.). Anal. Found: C, 55.82; H, 4.49. C₃₅H₃₅Fe₂O₆PSi₂ Calcd.: C, 56.01; H, 4.70%. IR (KBr): $[\nu_{co}/cm^{-1}]$ 1958.6 vs., 1737.1 vs. ¹H NMR (200 MHz, CDCl₃): $\delta_{\rm H}$ 7.33(m, 15H), 5.39(s, 2H), 4.68(s, 2H), 4.43(s, 2H), 3.50(s, 2H), 0.15(s, 6H) ppm.

2.2. Preparation of 2 and 3

Complexes 2 and 3 were prepared by the reaction of $(Me_2SiSiMe_2)[CpFe(CO)]_2(\mu-CO)_2$ and $P(OEt)_3$ or PPh₃ in 63% or 32% yield respectively using the similar method described for 1.

Complex **2**, m.p. 203°C (dec.). Anal. Found: C, 45.50; H, 5.59. $C_{23}H_{35}Fe_2O_6PSi_2$ Calcd.: C, 45.56; H, 5.82%. IR (KBr): [ν_{co}/cm^{-1}] 1956.3 vs., 1741.2 vs. ¹H NMR (90 MHz, CDCl₃): δ_H 5.12(s, 2H), 4.80(s, 2H), 4.64(s, 2H), 4.42(s, 2H), 3.94(q, 6H), 1.32(t, 9H), 0.31(s, 6H), 0.19(s, 6H) ppm.

Complex **3**, m.p. 207°C (dec.). Anal. Found: C, 60.07; H, 5.22. $C_{35}H_{35}Fe_2O_3PSi_2$ Calcd.: C, 59.84; H, 5.02%. IR (KBr): [ν_{co} /cm⁻¹] 1960.5 vs., 1735.1 vs. ¹H NMR (200 MHz, CDCl₃): δ_H 5.20(s, 2H), 5.08(s, 2H), 4.78(s, 2H₄), 4.56 (s, 2H), 0.41(s, 6H), 0.23(s, 6H) ppm.

2.3. Rearrangement reaction

0.35 g of **1** was heated in refluxing xylene (30 ml). The color changed to light rapidly and became orange yellow after about 30 min. After removal of solvent, the residue was resolved in CH_2Cl_2 , filtered through a Al_2O_3 column (3×15 cm) and eluted with CH_2Cl_2 . The yellow solid obtained was recrystallized from CH_2Cl_2 /pentane to give

0.21 g (60%) of **4** as light yellow solid, m.p.146–147°C. Anal. Found: C, 55.77; H, 4.61. $C_{35}H_{35}Fe_2O_6PSi_2$ Calcd.: C, 56.01; H, 4.70%. IR (KBr): $[\nu_{co}/cm^{-1}]$ 1983.2 vs., 1917.6 vs. ¹H NMR (90 MHz, CDCl₃): δ_H 7.38–7.15 (m, 15H), 5.30 (d, 2H), 5.06(d, 2H), 4.78(s, 2H), 4.38(m, 2H), 0.62 (s, 3H), 0.58 (s, 3H), 0.49 (s, 3H), 0.34(s, 3H) ppm.

The rearrangement reactions of 2 and 3 were carried out under similar conditions. The reactions were completed after about 30 min and the corresponding rearrangement products 5 and 6 were obtained in 68% and 48% yield, respectively.

Complex **5**, m.p. 122–3°C. Anal. Found: C, 45.50; H, 5.59. $C_{23}H_{35}Fe_2O_6PSi_2$ Calcd.: C, 45.56; H, 5.82%. IR (KBr): $[\nu_{co}/cm^{-1}]$ 1981.2 vs., 1912.5 vs. ¹H NMR (200 MHz, CDCl₃): δ_H 5.08(s, 2H), 4.98(s, 2H), 4.66(t, 2H), 4.30(s, 2H), 3.96(q, 6H), 1.30(t, 9H), 0.56 (s, 3H), 0.49(s, 3H), 0.42(s, 3H), 0.26(s, 3H) ppm.

Complex **6**, m.p. 197°C (dec.). Anal. Found: C, 59.60; H, 4.89. $C_{35}H_{35}Fe_2O_3PSi_2$ Calcd.: C, 59.84; H, 5.02%. IR (KBr): $[\nu_{co}/cm^{-1}]$ 1983.9 vs., 1916.3 vs., 1891.5 vs. ¹H NMR (200 MHz, CDCl₃): δ_H 7.52–7.37(m, 15H), 5.33(s, 1H), 5.07(t, 3H), 4.83(s, 1H), 4.70(s, 1H), 4.39(s, 1H), 2.82(s, 1H), 0.70(s, 3H), 0.54(s, 3H), 0.40(s, 3H), -0.66(s, 3H) ppm.

2.4. Crystallographic studies

Crystals of **1** suitable for X-ray diffraction were obtained from benzene/pentane solution. All data were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated MoK α (λ =0.71073 Å) radiation. Corrections for empirical absorption were applied to the intensity data. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached carbon atoms were not refined. All calculations were performed using the teXsan Crystallographic Software Package [15] on a Silicon Graphics Indy computer.

Crystals of 4 suitable for X-ray diffraction were obtained from CH_2Cl_2 /pentane solution. All data were collected on the Rigaku AFC7R diffractometer and the structure was determined as described for **1**.

3. Results and discussion

3.1. Synthesis of 1-3 and their thermal rearrangement reaction

Photolysis of tetramethyldisilane-bridged bis(cyclopentadienyl) tetracarbonyl di-iron in the presence of phosphite or phosphine ligand afforded the corresponding Fe-Fe bond complexes with one carbonyl replaced by a phosphite [(Me₂SiSiMe₂)Cp₂Fe₂(CO) or phosphine ligand: $(PR_3)(\mu-CO)_2$ (R=OPh, 1; OEt, 2; Ph, 3) (Scheme 2). Similar to the case of other bridged analogs, $E[CpFe(CO)]_{2}(\mu-CO)_{2}$ $[E=CH(NMe_2)CH(NMe_2)]$, CMe₂CMe₂], only one carbonyl was replaced even when the irradiation time was extended [14], indicating that the rearrangement reaction between Si-Si and Fe-Fe bonds could not take place under irradiation.

When these complexes were heated in refluxing xylene, they were converted to the corresponding rearrangement products, $[(Me_2SiCpFe)_2(CO)_3(PR_3)]$ (R=OPh, 4; OEt, 5; Ph, 6). It was found that the rearrangement that required more than 10 h could be accomplished in only 30 min after phosphite or phosphine substitution. This may be rationalized by the fact that the Fe–Fe bond becomes weaker after phosphite or phosphine ligand substitution. On the other hand, phosphite or phosphine ligand substitution could make the iron-centered radical more stable. The fact that the rearrangement reaction rate increases significantly after phosphite or phosphine ligand substitution also indicates that the cleavage of Fe–Fe bond is a key step for the rearrangement reaction and it supports the mechanism suggested by the present authors [6].

3.2. Spectroscopy

Complexes 1–6 were characterized by IR, ¹H NMR spectra and elemental analysis. Compared to the parent complexes, the splitting of silicon methyl and cyclopen-

tadienyl protons in ¹HNMR spectra of a phosphite or phosphine ligand substituted complex became more clear. Another aspect of the ¹HNMR spectra worth noting is the shielding effect by aromatic ring current of a phosphite or phosphine ligand. For example, the two protons of cyclopentadienyl group in complex **1** appeared at a much higher field (δ 3.50) than other cyclopentadienyl protons. It is evident that the two protons were shielded by an aromatic ring current of P(OPh)₃. It has also been substantiated by X-ray analysis. A more evident example is that one proton of cyclopentadienyl group appeared at δ 2.82 and protons of a silicon methyl group appeared at δ -0.66 in complex **6**. Such an upfield shift is evidently due to the shielding effect of a nearby aromatic ring current.

3.3. Crystallography

The crystal structures of **1** and **4** were determined by X-ray diffraction analysis. The molecular structures of 1 and 4 are presented in Figs. 1 and 2, respectively. A summary of the crystallographic results is presented in Table 1. Tables 2 and 3 provide selected bond distances and angles of 1 and 4, respectively. In 1, the dihedral angle between two cyclopentadienyl ring planes is 88.22°. Si(1) and Si(2) deviate from the linked cyclopentadienyl plane by 0.152 Å and 0.205 Å, respectively. Si(1), Si(2), Fe(1)and Fe(2) are co-planar on the whole. C(8) and C(17) lie on the same side of the plane and the distances to the plane are 0.413 Å and 0.450 Å, respectively. It indicates that the six-membered ring formed from the above atoms takes a boat conformation. The fragment Fe(1)-C(1)-O(1) is no longer linear (172.6°) due to the steric effect of $P(OPh)_3$. From Fig. 1 it can be seen that C(14) and C(15) are in the fielding area of aromatic ring C(30)-C(35) which accounts for the high field shifts in its ¹H NMR spectrum.

Unlike many rearrangement products, **4** no longer has C_i symmetry owing to the bulky P(OPh)₃ substitution. The dihedral angle between two cyclopentadienyl ring planes is 11.12°. Like many analogues, the six-member ring Fe(1)–Fe(2)–Si(1)–Si(2)–C(2)–C(11) still takes a chair conformation but with somewhat twisted (Fe(1), Fe(2), C(2))





Fig. 1. The molecular structure of 1.

and C(11) are planar, Si(1) and Si(2) deviate from the plane by 0.569 Å and 0.722 Å). Si(1) and Si(2) deviate from the linked cyclopentadienyl plane by 0.401 Å and 0.202 Å, respectively.

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4. Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge We greatly appreciate financial support from the National Natural Science Foundation of China, the Doctoral Foundation of State Education Department of China and State Key Laboratory of Elemento-Organic Chemistry of Nankai University.



Fig. 2. The molecular structure of 4.

Table 1	
Summary of crystal data and data collection and refinement for 1 and	14

	1	4
Formula	$C_{35}H_{35}Fe_{2}O_{6}PSi_{2}\cdot 1/2C_{6}H_{6}$	$C_{35}H_{35}Fe_2O_6PSi_2$
$M (g \text{ mol}^{-1})$	789.55	750.50
Crystal system	Monoclinic	Monoclinic
Space group	C2/c(No.15)	$P2_1/n(No.14)$
a (Å)	25.880(4)	15.504(3)
b (Å)	9.431(1)	11.029(2)
c (Å)	31.499(7)	21.183(2)
β (°)	107.08(2)	103.935(9)
$V(\text{\AA}^3)$	7349(2)	3515.5(9)
Ζ	8	4
$Dc (g/cm^3)$	1.427	1.418
F(000)	3272	1552
Temperature (K)	298(±1)	301(±1)
μ (MoK α) (cm ⁻¹)	9.42	9.81
$2\theta_{\rm max}$ (°)	45	48
Reflections collected	5276	6093
Independent reflections	5185	5856
Observed reflections $[I > 3\sigma(I)]$	3130	3616
Number of refined parameters	427	415
Goodness of fit	2.06	2.91
Rint	0.028	0.025
Final R and $R_{\rm w}$	0.037 and 0.040	0.061 and 0.064
Maximum Δ/σ	0.01	0.01
Max. residual peak (e $Å^3$)	0.59	1.07

Table 2

Selected bond distances (Å) and bond angles (°) of $\boldsymbol{1}^a$

Fe(1)–Fe(2)	2.540(1)	Si(1)-Si(2)	2.351(2)	Si(1)-C(8)	1.863(6)
Fe(1) - C(8)	2.179(6)	Si(2)–C(17)	1.857(5)	Fe(2)–C(17)	2.167(5)
Fe(2)–P(1)	2.120(2)	P(1)–O(4)	1.602(4)	P(1)–O(5)	1.607(4)
P(1)–O(6)	1.625(3)	O(4)–C(18)	1.405(6)	O(5)–C(24)	1.396(6)
O(6)-C(30)	1.399(6)	Fe(1)-PL(1)	1.754	Fe(2)-PL(2)	1.752
Si(1)-PL(1)	0.152	Si(2)-PL(2)	0.205		
Fe(2)-Fe(1)-C(8)		108.6(1)	Fe(1)-Fe(2)-C(17)		106.2(1)
Fe(1)-C(8)-Si(1)		130.7(3)	Fe(2)-C(17)-Si(2)		132.2(3)
Si(1)-Si(2)-C(17)		113.8(2)	Si(2)–Si(1)–C(8)		113.3(2)
Fe(1)-Fe(2)-P(1)		104.45(5)	Fe(1)-C(1)-O(1)		172.6(5)
Fe(2) - P(1) - O(4)		116.2(1)	Fe(2)-P(1)-O(5)		119.5(1)
Fe(2)-P(1)-O(6)		119.7(1)	O(4)-P(1)-O(5)		97.8(2)
O(4)-P(1)-O(6)		103.3(2)	O(5)–P(1)–O(6)		96.4(2)
P(1) - O(4) - C(18)		124.1(3)	P(1)-O(5)-C(24)		127.3(3)
P(1)-O(6)-C(30)	125.3(3) PL(1)–PL(2)			88.14	

^a PL=The plane of five-membered ring.

Table 3

Table 5									
Selected	bond	distances	(Å)	and	bond	angels	(°)	of 4	a

Fe(1)–Si(1)	2.326(2)	Fe(2)–Si(2)	2.316(2)	Fe(1)–C(2)	2.112 (7)
Si(1)–C(11)	1.900(7)	Si(2)-C(2)	1.877(7)	Fe(2)–C(11)	2.136(7)
Fe(1) - P(1)	2.095(2)	P(1)–O(1)	1.599(5)	P(1)–O(2)	1.592(6)
P(1)–O(3)	1.640(4)	O(1)–C(18)	1.408(9)	O(2)–C(24)	1.424(9)
O(3)-C(30)	1.388(9)	Fe(1)-PL(1)	1.717	Fe(2)-PL(2)	1.727
Si(2)-PL(1)	0.202	Si(1)-PL(2)	0.401		
Si(1) - Fe(1) - C(2)		100.6(2)	Si(2)-Fe(2)-C(11)		98.4(2)
P(1) - Fe(1) - Si(1)		93.74(8)	P(1)-Fe(1)-C(2)		160.1(2)
Fe(1)-Si(1)-C(11)		111.1(2)	Fe(1)-C(2)-Si(2)		132.3(4)
Fe(2)-Si(2)-C(2)		110.6(2)	Fe(2)-C(11)-Si(1)		138.5(4)
Fe(1) - P(1) - O(1)		121.2(2)	Fe(1) - P(1) - O(2)		112.3(2)
Fe(1) - P(1) - O(3)		119.0(2)	O(1)-P(1)-O(2)		103.2(3)
O(1)–P(1)–O(3)		96.1(2)	O(2)-P(1)-O(3)		102.2(3)
P(1) - O(1) - C(18)		130.4(4)	P(1)-O(2)-C(24)		125.6(5)
P(1) - O(3) - C(30)		122.9(4)	PL(1)–PL(2)		11.12

 $^{\rm a}\,\text{PL}{=}\text{The}$ plane of five-membered ring.

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