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Novel Rearrangement Reactions. 4. Thermal Rearrangement of $[(\eta^5{:}\eta^5\text{-}t\text{-BuC}_5\text{H}_3\text{Me}_2\text{SiSiMe}_2\text{C}_5\text{H}_3\text{-}t\text{-Bu})\text{Fe}_2(\text{CO})\text{P}(\text{OPh})_3(\mu\text{-CO})_2]$ Containing a Bulky Phosphite Ligand

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Photolysis of *cis*-$(\text{Me}_2\text{SiSiMe}_2)[(\eta^5\text{-}t\text{-BuC}_5\text{H}_3)\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$ (**2c**) in the presence of $\text{P}(\text{OPh})_3$ ligands afforded only *cis*-$[(\eta^5{:}\eta^5\text{-}t\text{-BuC}_5\text{H}_3\text{Me}_2\text{SiSiMe}_2\text{C}_5\text{H}_3\text{-}t\text{-Bu})\text{Fe}_2(\text{CO})\text{P}(\text{OPh})_3(\mu\text{-CO})_2]$ (**3c**), whereas similar treatment of **2t** yielded only the trans isomer **3t**. When **3c** and **3t** were heated, in xylene, the cis compound **(3c)** rearranged to the trans product $[\{\text{Me}_2\text{Si}(\eta^5\text{-}t\text{-BuC}_5\text{H}_3)\text{Fe}\}_2(\text{CO})_3\text{P}(\text{OPh})_3]$ (**4t**), while the trans compound (**3t**) afforded the cis product $[\{\text{Me}_2\text{Si}(\eta^5\text{-}t\text{-BuC}_5\text{H}_3)\text{Fe}\}_2(\text{CO})_3\text{P}(\text{OPh})_3]$ (**4c**); thus, the rearrangement is stereospecific.

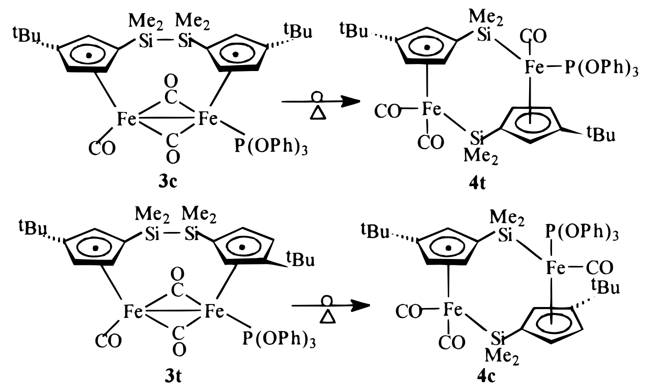
Introduction

We recently reported a novel rearrangement reaction involving Si−Si and Fe−Fe bonds in the bridged dinuclear iron complex $(\text{Me}_2\text{SiSiMe}_2)[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$ (**1**).[1] A detailed investigation of thermal rearrangement in the *tert*-butyl-substituted analogue $(\text{Me}_2\text{SiSiMe}_2)[(\eta^5\text{-}t\text{-BuC}_5\text{H}_3)\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$ (**2**) indicated that the reaction is stereospecific, and an alternative mechanism was subsequently proposed.[2] It was of interest to examine whether the rearrangement can proceed smoothly and to determine the rearrangement stereochemistry when a carbonyl ligand is replaced by a phosphite ligand. We report here an investigation of the synthesis of $[(\eta^5{:}\eta^5\text{-}t\text{-BuC}_5\text{H}_3\text{Me}_2\text{SiSiMe}_2\text{C}_5\text{H}_3\text{-}t\text{-Bu})\text{Fe}_2(\text{CO})\text{P}(\text{OPh})_3(\mu\text{-CO})_2]$ (**3**) and its thermal rearrangement.

Results and Discussion

Synthesis and Thermal Rearrangement. The synthesis of the *tert*-butyl-substituted complex $(\text{Me}_2\text{SiSiMe}_2)[(\eta^5\text{-}t\text{-BuC}_5\text{H}_3)\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$ (**2**), existing as a mixture of cis and trans isomers (**2c** and **2t**), has been described recently.[2] Photolysis of cis-$(\text{Me}_2\text{SiSiMe}_2)[(\eta^5\text{-}t\text{-BuC}_5\text{H}_3)\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$ (**2c**) in the presence of $\text{P}(\text{OPh})_3$ ligands for 40 h afforded only *cis*-$[(\eta^5{:}\eta^5\text{-}t\text{-BuC}_5\text{H}_3\text{Me}_2\text{SiSiMe}_2\text{C}_5\text{H}_3\text{-}t\text{-Bu})\text{Fe}_2(\text{CO})\text{P}(\text{OPh})_3(\mu\text{-CO})_2]$ (**3c**), whereas similar treatment of **2t** yielded only the trans isomer **3t**.[3] This indicated that the CO substitution reaction of bridged diiron species by a phosphite ligand did not influence the substituent configuration. Like other bridged analogues, $(\text{E})[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$ (E = CMe_2CMe_2, $\text{CH}(\text{NMe}_2)\text{CH}(\text{NMe}_2)$),[4] more than one carbonyl ligand could not be replaced by $\text{P}(\text{OPh})_3$ ligands despite prolongation of the reaction time.

Scheme 1



Study of the subsequent rearrangement reactions of **3c** and **3t** revealed the same stereospecificity as exhibited in those of **2c** and **2t**. When the cis substrate **3c** was heated in boiling xylene for 1 h, only the trans product **4t** was obtained in 55% yield, whereas similar treatment of the trans substrate **3t** afforded only the cis product **4c** in 50% yield (Scheme 1).[5] Although the rearrangement stereospecificity did not change, the rearrangement became much more facile when one carbonyl ligand was replaced by a phosphite ligand. The rearrangement that required 24 h before substitution could be accomplished in only 1 h.

Complexes **3c** and **3t** are dark red and stable in the solid state, whereas **4c** and **4t** are light yellow and

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[†] Nankai University.

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(5) The cis and trans isomers (**4c** and **4t**) were designated only according to the *tert*-butyl configuration of their precursors without $\text{P}(\text{OPh})_3$ ligands.

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Table 1. Physical and Spectral Data for Compounds 3 and 4

compd	yield (%)	mp (°C)	IR ν_{CO}, cm^{-1} (KBr disk)	^{1}H NMR δ, ppm ($CDCl_3$)	^{31}P NMR δ, ppm ($CDCl_3$)
3c	61−67	148−150	1989 (w), 1948 (s), 1766 (w), 1729 (s)	0.02 (s, 3H, SiMe), 0.13 (s, 3H, SiMe), 0.40 (s, 3H, SiMe), 0.51 (s, 3H, SiMe), 1.33 (s, 9H, *t*-Bu), 1.44 (s, 9H, *t*-Bu), 3.29 (s, 1H, Cp), 3.68 (s, 1H, Cp), 3.75 (s, 1H, Cp), 4.92 (s, 1H, Cp), 5.16 (d, 1H, Cp), 5.28 (s, 1H, Cp), 6.87−7.16 (m, 15H, Ph)	77.34
3t	71	160−161	1984 (w), 1950 (s), 1765 (w), 1730 (s)	0.05 (s, 3H, SiMe), 0.14 (s, 3H, SiMe), 0.37 (s, 3H, SiMe), 0.58 (s, 3H, SiMe), 1.31 (s, 9H, *t*-Bu), 1.33 (s, 9H, *t*-Bu), 3.52 (s, 1H, Cp), 3.61 (s, 1H, Cp), 3.83 (s, 1H, Cp), 4.77 (s, 1H, Cp), 5.06 (s, 1H, Cp), 5.17 (d, 1H, Cp), 6.99−7.11 (m, 15H, Ph)	77.73
4c	53	200−201	1982 (s), 1930 (s), 1916 (s)	0.28 (s, 3H, SiMe), 0.43 (s, 3H, SiMe), 0.51 (s, 3H, SiMe), 0.60 (s, 3H, SiMe), 1.05 (s, 9H, *t*-Bu), 1.27 (s, 9H, *t*-Bu), 3.21 (s, 1H, Cp), 4.41 (s, 1H, Cp), 4.55 (m, 2H, Cp), 5.06 (s, 1H, Cp), 5.14 (s, 1H, Cp), 6.95−7.17 (m, 15H, Ph)	66.34
4t	60	168−169	1981 (s), 1914 (s)	0.33 (s, 3H, SiMe), 0.47 (s, 3H, SiMe), 0.53 (s, 3H, SiMe), 0.62 (s, 3H, SiMe), 0.98 (s, 9H, *t*-Bu), 1.06 (s, 9H, *t*-Bu), 3.33 (s, 1H, Cp), 4.37 (s, 1H, Cp), 4.57 (d, 1H, Cp), 4.95 (s, 2H, Cp), 5.14 (s, 1H, Cp), 6.92−7.20 (m, 15H, Ph)	66.97

rather stable in solution as well as in the solid state. All decomposed on a silica column; therefore, an alumina column was employed to isolate and purify them. The IR spectra of **3c** and **3t** exhibited almost identical absorptions, except for a slight shift in frequencies (Table 1). The terminal carbonyl groups in the IR spectrum of **4c** gave rise to two absorptions (1981 and 1914 cm^{-1}), corresponding to symmetrical and antisymmetrical stretching vibrational modes. The two bands have nearly equal intensity, indicating that the OC−Fe−CO angle is approximately 90°. This conclusion has been confirmed by single-crystal X-ray diffraction of **4c** (C(13)−Fe(2)-C(14), 94.3(2)°). A similar observation was made in analogues (e.g., 92.7(2) and 92.0(2)° in [$Me_2Sn(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$,[6] 92.3(3)° in [$Me_2Si(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$,[1] 94.3(1)° in *trans*-[$Me_2Si(\eta^5\text{-}t\text{-}BuC_5H_3)Fe(CO)_2]_2$[2]). In the ^{1}H NMR spectra of all isomers, four chemically inequivalent silicon methyl groups exhibited four singlets. This differed from the one or two singlets observed in the ^{1}H NMR spectra of the precursors without the $P(OPh)_3$ ligand. The two *tert*-butyl groups in the ^{1}H NMR spectra of all isomers displayed two singlets, attributable to their different chemical environments. The ^{1}H NMR spectra of **3c** and **3t** exhibited two groups of cyclopentadienyl proton resonances of equal intensity, each consisting of three peaks. This is consistent with an asymmetric molecular structure containing two nonequivalent cyclopentadienyl rings. The group to higher field is assigned to the cyclopentadienyl ring bonded to the same iron atom as the phosphite ligand.[7] Although the cyclopentadienyl proton resonances in the ^{1}H NMR spectra of **4c** and **4t** were not divided into two different groups, there was one proton resonance shifted much more upfield than normal cyclopentadienyl protons, attributed to the shielding function of phenyl rings in the phosphite ligand. A similar phenomenon was observed in **3c** and **3t** but not in the analogue [$Fe_2\{\eta^5{:}\eta^5\text{-}C_5H_4CH(NMe_2)CH(NMe_2)\text{-}C_5H_4\}(CO)P(OEt)_3(\mu\text{-}CO)_2$].[8] Therefore, it appears reasonable that the proton is likely to fall in the shielding range of phenyl rings. The ^{29}Si NMR spectra of **4c** and **4t** exhibited one singlet and one doublet, and the latter is due to the coupling between silicon and phosphorus. The molecular structures of **3t** and **4c** were determined by X-ray diffraction.

Table 2. Selected Geometrical Details of Complex 3t

Bond Distances (Å)			
Fe(1)−Fe(2)	2.542(1)	Si(1)−Si(2)	2.363(2)
Fe(1)−P	2.121(1)	Fe(1)−C(2)	1.896(3)
Fe(1)−C(3)	1.910(3)	Fe(2)−C(1)	1.742(4)
Fe(2)−C(2)	1.974(3)	Fe(2)−C(3)	1.927(3)
P−O(4)	1.602(2)	P−O(5)	1.612(2)
P−O(6)	1.607(2)	C(1)−O(1)	1.151(4)
C(2)−O(3)	1.181(4)	C(3)−O(2)	1.187(4)
Fe(1)−Cp(1)[a]	1.760	Fe(2)−Cp(2)[a]	1.768
Bond Angles (deg)			
Fe(2)−Fe(1)−P	107.07(3)	Fe(1)−Fe(2)−C(1)	104.8(1)
Fe(1)−Fe(2)−C(6)	109.61(8)	Fe(2)−Fe(1)−C(18)	105.38(8)
Fe(1)−C(3)−Fe(2)	83.0(1)	Fe(1)−C(2)−Fe(2)	82.1(1)
Fe(2)−C(6)−Si(2)	126.9(2)	Fe(1)−C(18)−Si(1)	132.1(2)
Fe(1)−P−O(4)	116.72(9)	Fe(1)−P−O(5)	114.87(9)
Fe(1)−P−O(6)	113.90(9)		

[a] Distance from the centroid of the Cp ring to the corresponding Fe atom.

Molecular Structures of 3t and 4c. The molecular structure of **3t** is presented in Figure 1. Table 2 provides selected bond distances and angles. The molecule of **3t** is analogous to that of the parent complex **2t**, except that a terminal carbonyl group is replaced by a $P(OPh)_3$ ligand. The six-membered ring Fe(1)−Fe(2)−C(6)−Si(2)−Si(1)−C(18), constituting its molecular framework, adopts an approximate boat conformation (the Fe(1), Fe(2), Si(1), and Si(2) atoms are approximately coplanar, with C(6) and C(18) atoms deviating from this plane by 0.539 and 0.436 Å, respectively). The Fe−Fe distance (2.542(1) Å) is equal to those of **2t** and the nonbridged analogue *cis*-[$Fe_2(CO)_3P(OPh)_3(\eta^5\text{-}C_5H_5)_2$] (**5**)[9] (2.542(2) and mean 2.545(2) Å, respectively). The Si−Si distance (2.363(2) Å) is slightly longer than that (2.350(4) Å) of **2t** as a consequence of the $P(OPh)_3$ substitution. The P−Fe and P−O distances are close to those in **5**.[9] The dihedral angle between two cyclopentadienyl rings is 91.3°, similar to those in related analogues: e.g., 92.5°, **2t**; 91.9°, **2c**; 92.8°, *cis*-[$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$];[10] 97.2°, [$(\eta^5{:}\eta^5\text{-}C_5H_4SiMe_2C_5H_4)Fe_2(CO)_4$];[11] 88.8°, [$\eta^5{:}\eta^5\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4$]-

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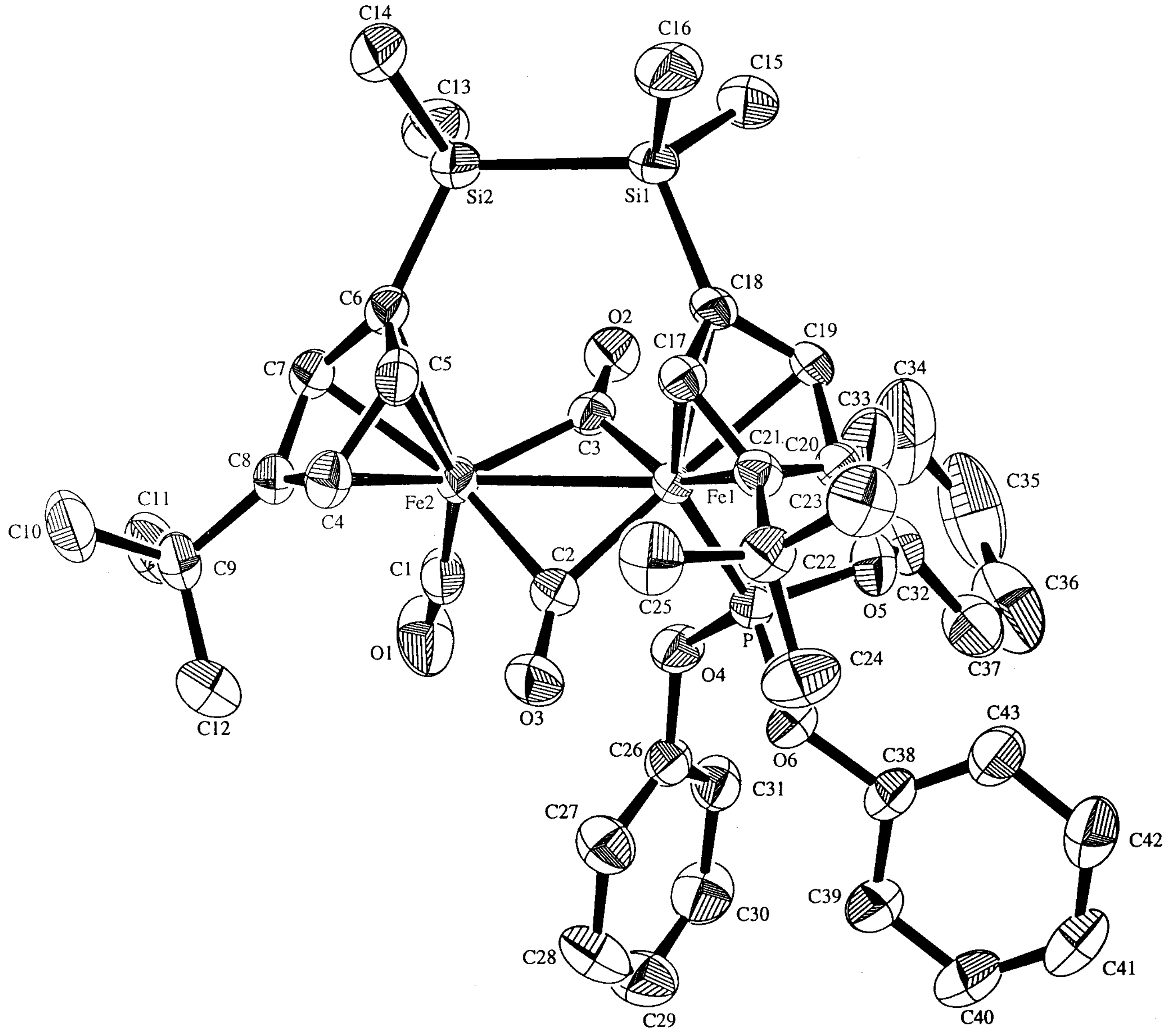

Figure 1. Molecular structure of *trans*-[(η^5:η^5-*t*-$BuC_5H_3Me_2SiSiMe_2C_5H_3$-*t*-Bu)$Fe_2(CO)P(OPh)_3(\mu\text{-}CO)_2$] (**3t**).

$Fe_2(CO)_4$.[12] The angle between two $Fe_2(\mu\text{-}CO)$ planes is 153.5°, less than those in its analogue (164° in **5**;[9] 165.3° in **2c**). The Si(1) and Si(2) atoms deviate from the linked cyclopentadienyl rings by 0.236 and 0.076 Å, respectively. The silicon methyl groups adopt an almost eclipsed conformation (the smaller C−Si−Si−C torsion angles fall in the range of 8.6(2)−10.6(2)°).

The molecular structure of **4c** is presented in Figure 2. Table 3 provides selected bond distances and angles. The molecule of **4c** consists of one [Me_2Si(η^5-*t*-BuC_5H_3)-$Fe(CO)_2$] and one [Me_2Si(η^5-*t*-BuC_5H_3)$FeP(OPh)_3(CO)$] moiety linked to each other by two Si−Fe bonds. **4c** is unsymmetrical, and the six-membered ring Fe(1)−Si(1)−C(5)−Fe(2)−Si(2)−C(18), constituting its molecular framework, adopts a twist-boat conformation. The dihedral angle between two cyclopentadienyl rings is 18.8°, less than that (68.98°) in its parent analogue *cis*-[Me_2Si(η^5-*t*-BuC_5H_3)$Fe(CO)_2]_2$.[2] The mean Fe−Si distance (2.312 Å) is almost equal to that (2.317 Å) in the parent analogue. The Fe−P distance (2.104 Å) is

Table 3. Selected Geometrical Details of Complex 4c

	Bond Distances (Å)		
Fe(1)−Si(1)	2.317(1)	Fe(2)−Si(2)	2.307(1)
Fe(1)−C(1)	1.730(4)	Fe(1)−P	2.104(1)
Fe(2)−C(13)	1.737(4)	Fe(2)−C(14)	1.735(4)
C(1)−O(1)	1.151(4)	C(13)−O(5)	1.158(4)
C(14)−O(6)	1.147(4)	P−O(2)	1.624(2)
P−O(3)	1.610(3)	P−O(4)	1.621(3)
Fe(1)−Cp(1)[a]	1.742	Fe(2)−Cp(2)[a]	1.714
	Bond Angles (deg)		
Si(1)−Fe(1)−C(18)	93.18(9)	Fe(1)−C(18)−Si(2)	141.8(2)
Fe(2)−Si(2)−C(18)	115.9(1)	Si(2)−Fe(2)−C(5)	97.35(10)
Fe(2)−C(5)−Si(1)	129.9(2)	Fe(1)−Si(1)−C(5)	115.4(1)
C(1)−Fe(1)−P	91.5(1)	C(13)−Fe(2)−C(14)	94.3(2)
Fe(1)−P−O(2)	119.2(1)	Fe(1)−P−O(3)	113.3(1)
Fe(1)−P−O(4)	120.83(10)		

[a] Distance from the centroid of Cp ring to the corresponding Fe atom.

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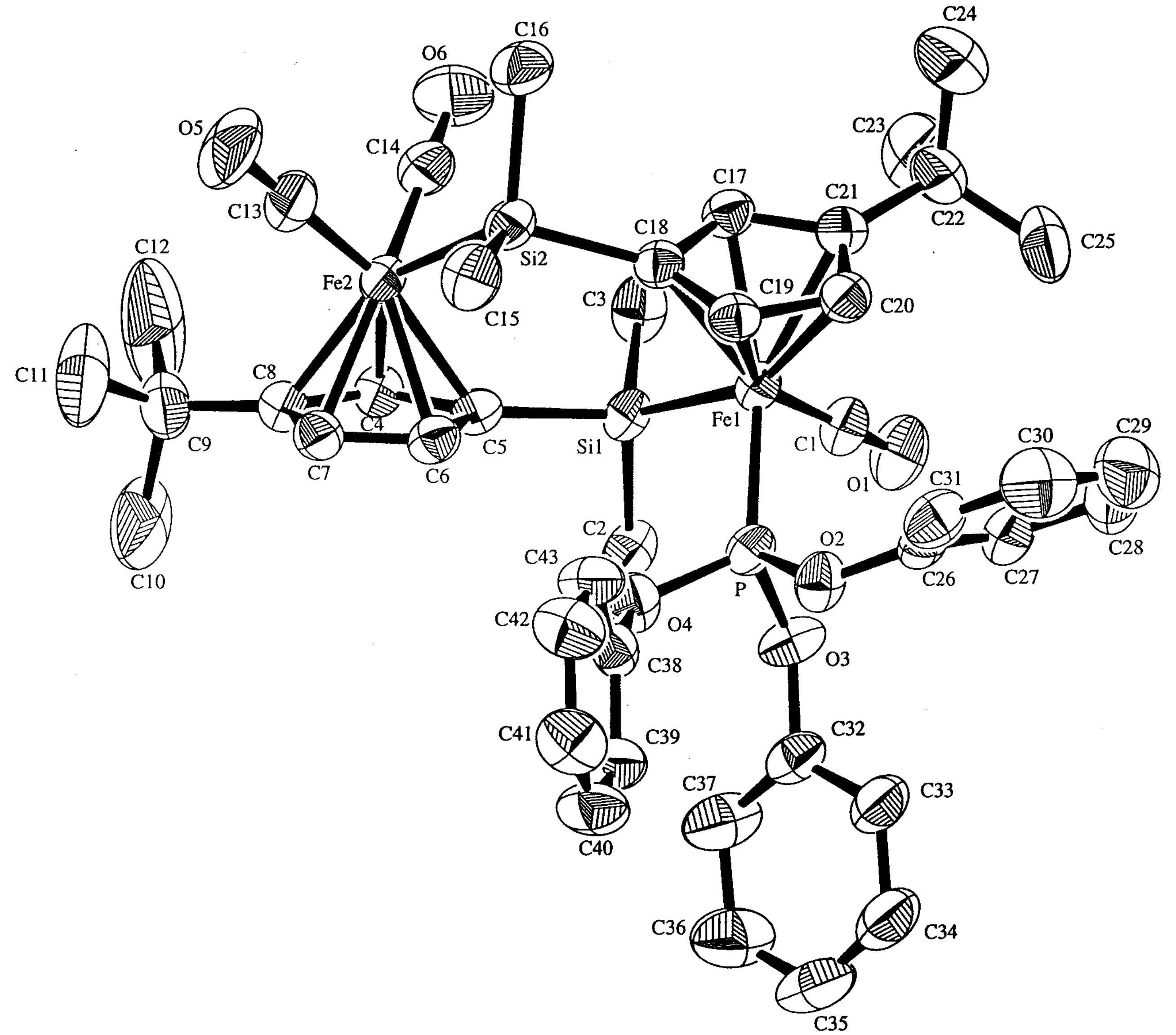

Figure 2. Molecular structure of *cis*-[{$Me_2Si(\eta^5$-*t*-$BuC_5H_3)Fe\}_2(CO)_3P(OPh)_3$] (**4c**).

shorter than those in analogues (2.121(1) Å in **3t**, 2.126(3) Å in **5**[9]). The Si(1) and Si(2) atoms are bent out of the linked cyclopentadienyl rings by 0.143 and 0.550 Å, respectively. In addition, the distance (1.742 Å) from the Fe(1) atom to Cp(1) is larger than that (1.714 Å) from the Fe(2) atom to Cp(2), probably due to the electronic effect of the phosphite ligand and the steric repulsion between it and the close *tert*-butyl group.

Mechanism. In comparison with the parent complex **2**, a carbonyl ligand of complex **3** was replaced by a phosphite ligand. The bulky phosphite ligand did not hinder the smooth progression of the rearrangement and, in fact, greatly accelerated it. Thus, there remains the question of why the thermal rearrangement of phosphite-substituted complex **3** occurs more readily than that of **2**. According to the mechanism we proposed previously,[2] the rearrangement velocity should be closely related to the degree of dissociation of Fe−Fe bonds and the stability of iron-centered radicals formed upon dissociation. It is known that metal−metal bonds often are destabilized with respect to homolytic dissociation on substitution of small ligands by more sterically demanding ligands. It has also been found that bulky substituents, either on the Cp ligand (Me, Ph) or in place of a carbonyl ligand (phosphines, phosphites), greatly enhance the extent of homolysis of the chromium−chromium bond.[13] Thus, it appears reasonable that the bulkier $P(OPh)_3$ ligands enhance thermal homolysis of the iron−iron bonds and possibly stabilize iron-centered radicals by dispersing the charge.

Complex **3** showed the same rearrangement stereospecificity (i.e., the cis isomer **3c** yields the trans product **4t**, whereas the trans isomer **3t** affords the cis product **4c**) as its precursor **2**. By analogy with the mechanism for the rearrangement of **2**, an alternative mechanism for formation of the cis product **4c** (or the trans product

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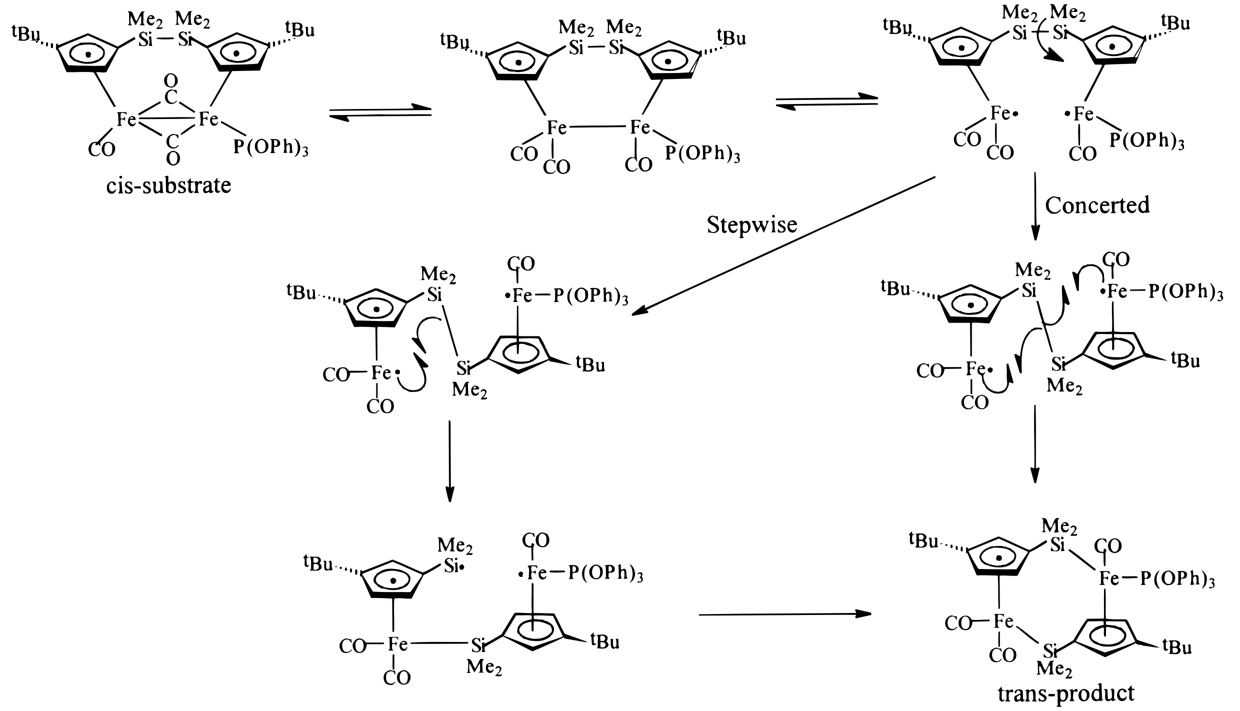
Scheme 2



4t) is proposed (Scheme 2). The mechanism involves either a concerted or stepwise pathway. If the rearrangement proceeds via a stepwise pathway, the iron-centered radical without the P(OPh)$_3$ ligand first will attack at the Si−Si bond because of its smaller steric bulk.

Over the course of photolysis of 40 h, we did not detect and isolate any rearrangement product formed from either **2** or **3**. In addition, photolysis of **1** in the absence of phosphite ligands did not produce the corresponding rearrangement product. This indicates that photolysis cannot induce the progression of the rearrangement. It is intriguing that Vollhardt et al. reported a reversible photochemical isomerization of (fulvalene)tetracarbonyldiruthenium, $Ru_2(CO)_4(\eta^5{:}\eta^5\text{-}C_{10}H_8)$, and its mechanism.[14] The forward reaction is induced by irradiation with long-wavelength light or even sunlight. On heating, the rearranged photoproduct $[(\eta^5\text{-}C_5H_4)Ru(CO)_2]_2$ reverts to the original complex, with a net energy release of about 30 kcal/mol. The rearrangement requires photoinduction, while our rearrangement is a thermal process involving the homolysis of metal−metal bonds.

Experimental Section

Schlenk and vacuum-line techniques were employed for manipulations of air- and moisture-sensitive compounds. Solvents were distilled from appropriate drying agents under argon before use. Tetrahydrofuran, toluene, xylene, and benzene were distilled from sodium/benzophenone ketyl and purged with argon prior to use. ^{1}H and ^{29}Si NMR spectra were obtained on a Bruker AC-P200 spectrometer using CHCl$_3$ (δ 7.24 ppm) and SiMe$_4$ as an internal standard, while phosphorus (^{31}P NMR) spectra were obtained on the same spectrometer using 85% H$_3$PO$_4$ as an external standard. Elemental analyses were performed with a Perkin-Elmer 240C analyzer. Infrared spectra were obtained as KBr disks and recorded on a Nicolet 5DX FT-IR spectrometer.

Table 4. Summary of X-ray Diffraction Data

	3t	4c
formula	$C_{43}H_{51}Fe_2O_6PSi_2$	$C_{43}H_{51}Fe_2O_6PSi_2$
fw	862.71	862.71
space group	$P\bar{1}$	$P\bar{1}$
cryst syst	triclinic	triclinic
Z	2	2
a (Å)	11.835(4)	15.235(9)
b (Å)	18.787(4)	15.451(7)
c (Å)	10.294(3)	11.461(3)
α, deg	98.84(2)	110.42(3)
β, deg	112.66(2)	90.60(4)
γ, deg	86.61(2)	60.86(3)
V (Å^3)	2087(1)	2166(2)
d_{calc} (g cm^{-3})	1.373	1.323
μ, cm^{-1}	8.36	8.05
R^a	0.032	0.034
$R_w{}^b$	0.043	0.046
goodness of fit	1.73	1.83

[a] $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2]^{1/2}$.

Preparation of $[(\eta^5{:}\eta^5\text{-}t\text{-}BuC_5H_3Me_2SiSiMe_2C_5H_3\text{-}t\text{-}Bu)Fe_2(CO)P(OPh)_3(\mu\text{-}CO)_2]$ (3). A solution of 0.55 g (0.95 mmol) of **2c** and 1.10 g (3.55 mmol) of P(OPh)$_3$ in 40 mL of benzene, thoroughly degassed, was irradiated with a 300 W high-pressure mercury lamp for 40 h. TLC monitoring of the reaction indicated the disappearance of reactant **2c**. Solvent was removed under vacuum, the dark red oil residue was chromatographed (neutral alumina, 200−300 mesh/dichloromethane), and the products were recrystallized from dichloromethane/hexane mixtures to give 0.50 g of dark red crystals of **3c**. Anal. Calcd for $C_{43}H_{51}Fe_2O_6PSi_2$: C, 59.87; H, 5.96. Found: C, 59.75; H, 5.90.

A solution of 0.37 g (0.64 mmol) of **2t** and 0.74 g (2.38 mmol) of P(OPh)$_3$ in 40 mL of benzene, thoroughly degassed, was irradiated with the above lamp for 40 h. Treatment similar to that described above afforded 0.39 g of dark red crystals of **3t**. Anal. Calcd for $C_{43}H_{51}Fe_2O_6PSi_2$: C, 59.87; H, 5.96. Found: C, 59.78; H, 5.43.

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[14] (a) Vollhardt, K. P. C.; Weidman, T. W. *J. Am. Chem. Soc.* **1983,** *105,* 1676. (b) Boese, R.; Cammack, J. K.; Matzger, A. J.; Pflug, K.; Tolman, W. B.; Vollhardt, K. P. C.; Weidman, T. W. *J. Am. Chem. Soc.* **1997,** *119,* 6757.

Thermal Rearrangement Reaction of 3c and 3t. A 0.30 g amount of **3c** in 25 mL of xylene was heated at reflux for 1 h. The solvent was removed under vacuum. The residue was introduced to an alumina column in a minimum of dichloromethane. Elution with petroleum ether yielded 0.18 g of light yellow crystals of **4t**. Anal. Calcd for $C_{43}H_{51}Fe_2O_6PSi_2$: C, 59.87; H, 5.96. Found: C, 59.80; H, 5.95. ^{29}Si NMR ($CDCl_3$): δ 33.7 (s), 31.5 (d, $^2J_{PSi} = 48.5$ Hz).

A 0.30 g amount of **3t** in 25 mL of xylene was refluxed for 1 h. Treatment similar to that described above gave 0.16 g of light yellow crystals of **4c**. Anal. Calcd for $C_{43}H_{51}Fe_2O_6PSi_2$: C, 59.87; H, 5.96. Found: C, 59.87; H, 5.57. ^{29}Si NMR ($CDCl_3$): δ 34.8 (s), 31.2 (d, $^2J_{PSi} = 45.7$ Hz).

Crystallographic Studies. Crystals of **3t** and **4c** suitable for X-ray diffraction were obtained from hexane/dichloromethane solution. All data sets were collected on a Rigaku AFC 7R diffractometer with graphite-monochromated Mo Kα radiation. The corrections for empirical absorption were applied to intensity data. The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan Crystallographic Software Package of Molecular Structure Corp. Neutral atom scattering factors were taken from the tabulation of Cromer and Waber.[15] A summary of the crystallographic results is presented in Table 4.

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Supporting Information Available: Tables of final positional and thermal parameters of the non-hydrogen atoms, general temperature factors, and bond distances and angles for **3t** and **4c** (24 pages). Ordering information is given on any current masthead page.

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(15) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.