3474 *Organometallics* **1997,** *16,* 3474−3481

Novel Rearrangement Reactions. 1. Molecular Rearrangement via Metathesis between Intramolecular Si−Si and Fe−Fe Bonds

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Received January 24, 1997[⊗]

Thermal treatment of t-Bu$C_5H_4Me_2SiSiMe_2C_5H_4$-t-Bu with $Fe(CO)_5$ in xylene gave the diiron complex $(Me_2SiSiMe_2)[(\eta^5\text{-}t\text{-}BuC_5H_3)Fe(CO)]_2(\mu\text{-}CO)_2$ (**3**), existing as a mixture of cis and trans isomers (**3c** and **3t**) which were separated by preparative TLC. When the two isomers were heated respectively in xylene, the cis substrate (**3c)** rearranged to the trans product $[Me_2Si(\eta^5\text{-}t\text{-}BuC_5H_3)Fe(CO)_2]_2$ (**4t**), while the trans substrate (**3t**) afforded the cis product $[Me_2Si(\eta^5\text{-}t\text{-}BuC_5H_3)Fe(CO)_2]_2$ (**4c**). This indicates that the rearrangement reaction is stereospecific. Complexes $[(\eta^5{:}\eta^5\text{-}C_5H_4Me_2SiSiMe_2C_5R_3R')Fe(CO)]_2(\mu\text{-}CO)_2$ ($R = H$, $R' =$ t-Bu, **5**; $R = R' =$ Me, **6**), containing different cyclopentadienyl groups, were prepared similarly. Their respective rearrangement reactions only yielded the corresponding unsymmetrical products $[(Me_2Si)(\eta^5\text{-}C_5H_4)Fe(CO)_2][(Me_2Si)(\eta^5\text{-}C_5R_3R')Fe(CO)_2]$ ($R = H$, $R' = t$-Bu, **7**; $R = R' =$ Me, **8**); no symmetrical disproportionation products were detected. This indicates that the reaction proceeds via an intramolecular rather than intermolecular pathway. The conclusion is further confirmed by the fact that no crossover product was formed in subsequent rearrangement between two different substrates. Probing the reaction by ESR spectroscopy shows that the reaction proceeds via an intermediate containing iron-centered radicals. On the basis of these experimental facts, an alternative mechanism for the rearrangement reaction is proposed. Molecular structures of **3c**, **3t**, **4t**, and **4c** were determined by X-ray diffraction.

Introduction

There is currently considerable interest in the synthesis and study of a variety of metal−metal-bonded transition-metal complexes,[1] largely owing to their important roles in many catalytic processes. Some important metal−metal-bonded systems are bridged binuclear complexes.[2] These systems are suitable for studying interactions between two metal reaction sites, since the existence of a bridge inherently holds the two metals in close proximity. In particular, bridged bis(cyclopentadienyl)tetracarbonyldiiron derivatives, in which two (cyclopentadienyl)iron units are linked together by certain alkyl or silyl groups, have been receiving attention.[3] Such bridging linkages result in special structural features and reactivity.[4]

Recently in the preparation of the disilane-bridged bis(cyclopentadienyl)tetracarbonyldiiron complex $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)]_2(\mu\text{-}CO)_2$ (**1**), a novel molecular rearrangement via a metathetical reaction between the Si−Si and Fe−Fe bonds was observed (Scheme 1).[5] Complex **1**, when heated in boiling xylene, converts smoothly to complex **2**, which has a novel cyclic structure. The formation of **2** from **1** implies formally the rupture of one Si−Si and one Fe−Fe bond and the formation of two Si−Fe bonds. This process is somewhat similar to the base-induced migrations of Si from Cp to metal.[6] As far as their structures are concerned, the molecular framework in complexes **1** and **2** may be considered to be a six-membered ring consisting of two

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

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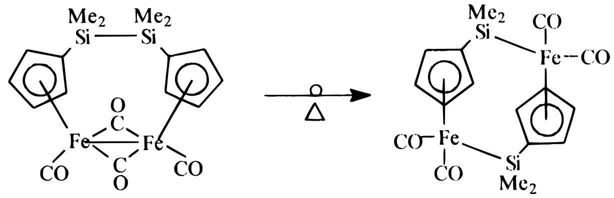
S0276-7333(97)00047-2 CCC: $14.00

Scheme 1



1 2

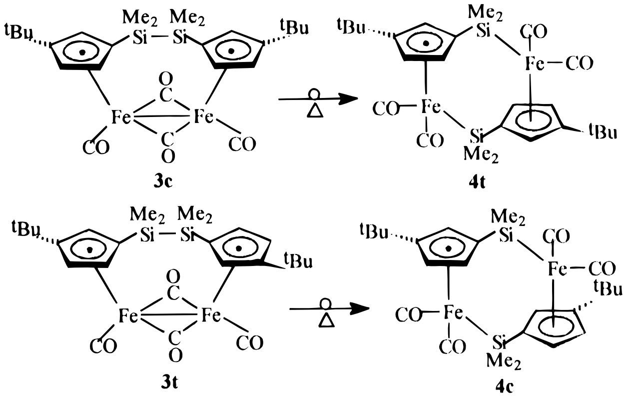
silicon, two iron, and two bridgehead carbon atoms of the cyclopentadienyl rings. Complex **1** is unsymmetrical, and the six-membered ring has a twist-boat conformation, while complex **2** has C_i symmetry, and the corresponding six-membered ring has a precise chair conformation.

In order to gain an insight into the reaction mechanism, detailed investigations of the stereochemistry of the reaction, reaction intermediate, and crossover reactions were conducted. An alternative mechanism has been proposed to account for the rearrangement reaction.

Results

Stereospecificity of the Reaction. To probe the effect of bulky substituent groups of the cyclopentadienyl rings on the rearrangement reaction, the *tert*-butyl-substituted analogue (Me$_2$SiSiMe$_2$)[(η^5-*t*-BuC$_5$H$_3$)Fe(CO)]$_2$(μ-CO)$_2$ (**3**) was synthesized by the same approach as was used for **1**. The expected product **3** (33%) and a small amount of rearrangement product **4** (2.2%) were obtained, showing that the *tert*-butyl group in complex **3** does not hinder the rearrangement reaction. It should be noted that complex **3** exists as a mixture of two isomers (*cis*-**3** (**3c**), *trans*-**3** (**3t**)).[7] Pure cis and trans isomers were separated by preparative TLC. ^{1}H NMR spectroscopy indicated that complex **4** also exists as a mixture of two isomers (*trans*-**4** (**4t**), *cis*-**4** (**4c**)),[8] which could not be separated by general chromatographic methods owing to their almost equal R_f values.

Scheme 2



Study of the subsequent rearrangement reactions of **3c** and **3t** revealed a significant feature of the stereochemistry of the reaction. When cis substrate **3c** was heated at reflux in xylene for 24 h, only the trans product **4t** was obtained in 60% yield, while similar treatment of trans substrate **3t** afforded only the cis product **4c** in 55% yield (Scheme 2). This strongly indicates that the rearrangement reaction is stereospecific. Complexes **3c** and **3t** are deep red crystals stable in the solid state, whereas complexes **4c** and **4t** are light yellow crystals rather stable in solution as well as in the solid state. The IR and ^{1}H NMR spectra of the respective cis and trans isomers of both reactants and products exhibited considerable differences. In the ^{1}H NMR spectrum of **3c**, the silicon methyls only exhibited a singlet (δ 0.23 ppm), attributable to an accidental degeneracy. This is different from the two singlets (δ 0.18 and 0.23 ppm) in the NMR spectrum of **3t**. In addition, the bridging carbonyl groups in the IR spectrum of **3c** gave rise to two absorptions (1794.5, 1753.5 cm^{-1}), different from the one carbonyl absorption (1769.9 cm^{-1}) of **3t**, which is attributable to the difference in the molecular symmetry of the two isomers. The silicon methyls in the ^{1}H NMR spectra of **4c** and **4t** exhibited two singlets, with significant chemical shift differences ($\Delta\delta$ 0.02 ppm for **4c**, 0.1 ppm for **4t**). All of their molecular structures were determined by single-crystal X-ray diffraction.

The molecular structure of **3c** is presented in Figure 1. Table 1 provides selected bond distances and angles and torsion angles. The molecule of **3c** has mirror symmetry except for some twist about the Si−Si bond, with the two *tert*-butyl groups oriented in the same direction. The six-membered ring Si(1)−Si(2)−C(8)−Fe(2)−Fe(1)−C(10), constituting its molecular framework, takes a twist-boat conformation. The Fe−Fe and Si−Si distances (2.5480(8), 2.357(2) Å) are longer than those (2.526(2), 2.346(4) Å) in the parent analogue, **1**, presumably as a consequence of the bulky *tert*-butyl substituents. The dihedral angle between the cyclopentadienyl rings is 91.98°, similar to those in related analogues: *e.g.*, 92.8°, *cis*-[(η^5-C$_5$H$_5$)$_2$Fe$_2$(CO)$_4$];[9] 97.2°, [(η^5:η^5-C$_5$H$_4$SiMe$_2$C$_5$H$_4$)Fe$_2$(CO)$_4$];[3c] 88.8°, [η^5:η^5-C$_5$H$_4$-CH(NMe$_2$)CH(NMe$_2$)C$_5$H$_4$]Fe$_2$(CO)$_4$.[10] The angle between the Fe$_2$(μ-CO)$_2$ planes is 165.29°, less than that in its parent analogue (178.69°), possibly owing to the large steric repulsion between the *tert*-butyl groups and the bridging carbonyls. Si(1) and Si(2) deviate from the linked cyclopentadienyl plane by 0.120 and 0.240 Å, respectively. The silicon methyls are partly eclipsed relative to one another (the smaller C−Si−Si−C torsion angles fall in the range of 18.0(3)−19.3(3)°).

The molecular structure of **3t** is presented in Figure 2. The quality of this structure is poor due to poor crystal quality, but it serves to establish the connectiv-

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(7) Cis isomer **3c** was designated according to the cis arrangement of two *tert*-butyl groups substituted at identical positions of the corresponding Cp rings, which was confirmed by single-crystal X-ray diffraction. Trans isomer **3t** was similarly designated in contrast to the cis isomer.

(8) Trans isomer **4t** was designated according to the trans arrangement of two substituted *tert*-butyl groups in the opposite direction, which was confirmed by single-crystal X-ray diffraction. Trans isomer **3t** was similarly designated in contrast to the cis isomer.

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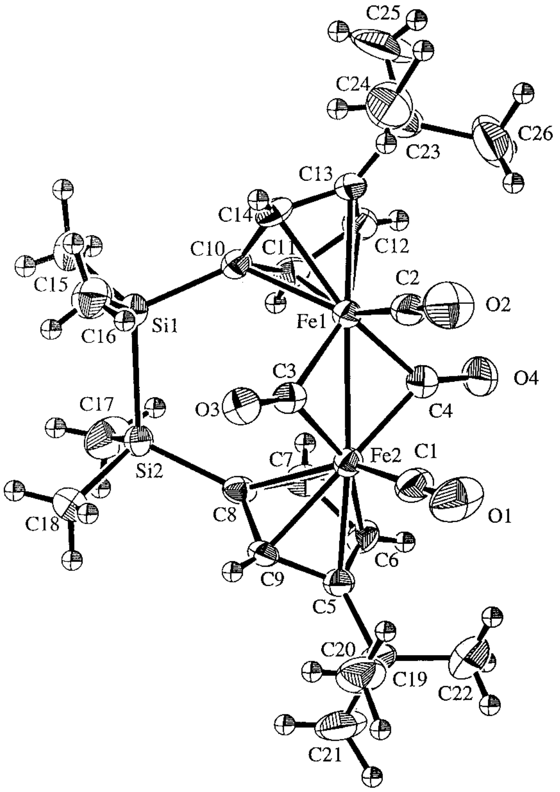


Figure 1. Molecular structure of (Me$_2$SiSiMe$_2$)[(η^5-*t*-BuC$_5$H$_3$)Fe(CO)]$_2$(μ-CO)$_2$ (**3c**).

Table 1. Selected Geometrical Details of Complex 3c

	Bond Distances (Å)		
Fe(1)−Fe(2)	2.5480(8)	Si(1)−Si(2)	2.357(2)
Fe(1)−C(2)	1.750(5)	Fe(1)−C(3)	1.929(4)
Fe(1)−C(4)	1.944(4)	Fe(1)−Cp(1)[a]	1.754
Fe(2)−C(1)	1.751(5)	Fe(2)−C(3)	1.911(4)
Fe(2)−C(4)	1.936(4)	Fe(2)−Cp(2)[a]	1.757
C(3)−O(3)	1.174(4)	C(4)−O(4)	1.160(5)
C(1)−O(1)	1.146(5)	C(2)−O(2)	1.151(5)
Si(2)−C(8)	1.889(4)	Si(1)−C(10)	1.878(4)
	Bond Angles (deg)		
Fe(2)−Fe(1)−C(2)	98.2(1)	Fe(1)−Fe(2)−C(1)	97.2(1)
Fe(2)−Fe(1)−C(10)	110.4 (1)	Fe(1)−Fe(2)−C(8)	105.5(1)
Fe(1)−C(3)−Fe(2)	83.1(2)	Fe(1)−C(4)−Fe(2)	82.1(2)
Fe(2)−C(8)−Si(2)	132.4(2)	Fe(1)−C(10)−Si(1)	128.4(2)
Si(2)−Si(1)−C(10)	109.8(1)	Si(1)−Si(2)−C(8)	116.2(1)
	Torsion Angles (deg)		
C(15)−Si(1)−Si(2)−C(17)			19.3(3)
C(15)−Si(1)−Si(2)−C(18)			−101.9(3)
C(15)−Si(1)−Si(2)−C(17)			139.1(3)
C(15)−Si(1)−Si(2)−C(18)			18.0(3)

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

ity. Table 2 provides selected bond distances and angles and torsion angles. The molecule of **3t** is similar to that of **3c**. It is different in that the substituent groups on the ring are trans to each other. Like **3c**, the six-membered ring also adopts a twist-boat conformation. The silicon methyl groups in the bridge take an almost eclipsed conformation (the smaller C−Si−Si−C torsion angles fall in the range of 6.0(6)−10.4(7)°). The remaining molecular parameters are almost equivalent to those in **3c**.

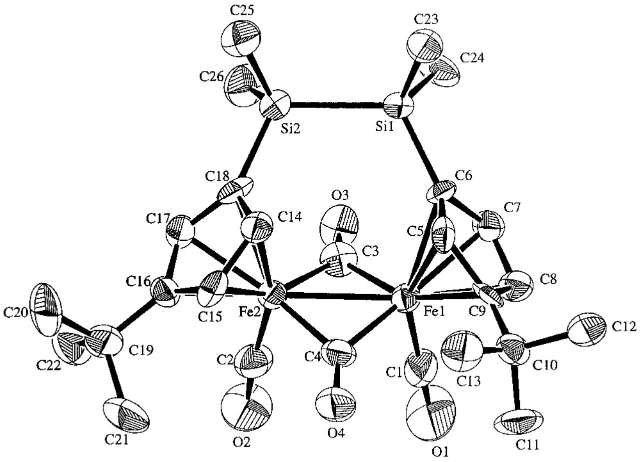


Figure 2. Molecular structure of (Me$_2$SiSiMe$_2$)[(η^5-*t*-BuC$_5$H$_3$)Fe(CO)]$_2$(μ-CO)$_2$ (**3t**). Hydrogen atoms are omitted for clarity.

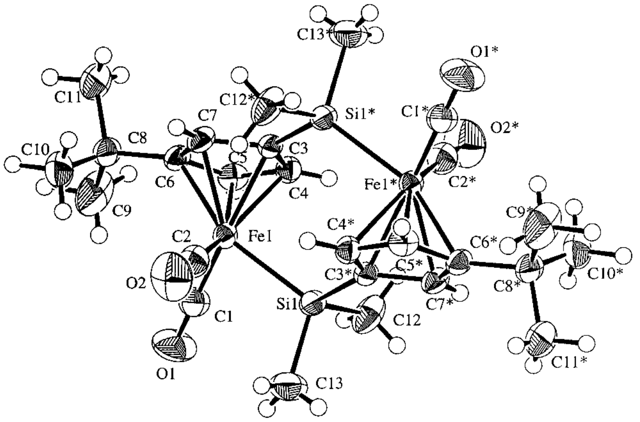


Figure 3. Molecular structure of [Me$_2$Si(η^5-*t*-BuC$_5$H$_3$)Fe(CO)$_2$]$_2$ (**4t**).

Table 2. Selected Geometrical Details of Complex 3t

	Bond Distances (Å)		
Fe(1)−Fe(2)	2.542(2)	Si(1)−Si(2)	2.350(4)
Fe(1)−C(1)	1.76(1)	Fe(1)−C(3)	1.90(1)
Fe(1)−C(4)	1.90(1)	Fe(1)−Cp(1)[a]	1.761
Fe(2)−C(2)	1.74(1)	Fe(2)−C(3)	1.91(1)
Fe(2)−C(4)	1.90(1)	Fe(2)−Cp(2)[a]	1.762
C(3)−O(3)	1.19(1)	C(4)−O(4)	1.20(1)
C(1)−O(1)	1.14 (1)	C(2)−O(2)	1.18(1)
Si(2)−C(18)	1.89(1)	Si(1)−C(6)	1.873(9)
	Bond Angles (deg)		
Fe(2)−Fe(1)−C(1)	101.4(4)	Fe(1)−Fe(2)−C(2)	99.6(4)
Fe(2)−Fe(1)−C(6)	105.9 (3)	Fe(1)−Fe(2)−C(18)	110.8(3)
Fe(1)−C(3)−Fe(2)	83.7(5)	Fe(1)−C(4)−Fe(2)	83.9(5)
Fe(2)−C(18)−Si(2)	126.1(6)	Fe(1)−C(6)−Si(1)	130.2(5)
Si(2)−Si(1)−C(6)	117.0(3)	Si(1)−Si(2)−C(18)	111.4(4)
	Torsion Angles (deg)		
C(23)−Si(1)−Si(2)−C(25)			6.0(6)
C(23)−Si(1)−Si(2)−C(26)			128.0(7)
C(24)−Si(1)−Si(2)−C(25)			−111.6(6)
C(24)−Si(1)−Si(2)−C(26)			10.4(7)

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

The molecular structure of **4t** is illustrated in Figure 3. Selected bond distances and angles are listed in Table 3. Molecules of **4t** consist of two [Me$_2$Si(η^5-*t*-BuC$_5$H$_3$)Fe(CO)$_2$] moieties linked to each other by two Si−Fe bonds. The molecule has C_i symmetry, and the six-membered ring Si(1)−Fe(1)−C(3)−Si(1*)−Fe(1*)−C(3*) takes a typical chair conformation. What is noteworthy herein is that Pannell et al. recently reported an analogous tin complex unexpectedly obtained

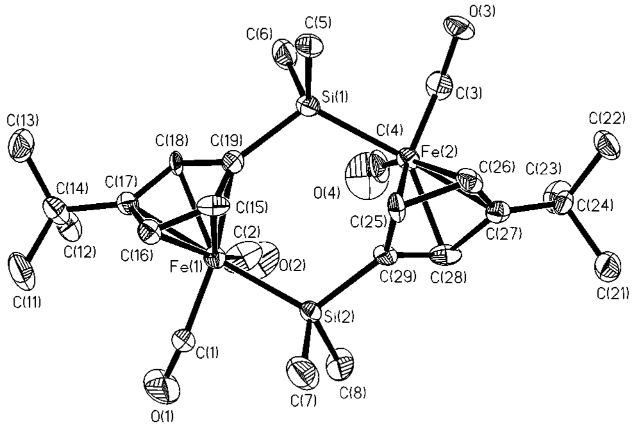


Figure 4. Molecular structure of $[Me_2Si(\eta^5\text{-}t\text{-}BuC_5H_3)Fe(CO)_2]_2$ (**4c**). Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 4t

Bond Distances (Å)			
Fe(1)−Si(1)	2.3148(8)	Fe(1)−C(1)	1.738(3)
Fe(1)−C(2)	1.731(3)	Fe(1)−C(3)	2.113(2)
Fe(1)−C(4)	2.086(3)	Fe(1)−C(5)	2.095(3)
Fe(1)−C(6)	2.129(2)	Fe(1)−C(7))	2.090(3
Fe(1)−Cp(1)[a]	1.723	C(1)−O(1)	1.156(3)
C(2)−O(2)	1.158(3)	Si(1)−C(12)	1.880(3)
Si(1)−C(13)	1.878(4)		
Bond Angles (deg)			
Si(1)−Fe(1)−C(1)	84.77(9)	Si(1)−Fe(1)−C(2)	87.01(9)
Si(1)−Fe(1)−C(3)	98.80(7)	Fe(1)−C(3)−Si(1*)	131.9(1)
Fe(1)−Si(1)−C(3*)	113.79(8)	Fe(1)−Si(1)−C(12)	114.3(1)
Fe(1)−Si(1)−C(13)	113.1(1)	C(1)−Fe(1)−C(2)	94.3(1)
C(12)−Si(1)−C(13)	106.2(2)	Fe(1)−C(6)−C(8)	130.2(2)

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

in a base-induced migration reaction which has a structure similar to that of complex **2**, and the corresponding six-membered ring of which also takes a chair conformation.[11] It appears that such a chair conformation contributes greatly to the considerable stability of this type of complex. The Fe−Si distance of **4t** (2.3148(8) Å) is almost equivalent to that in its parent analogue **2** (2.315(2) Å), much shorter than the average Si−Si and Fe−Fe bond distances in complex **3c** and slightly shorter than those in acyclic molecules of the same kind (2.346−2.363 Å),[12] which further accounts for the greater stability of the rearrangement products and presumably provides the driving force for the rearrangement.

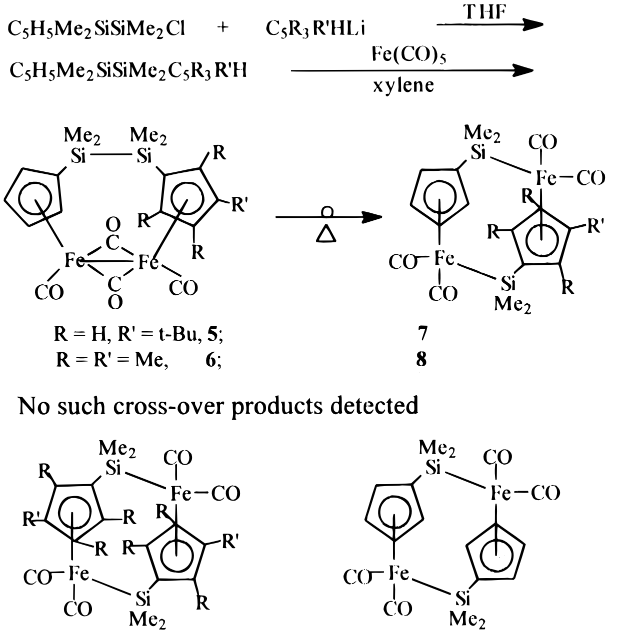
The molecular structure of **4c** is illustrated in Figure 4. Selected bond distances and angles are listed in Table 4. The molecule of **4c** also consists of two $[Me_2Si(\eta^5\text{-}t\text{-}BuC_5H_3)Fe(CO)_2]$ moieties linked to each other by two Si−Fe bonds. Unlike the trans isomer **4t**, **4c** is unsymmetrical, and the corresponding six-membered ring is in a twist-boat conformation. The dihedral angle between the two cyclopentadienyl rings is 68.98°, and the average Fe−Si distance (2.317 Å) is almost equal to that in the trans isomer. In addition, the closest intramolecular contact between two oxygen atoms (O(2)···O(4)) is 3.099 Å, approximately equal to twice the van der Waals radius (1.52 Å) of the oxygen atom,[13] which indicates a stronger interaction between the two atoms, resulting in larger isotropic thermal parameters.

Table 4. Selected Bond Distances (Å) and Angles (deg) for 4c

Bond Distances (Å)			
Fe(1)−Si(2)	2.311(8)	Fe(2)−Si(1)	2.322(8)
Fe(1)−C(1)	1.812(9)	Fe(1)−C(2)	1.731(6)
Fe(1)−Cp(1)[a]	1.7069	Fe(2)−C(3)	1.662(10)
Fe(2)−C(4)	1.728(8)	Fe(2)−Cp(2)[a]	1.7293
C(3)−O(3)	1.236(11)	C(4)−O(4)	1.186(9)
C(1)−O(1)	1.087(12)	C(2)−O(2)	1.126(8)
Si(1)−C(19)	1.913(13)	Si(2)−C(29)	1.882(12)
Bond Angles (deg)			
Si(2)−Fe(1)−C(19)	100.3(4)	Fe(1)−C(19)−Si(1)	131.0(5)
Fe(2)−Si(1)−C(19)	116.0(3)	Si(1)−Fe(2)−C(29)	99.0(4)
Fe(2)−C(29)−Si(2)	133.4(5)	Fe(1)−Si(2)−C(29)	114.9(3)
C(1)−Fe(1)−C(2)	94.4(4)	C(3)−Fe(2)−C(4)	93.1(4)
C(5)−Si(1)−C(6)	106.8(4)	C(7)−Si(2)−C(8)	102.9(4)

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

Scheme 3



Crossover Experiments. To examine whether this reaction takes place via an intramolecular or intermolecular pathway, we synthesized binuclear (Fe−Fe) complexes **5** and **6** containing bridged, unsymmetrically substituted bis(cyclopentadienyl) ligands and conducted studies of their rearrangement reactions. The results showed that when complexes **5** and **6** were heated in xylene, respectively, only the corresponding unsymmetrical rearrangement products **7** and **8**, but no symmetrical disproportionation products, were detected and isolated (Scheme 3). This indicated that the rearrangement reaction proceeds via an intramolecular rather than an intermolecular pathway. The conclusion was further confirmed by the crossover reactions between two different substrates. TLC monitoring of the outcome of a reaction between substrates **1** and **3c** indicated that only their respective rearrangement products **2** and **4t**, but no crossover product **7**, were formed (Scheme 4).

ESR Experiments. To investigate reaction intermediates possibly existing in the rearrangement process, the rearrangement reaction of complex **1** was monitored *in situ* by ESR spectroscopy. When a quartz

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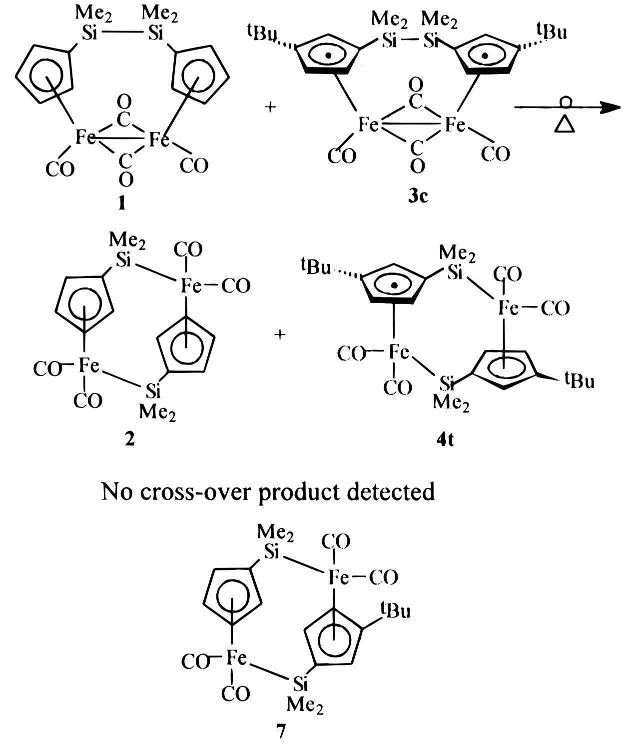
Scheme 4



tube containing a solution of complex **1** in xylene was heated in the cavity of an ESR spectrometer, a rather strong ESR signal ($g = 2.049$) was detected (Figure 5), which indicated the presence of iron-centered radicals ($g = 2.0446-2.0504$)[14] rather than silicon-centered radicals ($g = 2.0026-2.0036$).[15] A similar ESR signal ($g = 2.052$) also was detected in the nonbridged analogue $[(\eta^5\text{-}C_5Me_4H)_2Fe_2(CO)_4]$ by this method. In addition, an activation enthalpy of approximately 23 kcal/mol for the iron-iron cleavage step in the analogue $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$ has been reported.[16] These results strongly support the thermal homolysis of the iron–iron bond in complex **1**. In comparison to allyliron carbonyl complex $[(\eta^3\text{-}C_3H_5)_2Fe(CO)_3]_2$, which exists in solution in equilibrium with the green, monomeric $[(\eta^3\text{-}C_3H_5)_2\text{-}Fe(CO)_3]$,[14] complex **1** would also be presumed to exist in a similar equilibrium of the thermal homolysis in boiling xylene.

Discussion

Mechanism. As an intramolecular pathway with high stereospecificity, the rearrangement reaction may be conceived to proceed via the following path.

The pathway for formation of trans product **4t** (or cis product **4c**) may be considered to proceed by (i) initial pairwise opening of the carbonyl bridges to give a nonbridged tautomer, (ii) subsequent thermal homolysis of the Fe–Fe bond, (iii) suitable rotation about the Si–Si bond, and (iv) concerted (or stepwise) attack of iron radicals at the Si–Si bond to complete the reaction (Scheme 5). In step i, equilibrium between the bridged and nonbridged structures has been observed previously not only in a diiron complex[17] but also in other binuclear systems.[18] Thermal homolysis of the Fe–Fe bond in step ii has been confirmed by the detection of an iron radical ESR signal. In addition, note that thermal homolysis of the metal–metal bond is well-known.[19] The assumption of suitable rotation along the Si–Si single bond is a key requirement of the mechanism, which not only ensures a successful interconversion of the cis substrate (or trans substrate) into the trans product (or cis product) but satisfactorily accounts for the stereospecificity of the rearrangement reaction.

Figure 5. ESR spectrum of $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)]_2(\mu\text{-}CO)_2$ (**1**) maintained at 145 °C for 45 min.

However, it should be pointed out that although we did not detect the silicon-centered radical ESR signal, it is not entirely certain that two iron radicals attack concertedly at the Si–Si bond in the path. It is possible that the ESR spectrometer cannot detect the ESR signal of the intermediate simultaneously containing iron and silicon radicals formed via a stepwise attack owing to its extremely short life time and lower concentration. The possibility that two Si–Fe bonds formed via a stepwise process cannot be ruled out.

Reaction Extension. The rearrangement reaction may be considered as a σ-bond metathesis between intramolecular Si–Si and Fe–Fe bonds. Under general conditions, the reaction between Si–Si and Fe–Fe bonds is difficult, so that few examples of this type have been reported.[20] When a solution of $PhMe_2SiSiMe_2Ph$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)_2$ in xylene was heated under reflux, no reaction took place.[21] Similar treatment of the trisilane-bridged analogue $[\eta^5{:}\eta^5\text{-}C_5H_4(SiMe_2)_3C_5H_4][Fe(CO)]_2(\mu\text{-}CO)_2$ does not lead to occurrence of the rearrangement reaction between Si–Si and Fe–Fe bonds.[22] This indicates that the occurrence of the rearrangement reaction is dependent on the cyclic structure of the substrate. This conclusion is supported further by the latest results that the digermane-bridged analogue $(Me_2GeGeMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)]_2(\mu\text{-}CO)_2$ of structure similar to complex **1** also smoothly undergoes a similar rearrangement.[23] It is intriguing that the diruthenium(*Ru–Ru*) analogue of **1** was recently shown

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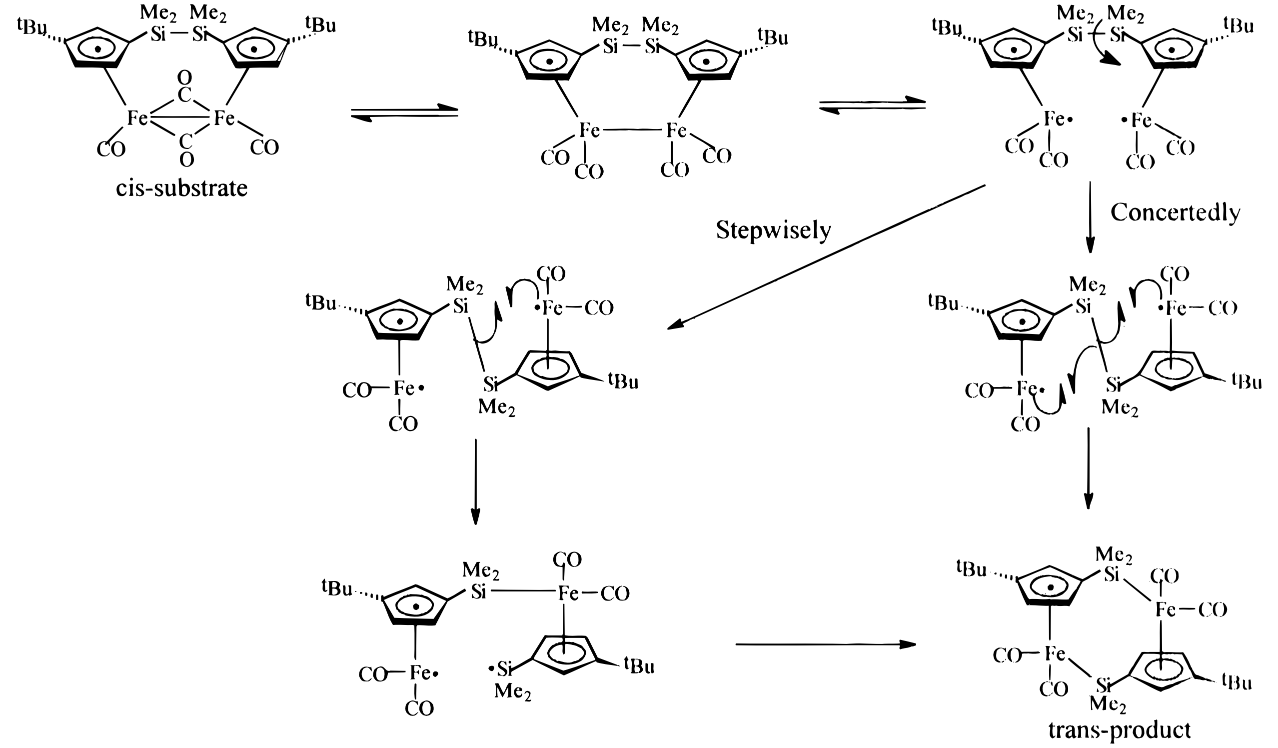
Scheme 5



to undergo a similar reaction.[24] Detail of these results will be published later. Finally, we note that this rearrangement is a common reaction of many complexes with the above-noted structure.

Experimental Section

General Considerations. Schlenk and vacuum-line techniques were employed for all manipulations of air- and moisture-sensitive compounds. Reaction solvents were distilled from appropriate drying agents under argon before use. Tetrahydrofuran, toluene, and xylene were distilled from sodium/benzophenone ketyl and purged with an argon atmosphere prior to use. *o*-Xylene used in ESR experiments was treated with concentrated sulfuric acid and distilled from sodium/benzophenone ketyl under an argon atmosphere. *t*-BuC_5H_5,[25] $C_5H_5Me_2SiSiMe_2Cl$,[26] $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)]_2(\mu\text{-}CO)_2$ (**1**),[5] and $[Me_2Si(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$ (**2**)[5] were prepared according to literature methods. Proton (^1H NMR) spectra were obtained on a Bruker AC-P200 or JEOL FX-90Q spectrometer. Chemical shifts are positive downfield from external $SiMe_4$. Elemental analyses were performed using a Perkin-Elmer 240C spectrometer. Infrared spectra were obtained as KBr disks and recorded on a Nicolet 5DX FT-IR spectrometer. ESR spectra were recorded on a JEOL JES-FEIXG spectrometer.

Preparation of (*t*-Bu)$C_5H_4Me_2SiSiMe_2C_5H_4$(*t*-Bu). A solution of 8.0 g (65.6 mmol) of *t*-BuC_5H_5 in 50 mL of THF, cooled to −20 °C, was treated dropwise (~30 min) with 34.5 mL of a 1.90 M hexane solution of BuLi (65.6 mmol) to give a light yellow solution, which was warmed to room temperature and then stirred for an additional 4 h. The mixture was cooled again to −20 °C, and a solution of 6.13 g (32.8 mmol) of $ClMe_2SiSiMe_2Cl$ in 20 mL of THF was added dropwise (~30 min). The reaction mixture was slowly warmed to room temperature, stirred for 2 h, and subsequently refluxed for an additional 2 h. Water (100 mL) was added to the mixture. The aqueous layer was separated and extracted twice with 60 mL of ether. The organic and ether extracts were combined and dried with sodium sulfate overnight. The solvent was removed under reduced pressure and the residue was introduced to a silica column in the minimum amount of hexane. Elution with hexane developed a light yellow band which afforded 7.0 g (60%) of yellow oil. It was identified as (*t*-Bu)$C_5H_4Me_2SiSiMe_2C_5H_4$(*t*-Bu) and could be used in the following reaction without further purification. ^1H NMR ($CDCl_3$): δ 0.02 (s, 12H, $SiMe_2$), 1.22 (s, 18H, CMe_3), 3.00, 3.40 (2 br m, 2H, *H*C_5H_3), 6.00−6.80 (2 br m, 6H, C_5H_3).

Preparation of $(Me_2SiSiMe_2)[(\eta^5\text{-}t\text{-}BuC_5H_3)Fe(CO)]_2(\mu\text{-}CO)_2$ (3). A solution of 2.50 g (7.0 mmol) of *t*-$BuC_5H_4Me_2SiSiMe_2C_5H_4$-*t*-Bu and 2.94 g (15.0 mmol) of $Fe(CO)_5$ in 30 mL of xylene was refluxed for 10 h. The solvent was removed under vacuum to give a dark crude product, which was introduced into an alumina column in the minimum amount of dichloromethane. Elution with hexane developed a yellow band which upon evaporation afforded 0.10 g (2%) of yellow crystals (**4**). Elution with hexane−dichloromethane (3:1) gave a red band which afforded 1.42 g (33%) of deep red crystals (**3**) as a mixture of cis and trans isomers which later were separated by preparative TLC (silica G). A 1.42 g amount of deep red crystals of **3** was dissolved in a minimum volume of dichloromethane and the solution chromatographed by preparative TLC to develop two red bands. The first band gave 0.50 g (35%) of deep red crystals (**3t**) and the second band 0.70 g (50%) of purple-red crystals (**3c**). ^1H NMR of the above yellow crystals (**4**) indicated that they were also a mixture of two isomers which could not be separated by chromatographic methods. For **4**: ^1H NMR ($CDCl_3$): δ 0.38, 0.44, 0.46, 0.48 (s, s, s, s, 12H, $SiMe_2$), 1.24, 1.27 (s, s, 18H, CMe_3), 4.64−4.94 (m, 6H, Cp H). For **3c**: mp 190−191 °C. Anal. Calcd for $C_{26}H_{36}Fe_2O_4Si_2$: C, 53.80; H, 6.25. Found: C, 53.77; H, 6.02. ^1H NMR ($CDCl_3$): δ 0.23 (s, 12H, $SiMe_2$), 1.33 (s, 18H, CMe_3), 4.63, 5.23 (d, s, 6H, Cp H). IR (ν_{CO}, cm^{-1}): 1983.2, 1934.0, 1794.5, 1753.5. For **3t**: mp 162−163 °C. Anal. Calcd for $C_{26}H_{36}Fe_2O_4Si_2$: C, 53.80; H, 6.25. Found: C, 53.63; H, 6.07. ^1H NMR ($CDCl_3$): δ 0.18, 0.28 (s, s, 12H, $SiMe_2$), 1.33 (s, 18H,

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Table 5. Summary of X-ray Diffraction Data

	3t	**3c**	**4c**	**4t**
formula	$C_{26}H_{36}Fe_2O_4Si_2$	$C_{26}H_{36}Fe_2O_4Si_2$	$C_{26}H_{36}Fe_2O_4Si_2$	$C_{26}H_{36}Fe_2O_4Si_2$
fw	580.43	580.43	580.43	580.43
space group	$P2_1/n$	$P2_1/c$	Cc	$P\bar{1}$
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
Z	4	4	4	1
a (Å)	10.115(8)	6.784(1)	20.359(4)	10.689(3)
b (Å)	25.731(9)	21.416(5)	7.717(2)	10.974(2)
c (Å)	12.036(7)	19.271(2)	20.620(4)	7.533(1)
α, deg	90	90	90	91.38(2)
β, deg	114.63(4)	97.27(1)	117.02(3)	109.78(2)
γ, deg	90	90	90	118.54(2)
V (Å^3)	2847(2)	2777.1(9)	2887(3)	711.8(3)
d_{calcd} (g cm^{-3})	1.340	1.388	1.335	1.354
cryst size (mm)	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30
radiation (Å^3)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, cm^{-1}	11.29	11.59	11.13	11.30
data collection method	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
max 2θ, deg	50.0	43.0	46.0	42.0
total no. of observns	5444	3485	3619	1557
no. of unique data, $I > 3\sigma(I)$	2624	2357	2059	1448
final no. of variables	307	451	307	227
R^a	0.097	0.029	0.034	0.022
$R_w{}^b$	0.120	0.044	0.040	0.031
goodness of fit	4.10	1.44	0.74	1.62

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

CMe_3), 4.58, 5.26 (s, s, 6H, Cp H). IR (ν_{CO}, cm^{-1}): 1983.2, 1925.8, 1769.9.

Rearrangement Reaction of Complexes 3c and 3t. Complex **3t** (0.17 g) in 25 mL of xylene was refluxed for 24 h. The product was separated by column chromatography (Al_2O_3/hexane), giving 80 mg (55%) of yellow crystals of **4c**: mp 172−173 °C. Anal. Calcd for $C_{26}H_{36}Fe_2O_4Si_2$: C, 53.80; H, 6.25. Found: C, 54.05; H, 6.38. ^{1}H NMR ($CDCl_3$): δ 0.44, 0.46 (s, s, 12H, $SiMe_2$), 1.24 (s, 18H, CMe_3), 4.77, 4.86 (m, s, 6H, Cp H). IR (ν_{CO}, cm^{-1}): 1991.4, 1975.0, 1917.6.

Complex **3c** (0.20 g) in 20 mL of xylene was similarly refluxed for 24 h, yielding 0.12 g (60%) of yellow crystals of **4t**: mp 237−238 °C. Anal. Calcd for $C_{26}H_{36}Fe_2O_4Si_2$: C, 53.80; H, 6.25. Found: C, 53.84; H, 6.36. ^{1}H NMR ($CDCl_3$): δ 0.38, 0.48 (s, s, 12H, $SiMe_2$), 1.27 (s, 18H, CMe_3), 4.64, 4.94 (s, s, 6H, Cp H). IR (ν_{CO}, cm^{-1}): 1975.0, 1934.0.

Preparation of [η^5:η^5-$C_5H_4Me_2SiSiMe_2C_5H_3$-*t*-Bu][Fe(CO)]$_2$(μ-CO)$_2$ (5) and [η^5:η^5-$C_5H_4Me_2SiSiMe_2C_5Me_4$][Fe(CO)]$_2$($\mu$-CO)$_2$ (6) and Their Rearrangement Reaction. A solution of 2.4 g (19.6 mmol) of *t*-BuC_5H_5 in 30 mL of THF, cooled to −20 °C, was treated dropwise with 8.5 mL of a 2.30 M hexane solution of BuLi (19.6 mmol) to give a light yellow solution, which was warmed to room temperature and then was stirred for an additional 4 h. The mixture was cooled again to −20 °C, and a solution of 4.2 g (19.6 mmol) of $C_5H_5Me_2SiSiMe_2Cl$ in 20 mL of THF was added dropwise (~30 min). The reaction mixture was slowly warmed to room temperature, stirred for 2 h, and subsequently refluxed for an additional 2 h. Water (50 mL) was added to the mixture. The aqueous layer was separated and extracted twice with 30 mL of ether. The organic and ether extracts were combined and dried with sodium sulfate overnight. The solvent was removed under reduced pressure, and the residue was introduced to a silica column in the minimum amount of hexane. Elution with hexane developed a light yellow band which afforded 3.2 g (54%) of yellow oil. It could be used in the following reaction without further purification.

$C_5H_5Me_2SiSiMe_2C_5HMe_4$ was also prepared in 35% yield by a similar procedure.

A solution of 2.0 g (6.6 mmol) of $C_5H_5Me_2SiSiMe_2C_5H_3$-*t*-Bu and 4.4 g (22.5 mmol) of $Fe(CO)_5$ in 40 mL of xylene was refluxed for 13 h. Cooling and distilling of xylene under reduced pressure gave a dark crude product, which was passed through a short alumina column with dichloromethane to remove decomposed residues. The solution was reduced to a minimum volume and then subjected to column chromatography on silica H. Elution with hexane−acetone (10:1) developed a yellow band and a red band, which afforded 1.30 g (38%) of yellow crystals (**7**) and 0.41 g (12%) of red crystals (**5**), respectively. For **5**: mp 161−162 °C. Anal. Calcd for $C_{22}H_{28}Fe_2O_4Si_2$: C, 50.40; H, 5.38. Found: C, 50.38; H, 5.29. ^{1}H NMR ($CDCl_3$): δ 0.38, 0.46 (s, s, 12H, $SiMe_2$), 1.30 (s, 9H, CMe_3), 4.18, 4.65, 5.16, 5.36 (s, d, s, s, 7H, Cp H). IR (ν_{CO}, cm^{-1}): 1982.3, 1935.7, 1791.0, 1748.3. For **7**: mp 125−126 °C. Anal. Calcd for $C_{22}H_{28}Fe_2O_4Si_2$: C, 50.40; H, 5.38. Found: C, 50.38; H, 5.21. ^{1}H NMR ($CDCl_3$): δ 0.41, 0.49 (s, s, 12H, $SiMe_2$), 1.27 (s, 9H, CMe_3), 4.71, 4.73, 4.92, 5.05 (d, s, d, s, 7H, Cp H). IR (ν_{CO}, cm^{-1}): 1972.2, 1915.1.

Complex **5** (0.35 g) in 30 mL of xylene was refluxed for 10 h; only a yellow band with the same R_f value as complex **7** was detected by TLC using different developers. The solvent was removed to yield 0.19 g (54%) of yellow crystals, which were identified as complex **7** by ^{1}H NMR (200 MHz).

A similar reaction of 1.80 g (6.0 mmol) of $C_5H_5Me_2SiSiMe_2C_5HMe_4$ with 2.90 g (15.0 mmol) of $Fe(CO)_5$ in 30 mL of xylene yielded 0.25 g (8%) of yellow crystals (**8**) and 0.54 g (17%) of deep red crystals (**6**), respectively. For **6**: mp 155.5−156.5 °C. Anal. Calcd for $C_{22}H_{28}Fe_2O_4Si_2$: C, 50.40; H, 5.38. Found: C, 50.40; H, 5.44. ^{1}H NMR ($CDCl_3$): δ 0.19, 0.21 (s, s, 12H, $SiMe_2$), 1.74, 1.92 (s, s, 12H, C_5Me_4), 4.68, 5.36 (s, s, 4H, Cp H). IR (ν_{CO}, cm^{-1}): 1970.8, 1929.3, 1757.3. For **8**: mp 135−136 °C. Anal. Calcd for $C_{22}H_{28}Fe_2O_4Si_2$: C, 50.40; H, 5.38. Found: C, 50.58; H, 5.49. ^{1}H NMR ($CDCl_3$): δ 0.38, 0.53 (s, s, 12H, $SiMe_2$), 1.94, 1.98 (s, s, 12H, C_5Me_4), 4.77, 4.98 (d, t, 4H, Cp H). IR (ν_{CO}, cm^{-1}): 1989.6, 1964.7, 1940.4, 1920.0, 1899.6.

Complex **6** (0.30 g) in 30 mL of xylene was refluxed for 10 h, similarly yielding only 0.17 g (57%) of yellow crystals, which were identified as complex **8** by ^{1}H NMR (200 MHz).

Crossover Reaction. A solution of 100 mg (0.12 mmol) of ($Me_2SiSiMe_2$)[(η^5-C_5H_4)Fe(CO)]$_2$(μ-CO)$_2$ (**1**) and 120 mg (0.12 mmol) of **3c** in 25 mL of xylene was refluxed for 10 h. Two bands (R_f 0.73, 0.68), respectively corresponding to the products **4t** and **2** formed via the rearrangement reaction of the substrates **3c** and **1**, were detected by TLC. No crossover product **7** (R_f 0.70) was detected.

ESR Experiments. To a dry quartz tube was added 20 mg of complex **1**. The tube was evacuated and filled with argon. *o*-Xylene (1 mL) was added by syringe. The reaction mixture was heated in the cavity of an ESR spectrometer and maintained at 145 °C. After 15 min, a clear ESR signal appeared; 45 min later the signal reached the maximum value ($g = 2.049$, peak width 191.2 G). The signal began to attenuate after 1 h.

A similar ESR signal ($g = 2.052$, peak width 168.2 G) was obtained when $[(\eta^5\text{-C}_5\text{HMe}_4)\text{Fe(CO)}]_2(\mu\text{-CO})_2$[27] was examined by an identical procedure. However, the signal intensity did not change after a long period of time.

Molecular Structure Determination. Crystals suitable for X-ray diffraction were obtained from hexane/dichloromethane solution. All data sets were collected on Enraf-Nonius CAD-4 or Rigaku AFC 7R diffractometers with graphite-monochromated Mo Kα radiation. Data were corrected in the usual fashion for Lorentz−polarization, and empirical absorption corrections using the program DIFBAS were applied for **3c**, **3t**, and **4t** (range of transmission factors 0.88−1.00, 0.74−1.06, 0.90−1.00, respectively). All calculations for **3c**, **3t**, and **4c** were performed using the teXsan Crystallographic Software Package of Molecular Structure Corp., while for **4c** PDP11/44 and IBM 486 computers were used. The structures of **3c**, **3t**, **4t**, and **4c** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms for **3c**, **3t**, and **4t** were refined isotropically. For **3t** hydrogen atoms were included but not refined. Neutral atom scattering factors were taken from the tabulation of Cromer and Waber.[28] The poor fit ($R = 9.7\%$, GOF $= 4.10$) for **3t** reflects poor crystal quality. Over 100 crystals were examined, and 4 complete data sets were collected, but 3 data sets could not be solved owing to the rapid decrease of diffraction intensity over the course of data collection. The present data were obtained when a Rigaku AFC 7R diffractometer instead of an Enraf-Nonius CAD-4 was used. The results of the X-ray diffraction study on **3t** are included in the text mainly because it is a further confirmation for the configuration of **3t**. Selected bond distances and angles for **3c**, **3t**, **4t**, and **4c** are given in Tables 1−4, respectively. A summary of the crystallographic results is presented in Table 5.

Acknowledgment. This work was financially supported by the National Science Foundation of the People's Republic of China.

Supporting Information Available: Tables of final positional and thermal parameters of the non-hydrogen atoms, general temperature factors, calculated hydrogen atom positions, and bond distances and angles for **3c**, **3t**, **4t**, and **4c** (32 pages). Ordering information is given on any current masthead page.

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[27] $[(\eta^5\text{-C}_5\text{HMe}_4)\text{Fe(CO)}]_2(\mu\text{-CO})_2$ was obtained in 65% yield when a solution of $C_5H_2Me_4$ and $Fe(CO)_5$ in xylene was heated to reflux. Mp: 180 °C dec. Anal. Calcd for $C_{22}H_{26}Fe_2O_4$: C, 57.01; H, 5.80. Found: C, 56.69; H, 5.62. ^{1}H NMR ($CDCl_3$): δ 1.70 (s, 12H, CpMe), 1.74 (s, 12H, CpMe), 3.84 (s, 12H, Cp H). IR (ν_{CO}, cm^{-1}): 1975.0, 1942.2, 1753.5, 1734.2.

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