Organometallics **1997,** *16,* 4620−4625

Novel Rearrangement Reactions. 2. Thermal Rearrangement Stereospecificity of Complex $(Me_2SiSiMe_2)[(\eta^5\text{-}IndH_4)Fe(CO)]_2(\mu\text{-}CO)_2$

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Received May 27, 1997[⊗]

The catalytic hydrogenation of the indenyl complex $(Me_2SiSiMe_2)[(\eta^5\text{-}Ind)Fe(CO)]_2(\mu\text{-}CO)_2$ (**2**) in CH_2Cl_2 afforded the tetrahydroindenyl complex $(Me_2SiSiMe_2)[(\eta^5\text{-}IndH_4)Fe(CO)]_2(\mu\text{-}CO)_2$ (**3**), existing as a mixture of cis and trans isomers (**3c** and **3t**), which were separated by column chromatography. When the two isomers were heated in xylene, respectively, the cis substrate **3c** rearranged to the trans product $[Me_2Si(\eta^5\text{-}IndH_4)Fe(CO)_2]_2$ (**4t**), while the trans substrate **3t** yielded the cis product $[Me_2Si(\eta^5\text{-}IndH_4)Fe(CO)_2]_2$ (**4c**). This indicates that the rearrangement reaction is stereospecific, which is consistent with the result observed in the rearrangement of complex $(Me_2SiSiMe_2)[(\eta^5\text{-}t\text{-}BuC_5H_3)Fe(CO)]_2(\mu\text{-}CO)_2$ (**5**). By analogy with the mechanism proposed based on detailed investigations of **5**, the pathway for formation of **4** is described. Molecular structures of **3c**, **3t**, **4t**, and **4c** were determined by X-ray diffraction.

Introduction

Considerable attention is presently focused on the synthesis and study of a variety of transition metal complexes which activate or contain a silicon−silicon bond.[1] The metal cyclopentadienyl complexes containing an oligosilyl group bonded to the cylcopentadienyl ring or direct metal−silicon bonds exhibit unique chemical properties such as base-induced migration,[2] photo isomerization,[3] and silylene elimination.[4]

We recently reported a novel rearrangement reaction between Si−Si and Fe−Fe bonds in a binuclear iron complex $(Me_2SiSiMe_2)$ $[(\eta^5\text{-}C_5H_4)Fe(CO)]_2(\mu\text{-}CO)_2$ (**1**).[5] The reaction involves formally the rupture of one Si−Si and one Fe−Fe bond and the formation of two Si−Fe bonds. Accordingly, it may be considered as a σ-bond metathesis between intramolecular Si−Si and Fe−Fe bonds. An alternative mechanism was subsequently proposed on the basis of detailed investigations of the rearrangement stereospecificity, reaction intermediate, and crossover reaction.[6] The special cyclic structure of indenyl ligands promoted us to synthesize related indenyl analogues and to further examine the reaction stereospecificity.

Results and Discussion

Stereospecificity of the Reaction. We recently reported that complex $(Me_2SiSiMe_2)[(\eta^5\text{-}Ind)Fe(CO)]_2$-$(\mu\text{-}CO)_2$ (**2**), existing as a mixture of cis and trans isomers, was synthsized by heating the ligand $C_9H_7Me_2$-$SiSiMe_2C_9H_7$ and $Fe(CO)_5$ in boiling heptane for 5 days.[7] The two isomers could not be separated by general chromtographic methods due to their almost equal R_f values. The separation of cis and trans isomers is essential to investigate the rearrangement strereospecificity. Accordingly, **2** was catalytically hydrogenated to the corresponding tetrahydroindenyl complex $(Me_2SiSiMe_2)[(\eta^5\text{-}IndH_4)Fe(CO)]_2(\mu\text{-}CO)_2$ **(3)** (Scheme 1). It was found that the pure cis and trans isomers (**3c** and **3t**) could be separated by column chromatography.[8]

Study of the subsequent respective rearrangement reactions of **3c** and **3t** revealed a significant feature of the stereochemistry of the reaction. When the cis substrate **3c** was heated in refluxing xylene for 36 h, only the trans product **4t** was obtained in 9% yield,

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[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

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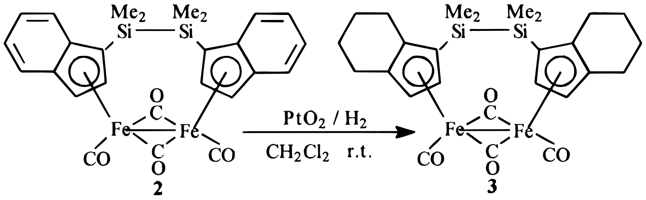
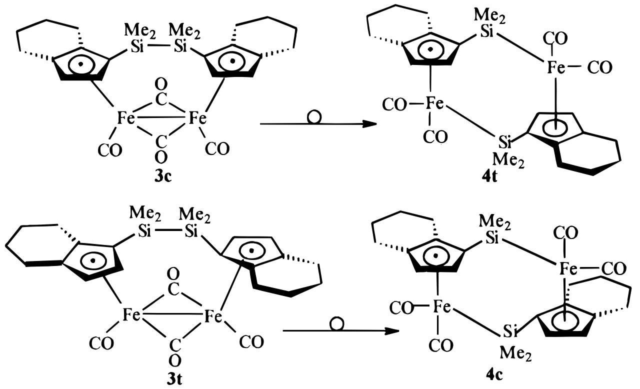
Scheme 1



Scheme 2



while similar treatment of the trans substrate **3t** afforded only the cis product **4c** in almost identical yield (Scheme 2). This suggests that the rearrangement reaction is stereospecific, which is consistent with the result observed in the rearrangement reaction of the analogue (Me$_2$SiSiMe$_2$)[(η^5-t-BuC$_5$H$_3$)Fe(CO)]$_2$(μ-CO)$_2$ (**5**).[6] The lower rearrangement yields reflect poorer thermal stability of the two substrates **3c** and **3t** since the two rearrangement products **4c** and **4t** are comparatively stable even in boiling xylene. However, apparently this does not influence the smooth progression of the rearrangement reaction.

Complexes **3c** and **3t** are air-stable dark-red crystals, while **4c** and **4t** are yellow crystals stable in the solid state as well as in solution at room temperature. The IR spectra of both **3c** and **3t** exhibited four completely identical strong absorptions, two for bridging carbonyl ligands and the other two for terminal carbonyl ligands, indicating considerable similarity of the two isomers. Both **4c** and **4t** showed two strong absorptions for terminal carbonyl ligands at the same position. These results are completely in accord with their structures as determined by X-ray diffraction analysis. The ^{1}H NMR spectrum of **3c** showed two singlets at 0.04 and 0.30 ppm (Me$_2$SiSiMe$_2$), one multiplet at 1.59−3.07 ppm (fused tetrahydrobenzo rings of the indenyl ligands), and two groups of resonances at 4.21 and 5.16 ppm (A and B parts of the Cp AB spin system), which is very similar to that of **3t**. The ^{1}H NMR spectrum of **4c** indicated two singlets at 0.38 and 0.54 ppm (Me$_2$Si), two multiplets for α and β parts of the fused tetrahydrobenzo rings, and two groups of resonances at 4.74 and 4.47 ppm (A and B parts of the Cp AB spin system), which is analogous to that of **4t** except for the slight changes of chemical shifts. All of their molecular structures were determined by single-crystal X-ray diffraction.

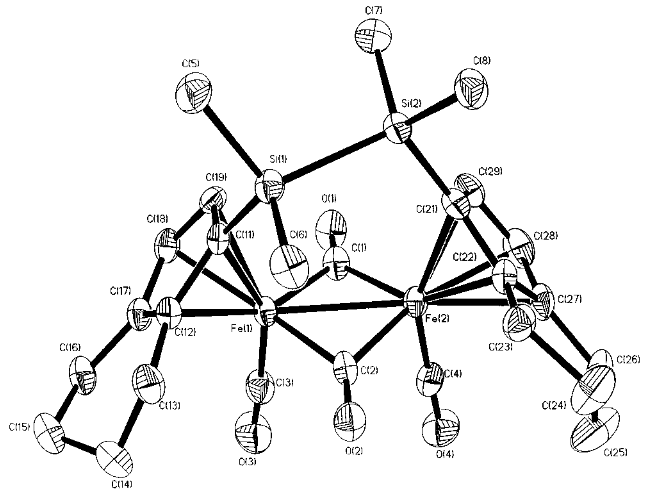


Figure 1. Molecular structure of (Me$_2$SiSiMe$_2$)[(η^5-IndH$_4$)Fe(CO)]$_2$(μ-CO)$_2$ (**3c**). Hydrogen atoms are omitted for clarity.

Table 1. Selected Geometrical Details of Complex 3c

Bond Distances (Å)			
Fe(1)−Fe(2)	2.560(1)	Si(1)−Si(2)	2.325(2)
Fe(1)−C(1)	1.930(5)	Fe(1)−C(2)	1.924(5)
Fe(1)−C(3)	1.734(7)	Fe(1)−Cp(1)[a]	1.747
Fe(2)−C(1)	1.911(5)	Fe(2)−C(3)	1.949(5)
Fe(2)−C(4)	1.748(7)	Fe(2)−Cp(2)[a]	1.755
C(1)−O(1)	1.174(4)	C(2)−O(2)	1.162(7)
C(3)−O(3)	1.156(8)	C(4)−O(4)	1.156(8)

Bond Angles (deg)			
Fe(2)−Fe(1)−C(3)	96.5(2)	Fe(1)−Fe(2)−C(1)	97.8(2)
Fe(2)−Fe(1)−C(11)	108.0 (1)	Fe(1)−Fe(2)−C(8)	107.8(1)
Fe(1)−C(1)−Fe(2)	83.6(2)	Fe(1)−C(2)−Fe(2)	82.7(2)
Fe(2)−C(21)−Si(2)	132.0(3)	Fe(1)−C(11)−Si(1)	132.2(3)
Si(2)−Si(1)−C(11)	108.5(2)	Si(1)−Si(2)−C(21)	113.0(2)

Torsion Angles (deg)			
C(5)−Si(1)−Si(2)−C(7)	−43.0(7)	C(6)−Si(1)−Si(2)−C(7)	−162.5(7)
C(5)−Si(1)−Si(2)−C(8)	74.6(7)	C(6)−Si(1)−Si(2)−C(8)	−44.8(7)

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

Molecular Structures of 3c, 3t, 4c, and 4t. The molecular structure of **3c** is presented in Figure 1. Table 1 provides selected bond distances, bond angles, and torsion angles. The molecule of **3c** has mirror symmetry except for some twist about the Si−Si bond, with the two fused tetrahydrobenzo rings oriented in the same direction. The six-membered ring, Si(1)−Si(2)−C(21)−Fe(2)−Fe(1)−C(10) constituting its molecular framework, adopts a twist boat conformation. The Fe−Fe distance [2.560(1) Å] is longer than that [2.526(2) Å] in the parent analogue, **1**, presumably due to the repulsion between the two fused six-membered rings. The longer Fe−Fe bond length results in a slight compression of the Si−Si bond [2.325(2), {2.346(4) Å in **1**}]. The dihedral angle (103.4°) between the two cyclopentadienyl rings is larger than those in many analogues: *e.g.*, 91.98°, **1**;[5] 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)$_4$];[10] and

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(8) The chiral *ansa*-metallocene catalysts for the stereoselective polymerization of α-olefins and other monomers are prepared as a mixture of two isomers, denominated as *rac* and *meso* diastereomers, respectively. According to the denomination, **3c** should be named a *meso* isomer, while **3t** should be named a *rac* isomer. In order to discuss the rearrangement stereospecifity conveniently, **3c** with approximate C_s symmetry was designated as *cis* isomer, while **3t** with approximate C_2 symmetry was designated as trans isomer.

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Table 2. Selected Geometrical Details of Complex 3t

	Bond Distances (Å)		
Fe(1)−Fe(1a)	2.563(1)	Si(1)−Si(1a)	2.323(3)
Fe(2)−Fe(3)	2.563(2)	Si(2)−Si(3)	2.334(2)
Fe(1)−C(1)	1.969(5)	Fe(1)−C(2)	1.744(6)
Fe(2)−C(3)	1.895(5)	Fe(2)−C(4)	1.987(6)
Fe(2)−C(5)	1.732(5)	Fe(3)−C(3)	1.959(5)
Fe(3)−C(4)	1.898(5)	Fe(3)−C(6)	1.739(6)
C(1)−O(1)	1.143(5)	C(2)−O(2)	1.163(7)
C(3)−O(3)	1.161(5)	C(4)−O(4)	1.147(6)
C(5)−O(5)	1.168(7)	C(6)−O(6)	1.157(7)
Si(1)−C(17)	1.865(5)	Si(2)−C(27)	1.878(5)
Si(3)−C(37)	1.876(5)	Fe(1)−Cp(1)[a]	1.752
Fe(2)−Cp(2)[a]	1.742	Fe(3)−Cp(3)[a]	1.752
	Bond Angles (deg)		
Fe(1a)−Fe(1)−C(2)	96.6(2)	Fe(1)−C(1)−Fe(1a)	82.2(2)
Fe(1a)−Fe(1)−C(17)	107.7(1)	Fe(1)−C(17)−Si(1)	130.6(3)
Si(1a)−Si(1)−C(17)	108.4(2)	Fe(2)−Fe(3)−C(6)	96.8(3)
Fe(3)−Fe(2)−C(5)	96.8(2)	Fe(3)−Fe(2)−C(37)	108.3(1)
Fe(2)−C(37)−Si(3)	130.9(3)	Si(2)−Si(3)−C(37)	108.4(2)
Si(3)−Si(2)−C(27)	110.0(2)	Fe(3)−Si(27)−Si(2)	128.7(3)
Fe(2)−Fe(3)−C(27)	108.7(1)	Fe(2)−C(3)−Fe(3)	83.4(2)
Fe(2)−C(4)−Fe(3)	82.5(2)	C(41)−Si(1)−C(42)	109.3(3)
C(43)−Si(2)−C(44)	109.1(3)	C(45)−Si(3)−C(46)	108.1(3)
	Torsion Angles (deg)		
C(41)−Si(1)−Si(1a)−C(41a)	69.8(4)	C(43)−Si(2)−Si(3)−C(45)	51.1(5)
C(41)−Si(1)−Si(1a)−C(42a)	−49.3(4)	C(43)−Si(2)−Si(3)−C(46)	−68.6(6)
C(42)−Si(1)−Si(1a)−C(41a)	−49.3(4)	C(44)−Si(2)−Si(3)−C(45)	169.6(5)
C(42)−Si(1)−Si(1a)−C(42a)	−168.5(4)	C(44)−Si(2)−Si(3)−C(46)	50.0(5)

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

88.8°, $[\eta^5,\eta^5\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4]Fe_2(CO)_4$.[11] This value is nearly close to the largest one, 109° in $(CH_3)_2C[(\eta^5\text{-}C_5H_4)_2Fe_2(CO)_4]$,[12] among the complexes of this type reported so far. The silicon methyl groups are staggered relative to one another [the smaller C−Si−Si−C torsion angles fall in the range of 43.0(7)−74.6(7)°], indicating the twist extent of the molecule.

The molecular structure of **3t** is presented in Figure 2. Table 2 provides selected bond distances and angles. The molecule of **3t** is similar to that of **3c**. It is different in that the fused tetrahydrobenzo rings adopt a trans arrangement. Like **3c**, the correspoding six-membered ring also adopts a twist boat conformation. It should be noted that there are two independent molecules with the ratio of 1:2 (A/B) in the unit cell: one (A) has C_2 symmetry, and the other (B) is unsymmetrical. The dihedral angle between the two Cp rings is 77.33° for A and 74.83° for B, nearly close to the smallest value, 73.2° in $(CH_2)_3[(\eta^5\text{-}C_5Me_4)Fe(CO)]_2(\mu\text{-}CO)_2$,[13] among the complexes of this type reported so far. This indicates larger difference between cis and trans isomers (**3c** and **3t**), The silicon methyl groups in the bridge adopt a staggered conformation [the smaller C−Si−Si−C torsion angles fall in the range of 49.3(4)−69.8(4)° for A and 50.0(5)−68.6(6)° for B]. The Si atoms are bent out of the linked cyclopentadienyl ring planes by 0.1836 Å for A, and 0.0926 and 0.1770 Å for B.

The molecular structure of **4t** is illustrated in Figure 3. Selected bond distances and angles are listed in Table 3. The molecule of **4t** consists of two $[Me_2Si(\eta^5\text{-}IndH_4)Fe(CO)_2]$ moities linked to each other by two Si−Fe bonds. Like many analogues,[5,14] **4t** has *Ci* symmetry, and the six-membered ring Fe(1)−Si(1)−C(11a)−Fe(1a)−Si(1a)−C(11) constituting its molecular framework adopts a stable chair conformation. This indicates that the larger tetrahydroindenyl ligands fail to influence the stable cyclic structure. The Fe−Si distance [2.316(2) Å] is close to that in its analogue[5] [2.315(2) Å] and slightly shorter than those in acyclic molecules of the same type (2.346−2.363 Å),[15] which further accounts for the greater stability of the rearrangement products and presumably provides the driving force for the rearrangement.

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

	Bond Distances (Å)		
Fe(1)−Si(1)	2.303(3)	Fe(2)−Si(2)	2.337(3)
Fe(1)−C(1)	1.731(8)	Fe(1)−C(2)	1.711(9)
Fe(1)−Cp(1)[a]	1.721	Fe(2)−C(3)	1.72(1)
Fe(2)−C(4)	1.76(1)	Fe(2)−Cp(2)[a]	1.748
C(3)−O(3)	1.17(1)	C(4)−O(4)	1.141(9)
C(1)−O(1)	1.168(8)	C(2)−O(2)	1.155(9)
Si(1)−C(11)	1.880(8)	Si(2)−C(21)	1.888(9)
	Bond Angles (deg)		
Si(2)−Fe(2)−C(11)	97.8(3)	Fe(2)−C(11)−Si(1)	138.0(4)
Fe(1)−Si(1)−C(11)	116.3(2)	Si(1)−Fe(1)−C(21)	100.3(2)
Fe(1)−C(21)−Si(2)	129.1(4)	Fe(2)−Si(2)−C(21)	111.0(2)
C(1)−Fe(1)−C(2)	94.7(4)	C(3)−Fe(2)−C(4)	96.1(4)
C(5)−Si(1)−C(6)	104.3(4)	C(7)−Si(2)−C(8)	103.7(4)

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

The molecular structure of **4c** is illustrated in Figure 4. Selected bond distances and angles are listed in

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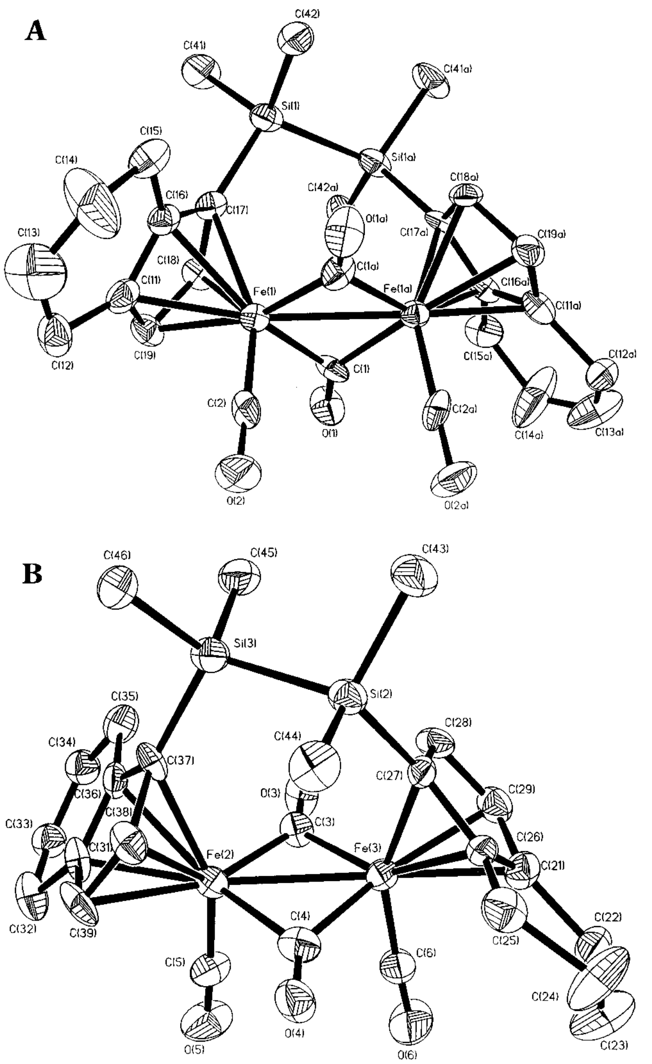


Figure 2. Molecular structure of ($Me_2SiSiMe_2$)[(η^5-$IndH_4$)Fe(CO)]$_2$(μ-CO)$_2$ (**3t**), showing labeling scheme for the two independent molecules present as a ratio of 1:2 (A/B) in the crystal structure. Hydrogen atoms are omitted for clarity.

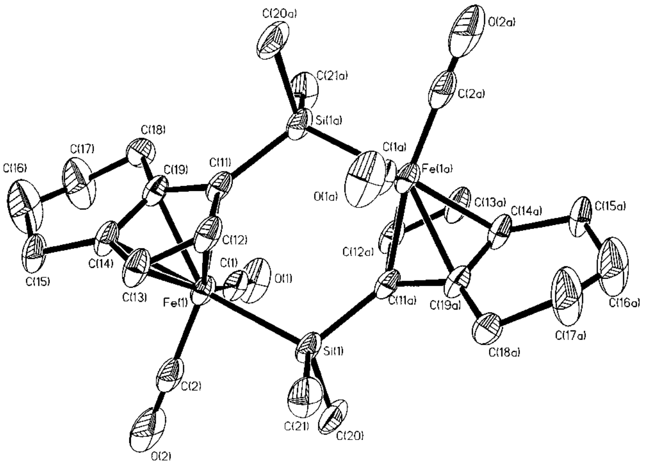


Figure 3. Molecular structure of [Me_2Si(η^5-$IndH_4$)Fe(CO)$_2$]$_2$ (**4t**). Hydrogen atoms are omitted for clarity.

Table 4. The molecule of **4c** also consists of two [Me_2Si(η^5-$IndH_4$)Fe(CO)$_2$] moieties linked to each other by two Si−Fe bonds. Unlike the trans isomer **4t**, **4c** is unsymmetric, and the corresponding six-membered ring adopts a twist boat conformation. The dihedral angle between two cyclopentadienyl rings is 30.8°, smaller than that in *cis*-[Me_2Si(η^5-*t*-BuC_5H_3)Fe(CO)$_2$]$_2$.[6] The two Fe−Si bond distances have a difference of 0.034 Å, but the mean bond length (2.320 Å) is rather close to that in **4t**. The unbalanced coordination presumably results from stronger interaction between the two cis-fused tetrahydrobenzo rings. The Si atoms are bent out of the linked Cp rings by 0.4188 and 0.1168 Å, respectively, indicating that the molecule is rather twisted.

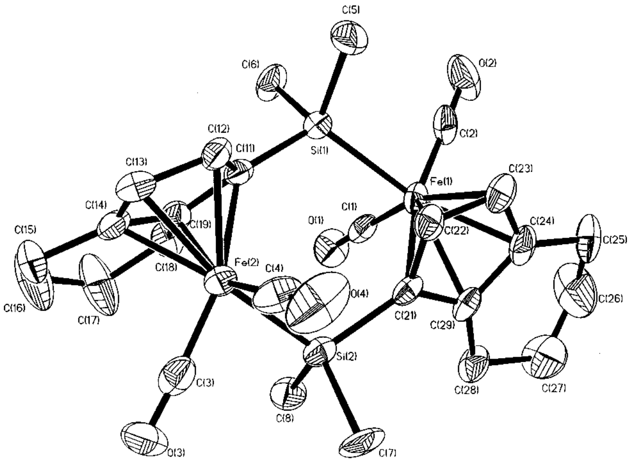


Figure 4. Molecular structure of [Me_2Si(η^5-$IndH_4$)Fe(CO)$_2$]$_2$ (**4c**). Hydrogen atoms are omitted for clarity.

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

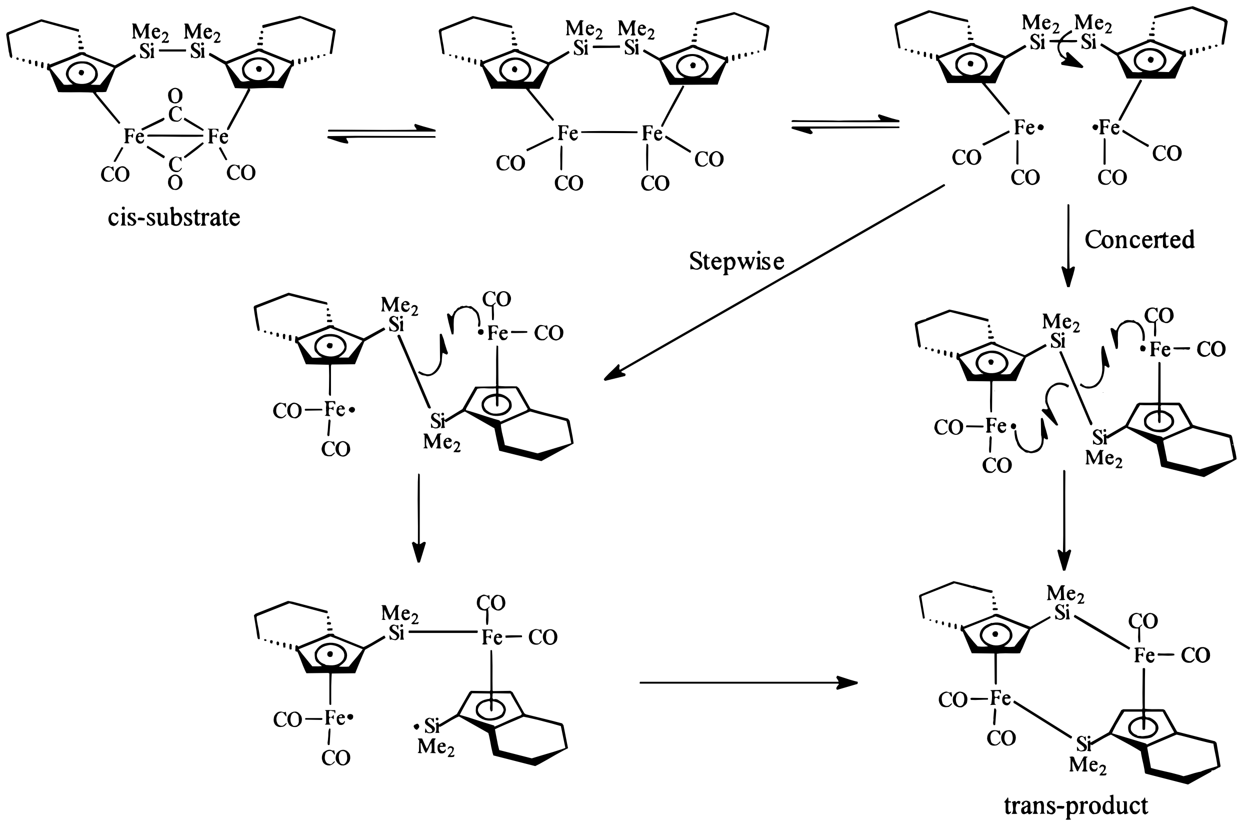
Bond Distances (Å)			
Fe(1)−Si(1)	2.316(2)	Fe(1)−C(1)	1.727(7)
Fe(1)−C(2)	1.730(6)	Fe(1)−C(11)	2.091(5)
Fe(1)−C(12)	2.078(6)	Fe(1)−C(13)	2.087(7)
Fe(1)−C(14)	2.111(6)	Fe(1)−C(19)	2.113(6)
Fe(1)−Cp(1)[a]	1.708	C(1)−O(1)	1.161(7)
C(2)−O(2)	1.144(7)	Si(1)−C(20)	1.895(7)
Si(1)−C(21)	1.904(7)		
Bond Angles (deg)			
Si(1)−Fe(1)−C(1)	89.1(3)	Si(1)−Fe(1)−C(2)	85.5(2)
Si(1)−Fe(1)−C(11)	101.8(2)	Fe(1)−C(11)−Si(1a)	132.7(3)
Fe(1)−Si(1)−C(11a)	111.8(2)	Fe(1)−Si(1)−C(20)	113.2(2)
Fe(1)−Si(1)−C(21)	112.4(2)	C(1)−Fe(1)−C(2)	94.1(3)
C(20)−Si(1)−C(21)	106.1(3)	Fe(1)−C(14)−C(15)	128.8(4)
Fe(1)−C(19)−C(18)	127.6(4)		

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

Mechanism. In comparison with the analogue **5** with a *tert*-butyl substituent at β position, the tetrahydroindenyl complex **3** exhibits the structural specialty, with a fused tetrahydrobenzo ring linked to α and β positions of the cyclopentadienyl rings. However, this does not influence the smooth advancement of the rearrangement. Complex **3** shows the same rearrangement stereospecifity (i.e., the cis isomer **3c** yields the trans product **4t**, while the trans isomer **3t** affords the cis product **4c**) as the analogue **5**. By analogy with the mechanism described in the previous paper in this series,[6] the pathway for formation of trans product **4t** (or cis product **4c**) is proposed as illustrated in Scheme 3.

This pathway invloves (i) the initial pairwise opening of the CO bridges to give a nonbridged tautomer, which was not only confirmed by the detailed investigation of cis−trans isomerization in analogue [(η^5-C_5H_5)$_2$$Fe_2(CO)_4$][16] but was also observed in binuclear ruthenium complexes in which bridged and nonbridged structures

Scheme 3



are present in detectable amounts,[17] and (ii) the subsequent thermal homolysis of Fe–Fe bonds, which was corrogated by the detection of an iron-centered radical ESR signal.[6] Such cleavage is hindered by a barrier of an order of magnitude of ~23 kcal/mol.[18]

The rearrangement reaction proceeds by either a concerted or stepwise pathway. The key requirement of the two paths is a suitable rotation of two [$Me_2Si(\eta^5$-$IndH_4)Fe(CO)_2$] moieties about the Si–Si bond, which not only ensures a successful interconversion of cis substrate (or trans substrate) into trans product (or cis product) but satisfactorily accounts for the stereospecificity of the rearrangement reaction.

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, heptane, and xylene were distilled from sodium/benzophenone ketyl and purged with argon atmosphere prior to use. ($Me_2SiSiMe_2$)[(η^5-Ind)Fe(CO)]$_2$(μ-CO)$_2$ (**2**)[7] was prepared according to a literature method. Proton (^1H NMR) spectra were obtained using $CHCl_3$ (δ 7.24 ppm) as an internal standard on a Bruker AC-P200 spectrometer. Elemental analyses were performed by a Perkin-Elmer 240C analyzer. Infrared spectra were obtained as KBr disk and recorded on a Nicolet 5DX FT-IR spectrometer.

Preparation of ($Me_2SiSiMe_2$)[(η^5-$IndH_4$)Fe(CO)]$_2$(μ-CO)$_2$ (3). To a solution of **2** (1.25 g, 2.20 mmol) in CH_2Cl_2 (50 mL) was added PtO_2 (50 mg, 1.90 mmol). The mixture was stirred under hydrogen atmosphere (1 atm) at 30 °C for 24 h. The catalyst was removed by filtration. The solvent was reduced to a minimum volume under vacuum and then was subjected to column chromatography on silica gel. Elution with CH_2Cl_2/petroleum ether (1:1) developed two red bands. The first band gave 0.40 g (31%) of dark-red crystals (**3t**), and the second band yielded 0.18 g (14%) of deep-red crystals (**3c**). For **3c**. Anal. Calcd for $C_{26}H_{36}Fe_2O_4Si_2$: C, 54.18; H, 5.60. Found: C, 53.83; H, 6.03. IR (ν_{CO}, cm^{-1}): 1983.2, 1934.0, 1802.7, 1761.7. ^1H NMR ($CDCl_3$): δ 5.06 (d, J = 2.69 Hz, 2H, Cp-H), 4.21(d, J = 2.69 Hz, 2H, Cp-H), 3.07–1.59 (m, 16H, C_4H_8), 0.30, 0.04 (s, s, 12H, $SiMe_2$). For **3t**. Anal. Calcd for $C_{26}H_{36}Fe_2O_4Si_2$: C, 54.18; H, 5.60. Found: C, 54.12; H, 5.84. IR (ν_{CO}, cm^{-1}): 1983.2, 1934.0, 1802.7, 1761.7. ^1H NMR ($CDCl_3$): δ 5.16 (d, J = 2.16 Hz, 2H, Cp-H), 4.49 (d, J = 2.16 Hz, 2H, Cp-H), 3.00–1.45 (m, 16H, C_4H_8), 0.30, 0.04 (s, s, 12H, $SiMe_2$).

Rearrangement Reaction of Complexes 3c and 3t. 3t (0.20 g, 0.34 mmol) was heated in refluxing xylene (50 mL) for 24 h. The reaction process was accompanied by major decomposition. TLC monitoring of the reaction indicated that only one product was formed. The solvent was removed under reduced pressure and then subjected to column chromatography on silica gel using petroleum ether as eluent. The yellow band afforded 18 mg (9.2%) of **4c** as light yellow crystals. For **4c**. Anal. Calcd for $C_{26}H_{36}Fe_2O_4Si_2$: C, 54.18; H, 5.60. Found: C, 54.07; H, 5.78. IR (ν_{CO}, cm^{-1}): 1976.8, 1919.9. ^1H NMR ($CDCl_3$): δ 4.63 (d, J = 2.07 Hz, 2H, Cp-H), 4.21 (d, J = 2.07 Hz, 2H, Cp-H), 2.68–2.31, 1.91–1.40 (m, m, 16H, C_4H_8), 0.56, 0.40(s, s, 12H, $SiMe_2$).

Similar treatment of **3c** afforded 16 mg (8.9%) of **4t** as light yellow crystals. For **4c**. Anal. Calcd for $C_{26}H_{36}Fe_2O_4Si_2$: C, 54.18; H, 5.60. Found: C, 54.18; H, 5.75. IR (ν_{CO}, cm^{-1}):

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Table 5. Summary of X-ray Diffraction Data

	3c	**3t**	**4c**	**4t**
formula	$C_{26}H_{32}Fe_2O_4Si_2$	$C_{26}H_{32}Fe_2O_4Si_2$	$C_{26}H_{32}Fe_2O_4Si_2$	$C_{26}H_{32}Fe_2O_4Si_2$
formula weight	576.41	576.41	576.41	576.41
space group	$P2_1/n$	$C2/c$	$P\bar{1}$	$P\bar{1}$
crystal system	monoclinic	monoclinic	triclinic	triclinic
Z	4	12	2	1
a (Å)	8.269(2)	23.514(5)	8.447(3)	7.683(2)
b (Å)	20.208(4)	17.085(3)	12.160(3)	9.795(3)
c (Å)	15.912(3)	20.925(4)	13.814(5)	11.044(4)
α, deg	90	90	76.07(2)	59.07(3)
β, deg	101.18(3)	111.28(3)	73.17(3)	65.21(3)
γ, deg	90	90	88.30(2)	74.92(2)
volume (Å^3)	2608(1)	7833(5)	1317(1)	646.1(2)
d_{calc} (g cm^{-1})	1.468	1.466	1.453	1.481
crystal size (mm)	0.20 × 0.30 × 0.30	0.30 × 0.30 × 0.40	0.20 × 0.30 × 0.20	0.20 × 0.30 × 0.40
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}	12.31	12.30	12.192	12.43
data collection method	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
max 2θ, deg	46.0	46.0	46.0	46.0
total no. of observns	3265	5378	3477	1690
no. of unique data, $I > 3\sigma(I)$	2205	2312	1954	1617
final no. of variables	307	652	307	154
R^a	0.034	0.051	0.052	0.049
$R_w{}^b$	0.039	0.045	0.064	0.059
goodness of fit	0.95	4.023	2.28	1.22

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

1975.0, 1925.0. ^{1}H NMR (CDCl$_3$): δ 4.74 (d, $J = 2.07$ Hz, 2H, Cp-H), 4.47 (d, $J = 2.07$ Hz, 2H, Cp-H), 2.72−2.30, 2.00−1.59 (m, m, 16H, C_4H_8), 0.54, 0.38 (s, s, 12H, SiMe$_2$).

Molecular Structure Determination. Crystals suitable for X-ray diffraction were obtained from hexane/dichloromethane solution. All data sets were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation. Empirical absorption corrections using the program DIFBAS were applied to intensity data. All calculations were performed on a PDP11/44 computer using the SDP-PLUS program system. The structures were solved by a direct phase determination method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms for **3c** and **3t** were refined isotropically. For **4c** and **4t**, hydrogen atoms were not included in the refinement and calculations of structure factors. Neutral atom scattering factors were taken from the tabulation of Cromer and Waber.[19] Selected bond distances and angles for **3c**, **3t**, **4c**, and **4t** are given in Tables 1−4, respectively. A summary of the crystallographic results is presented in Table 5.

Acknowledgment. We are grateful to the National Science Foundation of the P. R. China and the Doctoral Foundation of State Education Commission of the P. R. China for financial support of this work.

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**, **4c**, and **4t** (19 pages). Ordering information is given on any current masthead page.

OM970437O

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