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Novel Rearrangement Reactions. 6. Thermal Rearrangement of Disilyl-Bridged Diiron Complexes Containing Isocyanide Ligands and Stereochemistry of the Rearranged Products

Yongqiang Zhang, Xiuli Sun, Baiquan Wang, Shansheng Xu, and Xiuzhong Zhou*

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

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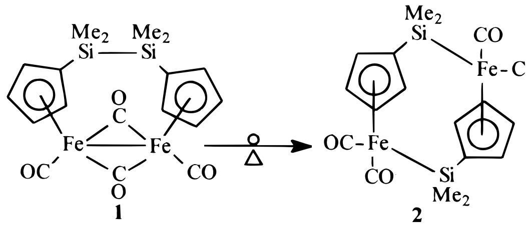
Treatment of ($Me_2SiSiMe_2$)[(η^5-$C_5H_3R^1$)Fe(CO)]$_2$(μ-CO)$_2$ (R^1 = H (**1**), R^1 = *t*-Bu (**5**)) with R^2NC (R^2 = C_6H_{11}, *t*-Bu) in benzene afforded isocyanide-substituted complexes [(η^5:η^5-$C_5H_3R^1$-$Me_2SiSiMe_2C_5H_3R^1$)Fe_2(CO)(CNR^2)(μ-CO)$_2$] (R^1 = H, R^2 = C_6H_{11} (**3**), R^2 = *t*-Bu (**4**); R^1 = R^2 = *t*-Bu (**6**)). Further investigations indicated that the cis substrate **5c** afforded only the cis product (**6c**), while the trans substrate **5t** afforded only the trans product (**6t**). When **3** and **4** were heated respectively in xylene, three different rearranged products [{(Me_2Si)(η^5-C_5H_4)Fe(CO)L_1}{(Me_2Si)(η^5-C_5H_4)Fe(CO)L_2}] (L_1 = L_2 = CO (**2**); L_1 = C_6H_{11}NC, L_2 = CO (**7**), L_2 = C_6H_{11}NC (**9**); L_1 = *t*-BuNC, L_2 = CO (**8**), L_2 = *t*-BuNC (**10**)) were obtained. Similarly, thermal treatment of **6t** afforded three different cis rearranged products, **11c**, **12c**, and **13c**, while treatment of **6c** yielded three different trans rearranged products, **11t**, **12t**, and **13t**. This indicated that the rearrangement still follows the reaction mechanism proposed previously on the basis of the intramolecular nature of this reaction if we only take into account the configuration of two *tert*-butyl groups on the Cp rings. To explain the formation of three different products, an alternative mechanism involving free ligand exchange to form three different iron-centered radical intermediates is proposed as a supplement to the previous mechanism. The complex stereochemistry in the molecules of **12** and **13** is discussed. Molecular structures of **8**, **9t**, **12t**, and **13c** have been determined by single-crystal X-ray diffraction.

Introduction

Extensive investigations on a variety of transition metal complexes that activate or contain a silicon−silicon bond revealed some unique chemical properties such as base-induced migration,[1] photoisomerization,[2] and silylene elimination and rearrangement.[3] We recently observed that when the dinuclear iron complex ($Me_2SiSiMe_2$)[(η^5-C_5H_4)Fe(CO)]$_2$(μ-CO)$_2$ (**1**) was heated at reflux in xylene, an intramolecular rearrangement reaction between Si−Si and Fe−Fe bonds occurred, during which one Fe−Fe bond and one Si−Si bond were cleaved and two Si−Fe bonds were simultaneously formed (eq 1).[4] On the basis of detailed investigations



1 2 (1)

of the rearrangement stereospecificity, reaction intermediates, and crossover reaction, an alternative mechanism was subsequently proposed,[5] which was further confirmed by investigating thermal rearrangement reactions of tetrahydroindenyl complexes ($Me_2SiSiMe_2$)[(η^5-$IndH_4$)Fe(CO)]$_2$(μ-CO)$_2$ and phosphite-substituted

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* Corresponding author. Fax: 0086-22-23502458. Tel: 0086-22-23504781. E-mail: zhouxz@public1.tpt.tj.cn.

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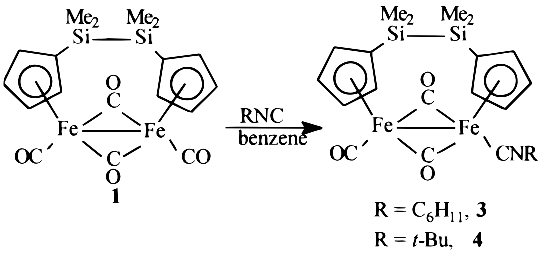
complexes $[(\eta^5{:}\eta^5\text{-}t\text{-BuC}_5\text{H}_3\text{Me}_2\text{SiSiMe}_2\text{C}_5\text{H}_3\text{-}t\text{-Bu})\text{Fe}_2(\text{CO})\text{P}(\text{OPh})_3(\mu\text{-CO})_2]$.[6] More recently ruthenium and germanium analogues have been shown to undergo similar rearrangement.[7] We report herein thermal rearrangements of disilyl-bridged diiron complexes with a terminal-substituted isocyanide ligand and stereochemistry and structures of the rearranged products.

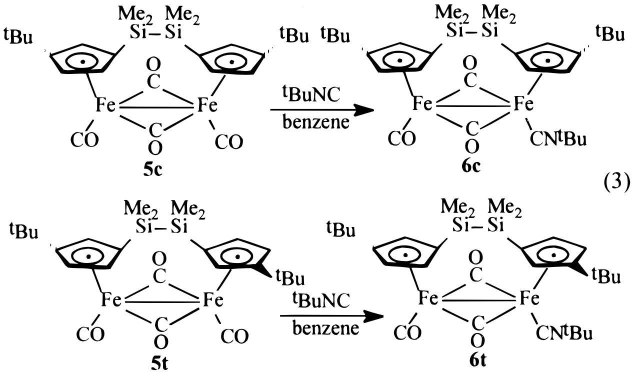
Results and Discussion

CO-Substitution Reactions of $(\text{Me}_2\text{SiSiMe}_2)[(\eta^5\text{-C}_5\text{H}_4)\text{Fe(CO)}]_2(\mu\text{-CO})_2$ (1). The replacement of carbonyl groups by isocyanide ligands in diiron complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2$[8] and its bridging analogues,[9] either by photolysis or themal process in benzene, was well established. Treatment of **1** with a 3-fold excess amount of isocyanide ligands in bezene at ambient temperature afforded isocyanide-subsitituted complexes **3** and **4** (eq 2). The investigations indicated that only one terminal CO group was replaced, whether at ambient temperature or in boiling bezene, which is in contrast to the case in the nonbridged analogue $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2$. The ^{1}H NMR spectra of **3** and **4** exhibit two groups of cyclopentadienyl proton resonance of equal intensity, each consisting of two singlets (α and β parts of the Cp ring). 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 atoms as the isocyanide ligands.[6b,10] Their IR spectra exhibit absorptions of only terminal isocyanide ligands (KBr, 2105 (**3**) and 2110 (**4**) cm^{-1}; CH$_2$Cl$_2$, 2112 (**3**) and 2115(**4**) cm^{-1}). This indicates that **3** and **4** exist as isocyanide terminal isomers in the solid state as well as in solution. This also implies that the process of bridge-terminal interchange between isocyanide ligands and carbonyl groups, suggested as the Adams−Cotton mechanism,[11] cannot occur at room temperature.



R = C$_6$H$_{11}$, **3**
R = *t*-Bu, **4**
(2)

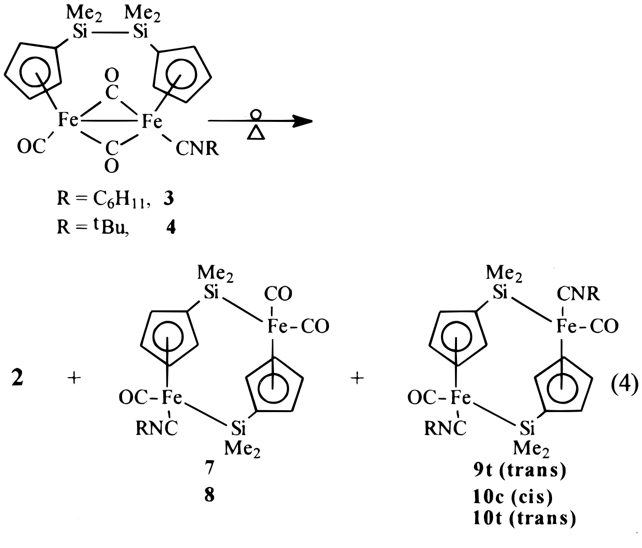
CO-Substitution Reactions of $(\text{Me}_2\text{SiSiMe}_2)[(\eta^5\text{-}t\text{-BuC}_5\text{H}_3)\text{Fe(CO)}]_2(\mu\text{-CO})_2$ (5). The cis isomer **5c** and a 3-fold excess amount of *tert*-butyl isocyanide ligands were refluxed in bezene to afford only the cis isocyanide-substituted complex **6c**, whereas similar treatment of **5t** yielded only the trans isomer **6t** (eq 3). This indicated that the CO-substitution reaction of bridged diiron species by isocyanide ligands did not influence the substituent configuration. Compared with the parent complex **1**, whose CO-substitution reaction could proceed facilely at room temperature, the CO-substitution reaction of **5** was more difficult. This should be attributed to substitution of bulky *tert*-butyl groups on the Cp rings.



(3)

The cis isomer **6c** is dark red crystals, while the trans isomer **6t** is green solids. In the ^{1}H NMR spectrum of **6c**, four chemically nonequivalent silicon methyl groups exhibit three singlets, suggesting the overlap of two silicon methyl proton signals, and two chemically nonequivalent *tert*-butyl groups on the Cp rings indicate one singlet. Four silicon methyl groups of **6t** exhibit four singlets, and two *tert*-butyl groups show two rather close singlets. Their IR spectra give rise to only absorptions of terminal isocyanide ligands. This indicates that only terminal carbonyl groups were replaced by *tert*-butyl isocyanide ligands.

Thermal Rearrangement Reactions of 3 and 4. Complex **3** was heated at reflux in xylene for 24 h, surprisingly affording three different products, **2** without substituted isocyanide ligands, **7** with a monosubstituted isocyanide ligand (the expected rearranged product), and **9** with disubstituted isocyanide ligands. Similar treatment of **4** also afforded three different products: **2**, **8**, and **10** (eq 4). Since each iron atom in



R = C$_6$H$_{11}$, **3**
R = ^{t}Bu, **4**
9t (trans)
10c (cis)
10t (trans)
(4)

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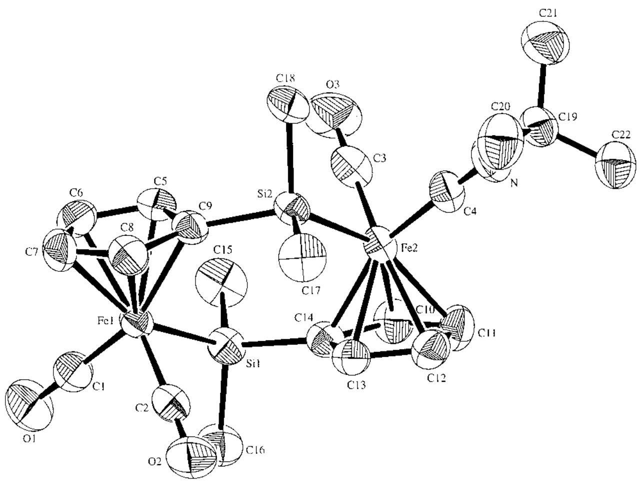

Figure 1. ORTEP drawing of **8**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 8

Bond Distances (Å)			
Fe(1)−Si(1)	2.320(1)	Fe(2)−Si(2)	2.296(1)
Fe(1)−C(1)	1.733(4)	Fe(1)−C(2)	1.737(4)
Fe(2)−C(3)	1.726(4)	Fe(2)−C(4)	1.810(4)
C(4)−N	1.163(4)	N−C(19)	1.451(4)
Fe(1)−Cp(1)	1.728[a]	Fe(2)−Cp(2)	1.732[a]
Bond Angles (deg)			
Fe(1)−C(9)−Si(2)	132.7(2)	Fe(2)−C(14)−Si(1)	128.8(2)
Fe(1)−Si(1)−C(14)	111.1(4)	Fe(2)−Si(2)−C(9)	113.6(1)
Si(1)−Fe(1)−C(9)	99.14(9)	Si(2)−Fe(2)−C(14)	100.74(9)
Fe(2)−C(4)−N	178.3(3)	C(4)−N−C(19)	167.5(4)

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

the molecules of **9** and **10** is linked with four different ligands, each of them can be considered as a chiral center. Thus the isomer with two isocyanide ligands adopting a trans configuration is meso, while the other one with two isocyanide ligands taking a cis configuration is racemic.

For complex **9** with disubstituted cyclohexyl isocyanide ligands, only the trans isomer **9t** (meso) was isolated, which has been determined by single-crystal X-ray diffraction. While for complex **10**, with *tert*-butyl isocyanide ligands, both the cis and trans isomers **10c** (rac) and **10t** (meso) were obtained. The ^{1}H NMR spectra of the rearranged products **7** and **8** show that the four methyl groups on the silicon atoms are all nonequivalent. The ^{13}C NMR spectrum of **8** exhibits four singlets for four silicon methyl groups, 10 singlets for two cyclopentadienyl rings, three singlets for carbonyl groups, and one singlet for one isocyanide ligand. The ^{29}Si NMR signals of **8** appear at 35.5 and 35.7 ppm. These indicate that **8** has a completely asymmetric molecular structure, which has been confirmed by single-crystal X-ray diffraction studies. **10c** and **10t** have almost identical ^{1}H NMR spectra except for different silicon methyl resonances. The isomer with two singlets for the silicon methyl groups is assigned to the trans isomer **10t** (meso) by comparing its ^{1}H NMR spectrum with that of **9t**.

X-ray Structure Determinations of 8 and 9t. The ORTEP drawing of **8** is shown in Figure 1. Selected bond distances and angles are summarized in Table 1. The molecule is completely asymmetric, and the six-membered ring Fe1−C9−Si2−Fe2−C14−Si1 constituting the molecular framework adopts a twist-boat conformation. This is different from the parent analogue **2**,[4] which has C_i symmetry, and the corresponding six-membered ring adopts a chair conformation. The two Fe−Si bonds (2.320(1) and 2.296(1) Å) is different: one is much close to that of **2** (2.315(2) Å), and the other linked with isocyanide ligands is shorter than that of **2**. This indicates that the weaker interaction between isocyanide ligands and iron atoms strengthens the Fe−Si bond. The dihedral angle between the two Cp ring planes is 7.11°, while the two Cp rings of **2** are parallel to each other. The Si(1) and Si(2) atoms are bent out of the corresponding Cp rings by 0.109 and 0.226 Å, respectively.

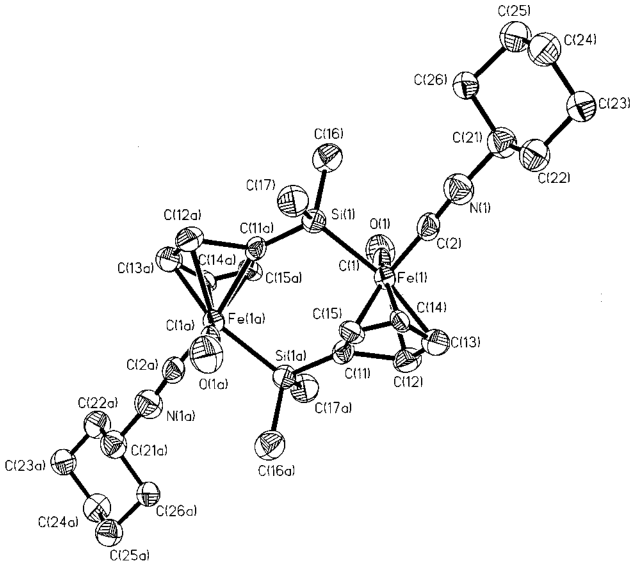

Figure 2. ORTEP drawing of **9t**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 9t

Bond Distances (Å)			
Fe(1)−Si(1)	2.285(3)	Fe(1)−C(1)	1.735(9)
Fe(1)−C(2)	1.786(7)	N(1)−C(21)	1.431(9)
C(2)−N(1)	1.165(8)	Si(1)−C(11a)	1.885(7)
Bond Angles (deg)			
Fe(1)−C(11)−Si(1a)	131.4(4)	Fe(1)−Si(1)−C(11a)	112.9(3)
Si(1)−Fe(1)−C(11)	100.4(2)	C(1)−Fe(1)−C(2)	95.3(4)
Fe(1)−C(2)−N(1)	177.8(7)	C(2)−N(1)−C(21)	175.2(8)

The ORTEP drawing of **9t** is shown in Figure 2. Selected bond distances and angles are summarized in Table 2. The molecule consists of two $(Me_2Si)[(\eta^5\text{-}C_5H_4)\text{-}Fe(CO)(CNC_6H_{11})]$ moieties linked to each other by two head-to-tail Fe−Si bonds. The molecule has C_i symmetry, with two isocyanide ligands adopting a trans configuration. The six-membered ring Fe1−C11−Si1a−Fe1a−C11a−Si1 constituting the molecular framework adopts a precise chair conformation. The cyclohexyl group adopts a chair conformation, with the isocyanide ligand being equitorial. The Fe−Si bond (2.285(3) Å) is shorter than that of **2** (2.315(2) Å) and much shorter than those in acyclic molecules (2.346−2.363 Å),[12] which accounts for greater stability of the rearranged products.

Thermal Rearrangement Reactions of 6c and 6t. As described above, thermal treatment of **6c** in boiling xylene for 24 h surprisingly afforded three different

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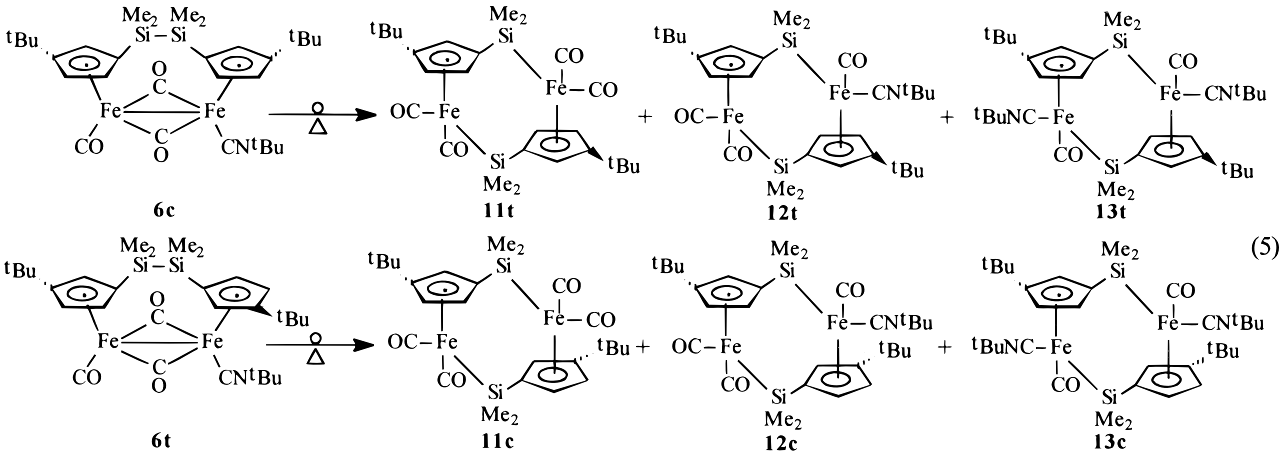
(12) Parkanyi, L.; Pannell, K. H.; Hernadez, C. *J. Organomet. Chem.* **1983**, *252*, 127.

Chart 1



products: **11t**[5] (the rearranged product of **5c**), **12t** (the expected rearranged product), and **13t**.[13] Similar treatment of **6t** also yielded three different products: **11c**[5] (the rearranged product of **5t**), **12c** (the expected rearranged product), and **13c** (eq 5, in Chart 1).[14] Although the rearrangement results became more complex when the CO groups in diiron complexes were replaced by isocyanide ligands, further investigations indicated that the rearrangement reaction is still stereospecific if we only consider the configuration of two *tert*-butyl groups on the Cp rings. The ^{1}H NMR spectra of **12t** and **12c** show the *tert*-butyl group of the isocyanide ligand more downfield than those on the Cp rings ($\Delta\delta$ 0.10 (**12t**) and 0.16 ppm (**12c**)). In contrast, their substrates **6c** and **6t** show *tert*-butyl groups on the Cp rings more downfield than that of the isocyanide ligand ($\Delta\delta$ 0.22 ppm for **6c** and **6t**).

Stereochemistry of the Rearranged Products 12 and 13. In the molecules of **12** and **13**, one or two CO groups coordinated to iron atoms are replaced by isocyanide ligands. This increases stereogenic centers in these molecules, which further complicates their stereochemistry. The molecules of the rearranged products with an isocyanide ligand have three stereogenic centers that theoretically imply eight stereomers, four pairs of enationmers. In the molecules of the rearranged products with disubstituted isocyanide ligands there exist four stereogenic centers, which imply possible existence of 16 stereomers. However, the symmetry reduces the number of stereomers. Thus there exist 10 stereomers, two of which have C_i symmetry and are meso and the remaining eight constituting four racemates, namely, four pairs of enationmers. All possible isomers are shown in Tables 3 and 4.[15]

Table 3. All Possible Stereoisomers of 12 (L_1 = *t*-BuNC, L_2 = CO)[a]

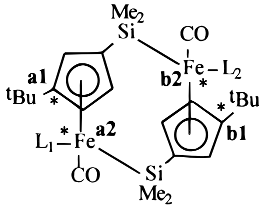
t-Bu	a1	b1	a2	
trans	R(S)	S(R)	R(S)	A(A*)
cis	R(S)	S(R)	S(R)	B(B*)
	R(S)	R(S)	R(S)	C(C*)
	R(S)	R(S)	S(R)	D(D*)

[a] A*, B*, C*, and D* mean the enantiomers of A, B, C, and D.

Table 4. All Possible Stereoisomers of 13 (L_1 = L_2 = *t*-BuNC)[a]

t-Bu	a1	b1	a2	b2	
trans	R	S	R	S	E
	R	S	S	R	F
cis	R(S)	S(R)	R(S)	R(S)	G(G*)
	R(S)	R(S)	R(S)	S(R)	H(H*)
	R(S)	R(S)	R(S)	R(S)	I(I*)
	R(S)	R(S)	S(R)	S(R)	J(J*)

[a] G*, H*, I*, and J* mean the enantiomers of G, H, I, and J.



For the monosubstituted product **12**, only two racemates, two pairs of enationmers, **12c** and **12t**, were obtained. **12c** may be assigned to isomer **C**(**C***) by analogy with the molecular structure of its phosphite-substituted analogue cis-[{(Me_2Si)(η^5-*t*-BuC_5H_3)Fe$(CO)_2$}{(Me_2Si)(η^5-*t*-BuC_5H_3)FeP$(OPh)_3$(CO)}].[6b] **12t** has the molecular structure of **A**(**A***), which has been confirmed by single-crystal X-ray diffraction. For the disubstituted product **13**, only two racemates, **13c** and **13t**, were isolated. The ^{1}H NMR spectrum of **13t** shows three singlets for four silicon methyl groups and two singlets for two *tert*-butyl groups on the Cp rings as well as two singlets for two *tert*-butyl groups of isocyanide ligands. This indicates that the molecule is asymmetric and its structure cannot be assigned to be isomers **E** and **F** with C_i symmetry. Thus **13t** should have the molecular structure of **G**(**G***), as determined by single-crystal X-ray diffraction (see Supporting Information). **13c** has an ^{1}H NMR spectrum almost identical to that of **13t**

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[13] The trans isomers (**11t**, **12t**, and **13t**) were designated according to the trans configuration of *tert*-butyl groups on the Cp rings and without consideration of the configuration of isocyanide ligands. Thus thermal rearrangement of the cis substrate afforded only the trans products.

[14] The cis isomers (**11c**, **12c**, and **13c**) were designated according to the cis configuration of *tert*-butyl groups on the Cp rings and without consideration of the configuration of isocyanide ligands. Thermal rearrangement of the trans substrate afforded only the cis products. Therefore, the rearrangement reaction still follows the high stereospecificity reported before.

[15] Although the Cp carbon atoms (**1a** and **1b**) linked with *tert*-butyl groups are not chiral centers, we consider them as chiral centers in order to discuss stereochemistry more simply and conveniently. In fact this designation does not influence the result of stereochemistry in the molecules of **12** and **13**.

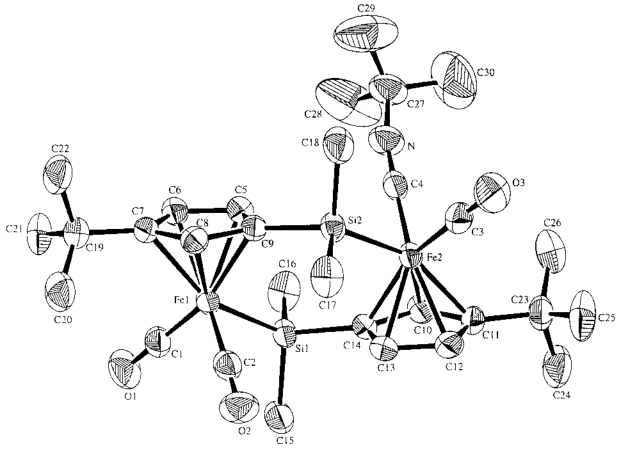

Figure 3. ORTEP drawing of **12t**.

Table 5. Selected Bond Distances (Å) and Angles (deg) for 12t

Bond Distances (Å)			
Fe(1)−Si(1)	2.317(1)	Fe(2)−Si(2)	2.303(1)
Fe(1)−C(1)	1.741(4)	Fe(1)−C(2)	1.747(4)
Fe(2)−C(3)	1.724(4)	Fe(2)−C(4)	1.804(4)
C(4)−N	1.165(4)	N−C(27)	1.444(4)
Fe(1)−Cp(1)[a]	1.722	Fe(2)−Cp(2)[a]	1.727
Bond Angles (deg)			
Fe(1)−C(9)−Si(2)	130.2(2)	Fe(2)−C(14)−Si(1)	133.7(2)
Fe(1)−Si(1)−C(14)	113.1(1)	Fe(2)−Si(2)−C(9)	112.63(10)
Si(1)−Fe(1)−C(9)	100.64(9)	Si(2)−Fe(2)−C(14)	100.00(9)
Fe(2)−C(4)−N	178.3(3)	C(4)−N−C(27)	167.6(4)

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

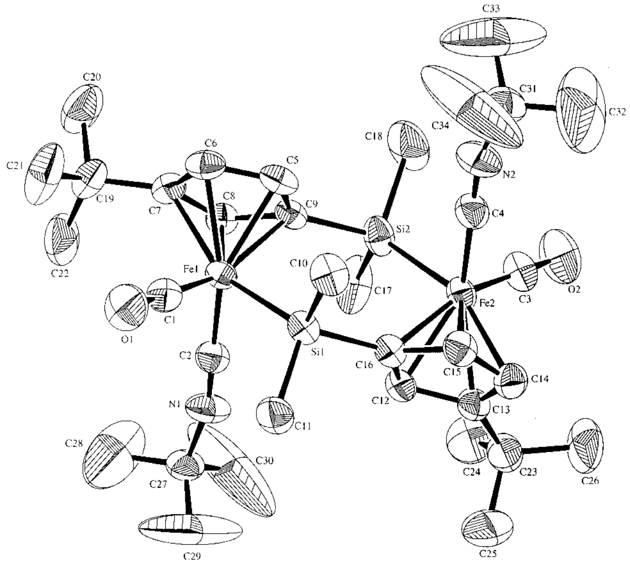

Figure 4. ORTEP drawing of **13c**.

Table 6. Selected Bond Distances (Å) and Angles (deg) for 13c

Bond Distances (Å)			
Fe(1)−Si(1)	2.289(2)	Fe(2)−Si(2)	2.306(2)
Fe(1)−C(1)	1.722(5)	Fe(1)−C(2)	1.797(5)
Fe(2)−C(3)	1.723(5)	Fe(2)−C(4)	1.798(5)
C(2)−N(1)	1.158(5)	N(1)−C(27)	1.443(6)
C(4)−N(2)	1.162(5)	N(2)−C(31)	1.433(6)
Fe(1)−Cp(1)[a]	1.725	Fe(2)−Cp(2)[a]	1.733
Bond Angles (deg)			
Fe(1)−C(9)−Si(2)	133.0(2)	Fe(2)−C(16)−Si(1)	133.3(2)
Fe(1)−Si(1)−C(16)	115.2(1)	Fe(2)−Si(2)−C(9)	116.1(1)
Si(1)−Fe(1)−C(9)	98.7(1)	Si(2)−Fe(2)−C(16)	98.7(1)
Fe(1)−C(2)−N(1)	177.1(4)	C(2)−N(1)−C(27)	165.3(5)
Fe(2)−C(4)−N(2)	178.3(3)	C(4)−N(2)−C(31)	164.3(6)

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

except for the difference of the proton signals on the Cp rings. The molecular structure of **13c** has been determined to be **H**(**H***) by single-crystal X-ray diffraction.

X-ray Structure Determinations of 12t and 13c. The ORTEP drawing of **12t** is shown in Figure 3. Selected bond distances and angles are summarized in Table 5. The molecule consists of one [$(Me_2Si)(\eta^5\text{-}t\text{-}BuC_5H_3)Fe(CO)_2$] moiety and one [$(Me_2Si)(\eta^5\text{-}t\text{-}BuC_5H_4)Fe(CO)(CN\text{-}t\text{-}Bu)$] moiety linked to each other by two head-to-tail Fe−Si bonds. **12t** is asymmetric, with two *tert*-butyl groups on the Cp rings adopting a trans configuration. The six-membered ring Fe1−C9−Si2−Fe2−C14−Si1 constituting the molecular framework adopts a twist-boat conformation. The two Fe−Si bonds (2.317(1) and 2.303(1) Å) are close to that of **11t** (2.3148(8) Å).[5] The dihedral angle between the two Cp ring planes is 5.22°, while the two Cp rings of **11t** are parallel to each other. The Si(1) and Si(2) atoms are bent out of the corresponding Cp rings by 0.271 and 0.151 Å, respectively. The distance from the centroid of the Cp ring to the corresponding Fe atom (mean 1.725 Å) is equal to that in its parent analogue **11t** (1.723 Å).

The ORTEP drawing of **13c** is shown in Figure 4. Selected bond distances and angles are summarized in Table 6. The molecule consists of two [$(Me_2Si)(\eta^5\text{-}t\text{-}BuC_5H_3)Fe(CO)(CN\text{-}t\text{-}Bu)$] moieties linked to each other by two head-to-tail Fe−Si bonds. **13c** is also asymmetric, with two *tert*-butyl groups on the Cp rings adopting a cis configuration and two isocyanide *tert*-butyl groups taking a trans configuration. The six-membered ring Fe1−C9−Si2−Fe2−C16−Si1 constituting the molecular framework adopts a twist-boat conformation. The two Fe−Si bonds (2.289(2) and 2.306(9) Å) are slightly shorter than that of the parent complex **11c** (mean 2.317 Å).[5] The coordinated isocyanide ligands are not as collinear as usual (C4−N2−C31 164.3(6)° and C2−N1−C27 165.3(5)°) due to the high steric congestion of four *tert*-butyl groups. The two Cp rings are almost parallel to each other (dihedral angle 2.1°). The Si(1) and Si(2) atoms are bent out of the corresponding Cp rings by 0.281 and 0.232 Å, respectively.

Mechanism. Although the stereochemistry of the rearrangement appears rather complex when CO groups are replaced by *tert*-butyl isocyanide ligands, the rearrangement reaction still follows the high stereospecificity reported previously (that is, the cis substrate affords the trans product, while the trans substrate produces the cis product) if we only take into account the configuration of two *tert*-butyl groups on the Cp rings. Therefore, the reaction mechanism proposed previously on the basis of the intramolecular nature of this reaction is also applied to the rearrangement of isocyanide-substituted analogues.[5,6b]

However, there still remains the question of why the thermal rearrangement exhibited such a complex stereochemistry and three different rearranged products when CO groups were replaced by isocyanide ligands. It is known that $Cp^*Fe(CO)_2^{\bullet}$ can undergo very rapid CO exchange with free CO dissolved in the solution.[16] Since isocyanide ligands are isostructural to CO groups,

Scheme 1

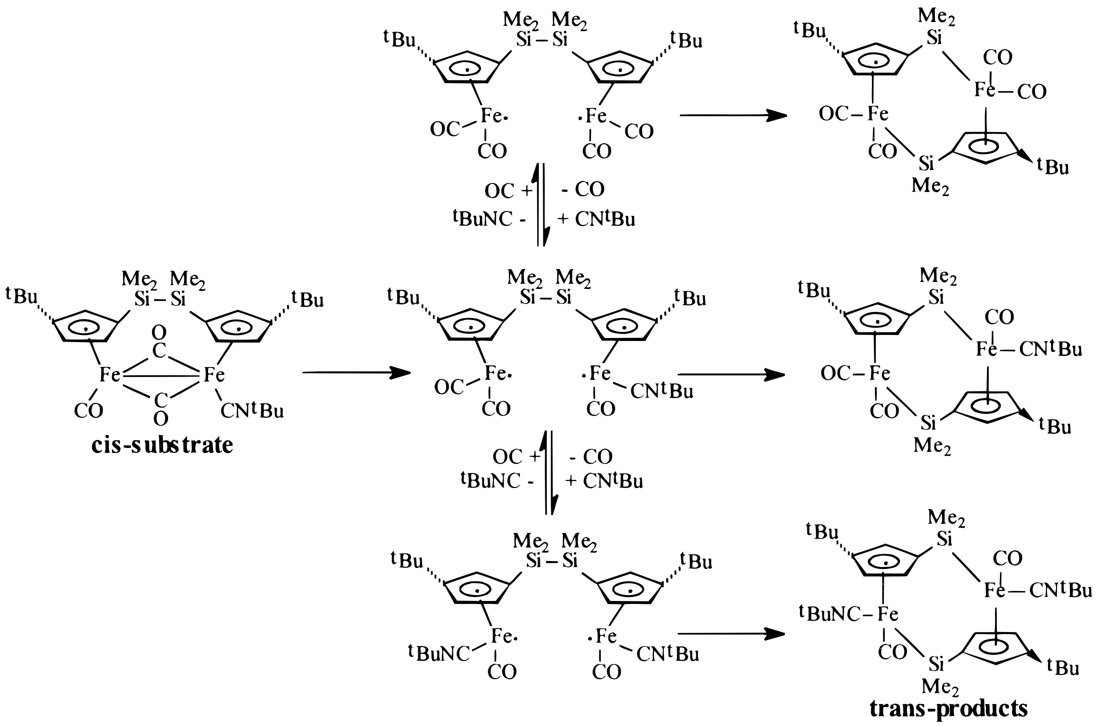

Table 7. Yields of Thermal Reaction Products of 3, 4, 6c, and 6t

substrate	thermal reaction products (yield)		
3	**2** (8%)	**7** (20%)	**9t** (4%)
4	**2** (13%)	**8** (27%)	**10c** (2%), **10t** (3%)
	2 (11%)[a]	**8** (4%)[a]	**10c** (12%), **10t** (6%)[a]
6c	**11t** (9%)	**12t** (40%)	**13t** (3%)
6t	**11c** (7%)	**12c** (30%)	**13c** (2%)

[a] In the presence of *t*-BuNC (2 equiv).

we can assume that iron-centered radical intermediates should undergo very rapid ligand exchange with free CO and isocyanide ligands dissolved in xylene. A possible mechanism involving free ligand exchange is proposed as a supplement to the previously reported mechanism (Scheme 1). The mechanism involves (i) initial ligand exchange to form three different iron-centered radical intermediates, and (ii) subsequent attack of every different iron-centered radical at the Si–Si bond by a concerted or stepwise pathway as proposed previously.[5,6b] Since isocyanide ligands can freely replace any CO group, any isomer could possibly appear in the reaction products. Why did we obtain only some isomers? Simple steric factors will make some isomers energetically favored and facilely formed. However, we do not exclude the possibility that other isomers could not be isolated owing to insufficient quantities .

It seems reasonable that an alternative mechanism involves (i) the disproportionation of the starting substrate to form the other two substrates which thermally rearrange to the corresponding products or (ii) the disproportionation of the rearranged product from the starting substrate to form the other two products. However, its drawback is rather evident if we carefully investigate the rearrangement results. First, if the rearrangement should proceed by a disproportionation process rather than a ligand exchange process, the first rearranged products would have the same yield as the third ones. But all experimental results indicate that the yields of the first products are twice or three times as much as those of the third ones (Table 7). In addition, IR monitoring of the rearrangement reaction of **4** indicated that the other two substrates, **1** and $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CN\text{-}t\text{-}Bu)]_2(\mu\text{-}CO)_2$, did not form over the course of the rearrangement. Second, the assumption that the rearranged product of the starting substrate disproportionately forms the other two products can be excluded by the fact that thermal treatment of a solution of **8** in xylene for 24 h did not yield **2** and **10**. Therefore, the disproportionation process is impossible. Furthermore, we studied the thermal rearrangement of **4** in the presence of *t*-BuNC. The experimental result showed that the yield of the expected rearrangement product **8**, with the monosubstituted isocyanide ligand, decreases significantly and the yield of the product **10**, with disubstituted isocyanide ligands, increases evidently in the presence of 2 equiv of *t*-BuNC. This indicated that the presence of excess isocyanide ligand promoted the ligand exchange between iron-centered radical intermediates and isocyanide ligand. Because the starting material badly decomposed during the thermal rearrangement and a large amount of CO was produced, the yield of the product **2**, without a substituted isocyanide ligand, did not appear to change. This further supported the mechanism involving free ligand exchange during the thermal rearrangement.

In contrast, a $P(OPh)_3$-substituted disilyl-bridged diiron complex did not undergo scrambling of $P(OPh)_3$ during the thermal rearrangement reaction.[6b] This can be attributed to the fact that the replacement of carbonyl groups by isocyanide ligands in diiron complex occurs either by photolysis or by a themal process in

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(16) Moore, B. D.; Poliakoff, M.; Turner, J. T. *J. Am. Chem. Soc.* **1986**, *108*, 1819.

Table 8. Summary of X-ray Diffraction Data

	8	9t	12t	13c
formula	$C_{22}H_{29}Fe_2NO_3Si_2$	$C_{30}H_{44}Fe_2N_2O_2Si_2$	$C_{30}H_{45}Fe_2NO_3Si_2$	$C_{34}H_{54}Fe_2N_2O_2Si_2$
fw	523.34	632.56	635.56	690.68
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
Z	4	2	2	4
a (Å)	14.931(5)	10.733(2)	12.065(3)	12.138(6)
b (Å)	10.207(3)	9.466(1)	16.458(4)	20.892(9)
c (Å)	16.508(3)	15.564(2)	9.296(3)	15.484(4)
α (deg)	90	90	105.45(2)	90
β (deg)	103.32(2)	98.33(1)	93.66(2)	98.64(3)
γ (deg)	90	90	70.91(2)	90
volume (Å^3)	2448(1)	1564.5(7)	1680.7(8)	3881(2)
D_{calc} (g·cm^{-3})	1.420	1.343	1.256	1.182
cryst size (mm)	0.20 × 0.20 × 0.40	0.20 × 0.20 × 0.40	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30
radiation (Å^3)	Mo Kα (0.71069)	Mo Kα (0.71073)	Mo Kα (0.71069)	Mo Kα (0.71069)
μ (cm^{-1})	13.04	10.297	9.62	8.37
data collection method	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
max 2θ (deg)	50.0	46.0	49.7	49.9
total no. of observns	4152	2423	4657	5837
no. of unique data, $I > 3\sigma(I)$	3045	1284	3309	3740
final no. of variables	272	172	344	380
R^a	0.033	0.053	0.029	0.040
$R_w{}^b$	0.043	0.063	0.037	0.050
goodness of fit	1.75	2.13	1.38	1.70

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

benzene, whereas the replacement by phosphite ligands occurs only by photolysis.

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, benzene, toluene, and xylene were distilled from sodium/benzophenone ketyl and purged with argon atmosphere prior to use. Isocyanide ligands $C_6H_{11}NC$ and *t*-BuNC,[17] $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)]_2(\mu\text{-}CO)_2$ (**1**),[4] and $(Me_2SiSiMe_2)[(\eta^5\text{-}t\text{-}BuC_5H_3)\,Fe(CO)]_2(\mu\text{-}CO)_2$ (**5**)[5] were prepared according to literature methods. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained on a BRUKER AC-P 200 spectrometer using $CHCl_3$ (δ 7.24 ppm for ^{1}H and 77.0 ppm for ^{13}C) and $SiMe_4$ as an internal standard. Elemental analyses were performed by a Perkin-Elmer 240C instrument. Infrared spectra were obtained as KBr disks and recorded on a Nicolet 5DX FT-IR spectrometer.

Preparation of $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)_2Fe_2(CO)(CNR)]$-$(\mu\text{-}CO)_2$ (3, R = C_6H_{11}; 4, R = *t*-Bu). A solution of 0.60 g (1.28 mmol) of **1** and 0.21 g (1.92 mmol) of $C_6H_{11}NC$ in 40 mL of benzene was stirred for 11 h. TLC monitoring of the reaction indicated the disappearance of **1**. The solvent was removed under vacuum, the dark red oil residue was chromatographed (neutral alumina, 200−300 mesh, dichloromethane), and the products were recrystallized from hexane to afford 0.50 g (71%) of dark red crystals of **3**. Mp: 164−6 °C. Anal. Calcd for $C_{24}H_{31}$-$Fe_2NO_3Si_2$: C, 52.47; H, 5.69; N, 2.55. Found: C, 52.11; H, 5.71; N, 2.52. ^{1}H NMR ($CDCl_3$) δ: 0.24 (s, 12H, $SiMe_2$), 1.21−1.55 (2 brm, 10H, $(CH_2)_5$), 3.34 (brm, 1H, NCH), 4.55, 4.61, 5.15, 5.27 (s, s, s, s, 8H, Cp). IR (ν_{CO}, cm^{-1}): 2105(m), 1944(s), 1778(m), 1729(s) (KBr); 2112(s), 1945(m), 1741(s) (CH_2Cl_2).

A solution of 0.60 g (1.28 mmol) of **1** and 0.33 g (3.84 mmol) of *t*-BuNC in 30 mL of benzene was stirred at room temperature for 20 h. Treatment similar to that described above afforded 0.50 g (75%) of dark red crystals of **4**. Mp: 113−4 °C. Anal. Calcd for $C_{22}H_{29}Fe_2NO_3Si_2$: C, 50.49; H, 5.59; N, 2.68. Found: C, 50.21; H, 5.76; N, 2.84. ^{1}H NMR ($CDCl_3$): δ 0.24 (s, 12H, $SiMe_2$), 1.14 (s, 9H, *t*-Bu), 4.53, 4.59, 5.12, 5.27 (s, s, s, s, 8H, Cp). IR (ν_{CO}, cm^{-1}): 2110(m), 1996(w), 1951(s), 1781(w), 1732(s) (KBr); 2115(s), 1950(m), 1738(s) (CH_2Cl_2).

Preparation of $(Me_2SiSiMe_2)[(\eta^5\text{-}t\text{-}BuC_5H_3)_2Fe_2(CO)$-$(CN\text{-}t\text{-}Bu)](\mu\text{-}CO)_2$ (6c and 6t). A solution of 0.80 g (1.38 mmol) of **5c** and 0.36 g (4.14 mmol) of *t*-BuNC in 40 mL of benzene was refluxed for 3 h. TLC monitoring of the reaction indicated the disappearance of **5c**. The solvent was removed under vacuum, the dark red oil residue was chromatographed (neutral alumina, 200−300 mesh, dichloromethane/hexane 1:1), and the products were recrystallized from dichloromethane/hexane mixtures to give 0.65 g (74%) of dark red crystals of **6c**. Mp: 149−150 °C. Anal. Calcd for $C_{30}H_{45}Fe_2NO_3Si_2$: C, 56.70; H, 7.14; N, 2.20. Found: C, 56.48; H, 7.11; N, 2.34. ^{1}H NMR ($CDCl_3$): δ 0.15, 0.20, 0.26 (s, s; s, 3H, 6H, 3H, $SiMe_2$), 1.12 (s, 9H, *t*-BuNC), 1.34 (s, 18H, t-BuCp), 4.40, 4.52, 5.00, 5.15 (s, d, s, s, 1H, 3H, 1H, 1H, Cp). IR (ν_{CO}, cm^{-1}): 2119(m), 1943(s), 1741(s).

Treatment similar to that of **5t** as described above afforded green solids of **6t** (64%). Mp: 162−3 °C. Anal. Calcd for $C_{30}H_{45}$-$Fe_2NO_3Si_2$: C, 56.70; H, 7.14; N, 2.20. Found: C, 56.85; H, 7.11; N, 2.54. ^{1}H NMR ($CDCl_3$): δ 0.12, 0.22, 0.23, 0.30 (s, s; s, s, 3H, 3H, 3H, 3H, $SiMe_2$), 1.12 (s, 9H, *t*-BuNC), 1.33, 1.34 (s, s, 9H, 9H, t-BuCp), 4.26, 4.32, 4.49, 4.53, 5.01, 5.13 (s, s, s, d, s, s, 1H, 1H, 1H, 1H, 1H, 1H, Cp). IR (ν_{CO}, cm^{-1}): 2123(m), 2079(w,sh), 1929(s), 1746(s), 1740(s).

Thermal Rearrangement Reactions of 3 and 4. A solution of **3** (0.30 g) in 25 mL of xylene was heated at reflux for 20 h. The solvent was removed under vacuum, and the brown residue was chromatographed (neutral alumina, 200−300 mesh, dichloromethane/hexane, 1:5) to afford three light yellow bands (R_f values: 0.62, 0.48, 0.34). Evaporation of solvents afforded three different yellow crystals: **2**, 20 mg (8%), **7**, 60 mg (20%), and **9t**, 15 mg (4%). **7**: Mp: 88−90 °C. Anal. Calcd for $C_{24}H_{31}Fe_2NO_3Si_2$: C, 52.47; H, 5.69; N, 2.55. Found: C, 52.66; H, 5.77; N, 2.57. ^{1}H NMR ($CDCl_3$): δ 0.34, 0.38, 0.41, 0.44 (s, s, s, s, 3H, 3H, 3H, 3H, $SiMe_2$), 1.31−1.85 (3brm, 10H, $(CH_2)_5$), 3.65 (brm, 1H, NCH), 4.70−4.89 (brm, 6H, Cp), 4.99 (s, 2H, Cp). IR (ν_{CO}, cm^{-1}): 2113(s), 1992(vw,sh), 1908(s). **9t**: Mp: 182−4 °C. Anal. Calcd for $C_{30}H_{42}Fe_2N_2O_2Si_2$: C, 57.15; H, 6.71; N, 4.44. Found: C, 57.25; H, 6.85; N, 4.40. ^{1}H NMR ($CDCl_3$): δ 0.31, 0.35 (s, s, 6H, 6H, $SiMe_2$), 1.33−1.84 (3brm, 10H, $(CH_2)_5$), 3.66 (brm, 1H, NCH), 4.66, 4.82 (s, s, 4H, 4H, Cp). IR (ν_{CO}, cm^{-1}): 2112(s), 1985(vw,sh), 1922(s).

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[17] Schuster, R. E.; Scott, J. E.; Casanova, J. *Org. Synth.* **1966**, *47*, 75.

A solution of **4** (0.70 g) in 30 mL of xylene was heated at reflux for 24 h. Treatment similar to that described above afforded four different light yellow bands. Evaporation of solvents afforded four yellow crystals: **2**, 80 mg (13%), **8**, 0.19 g (27%), **10t**, 15 mg (2%), and **10c**, 20 mg (3%). **8**: Mp: 123−4 °C. Anal. Calcd for $C_{22}H_{29}Fe_2NO_3Si_2$: C, 50.49; H, 5.59; N, 2.68. Found: C, 50.57; H, 5.47; N, 2.69. ^1H NMR ($CDCl_3$): δ 0.35, 0.39, 0.42, 0.44 (s, s, s, s, 3H, 3H, 3H, 3H, $SiMe_2$), 1.39 (s, 9H, *t*-BuNC), 3.65 (brm, 1H, NCH), 4.98−5.02, (brm, 8H, Cp). ^{13}C NMR ($CDCl_3$): δ 6.35, 6.77, 7.06, 7.22 ($SiMe_2$), 40.0 ($C(CH_3)_3$), 57.3 ($C(CH_3)_3$), 80.8, 82.9, 83.3, 84.0, 90.6, 92.8, 92.9, 93.8 (Cp), 92.2, 98.9 (*ipso* Cp), 171.3 (*t*-BuN*C*), 216.1, 216.3, 218.7 (Fe−CO). ^{29}Si NMR ($CDCl_3$): δ 35.5, 35.7. IR (ν_{CO}, cm^{-1}): 2100(m), 2074(w,sh), 1983(s), 1959(w), 1920(s). **10t**: Mp: 200 °C (dec). Anal. Calcd for $C_{26}H_{38}Fe_2N_2O_2Si_2$: C, 53.99; H, 6.62; N, 4.84. Found: C, 54.02; H, 6.37; N, 5.12. ^1H NMR ($CDCl_3$): δ 0.32, 0.35 (s, s, 6H, 6H, $SiMe_2$), 1.38 (s, 18H, *t*-BuNC), 4.64, 4.70, 4.84 (s, s, s, 4H, 2H, 2H, Cp). IR (ν_{CO}, cm^{-1}): 2103(m), 2063(w, sh), 1917(s), 1871(vw). **10c**: Mp: 198−9 °C (dec). Anal. Calcd for $C_{26}H_{38}Fe_2N_2O_2Si_2$: C, 53.99; H, 6.62; N, 4.84. Found: C, 54.01; H, 6.47; N, 5.11. ^1H NMR ($CDCl_3$): δ 0.34 (s, 12H, $SiMe_2$), 1.38 (s, 18H, *t*-BuNC), 4.64, 4.82 (s, s, 4H, 4H, Cp). IR (ν_{CO}, cm^{-1}): 2101(m), 2068(m), 1917(s), 1904(s).

Thermal Rearrangement Reactions of 4 in the Presence of *t*-BuNC. A solution of 1.14 g (2.18 mmol) of **4** and 0.37 g (4.36 mmol) of *t*-BuNC in 50 mL of xylene was refluxed for 24 h. TLC monitoring of the reaction indicated the disappearance of **4**. Treatment similar to that described above afforded four different light yellow bands. Evaporation of solvents afforded four yellow crystals: **2**, 110 mg (11%), **8**, 45 mg (4%), **10t**, 70 mg (6%), and **10c**, 149 mg(12%).

Thermal Rearrangement Reactions of 6c and 6t. A solution of **6c** (0.45 g) in 20 mL of xylene was heated at reflux for 24 h. The solvent was removed under vacuum, and the brown residue was chromatographed (neutral alumina, 200−300 mesh, dichloromethane/hexane, 1:10) to afford three light yellow bands. Evaporation of solvents afforded three different yellow crystals: **11t**, 35 mg (9%), **12t**, 0.18 g (40%) and **13t**, 15 mg (3%). **12t**: Mp: 158−9 °C. Anal. Calcd for $C_{30}H_{45}Fe_2NO_3Si_2$: C, 56.70; H, 7.14; N, 2.20. Found: C, 56.80; H, 7.10; N, 2.40. ^1H NMR ($CDCl_3$): δ 0.25, 0.35, 0.41, 0.43 (s, s; s, s, 3H, 3H, 3H, 3H, $SiMe_2$), 1.27 (s, 18H, *t*-BuCp), 1.37 (s, 9H, *t*-BuNC), 4.41, 4.46, 4.61, 4.74, 4.93 (d, s, s, s, s, 1H, 1H, 2H, 1H, 1H, Cp). IR (ν_{CO}, cm^{-1}): 2100(m), 2069(m), 1982(s), 1941(s), 1915(s). **13t**: Mp: 205 °C (dec). Anal. Calcd for $C_{34}H_{54}Fe_2N_2O_2Si_2$: C, 59.13; H, 7.88; N, 4.06. Found: C, 58.88; H, 7.66; N, 4.16. ^1H NMR ($CDCl_3$): δ 0.24, 0.36, 0.39 (s, s, s, 6H, 3H, 3H, $SiMe_2$), 1.27, 1.28 (s, s, 9H, 9H, *t*-BuCp), 1.36, 1.39 (s, s, 9H, 9H, *t*-BuNC), 4.32, 4.42, 4.53, 4.67, 4.76 (s, s, s, s, s, 2H, 1H, 1H, 1H, 1H, Cp). IR (ν_{CO}, cm^{-1}): 2106(m), 2074(m), 1985(w), 1915(s), 1900(s, sh).

Treatment similar to that of **6t** (0.50 g) as described above afforded three light yellow crystals: **11c**, 30 mg (7%), **12c**, 0.15 (30%), and **13c**, 10 mg (2%). **12c**: Mp: 145−6 °C. Anal. Calcd for $C_{30}H_{45}Fe_2NO_3Si_2$: C, 56.70; H, 7.14; N, 2.20. Found: C, 56.91; H, 7.03; N, 2.46. ^1H NMR ($CDCl_3$): δ 0.34, 0.35, 0.42 (s, s; s, 3H, 3H, 6H, $SiMe_2$), 1.22, 1.23 (s, s, 9h, 9H, *t*-BuCp), 1.38 (s, 9H, *t*-BuNC), 4.52, 4.64, 4.70, 4.76, 4.87 (s, s, s, s, s, 1H, 2H, 1H, 1H, 1H, Cp). IR (ν_{CO}, cm^{-1}): 2105(m), 2073(m), 1981(s), 1920(s). **13c**: Mp: 215−6 °C. Anal. Calcd for $C_{34}H_{54}Fe_2N_2O_2Si_2$: C, 59.13; H, 7.88; N, 4.06. Found: C, 58.64; H, 7.56; N, 4.26. ^1H NMR ($CDCl_3$): δ 0.30, 0.34, 0.36 (s, s; s, 6H, 3H, 3H, $SiMe_2$), 1.19, 1.25 (s, s, 9H, 9H, *t*-BuCp), 1.38, 1.40 (s, s, 9H, 9H, *t*-BuNC), 4.41, 4.55, 4.67 (s, s, t, 2H, 3H, Cp). IR (ν_{CO}, cm^{-1}): 2101(m), 2062(m), 1910(s), 1897(s).

Crystallographic Studies. Crystals suitable for X-ray diffraction were obtained from hexane/dichloromethane solutions. All data sets were collected on Enraf-Nonius CAD-4 (**9t**) or Rigaku AFC 7R (**8**, **12t**, and **13c**) diffractometers with graphite-monochromated Mo Kα radiation. The corrections for empirical absorption were applied to intensity data. All structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. All calculations for **8**, **12t**, and **13c** were performed using the teXsan Crystallographic Software Package of Molecular Structure Corp., while for **9t** PDP11/44 and Pentium MMX/166 computers was used. Neutral atom scattering factors were taken from the tabulations of Cromer and Waber.[18] A summary of the crystallographic results is presented in Table 8.

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Supporting Information Available: Tables of final postional and thermal parameters of the non-hydrogen atoms, general temperature factors, and bond distances and angles for **8**, **9t**, **12t**, **13t**, and **13c**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9902683

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