Organometallics **2006,** *25,* 133−139

Stereochemistry of the Thermal Rearrangement through Intramolecular Metathesis of Si−Si and Fe−Fe Bonds: First Evidence for a Nonconcerted Mechanism

Huailin Sun,* Yanbin Pan, Xuebin Huang, Zhonghuai Guo, Zhensheng Zhang, Huili Zhang, Jinmeng Li, and Fei Wang

Department of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

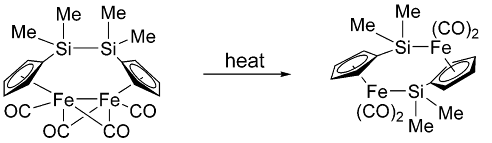
Received July 25, 2005

meso and *rac* isomers of $(\eta^5{:}\eta^5\text{-}C_5H_4RMeSiSiMeRC_5H_4)Fe_2(CO)_2(\mu\text{-}CO)_2$ (R = Ph, *n*-Bu) were synthesized and successfully separated for the first time. They were found to undergo the title rearrangement reaction in a nonstereospecific fashion, to give the products $[RMeSi\text{-}\eta^5\text{-}C_5H_4Fe(CO)_2]_2$ as mixtures of *meso* and *rac* isomers in ratios of about 1:1. This is direct evidence to rule out the concerted free radical mechanism that is currently used to explain this reaction. A new mechanism involving activation of the Si−Si bond by a coordinatively unsaturated iron center is suggested.

Introduction

Facile activation of Si−Si bonds by transition metals has been of interest in recent years because it leads to many intriguing reactions.[1,2] This kind of activation has most frequently been found to occur intramolecularly in transition-metal systems containing Si−Si bonds. Among the systems that have been studied, those with Si−Si bonds linked directly to transition-metal centers have received the most attenton.[3] Also studied have been systems with Si−Si bonds linked to the metal centers through an η^1-methylene or η^4-butadiene ligand.[4,5] However, intramolecular activation of Si−Si bonds by transition metals has remained largely unexplored until very recently. This situation has been changed, however, by the finding that a Si−Si bond linked to a η^5-cyclopentadienyl ligand could also be activated by intramolecular transition metals.[6]

The latter kind of Si−Si bond activation was first reported by Sun et al. in 1993.[6a] It took place in the cyclic structure of $(\eta^5{:}\eta^5\text{-}C_5H_4Me_2SiSiMe_2C_5H_4)Fe_2(CO)_2(\mu\text{-}CO)_2$ (**1**) under thermal conditions and proceeded formally via metathesis of the Si−Si and Fe−Fe bonds, to give the rearranged product $[Me_2Si\text{-}\eta^5\text{-}C_5H_4Fe(CO)_2]_2$ (**2**) containing two Si−Fe bonds (eq 1).



1 **2** (1)

This was a completely new reaction type,[7] and its mechanism was far from easy to understand at that time. Of particular interest is that this reaction could occur in other cyclic complexes similar to **1**, including those with a Ge−Ge bond in place of the Si−Si bond and/or a Ru−Ru bond in place of the Fe−Fe bond,[8] demonstrating the general importance of the rearrangement process.

In the past dozen years, much progress has been achieved in revealing details of the reaction, including its thermally induced character,[6] its intramolecular nature,[9,10] and its phosphorus ligand

---

* To whom correspondence should be addressed. E-mail: sunhl@nankai.edu.cn.

(1) For reviews containing this subject, see: (a) Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 419−421. (b) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351−1374. (c) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175−229. (d) Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317−1350. (e) Suginome, M.; Ito, Y. *J. Chem. Soc., Dalton Trans.* **1998**, 1925−1934. (f) Beletskaya, I.; Moberg, C. *Chem. Rev.* **1999**, *99*, 3435−3461. (g) Suginome, M.; Ito, Y. *Chem. Rev.* **2000**, *100*, 3221−3256.

(2) Some recent papers: (a) Nlate, S.; Herdtweck, E.; Fischer, R. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1861−1863. (b) Tamao, K.; Sun, G.-R.; Kawachi, A. *J. Am. Chem. Soc.* **1995**, *117*, 8043−8044. (c) Mitchell, G. P.; Tilley, T. D. *Organometallics* **1996**, *15*, 3477−3479. (d) Suginome, M.; Oike, H.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 1665−1666. (e) Suginome, M.; Oike, H.; Park, S.-S.; Ito, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 289−299. (f) Suginome, M.; Kato, Y.; Takeda, N.; Oike, H.; Ito, Y. *Organometallics* **1998**, *17*, 495−497. (g) Murakami, M.; Yoshida, T.; Ito, Y. *Chem. Lett.* **1996**, 13−14. (h) Schubert, U.; Pfeiffer, J.; Stöhr, F.; Sturmayr, D.; Thompson, S. *J. Organomet. Chem.* **1997**, *548*, 57−63. (i) Pannell, K. H.; Kobayashi, T.; Cervantes-Lee, F.; Zhang, Y. *Organometallics* **2000**, *19*, 1−3. (j) Zhang, Y. Q.; Pannell, K. H. *Organometallics* **2002**, *21*, 503−510. (k) Tobita, H.; Sato, T.; Okazaki, M.; Ogino, H. *J. Organomet. Chem.* **2000**, *611*, 314−322. (l) Ueno, K.; Asami, S.; Watanabe, N.; Ogino, H. *Organometallics* **2002**, *21*, 1326−1328. (m) Naka, A.; Ishikawa, M.; Cha, S. H.; Lee, K. K.; Kwak, Y. W. *J. Organomet. Chem.* **2002**, *645*, 47−53. (n) Williams, N. A.; Uchimaru, Y.; Tanaka, M. *Dalton Trans.* **2003**, 236−243.

(3) (a) Ueno, K.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1988**, *110*, 4092−4093. (b) Pannell, K. H.; Sharma, H. K.; Kapoor, R. N.; Cervantes-Lee, F. *J. Am. Chem. Soc.* **1997**, *119*, 9315−9316.

(4) Zhang, Y.; Cervantes-Lee, F.; Pannell, K. H. *J. Am. Chem. Soc.* **2000**, *11*, 2229−2235.

(5) Nakadaira, Y.; Kobayashi; T.; Sakurai, H. *J. Organomet. Chem.* **1979**, *165*, 399−405.

(6) (a) Sun, H.; Xu, S.; Zhou, X.; Wang, H.; Yao, X. *J. Organomet. Chem.* **1993**, *444*, C41−C43. (b) Sun, H.; Zhou; X.; Yao, X.; Wang, H. *Polyhedron* **1996**, *15*, 4489−4495. (c) Sun, H.; Zhang, Z.; Pan, Y.; Yang, J.; Zhou, X. *Inorg. Chem.* **2003**, *42*, 4076−4081.

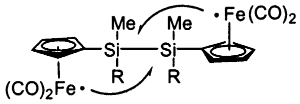
(7) Similar rearrangements, but not involving Si−Si bonds, are known. For example, see: (a) Bitterwolf, T. E.; Shade, J. E.; Hansen, J. A.; Rheingold, A. L. *J. Organomet. Chem.* **1996**, *514*, 13−21. (b) Boese, R.; Cammack, J. K.; Matzger, A. J.; Pflug, K.; Tolman, W. B.; Vollhardt, K. P. C.; Weidman, T. W. *J. Am. Chem. Soc.* **1997**, *119*, 6757−6773. (c) Fox, T.; Burger, P. *Eur. J. Inorg. Chem.* **2001**, 795−803.

(8) (a) Zhou, X.; Xie, W.; Xu, S. *Chin. Chem. Lett.* **1996**, *7*, 385−386. (b) Xie, W.; Wang, B.; Dai, X.; Xu, S.; Zhou, X. *Organometallics* **1998**, *17*, 5406−5410. (c) Xie, W.; Wang, B.; Dai, X.; Xu, S.; Zhou, X. *J. Chem. Soc., Dalton Trans.* **1999**, 1141−1146. (d) Xie, W.; Wang, B.; Xu, S.; Zhou, X. *Polyhedron* **1999**, *18*, 1647−1651. (e) Zhang, Y.; Xu, S.; Zhou, X. *Organometallics* **1997**, *16*, 6017−6020. (f) Zhang, Y.; Wang, B.; Xu, S.; Zhou, X.; Sun, J. *J. Organomet. Chem.* **1999**, *584*, 356−360.

(9) Sun, H.; Huang, X.; Hu, Z.; Zhang, Z.; Leng, X.; Weng, L. *Inorg. Chim. Acta* **2003**, *348*, 8−14.

10.1021/om050622z CCC: $33.50

Chart 1



enhancing effect.[11] However, some difficulties in understanding the mechanism still exist. Our most recent results demonstrated that the ring containing the Si−Si bond in **1** is not significantly strained.[6c,12] This implies that cleavage of the rather thermally stable[13] Si−Si bond requires activation by transition metals. In addition, an ongoing study by our group[14] revealed first-order kinetics for the disappearance of the substrate, confirming an unimolecular process.[9] Thus, how the Si−Si bond is activated by an intramolecular transition-metal center becomes the key to understanding the mechanism.

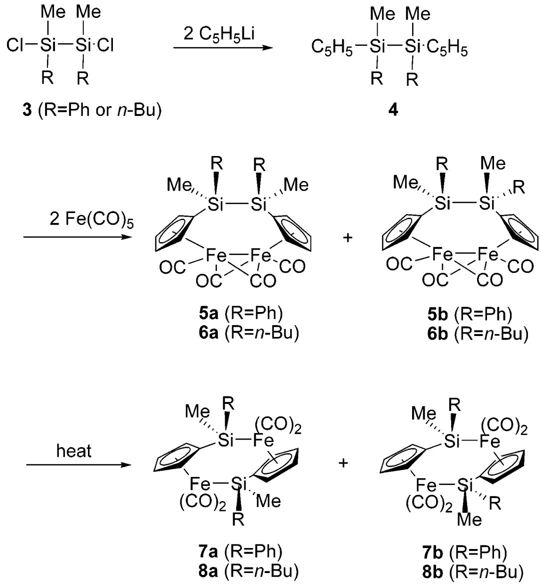
Several possible mechanisms have been considered or suggested for this reaction. Of these, the free radical mechanism proposed by Zhou et al. has been the most widely accepted.[10,15] This mechanism involves attack on the Si−Si bond by two iron-centered free radicals, produced by homolytic rupture of the weak Fe−Fe bond, to result in formation of two Si−Fe bonds in either a stepwise or a concerted pathway. It was recently found, however, that the stepwise pathway is less possible because it is not consistent with the regiospecific cleavage of the Si−Si bond in the cyclic structure when additional Si−Si bonds outside the cyclic structure are present.[9] Under this circumstance, whether the concerted free radical pathway is followed constitutes a challenging question.

The best way to address this issue is to study the stereochemistry. Since the concerted free radical pathway that involves simultaneous breaking of the Si−Si bond and formation of two Si−Fe bonds should inevitably lead to retention of stereoconfiguration at the silicon centers (Chart 1), the stereochemistry on silicon should be the object of study. Herein, we report the results of our study, which surprisingly demonstrate that the reaction is not stereospecific. Therefore, the concerted free radical mechanism that has long been used to explain this reaction has to be ruled out.

Results and Discussion

We introduced different substituents on silicon by using different disilanes, ClRMeSiSiMeRCl (**3**: R = Ph, *n*-Bu), prepared as 1:1 *meso* and *rac* mixtures according to literature procedures,[16] as the starting materials. The reaction of **3** with 2 equiv of C_5H_5Li produced $C_5H_5RMeSiSiMeRC_5H_5$ (**4**), which reacted subsequently with $Fe(CO)_5$ to give the desired complexes (η^5:η^5-$C_5H_4RMeSiSiMeRC_5H_4$)$Fe_2(CO)_2(\mu\text{-}CO)_2$ (**5**, R = Ph; **6**, R = *n*-Bu) as red crystals; meanwhile, the rearranged products [{RMeSi-η^5-$C_5H_4Fe(CO)_2$}$_2$] (**7**, R = Ph; **8**, R = *n*-Bu) were also obtained as yellow crystals (Scheme 1).

Scheme 1



Both **5** and **6** were mixtures of *meso* (or *cis*) and *rac* (or *trans*) isomers, as demonstrated by their ^{1}H NMR spectra, but the ratios had changed dramatically from those of the starting materials.[17] In the phenyl case, the *cis* (**5a**) and *trans* (**5b**) isomers were present in about an 8:1 ratio, which allowed easy isolation of the *cis* isomer by recrystallization. The low yield of the *trans* isomer made it difficult to isolate it in pure form. This shortcoming could be overcome by using *n*-butyl in place of phenyl (i.e. **6a**,**b**). In this case, the ratio of the *cis* (**6a**) to *trans* (**6b**) isomers was 1:1.1. The *trans* isomer was isolated by recrystallization of the mixture at −20 °C, taking advantage of its lower solubility. The more soluble *cis* isomer could be obtained from the mother liquor after repeated careful crystallizations.

The pure isomers were fully characterized by elemental analyses and spectroscopic methods. The IR spectra of all isomers showed very similar absorption bands for terminal CO groups at higher frequencies and for bridging CO groups at lower positions. The ^{1}H NMR spectra also are quite similar for each pair of isomers, but there were slight differences, e.g. in the chemical shifts of the Si−Me protons, which was used for quantitative determination of the ratios of the two isomers (vide supra). Better resolution of signals was observed in the ^{13}C NMR spectra, in which even the phenyl and *n*-butyl groups of the *cis* and *trans* isomers could be distinguished from one another. Of particular interest is that the bridging CO carbon atom gave rise to two signals for *cis* isomers but only one signal for *trans* isomers, which is in accord with their structures and can be taken as reliable evidence for assigning their *cis* and *trans* configurations.

More direct evidence for the configurations was achieved by an X-ray diffraction study of the molecular structures of **5a** (Figure 1) and **6b** (Figure 2), which clearly showed the *cis* arrangement of phenyl groups for **5a** and the *trans* relationship

---

(10) Zhou, X.; Zhang, Y.; Xie, W.; Xu, S.; Sun, J. *Organometallics* **1997**, *16*, 3474−3481.

(11) Sun, H.; Teng, X.; Huang, X.; Hu, Z.; Pan, Y. *J. Organomet. Chem.* **2000**, *595*, 268−275.

(12) Sun, H.; Zhang, Z.; Zhou, X. *Chin. J. Chem.* **2003**, *21*, 839−842.

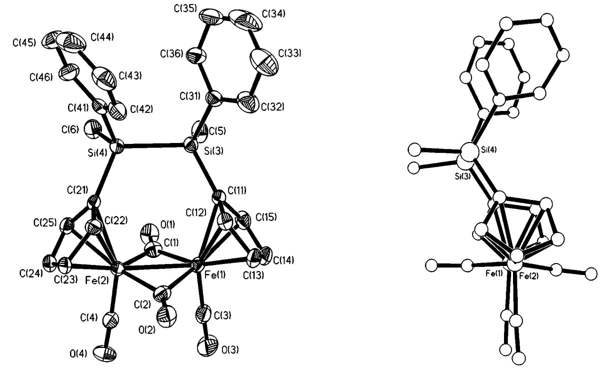
(13) West, R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1983; Vol. 9, p 365.

(14) Sun, H.; Wang, F.; et al. Unpublished results.

(15) (a) Wang, B.; Zhang, Y.; Xu, S.; Zhou. X. *Organometallics* **1997**, *16*, 4620−4625. (b) Zhang, Y.; Xu, S.; Tian, G.; Zhou, X.; Sun, J. *Organometallics* **1998**, *17*, 1122−1127. (c) Zhang, Y.; Sun, X.; Wang, B.; Xu, S.; Zhou, X. *Organometallics* **1999**, *18*, 4493−4500.

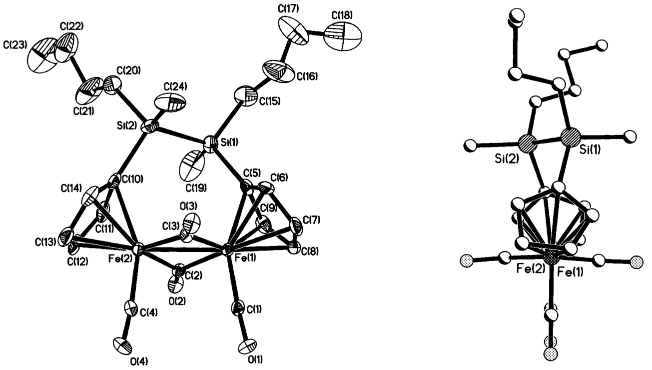
(16) (a) Tamao, K.; Kumada, M.; Ishikawa, M. *J. Organomet. Chem.* **1971**, *31*, 17−34. (b) Sakurai, H.; Yoshida, M.; Sakamoto, K. *J. Organomet. Chem.* **1996**, *521*, 287−293.

(17) Preferential formation of one of diastereoisomers is often reported for Si−Si bond-containing compounds. For recent examples, see: (a) El-Sayed, I.; Hatanaka, Y.; Muguruma, C.; Shimada, S.; Tanaka, M.; Koga, N.; Mikami, M. *J. Am. Chem. Soc.* **1999**, *121*, 5095−5096. (b) Bohme, U.; Gunther, B.; Rittmeister, B. *Inorg. Chem. Commun.* **2000**, *3*, 428−432. (c) Trankler, K. A.; Wyman, D. S.; Corey, J. Y.; Katz, E. E. *Organometallics* **2000**, *19*, 2408−2410. (d) Trankler, K. A.; Wyman, D. S.; Corey, J. Y.; Katz, E. E.; Rath, N. P. *Organometallics* **2001**, *20*, 5139−5148. (e) Kaats-Richters, V. E. M.; Cleij, T. J.; Jenneskens, L. W.; Lutz, M.; Spek, A. L.; van Walree, C. A. *Organometallics* **2003**, *22*, 2249−2258.



(a) (b)

Figure 1. (a) ORTEP plot of **5a** (30% probability level). Selected bond lengths (Å) and angles (deg): Si(3)−Si(4) = 2.359(2), Fe(1)−Fe(2) = 2.535(1), Si(3)−C(11) = 1.869(6), Si(4)−C(21) = 1.882(6), Fe(1)−C(11) = 2.167(6), Fe(2)−C(21) = 2.154(6); Si(3)−Si(4)−C(21) = 114.6(2), Si(4)−Si(3)−C(11) = 114.4(2), Fe(1)−Fe(2)−C(21) = 108.2(2), Fe(2)−Fe(1)−C(11) = 109.2(2), Fe(2)−C(21)−Si(4) = 133.6(3). (b) Side view of **5a**.



(a) (b)

Figure 2. (a) ORTEP plot of **6b** (15% probability level). Selected bond lengths (Å) and angles (deg): Si(1)−Si(2) = 2.339(7), Fe(1)−Fe(2) = 2.5518(16), Si(1)−C(5) = 1.895(10), Si(2)−C(10) = 1.916(12), Fe(1)−C(5) = 2.178(9), Fe(2)−C(10) = 2.154(10); Si(2)−Si(1)−C(5) = 106.9(4), Si(1)−Si(2)−C(10) = 106.7(4), C(10)−Fe(2)−Fe(1) = 108.4(3), C(5)−Fe(1)−Fe(2) = 107.9(3), Si(1)−C(5)−Fe(1) = 130.2(5). (b) Side view of **6b**.

of the two *n*-butyl groups for **6b**. Interestingly, the two molecules have very different conformations. In the molecule of **5a**, the two Cp groups are eclipsed with respect to each other. The Si−Si bond links two Cp groups from one side but not on the top of the molecule (Figure 1b), giving a boatlike conformation for the six-membered cyclic structure composed of two silicon, two iron, and two bridgehead Cp carbon atoms. This is due to the fact that the Si−Si bond is too long to fit into the space between two Cp groups on the top, to form a coplanar conformation in the six-membered ring. In the molecule of **6b**, the two Cp groups are staggered. The Si−Si bond stays on the top but twists away from the direction parallel to the axis of the Fe−Fe bond (Figure 2b), to minimize the molecular strain caused by the long Si−Si bond. This produces a twisted-boat conformation for the six-membered cyclic structure. These two molecules provide the representative conformations that the cyclic structure could adopt without causing significant ring strain.

The length of the Si−Si bond of **5a** is 2.359(2) Å, identical with that in $(PhMeSi)_6$ (2.359 Å);[18] while the Si−Si bond length of **6b** is 2.339(7) Å, comparable to that in $(Me_2Si)_6$ (2.338 Å).[19] The lengths of the Fe−Fe bonds are 2.535(1) Å for **5a** and 2.5518(16) Å for **6b**. The former is nearly identical with the Fe−Fe bond length in the parent complex *cis*-$[CpFe(CO)_2]_2$ (2.531(2) Å),[20] whereas the latter is slightly longer than that of the former. This lengthening of the Fe−Fe bond in the latter case should be due to the twisted-boat conformation, which tends to compress the Si−Si bond but extend the Fe−Fe bond. This conformational change is also accompanied by the reduction of the dihedral angle between two Cp planes from 79.2° for **5a** to 73.4° for **6b**.

Next, the thermal rearrangements of the pure isomers were studied. Upon heating in *p*-xylene at the reflux temperature, all pure isomers, i.e., **5a** and **6a**,**b**, were transformed gradually into their respective rearranged products, which were yellow crystals (Scheme 1). Analyses of these products were carried out using ^1H and ^{13}C NMR spectroscopy, to see if they could be single isomers, as expected according to the concerted free radical mechanism. To our surprise, however, these products were mixtures of *cis* (or *rac*) and *trans* (or *meso*) isomers in ratios of about 1:1. Specifically, the mixture obtained from **5a** was composed of the *cis* (**7a**) and *trans* (**7b**) isomers in a 46:54 ratio, as determined by ^1H NMR spectroscopic methods, while **6a**,**b** produced mixtures containing the *cis* (**8a)** and *trans* (**8b)** isomers in ratios of 45:55 and 52:48, respectively, as determined by ^{13}C NMR spectroscopy (vide infra).

Separation and complete characterization of the rearranged isomers were accomplished. Taking advantage of the fact that the *trans* isomers were significantly less soluble than the corresponding *cis* isomers, *trans* isomers **7b** and **8b** were easily isolated in pure form by fractional crystallization. *cis* isomers **7a** and **8a** also were obtained from the mother solution by repeated crystallization. All isomers were pure by elemental analysis. Their IR spectra generally showed two CO absorption bands at relatively high frequencies, consistent with the existence of only terminal CO groups. It was impressive that all ^1H and ^{13}C NMR peaks for **7a**,**b** could be found in the spectrum of their mixture, and the signals due to Si−Me protons were used for determination of their ratio. On the other hand, although all peaks of the ^1H NMR spectra of **8a**,**b** appeared in their mixture, the chemical shifts were too close to be analyzed quantitatively. Fortunately, the ^{13}C NMR spectra of the isomers exhibited enough differences, and the signals due to Si−Me carbon atoms were used to determine the ratio of the two isomers (see the Experimental Section).

In addition, the molecular structures of **7b** (Figure 3) and **8b** (Figure 4) were determined by X-ray diffraction methods. The results demonstrated that both molecules have the expected *trans* configurations. These molecules are centrosymmetric in the crystalline state. The six-membered rings composed of two silicon, two iron, and two bridgehead Cp carbon atoms adopted standard chairlike conformations. Compared with the boatlike conformations before rearrangement, the formation of these strainless chairlike conformations must be accompanied by relaxation of the molecular strain that might exist to some extent in the starting complexes. This was expected to constitute one of the driving forces for this reaction described in the previous paper.[6a] The exact way in which the molecular strain acts as the driving force is to be investigated in a following paper. The

---

(18) Chen, S. M.; Davia, L. D.; Haller, K. J.; Wadsworth, C. L.; West, R. *Organometallics* **1983**, *2*, 409−414.

(19) Carrell, H. L.; Donohue, J. *Acta Crystallogr., Sect. B* **1972**, *28*, 1566−1571.

(20) Bryan, R. F.; Greene, P. T.; Newlands, M. J.; Field, D. S. *J. Chem. Soc. A* **1970**, 3068−3074.

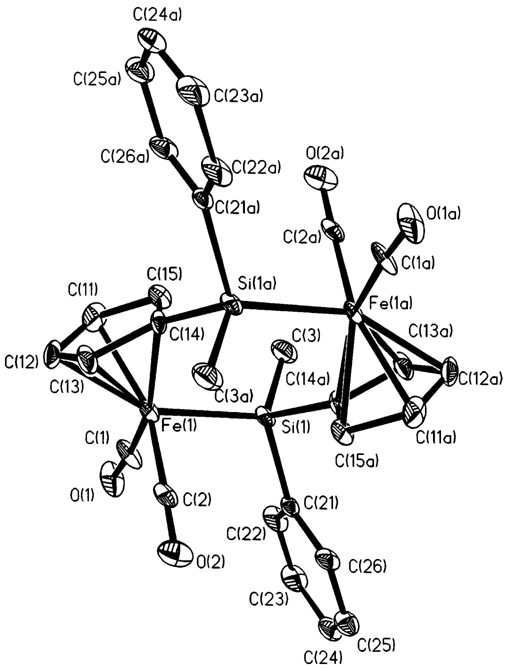


Figure 3. ORTEP plot of **7b** (30% probability level). Selected bond lengths (Å) and angles (deg): Fe(1)−Si(1) = 2.312(2), Si(1)−C(14a) = 1.911(7), Fe(1)−C(14) = 2.098(5), Fe(1)−C(1) = 777(7), Fe(1)−C(2) = 1.752(9); Si(1)−Fe(1)−C(14) = 99.6(2), Fe(1)−Si(1)−C(14a) = 112.6(2), Fe(1)−C(14)−Si(1a) = 130.2(3), C(3)−Si(1)−C(21) = 105.7(4), C(1)−Fe(1)−C(2) = 94.4(4).

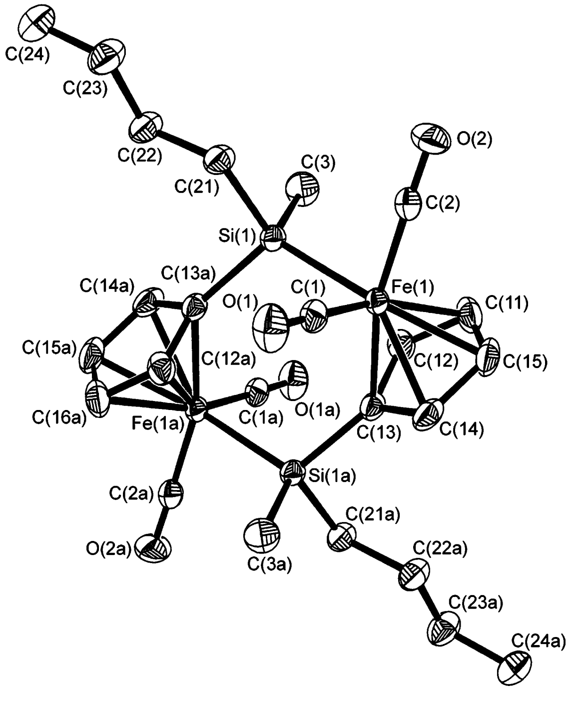


Figure 4. ORTEP plot of **8b** (30% probability level). Selected bond lengths (Å) and angles (deg): Fe(1)−Si(1) = 2.319(1), Si(1)−C(13a) = 1.882(2), Fe(1)−C(13) = 2.103(2); Si(1)−Fe(1)−C(13) = 99.5(1), Fe(1)−C(13)−Si(1a) = 132.8(1), Fe(1)−Si(1)−C(13a) = 112.1(1).

lengths of the Si−Fe bonds are 2.312(2) Å for **8b** and 2.319(1) Å for **9b**, which are much shorter than the averages of the Si−Si and Fe−Fe bonds for **6a** (2.447 Å) and **7b** (2.445 Å), demonstrating extraordinary stability of the Si−Fe bonds (see below). The formation of the highly stable Si−Fe bonds may be another driving force for the metathesis reaction.[6a]

The results obtained above unambiguously demonstrated that the rearrangement reaction is nonstereospecific. This indicates that cleavage of the Si−Si bond and formation of two Si−Fe bonds were not taking place simultaneously but were following a stepwise pathway, during the course of which stereorandomization has occurred.[21] Therefore, the concerted free radical mechanism stated above has to be ruled out. This means that the whole free radical mechanism does not work for the reaction, given that the stepwise free radical pathway has already been excluded as mentioned above. In other words, it seems that the iron-centered free radicals are not able to break the Si−Si bond, although they may be formed during the reaction process. This actually should not be very surprising. We note that the free radical mechanism has been proposed mainly on the basis of an in situ ESR observation of a paramagnetic signal that has been attributed to the iron-centered free radical,[10] whereas the observation of the free radical does not mean it has to be responsible for cleavage of the Si−Si bond.[22]

In fact, almost all Si−Si bond activation reactions reported to date have been proven or are believed to follow an oxidative addition mechanism that involve cleavage of Si−Si bonds by coordinatively unsaturated metal centers. To our knowledge, the above free radical mechanism would be the only example of an intramolecular Si−Si bond activation explained without using the oxidative addition mechanism. Now, the ruling out of the free radical mechanism would strongly suggest that an oxidative addition mechanism should be seriously considered.

Obviously, to generate a vacant coordination site on a metal center is a prerequisite for oxidative addition of the Si−Si bond to occur. In principle, there are two possible pathways to produce such a vacant coordination site on the iron centers according to the ligands existing in the present system: dissociation of CO ligand or η^5−η^3 slippage[23,24] of the Cp group. At high temperatures, both processes would be possible, to afford **9** and **10**, respectively (see Scheme 2). The Si−Si bond would then add to the coordinatively unsaturated iron center, resulting in oxidative adducts **11** and **12**. These adducts should be thermally unstable, due especially to the existence of the four-membered cyclic structures containing an Fe−Fe bond. They would be further transformed, through cleavage of the weak Fe−Fe bond, into **13** and **14**. The η^6- and η^4-silafulvene structures in the latter species would also tend to resume a η^5-Cp coordination form through breaking the Fe−Si linkages, promoted probably by recombination of CO and η^3−η^5 backward slippage of Cp, leading to the key intermediate **15**. The latter contains a silicon-

---

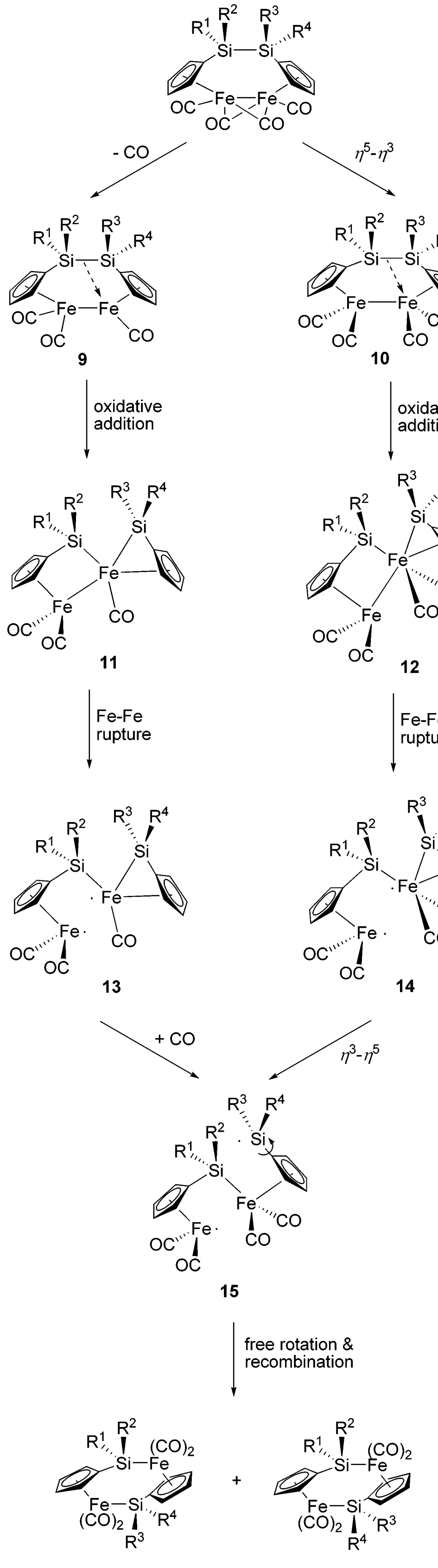
(21) The stereorandomization cannot take place after the rearrangement. This has been confirmed experimentally by treating the pure isomers of the rearranged products under thermal conditions.

(22) In fact, the in situ ESR observation is also questionable, since there are always a large amount of unidentified decomposition products being formed during the reaction process (up to 40% for the reaction shown in eq 1[6a]), which renders the system very complicated and not suitable for in situ ESR study.

(23) For reviews, see: (a) Joseph, M. O.; Charles, P. C. *Chem. Rev.* **1987**, *87*, 307−318. (b) Calhorda, M. J.; Romao, C. C.; Veiros, L. F. *Chem. Eur. J.* **2002**, *8*, 868−875.

(24) For recent papers, see: (a) Calhorda, M. J.; Gamelas, C. A.; Romao, C. C.; Veiros, L. F. *Eur. J. Inorg. Chem.* **2000**, 331−340. (b) Simanko, W.; Sapunov, V. N.; Schmid, R.; Kirchner, K. *Organometallics* **1998**, *17*, 2391−2393. (c) Yan, X.; Cherenga, A. N.; Metzler, N.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1997**, 2091−2099. (d) Green, J. C.; Perkin, R. P. G.; Yan, X.; Haaland, A.; Scherer, W.; Tafipolsky, M. A. *J. Chem. Soc., Dalton Trans.* **1997**, 3219−3224. (e) Zhang, S.; Brown, T. L. *J. Am. Chem. Soc.* **1993**, *115*, 1779−1789. (f) Yang, H.; Kotz, K. T.; Asplund, M. C.; Harris, C. B. *J. Am. Chem. Soc.* **1997**, *119*, 9564−9565. (g) Dunwoody, N.; Lees, A. J. *Organometallics* **1997**, *16*, 5770−5778. (h) Vest, P.; Anhaus, J.; Bajaj, H. C.; van Eldik, R. *Organometallics* **1991**, *10*, 818−819. (i) Butts, M. D.; Bergman, R. G. *Organometallics* **1994**, *13*, 1899−1910.

Scheme 2



centered free radical, which would allow for free rotation around the Si−Cp bond, resulting in stereorandomization in the final products.

Of the two pathways, evidence accumulated up to now seems to support the latter rather than the former. For example, photochemical conditions that could induce CO loss did not lead to the rearrangement.[6,25] In addition, η^4-silatrimethylenemethane complexes that closely resemble the η^4-silafulvene coordination form in **12** and **14** have been structurally characterized,[26] whereas a η^6-silafulvene complex such as those in **11** and **13** is entirely unknown. To further distinguish between the two oxidative addition pathways[27] is not the task of the present paper, however. What we wish to point out here is that, according to the experimental results obtained up to now, it seems that an oxidative addition mechanism is most probably followed by the present reaction.

In summary, we have successfully studied the stereochemistry of the title reaction and demonstrated that the reaction does not have stereospecificity. This provides direct evidence to rule out the possibility of the concerted free radical mechanism that is currently used to explain this reaction. A new mechanism involving activation of the Si−Si bond by oxidative addition to a coodinatively unsaturated iron center has been suggested. Further study of the latter mechanism, aiming at revealing underlying principles that control the Si−Si bond activation, is actively underway.

Experimental Section

General Considerations. All reactions were carried out under an argon atmosphere by using standard Schlenk and vacuum-line techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity-plus 400 or Mercury-300BB spectrometer. A longer delay time of 5 s was used in quantitative ^{1}H NMR analyses, and a gated decoupling mode was applied for ^{13}C NMR determination of ratios of the isomers. IR spectra were recorded using a Bruker Smart 1000 instrument. Elemental analyses were performed using a Vario EL instrument. THF, *n*-hexane, and *p*-xylene were dried by refluxing with sodium in the presence of benzophenone and distilled before use. ClPhMeSiSiMePhCl[16a] and Cl(*n*-Bu)MeSiSiMe(*n*-Bu)Cl[16b] were prepared according to the literature methods. Other chemicals were used as purchased.

Synthesis of (η^5:η^5-C_5H_4PhMeSiSiMePhC_5H_4)$Fe_2(CO)_2(\mu$-$CO)_2$ (5). To a stirred solution of C_5H_5Li, prepared from C_5H_6 (3.0 g, 0.045 mol) in THF (40 mL) and *n*-butyllithium in hexane (33 mL, 1.37 M, 0.045 mol) at −78 °C, was added ClPhMeSiSiMePhCl (**3**, R = Ph; 6.2 g, 0.02 mol) in THF (40 mL). After it was warmed to room temperature, stirring was continued for 12 h. The mixture was hydrolyzed with water, extracted with petroleum ether (100 mL), and then dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to give a waxlike solid of C_5H_5PhMeSiSiMePhC_5H_5 (**4**, R = Ph), which was used, without further purification, to react with $Fe(CO)_5$ (8.8 g, 0.045 mol) in refluxing *p*-xylene (40 mL) for 12 h. Then, the solvent was distilled off under reduced pressure (unreacted $Fe(CO)_5$, which is poisonous, should be collected with a liquid nitrogen trap!). The solid residue was separated through a column (neutral Al_2O_3, petroleum ether/benzene 2:1) to give a red band following a yellow band, from which dark red crystals of the desired complex **5** (1.4 g, 12% yield) and yellow crystals of the rearranged product **7** (0.25 g, 2% yield) were obtained, respectively. On the basis of ^{1}H NMR spectroscopy, **5** contained the *cis* (**5a**) and *trans* (**5b**) isomers in a ratio of about 8:1. Recrystallization of this mixture with hexane containing a small

---

(25) Xie, W.; Wang, B.; Xu, S.; Zhou, X.; Cheng, K. *Polyhedron* **1999**, *18*, 2645−2650.

(26) Ando, W.; Yamamoto, T.; Saso, H.; Kabe, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2791−2793.

(27) One of the reviewers of this paper provided the valuable suggestion that there is a third possible pathway to generate a vacant coordination site on the iron center: i.e., through changing one of the bridging CO groups into a terminal one and breaking the Fe−Fe bond. This pathway, which would involve formation of intermediates with coordination modes rather similar to those of the CO-loss pathway, will be considered together with the CO-loss mechanism in a forthcoming paper.

Table 1. Crystal Data and Structure Refinement Details for 5a, 6b, 7b, and 8b

	5a	**6b**	**7b**	**8b**
formula	$C_{28}H_{24}Fe_2O_4Si_2$	$C_{24}H_{32}Fe_2O_4Si_2$	$C_{28}H_{24}Fe_2O_4Si_2$	$C_{24}H_{32}Fe_2O_4Si_2$
fw	592.37	552.38	592.37	552.39
temp (K)	299(1)	293(2)	299(1)	299(1)
cryst syst	monoclinic	orthorhombic	monoclinic	triclinic
space group	$P2_1/c$	*Pbcn*	$P2_1/c$	$P\bar{1}$
a (Å)	9.526(2)	30.520(7)	10.627(2)	7.687(1)
b (Å)	13.921(3)	8.022(4)	8.102(2)	8.173(2)
c (Å)	20.577(4)	21.531(6)	15.689(3)	10.752(5)
α (deg)	90	90	90	86.55(3)
β (deg)	102.03(3)	90	102.34(3)	77.42(2)
γ (deg)	90	90	90	79.17(2)
V (Å^3)	2669(1)	5271(3)	1320(1)	647.4(3)
Z	4	8	2	1
ρ_{calcd} (g cm^{-3})	1.474	1.392	1.491	1.417
μ (mm^{-1})	1.2058	1.218	1.2193	1.2370
cryst size (mm)	0.25 × 0.35 × 0.40	0.15 × 0.20 × 0.25	0.20 × 0.30 × 0.40	0.25 × 0.35 × 0.35
θ range (deg)	2−25	1.33−25	2−25	2−25
index ranges	$-11 \le h \le 11$	$-36 \le h \le 28$	$-12 \le h \le 12$	$-9 \le h \le 9$
	$0 \le k \le 16$	$-8 \le k \le 9$	$0 \le k \le 9$	$9 \le k \le 9$
	$0 \le l \le 24$	$-21 \le l \le 25$	$0 \le l \le 18$	$0 \le l \le 12$
no. of rflns collected	5029	19 450	2547	2395
no. of indep rflns	4222	4359	2043	2194
no. of obsd rflns	2854 ($I \geq 3\sigma(I)$)	2291 ($I \geq 2\sigma(I)$)	1334 ($I \geq 3\sigma(I)$)	1937 ($I \geq 3\sigma(I)$)
refinement method	on F	on F^2	on F	on F
no. of params	325	308	163	145
goodness of fit	1.12	1.042	1.14	1.12
R1 index (obsd data)	0.045	0.089	0.069	0.028
wR2 index (obsd data)	0.059	0.158	0.070	0.035
largest diff peak/hole (e Å^{-3})	0.55/−0.66	0.496/−0.313	0.44/−0.74	0.24/−0.39

portion of CH_2Cl_2 afforded pure **5a**. **5b** was not obtained in pure form due to its low yield. Data for **5a** are as follows. Mp: 171−173 °C. IR (KBr): ν_{CO} 1989 (s), 1952 (m), 1758 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.75 (s, 6H, $SiCH_3$); 4.63, 5.13, 5.35, 5.56 (m, 2H:2H:2H:2H, C_5H_4); 7.16, 7.24 (m, 8H:2H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ −3.2 (s, $SiCH_3$); 88.2, 88.7, 89.6, 95.9, 98.6 (C_5H_4); 128.1, 129.4, 134.7, 135.1 (C_6H_5); 209.8 (terminal CO); 270.8, 272.4 (bridging CO). Anal. Calcd for $C_{28}H_{24}O_4Fe_2Si_2$: C, 56.77; H, 4.08. Found: C, 56.75; H, 4.24. Data for **5b** are as follows. ^{1}H NMR ($CDCl_3$): δ 0.62 (s, 6H, SiMe); 5.04, 5.45, 5.51 (m, 4H:2H:2H, C_5H_4); 7.20, 7.28 (m, 8H:2H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ −4.7 ($SiCH_3$); 86.6, 87.6, 88.2, 98.6, 100.0 (C_5H_4); 128.3, 129.5, 135.1, 135.7 (C_6H_5); 209.3 (terminal CO); 271.7 (bridging CO).

Synthesis of [η^5:η^5-C_5H_4(*n*-Bu)MeSiSiMe(*n*-Bu)C_5H_4]Fe_2-$(CO)_2$(μ-CO)$_2$ (6). Using the same procedures mentioned above, C_5H_5(*n*-Bu)MeSiSiMe(*n*-Bu)C_5H_5 (**4**, R = *n*-Bu) was prepared from the reaction of Cl(*n*-Bu)MeSiSiMe(*n*-Bu)Cl (**3**, R = *n*-Bu; 4.9 g, 0.018 mol) and C_5H_5Li (0.04 mol). The crude product, which is an oil, was refluxed with $Fe(CO)_5$ (8.1 g, 0.041 mol) in *p*-xylene (20 mL) for 10 h. After workup in the same way as mentioned above, the solid residue was separated through a column (neutral Al_2O_3). Elution with petroleum ether gave a yellow band, from which yellow crystals of the rearranged product **8** (1.0 g, 10% yields) were obtained. Further elution with petroleum ether/ether (2:1) gave a red band, from which dark red crystals of the desired complex **6** (1.2 g, 12% yields) were obtained. ^{1}H NMR analysis showed that **6** was a mixture of *cis* (**6a**) and *trans* (**6b**) isomers in a ratio of 1:1.4. Fractional crystallization of this mixture with hexane at −20 °C gave pure **6b**. After several portions of the *trans* isomer were removed, **6a** was obtained from the mother liquid through careful crystallization at −20 °C. Data for **6a** are as follows. Mp: 116−118 °C. IR (KBr): ν_{CO} 1991 (s), 1973 (s), 1947 (m), 1931 (m), 1817 (w), 1763 (s) cm^{-1}. IR (hexane): ν_{CO} 2001 (s), 1961 (m), 1813 (w), 1785 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.33 (s, 6H, $SiCH_3$); 0.70 (m, 4H, $SiCH_2$); 0.84 (t, $^3J_{H-H}$ = 7.0 Hz, 6H, CCH_3); 1.30 (m, 8H, CCH_2CH_2C); 4.50, 4.85, 5.33, 5.44 (m, 2H:2H:2H:2H, C_5H_4). ^{13}C NMR ($CDCl_3$): δ −5.2 ($SiCH_3$); 13.7, 14.1, 26.4, 26.7 (*n*-Bu); 87.9, 88.1, 91.0, 95.7, 97.1 (C_5H_4); 209.7 (terminal CO); 271.9, 272.4 (bridging CO). Anal. Calcd for $C_{24}H_{32}O_4Si_2Fe_2$: C, 52.18; H, 5.84. Found: C, 52.39; H, 5.62. Data for **6b** are as follows. Mp: 158−159 °C. IR (KBr): ν_{CO} 1993 (s), 1946 (m), 1765 (s) cm^{-1}. IR (hexane): ν_{CO} 2001 (s), 1960 (m), 1785 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.36 (s, 6H, $SiCH_3$); 0.67 (m, 4H, $SiCH_2$); 0.84 (t, $^3J_{H-H}$ = 7.1 Hz, 6H, CCH_3); 1.26 (m, 8H, CCH_2CH_2C); 4.69, 4.81, 5.34, 5.41 (m, 2H:2H:2H:2H, C_5H_4). ^{13}C NMR ($CDCl_3$): δ −5.5 ($SiCH_3$); 13.7, 14.8, 26.4, 26.6 (*n*-Bu); 86.9, 87.8, 90.2, 97.2, 97.9 (C_5H_4); 209.7 (terminal CO); 272.2 (bridging CO). Anal. Calcd for $C_{24}H_{32}O_4Si_2Fe_2$: C, 52.18; H, 5.84. Found: C, 51.96; H, 5.87.

Synthesis of [PhMeSi-η^5-$C_5H_4Fe(CO)_2$]$_2$ (7). Pure **5a** (200 mg, 0.34 mmol) was refluxed in *p*-xylene (50 mL) for 18 h. After the mixture was cooled to room temperature, the solvent was distilled off under reduced pressure. The solid residue was purified through a column (neutral Al_2O_3, chloroform) to give a yellow band, from which yellow crystals of **7** (118 mg, 59% yield) were obtained. ^{1}H and ^{13}C NMR spectroscopic analyses of the product showed that it was a mixture of *cis* (**7a**) and *trans* (**7b**) isomers**.** The ratio of the isomers was determined by the ^{1}H NMR method to be 46:54. They were separated from each other by fractional crystallization with CH_2Cl_2. In this solvent **7a** was much more soluble than **7b**. Data for **7a** are as follows. Mp: 200−201 °C. IR (KBr): ν_{CO} 1989 (s), 1936 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.78 (s, 6H, $SiCH_3$); 4.80, 5.13, 5.20, 5.24 (m, 2H:2H:2H:2H, C_5H_4); 7.30, 7.51 (m, 6H:4H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 6.3 ($SiCH_3$); 84.1, 84.8, 93.2, 94.2, 95.2 (C_5H_4); 127.9, 128.6, 133.8, 144.4 (C_6H_5); 215.3, 215.4 (CO). Anal. Calcd for $C_{28}H_{24}O_4Fe_2Si_2$: C, 56.77; H, 4.08. Found: C, 56.63; H, 4.36. Data for **7b** are as follows. Mp: >360 °C. IR (KBr): ν_{CO} 1984 (s), 1937 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.88 (s, 6H, $SiCH_3$); 4.92, 5.16, 5.20, 5.33 (m, 2H:2H:2H:2H, C_5H_4); 7.25, 7.45 (m, 6H:4H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 5.2 ($SiCH_3$); 84.3 (2C), 93.1, 93.7, 96.1 (C_5H_4); 127.6, 128.4, 133.8, 141.2 (C_6H_5); 214.7, 216.4 (CO). Anal. Calcd for $C_{28}H_{24}O_4Fe_2Si_2$: C, 56.77; H, 4.08. Found: C, 56.79; H, 4.22.

Synthesis [(*n*-Bu)MeSi-η^5-$C_5H_4Fe(CO)_2$]$_2$ (8). Pure **6a** (200 mg, 0.36 mmol) was refluxed in *p*-xylene (20 mL) for 13 h. After the solvent was removed, the solid residue was purified through a column (neutral Al_2O_3, hexane) to afford a yellow band, from which yellow crystals of **8** (138 mg, 69% yield) were obtained. ^{1}H and ^{13}C NMR spectroscopic analyses showed that it was a mixture of *cis* (**8a**) and *trans* (**8b**) isomers. The ratio was determined by ^{13}C NMR spectroscopy to be 45:55. Further developing with hexane/

ether (2:1) gave a red band, from which a small amount of **6a** (3 mg, 1.5% yield) was recovered. Similar treatment of **6b** (100 mg) afforded **8** (60 mg, 60% yield) as a mixture of **8a** and **8b** in a ratio of 52:48. The two isomers were separated from each other by fractional crystallization in hexane. Data for **8a** are as follows. Mp: 116−117 °C. IR (KBr): ν_{CO} 1985 (s), 1934 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.45 (s, 6H, $SiCH_3$); 0.87 (t, $^3J_{H-H} = 6.9$ Hz, 6H, CCH_3); 0.95 (m, 4H, $SiCH_2$); 1.29 (m, 8H, CCH_2CH_2C); 4.93, 4.96, 5.03 (m, 2H:2H:4H, C_5H_4). ^{13}C NMR ($CDCl_3$): δ 4.5 ($SiCH_3$); 13.8, 23.3, 26.5, 27.6 (*n*-Bu); 83.5, 83.9, 93.0, 94.0, 95.7 (C_5H_4); 215.7, 215.8 (CO). Anal. Calcd for $C_{24}H_{32}O_4Si_2Fe_2$: C, 52.18; H, 5.84. Found: C, 52.15; H, 5.63. Data for **8b** are as follows. Mp: 134−135 °C. IR (KBr): ν_{CO} 1986 (s), 1926 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.46 (s, 6H, $SiCH_3$); 0.87 (t, $^3J_{H-H} = 6.9$ Hz, 6H, CCH_3); 0.92 (m, 4H, $SiCH_2$); 1.30 (m, 8H, CCH_2CH_2C); 4.90, 4.99, 5.04 (m, 2:4:2, 8H, C_5H_4). ^{13}C NMR ($CDCl_3$): δ 4.3 ($SiCH_3$); 13.8, 23.3, 26.5, 27.6 (*n*-Bu); 83.6, 83.8, 93.3, 94.0, 95.3 (C_5H_4); 215.7, 215.9 (CO). Anal. Calcd for $C_{24}H_{32}O_4Si_2Fe_2$: C, 52.18; H, 5.84. Found: C, 52.00; H, 5.89.

X-ray Crystallography. Single crystals of **5a**, **6b**, **7b**, and **8b** suitable for X-ray diffraction analyses were obtained from hexane/CH_2Cl_2, chloroform, hexane/CH_2Cl_2, and hexane, respectively. Data collections were performed on an Enraf-Nonius CAD-4 diffractometer for **5a**, **7b**, and **8b** and on a Bruker SMART 1000 diffractometer for **6b**, using a $2\theta/\omega$ scan technique with Mo Kα ($\lambda = 0.710\,73$ Å) radiation. All structures were solved by direct methods and refined using standard least-squares and Fourier techniques. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added theoretically and refined with isotropic thermal parameters. It was noted that the quality of the crystallographic data for **6b** was affected by dynamic disorder of *n*-butyl groups. Positional disorder of the silicon atoms was also observed (with 20% occupancy), but groups attached to them could not be located. Crystal and structure refinement data are shown in Table 1.

Acknowledgment. We thank the National Natural Science Foundation of China for financial support (Grant Nos. 29872020 and 20372036).

Supporting Information Available: CIF files giving X-ray structural data for complexes **5a**, **6b**, **7b**, and **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050622Z