Synthesis and Properties of Structural Variants of the Si−Si Bridged Bis(cyclopentadienyl)tetracarbonyldiiron Complexes: Modification on the Bridge

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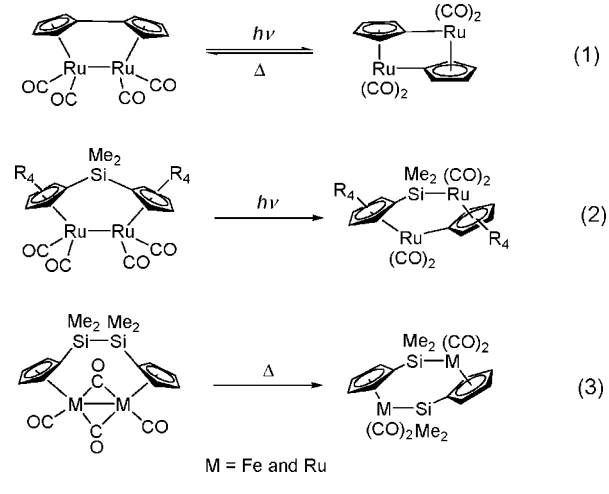
A series of new structural variants of the Si−Si bridged bis(cyclopentadienyl)tetracarbonyldiiron complex (η^5,η^5-$C_5H_4XC_5H_4$)$Fe_2(CO)_4$, where X = MeSi[μ-$(CH_2)_4$]SiMe (**3**), CH_2SiMe_2 (**7**), and $SiMe_2SiPh_2$ (**10**), were synthesized and their properties studied with emphasis on the thermal rearrangement that had been demonstrated to occur when X = $SiMe_2SiMe_2$. It was found that the presence of the cyclic structure on the Si−Si bridge for complex **3** prohibited the thermal rearrangement, but oxygen insertion into the Si−Si bond took place under thermal conditions to give the new Si−O−Si bridged complex {η^5,η^5-$C_5H_4MeSi(\mu$-O)[μ-$(CH_2)_4$]$SiMeC_5H_4$}$Fe_2(CO)_4$ (**4**). Using CH_2SiMe_2 as the bridging group in complex **7** also resulted in failure of the rearrangement because the C−Si bond could not be activated by the iron center. Complex **10**, with the unsymmetric bridging group $SiMe_2SiPh_2$, underwent thermal rearrangement, producing the expected product *cyclic*-[(Me_2Si-η^5-C_5H_4)$Fe(CO)_2$(Ph_2Si-η^5-C_5H_4)$Fe(CO)_2$]− (**11**) with two Si−Fe bonds. When the reaction was performed in the presence of $P(OPh)_3$, incorporation of the phosphite ligand in the rearranged product took place, providing two regioisomers, *cyclic*-{(Me_2Si-η^5-C_5H_4)$Fe(CO)[P(OPh)_3]$(Ph_2Si-η^5-C_5H_4)$Fe(CO)_2$}− (**12a**) and *cyclic*-{(Me_2Si-η^5-C_5H_4)$Fe(CO)_2$(Ph_2Si-η^5-C_5H_4)$Fe(CO)[P(OPh)_3]$}− (**12b**), in a 1:1.8 ratio. The reaction of **10** with I_2 led to Fe−Fe bond cleavage, affording di-iodide (η^5,η^5-$C_5H_4Me_2SiSiPh_2C_5H_4$)$[Fe(CO)_2I]_2$ (**13**). The molecular structures of **3**, **4**, **7**, **10**, **11**, and **13** have been determined by X-ray diffraction methods.

Introduction

Ring-bridged bis-cyclopentadienyl bimetallic complexes (η^5,η^5-$C_5H_4XC_5H_4$)$M_2(CO)_4$ (M = Fe and Ru, X = alkyl and silyl) have received continuous attention during the past several decades due to their unique structural and chemical properties.[1] Interest in such complexes was initially focused on the structural feature of the *cis* conformation due to the constraint of the two cyclopentadienyl (Cp) groups by the bridging group and the possible cooperative behaviors of the two metal centers located in close proximity.[2,3] Recently, a number of interesting new reactions have been found to occur in such systems. Besides the reversible "twisting" reaction involving activation of the C−H bond on the Cp ring,[4,5] a series of topologically similar skeleton rearrangements involving activation of the bridging C−C, C−Si, and Si−Si bonds by the metal centers have been reported (eqs 1−3).



The first example is the photochemically induced rearrangement of the diruthenium complex (η^5,η^5-C_5H_4-C_5H_4)$Ru_2(CO)_4$ with directly linked Cp rings, reported by Vollhardt and co-

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workers, which could be thermally reversed (eq 1).[6] Another example is the photochemical rearrangement of the silicon-bridged diruthium complexes (η^5,η^5-$C_5R_4SiMe_2C_5R_4$)$Ru_2(CO)_4$, reported first by Bitterwolf and co-workers as a side process and developed later by Burger into the clean reaction (eq 2).[4,7] In 1993, we reported the synthesis of the first Si−Si bridged diiron complex (η^5,η^5-$C_5H_4Me_2SiSiMe_2C_5H_4$)$Fe_2(CO)_4$, which has resulted in the finding of the thermal rearrangement via metathesis of the Si−Si and Fe−Fe bonds (eq 3).[8,9] Since then, considerable effort has been devoted to investigation of the scope and mechanism of the thermal rearrangement. During this course, many analogous complexes have been synthesized by introducing various substituents onto the Cp rings and by using phosphines and isocyanides to replace the CO ligand. Most of these studies, however, have been restricted to the use of the same $Me_2SiSiMe_2$ bridge, and little has been done for modification of the bridge structure.

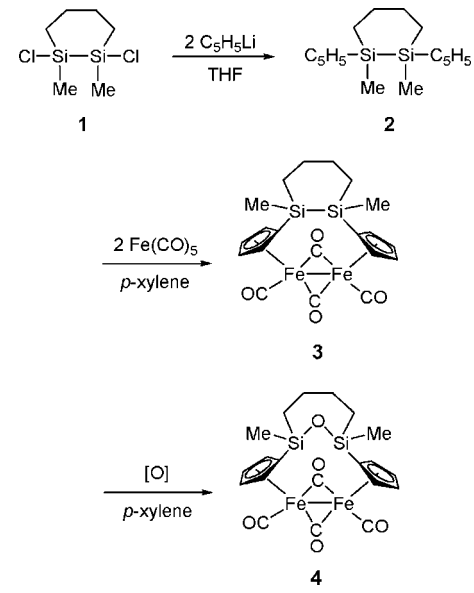
Very recently, we have reported the use of the phenyl- and *n*-butyl-substituted groups PhMeSiSiMePh and (*n*-Bu)MeSiSiMe(*n*-Bu) as the bridge for study of the stereochemistry of the thermal rearrangement.[8c] Herein, we describe further modification of the Si−Si bridge by using a series of novel bridging groups, including MeSi[μ-$(CH_2)_4$]SiMe, with the Si−Si bond being constrained by the cyclic structure, CH_2SiMe_2 with a Si−C bond replacing the Si−Si bond, and $SiMe_2SiPh_2$ with an unsymmetric Si−Si structure. The structural and chemical properties of the new complexes were studied, which provided helpful information for understanding the scope and some details of the thermal rearrangement. It should be noted that the syntheses of some of the complexes have been briefly mentioned in the previous communication.[10]

Results and Discussion

Complex with a Cyclic Structure on the Bridge. Synthesis of the complex with a cyclic structure on the Si−Si bridge was accomplished by using 1,2-dichloro-1,2-dimethyl-1,2-disilacyclohexane (**1**) as the starting material. Thus, the reaction of **1**, prepared by the literature procedures,[11] with 2 equiv of cyclopentadienyllithium provided the biscyclopentadienyl ligand **2**; the latter reacted subsequently with pentacarbonyliron in refluxing *p*-xylene, producing the desired complex **3**(Scheme 1).

^{1}H and ^{13}C NMR analysis of the product indicated that it was a single isomer, with either the *cis* or the *trans* conformation for the two methyl groups at the Si−Si bridge. The molecular structure determined by the X-ray diffraction method clearly demonstrated that the two methyl groups were in a *trans* relationship (Figure 1). The Si−Si bridge stayed on the top of the molecule but twisted away from the direction parallel to the Fe−Fe bond (for a side view of the molecule, see Figure S1 in the Supporting Information), which is similar to the *trans* isomer of the (*n*-Bu)MeSiSiMe(*n*-Bu)-bridged complex[8c] and is believed to be due to the Si−Si bond being longer than the space between two the Cp groups on the top. The six-membered ring on the bridge adopted a chair-like conformation. The length of the Si−Si bond [2.306(2) Å] is shorter than that in the above *n*-butyl-substituted complex [2.339(7) Å], while the Fe−Fe bond [2.581(1) Å] is slightly longer than in the *n*-butyl case [2.5518(16) Å].[8c]

Scheme 1



One of the significant features of **3** was that it did not undergo thermal rearrangement through metathesis of the Si−Si and Fe−Fe bonds owing to the presence of the cyclic structure on the bridge. It could be slowly transformed into a new product, however, upon refluxing in *p*-xylene, as indicated by TLC

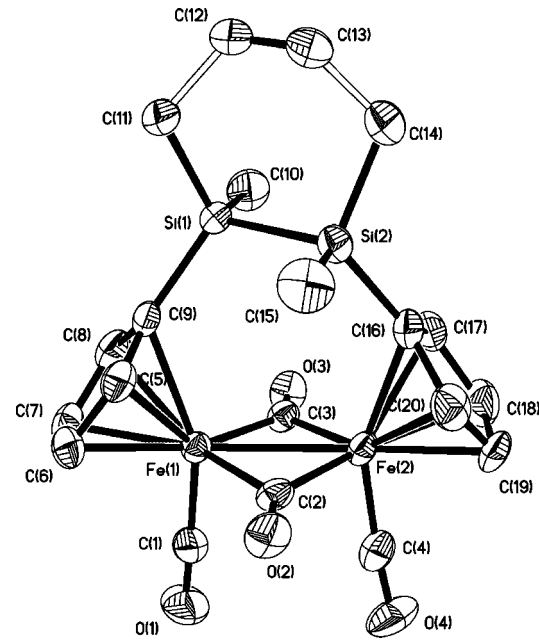


Figure 1. ORTEP plot of **3** (30% probability level). Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) 2.581 (1), Si(1)−Si(2) 2.306(2); Si(1)−Si(2)−C(16) 109.08(13), Si(2)−Si(1)−C(9) 109.18(12).

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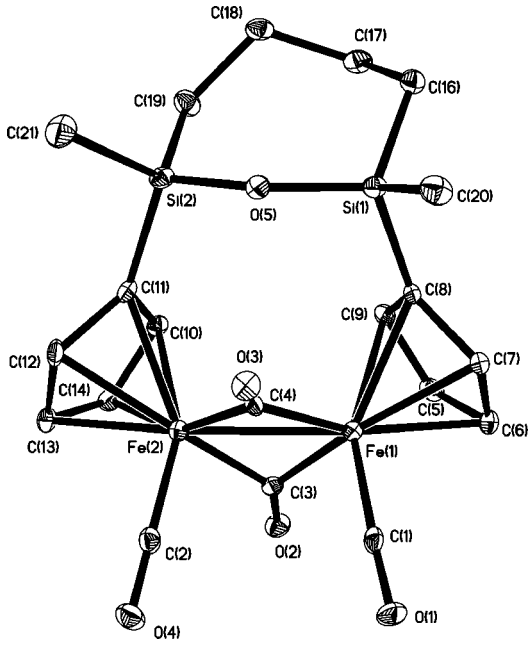


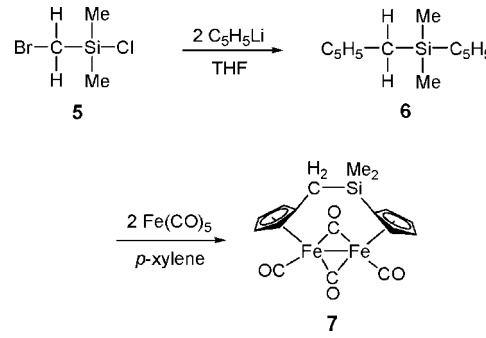
Figure 2. ORTEP plot of **4** (30% probability level). Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) 2.5386(14), Si(1)−O(5) 1.621(3), Si(2)−O(5) 1.622(3); Si(1)−O(5)−Si(2) 145.39(18).

monitoring of the reaction process. This product after isolation was found to be complex **4**, with the Si−O−Si bridge (Scheme 1). X-ray diffraction study revealed that the two methyl groups on the Si−O−Si bridge of this complex were in a *cis* relationship, indicating that inversion of the conformation on the bridge has occurred (Figure 2). Compared with other *cis*-conformed Si−Si bridged complexes previously reported, the Si−O−Si bridge in this complex is tilted to a greater extent toward one side of the molecule, due probably to the lengthening of the bridge (for a side view of the molecule, see Figure S2 in the Supporting Information). The two Cp groups were in a nearly eclipsed conformation. The length of the Fe−Fe bond is 2.5386(14) Å, which is shorter than that before oxygen insertion.

Clearly, insertion of oxygen into the Si−Si bond has taken place, and the conformation of the groups at the bridge has inversed. Although the mechanism of the process has not been clarified yet, it is likely that the oxygen insertion might be caused by the trace amount of molecular oxygen in the inert gas, since similar insertion of oxygen into the Si−Si bond of the starting cyclic compound **1** has been found to facilely occur upon exposure to the air. In addition, the change of the conformation of the bridge might be attributed to the high reaction temperature that would result in formation of thermal dynamic products. These points will be addressed elsewhere in the future.

Complex with the C−Si Bridge. In the past, the thermal rearrangement of the Si−Si bridged bis(cyclopentadienyl)diiron complexes has been found to extensively occur. However, whether such rearrangement could take place for the C−Si bond bridged analogous complex has never been tested. In fact, there has never been any report of C−Si bridged bis-cyclopentadienyl bimetallic complexes, although a large number of C−C and Si−Si bridged systems exist in the literature. To our knowledge, the only report of the C−Si bridged complexes was the bis-fluorenyl zirconium and hafnium mononuclear compounds.[12,13]

Scheme 2



Thus, we synthesized the first C−Si bridged bis-cyclocpentadienyl complex, which was accomplished by using bromomethyldimethylchlorosilane (**5**) as the starting material, which reacted with 2 equiv of cyclopentadienyl lithium, producing the bis-cyclopentadienyl ligand **6**; the latter reacted subsequently with pentacarbonyliron under thermal conditions, providing the desired complex **7** (Scheme 2).

The molecular structure of **7** was determined by the X-ray diffraction method (Figure 3). In the crystalline state, the CH_2SiMe_2 bridge in the complex moved to one side of the molecule, similar to the $Me_2SiSiMe_2$-bridged case,[8a] but the carbon atom of the bridge was quite close to the top, as the result of the shortening of the C−Si bridge (1.883 Å) as compared to the Si−Si bond (2.346 Å).[8a] The two Cp groups took a partially staggered conformation (for a side view of the molecule, see Figure S3 in the Supporting Information). The Fe−Fe bond (2.550 Å) is slightly longer than in the $Me_2SiSiMe_2$-bridged complex (2.526 Å).[8a] All other bond lengths and angles are normal, indicating that there is not much strain in the molecule.

It was found that complex **7** did not undergo thermal rearrangement when refluxed in *p*-xylene. This result remained unchanged even after substitution of a CO ligand with $P(OPh)_3$,[10] which has been well known to be able to accelerate

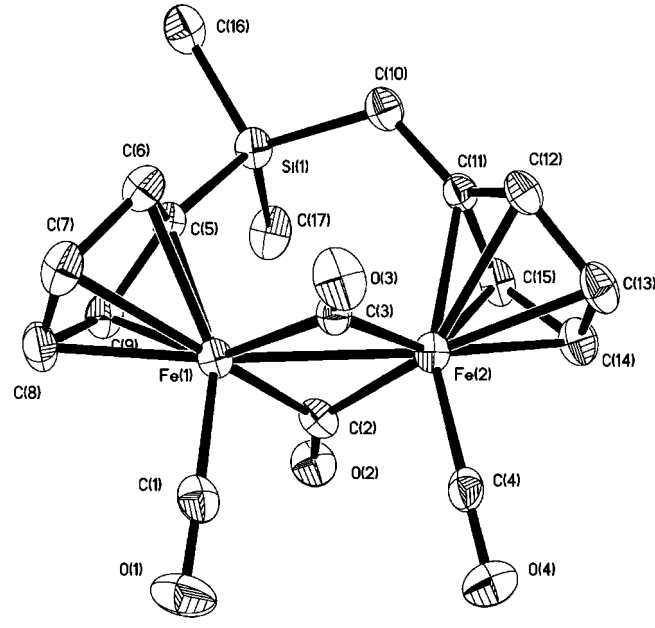


Figure 3. ORTEP plot of **7** (30% probability level). Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) 2.550(2), Si(1)−C(10) 1.883(3),C(10)−C(11)1.475(8),Si(1)−C(5)1.881(7);Si(1)−C(10)−C(11) 120.8(4), C(10)−Si(1)−C(5) 107.8(3).

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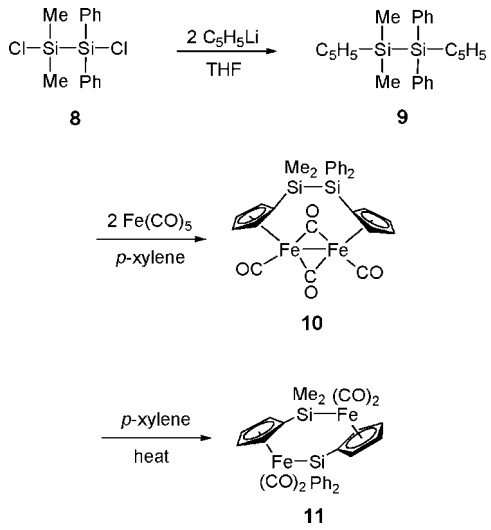
Scheme 3



the thermal rearrangement.[14] This means that the C−Si bond could not be activated by the iron center, according to the previously suggested mechanism of thermal rearrangement,[8c] which is also in accordance with the notion that the C−Si bond should be much more difficult to activate by transition metals than Si−Si bonds.[15]

Complex with the Unsymmetric Si−Si Bridge. Previous works on the Si−Si bridged complexes were restricted to the use of symmetric bridges, such as $Me_2SiSiMe_2$, (*n*-Bu)MeSiSiMe(*n*-Bu), and PhMeSiSiMePh. The synthesis of the first unsymmetric Si−Si bridged complex was accomplished here by using 1,2-dichloro-1,1-diphenyl-2,2-dimethyldisilane (**8**) as the starting material, which reacted with cyclopentadienyllithium and then with pentacarbonyliron in a similar fashion to those described above. Complex **10** was obtained as dark red crystals. Meanwhile, the rearranged product **11** was obtained as yellow crystals. The rearrangement from **10** to **11** was confirmed by heating of the former in refluxing *p*-xylene (Scheme 3).

Both complexes were fully characterized and their molecular structures determined by X-ray diffraction methods. Complex **10** (Figure 4) took a conformation very similar to that of the parent complex with the $Me_2SiSiMe_2$ bridge; that is, the Si−Si bond stayed on the top of the molecule but twisted away from the direction parallel to the Fe−Fe bond (for a side view of the molecule, see Figure S4 in the Supporting Information). This has been attributed to fact that the Si−Si bond is somewhat longer than the space between the two Cp groups. The Si−Si bond (2.3348 Å) is slightly shorter than that in the parent complex (2.346 Å), while the Fe−Fe bond (2.5593 Å) is a little longer than in the same complex (2.526 Å).[8c]

Complex **11** took a chair-like conformation for the six-membered ring of the skeleton (Figure 5). The lengths of the two Si−Fe bonds have little difference, with one (2.3200 Å) slightly longer than the other (2.3093 Å), due to the steric reasons. Both bonds are much shorter than the lengths of either Si−Si or Fe−Fe bonds, indicating the extraordinary stability of the Si−Fe linkage, which is believed to be one of the major driving forces for the thermal rearrangement.

Properties of the New $Me_2SiSiPh_2$-Bridged Complex. The thermal rearrangement of the newly obtained unsymmetric

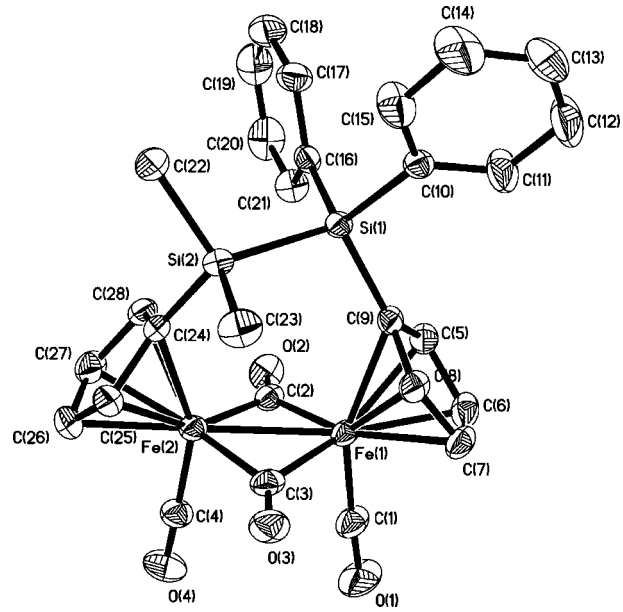


Figure 4. ORTEP plot of **10** (30% probability level). Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) 2.5593(7), Si(1)−Si(2) 2.3348(11), Si(1)−C(9) 1.874(3), Si(2)−C(24) 1.877(3); Si(2)−Si(1)−C(9) 108.02(9), Si(1)−Si(2)−C(24) 106.45(9).

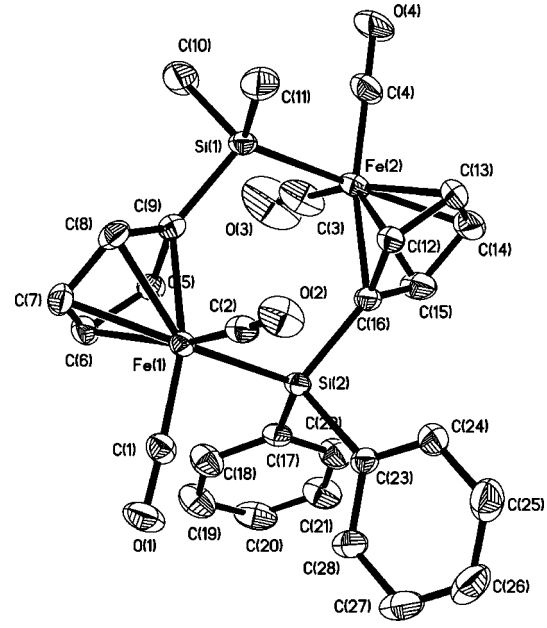


Figure 5. ORTEP plot of **11** (30% probability level). Selected bond lengths (Å) and angles (deg): Si(1)−Fe(2) 2.3093(10), Si(2)−Fe(1) 2.3200(9), Si(1)−C(9) 1.879(3), Si(2)−C(16) 1.899(3); Fe(1)−Si(2)−C(16) 111.72(9), Fe(2)−Si(1)−C(9) 112.88(9).

Si−Si bridged complex **10** was also performed in the presence of the phosphite ligand $P(OPh)_3$. A pair of *cis* and *trans* isomers, **12a** and **12b**, were obtained through incorporation of the phosphite into the rearranged products (Scheme 4). The ratio of **12a** and **12b** was about 1:1.8; that is, the *trans* isomer, having the phosphite ligand and the larger $SiPh_2$ group at opposite sides, was produced preferentially.

The incorporation of the phosphite ligand into the rearranged products should be accomplished by ligand substitution prior to the rearrangement, according to our previous knowlegde.[14] Such ligand substitution would produce two regioisomers, **10′a** and **10′b** (Scheme 4), in nearly equal amounts that should be

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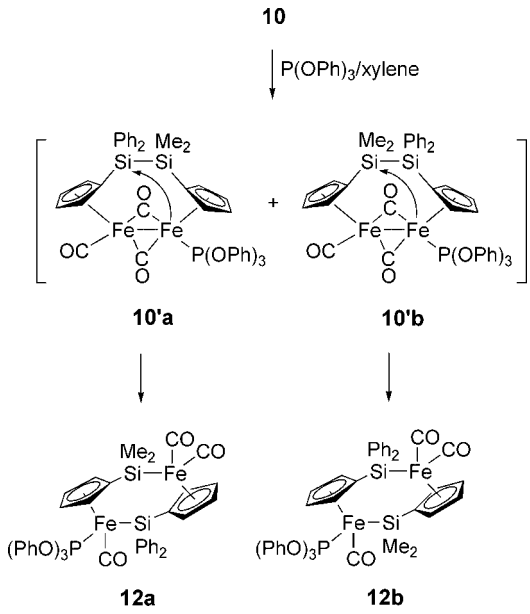
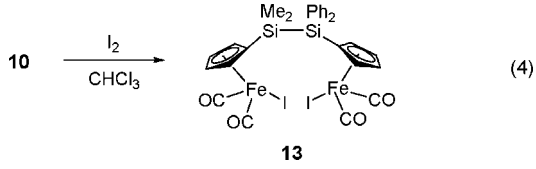
Scheme 4



in fast equilibrium owing to migration of the phosphite ligand between two iron centers.[10] Their subsequent rearrangements leading to preferential formation of the *trans* rearranged product may be rationalized on the basis of our previously suggested mechanism of the thermal rearrangement,[8c] by the fact that the initial formation of the Si−Fe bond between the phosphite-substituted iron and the silicon should be the rate-determining step of the rearrangement process and that in this step there should be much less steric hindrance between $P(OPh)_3$ and $SiMe_2$ for the formation of the *trans* product than between $P(OPh)_3$ and $SiPh_2$ for the formation of the *cis* isomer.

The reaction of **10** with molecular iodine was performed also, which produced the di-iodide **13** through cleavage of the Fe−Fe bond (eq 4). The molecular structure of this molecule determined by the X-ray diffraction method showed that the Si−Si bond (2.367 Å) is slightly longer than that before breaking of the cyclic structure (2.335 Å) (Figure 6). This demonstrates once again that there is no obvious molecular strain on the bridge of the complex.[8b]



(4)

Concluding Remarks. A variety of structural variants of the Si−Si bridged bis(cyclopentadienyl)tetracarbonyldiiron complexes have been synthesized and their structures and properties studied, providing helpful information for complete understanding of the scope and the details of the thermal rearrangement. Further effort for final clarification of the reaction mechanism should be directed toward isolation or trapping of the reactive intermediates after activation of the Si−Si bond by the metal center.[8c] Such study would be of interest because it might provide useful knowledge for activation of other stable σ-bonds such as C−Si and C−C in related systems.

Experimental Section

General Procedures. All reactions were carried out under a nitrogen or argon atmosphere using vacuum line and Schlenk techniques. THF and *p*-xylene were distilled from sodium/benzophenone. Chloroform was dried by refluxing over P_2O_5 and distilled under an inert atmosphere. Elemental analysis was performed using an Elementary Vario EL instrument. IR spectra were recorded with a Magna-560 FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded with Varian Unity Plus-400 and Bruker Avance 300 spectrometers. 1,2-Dichloro-1,2-diphenyl-1,2-disilacyclohexane (**1**) and $ClPh_2SiSiMe_2Cl$ (**8**) were prepared according to the literature procedures. $BrCH_2SiMe_2Cl$ (**5**) was purchased from Alderich.

Synthesis of $\{\eta^5,\eta^5$-$C_5H_4MeSi[\mu$-$(CH_2)_4]SiMeC_5H_4\}Fe_2(CO)_4$(3). A 3.63 g (17 mmol) amount of 1,2-dichloro-1,2-diphenyl-1,2-disilacyclohexane (**1**) was added dropwise to a solution of cyclopentadienyllithium prepared from 3.51 g (53 mmol) of cyclopentadiene and 28 mL of *n*-butyllithium (1.45 M, 41 mmol) in 45 mL of THF at −78 °C. The resulting mixture was allowed to warm to room temperature and stirred overnight. It was then heated at reflux for 7 h. After cooling to room temperature, it was hydrolyzed with a saturated solution of ammonium chloride, extracted three times with 100 mL of ether, and then dried over anhydrous magnesium sulfate. Removing the solvent under reduced pressure afforded a crude product of 1,2-dicyclopentadienyl-1,2-diphenyl-1,2-disilacyclohexane (**2**) as an oil, which was used directly for the next reaction without further purification.

The oil product obtained above was added into a 250 mL flask containing 80 mL of *p*-xylene and 10 g (52 mmol) of pentacarbonyliron. The resulting mixture was refluxed for 11 h. After cooling to room temperature, the solvent was removed under reduced pressure (unreacted pentacarbonyliron should be collected in a liquid nitrogen trap!) to give a semisolid residue. This residue was dissolved in a minimum amount of benzene and purified through a column (silica, petroleum ether/dichloromethane, 2:1, v/v). Collection of the red band afforded 310 mg of **3** (4% total yield) as dark red crystals, mp 252−253 °C. IR (KBr): ν_{CO} 1760 (s), 1941 (s), 1989 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.55 (s, 6H, CH_3), 0.65 (m, 2H, CH_2), 1.00 (m, 2H, CH_2), 1.26 (m, 2H, CH_2), 2.02 (m, 2H, CH_2), 4.98 (s, 2H, Cp), 5.08 (s, 2H, Cp), 5.29 (s, 2H, Cp), 5.40 (s, 2H, Cp). ^{13}C NMR ($CDCl_3$): δ −6.51 (CH_3), 17.00 (CH_2), 26.03 (CH_2), 84.89 (Cp), 87.71 (Cp), 87.85 (Cp), 100.30 (Cp), 101.16 (Cp), 209.48 (terminal CO), 271.40 (bridging CO). Anal. Calcd for $C_{20}H_{22}O_4Si_2Fe_2$: C, 48.60; H, 4.49. Found: C, 48.61; H, 4.58.

Synthesis of $\{\eta^5,\eta^5$-$C_5H_4MeSi(\mu$-$O)[\mu$-$(CH_2)_4]SiMeC_5H_4\}Fe_2(CO)_4$(4). To a 100 mL flask was added 110 mg (0.24 mmol) of **3** and 20 mL of *p*-xylene. The mixture was refluxed for 18 h while stirring magnetically. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in a small amount of dichloromethane and separated through a column (neutral alumina). Elution with the mixed solvent of petroleum ether and dichloromethane (v/v = 1:1) gave a red band, from which 8 mg (7% yield) of **4** was obtained as dark red crystals, mp 115−116 °C. IR (KBr): ν_{CO} 1778 (s), 1815 (w), 1946 (s), 1996 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.39 (s, 6H, CH_3), 0.80 (m, 4H, CH_2), 1.68 (m, 4H, CH_2), 4.27 (s, 2H, Cp), 5.03 (s, 2H, Cp), 5.27 (s, 2H, Cp), 5.49 (s, 2H, Cp). ^{13}C NMR ($CDCl_3$): δ −0.50 (CH_3), 18.29 (CH_2), 24.61 (CH_2), 89.31 (Cp), 89.77 (Cp), 92.32 (Cp), 92.76 (Cp), 96.67 (Cp), 210.12 (terminal CO), 267.94 (bridging CO), 271.23 (bridging CO). Anal. Calcd for $C_{20}H_{22}O_5Si_2Fe_2$: C, 47.08; H, 4.35. Found: C, 47.36; H, 4.55.

Synthesis of $(\eta^5,\eta^5$-$C_5H_4CH_2SiMe_2C_5H_4)Fe_2(CO)_4$(7). To a 500 mL flask containing 15.6 g (0.20 mol) of cyclopentadiene and 180 mL of THF was added 14 mL (1.77 M, 25 mmol) of a solution of *n*-butyllithium in hexane at −78 °C. The mixture was stirred at room temperature for 1 h. It was then cooled to −78 °C once again, and 12.2 g (65 mmol) of $BrCH_2SiMe_2Cl$ in 60 mL of THF was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. It was then refluxed for 9 h. After

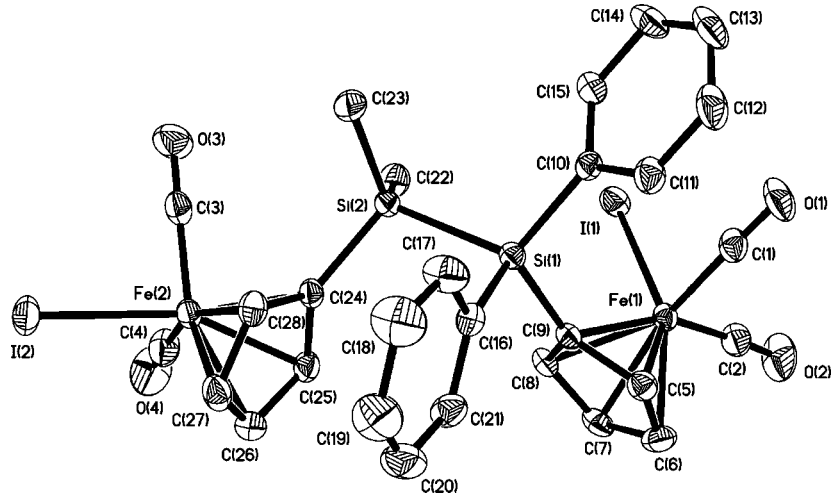


Figure 6. ORTEP plot of **13** (30% probability level). Selected bond lengths (Å) and angles (deg): Si(1)−Si(2) 2.3666(16), Fe(1)−I(1) 2.5986(8), Fe(2)−I(2) 2.6091(7), Si(1)−C(9) 1.892(4), Si(2)−C(24) 1.885(4); Si(1)−Si(2)−C(24) 100.83(13), Si(2)−Si(1)−C(9) 113.89(13).

Table 1. Crystal Data and Structure Refinement for 3, 4, and 7

	3	**4**	**7**
formula	$C_{20}H_{22}Fe_2O_4Si_2$	$C_{20}H_{22}Fe_2O_5Si_2$	$C_{17}H_{16}O_4Fe_2Si$
fw	494.26	510.26	424.09
temperature [K]	294(2)	113(2)	293(2)
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/n$	$P2(1)/n$
a [Å]	7.747(4)	15.109(9)	7.876(5)
b [Å]	10.621(5)	8.955(5)	25.804(8)
c [Å]	14.710(7)	16.008(9)	8.950(6)
α [deg]	85.807(6)	90	90
β [deg]	78.435(8)	109.277(8)	108.951(13)
γ [deg]	68.61	90	90
V [Å^3]	1104.2(9)	2044(2)	1720.3(17)
Z	2	4	4
ρ_{calc} [g/cm^{-3}]	1.480	1.658	1.637
μ [mm^{-1}]	1.444	1.566	1.773
cryst size [mm]	0.24 × 0.20 × 0.12	0.24 × 0.22 × 0.20	0.32 × 0.20 × 0.18
θ range [deg]	1.41 to 25.02	1.61 to 27.77	2.53 to 26.44
index ranges	$-8 \le h \le 9$	$-19 \le h \le 19$	$-8 \le h \le 9$
	$-12 \le k \le 11$	$-11 \le k \le 11$	$-23 \le k \le 32$
	$-17 \le l \le 16$	$-20 \le l \le 20$	$-11 \le l \le 10$
no. of reflns collected	5539	18 399	9481
no. of indep reflns	3861	4730	3435
no. of obsd reflns [$I \ge 2\sigma(I)$]	2487	4015	1627
no. of params	384	265	219
goodness of fit	1.021	1.129	0.925
R_1 indices (obsd data)	0.0404	0.0590	0.0693
wR_2 indices (obsd data)	0.0815	0.1088	0.1106
largest diff peak/hole [e Å^{-3}]	0.525/−0.294	0.454/−0.536	0.665/−0.661

cooling to room temperature, the mixture was hydrolyzed with a saturated solution of ammonium chloride, extracted with ether, washed with water, and dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure gave 12.8 g of the crude product **6** as an oil, which was used directly for the next reaction without further purification.

To a 250 mL flask containing 100 mL of *p*-xylene were added the oil product obtained above and 33.0 g (0.17 mol) of pentacarbonyliron. The mixture was refluxed for 20 h. After cooling to room temperature, the solvent was removed under reduced pressure (unreacted pentacarbonyliron should be collected in a liquid nitrogen trap!) to give a solid residue, which was purified through a neutral alumina column. Elution with petroleum ether/dichloromethane (2:1) gave a red band, from which 0.93 g of **7** (22% yield) was obtained as dark red crystals,[16] mp 184−186 °C. IR (KBr): ν_{CO} 1982 (s), 1937 (s), 1810 (s), 1770 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.22 (s, 6H, $SiMe_2$), 1.46 (s, 2H, CH_2), 4.64 (m, 2H, C_5H_4), 4.86 (m, 2H, C_5H_4), 5.12 (m, 2H, C_5H_4), 5.42 (m, 2H, C_5H_4). ^{13}C NMR ($CDCl_3$): δ −1.04 ($SiMe_2$), 14.12 (CH_2), 82.62 (C_5H_4), 83.66 (C_5H_4), 96.70 (C_5H_4), 88.77 (C_5H_4), 94.53 (C_5H_4), 99.46 (C_5H_4), 99.82 (C_5H_4), 102.75 (C_5H_4), 209.82 (terminal CO), 209.93 (terminal CO), 272.93 (bridging CO). Anal. Calcd for $C_{17}H_{16}O_4Fe_2Si$: C, 48.11; H, 3.77. Found: C, 47.94; H, 3.55.

Synthesis of (η^5,η^5-$C_5H_4SiMe_2SiPh_2C_5H_4$)$Fe_2(CO)_4$(10). A 7.84 g (25 mmol) amount of $ClPh_2SiSiMe_2Cl$ was added dropwise to a solution of cyclopentadienyllithium, prepared from 5.05 g (77 mmol) of cyclopentadiene and 40 mL of *n*-butyllithium (1.50 M, 60 mmol) in 120 mL of THF at −78 °C. The resulting mixture was allowed to warm to room temperature and then stirred

(16) The structure assignment of the byproduct in a previous study of **7**, without support of X-ray diffraction data, appears now to be incorrect. Therefore, its structure still remains to be determined. See: Sun, H.; Zang, H.; Zang, Z. *Chin. J. Chem.* **2006**, *24*, 1476–1479.

Table 2. Crystal Data and Structure Refinement for 10, 11, and 13

	10	11	13
formula	$C_{28}H_{24}Fe_2O_4Si_2$	$C_{28}H_{24}Fe_2O_4Si_2$	$C_{28}H_{24}Fe_2I_2O_4Si_2$
fw	592.35	592.35	846.15
temperature [K]	294(2)	294(2)	294(2)
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2(1)/n$	$P\bar{1}$
a [Å]	10.1855(17)	10.4845(18)	10.1097(17)
b [Å]	11.2228(19)	11.743(2)	11.2601(18)
c [Å]	12.895(2)	21.997(4)	14.787(2)
α [deg]	77.310(3)	90	82.990(2)
β [deg]	69.295(3)	93.391(3)	81.164(3)
γ [deg]	78.967(3)	90	69.457(2)
V [Å^3]	1334.6(4)	2703.5(8)	1553.3(4)
Z	2	4	2
ρ_{calc} [g/cm^{-3}]	1.474	1.455	1.809
μ [mm^{-1}]	1.209	1.194	3.029
cryst size [mm]	0.26 × 0.16 × 0.14	0.24 × 0.18 × 0.12	0.24 × 0.20 × 0.12
θ range [deg]	1.71 to 25.01	1.85 to 26.37	1.40 to 25.01
index ranges	$-6 \le h \le 12$	$-13 \le h \le 8$	$-12 \le h \le 9$
	$-13 \le k \le 13$	$-13 \le k \le 14$	$-12 \le k \le 13$
	$-15 \le l \le 15$	$-25 \le l \le 27$	$-17 \le l \le 16$
no. of reflns collected	6811	14 844	7941
no. of indep reflns	4680	5486	5435
no. of obsd reflns [$I \ge 2\sigma(I)$]	3613	3859	4004
no. of params	327	327	345
goodness of fit	1.041	1.016	1.001
R_1 indices (obsd data)	0.0324	0.0361	0.0310
wR_2 indices (obsd data)	0.0784	0.0797	0.0643
largest diff peak/hole [e Å^{-3}]	0.303/−0.268	0.579/−0.441	0.425/−0.589

overnight. After refluxing for 2 h, it was cooled to room temperature again. It was then hydrolyzed with 150 mL of a saturated solution of ammonium chloride, extracted three times with 100 mL of ether, and dried with anhydrous magnesium sulfate. Removing the solvent under reduced pressure afforded the crude product of **9** as an oil, which was used directly in the next reaction without further purification.

The oil product obtained above was added into a 250 mL flask containing 100 mL of *p*-xylene and 10 g (52 mmol) of pentacarbonyliron. The resulting mixture was refluxed for 8 h. After cooling to room temperature, the solvent was removed under reduced pressure (unreacted pentacarbonyliron should be collected in a liquid nitrogen trap!) to give a semisolid residue, which was dissolved in a small amount of benzene and purified through a silica column. Elution with petroleum ether/dichloromethane (4:1, v/v) afforded a yellow band, from which 0.35 g of compound **11** (2.3% total yield) was obtained as yellow crystals (for the data of the complex, see below).

Further elution with petroleum ether/dichloromethane (1:1, v/v) gave a red band, from which 3.5 g of compound **10** (24% total yield) was obtained as dark red crystals, mp 189−190 °C. IR (KBr): ν_{CO} 1987 (s), 1942 (m), 1766 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.36 (s, 6H, $SiMe_2$), 4.92 (m, 2H, C_5H_4), 4.95 (m, 2H, C_5H_4), 5.41 (m, 2H, C_5H_4), 5.45 (m, 2H, C_5H_4), 7.38 (m, 6H, Ph), 7.44 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$): δ −1.378 ($SiMe_2$), 87.21 (C_5H_4), 87.44 (C_5H_4), 87.68 (C_5H_4), 90.14 (C_5H_4), 98.29 (C_5H_4), 99.34 (C_5H_4), 128.36 (Ph), 129.76 (Ph), 134.10 (Ph), 135.84 (Ph), 209.60 (terminal CO), 209.65 (terminal CO), 271.19 (bridging CO). Anal. Calcd for $C_{28}H_{24}Si_2Fe_2O_4$: C, 56.77; H, 4.08. Found: C, 56.77; H, 3.87.

Synthesis of *cyclo*-[(Me$_2$Si-η^5-C$_5$H$_4$)Fe(CO)$_2$(Ph$_2$Si-η^5-C$_5$H$_4$)-Fe(CO)$_2$]− (11). To a 50 mL flask was added 88 mg (0.15 mmol) of **10** and 20 mL of *p*-xylene. The mixture was refluxed for 8 h while stirring magnetically. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in a small amount of dichloromethane and separated through a column (neutral alumina). Elution with petroleum ether gave a light yellow band, from which 33 mg (38% yield) of **11** was obtained as yellow crystals, mp 194−195 °C. IR (KBr): ν_{CO} 1990 (s), 1929 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.50 (s, 6H, $SiMe_2$), 5.02 (m, 2H, C_5H_4), 5.08 (m, 2H, C_5H_4), 5.24 (m, 2H, C_5H_4), 5.24 (m, 2H, C_5H_4), 7.28 (m, 6H, Ph), 7.40 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$): δ 6.96 ($SiMe_2$), 84.00 (C_5H_4), 84.48 (C_5H_4), 93.46 (C_5H_4), 93.64 (C_5H_4), 94.95 (C_5H_4), 97.67 (C_5H_4), 127.53 (Ph), 128.48 (Ph), 135.33 (Ph), 142.44 (Ph), 215.22 (CO), 215.38 (CO). Anal. Calcd for $C_{28}H_{24}Si_2Fe_2O_4$: C, 56.77; H, 4.08. Found: C, 56.85; H, 4.00.

Synthesis of *cyclo*-{(Me$_2$Si-η^5-C$_5$H$_4$)Fe(CO)[P(OPh)$_3$](Ph$_2$Si-η^5-C$_5$H$_4$)Fe(CO)$_2$}− (12a) and *cyclo*-{(Me$_2$Si-η^5-C$_5$H$_4$)Fe(CO)$_2$(Ph$_2$Si-η^5-C$_5$H$_4$)Fe(CO)[P(OPh)$_3$]}− (12b). To a 50 mL flask were added 125 mg (0.21 mmol) of **10**, 335 mg (1.1 mmol) of $P(OPh)_3$, and 20 mL of *p*-xylene. The mixture was refluxed for 3 h, while stirring magnetically. After removal of the solvent under reduced pressure, the residue was dissolved in a small amount of dichloromethane and separated through a column (neutral alumina). Elution with petroleum ether/ dichloromethane (v/v = 1:1) gave a light yellow band, from which 145 mg (78% yield) of a mixture of **12a** and **12b** was obtained as a yellow crystalline solid. The ratio of the two isomers was determined by ^{1}H NMR spectroscopy to be 1:1.8. Fractional crystallization of the mixture at −20 °C gave pure crystals of **12a** first and then **12b**. **12a**: mp 198−201 °C. IR (KBr): ν_{CO} 1932 (vs), 1946 (s), 1991 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.59 (s, 3H, $SiMe_2$), 0.60 (s, 3H, $SiMe_2$), 4.28 (m, 1H, Cp), 4.38 (m, 1H, Cp), 4.79 (m, 1H, Cp), 4.91 (m, 1H, Cp), 4.96 (m, 1H, Cp), 5.16 (m, 1H, Cp), 5.30 (m, 2H, Cp), 7.00 (d, J = 7.8 Hz, 6H, Ph), 7.08−7.29 (m, 17H, Ph), 7.45 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 6.81 (Me), 8.87 (Me), 80.70 (C_5H_4), 83.53 (C_5H_4), 83.88 (C_5H_4), 84.46 (C_5H_4), 90.56 (C_5H_4), 92.13 (C_5H_4), 93.81 (C_5H_4), 95.03 (C_5H_4), 96.13 (C_5H_4), 101.24 (C_5H_4), 121.08 (Ph), 124.35 (Ph), 126.99 (Ph), 127.23 (Ph), 127.74 (Ph), 128.11 (Ph), 129.48 (Ph), 135.12 (Ph), 135.43 (Ph), 142.55 (Ph), 143.93 (Ph), 152.01 (J = 11.6 Hz, Ph), 215.42 (CO), 216.08 (CO). Anal. Calcd for $C_{45}H_{39}Si_2Fe_2O_6P$: C, 61.80; H, 4.49; Found: C, 61.95; H, 4.47. **12b**: mp 205−207 °C. IR (KBr): ν_{CO} 1928 (vs), 1985 (s), 1990 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.44 (s, 3H, $SiMe_2$), 0.49 (s, 3H, $SiMe_2$), 4.30 (m, 1H, Cp), 4.72 (m, 1H, Cp), 4.88 (m, 1H, Cp), 4.91 (m, 1H, Cp), 4.94 (m, 1H, Cp), 5.16 (m, 1H, Cp), 5.29 (m, 1H, Cp), 5.35 (m, 1H, Cp), 6.65 (d, J = 7.2 Hz, 6H, Ph), 7.00 (m, 4H, Ph), 7.08−7.13 (m, 11H, Ph), 7.45 (m, 2H, Ph), 7.59 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 6.58 (Me), 7.31 (Me), 81.88 (C_5H_4), 84.48 (C_5H_4),

83.22 (C_5H_4), 83.37 (C_5H_4), 83.55 (C_5H_4), 89.72 (C_5H_4), 93.11 (C_5H_4), 94.01 (C_5H_4), 94.74 (C_5H_4), 95.10 (C_5H_4), 96.93 (C_5H_4), 120.95 (Ph), 124.16 (Ph), 126.71 (Ph), 126.81 (Ph), 127.25 (Ph), 127.63 (Ph), 129.19 (Ph), 136.44 (Ph), 136.78 (Ph), 144.36 (Ph), 144.96 (Ph), 152.97 (J = 13.0 Hz, Ph), 215.51 (CO), 215.63 (CO), 218.19 (J = 41 Hz, CO). Anal. Calcd for $C_{45}H_{39}Si_2Fe_2O_6P$: C, 61.80; H, 4.49. Found: 61.80; 4.34.

Synthesis of (η^5,η^5-$C_5H_4Me_2SiSiPh_2C_5H_4$)[Fe(CO)$_2$I]$_2$(13). To a 50 mL flask were added 107 mg (0.18 mmol) of **10** and a solution of I_2 in $CHCl_3$ (27 mg/mL, 1.7 mL, 0.18 mmol). The mixture was magnetically stirred for 1 h and washed three times with a saturated solution of sodium sulfite and then another three times with water. The resulting solution was dried over sodium sulfate. After removal of the solvent, the residue was dissolved in a small amount of dichloromethane and separated through a column (neutral alumina). Elution with petroleum ether/chloroform (v/v; 1:1) gave a brown band, from which 91 mg (60% yield) of **13** was obtained as dark brown crystals, mp 126−127 °C. IR (KBr): 2040 (s), 2029(s) 2001 (s), 1978 (s) cm^{-1}.^{1}H NMR ($CDCl_3$): δ 0.70 (s, 6H, $SiMe_2$), 4.71 (m, 2H, Cp), 4.88 (m, 2H, Cp), 5.05 (m, 2H, Cp), 5.28 (m, 2H, Cp), 7.46 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$): δ −2.01, −1.95 ($SiMe_2$), 83.50 (Cp), 84.56 (Cp), 85.67 (Cp), (Cp), 87.46 (Cp), 92.73 (Cp), 93.58 (Cp), 128.64 (Ph), 130.56 (Ph), 132.16 (Ph), 136.03 (Ph), 212.67 (CO), 213.16 (CO). Anal. Calcd for $C_{28}H_{24}Si_2Fe_2O_4I_2$: C, 39.75; H, 2.84. Found: C, 39.28; H, 3.15.

X-ray Crystallography. Single crystals of **3**, **4**, **7**, **10**, **11**, and **13** suitable for X-ray diffraction analyses were obtained from hexane/CH_2Cl_2 solvents. Data collections were performed on a Bruker SMART 1000 diffractometer, using the $2\theta/\omega$ scan technique with Mo Kα (λ = 0.71073 Å) radiation. All structures were solved by direct methods and refined using standard least-squares and Fourier techniques. Non-hydrogen atoms are refined with anisotropic thermal parameters. Hydrogen atoms were added theoretically and refined with isotropic thermal parameters. Crystal and structure refinement data are shown in Tables 1 and 2.

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Supporting Information Available: The side views of the molecular structures of **3**, **4**, **7**, and **10**, and CIF files giving X-ray structural data for complexes **3**, **4**, **7**, **10**, **11**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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