Lewis Acid-Catalyzed Friedel−Crafts Alkylation of Ferrocene with Allylchlorosilanes

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Friedel−Crafts alkylations of ferrocene, **1**, with allylchlorosilanes in the presence of Lewis acid catalysts under mild conditions gave regiospecific [1-methyl-2-(alkylchlorosilyl)ethyl]-ferrocenes in fair to good yields depending upon the substituents on silicon, along with small amounts of dialkylated products. The alkylation of ferrocene with 1.2 equiv of (2-methylallyl)-dimethylchlorosilane, **2b**, at 0 °C gave monoalkylated ferrocene **3b** and an isomeric mixture of dialkylated products in 76% and 4% yields, respectively. The yield of the dialkylated ferrocene mixture increased to 21% when 2 equiv of alkylating agent **2b** was used. The two components of the dialkylated product mixture were identified as 1,1′-dialkylated ferrocene **4b** (17%), and 1,3-dialkylated ferrocene **4b′** (4%). A higher yield of the 1,1′-diadduct compared to the 1,3-diadduct indicates that the electron-donating alkylsilyl group does not greatly enhance a second alkylation on the same ring. The reactivities of allylchlorosilanes in the ferrocene alkylations decrease in the following order: allyldialkylchlorosilane > allyl(alkyl)-dichlorosilane ≫ allyldichlorosilane ≈ allyltrichlorosilane. The catalytic efficiencies of Lewis acids for the alkylations decrease in the following order: $HfCl_4 > ZrCl_4 > AlCl_3 > AlBr_3 > TiCl_4$.

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Introduction

Ferrocene behaves in many respects like an electron-rich aromatic compound, which is activated toward electrophilic reaction.[1] For example, the Friedel−Crafts type acylation of ferrocene with acyl halides proceeds under mild conditions and gives acylferrocenes in yields over 80%.[2] In the acylation reaction, ferrocene is 10^6 times more reactive than benzene. However, the Friedel−Crafts type alkylation of ferrocene with alkyl halides or olefins is different from that of benzene with respect to reactivity and yields. The yields of ferrocene alkylations are often very low, and the separation of alkylated byproducts is tedious.[3,4] Therefore, alkylated ferrocenes are rare and are generally prepared by multistep processes.

The Friedel−Crafts type alkylation of ferrocene with alkyl bromide in the presence of aluminum chloride catalyst to give alkylferrocenes was first reported by Nesmeyanov and Kochetkova.[5] In the alkylation of ferrocene with ethyl bromide, monoethylated product was obtained in only 4% yield along with the di- and trialkylated products in 3.5% yield, respectively.[5] These researchers also reacted ferrocene with ethylene and obtained a 20.5% yield of alkylated product.[6] Alkylations of ferrocene with other alkylating agents such as 2-chloroethanol,[7] 1,2-dibromoethane,[7] methyl chloromethyl ether,[4] and chloro- and aminoorganosilanes[8] have been reported, but the yields were poor except for the alkylation involving 1,2-dibromoethane. Alkylation with 1,2-dibromoethane gave a mixture of mono- and polyethylated products in approximately 90% yield; however, 30 equiv of 1,2-dibromoethane and 5 equiv of $AlCl_3$ were required.

Sollott and Peterson first reported that ferrocene could be silylated with chloro- and aminosilanes analogously to Friedel−Crafts alkylations with alkyl halides.[8] Alkylations with aminochlorosilanes afforded hydroxysilylferrocenes in good to moderate yields. On the other hand, chlorophenylsilanes gave only low yields of phenylsilylferrocenes. These results indicated that a silylenium ion intermediate was generated via cleavage of silicon−halogen bonds under the reaction conditions. Olah and co-workers later reported the trialkylsilylation of ferrocene using a catalyst consisting of a 2:1 mixture of aluminum chloride and sterically hindered tertiary amines in order to prevent the protodesilylation of the product.[9]

Recently, we reported Friedel−Crafts type alkylations of aromatic compounds with allylchlorosilanes[10] and vinylchlorosilanes[11,12] in the presence of Lewis acid catalysts. Alkylations with allylchlorosilanes proceeded

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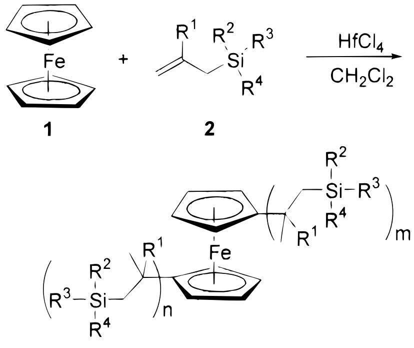
smoothly at temperatures as low as −45 °C and gave 3-arylsilabutanes regiospecifically in good yields. Alkylations of substituted benzenes with vinylchlorosilanes also proceeded in good yields at room temperature to give polyalkylated products having up to six 2-silylethyl groups. Allylchlorosilanes were found to be more reactive than vinylchlorosilanes. In the alkylation reactions, the reactivities of the allylchlorosilanes increased as the number of chlorine atoms on the silicon increased, but decreased as the number of methyl groups increased.[13] Allyltrimethylsilane did not give alkylated products but instead dimerized to give the allylsilylation product.[14] In an extension of this study, the alkylation of ferrocene with allylchlorosilanes was attempted in the presence of various Lewis acids. In the present paper, we wish to report a convenient one-step synthesis of alkylferrocenes containing alkylchlorosilyl groups in β-positions relative to the ferrocene ring.

Results and Discussion

Lewis Acid-Catalyzed Alkylation of Ferrocene (1) with Allyldimethylchlorosilane (2a). The alkylation of **1** with **2a** as a representative allylchlorosilane was carried out using different Lewis acids as catalyst in various solvent systems (eq 1). For the $HfCl_4$-catalyzed alkylations, different mole ratios of $HfCl_4$/**2a** were used. These results are summarized in Table 1.



1 **2**

(1)

3 (m + n = 1)
4 (m + n = 2)
a: R^1 = H, R^2 = R^3 = Me, R^4 = Cl
b: R^1 = Me, R^2 = R^3 = Me, R^4 = Cl
c: R^1 = H, R^2 = Me, R^3 = R^4 = Cl
d: R^1 = H, R^2 = *i*-Pr, R^3 = R^4 = Cl
e: R^1 = H, R^2 = *n*-Hex, R^3 = R^4 = Cl
f: R^1 = H, R^2 = H, R^3 = R^4 = Cl
g: R^1 = H, R^2 = R^3 = R^4 = Cl

Although numerous Lewis acids have been used as catalysts for Friedel−Crafts alkylations,[15] $AlCl_3$ is known as one of the most active catalysts for alkylations involving organosilanes.[13] The alkylation of **1** with **2a** in the presence of $AlCl_3$ catalyst at 0 °C in methylene chloride solution for 1.5 h (entry 1) gave the monoadduct [1-methyl-2-(dimethylchlorosilyl)ethyl]ferrocene (**3a**) in 74% yield, along with the diadducts, bis[1-methyl-2-(dimethylchlorosilyl)ethyl]ferrocenes (**4a**, 6%). We also found that ferrocene had a tendency to be easily oxidized, in which case it formed a greenish complex with $AlCl_3$.[16] As the nonreactive complex was formed, the catalytic activity of $AlCl_3$ was reduced.

Table 1. Lewis Acid-Catalyzed Alkylation of 1 with 2a

entry no.	Lewis acid	equiv[c]	reaction conditions[a] solvent	temp (°C)	time (h)	products (%)[b] **3a**	**4a**
1	$AlCl_3$	0.1	CH_2Cl_2	0	1.5	74	6
2	$AlBr_3$	0.1	CH_2Cl_2	0	1.5	71	7
3	$TiCl_4$	0.1	CH_2Cl_2	0	1.5	0	0
4	$ZrCl_4$	0.1	CH_2Cl_2	0	1.5	78	10
5	$HfCl_4$	0.1	CH_2Cl_2	0	1.5	86	8
6	$HfCl_4$	0.05[d]	CH_2Cl_2	0	2	34	0
7	$HfCl_4$	0.2	CH_2Cl_2	0	1	78	9
8	$HfCl_4$	0.4	CH_2Cl_2	0	1	72	15
9	$HfCl_4$	0.8	CH_2Cl_2	0	0.75	60	6
10	$HfCl_4$	0.1	$CHCl_3$	0	3	83	6
11	$HfCl_4$	0.1	CCl_4[e]	rt	9	41	0
12	$HfCl_4$	0.1	hexane[f]	reflux	8	37	0

[a] 1:4 mixture of **2a** and **1** was used. [b] GLC yields. [c] Equiv of Lewis acid was based on **2a** used. [d] 62% of unreacted **2a** was recovered. [e] 55%. [f] 60% of unreacted **2a** was recovered.

As shown in Table 1, $AlBr_3$ showed comparable catalytic activity to $AlCl_3$, while $TiCl_4$ was inactive. Among the group 4 transition metal chlorides, $ZrCl_4$ and $HfCl_4$ were highly active and afforded the alkylation products **3a** and **4a** in 88% and 94% yields, respectively. Catalytic activities increased as the size of the metal increased from aluminum to hafnium, with titanium being the exception. Among the Lewis acid catalysts used, $HfCl_4$ was the best catalyst for the alkylation of **1**. It is interesting to note that mild Lewis acids such as $HfCl_4$ and $ZrCl_4$ were more effective than $AlCl_3$ and $AlBr_3$, both known to be strong Lewis acids. The higher activity of $HfCl_4$ than $AlCl_3$ may be due to the easy complexation of $AlCl_3$ to ferrocene.[9]

To find the optimum conditions for the alkylation, the $HfCl_4$-catalyzed alkylation was carried out using various amounts of the catalyst with respect to **2a**. The rate of alkylation increased as the amounts of $HfCl_4$ increased from 0.05 to 0.8, but the amount of diadduct products formed in the reaction also increased. The reaction with 0.05 equiv of $HfCl_4$ was very slow and gave only a 34% yield of product after a 2 h reaction period, suggesting that insufficient catalyst was present for effective alkylation. As shown in entry 5 of Table 1, the reaction of **1** with **2a** in methylene chloride at 0 °C for 1.5 h gave **3a** in 86% yield. The same reaction in chloroform (entry 10) for 3 h gave **3a** in 83% yield. When carbon tetrachloride or hexane was used as the solvent (entries 11 and 12), higher reaction temperatures were required and the yields were only around 40%. Among the solvents used, methylene chloride was found to be the most effective solvent.

Alkylation of 1 with Allylchlorosilanes (2a−g). The alkylation of **1** with **2a**−**g** was carried out in the presence of $HfCl_4$ catalyst in methylene chloride at temperatures ranging from 0 °C to reflux temperature and afforded the corresponding regiospecific alkylated products, [1-methyl-2-(alkylchlorosilyl)ethyl]ferrocenes, **3a**−**g**, in fair to good yields depending upon the substituents on silicon (eq 1). The results obtained using optimum reaction conditions are summarized in Table 2.

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Table 2. HfCl$_4$-Catalyzed Alkylation of 1 with Allylchlorosilanes

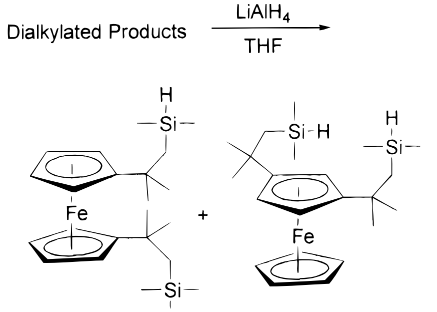
entry no.	allylsilane **2**	reaction conditions[a] HfCl$_4$ (equiv)	temp (°C)	time (h)	products (%)[b] **3**	**4**
13	**2a**	0.1	0	1.5	**3a**, 86	**4a**, 8
14	**2b**	0.2	0	1	**3b**, 76	**4b**, 4
		0.1	0	1.5	trace	0
15	**2c**	0.4	reflux	7	**3c**, 82	0
16	**2d**	0.4	reflux	7	**3d**, 84	0
17	**2e**	0.4	reflux	6	**3e**, 90	0
18	**2f**[c]	0.8	reflux	16	trace	0
19	**2g**	0.8	reflux	16	trace	0

[a] 1:4 reaction of **2** and **1** was carried out in the presence of HfCl$_4$ based on **2** used. [b] GLC yields. [c] Polymeric materials were obtained as major products.

As shown in Table 2, the alkylations of **1** with **2** in the presence of hafnium chloride catalyst at 0 °C or reflux temperature gave monoalkylated ferrocenes, along with small amounts of dialkylated ferrocenes. The yields of monoadducts ranged from trace amounts to 90% depending upon the substituents on the silicon atom and the amount of catalyst used. The yields of dialkylation products generally ranged from 0% to 8%. The reactivity of **2** in the alkylation of **1** depended upon the substituents on the silicon atom. The reactivity increased as the number of alkyl groups on the silicon atom of **2** increased. The HfCl$_4$-catalyzed alkylation of **1** with **2a** at 0 °C for 1.5 h afforded **3a** in 86% yield and **4a** as an isomeric mixture in 8% yield. In the case of **2b**, 0.2 equiv of HfCl$_4$ was required because of the lower reactivity of **2b**, presumably due to the steric hindrance of the methyl group on the β-carbon of the allyl group. The alkylations with allyl(alkyl)dichlorosilanes (**2c**, **2d**, **2e**) required 0.4 equiv of HfCl$_4$ catalyst and reflux temperatures to give the alkylated products in high yields (82−90%). However, allyldichlorosilane (**2f**) and allyltrichlorosilane (**2g**) were relatively unreactive, suggesting that the formation of the β-silyl cation intermediate is largely retarded because of the less effective $\sigma-\pi$ conjugation due to the electronegative chlorine atoms on silicon.[10] The reactivity of **2** in the alkylation of **1** decreased in the following order: allyldialkylchlorosilanes > allylalkyldichlorosilanes ≫ allyldichlorosilane ≈ allyltrichlorosilane. This reactivity order is opposite the reactivity order for the alkylations of substituted benzenes.[14] Considering that alkylations of both substituted benzenes and ferrocene are electrophilic substitution reactions, this reactivity difference is not clear but likely related to the complexation of ferrocene with the Lewis acid catalysts.

Characterization of Dialkylated Ferrocenes. Identification of the dialkylated products, **4a**, was complicated by the fact that there are three possible structural isomers and two diastereomers for each structural isomer. For simplicity, **2b** was used as a representative allylchlorosilane for the preparation of dialkylated ferrocenes. When **1** was reacted with 2 equiv of **2b** in the presence of hafnium chloride at 0 °C, monoalkylated product, **3b**, was obtained in 67% yield as the major product along with the isomeric mixture of dialkylated products in 21% yield. GLC analysis of the dialkylated product mixture showed two components in a ratio of 17:4. The ^{13}C NMR spectrum showed no diastereomers, as expected. The structures of the isomeric dialkylation products were deduced from identification of the corresponding reduced compounds obtained from reaction with lithium aluminum hydride (eq 2). The reduced compounds are stable toward the atmosphere and allowed a better separation of isomers by preparative GLC. Subsequent NMR spectral analysis allowed assignment of the structure of each isomer.

In the identification of the isomers, the ^{1}H NMR chemical shifts of the cyclopentadienyl hydrogens were very helpful. In the ^{1}H NMR spectra of the reduced diadducts, the protons of the nonalkylated ring appeared as a singlet at 4.12 ppm,[17] notably downfield compared to the signals corresponding to mono- and dialkylated rings. In comparison to the literature values for dialkylated ferrocenes,[18] the two singlets at 4.02 and 4.06 ppm with an integration ratio of 1:1 can be easily assigned to the two sets of the ring protons of the heteroannularly disubstituted ferrocene in 2,5- and 3,4-positions, respectively. Two different proton signals appearing at 3.93 and 3.96 ppm with an integration ratio of 1:2 were assigned to the ring protons of homoannularly disubstituted ferrocene. These results disclose the structures of the isomeric dialkylated ferrocenes, **5b** and **5b′**, to be 1,1′-dialkylated and 1,3-dialkylated ferrocenes as shown in eq 2. From these results, the two components in the dialkylation products can be deduced as 1,1′-bis[1,1-dimethyl-2-(dimethylchlorosilyl)ethyl]ferrocene (**4b**, 17%) and 1,3-bis[1,1-dimethyl-2-(dimethylchlorosilyl)ethyl]ferrocene (**4b′**, 4%).



5b (81%) **5b′** (19%)

(2)

Higher yields of 1,1′-diadduct than 1,3-diadduct indicate that the electron-donating alkylsilyl group does not greatly enhance a second alkylation on the same ring. In addition to this electronic reason, the 1,1′-diadduct should be favorable to minimize the steric interactions between two alkyl groups.

Experimental Section

All reactions and manipulations were carried out under prepurified dinitrogen using Schlenk techniques. Glassware was flame-dried before use. Dried solvents were employed in all reactions. Lewis acids and ferrocene were purchased from Aldrich Chemical Co. Allylhexyldichlorosilane, allylisopropyldichlorosilane, and (2-methylallyl)dimethylchlorosilane were prepared using Grignard reagents.[19] All other allylchlorosilanes were purchased from Gelest Chemical Co. All allylchlorosilanes were distilled before use. The reaction products were analyzed by GLC using a packed column (10% SE-30 or SE-

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54 on 80−100 mesh chromosorb W/AW, $^1/_8$ in. × 1.5 m) or a capillary column (SE-30, 30 m) with a Varian 3300 gas chromatograph, flame ionization detector, and Hitachi D-2500 integrator. Samples for characterization were purified by preparative GLC using a Donam system series DS 6200 gas chromatograph with a thermal conductivity detector and a 4 m by $^1/_8$ in. stainless steel column packed with 20% OV-101 on 80−100 mesh chromosorb P/AW. NMR spectra were recorded on a Varian Unity Plus 600 (FT, 600 MHz, ^{1}H) and a Varian Gem 300 (FT, 300 MHz, ^{1}H; 75 MHz, ^{13}C) spectrometer in $CDCl_3$ solvent. Mass spectra were obtained using a Hewlett-Packard 6890 GC/MS. HRMS (high-resolution mass (70 eV, EI) spectra) were performed by Korea Basic Science Institute, Seoul, Korea. Elemental analyses were performed by the chemical analysis laboratory of the Korea Institute of Science and Technology.

Typical Procedure for Reaction of 1 with 2a. A mixture of **1** (10.45 g, 56.2 mmol), **2a** (1.90 g, 14.1 mmol), and $HfCl_4$ (0.45 g, 1.41 mmol) in methylene chloride (100 mL) under a nitrogen atmosphere was stirred for 1.5 h at 0 °C, after which the solvent was removed by simple distillation. The remaining mixture was extracted with hexane (80 mL), and the dark green sticky solid was filtered off. Hexane was distilled off from the filtrate, and unreacted **1** was removed by recrystallization and sublimation. Vacuum distillation (bp 110−114 °C/0.6 mmHg) gave **3a** (3.0 g, 67% yield based on **2b**) and **4a** (0.81 g, 13%, bp 170−175 °C/0.6 mmHg) as an isomeric mixture.

Also, 0.15 g of unidentified high-boiling compounds was obtained. Data for **3a**: ^{1}H NMR (600 MHz) δ 0.43 (s, 3H, SiCH_3), 0.44 (s, 3H, SiCH_3), 1.10 (dd, J = 14.8, 9.6 Hz, 1H, CH_aH$_b$Si), 1.29 (dd, J = 14.8, 4.2 Hz, 1H, CH$_a$$H_b$Si), 1.33 (d, J = 6.6 Hz, 3H, CHCH_3), 2.79−2.82 (m, 1H, CHCH$_3$), 4.11 (s, 4H, C$_5$$H_4$), 4.17 (s, 5H, C$_5$$H_5$); ^{13}C NMR (75 MHz) δ 2.78, 2.97 (Si(CH$_3$)$_2$), 23.76 (CHCH$_3$), 28.87 (CHCH$_3$), 29.57 (CH$_2$Si), 65.73, 66.76, 66.93, 67.12 (C_5H$_4$), 68.43 (C_5H$_5$), 98.02 (*ipso*-*C* of Cp); HRMS (*m*/*e*) calcd for $C_{15}H_{21}SiClFe$ (M^+), 320.0450; found, 320.0451. Anal. Calcd for $C_{15}H_{21}SiClFe$: C, 56.18; H, 6.60. Found: C, 56.40; H, 6.79. Data for **4a**: ^{1}H NMR (300 MHz) δ 0.41 (s, 6H, Si(CH_3)$_2$), 0.42 (s, 6H, Si(CH_3)$_2$), 1.07 (dd, J = 14.8, 9.6 Hz, 2H, 2(CH_aH$_b$Si)), 1.25−1.29 (m, 2H, 2(CH$_a$$H_b$Si)), 1.31 (d, J = 6.7 Hz, 6H, 2(CHCH_3)), 2.72−2.85 (m, 2H, 2(CHCH$_3$)), 4.04−4.10 (s & m, 8H, C$_{10}$$H_8$ of isomeric dialkylated ferrocenes); ^{13}C NMR (75 MHz) δ 2.79, 2.98 (Si(CH$_3$)$_2$), 23.82 (CHCH$_3$), 28.86 (CHCH$_3$), 29.64 (CH$_2$Si), 64.43, 64.67, 65.42, 65.63, 66.15, 67.25, 67.82, 68.50, 69.0 (two C_5H$_4$'s of isomeric dialkylated ferrocenes), 98.01 (*ipso*-*C* of Cp); HRMS (*m*/*e*) calcd for $C_{20}H_{32}Si_2Cl_2Fe$ (M^+), 454.0769; found, 454.0767. Anal. Calcd for $C_{20}H_{32}Si_2Cl_2Fe$: C, 52.75; H, 7.08. Found for an isomeric mixture of **4a**: C, 52.90; H, 7.23.

Reaction of 1 with 2b. Using the procedure described in the reaction of **1** with **2a**, the reaction of **1** (1.05 g, 5.64 mmol) with **2b** (0.21 g, 1.41 mmol) in the presence of $HfCl_4$ (0.09 g, 0.28 mmol) gave **3b** (76%) and **4b** (4%). Data for **3b**: ^{1}H NMR (300 MHz) δ 0.28 (s, 6H, Si(CH_3)$_2$), 1.29 (s, 2H, SiCH_2), 1.42 (s, 6H, C(CH_3)$_2$), 4.09 (dd, J = 10.8, 1.8 Hz, 4H, C$_5$$H_4$), 4.16 (s, 5H, C$_5$$H_5$); ^{13}C NMR (75 MHz) δ 3.97 (Si(CH$_3$)$_2$), 31.37 (C(CH$_3$)$_2$), 32.92 (C(CH$_3$)$_2$), 38.25 (CH$_2$Si), 65.60, 67.12 (C_5H$_4$), 68.37 (C_5H$_5$), 102.43 (*ipso*-*C* of Cp); HRMS (*m*/*e*) calcd for $C_{16}H_{23}SiClFe$ (M^+), 334.0607; found, 334.0611. Anal. Calcd for $C_{16}H_{23}SiClFe$: C, 57.41; H, 6.93. Found: C, 57.40; H, 7.10.

Compounds **5b** and **5b′** were prepared first by the alkylation of **1** (1.05 g, 5.64 mmol) with **2b** (1.66 g, 11.2 mmol) in the presence of $HfCl_4$ (0.36 g, 1.12 mmol) at 0 °C to give **3b** (0.82 g, 67%) and a 4:1 mixture of **4b** and **4b′** (0.37 g, 21%). To a stirred solution of lithium aluminum hydride (0.06 g, 1.58 mmol) in 5 mL of dried THF was added dropwise a solution of 0.37 g (0.77 mmol) of the isomeric mixture of **4b** and **4b′** in 5 mL of THF. The resulting mixture was stirred for 1 h and hydrolyzed with water. The organic layer was extracted with 15 mL of diethyl ether, and the extracts were washed with aqueous $NaHCO_3$ and dried over anhydrous $MgSO_4$. The solvent was distilled off. The remaining products were vacuum distilled to give **5b** and **5b′** (0.32 g, 100%). A mixture of **5b** and **5b′** was purified using preparative GLC. Data for **5b**: ^{1}H NMR (300 MHz) δ −0.06 (d, J = 3.6 Hz, 12H, 2(Si(CH_3)$_2$)), 0.96 (d, J = 3.2 Hz, 4H, 2(SiCH_2)), 1.35 (s, 12H, 2(C(CH_3)$_2$)), 3.87 (sept, J = 3.6 Hz, 2H, 2(SiH)), 4.02 (s, 4H, C$_5$$H_4$), 4.06 (s, 4H, C$_5$$H_4$); ^{13}C NMR (75 MHz) δ −2.62 (Si(CH$_3$)$_2$), 31.07 (C(CH$_3$)$_2$), 32.86 (C(CH$_3$)$_2$), 33.95 (CH$_2$Si), 65.58, 67.52 (C_5H$_4$), 102.32 (*ipso*-*C* of Cp). Data for **5b′**: ^{1}H NMR (300 MHz) δ −0.02 (d, J = 3.6 Hz, 12H, 2(Si(CH_3)$_2$)), 0.97 (d, J = 3.1 Hz, 4H, 2(SiCH_2)), 1.33 (s, 12H, 2(C(CH_3)$_2$)), 3.91 (sept, J = 3.6 Hz, 2H, 2(SiH)), 3.93 (s, 1H, C$_5$$H_3$), 3.96 (s, 2H, C$_5$$H_3$), 4.12 (s, 5H, C$_5$$H_5$); ^{13}C NMR (75 MHz) δ −2.48 (Si(CH$_3$)$_2$), 30.84, 30.93 (C(CH$_3$)$_2$), 32.95 (C(CH$_3$)$_2$), 33.59 (CH$_2$Si), 62.81, 63.71 (C_5H$_3$), 68.55 (C_5H$_5$), 102.29 (*ipso*-*C* of Cp). Anal. Calcd for $C_{22}H_{38}Si_2Fe$: C, 63.74; H, 9.24. Found for a mixture of **5b** and **5b′**: C, 63.70; H, 9.29.

Reaction of 1 with 2c. Using the procedure described in the reaction of **1** with **2a**, the reaction of **1** (1.05 g, 5.64 mmol) with **2c** (0.22 g, 1.41 mmol) in the presence of $HfCl_4$ (0.18 g, 0.56 mmol) gave [1-methyl-2-(methyldichlorosilyl)ethyl]ferrocene (**3c**; 82%, bp 104−110 °C/0.6 mmHg). Data for **3c**: ^{1}H NMR (300 MHz) δ 0.74 (s, 3H, SiCH_3), 1.39 (dd, 1H, CH_aH$_b$Si overlapped with CHCH_3), 1.40 (d, J = 6.6 Hz, 3H, CHCH_3), 1.59(dd, J = 14.5, 4.2 Hz, 1H, CH$_a$$H_b$Si), 2.90−3.0 (m, 1H, C$HCH_3$), 4.12 (s, 4H, C$_5$$H_4$), 4.17 (s, 5H, C$_5$$H_5$); ^{13}C NMR (75 MHz) δ 6.61 (SiCH$_3$), 23.63 (CHCH$_3$), 28.74 (CHCH$_3$), 32.17 (CH$_2$Si), 65.74, 66.85, 67.11, 67.37 (C_5H$_4$), 68.51 (C_5H$_5$), 96.88 (*ipso*-*C* of Cp); HRMS (*m*/*e*) calcd for $C_{14}H_{18}SiCl_2Fe$ (M^+), 339.9904; found, 339.9901. Anal. Calcd for $C_{14}H_{18}SiCl_2Fe$: C, 49.29; H, 5.32. Found: C, 49.40; H, 5.49.

Reaction of 1 with 2d. Using the procedure described in the reaction of **1** with **2a**, the reaction of **1** (1.05 g, 5.64 mmol) with **2d** (0.26 g, 1.41 mmol) in the presence of $HfCl_4$ (0.18 g, 0.56 mmol) gave [1-methyl-2-(isopropyldichlorosilyl)ethyl]ferrocene (**3d**; 84%). Data for **3d**: ^{1}H NMR (300 MHz) δ 1.09 (d, J = 6.7 Hz, 3H, isopropyl-(CH_3)$_a$), 1.12(d, J = 6.7 Hz, 3H, isopropyl-(CH_3)$_b$), 1.16−1.25 (m, 1H, isopropyl-CH), 1.32 (dd, J = 15.1, 9.9 Hz, 1H, CH_aCH$_b$Si), 1.38 (d, J = 6.9 Hz, 3H, CHCH_3), 1.57 (dd, J = 15.2, 4.1 Hz, 1H, CH$_a$CH_bSi), 2.86−2.97 (m, 1H, CHCH$_3$), 4.09 (s, 4H, C$_5$$H_4$), 4.15 (s, 5H, C$_5$$H_5$); ^{13}C NMR (75 MHz) δ 16.11, 16.15 (CH(CH$_3$)$_2$ of isopropyl), 19.14(CH(CH$_3$)$_2$), 23.56(CHCH$_3$), 28.34(CHCH$_3$), 28.61 (CH$_2$Si), 65.78, 66.63, 67.05, 67.24 (C_5H$_4$), 68.46 (C_5H$_5$), 97.40 (*ipso*-*C* of Cp); HRMS (*m*/*e*) calcd for $C_{16}H_{22}SiCl_2Fe$ (M^+), 368.0217; found, 368.0221. Anal. Calcd for $C_{16}H_{22}SiCl_2Fe$: C, 52.05; H, 6.01. Found: C, 51.90; H, 6.14.

Reaction of 1 with 2e. Using the procedure described in the reaction of **1** with **2a**, the reaction of **1** (1.05 g, 5.64 mmol) with **2e** (0.32 g, 1.41 mmol) in the presence of $HfCl_4$ (0.18 g, 0.56 mmol) gave [1-methyl-2-(hexyldichlorosilyl)ethyl]ferrocene (**3e**; 90%, bp 165−170 °C/0.6 mmHg). Data for **3e**: ^{1}H NMR (300 MHz) δ 0.92 (t, J = 6.6 Hz, 3H, CH_3 of *n*-hexyl), 1.04 (t, J = 8.1 Hz, 2H, SiCH_2 of *n*-hexyl), 1.31−1.36 (m, 9H, SiCH$_2$-(CH_2)$_4$ and CH_aH$_b$Si), 1.39 (d, J = 6.7 Hz, 3H, CHCH_3), 1.56 (dd, J = 15.1, 4.5 Hz, 1H, CH$_a$$H_b$Si), 2.82−2.98 (m, 1H, C$HCH_3$), 4.07 (s, 4H, C$_5$$H_4$), 4.16 (s, 5H, C$_5$$H_5$); ^{13}C NMR (75 MHz) δ 14.13, 21.22, 21.34, 22.51, 30.70, 31.35 (carbons of *n*-hexyl at Si), 23.66 (CHCH$_3$), 28.66 (CHCH$_3$), 32.12 (CH$_2$Si), 65.75, 66.80, 67.07, 67.33(C_5H$_4$), 68.50 (C_5H$_5$), 97.09 (*ipso*-*C* of Cp); HRMS (*m*/*e*) calcd for $C_{19}H_{28}SiCl_2Fe$ (M^+), 410.0687; found, 410.0687. Anal. Calcd for $C_{19}H_{28}SiCl_2Fe$: C, 55.49; H, 6.86. Found: C, 55.65; H, 6.76.

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