Selective and Stepwise Bromodemethylation of the Silyl Ligand in Iron(II) Silyl Complexes with Boron Tribromide

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Treatment of $Cp^*(CO)_2FeSiMe_2R$ ($Cp^* = C_5Me_5$, R = Me and Ph) with 1 equiv of BBr_3 at room temperature afforded $Cp^*(CO)_2FeSiBrMeR$ (R = Me and Ph) and $MeBBr_2$ in high yields via bromodemethylation of the silyl ligand. $Cp^*(CO)_2FeSiBrMeR$ (R = Me and Ph) was further converted to $Cp^*(CO)_2FeSiBr_2R$ (R = Me and Ph) quantitatively on addition of another equivalent of BBr_3 and heating. Treatment of $Cp^*(CO)_2FeSiMe_2SiMe_3$ with 1 equiv of BBr_3 at room temperature led to selective bromodemethylation at the α-silicon atom to produce $Cp^*(CO)_2FeSiBrMeSiMe_3$, which was also converted to $Cp^*(CO)_2FeSiBr_2SiMe_3$ on heating with another equivalent of BBr_3 at 40 °C in quantitative yield. The solid-state structure of $Cp^*(CO)_2FeSiBr_2SiMe_3$ was confirmed by X-ray crystal structure determination.

Introduction

Transition-metal silyl complexes have attracted great interest because of their important roles in various reactions of organosilicon compounds with transition-metal complexes.[1] Although there are many reports on the synthesis, it was only recently demonstrated that direct introduction of functional groups on the silyl ligands is a useful method in synthesizing various derivatives of silyl complexes.[2−4] For example, Malisch et al. reported that regioselective halogenation of α-Si−H groups of $Cp(CO)_2MSiH_2SiH_3$ (M = Fe, Ru) proceeds on treatment with CX_4 (X = Cl, Br) or Br_2 to produce the corresponding $Cp(CO)_2MSiX_2SiH_3$ (M = Fe, Ru) in high yield.[2c] He also reported that hydroxylation of $Cp(CO)_2FeSiH_2SiH_3$ with dimethyldioxirane occurs regioselectively.[4d] Nevertheless, only a limited number of such examples have been reported so far.

Previously, Ueno et al. performed the reaction of a silyliron(II) complex $Cp^*(CO)_2FeSiMe_3$ ($Cp^* = C_5Me_5$) with a Lewis acid $GaCl_3$ that led to the cleavage of the iron−silicon bond to produce $Cp^*(CO)_2FeGaCl_2$ and $ClSiMe_3$ in almost quantitative yield.[5] In the course of our application of this method to the synthesis of boryl complexes by using BBr_3 instead of $GaCl_3$, we unexpectedly found that bromodemethylation of the silyl ligand of $Cp^*(CO)_2FeSiMe_3$ occurred to produce a bromosilyl derivative $Cp^*(CO)_2FeSiBrMe_2$ via cleavage of a silicon−carbon bond. The cleavage of a silicon−carbon bond is an important process in synthetic chemistry, but the cleavage of a Si−C(sp³) bond is quite rare even in organic synthesis.[6] Usually, the cleavage of a Si−C(sp²) bond is more favorable than that of a Si−C(sp³) bond: Trimethylsilyl-substituted arenes ($ArSiMe_3$, Ar = aryl) react with BX_3 to give $XSiMe_3$ and $ArBX_2$ via the selective cleavage of the Si−Ar bond.[7] We report here the details of bromodemethylation of silyliron complexes $Cp^*(CO)_2FeSiMe_2R$ (R = Me, Ph, and SiMe₃) with boron tribromide. The bromination occurs regioselectively and stepwise at the α-Si atom, and the methyl groups are chemoselectively substituted.

Results and Discussion

When a trimethylsilyliron(II) complex $Cp^*(CO)_2FeSiMe_3$ ($Cp^* = \eta^5$-C_5Me_5) (**1a**) was treated with 1 equiv of BBr_3 in C_6D_6 at room temperature, the reaction completed within 1 h to afford the bromodimethylsilyliron(II) complex $Cp^*(CO)_2FeSiMe_2Br$ (**2a**) quantitatively (eq 1) via bromodemethylation of the silyl group. Complex **2a** further reacted with another equivalent of BBr_3 in C_6D_6 on heating (40−60 °C) to lead to the quantitative formation of dibromomethylsilyliron(II) complex $Cp^*(CO)_2FeSiMeBr_2$ (**3a**). Complex **3a** was also obtained directly from the reaction of **1a** with more than 2 equiv of BBr_3 on heating in high yield. Analytically pure **2a** was obtained as yellow crystals by the prepara-

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(1) (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24. (b) Eisen, M. S. In *The Chemistry of Organic Silicon Compounds*, Vol. 2; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Chapter 35. (c) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.
(2) (a) Malisch, W.; Kuhn M. *Chem. Ber.* **1974**, *107*, 2835. (b) Malisch, W.; Ries, W. *Chem. Ber.* **1979**, *112*, 1304. (c) Malisch, W.; Jehle, H.; Möller, S.; Thum, G.; Reising, J.; Gbureck, A.; Nagel, V.; Fickert, C.; Kiefer, W.; Nieger, M. *Eur. J. Inorg. Chem.* **1999**, 1597.
(3) Nikonov, G. I.; Kuzmina, L. G.; Vyboishchikov, S. F.; Lemenovskii, D.; Howard, A. J. A. K. *Chem. Eur. J.* **1999**, *5*, 2947.
(4) (a) Malisch, W.; Lankat, R.; Fey, O.; Reising, J.; Schmitzer, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1917. (b) Malisch, W.; Neumayer, M.; Fey, O.; Adam, W.; Schuhmann, R. *Chem. Ber.* **1995**, *128*, 1257. (c) Möller, S.; Fey, O.; Malisch, W.; Seelbach, W. *J. Organomet. Chem.* **1996**, *506*, 239. (d) Malisch, W.; Jehle, H.; Saha-Möller, C.; Adam, W. *Eur. J. Inorg. Chem.* **1998**, 1585. (e) Malisch, W.; Hofmann, M.; Kaupp, G.; Käb, H.; Reising, J. *Eur. J. Inorg. Chem.* **2002**, 3235.

(5) Ueno, K.; Watanabe, T.; Ogino, H. *Appl. Organomet. Chem.* **2003**, *17*, 403.
(6) Brook, M. A. In *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, 2000; Chapter 16.
(7) (a) Haubold, W.; Herdtle, J. Gollinger, W.; Einholz, W. *J. Organomet. Chem.* **1986**, *315*, 1. (b) Kaufmann, D. *Chem. Ber.* **1987**, *120*, 853. (c) Kaufmann, D. *Chem. Ber.* **1987**, *120*, 901. (d) Gross, U.; Kaufmann, D. *Chem. Ber.* **1987**, *120*, 991.

tive scale reaction of **1a** with BBr$_3$ in hexane and following removal of the byproduct BBr$_2$Me under vacuum. Complex **3a** was also fully characterized by spectroscopic techniques. In contrast, no tribromosilyliron(II) complex Cp*(CO)$_2$FeSiBr$_3$ was detected even after **3a** and a large excess of BBr$_3$ were heated in C$_6$D$_6$ at 50 °C for 2 days. Analogous halodemethylation of **1a** did not occur when BCl$_3$ or AlCl$_3$ was used instead of BBr$_3$. The H/X exchange reaction of hydrosilyl complexes M-SiH$_n$R$_{3-n}$ with CX$_4$ (X = Cl, Br) or Br$_2$ has been known as almost the only method for halogenation of the silyl ligand in transition-metal silyl complexes.[2,3] To our knowledge, the reaction shown in eq 1 is the first example of halodemethylation of the silyl ligand in transition-metal silyl complexes.

$$ \tag{1} $$

1a (R = Me)   **2a** (R = Me)   **3a** (R = Me)
1b (R = Ph)   **2b** (R = Ph)   **3b** (R = Ph)
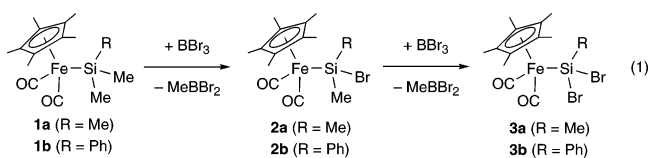
To get insight into the scope and limitation of this bromination reaction, we next investigated the reactions of BBr$_3$ with silyl complexes having not only methyl group(s) but also other substituent(s) simultaneously on a silicon atom. When Cp*(CO)$_2$FeSiMe$_2$Ph (**1b**) was treated with 1 equiv of BBr$_3$ in C$_6$D$_6$ at room temperature, a methyl group on the silyl ligand was selectively substituted to give Cp*(CO)$_2$FeSiMeBrPh (**2b**) (eq 1). The reaction of **2b** with BBr$_3$ at 60 °C further afforded dibromophenylsilyliron(II) complex Cp*(CO)$_2$FeSiBr$_2$Ph (**3b**) as a single product in quantitative yield. Complex **3b** was also obtained directly when **1b** was heated with more than 2 equiv of BBr$_3$. Interestingly, bromodephenylation never occurred under even more severe conditions. As mentioned in the Introduction, this selectivity is opposite that observed in the reactions of organosilicon compounds with Lewis acids BCl$_3$ and BBr$_3$, which cause the cleavage of Si−C(sp^2) bonds in preference to Si−C(sp^3) bonds at ambient temperature.[7] The latter type of selectivity was also observed in the bromodemethylation reactions of (silylcyclopentadienyl)zirconium complexes (Ph$_n$Me$_{3-n}$SiC$_5$H$_4$)$_2$ZrCl$_2$ (n = 1, 2) with BBr$_3$.[8]

This bromodemethylation was found to occur also regioselectively at the α-silicon atom in the case of a disilanyliron(II) complex. Thus, treatment of Cp*-(CO)$_2$FeSiMe$_2$SiMe$_3$ (**1c**) with 1 equiv of BBr$_3$ at room temperature produced Cp*(CO)$_2$FeSiMeBrSiMe$_3$ (**2c**) quantitatively (eq 2). Complex **2c** further reacted cleanly with another equivalent of BBr$_3$ to give Cp*(CO)$_2$-FeSiBr$_2$SiMe$_3$ (**3c**). These complexes **2c** and **3c** have been isolated and fully characterized by spectroscopic techniques (see Experimental Section). The structure of **3c** was confirmed by X-ray crystallography (vide infra). No β-silicon-substituted complex was observed even by addition of an excess of BBr$_3$ to **3c** and heating the mixture. These results imply that the iron fragment plays an important role in determining the chemo- and regioselectivity of this bromination reaction. It is worth
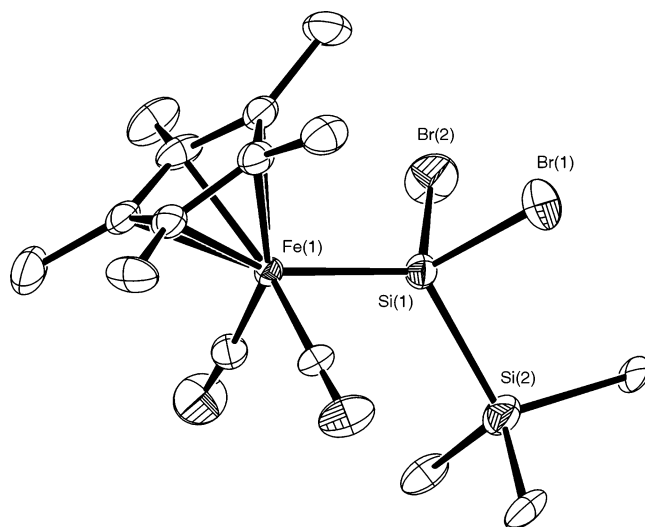
(8) (a) Deck, P. A.; Fisher, T. S.; Sloan Downey, J. *Organometallics* **1997**, *16*, 1193. (b) Deck, P. A.; Cheng, X.; Stoebenau, E. J.; Slebodnick, C.; Billodeaux, D. R., Fronczek, F. R. *Organometallics* **2000**, *19*, 5404.

Figure 1. Molecular structure of **3c**, showing 50% thermal ellipsoids. Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (deg): Fe−Si(1), 2.262-(2); Si(1)−Br(1), 2.281(2); Si−Br(2), 2.281(2); Si(1)−Si(2), 2.343(3); Fe−Si(1)−Br(1), 113.0(1); Fe−Si(1)−Br(2), 114.5-(1); Fe−Si(1)−Si(2), 123.7(1).

noticing that the regioselectivity of this reaction coincides with that of the above-mentioned halogenation of Cp(CO)$_2$FeSiH$_2$SiH$_3$ with CX$_4$ (X = Cl, Br) reported by Malisch et al.[2c] Unlike **1a**, the reaction of the Cp analogue, CpFe(CO)$_2$SiMe$_3$, with BBr$_3$ only produced a complicated mixture containing CpFe(CO)$_2$SiBrMe$_2$ (~30%) that could not be isolated.

$$ \tag{2} $$

1c   **2c**   **3c**
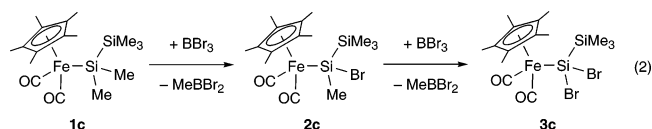
The X-ray crystal structure of **3c** (Figure 1) shows that two bromine atoms are attached to the α-silicon atom and the SiMe$_3$ group is located at the position farthest away from the bulky Cp* ligand. The Fe−Si(1) bond length (2.262(2) Å) is shorter than the Fe−Si bond lengths of trialkylsilyliron complexes (2.33−2.46 Å).[9] This tendency is often observed in halo-substituted silyl complexes in which interaction between the low-lying Si−X σ*-orbital and a symmetry-adapted, occupied d-orbital of the metal causes the shortening of the M−Si bond length.[10] The Si(1)−Si(2) bond length (2.343(3) Å) of **3c** is in the normal range of the values previously reported for disilanyliron complexes (2.33−2.39 Å).[9] The Si(1)−Br(1) and Si(1)−Br(2) bond lengths (2.281(2) and 2.281(2) Å) are at the longest extreme of the Si−Br bond lengths ever reported for organobromosilanes (2.20−2.28 Å).[9]

Finally, we investigated the effect of the substituents of the silyl ligand and the solvent on the reaction rate of the bromodemethylation. The results are summarized

(9) (a) Vancea, L.; Bennett, M. J.; Jones, C. E.; Smith, R. A.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 897. (b) Knorr, M.; Müller, J.; Schubert, U. *Chem. Ber.* **1987**, *120*, 879. (c) Pannell, K. H.; Lin, S.-H.; Kapoor, R. N.; Cervantes-Lee, F.; Pinon, M.; Parkanyi, L. *Organometallics* **1990**, *9*, 2454. (d) Nakazawa, H.; Yamaguchi, Y.; Kawamura, K.; Miyoshi, K. *Organometalics* **1997**, *16*, 4626. (e) Pannell, K. H.; Kobayashi, T.; Cervantes-Lee, F.; Zhang, Y. *Organometallcs* **2000**, *19*, 1.
(10) Lemke, F. R.; Galat, K. J.; Youngs, W. J. *Organometallics* **1999**, *18*, 1419.

Table 1. Effect of the Substituents of the Silyl Ligand and the Solvent on the Reaction Rate of the Bromodemethylation
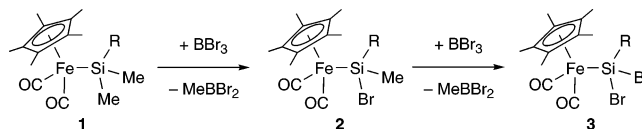
entry	compound	equiv of BBr₃	solvent	T (°C)	time (h)	product	yield (%)[b]
1	**1a** (R = Me)	1	C₆D₆	20	0.5	**2a**	quant.
2	**1b** (R = Ph)	1	C₆D₆	20	1	**2b**	quant.
3	**1c** (R = SiMe₃)	1	C₆D₆	20	0.2	**2c**	quant.
4	**2a** (R = Me)	1.2	C₆D₆	50	34	**3a**	quant.
5	**2b** (R = Ph)	1.2	C₆D₆	50	96	**3b**	quant.
6	**2c** (R = SiMe₃)	1.2	C₆D₆	50	2.5	**3c**	quant.
7	**2a** (R = Me)[c]	2	hexane	20	48	**3a**	7[d]
8	**2a** (R = Me)[c]	2	toluene	20	48	**3a**	47[d]
9	**2a** (R = Me)[c]	2	CH₂Cl₂	20	48	**3a**	83[d]

[a] A 0.10 M solution was used. [b] The yield was determined by ^{1}H NMR. [c] A 0.05 M solution was used. [d] The value shows the conversion (%).

in Table 1. The reaction was the fastest when the substituent on the α-silicon atom was a SiMe₃ group (see entries 4, 5, and 6). The reaction slowed as the substituent was changed from Me to Ph. Substitution of a bromine atom for a methyl group significantly deactivated the bromodemethylation (compare entries 1−2 and 4−5). Thus, the more electron-donating the substituents became, the faster the bromination reaction proceeded. With respect to the solvent effect, when the reaction of **2a** with 2 equiv of BBr₃ was carried out in hexane, toluene, or dichloromethane in the same concentration, the percentage of conversion from **2a** to **3a** after 48 h was 7%, 47%, and 83%, respectively (entries 7−9). Apparently, the more polar the solvent became, the faster the bromination reaction proceeded. This tendency suggests that the transition state or intermediate of this reaction is substantially more polarized than the starting complex **1a**. A possible intermediate is a cationic silylene complex [Cp*-(CO)₂Fe=SiR₂]⁺[BMeBr₃]⁻ produced by the abstraction of a methyl anion from **1a** with the Lewis acid BBr₃. The silylene ligand in the cationic part may be stabilized by coordination of either BMeBr₃⁻ or solvent. Many base-stabilized and also base-free cationic silylene complexes have been isolated and well-characterized.[1] It is well known that the silylene ligand in cationic silylene complexes is extremely electrophilic. This would be the driving force for the final step, i.e., bromide transfer from BMeBr₃⁻ to the silylene silicon.

Although this mechanism could rationalize the selective α-bromination of the disilanyl ligand, the preference of a methyl group to a phenyl group in bromination cannot be easily explained by this mechanism. Further investigations on the mechanism of this reaction are under way.

In summary, we found that the reaction of Cp*-(CO)₂FeSiMe₂R (R = Me, Ph, or SiMe₃) with BBr₃ causes selective and stepwise bromodemethylation of the silyl ligand to produce the corresponding bromosilyl complexes Cp*(CO)₂FeSiBrMeR and Cp*(CO)₂FeSiBr₂R. When R = SiMe₃, the bromodemethylation occurs selectively at the α-silicon atom. These bromination reactions proceed almost quantitatively under mild conditions. Electron-donating substituents on the α-sil-

icon atom of the silyl complexes and polar solvents accelerate the reaction. Application of this reaction toward other transition-metal silyl complexes is in progress.

Experimental Section

General Procedures. All manipulations were performed using either standard Schlenk tube techniques under nitrogen or argon atmosphere or vacuum line techniques, or in a drybox under nitrogen atmosphere. Hexane, toluene, and THF were dried over sodium benzophenone ketyl and freshly distilled under a nitrogen atmosphere. K[Cp*Fe(CO)₂],[11] Cp*Fe(CO)₂-SiMe₃ (**1a**),[12] and Cp*Fe(CO)₂SiMe₂SiMe₃ (**1c**) (Cp* = C₅Me₅)[13] were prepared by the literature procedures. NMR spectra were recorded on a Bruker ARX-300 Fourier transform spectrometer at room temperature. IR spectra were obtained on a HORIBA FT-730 spectrometer at room temperature. Mass spectra were recorded on a JEOL HX-110 spectrometer at the Instrumental Analysis Center for Chemistry, Tohoku University. Elemental analyses were performed at the Instrumental Analysis Center for Chemistry, Tohoku University.

Synthesis of Cp*Fe(CO)₂SiMe₂Ph (1b). A THF (15 mL) solution of K[Cp*Fe(CO)₂] (1.0 g, 3.5 mmol) was added to ClSiMe₂Ph (0.70 mL, 4.2 mmol) in THF (10 mL) at −46 °C with vigorous stirring. The reaction mixture was warmed to room temperature and stirred overnight. After removal of volatiles under reduced pressure, hexane (50 mL) was added to the residue and insoluble material was filtered off. The filtrate was concentrated to ca. 2 mL and cooled to −30 °C for 1 day to give orange crystals. Yield: 0.82 g (2.1 mmol, 60%). ^{1}H NMR (300 MHz, C₆D₆): δ 0.78 (s, 6H, SiMe), 1.34 (s, 15H, C₅Me₅), 7.20 (m, 1H, Ph), 7.27 (m, 2H, Ph), 7.78 (m, 2H, Ph). ^{13}C NMR (75.5 MHz, C₆D₆): δ 5.5 (SiMe), 9.4 (C₅*Me*₅), 94.8 (*C*₅Me₅), 127.6, 134.2, 146.3 (Ph), 218.3 (CO). ^{13}C NMR (75.5 MHz, CDCl₃): δ 5.0 (SiMe), 9.7 (C₅*Me*₅), 94.8 (*C*₅Me₅), 127.1, 127.5, 133.8, 146.0 (Ph), 217.8 (CO). ^{29}Si NMR (59.6 MHz, C₆D₆): δ 20.6. IR (KBr): ν_CO 1905, 1963 cm⁻¹. MS (EI, 70 eV): *m/z* 382 (M⁺, 17), 354 (M⁺ − CO, 16), 326 (M⁺ − 2CO, 98), 311 (M⁺ − 2CO − Me, 32), 135 ([SiMe₂Ph]⁺, 100). Anal. Calcd for C₂₀H₂₆FeO₂Si; C, 62.83; H, 6.85. Found: C, 62.74; H, 6.83.

Reaction of 1a with 1 Equiv of BBr₃: Formation of Cp*Fe(CO)₂SiBrMe₂ (2a). BBr₃ (70 μL, 0.74 mmol) was added dropwise to a hexane (10 mL) solution of Cp*Fe-(CO)₂SiMe₃ (200 mg, 0.624 mmol) at room temperature. The

(11) Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 1094.
(12) Randolph, C. L.; Wrighton, M. S. *Organometallics* **1987**, *6*, 365.
(13) Ueno, K.; Nakano, K.; Ogino, H. *Chem. Lett.* **1996**, 459.

mixture was stirred vigorously for 1 h. After removal of volatiles, hexane (10 mL) was added to the residue and insoluble material was filtered off. The solvent was removed from the filtrate under reduced pressure to give yellow crystals of **2a**. Yield: 239 mg (0.620 mmol, 99%). ^{1}H NMR (300 MHz, C_6D_6): δ 1.07 (s, 6H, SiMe), 1.46 (s, 15H, C_5Me_5). ^{13}C NMR (75.5 MHz, C_6D_6): δ 9.4 (C_5Me_5), 12.5 (SiMe), 96.1 (C_5Me_5), 216.0 (CO). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 71.8. IR (KBr): ν_{CO} 1934, 1981 cm^{-1}. MS (EI, 70 eV): m/z 384 (M$^+$, 6), 356 (M$^+$ − CO, 31), 328 (M$^+$ − 2CO, 32), 190 ([Fe(CO)$_4$SiMe$_2$]$^+$, 100). Anal. Calcd for $C_{14}H_{21}BrFeO_2Si$: C, 43.66; H, 5.50. Found: C, 43.60; H, 5.51.

Reaction of 1a with an Excess of BBr$_3$: Formation of Cp*Fe(CO)$_2$SiBr$_2$Me (3a). BBr$_3$ (200 μL, 2.12 mmol) was added dropwise to a toluene (10 mL) solution of **1a** (200 mg, 0.624 mmol) at room temperature. The mixture was stirred for 36 h at 40 °C. After removal of volatiles under reduced pressure, hexane (10 mL) was added to the residue and insoluble material was filtered. The solvent was removed from the filtrate to give yellow crystals of **3a**. Yield: 267 mg (0.593 mmol, 95%). ^{1}H NMR (300 MHz, C_6D_6): δ 1.42 (s, 15H, C_5-Me$_5$), 1.62 (s, 3H, SiMe). ^{13}C NMR (75.5 MHz, C_6D_6): δ 9.1 (C_5Me_5), 19.9 (SiMe), 97.2 (C_5Me_5), 214.3 (CO). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 68.9. IR (KBr): ν_{CO} 1950, 1998 cm^{-1}. Anal. Calcd for $C_{13}H_{18}Br_2FeO_2Si$: C, 34.70; H, 4.03. Found: C, 34.73; H, 3.91.

Reaction of 1b with 1 Equiv of BBr$_3$: Formation of Cp*Fe(CO)$_2$SiBrMePh (2b). 2b was obtained as orange crystals by a procedure similar to the reaction of **1a** with 1 equiv of BBr$_3$. BBr$_3$ (60 μL, 0.63 mmol), **1b** (200 mg, 0.523 mmol), and toluene (10 mL) were used, and the mixture was stirred at room temperature for 6 h. Yield: 234 mg (0.523 mmol, 100%). ^{1}H NMR (300 MHz, C_6D_6): δ 1.31 (s, 3H, SiMe), 1.33 (s, 15H, C_5Me_5), 7.15 (m, 1H, Ph), 7.24 (m, 2H, Ph), 7.98 (m, 2H, Ph). ^{13}C NMR (75.5 MHz, C_6D_6): δ 9.5 (C_5Me_5), 12.9 (SiMe), 96.3 (C_5Me_5), 127.9, 129.0, 134.0, 143.6 (Ph), 216.3, 216.9 (CO). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 63.7. IR (KBr): ν_{CO} 1930, 1982 cm^{-1}. MS (EI, 70 eV): m/z 446 (M$^+$, 14), 418 (M$^+$ − CO, 72), 390 (M$^+$ − 2CO, 100), 375 (M$^+$ − 2CO − Me, 59), 298 (M$^+$ − 2CO − Me − Ph, 10). Anal. Calcd for $C_{19}H_{23}BrFeO_2$-Si: C, 51.03; H, 5.18. Found: C, 51.05; H, 5.13.

Reaction of 1b with an Excess of BBr$_3$: Formation of Cp*Fe(CO)$_2$SiBr$_2$Ph (3b). 3b was obtained as orange crystals by a procedure similar to the reaction of **1a** with an excess of BBr$_3$. BBr$_3$ (130 μL, 1.38 mmol), **1b** (175 mg, 0.458 mmol), and toluene (10 mL) were used, and the mixture was stirred on heating at 80 °C for 24 h. The workup was performed using toluene. Yield: 234 mg (0.457 mmol, 100%). ^{1}H NMR (300 MHz, C_6D_6): δ 1.32 (s, 15H, C_5Me_5), 7.07 (m, 1H, Ph), 7.19 (m, 2H, Ph), 8.15 (m, 2H, Ph). ^{13}C NMR (75.5 MHz, C_6D_6): δ 9.0 (C_5Me_5), 96.8 (C_5Me_5), 127.8, 129.8, 133.5, 142.9 (Ph), 214.9 (CO). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 74.9. IR (KBr): ν_{CO} 1952, 2000 cm^{-1}. Anal. Calcd for $C_{18}H_{20}Br_2FeO_2Si$: C, 42.22; H, 3.94. Found: C, 42.05; H, 3.94.

Reaction of 1c with 1 Equiv of BBr$_3$: Formation of Cp*Fe(CO)$_2$SiBrMeSiMe$_3$ (2c). 2c was obtained as orange crystals by a procedure similar to the reaction of **1a** with 1 equiv of BBr$_3$. BBr$_3$ (60 μL, 0.63 mmol) and **1c** (200 mg, 0.528 mmol) were used. Yield: 230 mg (0.519 mmol, 98%). ^{1}H NMR (300 MHz, C_6D_6): δ 0.44 (s, 9H, β-SiMe), 1.15 (s, 3H, α-SiMe), 1.48 (s, 15H, C_5Me_5). ^{13}C NMR (75.5 MHz, C_6D_6): δ −0.6 (β-SiMe), 8.1 (α-SiMe), 9.5 (C_5Me_5), 96.2 (C_5Me_5), 216.2 (CO). ^{29}-Si NMR (59.6 MHz, C_6D_6): δ −25.6 (β-Si), 64.1 (α-Si). IR (KBr): ν_{CO} 1934, 1982 cm^{-1}. MS (EI, 70 eV): m/z 444 (M$^+$, 28), 414 (M$^+$ − CO, 86), 386 (M$^+$ − 2CO, 100), 369 (M$^+$ − SiMe$_3$, 32), 313 (M$^+$ − 2CO − SiMe$_3$, 36), 290 (M$^+$ − Br − SiMe$_3$, 87). Anal. Calcd for $C_{16}H_{27}BrFeO_2Si_2$: C, 43.35; H, 6.14. Found: C, 43.05; H, 6.08.

Reaction of 1c with an Excess of BBr$_3$: Formation of Cp*Fe(CO)$_2$SiBr$_2$SiMe$_3$ (3c). 3c was obtained as orange crystals by a procedure similar to the reaction of **1a** with an excess of BBr$_3$. BBr$_3$ (360 μL, 3.72 mmol), **1c** (470 mg, 1.24 mmol), and hexane (20 mL) were used, and the mixture was stirred on heating at 40 °C for 6 h. Yield: 595 mg (1.17 mmol, 94%). ^{1}H NMR (300 MHz, C_6D_6): δ 0.51 (s, 9H, β-SiMe), 1.47 (s, 15H, C_5Me_5). ^{13}C NMR (75.5 MHz, C_6D_6): δ −1.3 (β-SiMe), 9.1 (C_5Me_5), 97.5 (C_5Me_5), 214.6 (CO). ^{29}Si NMR (59.6 MHz, C_6D_6): δ −19.7 (β-Si), 84.0 (α-Si). IR (KBr): ν_{CO} 1945, 1994 cm^{-1}. Anal. Calcd for $C_{15}H_{24}Br_2FeO_2Si_2$: C, 35.45; H, 4.76. Found: C, 35.82; H, 4.82.

Reaction of 2a with BBr$_3$. BBr$_3$ (6 μL, 0.06 mmol) was added to a C_6D_6 (0.50 mL) solution of **2a** (20 mg, 0.052 mmol) in a Pyrex NMR tube at room temperature. The NMR tube was then degassed and sealed. The solution was heated at 50 °C. The reaction was monitored by ^{1}H NMR spectroscopy. After 34 h, **2a** was converted to give **3a** in quantitative yield.

Reaction of 2b with BBr$_3$. In a procedure similar to the reaction of **2a** with BBr$_3$, a C_6D_6 (0.50 mL) solution containing **2b** (23 mg, 0.052 mmol) and BBr$_3$ (6 μL, 0.06 mmol) was heated at 50 °C for 96 h to give **3b** in quantitative yield.

Reaction of 2c with BBr$_3$. In a procedure similar to the reaction of **2a** with BBr$_3$, a C_6D_6 (0.50 mL) solution containing **2c** (23 mg, 0.051 mmol) and BBr$_3$ (6 μL, 0.06 mmol) was heated at 50 °C for 2.5 h to give **3c** in quantitative yield.

Reactions of 2a with BBr$_3$ in Various Solvents. A typical procedure is as follows: BBr$_3$ (25 μL, 0.26 mmol) was added to a hexane (2.5 mL) solution of **2a** (50 mg, 0.13 mmol) at 20 °C. A small portion (50 μL) of the reaction mixture was collected periodically (every ca. 24 h for a week), and volatiles were removed in vacuo. The resulting residue was dissolved in C_6D_6, and the ^{1}H NMR spectrum was measured. Similarly, the reaction of **2a** with BBr$_3$ was performed in toluene and in CH$_2$Cl$_2$ at 20 °C and monitored by ^{1}H NMR spectroscopy.

X-ray Crystal Structure Determination of 3c. A single-crystal suitable for X-ray crystal structure determination was mounted on a glass fiber. The intensity data were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation to a maximum 2θ value of 55.0 at 150 K. A total of 44 images, corresponding to 220.0° oscillation angles, were collected with two different goniometer settings. Exposure time was 1.30 min per degree. Readout was performed in the 0.100 mm pixel mode. Numerical absorption collections were applied on the crystal shape. The structure was solved by Patterson and Fourier transform methods. All non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic displacement parameters based on F^2 with all reflections. All hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. The final residue R1 and the weighted R_w were R1 = 0.052 and R_w = 0.136 for 2297 reflections with $I > 2\sigma(I)$. All calculations were performed using the teXsan crystal structure analysis package.[14]

Crystallographic Information has been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 229770).

Supporting Information Available: Crystal structure data for **3c**, including tables of atomic coordinates, anisotropic thermal parameters, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) teXsan: Crystal Structure Analysis Package; Molecular Structure Corporation, 1985 & 1999.