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Functionalization of the μ-Silylene Ligand in $Cp_2Fe_2(CO)_3(\mu\text{-SiH}^t\text{Bu})$: Syntheses of μ-Halosilylene Complexes $Cp_2Fe_2(CO)_3(\mu\text{-SiX}^t\text{Bu})$ (X = Cl, Br, I) and Donor-Stabilized Cationic μ-Silylyne Complexes $[Cp_2Fe_2(CO)_3(\mu\text{-Si}^t\text{Bu}\cdot\text{Base})]I$ (Base = *N*-Methylimidazole, 4-(Dimethylamino)pyridine)

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Abstract: The μ-silylene complex $Cp_2Fe_2(CO)_3(\mu\text{-SiH}^t\text{Bu})$ (**1**) reacts with CCl_4, $CHBr_3$, and CH_2I_2 at room temperature to afford μ-halosilylene complexes $Cp_2Fe_2(CO)_3(\mu\text{-SiX}^t\text{Bu})$ (**2**, X = Cl; **3**, X = Br; **4**, X = I, respectively). The iodine atom on the silylene bridge in **4** is replaced by strong Lewis bases, *N*-methylimidazole (NMI) and 4-(dimethylamino)-pyridine (DMAP), to give the first donor-stabilized μ-silylyne dinuclear complexes $[Cp_2Fe_2(CO)_3(\mu\text{-Si}^t\text{Bu}\cdot\text{Base})]^+$ ($[\mathbf{7}]^+$, base = NMI; $[\mathbf{8}]^+$, Base = DMAP). The crystal structures of $[\mathbf{7}]I\cdot CD_3CN$ and $[\mathbf{8}]I$ have been determined by X-ray crystallography. Crystals of $[\mathbf{7}]I\cdot CD_3CN$ are orthorhombic, *Pbnm*, a = 16.371(4) Å, b = 17.043(3) Å, c = 9.975(1) Å, Z = 4, and R = 0.056. Crystals of $[\mathbf{8}]I$ are orthorhombic, *Pbnm*, a = 14.564(2) Å, b = 18.412(4) Å, c = 10.290(1) Å, Z = 4, and R = 0.070. These compounds have short Fe–Si bond lengths 2.262(2) Å ($[\mathbf{7}]I\cdot CD_3CN$) and 2.266(3) Å ($[\mathbf{8}]I$). In contrast, Si–N distances ($[\mathbf{7}]I\cdot CD_3CN$, 1.885(7) Å; $[\mathbf{8}]I$, 1.866(9) Å) are considerably longer than typical Si–N single bonds (ca. 1.75 Å), which is consistent with dative interaction between the nitrogen and silicon atoms. Spectroscopic properties of **2**–$[\mathbf{8}]^+$ are also discussed.

Introduction

Bridging ligands in transition-metal dinuclear complexes are placed in rather unusual circumstances arising from the strong electronic effect of two metal atoms. Therefore, the bridging units frequently show interesting reactivities, which are not observed in usual organic molecules or mononuclear complexes.[1,2] Bridging ligands are also regarded as the model of small molecules adsorbed on a metal surface.[3] From these viewpoints, reactivities of the dinuclear complexes bridged by carbon atoms, e.g., μ-carbene complexes[1] and μ-vinylidene complexes,[2] have been investigated extensively. In contrast, only few investigations have been reported with regard to the reactivity of the corresponding μ-silylene complexes, although it is an intriguing subject.[4–7]

Carbyne-bridged dinuclear complexes have remarkable reactivities,[8] which include formation of trinuclear clusters,[9] hydrocarbation toward olefins,[10] and formation of novel μ-carbene complexes by the reactions with nucleophiles.[11] However, there was no example of silylyne-bridged dinuclear complexes which correspond to μ-carbyne complexes, until we reported preliminarily a donor-stabilized silylyne diiron complex.[12] Malisch and Ries reported the abstraction reactions of a hydride and a chloride from the bridging silylene ligand in $[CpFe(CO)_2]_2(\mu\text{-SiXMe})$ (X = H, Cl) by CPh_3BF_4 and $AgBF_4$, respectively, but they resulted in the fluorination of the bridging silicon, instead of the formation of the silylyne-bridged cationic species.[6b] Quite recently, Tilley and his co-workers reported the synthesis of an osmium-substituted silylene complex $[(\eta\text{-}C_5Me_5)(PMe_3)_2Ru{=}Si\text{-}$

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(1) For example: (a) Sumner, C. E.; Riley, P. E.; Davis, R. E.; Petit, R. J. S. *J. Am. Chem. Soc.* **1980**, *102*, 1752. (b) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (c) Hermann, W. A.; Plank, J.; Ziegler, M. L.; Balbach, B. *J. Am. Chem. Soc.* **1980**, *102*, 5906. (d) Hahn, J. E. *Prog. Inorg. Chem.* **1984**, *31*, 205. (e) Jeffery, J. C.; Went, M. J. *Polyhedron* **1988**, *7*, 775. (f) Colborn, R. E.; Davies, D. L.; Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Orpen, A. G.; Guerchais, J. E.; Roue, J. *J. Chem. Soc., Dalton Trans.* **1989**, 1799 and references cited therein.

(2) For example: (a) King, R. B.; Saran, M. S. *J. Am. Chem. Soc.* **1973**, *95*, 1811. (b) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

(3) Reviews: (a) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (b) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.

(4) (a) Nicholson, B. K.; Mackay, K. M.; Gerlach, R. F. *Rev. Silicon, Germanium, Tin Lead Compd.* **1973**, *5*, 67. (b) Aylett, B. J. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 2. (c) Tilley, T. D. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24. (d) Tilley, T. D. *Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Chapters 9 and 10.

(5) Carre, F. H.; Morreu, J. J. *Inorg. Chem.* **1982**, *21*, 3099.

(6) (a) Malisch, W.; Ries, W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 120. (b) Malisch, W.; Ries, W. *Chem. Ber.* **1979**, *112*, 1304.

(7) (a) Wang, W.-D.; Eisenberg, R. *J. Am. Chem. Soc.* **1990**, *112*, 1833. (c) Wang, W.-D.; Eisenberg, R. *Organometallics* **1992**, *11*, 908.

(8) (a) Fischer, H.; Hoffmann, P.; Kreissl, F. R.; Schrock, R. R.; Schubert, U.; Weiss, K. *Carbyne Complexes*; VCH Publishers: New York, 1990. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1990. (c) Puddephatt, R. J. *Polyhedron* **1988**, *7*, 767.

(9) For example: (a) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89. (b) Abad, J. A.; Delgado, E.; Garcia, M. E.; Grosse-Ophoff, J.; Hart, I. J.; Jeffery, J. C.; Simmons, M. S.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 41. (c) Bermudez, M. D.; Delgado, E.; Elliott, G. P.; Tran-Huy, N. H.; Mayor-Real, F.; Stone, F. G. A.; Winter, M. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1235. (d) Green, M.; Howard, J. A. K.; James, A. P.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1986**, 187 and references cited therein.

(10) (a) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Marder, S. R.; Austin, E. A. *J. Am. Chem. Soc.* **1986**, *108*, 4043. (b) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Colborn, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 4053.

(11) (a) Casey, C. P.; Woo, L. K.; Fagan, P. J.; Palermo, R. E.; Adams, B. R. *Organometallics* **1987**, *6*, 447. (b) Casey, C. P.; Konings, M. S.; Marder, S. R. *Polyhedron* **1988**, *7*, 881. (c) Busetto, L.; Bordoni, S.; Zanotti, V.; Albano, V. G.; Braga, D. *Gazz. Chim. Ital.* **1988**, *118*, 667. (d) Aime, S.; Cordero, L.; Gobetto, R.; Bordoni, S.; Busetto, L.; Zanotti, V.; Albano, V. G.; Braga, D.; Grepioni, F. *J. Chem. Soc., Dalton Trans.* **1992**, 2961. (e) Schroeder, N. C.; Richardson, J. W., Jr.; Wang, S. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1985**, *4*, 1226. (f) Schroeder, N. C.; Funchess, R.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1989**, *8*, 521. (g) Aase, T.; Tilset, M.; Parker, V. D. *Organometallics* **1989**, *8*, 1558.

(12) Kawano, Y.; Tobita, H.; Ogino, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 843.

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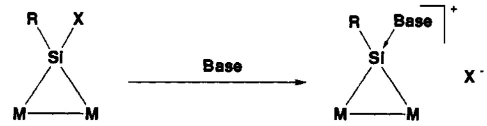
Scheme 1



(S-*p*-Tol){Os(CO)$_4$}]. They described the ligand in this complex as "a metal-substituted silylene or a bridging silylyne".[13] They reported also a phenanthroline-stabilized mononuclear silylyne complex [(η-C$_5$Me$_5$)(PMe$_3$)$_2$RuSi(S-*p*-Tol)·(phenanthroline)](OTf)$_2$.[14] Silylyne complexes also participate in the coordination chemistry of low-valent silicon species, which is a rapidly developing area.[4c,d,15-20]

Our approach for the synthesis of silylyne complexes includes the exchange of a halo group on the silylene bridge of the μ-silylene diiron complex with a strong Lewis base (Scheme 1).

The exchange of a halo group on a silicon atom with a strong Lewis base is well-known with regard to organosilicon systems. The 1:1 ionic adducts of R$_3$SiX (X = halides, triflate, or perchlorate) and a Lewis base, [R$_3$Si·Base]X, have been thoroughly investigated.[21-25] They are also useful as versatile silylation reagents.[21] The cationic μ-silylyne complexes are closely related to them and have a possibility to offer a new type of synthetic device.

This paper describes the synthesis of the first μ-silylyne dinuclear complexes and their crystal structures. The synthesis and characterization of the precursors, μ-halosilylene diiron complexes Cp$_2$Fe$_2$(CO)$_3$(μ-SiX^{t}Bu), are also described herein. The preliminary communication of the complexes has been published already.[26]

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere. Reagent-grade pentane, hexane, heptane, diethyl ether, and toluene were distilled under a nitrogen atmosphere from sodium–benzophenone ketyl immediately before use. Acetonitrile was distilled from CaH$_2$, then from P$_2$O$_5$, and finally from CaH$_2$. Benzene-d_6 and toluene-d_8 were dried over a potassium mirror and transferred into NMR tubes under vacuum before use. Acetonitrile-d_3 was distilled from CaH$_2$ three times. Carbon tetrachloride, bromoform, and diiodomethane were dried over P$_2$O$_5$ and then distilled. *N*-Methylimidazole (NMI) was distilled from sodium, and 4-(dimethylamino)pyridine (DMAP) was recrystallized from toluene. Cp$_2$Fe$_2$(CO)$_3$(μ-SiH^{t}Bu) (**1**) was prepared according to the procedure reported previously.[27] IR spectra were recorded on Jasco IR-810 and Bruker IFS66v spectrometers. ^{1}H NMR spectra were recorded on JEOL FX-90Q, Varian EM-390, and Varian XL-200 spectrometers at ambient temperature. ^{13}C NMR spectra were recorded on Varian XL-200 and Bruker AC-300 spectrometers. ^{29}Si NMR spectra were obtained on a Bruker AC-300 spectrometer by using a DEPT pulse sequence. Mass spectra and high-resolution mass spectra were recorded on a JEOL JMS HX-110 spectrometer. ^{1}H NMR, ^{13}C NMR, and IR data of the complexes obtained in this work are listed in Table 1. ^{29}Si NMR and UV–vis spectral data are listed in Table 2.

Synthesis of Cp$_2$Fe$_2$(CO)$_3$(μ-SiCl^{t}Bu) (2). Cp$_2$Fe$_2$(CO)$_3$(μ-SiH^{t}Bu) (**1**) (251 mg, 0.61 mmol) was dissolved in carbon tetrachloride (20 mL), and the red solution was stirred at room temperature. After 17.5 h, only one spot was observed on a silica gel TLC. The solution was filtered, and the filtrate was evaporated to give a red solid. Recrystallization of the solid from toluene–pentane afforded **2** (270 mg, 0.60 mmol, 99%) as red crystals. MS (EI) *m/z*: 446 (10, M$^+$), 418 (26, M$^+$ – CO), 390 (8, M$^+$ – 2CO), 362 (34, M$^+$ – 3CO), 215 (100, Cp$_2$Fe$_2$H$^+$). Exact MS. Calcd for C$_{17}$H$_{19}$ClFe$_2$O$_3$Si: 445.9491. Found: 445.9496.

Synthesis of Cp$_2$Fe$_2$(CO)$_3$(μ-SiBr^{t}Bu) (3). A solution of **1** (755 mg, 1.83 mmol) in bromoform (7 mL) was stirred at room temperature. After 80 min, volatiles were removed in vacuo and the residue was extracted with benzene (20 mL). The extract was filtered, and the filtrate was evaporated to dryness. The resulting red solid was recrystallized from toluene–heptane to give **3** (744 mg, 1.52 mmol, 83%) as red crystals. MS (EI) *m/z*: 490 (39, M$^+$), 462 (75, M$^+$ – CO), 406 (57, M$^+$ – 3CO), 215 (100, Cp$_2$Fe$_2$H$^+$). Exact MS. Calcd for C$_{17}$H$_{19}$BrFe$_2$O$_3$Si: 489.8986. Found: 489.8981.

Synthesis of Cp$_2$Fe$_2$(CO)$_3$(μ-SiI^{t}Bu) (4). To a solution of **1** (240 mg, 0.58 mmol) in dichloromethane (2 mL) was added CH$_2$I$_2$ (1 mL), and the mixture was stirred at room temperature. After 3 days, volatiles were removed in vacuo without warming. The red residue was then recrystallized from toluene–pentane to give **4** (215 mg, 0.40 mmol, 69%) as red needles. MS (EI) *m/z*: 538 (27, M$^+$), 510 (100, M$^+$ – CO), 454 (57, M$^+$ – 3CO). Exact MS. Calcd for C$_{17}$H$_{19}$Fe$_2$IO$_3$Si: 537.8847. Found: 537.8865.

Synthesis of Cp$_2$Fe$_2$(CO)$_3$(μ-SiMe^{t}Bu) (5). To a solution of **2** (143 mg, 0.32 mmol) in diethyl ether (10 mL) was added a diethyl ether solution of CH$_3$Li (3.9 mL of a 0.48 M solution, 1.9 mmol) with stirring over 4 h. After the solution was stirred for 4.5 h, the LiCl precipitate was removed by filtration. The filtrate was evaporated to dryness, and the residue was placed on a silica gel column (1.5 cmϕ × 12 cm) and eluted with a hexane–diethyl ether mixture (8:1). A trace amount of ferrocene was eluted, and then a red fraction was collected. Evaporation of the solvent and recrystallization of the residue from toluene gave **5** (95 mg, 0.22 mmol, 70%. MS (EI) *m/z*: 426 (29, M$^+$), 398 (63, M$^+$ – CO), 286 (100). Exact MS. Calcd for C$_{18}$H$_{21}$Fe$_2$O$_3$Si: 426.0037. Found: 426.0036. In the chromatographic column, the red fraction of **5** separated into two bands which are assignable to *trans* and *cis* isomers. However, neither of them could be isolated in a pure state because of their thermal interconversion.

Reaction of 2 with AgPF$_6$. To a solution of **2** (100 mg, 0.22 mmol) in CH$_3$CN (10 mL) was added a CH$_3$CN (4 mL) solution of AgPF$_6$ (119 mg, 0.47 mmol) dropwise over 10 min with stirring at –48 °C. A silver

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(13) Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1993**, *115*, 358.

(14) Grumbine, S. D.; Chadha, R. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1518.

(15) Lickiss, P. D. *Chem. Soc. Rev.* **1992**, 271 and references cited therein.

(16) (a) Straus, D. A.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 5872. (b) Straus, D. A.; Zhang, C.; Quimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673 (c) Straus, D. A.; Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 7801. (d) Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1993**, *115*, 7884.

(17) (a) Zybill, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 669. (b) Zybill, C.; Müller, G. *Organometallics* **1988**, *7*, 1368. (c) Zybill, C.; Wilkinson, D. L.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 583. (d) Leis, C.; Wilkinson, D. L.; Handwerker, H.; Zybill, C. *Organometallics* **1992**, *11*, 514. (e) Zybill, C.; Wilkinson, D. L.; Leis, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 203. (f) Probst, R.; Leis, C.; Gamper, S.; Herdtweck, E.; Zybill, C.; Auner, N. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1132. (g) Handwerker, H.; Leis, C.; Probst, R.; Bissinger, P.; Grohmann, A.; Kiprof, P.; Herdtweck, E.; Blumel, J.; Auner, N.; Zybill, C. *Organometallics* **1993**, *12*, 2162. (h) Handwerker, H.; Paul, M.; Blumel, J.; Zybill, C. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 2162. (i) Handwerker, H.; Paul, M.; Riede, J.; Zybill, C. *J. Organomet. Chem.* **1993**, *459*, 151.

(18) (a) Ueno, K.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1988**, *110*, 4092. (b) Tobita, H.; Ueno, K.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 3415. (c) Takeuchi, T.; Tobita, H.; Ogino, H. *Organometallics* **1991**, *10*, 835. (d) Koe, J. R.; Tobita, H.; Ogino, H. *Organometallics* **1992**, *11*, 2479. (e) Ueno, K.; Tobita, T.; Seki, S.; Ogino, H. *Chem. Lett.* **1993**, 1723.

(19) (a) Corriu, R.; Lanneau, G.; Priou, C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1130. (b) Corriu, R.; Lanneau, G.; Chauhan, B. *Organometallics* **1993**, *12*, 2001.

(20) (a) Woo, L. K.; Smith, D. A.; Young, V. G., Jr. *Organometallics* **1991**, *10*, 3977. (b) Lee, K. E.; Ariv, A. M.; Gladysz, J. A. *Chem. Ber.* **1991**, *124*, 309. (c) Jutzi, Z.; Möhrke, A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 893.

(21) (a) Bassindale, A. R.; Stout, T. *J. Organomet. Chem.* **1982**, *238*, C41. (b) Bassindale, A. R.; Stout, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1387. (c) Bassindale, A. R.; Stout, T. *J. Chem. Soc., Perkin Trans. 2*, **1986**, 221. (d) Bassindale, A. R.; Stout, T. *Tetrahedron Lett.* **1985**, *26*, 3403.

(22) (a) Chojinowski, J.; Cypryk, M.; Michalski, J. *J. Organomet. Chem.* **1978**, *161*, C31. (b) Barton, T. J.; Tully, C. R. *J. Org. Chem.* **1978**, *43*, 3649. (c) Lambert, J. B.; Schulz, W. J., Jr.; McConnell, J. A.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 2201.

(23) (a) Hensen, K.; Zengerly, T.; Pickel, P.; Klebe, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *22*, 725. (b) Hensen, K.; Zengerly, Müller, T.; Pickel, P. *Z. Anorg. Allg. Chem.* **1988**, *558*, 21.

(24) (a) Kira, M.; Hino, T.; Sakurai, H. *J. Am. Chem. Soc.* **1992**, *114*, 6697. (b) Kira, M.; Hino, T.; Sakurai, H. *Chem. Lett.* **1993**, 153. (c) Kira, M.; Hino, T.; Sakurai, H. *Chem. Lett.* **1992**, 555. (d) Bahr, S. R.; Boudjouk, P. *J. Am. Chem. Soc.* **1993**, *115*, 4514.

(25) (a) Emde, H.; Domsch, D.; Feger, H.; Frick, U.; Götz, A.; Hergott, H. H.; Hohmann, K.; Kober, W.; Krangeloh, K.; Oesterle, T.; Steppan, W.; West, W.; Simchen, G. *Synthesis* **1982**, 1. (b) Olah, G. A.; Narang, S. C. *Tetrahedron* **1982**, *38*, 2225.

(26) Tobita, H.; Kawano, Y.; Ogino, H. *Chem. Lett.* **1989**, 2155.

(27) (a) Tobita, H.; Kawano, Y.; Shimoi, M.; Ogino, H. *Chem. Lett.* **1987**, 2247. (b) Kawano, Y.; Tobita, H.; Ogino, H. *J. Organomet. Chem.* **1992**, *428*, 125.

Table 1. ^{1}H NMR, ^{13}C NMR, and IR Spectral Data for $\mathrm{Cp_2Fe_2(CO)_3(\mu\text{-}SiX^tBu)}$ (X = H, Cl, Br, I, Me) and $\mathrm{[Cp_2Fe_2(CO)_3(\mu\text{-}Si^tBu\cdot Base)]I}$ (Base = NMI, DMAP)

	^{1}H NMR δ/ppm^a	^{13}C NMR δ/ppm^b	IR $\tilde{\nu}$/cm^{-1} ^{c}
$\mathrm{Cp_2Fe_2(CO)_3(\mu\text{-}SiH^tBu)}$ (**1**)^d	1.33 (s, 9H, ^{t}Bu) 4.83 (s, 10H, Cp) 7.24 (s, 1H, SiH)^e	30.0 (C*Me*$_3$), 31.5 (*C*Me$_3$) 84.5 (Cp), 213.4 (CO) 277.6 (μ-CO)	2074 (w, νSiH) 1950 (vs), 1922 (m) ($\nu\mathrm{CO_{term}}$) 1720 (s, $\nu\mathrm{CO_{bridge}}$)
$\mathrm{Cp_2Fe_2(CO)_3(\mu\text{-}SiCl^tBu)}$ (**2**)	(*cis* isomer) 1.55 (s, 9H, ^{t}Bu) 4.24 (s, 10H, Cp)	29.1 (C*Me*$_3$), 38.8 (*C*Me$_3$) 87.1 (Cp), 212.8 (CO) 274.8 (μ-CO)	1952 (vs), 1918 (m) ($\nu\mathrm{CO_{term}}$) 1763 (s, $\nu\mathrm{CO_{bridge}}$)
	(*trans* isomer) 1.46 (s, 9H, ^{t}Bu) 4.36, 4.38 (s, 5H × 2, Cp)		
$\mathrm{Cp_2Fe_2(CO)_3(\mu\text{-}SiBr^tBu)}$ (**3**)	(*cis* isomer) 1.55 (s, 9H, ^{t}Bu) 4.24 (s, 10H, Cp)	29.3 (C*Me*$_3$), 38.9 (*C*Me$_3$) 87.5 (Cp), 212.6 (CO) 273.9 (μ-CO)	1952 (vs), 1924 (m) ($\nu\mathrm{CO_{term}}$) 1773 (s, $\nu\mathrm{CO_{bridge}}$)
	(*trans* isomer) 1.47 (s, 9H, ^{t}Bu) 4.34, 4.40 (s, 5H × 2, Cp)		
$\mathrm{Cp_2Fe_2(CO)_3(\mu\text{-}SiI^tBu)}$ (**4**)	(*cis* isomer) 1.56 (s, 9H, ^{t}Bu) 4.24 (s, 10H, Cp)	29.8 (C*Me*$_3$), 38.0 (*C*Me$_3$) 88.2 (Cp), 212.7 (CO) 273.4 (μ-CO)	1952 (vs), 1925 (m) ($\nu\mathrm{CO_{term}}$) 1772 (s, $\nu\mathrm{CO_{bridge}}$)
	(*trans* isomer) 1.46 (s, 9H, ^{t}Bu) 4.33, 4.40 (s, 5H × 2, Cp)		
$\mathrm{Cp_2Fe_2(CO)_3(\mu\text{-}SiMe^tBu)}$ (**5**)	(*cis* isomer) 1.42 (s, 9H, ^{t}Bu) 1.00 (s, 3H, SiMe) 4.08 (s, 10H, Cp)	13.6 (SiMe), 29.9 (C*Me*$_3$) 32.9 (*C*Me$_3$), 84.8 (Cp) 213.8 (CO), 278.6 (μ-CO)	1990, 1947, 1937 (sh), 1914($\nu\mathrm{CO_{term}}$) 1751, 1712 ($\nu\mathrm{CO_{bridge}}$)
	(*trans* isomer) 1.31 (s, 9H, ^{t}Bu) 1.15 (s, 3H, SiMe) 4.25, 4.44 (s, 5H × 2, Cp)	12.5 (SiMe), 30.2 (C*Me*$_3$) 34.5 (*C*Me$_3$), 84.0, 85.4 (Cp) 213.4, 215.4 (CO), 279.4 (μ-CO)	
$\mathrm{[Cp_2Fe_2(CO)_3(\mu\text{-}Si^tBu\cdot NMI)]I}$ ([**7**]I)^f	1.40 (s, 9H, ^{t}Bu) 3.83 (s, 3H, NMe) 5.10 (s, 10H, Cp) 7.29, 7.46, 8.82 (m, 1H × 3, NMI ring protons)	29.1 (NMe), 29.9 (C*Me*$_3$) 36.3 (*C*Me$_3$), 86.4 (Cp) 123.3, 128.6, 141.4 (NMI ring C) 213.6 (CO)^g	1980 (vs), 1932 (m) ($\nu\mathrm{CO_{term}}$) 1766 (s, $\nu\mathrm{CO_{bridge}}$)
$\mathrm{[Cp_2Fe_2(CO)_3(\mu\text{-}Si^tBu\cdot DMAP)]I}$ ([**8**]I)^f	1.38 (s, 9H, ^{t}Bu) 3.13 (s, 6H, NMe) 5.11 (s, 10H, Cp) 6.74, 8.31 (ABq, *J* = 7.8 Hz, 2 H × 2, DMAP ring protons)	30.1 (C*Me*$_3$), 37.7 (*C*Me$_3$) 40.2 (NMe), 86.3 (Cp) 106.5, 147.1, 156.6 (DMAP ring C) 213.2 (CO), 269.7 (μ-CO)	1977 (vs), 1934 (m) ($\nu\mathrm{CO_{term}}$) 1768 (s, $\nu\mathrm{CO_{bridge}}$)

[a] In $\mathrm{C_6D_6}$ unless otherwise noted. [b] In $\mathrm{CD_2Cl_2}$ unless otherwise noted. [c] KBr pellet. [d] From ref 27b. [e] In $\mathrm{CD_3CN}$. [f] ^{1}H and ^{13}C NMR spectra were measured in $\mathrm{CD_3CN}$. [g] No μ-CO signal could be observed due to the low solubility of [**7**]I in $\mathrm{CD_3CN}$.

Table 2. ^{29}Si NMR and UV–Vis Spectral Data for $\mathrm{[Cp_2Fe_2(CO)_3(\mu\text{-}SiX^tBu)]^n}$ (*n* = 0 for X = H, Cl, Br, I; *n* = 1+ for X = NMI, DMAP)

compound	X	^{29}Si NMR δ/ppm^a	UV–vis^b (the lowest energy band) λ_{max} (ϵ)/nm
1	H	254.4	512 (650)
2	Cl	276.3	515 (700)
3	Br	284.8	517 (680)
4	I	289.1	521 (700)
5	Me	267.4	
[**7**]I	NMI	251.5	
[**8**]I	DMAP	264.6	

[a] In $\mathrm{CD_2Cl_2}$. [b] In $\mathrm{CH_2Cl_2}$.

powder precipitated out immediately. The mixture was stirred for 15 min at this temperature and then allowed to warm to room temperature. The silver powder was removed by filtration, and the filtrate was evaporated to dryness. Molecular distillation of the residue gave a mixture of $\mathrm{CpFe(CO)_2SiClF^tBu}$ (**6a**) and $\mathrm{CpFe(CO)_2SiF_2{}^tBu}$ (**6b**) as an yellow oil (54 mg). The respective yields of **6a** and **6b** were calculated to be 19% and 62% on the basis of the ratio of **6a** and **6b** by ^{1}H NMR spectroscopy. **6a.** ^{1}H NMR (90 MHz, $\mathrm{C_6D_6}$): δ 1.19 (d, $^4J_{FH}$ = 1.2 Hz, 9H, ^{t}Bu), 4.12 (s, 5H, Cp). MS (EI) *m/z*: 316 (5, M$^+$). **6b.** ^{1}H NMR (90 MHz, $\mathrm{C_6D_6}$): δ 1.16 (t, $^4J_{FH}$ = 1.2 Hz, 9H, ^{t}Bu), 4.14 (s, 5H, Cp). MS (EI) *m/z*: 300 (5, M$^+$), 241 (100). IR spectrum of the mixture: 2005, 1954 (νCO), 842, 819, 792 (νSiF).

Synthesis of $\mathrm{[Cp_2Fe_2(CO)_3(\mu\text{-}Si^tBu\cdot NMI)]I\cdot CD_3CN}$ ([7]I·$\mathrm{CD_3CN}$). To a suspension of **4** (88 mg, 0.16 mmol) in acetonitrile (1 mL) was added NMI (14 mL, 0.18 mmol) with stirring. The mixture was allowed to stand at 40 °C for 30 min, then gradually cooled to room temperature. Diethyl ether was added, and the reaction mixture was cooled to –48 °C. After 2 h, the supernatant fluid was removed by a syringe. The red crystals thus obtained, [**7**]I·$\mathrm{CD_3CN}$, were washed with diethyl ether (2.5 mL, three times) and dried under vacuum. Yield: 65 mg (0.10 mmol, 66%). MS (FAB, sulfolane matrix) *m/z*: 493 (38, M$^+$), 411 (53, M$^+$ – NMI), 203 (100, CpFeNMI$^+$), 83 (74, NMI·H$^+$). Anal. Calcd for $\mathrm{C_{23}H_{28}Fe_2IN_3O_3Si}$: C, 41.78; H, 4.27; N, 6.35. Found: C, 41.41; H, 3.81; N, 6.77.

Synthesis of $\mathrm{[Cp_2Fe_2(CO)_3(\mu\text{-}Si^tBu\cdot DMAP)]I}$ ([8]I). The synthetic procedure of [**8**]I was almost the same as that of [**7**]I·$\mathrm{CD_3CN}$ except for the use of DMAP instead of NMI. The reaction of **4** (72 mg, 0.13 mmol) with DMAP (17 mg, 0.14 mmol) afforded [**8**]I (39 mg, 0.06 mmol, 44%) as red crystals. MS (FAB, sulfolane matrix) *m/z*: 533 (59, M$^+$), 411 (38, M$^+$ – DMAP), 243 (33, CpFeDMAP$^+$), 123 (100, DMAP·H$^+$). Anal. Calcd for $\mathrm{C_{24}H_{29}Fe_2IN_2O_3Si}$: C, 43.66; H, 4.43; N, 4.24. Found: C, 43.60; H, 4.62; N, 4.10.

X-ray Crystal Structure Determination. The crystals of [**7**]I·$\mathrm{CD_3CN}$ and [**8**]I used for X-ray struture analyses were grown by cooling acetonitrile-*d*$_3$ solutions of these complexes to 0 °C. The crystals were sealed in thin-wall glass capillaries under a nitrogen atmosphere. The intensity data were collected on a Rigaku AFC-6A automated four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The reflection data were corrected with Lorentz and polarization factors but not for absorption and extinction. In both cases, the systematic absence gave two possibilities for the space group (*Pbnm* and *Pbn*2$_1$). Analyses by both space groups showed no appreciable difference in *R* values. Therefore *Pbnm* was adopted as the space group, which has higher symmetry, for both crystals. Crystallographic and experimental data are listed in Table 3.

Table 3. Crystal Data for [**7**]I·CD_3CN and [**8**]I

	[**7**]I·CD_3CN	[**8**]I
formula	$C_{23}H_{25}D_3Fe_2IN_3O_3Si$	$C_{23}H_{29}Fe_2IN_2O_3Si$
fw	664.15	660.17
cryst system	orthorhombic	orthorhombic
space group	*Pbnm*	*Pbnm*
a/Å	16.371(4)	14.564(2)
b/Å	17.043(3)	18.412(4)
c/Å	9.975(2)	10.290(1)
U/Å^3	2783(1)	2759(1)
Z	4	4
d_{calcd}/g cm^{-3}	1.59	1.59
μ(Mo Kα)/cm^{-1}	22.60	22.78
cryst size/mm	0.45 × 0.30 × 0.30	0.35 × 0.10 × 0.15
temp/°C	21	21
2θ range/deg	3–60	3–60
scan mode	2θ-ω	2θ-ω
monochromator	graphite	graphite
scan rate/deg min^{-1}	4	2
2θ width/deg	$1.1 + 0.35 \tan\theta$	$1.08 + 0.35 \tan\theta$
no. of unique data	4530	4519
no. of data used with $\lvert F_o\rvert > 3\sigma\lvert F_o\rvert$	2125	2000
R	0.056	0.070
R_w[a]	0.065	0.086

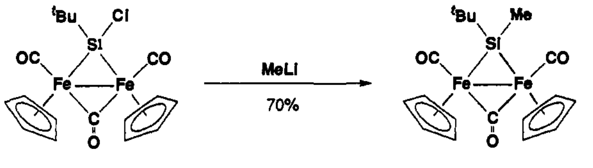
[a] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = [\sigma^2(|F_o|) + aF_o^2]^{-1}$, $a = 0.0008$ (for [**7**]I·CD_3CN) and 0.0024 (for [**8**]I).

The structures were solved by the heavy atom method. All the non-hydrogen atoms were located and refined by the block-diagonal least-squares method by applying anisotropic temperature factors. While some of the hydrogen atoms were found from difference Fourier synthesis and refined with isotropic temperature factors, the positions of other hydrogen atoms were calculated and fixed. Atomic scattering factors for non-hydrogen atoms and hydrogen atoms were taken from refs 28 and 29, respectively. Calculations were performed on a Nippon Electric Co. ACOS-2000 computer at the Tohoku University Computer Center using the Universal Program UNICS III.[30]

Results and Discussion

Synthesis of μ-Halosilylene Complexes. Substitution of the hydrogen atom on the silylene bridige of **1** by a halogen atom proceeds smoothly by reaction with an organic halide at room temperature (Scheme 2). Reaction of **1** with CCl_4 completed within 17.5 h to give red crystals of **2** in 99% yield. A similar chlorination reaction has been reported by Malisch and Ries for $Cp_2Fe_2(CO)_3(\mu\text{-SiHMe})$.[6a] Similarly, bromination and iodination of **1** have been achieved by treatment with $CHBr_3$ and CH_2I_2, respectively, to afford **3** (83%) and **4** (69%) (Scheme 2).

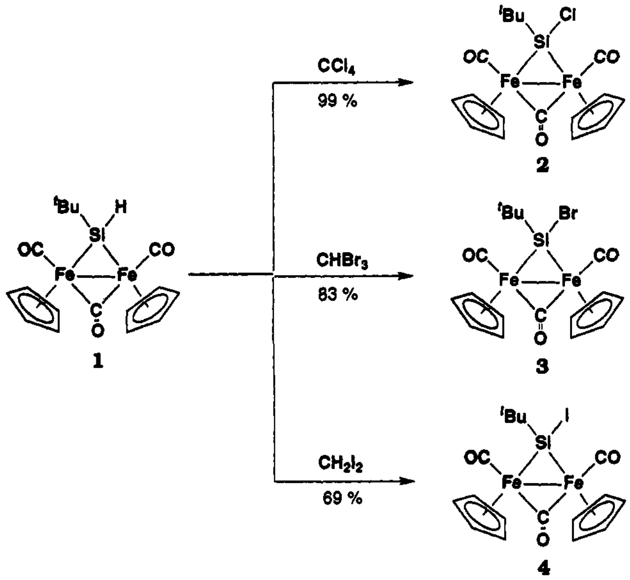
Nucleophilic substitution on the silicon atom of **2** has been attempted with several nucleophiles. Methyllithium reacted with **2** in diethyl ether to give **5** in 70% yield (eq 1). In the case of the reaction of **2** with ethyllithium, the desired ethyl derivative[31] was detected by silica gel TLC, but the amount of the product was too small to be isolated. The reactions with bulkier and more basic *tert*-butyllithium and potassium *tert*-butoxide only afforded intractable oily products. On the other hand, no reaction was observed between **2** and $p\text{-}CH_3C_6H_4MgCl$ or $Na[Fe(CO)_2Cp]$.



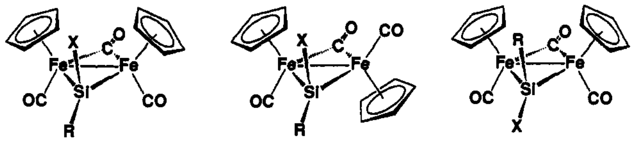
(1)

2 **5**

Scheme 2



Scheme 3



cis (X) *trans* *cis (R)*

Table 4. Ratio of *cis* and *trans* Isomers for $Cp_2Fe_2(CO)_3(\mu\text{-SiX}^t\text{Bu})$

		ratio of isomers/%	
compound	X	*cis*[a]	*trans*
1	H	100	0
2	Cl	93	7
3	Br	93	7
4	I	92	8
5	Me	62	38

[a] Only one of the two possible *cis* isomers has been observed by NMR spectroscopy in all cases. This is assignable to sterically less hindered *cis* (X) isomer.

For each $Cp_2Fe_2(CO)_3(\mu\text{-SiX}^t\text{Bu})$ (**1**–**5**), three geometric isomers are possible (Scheme 3). Complex **1** was found to exist as the *cis*(H) isomer exclusively.[27] In contrast to **1**, the *trans* isomers turned out to be observed for the complexes **2**-**5**. The ratios of *cis* and *trans* isomers of the five complexes (**1**–**5**) are shown in Table 4. The ratios indicate that steric interaction between the X atom and cyclopentadienyl rings is an important factor in determining the relative stability between *trans* and *cis* isomers. Especially, the methyl derivative **5** shows a significantly high proportion of *trans* isomer compared with those of hydro and halo derivatives **1**–**4**. This is probably because the steric interaction around the silicon atom in **5** is the largest by virtue of not only the bulkiness of the methyl group but also the shortness of the Si–Me bond. In fact, though the van der Waals radius of iodine (2.44 Å) is larger than that of the methyl group (2.0 Å),[32a] the proportion of the *trans* isomer of **4** is lower than that of **5** because the Si–I bond of **4** is much longer than the Si–C bond of **5**. Typical Si–I and Si–C bond lengths are 2.46 and 1.87 Å, respectively.[32b] Separation of isomers of **5** was unsuccessful because they interconvert with each other at room temperature.

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[28] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2A (pp 72–98), Table 2.3.1.1 (pp 149–150).

[29] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

[30] Sakurai, T.; Kobayashi, M. *Rikagaku Kenkyusho Hokoku* **1979**, *55*, 69–77.

[31] Kawano, Y.; Tobita, H.; Ogino, H. *Unpublished* results.

[32] (a) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972; pp 109. (b) *Ibid.* pp 107–108.

A similar behavior has been also observed by Malisch for $Cp_2Fe_2(CO)_3(\mu\text{-}SiHMe)$.[6a] Moreover, the free energies of activation for the interconversion of **5** were evaluated from the coalescence temperature[33] of ^1H NMR spectra: $\Delta G^{\ddagger}_{362\,K} = 83.1 \pm 1.0$ kJ mol^{-1} for *cis* → *trans* isomerization and $\Delta G^{\ddagger}_{362\,K} = 81.7 \pm 1.0$ kJ mol^{-1} for *trans* → *cis* isomerization. These values are close to the activation energies of the *cis–trans* isomerization of μ-carbene complexes $Cp_2Fe_2(CO)_3(\mu\text{-}CH_2)$[34] and $Cp_2Ru_2(CO)_3(\mu\text{-}CMe_2)$[35] and a μ-germylene complex $Cp_2Fe_2(CO)_3(\mu\text{-}GeMe_2)$.[36]

^{29}Si NMR and UV–Vis Spectra of $Cp_2Fe_2(CO)_3(\mu\text{-}SiX^tBu)$. As shown in Table 2, ^{29}Si NMR signals of **2–5** are observed in an extremely low field like those of **1**.[27] The values of chemical shifts of μ-halosilylene complexes $Cp_2Fe_2(CO)_3(\mu\text{-}SiX^tBu)$ are higher than those of **1** and increase in the order **2** (X = Cl) < **3** (X = Br) < **4** (X = I). To our knowledge, this is the first example of inverse halogen dependence in ^{29}Si NMR spectroscopy. Table 2 also shows the λ_{max}'s of the lowest energy UV–vis bands of these complexes, which increase (in other words, the HOMO–LUMO gaps decrease) in the order **1–2–3–4**.

Therefore, it is probable that the ^{29}Si NMR chemical shift has some relationship with the HOMO–LUMO gap. Indeed, according to Ramsey's expression (eq 2),[37] the paramagnetic

$$-\delta \sim \sigma_p = \left(\frac{-\mu_0}{4\pi}\right)\left(\frac{4\mu_B{}^2}{\Delta E}\right)[\langle r^{-3}\rangle_p P_i + \langle r^{-3}\rangle_d D_i] \qquad (2)$$

shielding constant σ_p, which dominates the chemical shifts δ of "heavy atoms" including ^{29}Si, decreases and leads to the downfield shift as the average electronic excitation energy ΔE decreases. This ΔE is supposed to correlate with the HOMO–LUMO gap because it has been elucidated that the frontier orbitals in dinuclear complexes with a metal–metal bond and bridging groups are localized on the three-membered ring constructed with the bridging unit and the two metals.[38]

Inverse halogen dependence is frequently found in metal nucleus NMR spectroscopy.[39] Also, in some cases, very good linear correlations have been observed between the chemical shift of the metal nucleus NMR and the λ_{max} in the UV–vis spectra.[40] However, in the case of complexes **1–4**, no linear correlation is seen between the ^{29}Si chemical shift and λ_{max} values (Figure 1). This can be explained by the change of the average radii of the valence orbitals $\langle r^{-3}\rangle_p$ and $\langle r^{-3}\rangle_d$ in eq 2, which depend on the atom X bonded to the bridging silicon.

Syntheses of Donor-Stabilized μ-Silylyne Complexes. In order to synthesize a silylyne-bridged diiron complex, we first attempted the chloride abstraction from **2** with $AgPF_6$. However, treatment of **2** with $AgPF_6$ in acetonitrile resulted in the precipitation of Ag metal. The subsequent workup did not give the desired μ-silylyne complex but gave monoiron complexes with fluorinated silyl groups, **6a,b** (eq 3).

We then examined the reactions of iodosilylene-bridged complex **4** with neutral Lewis bases. When a strong Lewis base NMI or DMAP was added to the acetonitrile solution of **4**, the iodo group on the bridging silicon was substituted by the base to afford the iodide salt of the cationic complex $[7]^+$ or $[8]^+$ in good yield (eq 4). Cations $[7]^+$ and $[8]^+$ are the first examples of donor-stabilized μ-silylyne dinuclear complexes. The iodide salts [**7**]I and [**8**]I were isolated as red crystalline solids which are moderately soluble in acetonitrile and sulfolane but insoluble in tetrahydrofuran, dichloromethane, and hydrocarbon solvents. The crystal of [**7**]I contains one molecule of acetonitrile per molecule. Although the crystals of [**7**]I and [**8**]I are stable toward air and moisture, the solutions of them are moisture sensitive. The unprecedented silylyne-bridged structures of [**7**]I·CD_3CN and [**8**]I were determined unequivocally by X-ray crystal structure analyses (*vide infra*).

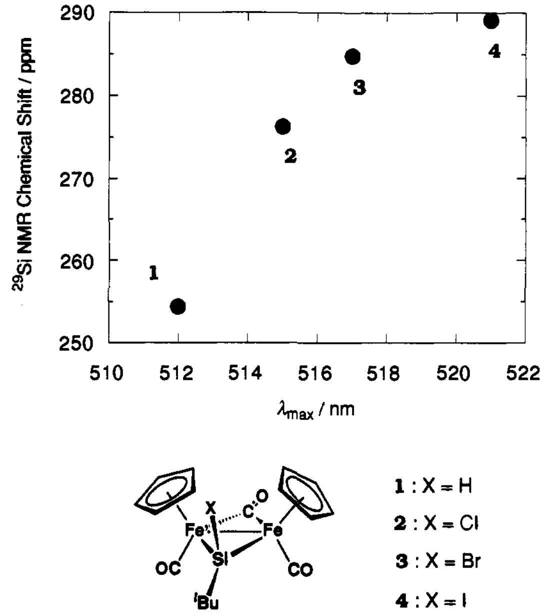
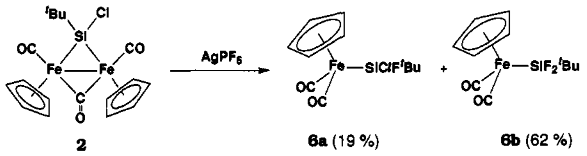
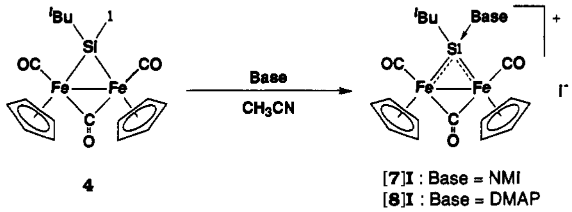


Figure 1. Relationship between ^{29}Si NMR chemical shift and λ_{max} for **1–4**.



(3)



(4)

In the infrared spectrum of [**7**]I·CD_3CN, the carbonyl stretching bands appear at 1980 and 1932 cm^{-1} (νCO_{term}) and 1766 cm^{-1} (νCO_{bridge}), all of which are higher in wavenumber than those of **1** by about 30 cm^{-1} on average (Table 1). In the ^1H NMR spectrum of [**7**]I, two singlets assignable to the Cp ligands and the *tert*-butyl group were observed at lower field than the corresponding signals of **1** and **4** in CD_3CN (**1**, δ 1.33 (^{t}Bu), 4.68 (Cp); **4**, δ 1.39 (^{t}Bu), 4.83 (Cp)). Also, the signals of NMI coordinated to the silicon atom shifted downfield compared with those of free NMI. These observations indicate that a positive charge is delocalized over the $SiFe_2C$ four-membered ring and the coordinated NMI ring. The FAB mass spectrum of [**7**]I in a sulfolane matrix clearly shows a peak for the cation of $[7]^+$ at $m/z = 493$. Interestingly, the spectrum also shows a strong peak

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(33) (a) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982. (b) Kost, D.; Carlson, E. H.; Raban, M. *J. Chem. Soc., Chem. Commun.* **1971**, 656.

(34) Altbach, M. I.; Muedas, C. A.; Korswagen, R. P.; Ziegler, M. L. *J. Organomet. Chem.* **1986**, *306*, 375.

(35) Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 2099.

(36) Adams, R. D.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1080.

(37) (a) Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699. (b) Jameson, C. J.; Gutowsky, H. S. *J. Chem. Phys.* **1964**, *40*, 1714. (c) Mason, J. *Multinuclear NMR*; Plenum Press: New York, 1987.

(38) For example: (a) Hoffmann, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 554. (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800. (c) Herrmann, W. A. *J. Am. Chem. Soc.* **1981**, *103*, 6852. (d) Clemente, D. A.; Rees, B.; Bandoni, G.; Biagini, M. C.; Reiter, B.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 887.

(39) Mason, J. *Chem. Rev.* **1987**, *87*, 1299.

(40) (a) Freeman, R.; Murray, G. R.; Richards, R. E. *Proc. R. Soc. London* **1957**, *A252*, 455. (b) Fujiwara, S.; Yajima, F.; Yamazaki, A. *J. Magn. Reson.* **1969**, *1*, 293.

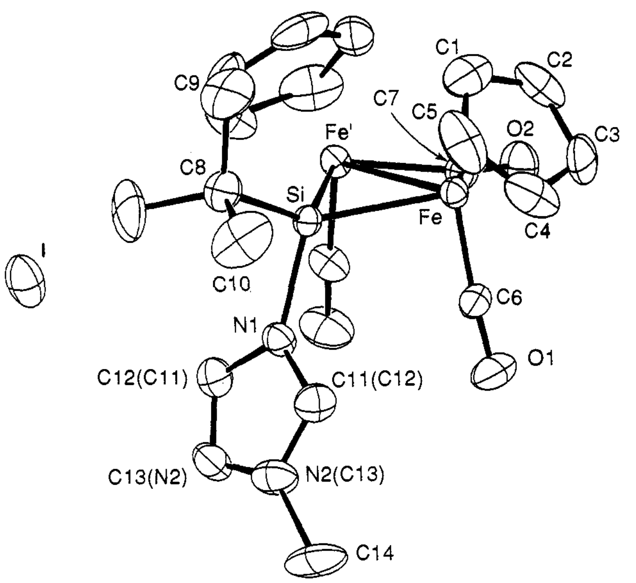

Figure 2. ORTEP diagram of $[Cp_2Fe_2(CO)_3(\mu\text{-Si}^t\text{Bu}\cdot\text{NMI})]I\cdot CD_3CN$ ($[7]I\cdot CD_3CN$ with atomic numbering scheme.

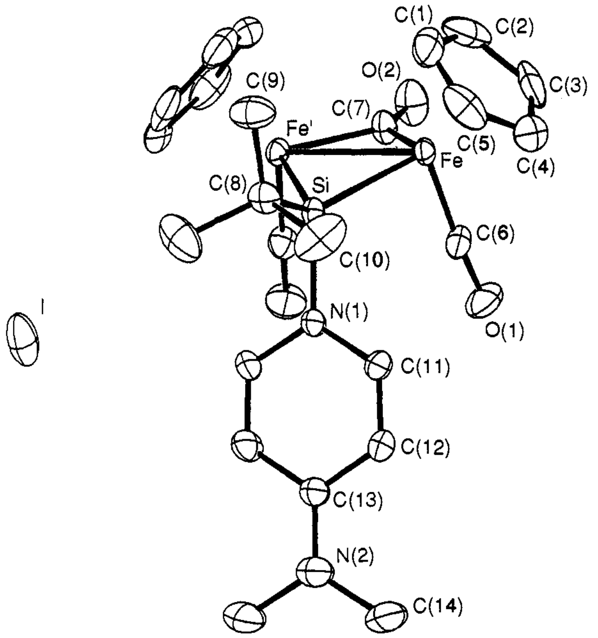

Figure 3. ORTEP diagram of $[Cp_2Fe_2(CO)_3(\mu\text{-Si}^t\text{Bu}\cdot\text{DMAP})]I$ ($[8]I$) with atomic numbering scheme.

at $m/z = 411$ which corresponds to $[Cp_2Fe_2(CO)_3(\mu\text{-Si}^t\text{Bu})]^+$. Thus, the base-free silylyne complex cation can be relatively stable in the gas phase.

When the bromo derivative **3** was used instead of **4**, the formation of $[7]^+$ was confirmed by ^{1}H NMR spectroscopy. In this case, however, the reaction reached to an equilibrium in which the equilibrium constant $K\ (=[[7]^+][I^-]/[3][NMI])$ was ca. 0.25 at ambient temperature in an acetonitrile-d_3 solution. When 1 equiv of $NaBPh_4$ was added to the mixture, the equilibrum shifted largely toward $[7]^+$, accompanied by precipitation of NaBr, but the isolation of the tetraphenylborate salt of $[7]^+$ was unsuccessful.

The spectroscopic behavior of the DMAP-coordinated complex $[8]^+$ closely resembles that of $[7]^+$.

Crystal Structures of $[7]I\cdot CD_3CN$ and $[8]I$. Crystals of $[7]I\cdot CD_3CN$ and $[8]I$ were grown by cooling their CD_3CN solutions. Figures 2 and 3 show the ORTEP diagrams for $[7]I\cdot CD_3CN$ and $[8]I$, respectively, involving the atomic numbering schemes. Selected interatomic distances and angles are listed in Tables 5 and 6. As the structural features of $[7]I\cdot CD_3CN$ and $[8]I$ except the coordinated bases are almost identical, the structure of $[7]I\cdot CD_3CN$, which has smaller standard deviations, is mainly discussed below.

Table 5. Selected Bond Distances (Å) and Angles (deg) for $[Cp_2Fe_2(CO)_3(\mu\text{-Si}^t\text{Bu}\cdot\text{NMI})]I\cdot CD_3CN$ ($[7]I\cdot CD_3CN$)

	Distances		
Si···I	5.388(2)	Fe–Fe′	2.626(2)
Si–Fe	2.262(2)	Si–N1	1.885(7)
Si–C8	1.910(9)	Fe–C6	1.745(6)
Fe–C7	1.913(8)	C6–O1	1.137(8)
C7–O2	1.185(12)	Fe–C(Cp)$_{av}$	2.088(11)
	Angles		
Fe–Si–Fe′	70.96(7)	Si–Fe–Fe′	54.52(6)
Fe–C7–Fe′	86.7(4)	C7–Fe–Fe′	46.7(2)
Si–Fe–C7	99.4(2)	C8–Si–N1	96.2(4)
Fe–Si–C8	130.7(3)	Fe–Si–N1	114.5(2)
Fe–C6–O1	176.0(6)	Fe–C7–O2	136.7(5)
dihedral angle between the Si–Fe–Fe′ plane and C7–Fe–Fe′ plane			161.8
dihedral angle between the two cyclopentadienyl rings			84.9
angle between the Si–Fe–Fe′ plane and Si–C8 vector			143.2
angle between the Si–Fe–Fe′ plane and Si–N1 vector			120.7
angle between the least squares plane of the NMI ring and Ni–Si vector			177.5

Table 6. Selected Bond Distances (Å) and Angles (deg) for $[Cp_2Fe_2(CO)_3(\mu\text{-Si}^t\text{Bu}\cdot\text{DMAP})]I$ ($[8]I$)

	Distances		
Si···I	5.565(2)	Fe–Fe′	2.633(2)
Si–Fe	2.266(3)	Si–N1	1.866(9)
Si–C8	1.947(11)	Fe–C6	1.738(8)
Fe–C7	1.912(9)	C6–O1	1.16(1)
C7–O2	1.18(1)	Fe–C(Cp)$_{av}$	2.09(1)
	Angles		
Fe–Si–Fe′	71.05(9)	Si–Fe–Fe′	54.48(7)
Fe–C7–Fe′	87.0(4)	C7–Fe–Fe′	46.5(3)
Si–Fe–C7	99.7(3)	C8–Si–N1	97.5(4)
Fe–Si–C8	128.8(3)	Fe–Si–N1	115.7(3)
Fe–C6–O1	176.0(7)	Fe–C7–O2	136.4(7)
dihedral angle between the Si–Fe–Fe′ plane and C7–Fe–Fe′ plane			164.3
dihedral angle between the two cyclopentadienyl rings			85.7
angle between the Si–Fe–Fe′ plane and Si–C8 vector			140.3
angle between the Si–Fe–Fe′ plane and Si–N1 vector			122.2

As shown in Figure 2, two Cp rings and the *tert*-butyl group in $[7]I\cdot CD_3CN$ are all located on the same side of the Fe–Si–Fe′–C(7) bicyclic ring. The dihedral angle between the two Cp rings is 84.8°. Coordination of the lone pair on the nitrogen atom of NMI to the Si atom in the silylyne ligand causes pyramidalization of the silicon atom. However, the angle between the Fe_2Si plane and the Si–C(8) bond (143.2°) is markedly enlarged from the calculated angle for an ideal tetrahedron (125.3°), apparently due to the large steric repulsion between the *tert*-butyl group and two cyclopentadienyl rings. The plane of the five-membered ring of NMI is parallel to the Fe–Fe bond, and the NMI ligand is disordered between the two possible orientations related by a crystallographic mirror plane.

The distance between the Si and I atoms (5.388(2) Å) is substantially longer than the sum of the effective van der Waals radii of silicon and iodine (4.08 Å).[41] This clearly indicates that the iodide merely exists as a counteranion and there is no chemical bond between Si and I. The Fe–Si bond length (2.262(2) Å) is shorter than the known values for neutral silylene-bridged diiron complexes **1** (2.270(1) and 2.272(1) Å)[27] and $Cp_2Fe_2(CO)_3\{\mu\text{-SiMe(SiMe}_3)\}$ (2.294(1) and 2.301(1) Å)[42] although the steric

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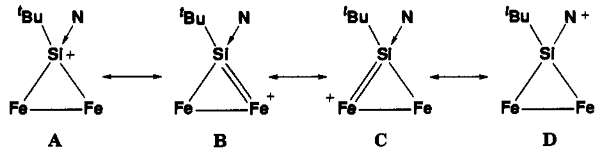
(41) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(42) Ueno, K.; Hamashima, N.; Shimoi, M.; Ogino, H. *Organometallics* **1991**, *10*, 959.

hindrance of the bridging unit in [7]I·CD$_3$CN ("Si^{t}Bu·NMI") is apparently larger than that in **1** ("SiH^{t}Bu"). This suggests the existence of partial unsaturated bond character between Fe and Si. On the other hand, the Si–N bond length (1.885(7) Å) is considerably longer than typical Si–N single bonds (ca. 1.75 Å).[43] Similar long Si–N bonds are also found in several cation–Lewis base adducts such as cationic silylene complex [(η-C$_5$Me$_5$)(PMe$_3$)$_2$-Ru=SiPh$_2$·NCMe]BPh$_4$·CH$_2$Cl$_2$ (1.932(8) Å)[16a,b] and halosilane–base adducts [Me$_3$Si·pyridine]X (1.858(9) Å (X = I), 1.856(7) Å (X = Br))[23a] and [Me$_3$Si·NMI]Cl (1.821(2) Å).[23b] The value therefore indicates that the Si–N interaction in [7]I·CD$_3$CN should be described as a dative bond.

The structural features and spectroscopic properties of [7]I·CD$_3$-CN and [**8**]I mentioned above support the bonding descriptions shown in eq 4. They could be also described as the combination of four resonance structures A–D (Scheme 4).

Scheme 4



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Supplementary Material Available: Tables of positional and thermal parameters, bond distances, and bond angles for [7]I·CD$_3$-CN and [**8**]I (10 pages); listing of structure factors (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(43) Sheldrick, W. S.; Wolfsberger, W. *Z. Naturforsch.* **1977**, *B32*, 22.