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Novel Silicon- and Tin-Containing Ferrocenophanes and Related Compounds as Lewis Acids†

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The syntheses of 1,1′-bis(chloromethyldimethylsilyl)ferrocene, fc$(SiMe_2CH_2Cl)_2$ (**2**), of the series of open-chain ferrocene- and silicon-containing organotin(IV) compounds $(FcMe_2SiCH_2)_2SnPh_2$ (**3**), $(FcMe_2SiCH_2SnXPh)_2CH_2$ (**4**, X = Ph; **7**, X = I; **8**, X = Cl; **9**, X = F), fc$(SiMe_2CH_2SnXR_2)_2$ (**5**, R = X = Ph; **6**, R = X = Me; **10**, R = Ph, X = I; **11**, R = Me, X = Cl; **12**, R = Ph, X = Cl; **13**, R = Ph, X = F), fc$(SiMe_2CH_2SnPh_2CH_2SiMe_2Fc)_2$ (**14**), and of the ferrocenophanes [fc$(SiMe_2CH_2SnXRCH_2SiMe_2)_2$fc] (**15**, R = X = Me; **16**, R = X = Ph; **17**, R = Ph, X = I; **18**, R = Ph, X = F; **19**, R = Ph, X = Cl; **20**, R = Me, X = Cl) and two of their chloride complexes {[fc$(SiMe_2CH_2SnClRCH_2SiMe_2)_2$fc·2Cl]$^{2-}$ 2[$(Ph_3P)_2N$]$^+$} (**22**, R = Me; **23**, R = Ph) are reported, and the molecular structures of **4**, **16**, **17**, **19**, **20**, **22**, and **23** are described. In solution, the halogen-substituted ferrocenophanes **17**−**19** undergo *cis*−*trans* isomerization, the rate of which is enhanced by addition of halide ions. Variable-temperature ^{119}Sn and ^{19}F NMR studies in solution indicate that the fluoro derivatives **9**, **13**, and **18** react with different molar equivalents of fluoride ions to give the 1:1 and 1:2 adducts [$(FcMe_2SiCH_2SnFPh)_2CH_2 \cdot nF$]$^{n-}$[$Bu_4N$]$^+_n$ (**9a**,**b**, $n = 1$; **9c**, $n = 2$), {[**13**·2F]$^{2-}$[Bu_4N]$^+_2$}, and {[**18**·F]$^-$[Bu_4N]$^+$} and {[**18**·2F]$^{2-}$[Bu_4N]$^+_2$}, respectively. A more extended electrochemical investigation points out that the species containing halogen-substituted tin groups are more sensitive to anions than their analogues containing diphenyltin groups.

Introduction

The synthesis of tailor-made host molecules for the selective complexation of anions or neutral donor molecules has become a topic of increasing interest over the last 2 decades.[1] Covalent fitting of Lewis acidic centers such as boron,[2] aluminum,[3] indium,[4] silicon,[5] germanium,[6] tin,[7,8] and mercury[9] in suitable organic molecule structures results in multidentate Lewis acidic host molecules which were shown to be efficient in coordinating anions and neutral Lewis bases. The guest selectivity and stability of the host−guest complexes of these

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† Dedicated to Professor Kalman Burger (A. Jozsef University, Szeged, Hungary) on the occasion of his 70th birthday. This paper includes part of the Ph.D. thesis of R. Altmann, Dortmund University, 1998. Part of this work was presented as posters at the XXXIIIth International Conference on Coordination Chemistry, Florence, Italy, Aug 30−Sept 4, 1998 (Book of Abstracts, p 436), and at the IXth International Conference on the Coordination and Organometallic Chemistry of Germanium, Tin, and Lead (ICCOC-GTL), Sept 20−25, 1998, Melbourne, Australia (Book of Abstracts, p 14).

(1) (a) Pierre, J. L.; Baret, P. *Bull. Soc. Chim. Fr.* **1983**, II-367 and references cited therein. (b) Dietrich, B. *Pure Appl. Chem.* **1993**, *65*, 1457 and references cited therein. (c) Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609 and references cited therein. (d) Beer, P. D.; Smith, D. K. *Progress in Inorganic Chemistry*; Wiley: New York, 1997; Vol. 46, p 1, and references cited therein. (e) Antonisse, M. M. G.; Reinhoudt, D. N. *Chem. Commun.* **1998**, 443.

(2) (a) Shriver, D. F.; Biallas, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 1078. (b) Katz, H. E. *J. Org. Chem.* **1985**, *50*, 5027. (c) Katz, H. E. *J. Am. Chem. Soc.* **1986**, *108*, 7640.

(3) (a) Sharma, V.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1992**, *114*, 7931. (b) Kaul, F. A. R.; Tschinkl, M.; Gabbai, F. P. *J. Organomet. Chem.* **1997**, *539*, 187. (c) Eisch, J. J.; Mackenzie, K.; Windisch, H.; Krüger, C. *Eur. J. Inorg. Chem.* **1999**, 153.

(4) (a) Gabbai, F. P.; Schier, A.; Riede, J.; Schichl, D. *Organometallics* **1996**, *15*, 4119. (b) Tschinkl, M.; Schier, A.; Riede, J.; Schmidt, E.; Gabbai, F. P. *Organometallics* **1997**, *16*, 4759. (c) Tschinkl, M.; Schier, A.; Riede, J.; Gabbai, F. P. *Inorg. Chem.* **1997**, *36*, 5706. (d) Gabbai, F. P.; Schier, A.; Riede, J. *Angew. Chem.* **1998**, *110*, 646.

(5) (a) Jung, M. E.; Xia, H. *Tetrahedron Lett.* **1988**, *29*, 297. (b) Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *Organometallics* **1992**, *11*, 2099. (c) Tamao, K.; Hayashi, T.; Ito, Y. *J. Organomet. Chem.* **1996**, *506*, 85. (d) Brondani, D.; Carré, F. H.; Corriu, R. J. P.; Moreau, J. J. E.; Man, M. W. C. *Angew. Chem.* **1996**, *108*, 349.

(6) Aoyagi, S.; Tanaka, K.; Takeuchi, Y. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1549.

(7) (a) Karol, T. J.; Hutchinson, J. P.; Hyde, J. R.; Kuivila, H. G.; Zubieta, J. A. *Organometallics* **1983**, *2*, 106. (b) Kuivila, H. G.; Karol, T. J.; Swami, K. *Organometallics* **1983**, *2*, 909. (c) Swami, K.; Hutchinson, J. P.; Kuivila, H. G.; Zubieta, J. A. *Organometallics* **1984**, *3*, 1687. (d) Austin, M.; Gebreyes, K.; Kuivila, H. G.; Swami, K.; Zubieta, J. A. *Organometallics* **1987**, *6*, 834. (e) Blanda, M. T.; Newcomb, M. *Tetrahedron Lett.* **1989**, *30*, 3501. (f) Newcomb, M.; Horner, J. H.; Blanda, M. T.; Squattrito, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 6294. (g) Horner, J. H.; Squatritto, P. J.; McGuire, N.; Riebenspies, J. P.; Newcomb, M. *Organometallics* **1991**, *10*, 1741.

(8) (a) Gielen, M.; Jurkschat, K.; Meunier-Piret, J.; Van Meerssche, M. *Bull. Soc. Chim. Belg.* **1984**, *93*, 379. (b) Jurkschat, K.; Kuivila, H. G.; Liu, S.; Zubieta, J. A. *Organometallics* **1989**, *8*, 2755. (c) Jurkschat, K.; Rühlemann, A.; Tzschach, A. *J. Organomet. Chem.* **1990**, *381*, C53. (d) Jurkschat, K.; Hesselbarth, F.; Dargatz, M.; Lehmann, J.; Kleinpeter, E.; Tzschach, A.; Meunier-Piret, J. *J. Organomet. Chem.* **1990**, *388*, 259. (e) Dakternieks, D.; Jurkschat, K.; Zhu, H.; Tiekink, E. R. T. *Organometallics* **1995**, *14*, 2512. (f) Altmann, R.; Jurkschat, K.; Schürmann, M.; Dakternieks, D.; Duthie, A. *Organometallics* **1997**, *16*, 5716. (g) Altmann, R.; Jurkschat, K.; Schürmann, M.; Dakternieks, D.; Duthie, A. *Organometallics* **1998**, *17*, 5858.

10.1021/om9905660 CCC: $19.00

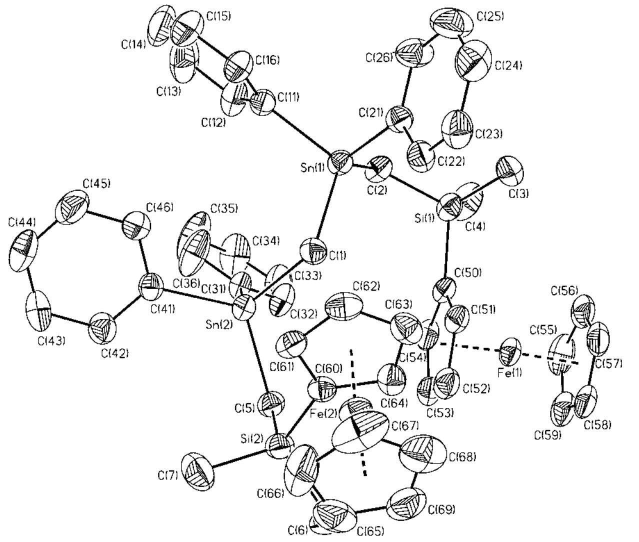

Figure 1. General view (SHELXTL-PLUS) of a molecule of **4** showing 30% probability displacement ellipsoids and the atom numbering.

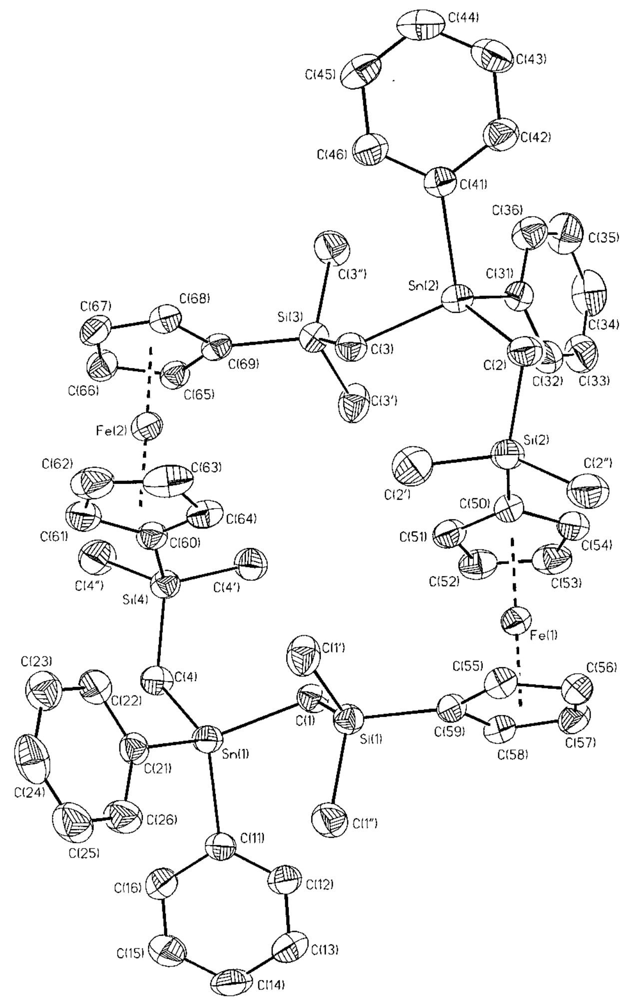

Figure 2. General view (SHELXTL-PLUS) of a molecule of **16** showing 30% probability displacement ellipsoids and the atom numbering.

compounds strongly depend on the preorganization of the host molecule; i.e., the more rigid the host, the better the selectivity to be expected.

Recent studies also demonstrated the utility of bidentate Lewis acids as catalysts in organic reactions involving carbonyl compounds,[10] and model host−guest complexes composed of bidentate mercury compounds and ketones have been isolated and fully characterized.[9h]

Electrochemical studies showed the potential ability of organotin(IV) halides to act as carriers in phosphate-selective electrodes.[11] Cyclic voltammetry was employed to study the anion recognition of ferrocene- or cobaltocene-containing host molecules.[1d,12]

One objective of our research is to study the host−guest activity of spacer-bridged organotin(IV) halides.[8,13] Because of their potential use in electrochemical sensing, we were interested in the synthesis of redox-active host molecules with Lewis acidic centers. Although ferrocene derivatives with organosilicon[14] or organotin[15] units have been described, there have been no reports on such derivatives containing both silicon and tin.

Following our preliminary communication on the structure of 1,1,3,3,14,14,16,16,18,18,29,29-dodecamethyl-3,14,18,29-tetrasila-1,16-distanna[5.5]ferrocenophane,[16] we report here the syntheses of novel silicon- and tin-

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(9) (a) Wuest, J. D.; Zacharie, B. *Organometallics* **1985**, *4*, 410. (b) Beauchamp, A. L.; Olivier, M. J.; Wuest, J. D.; Zacharie, B. *J. Am. Chem. Soc.* **1986**, *108*, 73. (c) Wuest, J. D.; Zacharie, B. *J. Am. Chem. Soc.* **1987**, *109*, 4714. (d) Yang, X.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 380. (e) Chistyakov, A. L.; Stankevich, I. V.; Gambaryan, N. P.; Struchkov, Yu. T.; Yanovsky, A. I.; Tikhonova, I. A.; Shur, V. B. *J. Organomet. Chem.* **1997**, *536*, 413. (f) Vaugeois, J.; Simard, M.; Wuest, J. D. *Organometallics* **1998**, *17*, 1208. (g) Wuest, J. D. *Acc. Chem. Res.* **1999**, *32*, 81. (h) Tschinkl, M.; Schier, A.; Riede, J.; Gabbai, F. P. *Organometallics* **1999**, *18*, 1747.

(10) (a) Ooi, T.; Tomoya, M.; Maruoka, K. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2347. (b) Ooi, T.; Takahashi, M.; Maruoka, K. *J. Am. Chem. Soc.* **1996**, *118*, 11307.

(11) (a) Chaniotakis, N. A.; Jurkschat, K.; Rühlemann, A. *Anal. Chim. Acta* **1993**, *282*, 345. (b) Tsagatakis, J. K.; Chaniotakis, N. A.; Jurkschat, K. *Helv. Chim. Acta* **1994**, *77*, 2191. (c) Chaniotakis, N. A.; Tsagatakis, J. K.; Jurkschat, K.; Willem, R. *React. Funct. Polym.* **1997**, *34*, 183. (d) Tsagatakis, J. K.; Chaniotakis, N. A.; Jurkschat, K *Quim. Anal.* **1997**, *16*, 105.

(12) (a) Beer, P. D. *Adv. Inorg. Chem.* **1992**, *39*, 79 and references cited therein. (b) Beer, P. D. *Acc. Chem. Res.* **1998**, *31*, 71 and references cited therein. (c) Togni, A.; Hayashi, T. *Ferrocenes*; VCH: Weinheim, Germany, 1995, and references cited therein. (d) Kingston, J. E.; Ashford, L.; Beer, P. D.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1999**, 251. (e) Scherer, M.; Sessler, J. L.; Gebauer, A.; Lynch, V. *J. Chem. Soc., Chem. Commun.* **1998**, 85. (f) Dong, T. Y.; Chang, C. K.; Cheng, C. H.; Lin, K. J. *Organometallics* **1999**, *18*, 1911.

(13) (a) Kühn, S. Ph.D. Thesis, University of Dortmund, 1997. (b) Hummeltenberg, R. Ph.D. Thesis, University of Dortmund, 1997. (c) Altmann, R.; Gausset, O.; Hummeltenberg, R.; Jurkschat, K.; Kühn, S.; Schürmann, M.; Zobel, B. In *Organosilicon Chemistry IV*; Auner, N., Weis, J. Eds.; Wiley-VCH: Weinheim, Germany, in press.

(14) (a) Park, J.; Seo, Y.; Cho, S.; Whang, D.; Kim, K.; Chang, T. *J. Organomet. Chem.* **1995**, *489*, 23. (b) Calhorda, M. J.; Lopes, P. E. M.; Schier, A.; Herrmann, R. J. *Organomet. Chem.* **1997**, *543*, 93. (c) MacLachlan, M. J.; Lough, A. J.; Geiger, W. E.; Manners, I. *Organometallics* **1998**, *17*, 1873. (d) Cervantes-Lee, F.; Sharma, H. K.; Pannell, K. H.; Derecskei-Kovacs, A.; Marynick, D. S. *Organometallics* **1998**, *17*, 3701. (e) Gomez-Elipe, P.; Resendes, R.; Macdonald, P. M.; Manners, I. *J. Am. Chem. Soc.* **1998**, *120*, 8348. (f) Palitzsch, W.; Pietzsch, C.; Jacob, K.; Edelmann, F. T.; Gelbrich, T.; Lorenz, V.; Puttnat, M.; Roewer, G. *J. Organomet. Chem.* **1998**, *554*, 139. (g) Rasburn, J.; Foucher, D. A.; Reynolds, W. F.; Manners, I.; Vancso, G. J. *J. Chem. Soc., Chem. Commun.* **1998**, 843. (h) Garcia, B.; Casado, C. M.; Cuadrado, I.; Alonso, B.; Moran, M.; Losada, J. *Organometallics* **1999**, *18*, 2349.

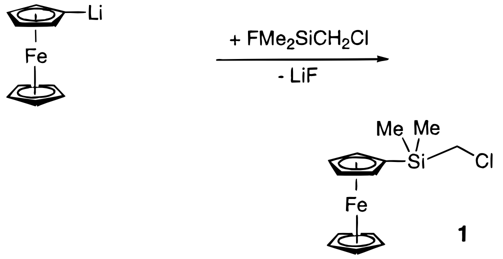
(15) (a) Clearfield, A.; Simmons, C. J.; Withers, H. P., Jr.; Seyferth, D. *Inorg. Chim. Acta* **1983**, *75*, 139. (b) Herberhold, M.; Steffl, U.; Milius, W.: Wrackmeyer, B. *Angew. Chem.* **1996**, *108*, 1927. (c) Rulkens, R.; Lough, A. J.; Manners, I. *Angew. Chem.* **1996**, *108*, 1929. (d) Herberhold, M.; Steffl, U.; Milius, W.: Wrackmeyer, B. *Z. Anorg. Allg. Chem.* **1998**, *624*, 386. (e) Herberhold, M.; Milius, W.; Steffl, U.; Vitzithum, K.; Wrackmeyer, B.; Herber, R. H.; Fontani, M.; Zanello, P. *Eur. J. Inorg. Chem.* **1999**, 145. (f) Sharma, H. K.; Cervantes-Lee, F.; Mahmoud, J. S.; Pannell, K. H. *Organometallics* **1999**, *18*, 399.

(16) Gausset, O.; Delpon-Lacaze, G.; Schürmann, M.; Jurkschat, K. *Acta Crystallogr.* **1998**, *C54*, 1425.

containing ferrocenophanes and of related open-chain derivatives. The complexing behavior toward halide ions and dihydrogen phosphate is investigated by means of NMR spectroscopy, X-ray analysis, and electrochemical techniques.

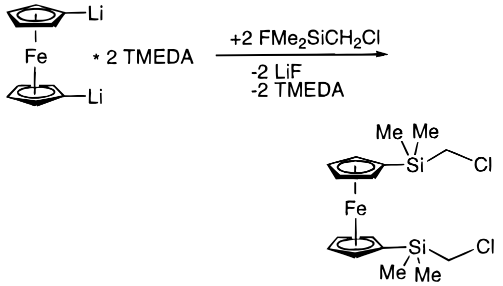
Results and Discussion

Synthetic Aspects. The reaction of lithioferrocene[17] and 1,1′-dilithioferrocene[18] with (chloromethyl)dimethylfluorosilane provided the ferrocene- and silicon-containing precursors $FcMe_2SiCH_2Cl$ (**1**) and $fc(SiMe_2CH_2Cl)_2$ (**2**), respectively, as red oils in good yields (eqs 1 and 2). Hereafter, Fc and fc refer to monosubstituted and 1,1′-disubstituted ferrocene units, respectively. The use of (chloromethyl)dimethylfluorosilane was preferred over the corresponding commercially available chlorosilane as, according to our experience, the former gives better yields in nucleophilic substitution reactions.



1

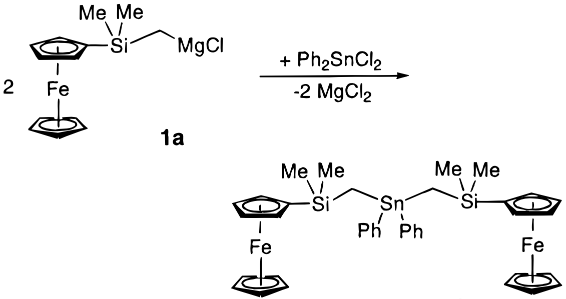
(1)



2

(2)

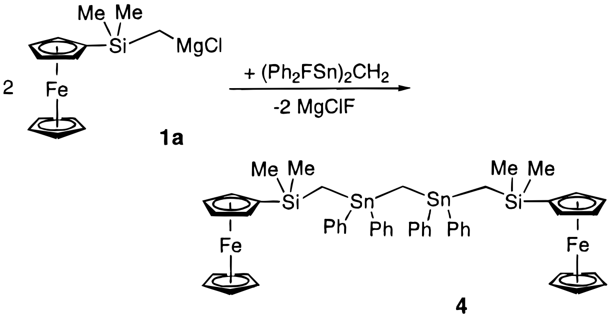
The reactions of the Grignard reagent **1a** with Ph_2SnCl_2 or $(Ph_2FSn)_2CH_2$[8e] afforded the mono- and ditin species $(FcMe_2SiCH_2)_2SnPh_2$ (**3**) and $(FcMe_2SiCH_2SnPh_2)_2CH_2$ (**4**), respectively, as red solids (eqs 3 and 4). The molecular structure of the methylene-bridged tetraorganotin species **4** is shown in Figure 1. The silicon and tin atoms in the methylene-bridged tetraorganotin species **4** each exhibit a tetrahedral configuration. The Sn−C, Si−C, and Fe−C bond lengths as well as the bond angles at silicon and tin are as expected (Table 1).[14c,d,16,19,20] The cyclopentadiene rings are eclipsed, as is shown by the torsion angles C(64)−centroid(cp1)−centroid(cp2)−C(69) and C(52)−centroid(cp3)−center(cp4)−C(58) of 0.0(7) and 0.8(7)°, respectively (Table 4). The cyclopentadiene rings within one ferrocene unit are slightly tilted by 2.5(3)° (Fe(1)) and 2.5(2)° (Fe(2)).



1a

3

(3)

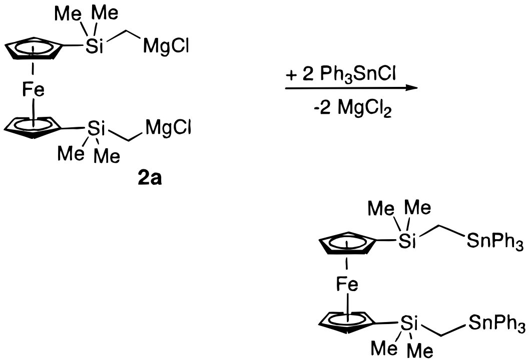


1a

4

(4)

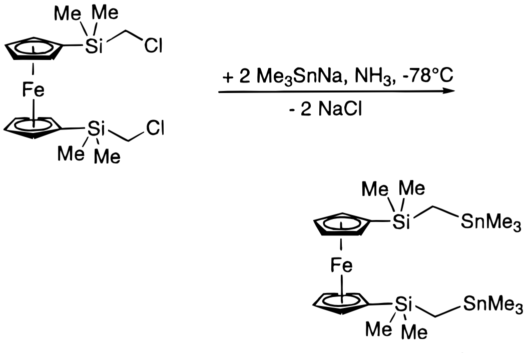
The reaction of the di-Grignard reagent **2a** with 2 molar equiv of Ph_3SnCl gave the 1,1′-difunctionalized ferrocene derivative $fc(SiMe_2CH_2SnPh_3)_2$ (**5**) (eq 5). Its trimethyltin-substituted analogue **6** was prepared by treatment of $fc(SiMe_2CH_2Cl)_2$ (**2**) with two molar equiv of Me_3SnNa in liquid ammonia (eq 6).



2a

5

(5)



6

(6)

Cleavage of the tin−phenyl and tin−methyl bonds by reaction of the corresponding derivatives **4**−**6** with iodine and dimethyltin dichloride provided the halogen-functionalized species **7**, **10**, and **11**, respectively (Schemes 1 and 2). Compounds **7** and **10** were converted into their corresponding chloro- and fluoro-substituted derivatives **8** and **9**, and **12** and **13**, respectively, by treatment with silver chloride or potassium fluoride (Schemes 1 and 2).

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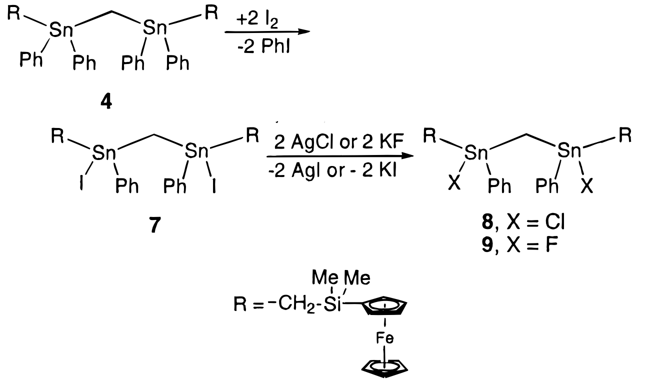
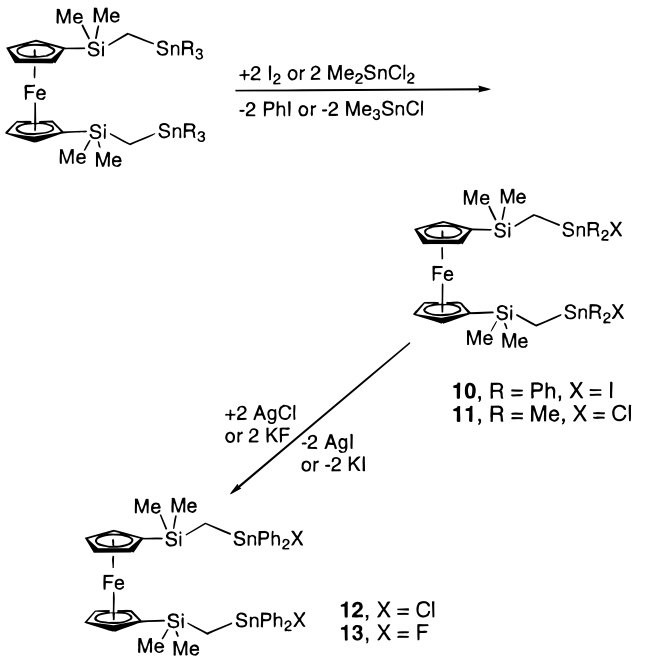
[17] (a) Rebiere, F.; Samuel, O.; Kagan, H. B. *Tetrahedron Lett.* **1990**, *31*, 3121. (b) Mueller-Westerhoff, U. T.; Yang, Z.; Ingram, G. *J. Organomet. Chem.* **1993**, *463*, 163. (c) Schottenberger, H.; Buchmeiser, M.; Polin, J.; Schwarzhans, K. E. *Z. Naturforsch.* **1993**, *48B*, 1524.

[18] Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Merrill, R. E.; Smart, J. C. *J. Organomet. Chem* **1971**, *27*, 241.

Scheme 1

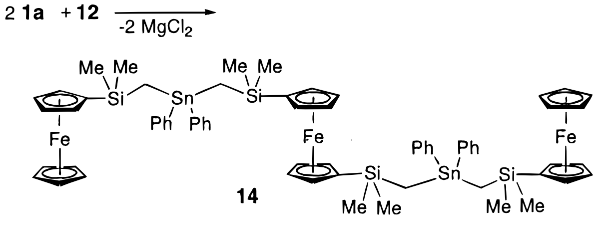


Scheme 2



Compounds **7**−**9** each contain two chiral tin atoms, but the ^{119}Sn NMR in CH_2Cl_2 gave no evidence for the corresponding pairs of diastereomers, which hints at intra- and/or intermolecular exchange processes being fast on the ^{119}Sn NMR time scale.

The reaction of **12** with 2 molar equiv of the Grignard reagent **1a** afforded fc($SiMe_2CH_2SnPh_2CH_2SiMe_2Fc)_2$ (**14**) as a species containing one ferrocenediyl as well as two ferrocenyl units (eq 7).



(7)

The reaction of the di-Grignard reagent **2a** with the organotin chlorides **11** and **12** provided the silicon- and tin-containing ferrocenophanes **15** and **16** (Figure 2), respectively, which were separated by fractional crystallization and size exclusion chromatography (Scheme 3). The compounds **15** and **16** are red crystalline solids.

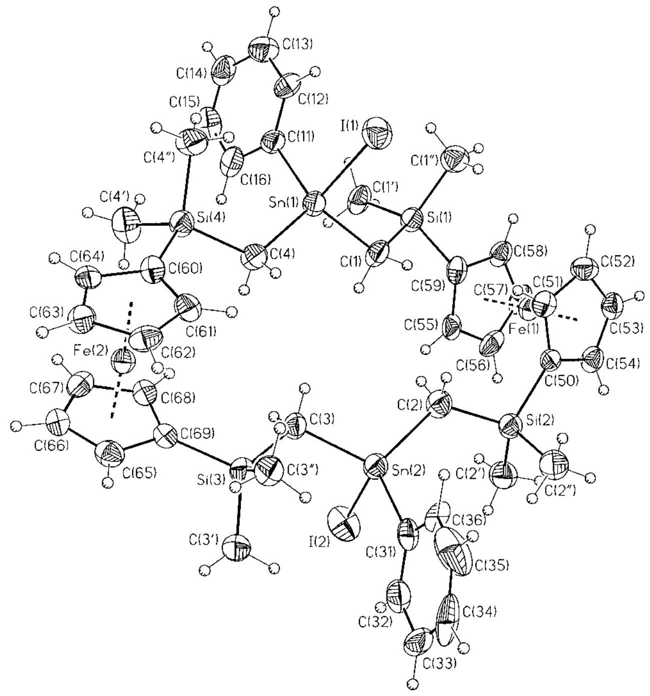
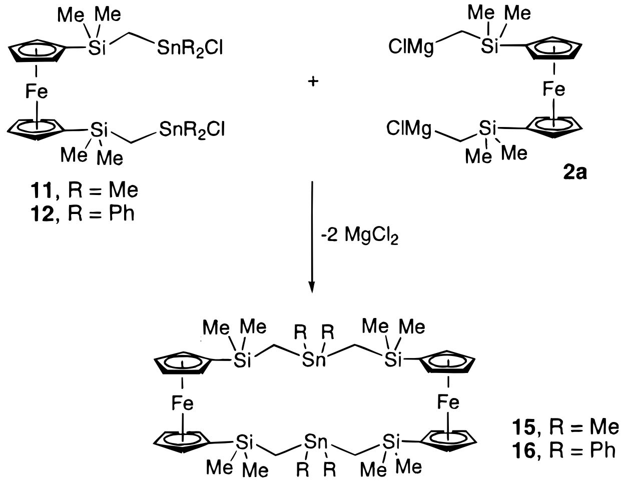


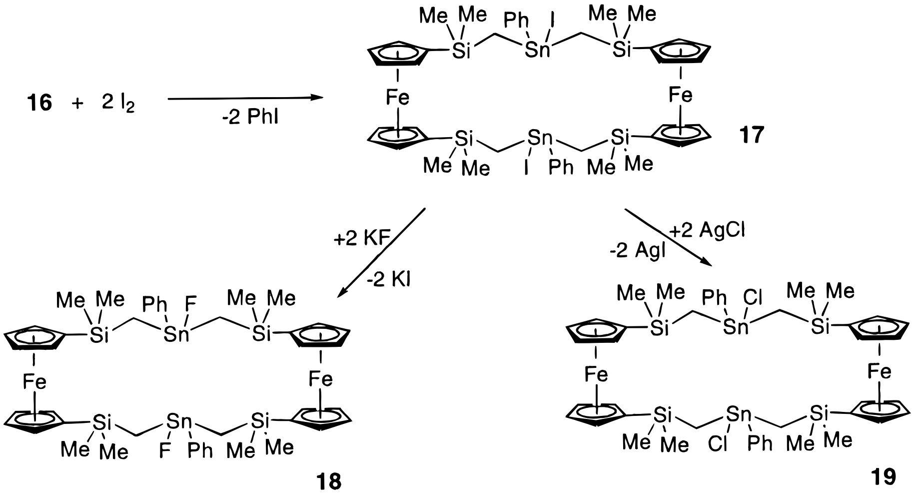
Figure 3. General view (SHELXTL-PLUS) of a molecule of **17** showing 30% probability displacement ellipsoids and the atom numbering.

Scheme 3



The reaction of the ferrocenophane **16** with 2 molar equiv of iodine quantitatively gave *trans*-fc($SiMe_2CH_2$-$SnIPhCH_2SiMe_2)_2$fc (**17**) as a red crystalline solid (Scheme 4, Figure 3). In $CDCl_3$ solution, compound **17** is in equilibrium with its *cis* isomer **17a**, as is evidenced by (i) two almost equally intense ^{119}Sn NMR signals at −13.1 and −13.4 ppm and (ii) the ^{13}C NMR spectrum showing 4 resonances for the methyl carbons at 0.60, 0.74, 0.84, and 0.97 ppm, 2 resonances for the methylene carbons at 4.32 and 4.37 ppm, 10 resonances for the cyclopentadiene carbons at 71.41, 71.48, 71.55, 71.61, 72.73, 72.78, 72.86, 72.95, 73.05, and 73.15 ppm, and 2 resonances for the *ipso* carbons of the phenyl groups at 139.59 and 139.67 ppm. However, the ^{1}H NMR spectrum displays only two broad resonances for the methyl protons at 0.18 ($w_{1/2} = 5.4$ Hz) and 0.37 ($w_{1/2} = 4.3$ Hz) ppm, which hints at *cis*−*trans* isomerization being fast on the ^{1}H NMR time scale. The rate of the *cis*−*trans*

Scheme 4



isomerization is enhanced upon addition of 0.1 molar equiv of Ph$_4$PI to the solution of **17**. Thus, the ^{119}Sn NMR spectrum at room temperature shows a single resonance at −13.5 ppm ($w_{1/2}$ = 52 Hz) and the ^{13}C NMR spectrum displays one broad signal for the methyl carbons at 0.77 ppm ($w_{1/2}$ = 13 Hz), one signal for the methylene carbons at 4.32 ppm ($w_{1/2}$ = 24.3 Hz), three resonances for the cyclopentadiene carbons at 71.63 ($w_{1/2}$ = 12.6 Hz), 72.87 ($w_{1/2}$ = 8.8 Hz), and 73.10 ($w_{1/2}$ = 21.4 Hz) ppm, and one resonance for the *ipso* carbons at 139.60 ppm. The *cis*−*trans* isomerization is likely to proceed via pentacoordinate tin species.

Treatment of **17** in diethyl ether with aqueous potassium fluoride yielded fc(SiMe$_2$CH$_2$SnFPhCH$_2$SiMe$_2$)$_2$fc (**18**) as an orange amorphous solid which shows a rather poor solubility in common organic solvents (Scheme 4). Its ^{19}F NMR spectrum in CD$_2$Cl$_2$ displayed two almost equally intense signals at −209.7 ($^1J(^{19}\mathrm{F}-^{119/117}\mathrm{Sn})$ = 2357/2256 Hz) and −210.7 ($^1J(^{19}\mathrm{F}-^{119/117}\mathrm{Sn})$ = 2369/2266 Hz) ppm and hints at the presence of *cis*−*trans* isomers. This is also supported by the ^{1}H NMR spectrum in CDCl$_3$, showing four methyl resonances at 0.22, 0.23, 0.38, and 0.39 ppm (integral ratio 7:6:6:7).

The reaction of the organotin iodide **17** with silver chloride in CH$_2$Cl$_2$/CH$_3$CN (1:1) afforded the chloro-substituted species *trans*-fc(SiMe$_2$CH$_2$SnClPhCH$_2$SiMe$_2$)$_2$-fc (**19**) as an orange crystalline solid (Scheme 4, Figure 4).

In contrast to the iodo-substituted ferrocenophane **17**, the ^{119}Sn NMR spectrum in CD$_2$Cl$_2$ at room temperature of the chloro-substituted derivative **19** displays only one signal at 95.4 ppm ($w_{1/2}$ = 29 Hz). At −80 °C two resonances of equal integral ratio at 99.8 and 99.7 ppm are observed. The ^{13}C NMR spectrum at room temperature displays a single broad resonance for the methyl carbons at 0.7 ppm ($w_{1/2}$ = 20 Hz), a single sharp resonance for the methylene carbons at 4.8 ($^1J(^{13}\mathrm{C}-^{119/117}\mathrm{Sn})$ = 279/266 Hz), three broad resonances for the cyclopentadienyl carbons at 71.6, 72.8, and 73.0 ppm, and four sharp signals for the phenyl carbons at 127.6, 128.6, 135.5, and 141.8 ppm. The ^{1}H NMR spectrum displays two broad signals for the methyl protons at 0.20 ($w_{1/2}$ = 12 Hz) and 0.38 ($w_{1/2}$ = 11 Hz), a singlet for the methylene protons at 0.70 ($w_{1/2}$ = 8 Hz), and the expected signals for the cyclopentadienyl and phenyl protons. The results indicate the *cis*−*trans* equilibrium to be fast on all NMR time scales at room temperature but slow on the ^{119}Sn NMR time scale at −80 °C.

The reaction of the methyl-substituted ferrocenophane fc(SiMe$_2$CH$_2$SnMe$_2$CH$_2$SiMe$_2$)$_2$fc[16] (**15**) with 2 molar equiv of Me$_2$SnCl$_2$ gave a solid crude product, from which the Me$_3$SnCl formed along the reaction and residual traces of Me$_2$SnCl$_2$ were removed in vacuo. The ^{119}Sn NMR spectrum in CH$_2$Cl$_2$ of the residue showed five resonances at (a) 168.8 ppm (integral 1.5), (b) 168.3 ppm (integral 3.8), (c) 167.3 ppm (integral 4), (d) 17.8 ppm (integral 1.0), and (e) 17.7 (integral 1.8) ppm and hints at both Sn−CH$_3$ and Sn−CH$_2$ bond cleavage (Scheme 5). With caution we assign two of the three signals (a)−(c) to the *cis/trans* mixture of fc(SiMe$_2$CH$_2$-SnClMeCH$_2$SiMe$_2$)$_2$fc (**20**), and the third one and the signal (d) or (e) to the open-chain derivative **21** (Scheme 5). The reaction mixture could not be separated in bulk quantity, but we succeeded in isolating a single crystal

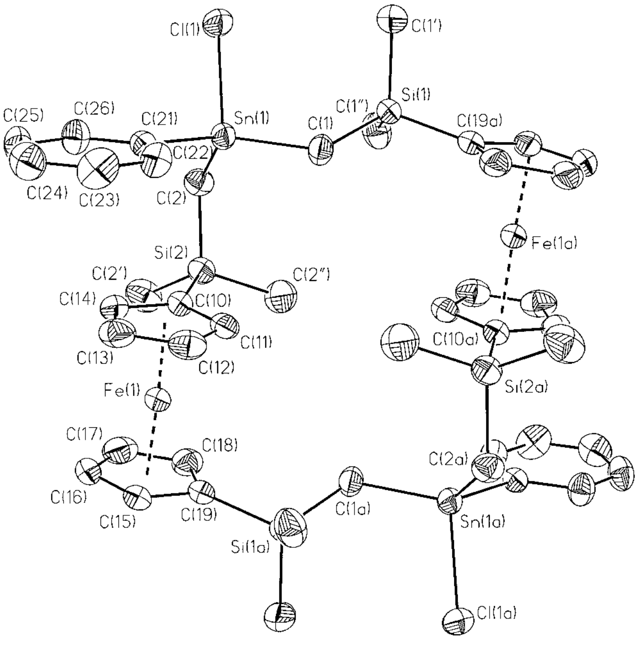
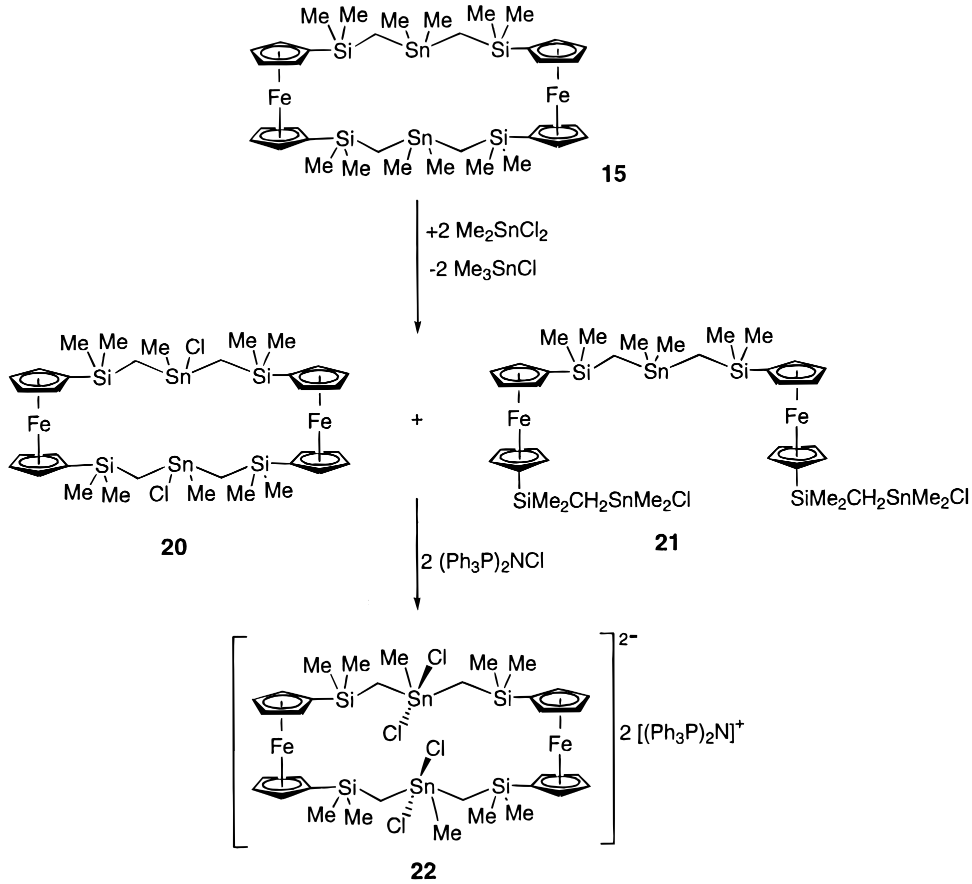


Figure 4. General view (SHELXTL-PLUS) of a molecule of **19** showing 30% probability displacement ellipsoids and the atom numbering (symmetry transformation used to generate equivalent atoms: (a) $-x + 1, -y + 1, -z + 1$).

Scheme 5



of *trans*-fc$(SiMe_2CH_2SnClMeCH_2SiMe_2)_2$fc (**20**), the molecular structure of which is shown in Figure 5. The addition of 2 molar equiv of $(Ph_3P)_2NCl$ to the crude reaction mixture according to Scheme 5 afforded in good yield the chloride complex {[fc$(SiMe_2CH_2SnClMeCH_2SiMe_2)_2$fc·2Cl]$^{2-}$2[$(Ph_3P)_2N$]$^+$} (**22**) (Figure 6) as orange crystals, indicating that the *cis/trans* mixture of fc$(SiMe_2CH_2SnClMeCH_2SiMe_2)_2$fc (**20**) was indeed the major species in this crude reaction mixture. The phenyl-substituted analogue of **22**, i.e., {[fc$(SiMe_2CH_2SnClPhCH_2SiMe_2)_2$fc·2Cl]$^{2-}$2[$(Ph_3P)_2N$]$^+$} (**23**) (Figure 7), was obtained as orange crystals by addition of 2 molar equiv of $(Ph_3P)_2NCl$ to a solution of the corresponding ferrocenophane **19**.

Molecular Structures of 16, 17, 19, 20, 22, and 23. The molecular structures of the ferrocenophanes **16**, **17**, **19**, and **20**, and two of their chloride complexes (**22** and **23**) are illustrated in Figures 2–7, showing the crystallographic numbering schemes and confirming the connectivities and stoichiometries of the compounds. Selected interatomic parameters are listed in Tables 2–4 and provide detailed information on the molecular geometries.

In contrast to the ferrocenophanes **16** and **17**, the related derivatives **19**, **20**, **22**, and **23** each show an inversion center. The silicon atoms in **16**, **17**, **19**, **20**, **22**, and **23** and the tin atoms in **16**, **17**, **19**, and **20** are essentially tetracoordinate; the corresponding bond distances are as expected.

The lattices of the chloride complexes **22** and **23** comprise discrete [fc$(SiMe_2CH_2SnClMeCH_2SiMe_2)_2$fc·2Cl]$^{2-}$ and [fc$(SiMe_2CH_2SnClPhCH_2SiMe_2)_2$fc·2Cl]$^{2-}$ anions, respectively, and [$(Ph_3P)_2N$]$^+$ countercations without significant interionic contacts. The compounds crystallize centrosymmetrically with 1 molar equiv of

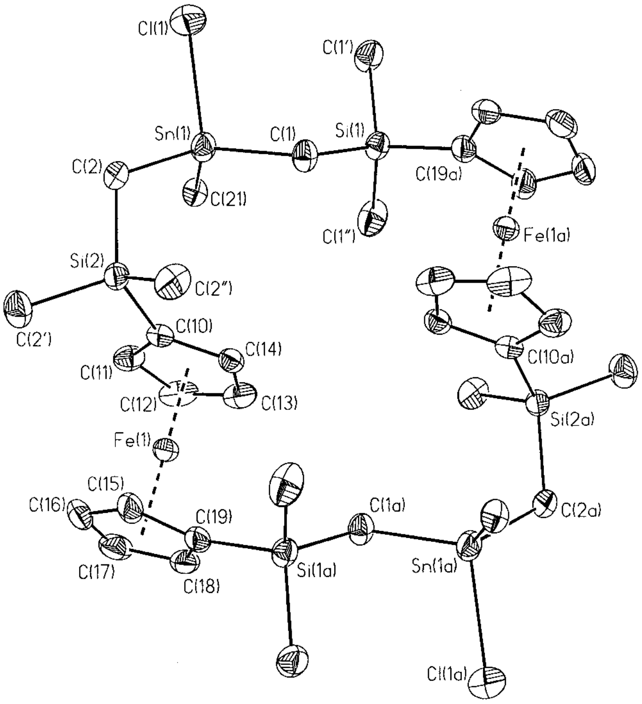


Figure 5. General view (SHELXTL-PLUS) of a molecule of **20** showing 30% probability displacement ellipsoids and the atom numbering (symmetry transformation used to generate equivalent atoms: (a) $-x + 1, -y, -z$).

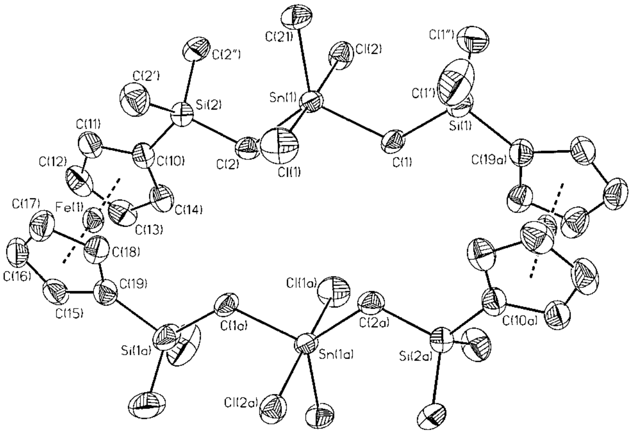


Figure 6. General view (SHELXTL-PLUS) of the dianion of **22** showing 30% probability displacement ellipsoids and the atom numbering. The $[(Ph_3P)_2N]^+$ countercations and dichloromethane molecule are omitted for clarity (symmetry transformation used to generate equivalent atoms: (a) $-x, y - 1, -z + 1$).

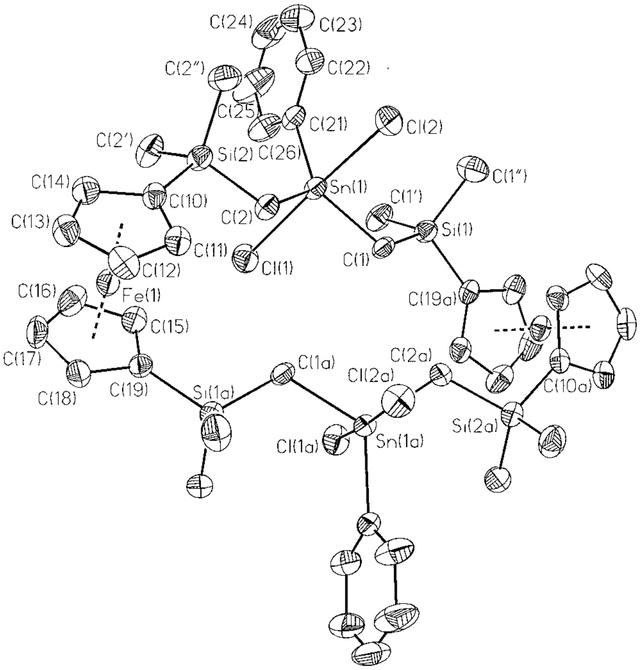


Figure 7. General view (SHELXTL-PLUS) of the dianion of **23** showing 30% probability displacement ellipsoids and the atom numbering. The $[(Ph_3P)_2N]^+$ countercations and dichloromethane molecule are omitted for clarity (symmetry transformation used to generate equivalent atoms: (a) $-x, y, -z + 1.5$).

Table 1. Selected Interatomic Bond Distances (Å) and Angles (deg) for 4

	Bond Distances		
Sn(1)−C(1)	2.124(3)	Si(1)−C(2)	1.857(3)
Sn(1)−C(11)	2.131(3)	Si(1)−C(3)	1.847(4)
Sn(1)−C(21)	2.150(4)	Si(1)−C(4)	1.865(3)
Sn(1)−C(2)	2.151(3)	Si(1)−C(50)	1.899(4)
Sn(2)−C(1)	2.128(3)	Si(2)−C(5)	1.855(4)
Sn(2)−C(31)	2.142(3)	Si(2)−C(6)	1.858(3)
Sn(2)−C(41)	2.146(3)	Si(2)−C(7)	1.855(4)
Sn(2)−C(5)	2.146(3)	Si(2)−C(60)	1.898(4)
	Bond Angles		
C(1)−Sn(1)−C(11)	110.15(13)	C(3)−Si(1)−C(2)	109.47(16)
C(1)−Sn(1)−C(21)	102.65(13)	C(3)−Si(1)−C(4)	110.8(2)
C(11)−Sn(1)−C(21)	105.41(14)	C(2)−Si(1)−C(4)	109.08(17)
C(1)−Sn(1)−C(2)	115.08(13)	C(3)−Si(1)−C(50)	109.01(18)
C(11)−Sn(1)−C(2)	107.02(13)	C(2)−Si(1)−C(50)	110.36(15)
C(21)−Sn(1)−C(2)	116.10(13)	C(7)−Si(1)−C(50)	108.11(18)
C(1)−Sn(2)−C(31)	110.58(13)	C(7)−Si(1)−C(5)	109.88(19)
C(1)−Sn(2)−C(41)	111.93(13)	C(5)−Si(1)−C(6)	110.0(2)
C(31)−Sn(2)−C(41)	103.60(12)	C(7)−Si(1)−C(6)	108.40(16)
C(1)−Sn(2)−C(5)	106.95(13)	C(5)−Si(2)−C(60)	109.61(17)
C(31)−Sn(2)−C(5)	108.70(12)	C(5)−Si(2)−C(60)	110.37(15)
C(41)−Sn(2)−C(5)	115.04(13)	C(6)−Si(2)−C(60)	108.61(17)
Sn(1)−C(1)−Sn(2)	122.54(16)	Si(2)−C(5)−Sn(2)	120.30(15)
Si(1)−C(2)−Sn(1)	120.05(17)		

dichloromethane in the unit cells. The tin atoms in the anions of both **22** and **23** exhibit a trigonal-bipyramidal configuration with the axial positions being occupied by the chlorine atoms (Figures 6 and 7). The carbon atoms C(1), C(2), and C(21) define the equatorial planes from which the tin atoms are displaced by 0.025(4) (**22**) and 0.018(3) Å (**23**) in the direction of Cl(1) and Cl(2), respectively. The Sn(1)−Cl(1) (2.616(2) Å (**22**), 2.649(1) Å (**23**)) and Sn(1)−Cl(2) (2.634(1) Å (**22**), 2.603(1) Å (**23**)) bond lengths are approximately 0.2−0.3 Å greater than the Sn−Cl bond lengths in **19** and **20**.

The cyclopentadiene rings of the ferrocenophanes **16**, **17**, **19**, **20**, **22**, and **23** show skew conformations between synclinal staggered and anticlinal eclipsed. The torsion angles fall in the range between 12.4(7)° for C(64)−centroid(cp1)−centroid(cp2)−C(69) (**16**) and 29.7(6)° for C(11)−centroid(cp1)−centroid(cp2)−C(19) (**19**) (Table 4). The cyclopentadiene ring tilts within the ferrocene units amount to between 1.4(3)° for **20** and 4.6(1)° for **17**.

The intramolecular Sn···Sn distances vary between 5.8219(6) Å for the chloride complex **23** and 9.4061(5) Å for the phenyl-substituted tetraorganotin derivative **16** (Table 4). Compared to this, the intramolecular Si···Si distances vary only between 7.518(3) Å (**16**) and 8.983(2) Å (**23**).

Complexation Behavior of Compounds 8, 12, and 19 toward Chloride Ions in Solution. The ^{119}Sn NMR chemical shifts of the organotin(IV) chlorides **8**, **12**, and **19** to which various amounts of $[(Ph_3P)_2N]^+Cl^-$ have been added are shown in Figure 8. As expected from earlier investigations on $(Ph_2XSn)_2CH_2$,[8c] the measurements clearly indicate for the methylene-bridged species **8** the exclusive formation of the 1:1 complex $\{[(FcMe_2SiCH_2SnClPh)_2CH_2{\cdot}Cl]^-[(Ph_3P)_2N]^+\}$ (**8b**). According to the substituent pattern at tin, the chloride complex **8b** should be a mixture of two diastereomers. However, the ^{119}Sn NMR spectra of **8b** in CD_2Cl_2 at room temperature as well as at −80 °C show only single resonances at −69.2 and −68.2 ppm, respectively, and indicate the epimerization to be fast on the NMR time scale at both temperatures or, less likely, the presence of one diastereomer only.

The slope for the system $fc(SiMe_2CH_2SnClPh_2)_2$ (**12**) + $n[(Ph_3P)_2N]^+Cl^-$ shows no point of saturation, even after the addition of 5 molar equiv of chloride ions. This implies that even at this chloride concentration there is a considerable population of uncomplexed ferrocene derivative **12** in the equilibrium.

For the ferrocenophane **19** the tin atoms reach their maximum low-frequency shift upon addition of 2−3 molar equiv of chloride ions. Nevertheless, the formation of a stable 1:2 complex of **19** with chloride ions was confirmed by isolation and X-ray analysis of **23** (Figure 7).

Table 2. Selected Interatomic Bond Distances (Å) and Angles (deg) for 16 and 17

	compd	
	16: X(1) = C(21); X(2) = C(41)	**17**: X(1) = I(1); X(2) = I(2)
	Bond Distances	
Sn(1)−X(1)	2.148(4)	2.7339(10)
Sn(2)−X(2)	2.147(4)	2.7430(11)
Sn(1)−C(4)	2:139(3)	2.129(7)
Sn(1)−C(11)	2.151(4)	2.147(9)
Sn(1)−C(1)	2.156(3)	2.145(7)
Sn(2)−C(31)	2.142(4)	2.148(11)
Sn(2)−C(3)	2.147(3)	2.134(8)
Sn(2)−C(2)	2.147(3)	2.118(8)
Si(1)−C(59)	1.859(4)	1.845(10)
Si(1)−C(1″)	1.867(4)	1.844(9)
Si(2)−C(50)	1.863(4)	1.884(9)
Si(2)−C(2)	1.866(3)	1.853(8)
Si(3)−C(69)	1.848(4)	1.850(9)
Si(3)−C(3)	1.862(4)	1.878(8)
Si(4)−C(4)	1.862(3)	1.869(8)
Si(4)−C(60)	1.867(4)	1.853(8)
	Bond Angles	
C(4)−Sn(1)−X(1)	108.96(15)	106.7(3)
C(4)−Sn(1)−C(11)	108.25(14)	113.7(3)
X(1)−Sn(1)−C(11)	104.92(15)	103.1(3)
C(4)−Sn(1)−C(1)	114.84(13)	112.9(3)
X(1)−Sn(1)−C(1)	111.48(13)	105.2(3)
C(11)−Sn(1)−C(1)	107.15(15)	114.1(3)
C(31)−Sn(2)−C(3)	111.63(14)	112.9(3)
C(31)−Sn(2)−C(2)	108.21(15)	114.4(4)
C(3)−Sn(2)−C(2)	115.30(13)	112.5(3)
C(31)−Sn(2)−X(2)	104.40(14)	105.2(4)
C(3)−Sn(2)−X(2)	107.03(14)	103.3(2)
C(2)−Sn(2)−X(2)	109.70(14)	107.5(3)
C(1)−Si(1)−C(59)	109.83(17)	109.4(4)
C(1)−Si(1)−C(1′)	110.12(18)	110.5(4)
C(59)−Si(1)−C(1′)	110.73(17)	106.6(4)
C(50)−Si(2)−C(2′)	111.72(18)	110.0(4)
C(50)−Si(2)−C(2)	108.94(17)	109.0(4)
C(2″)−Si(2)−C(2)	109.72(18)	112.6(4)
C(69)−Si(3)−C(3′)	110.56(17)	107.3(4)
C(69)−Si(3)−C(3)	110.39(17)	108.0(4)
C(3′)−Si(3)−C(3)	109.73(18)	109.6(4)
C(4′)−Si(4)−C(4)	109.34(18)	110.3(5)
C(4′)−Si(4)−C(4″)	109.8(2)	107.3(5)
C(4)−Si(4)−C(4″)	107.64(18)	111.2(4)
Si(1)−C(1)−Sn(1)	117.06(17)	117.8(4)
Si(2)−C(2)−Sn(2)	120.01(17)	122.0(5)
Si(3)−C(3)−Sn(2)	117.80(18)	118.0(4)
Si(4)−C(4)−Sn(1)	122.72(18)	119.7(4)

Table 3. Selected Interatomic Bond Distances (Å) and Angles (deg) for 19, 20, 22, and 23

	compd			
	19	**20**	**22**	**23**
	Bond Distances			
Sn(1)−C(1)	2.127(3)	2.125(5)	2.136(5)	2.135(3)
Sn(1)−C(2)	2.129(3)	2.118(5)	2.146(5)	2.122(4)
Sn(1)−C(21)	2.130(3)	2.123(4)	2.137(5)	2.155(4)
Sn(1)−Cl(1)	2.3914(8)	2.333(2)	2.616(2)	2.649(1)
Sn(1)−Cl(2)			2.634(1)	2.603(1)
Si(1)−C(19a)	1.853(3)	1.863(5)	1.856(7)	1.867(4)
Si(1)−C(1)	1.854(3)	1.863(5)	1.839(6)	1.851(4)
Si(1)−C(1′)	1.861(3)	1.865(3)	1.861(8)	1.872(4)
Si(1)−C(1″)	1.865(3)	1.852(6)	1.839(8)	1.853(4)
Si(2)−C(10)	1.855(4)	1.861(5)	1.870(6)	1.863(4)
Si(2)−C(2)	1.859(3)	1.867(5)	1.852(6)	1.857(3)
Si(2)−C(2′)	1.863(3)	1.867(5)	1.857(6)	1.871(4)
Si(2)−C(2″)	1.869(3)	1.855(5)	1.890(6)	1.848(4)
	Bond Angles			
Si(1)−C(1)−Sn(1)	117.5(2)	117.5(2)	121.2(3)	118.0(2)
Si(2)−C(2)−Sn(1)	116.7(1)	116.1(2)	117.9(3)	119.1(2)
C(1)−Sn(1)−C(2)	119.5(1)	115.1(2)	114.4(2)	114.9(1)
C(1)−Sn(1)−C(21)	112.8(1)	115.3(2)	122.0(2)	122.7(1)
C(2)−Sn(1)−C(21)	112.3(1)	113.2(2)	123.6(2)	122.5(1)
C(1)−Sn(1)−Cl(1)	105.81(9)	105.1(2)	91.6(2)	87.8(1)
C(2)−Sn(1)−Cl(1)	100.98(8)	103.8(1)	92.5(2)	88.6(1)
C(21)−Sn(1)−Cl(1)	102.93(8)	102.3(1)	88.1(2)	92.0(1)
C(1)−Sn(1)−Cl(2)			89.2(2)	90.8(1)
C(2)−Sn(1)−Cl(2)			91.0(2)	88.4(1)
C(21)−Sn(1)−Cl(2)			87.9(2)	92.2(1)
Cl(1)−Sn(1)−Cl(2)			175.74(6)	175.72(4)
C(19a)−Si(1)−C(1′)	106.4(2)	108.7(2)	110.7(3)	106.08(18)
C(19a)−Si(1)−C(1″)	109.5(2)	109.3(3)	107.5(4)	108.7(2)
C(1′)−Si(1)−C(1″)	108.7(2)	109.6(3)	108.6(5)	109.7(2)
C(19a)−Si(1)−C(1)	110.6(1)	110.5(2)	107.0(3)	111.4(2)
C(1′)−Si(1)−C(1)	111.6(2)	108.4(2)	110.1(4)	110.3(2)
C(1″)−Si(1)−C(1)	110.1(2)	110.3(3)	112.9(3)	110.6(2)
C(2″)−Si(2)−C(10)	109.3(2)	109.5(2)	106.0(3)	109.8(2)
C(2″)−Si(2)−C(2′)	111.2(2)	111.1(3)	108.5(3)	108.0(2)
C(10)−Si(2)−C(2′)	110.7(2)	110.6(2)	109.1(3)	109.5(2)
C(2″)−Si(2)−C(2)	110.2(2)	110.0(3)	110.6(3)	110.7(2)
C(10)−Si(2)−C(2)	107.0(1)	106.8(2)	110.8(37)	107.6(2)
C(2′)−Si(2)−C(2)	108.4(2)	108.7(3)	111.6(3)	111.4(2)

Complexation Behavior of Compounds 9, 13, and 18 toward Fluoride Ions in Solution. Temperature-dependent ^{19}F and ^{119}Sn NMR studies on solutions of bis(diorganofluorostannyl)methane derivative **9**, the ferrocenediyl derivative **13**, and the fluoro-substituted ferrocenophane **18**, to which different molar equivalents of fluoride anions have been added, reveal the formation in situ of the tetrabutylammonium organofluorostannates **9a/9b** (pair of diastereomers, ratio 0.4/1) **9c**, and **9d** (Chart 1), $\{[\mathbf{13}\cdot 2F]^{2-}[Bu_4N]^+{}_2\}$, and $\{[\mathbf{18}\cdot F]^{-}[Bu_4N]^+\}$ and $\{[\mathbf{18}\cdot 2F]^{2-}[Bu_4N]^+{}_2\}$, respectively. The complexes are kinetically stable on the ^{119}Sn NMR time scale below −50 °C but labile at room temperature. A detailed description of their NMR spectra is given in the Supporting Information.

Electrochemistry. In agreement with previous findings,[15e] all the derivatives studied here display a single, ferrocene-based, reversible oxidation, independent of their content of ferrocene subunits (see Supporting Information). An overall picture of the electrochemical consequences of adding progressive amounts of different anions (namely, chloride, fluoride, and dihydrogen phosphate) to the derivatives under study is given in the Supporting Information (Table 7a). As a preliminary consideration, the species **3**−**5**, **14**, and **16**, which contain diphenyltin moieties in the bridge, are all less sensitive to anion additions ($\Delta E^{\circ\prime} = 0{-}130$ mV) with respect to those species **9**, **12**, **13**, and **17**−**19** containing halogen-substituted tin groups ($\Delta E^{\circ\prime} = 70{-}560$ mV). This is to be expected, given the higher Lewis acidity of organotin halides as compared to tetraorganotin compounds. In a more detailed analysis, within the mono(ferrocene) derivatives, **5** is by no means affected by chloride ions, whereas it is slightly sensitive to fluoride ions ($\Delta E^{\circ\prime} \approx 40$ mV). However, it undergoes irreversible chemical reactions in the presence of dihydrogen phosphate ions. The chlorostannyl-substituted derivative **12** seems to be able to distinguish Cl^- ($\Delta E^{\circ\prime} \approx 220$ mV) from $H_2PO_4^-$ ($\Delta E^{\circ\prime} \approx 560$ mV) but suffers the presence of relatively high amounts of F^-. The fluorostannyl-substituted compound **13** is effective toward Cl^- ($\Delta E^{\circ\prime} \approx 190$ mV), but in the presence of an excess of either F^- or $H_2PO_4^-$ it undergoes chemical reactions which cause destruction of the original species. It is known that fluoride ions promote phenyl group migration when added to phenyl-substituted organotin compounds.[21] Within the diferrocenes, the phenyl-substituted ferrocenophane **16** has no propensity for

Table 4. Intramolecular Sn···Sn and Si···Si Distances (Å), Cyclopentadiene Ring Tilts (deg), and Torsion Angles (deg) for 4, 16, 17, 19, 20, 22, and 23

	compd						
	X1 = 3; X2 = 4; X3 = 2; Y1 = 59; Y2 = 50; Y3 = 64; Y4 = 69			X1 = 1a; X2 = X3 = 2a; Y1 = 19a; Y2 = 10a; Y3 = 11; Y4 = 19			
	4	**16**	**17**	**19**	**20**	**22**	**23**
Intramolecular Distances							
Sn···Sn		9.4061(5)	6.1975(9)	8.718(6)	8.829(3)	5.9091(8)	5.8219(6)
Si(1)···Si(X1)		7.518(3)	8.432(4)	8.684(2)	7.851(5)	9.184(4)	8.026(2)
Si(2)···Si(X2)		8.548(2)	9.117(4)	7.539(2)	8.458(4)	8.423(3)	8.983(2)
Torsion Angles of Cyclopentadiene Rings							
Si(1)−C(Y1)−C(Y2)−Si(X3)		79.2(2)	84.4(6)	90.9(2)	80.3(3)	78.9(4)	81.4(3)
Si(3)−C(69)−C(60)−Si(4)		76.7(4)	82.9(6)				
C(Y3)−cp(1)−cp(2)−C(Y4)[a]	0.0(7)	12.4(7)	15.2(7)	29.7(6)	17.1(5)	14.4(6)	15.8(5)
C(52)−cp(3)−cp(4)−C(58)[a]	0.8(7)	14.3(7)	16.5(9)				
Cyclopentadiene Ring Tilt							
at Fe(1)	2.5(3)	1.5(3)	1.7(1)	3.5(3)	1.4(3)	2.7(4)	2.3(2)
at Fe(2)	2.5(2)	3.0(3)	4.6(1)				

[a] cp = center of cyclopentadiene ring.

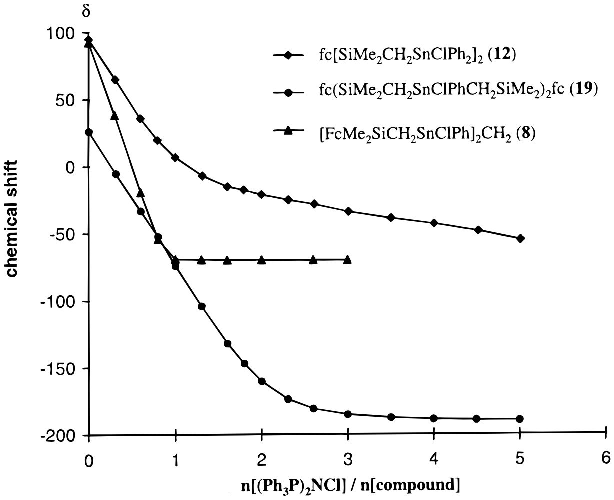
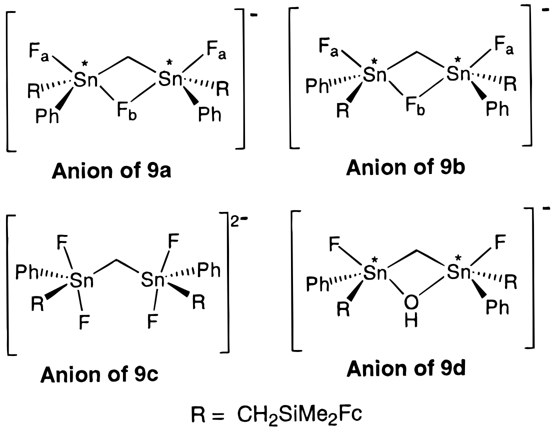


Figure 8. Plot of ^{119}Sn NMR chemical shift (ppm) versus the molar ratio $[(Ph_3P)N]^+Cl^-$/compound.

Chart 1



anion sensing via electrochemical techniques; whereas, somewhat surprising when considering their substituent pattern at tin, the mono- and ditin species **3** and **4**, respectively, could be effective in the selective recognition of dihydrogen phosphate ion ($\Delta E°' \approx 110$ and 60 mV, respectively) from chloride ion. Here again, some drawbacks occur in the concomitant presence of a large amount of fluoride ion, which is likely to be traced to fluoride ion promoted phenyl group migration.[21] The bis(fluorostannyl)methane derivative **9** is able to bind chloride ions ($\Delta E°' \approx 90$ mV), but it also undergoes irreversible chemical reactions in the presence of F^- or $H_2PO_4^-$, as on the other hand the iodo-substituted ferrocenophane **17** does, which upon oxidation in the presence of these anions decoordinates I^- ion, which in turn oxidizes more easily ($E_p = +0.24$ V) than the ferrocene complex itself. The fluoro-substituted ferrocenophane **18** could selectively recognize chloride ($\Delta E°' \approx 100$ mV) from fluoride ($\Delta E°' \approx 180$ mV) ions, but it also suffers the presence of $H_2PO_4^-$. Finally, as Figure 9 illustrates, the chloro-substituted ferrocenophane **19** seems to meet the criteria for an ideal transducer in molecular sensoring.[22] It exhibits cathodic shifts significantly dependent from the nature of the anion (Cl^-, $\Delta E°' \approx 130$ mV; F^-, $\Delta E°' \approx 210$ mV; $H_2PO_4^-$, $\Delta E°' \approx 480$ mV), without undergoing any chemical decomposition upon oxidation. It must be taken into account that in those cases where partial complexation caused slight separation between waves (as in the case of Figure 9B-(b)), differential pulse voltammetry succeeded in resolving them. The most anodic wave present in the cyclic voltammogram A(d) is due to the oxidation of the excess of chloride ions.

Finally, the triferrocene **14** seems to be somewhat effective toward dihydrogen phosphate ($\Delta E°' \approx 130$ mV) but is poorly sensitive to chloride and fluoride ions and is unable to distinguish them (in both cases, $\Delta E°' \approx 50$ mV).

A final comment concerns the fact that, at variance with the majority of electrochemical reports on anion receptors which involve formation of 1:1 complexes, some of the present organotin derivatives tend to form stepwisely 1:1 and 2:1 anion-to-ferrocenophane complexes.

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(19) (a) Davies, A. G.; Tse, M. W.; Kennedy, J. D.; McFarlane, W.; Pyne, G. S.; Ladd, M. F. C.; Povey, D. C. *J. Chem. Soc., Perkin Trans. 2* **1981**, 369. (b) Belsky, V. K.; Simonenko, A. A.; Reikhsfeld, V. O.; Saratov, I. E. *J. Organomet. Chem.* **1983**, *244*, 125. (c) Beauchamp, A. L.; Latour, S.; Olivier, M. J.; Wuest, J. D. *J. Organomet. Chem.* **1983**, *254*, 283. (d) Al-Juaid, S. S.; Dhaher, S. M.; Eaborn, C.; Hitchcock, P. B.; Smith, J. D. *J. Organomet. Chem.* **1987**, *325*, 117.

(20) Seiler, P.; Dunitz, J. D. *Acta Crystallogr.* **1979**, *B35*, 1068.

(21) (a) Dakternieks, D.; Zhu, H *Organometallics* **1992**, *11*, 3820. (b) Dakternieks, D.; Zhu, H *Inorg. Chim. Acta* **1992**, *196*, 19.

(22) Hansen, T. K.; Jørgensen, T.; Stein, P. C.; Becher, J. *J. Org. Chem.* **1992**, *57*, 6403.

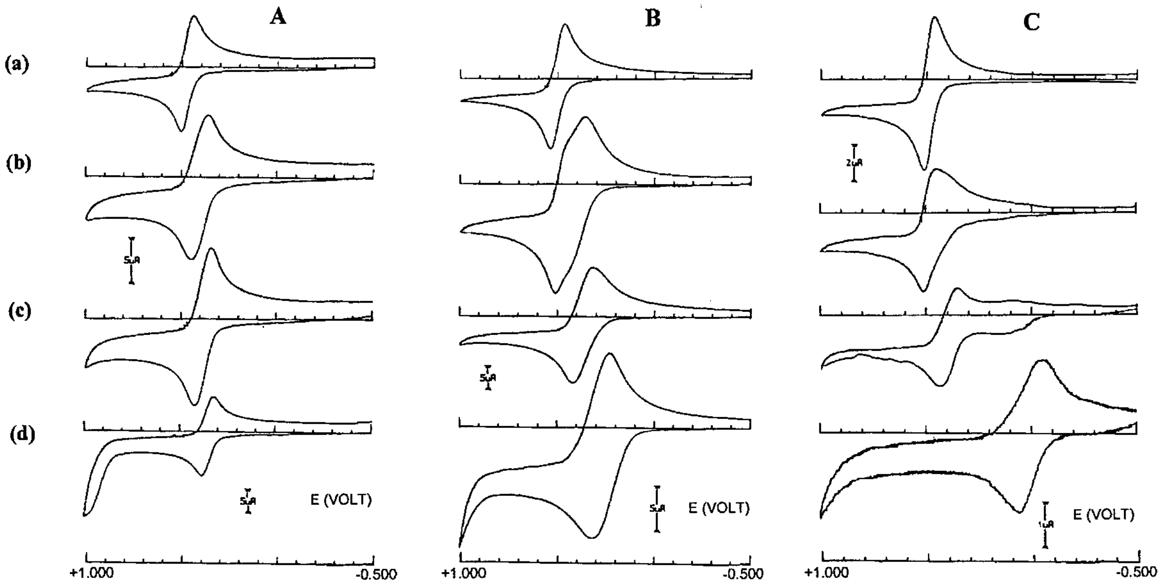

Figure 9. Representative cyclic voltammetric profiles recorded at a platinum electrode on CH_2Cl_2 solutions containing **19** upon progressive addition of Cl^- (A), F^- (B), and $H_2PO_4^-$ (C) anions, respectively. [anion]/[**19**] ratios: (a) 0.0/1; (b) 0.5/1; (c) 1/1; (d) 5/1. Scan rates: (A, B) 0.1 V s^{-1}; (C) 0.02 V s^{-1}.

Conclusion

A variety of ferrocene-containing organotin compounds, including novel ferrocenophanes, has been synthesized by employing the (dimethylsilyl)methylene group, $-Me_2SiCH_2-$, as a spacer between the ferrocene units and tin.

On the basis of the cathodic shifts of the oxidation process of the ferrocene subunits ($\Delta E°'$) as induced by anions, most of the compounds studied are potentially able to act as single anion receptors. However, the concomitant presence of chloride, fluoride, and dihydrogen phosphate ions could reduce their sensing ability. In this connection, only the chloro-substituted ferrocenophane **19** seems to be able to perform a selective recognition of these three anions. The origin for this somewhat unexpected difference between **19** and the related iodo- and fluoro-substituted derivatives **17** and **18**, respectively, is not obvious but might be traced to the interplay of the tin atoms in **19** having the right Lewis acidity and the chloride, in comparison to fluoride and iodide, being a poor leaving group.

Experimental Section

General Methods. All reactions were carried out under a dry nitrogen atmosphere. The solvents were purified by distillation from appropriate drying agents under nitrogen. Tetrabutylammmonium fluoride trihydrate and $(Ph_3P)_2NCl$ were commercial products. (Chloromethyl)dimethylfluorosilane and lithioferrocene were synthesized as described elsewhere.[17,23]

The experimental density of the crystals were measured using a Micromeritics Accu Pyc 1330 instrument. Elemental analyses were performed on an instrument from Carlo Erba Strumentazione (Model 1106), and the molecular weight determinations were measured osmometrically on a Knauer Dampfdruckosmometer.

NMR spectra were recorded on Bruker DRX400 and Bruker DPX300 FT NMR spectrometers with broad-band decoupling of ^{119}Sn at 149.21 and 111.92 MHz, respectively, ^{29}Si at 79.49 and 59.63 MHz, ^{19}F at 282.41 MHz, and ^{13}C at 100.61 MHz, using external and internal deuterium lock. ^1H, ^{13}C, ^{19}F, ^{29}Si, and ^{119}Sn NMR chemical shifts (δ) are given in ppm and are referenced to external Me_4Sn (^{119}Sn), $CFCl_3$ (^{19}F), and Me_4Si (^{29}Si, ^{13}C, ^1H), respectively. Temperatures were maintained using a Bruker temperature control system. The complexes for NMR investigations were generally prepared in situ, and the concentrations of the organotin halides were typically about 0.1–0.2 M.

Electrospray mass spectra were obtained with a Platform II single-quadrupole mass spectrometer (Micromass, Altrincham, U.K.) using an acetonitrile mobile phase and with a Finnigan MAT 90 spectrometer equipped with an ESI II electrospray ion source.

Material and apparatus for electrochemical investigations have been described elsewhere.[24] All the potential values are referred to the saturated calomel electrode (SCE). Under the present experimental conditions the one-electron oxidation of ferrocene occurs at $E°' = +0.38$ V. The concentrations of the electroactive compounds in cyclic voltammetry were around 1×10^{-3} mol dm^{-3}.

Synthesis of 1,1′-Bis[(chloromethyl)dimethylsilyl]ferrocene, fc(SiMe$_2$CH$_2$Cl)$_2$ (2). *n*-BuLi (105 mL, 166 mmol, 1.58 M solution in hexane) was added dropwise to a mixture of ferrocene (12.6 g, 68 mmol) and TMEDA (19.4 g, 166 mmol) in 600 mL of hexane. After it was stirred for 24 h, the mixture was added dropwise at −78 °C to a solution of (chloromethyl)dimethylfluorosilane[23] (21.5 g, 170 mmol) in 100 mL of hexane. The reaction mixture was stirred overnight at room temperature and then cooled to 0 °C and hydrolyzed with 100 mL of water. After filtration, the organic layer was separated, dried over Na_2SO_4, and filtered. The solvent was removed in vacuo, and ferrocene and ((chloromethyl)dimethylsilyl)ferrocene (**1**) were removed by Kugelrohr distillation in vacuo (5×10^{-3} Torr, 100–160 °C). Kugelrohr distillation of the dark red residue in vacuo afforded 24.0 g (89%) of $fc(SiMe_2CH_2Cl)_2$ as a red oil, bp 170–175 °C (5×10^{-3} Torr), which solidifies upon standing, mp 36–37 °C. $^{29}Si\{^1H\}$ NMR (CH_2Cl_2): δ −1.9. ^1H NMR ($CDCl_3$): δ 0.38 (s, 12H, CH_3), 2.86 (s, 4H, CH_2Cl), 4.12 (complex pattern, 4H, $H_{Cp-2,5}$), 4.34 (complex pattern, 4H, $H_{Cp-3,4}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −3.7 (CH_3), 30.9 (CH_2Cl),

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[23] (Chloromethyl)dimethylfluorosilane was synthesized by direct distillation from the flask after triphenyltin fluoride and (chloromethyl)dimethylchlorosilane were warmed to 100 °C over 18 h.

[24] Zanello, P.; Laschi, F.; Fontani, M.; Mealli, C.; Ienco, A.; Tang, K.; Jin, X.; Li, L. *J. Chem. Soc., Dalton Trans.* **1999**, 965.

67.7 (C_{cp-1}), 71.5 ($C_{cp-3,4}$), 73.1 ($C_{cp-2,5}$). Anal. Calcd for $C_{16}H_{24}Cl_2FeSi_2$ (395.25): C, 48.1; H, 6.1. Found: C, 48.3; H, 6.2.

Synthesis of Bis[(ferrocenyldimethylsilyl)methyl]diphenyltin, $(FcMe_2SiCH_2)_2SnPh_2$ (3). Lithioferrocene[17] (7.7 g, 40 mmol) was added in small portions at −78 °C to a magnetically stirred solution of (chloromethyl)dimethylfluorosilane[23] (6.1 g, 48 mmol) in 250 mL of hexane. The reaction mixture was stirred overnight at room temperature and then cooled to 0 °C and hydrolyzed with 100 mL of water. After filtration, the organic layer was separated, dried over Na_2SO_4, and filtered. The solvent was removed in vacuo, and ferrocene was removed by sublimation in vacuo (5×10^{-3} Torr, 100 °C). Kugelrohr distillation of the dark red residue in vacuo afforded 6.5 g (69%) of $FcMe_2SiCH_2Cl$ (**1**) as a red oil, bp 150−155 °C (5×10^{-3} Torr). $^{29}Si\{^1H\}$ NMR (CH_2Cl_2): δ −2.1. ^1H NMR ($CDCl_3$): δ 0.37 (s, 6H, CH_3), 2.87 (s, 2H, CH_2Cl), 4.12 (complex pattern, 2H, $H_{Cp-2,5}$), 4.13 (s, 5H, H_{Cp}), 4.37 (complex pattern, 2H, $H_{Cp-3,4}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −3.7 (CH_3), 31.1 (CH_2Cl), 67.1 (C_{cp-1}), 68.1 (C_{cp}), 71.1 ($C_{cp-3,4}$), 73.0 ($C_{cp-2,5}$).

A solution of Ph_2SnCl_2 (3.44 g, 10 mmol) in 25 mL of thf was added dropwise to a magnetically stirred solution of $FcMe_2SiCH_2MgCl$ prepared from **1** (6.50 g, 22 mmol) and Mg (1.07 g, 44 mmol) in 70 mL of thf. The reaction mixture was heated at reflux for 2 h, and two-thirds of the thf was distilled off, followed by addition of 100 mL of CH_2Cl_2. The reaction mixture was hydrolyzed under ice cooling with 100 mL of water. After filtration, the organic layer was separated, dried over Na_2SO_4, and filtered. The solvent was evaporated, and the resulting dark red residue was recrystallized from ethanol to give 6.8 g (86%) of $(FcMe_2SiCH_2)_2SnPh_2$ (**3**) as a red solid, mp 86−88 °C. $^{119}Sn\{^1H\}$ NMR (CH_2Cl_2): δ −51.5. $^{29}Si\{^1H\}$ NMR (CH_2Cl_2): δ −1.5 ($^2J(^{29}Si-^{119}Sn)$ = 20 Hz). ^1H NMR ($CDCl_3$): δ 0.08 (s, 12H, CH_3), 0.26 (s, $^2J(^1H-^{119/117}Sn)$ = 75/72 Hz, 4H, CH_2), 3.95 (complex pattern, 4H, $H_{Cp-2,5}$), 4.05 (s, 10H, H_{Cp}), 4.27 (complex pattern, 4H, $H_{Cp-4,3}$), 7.20−7.50 (complex pattern, 10H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −3.4 ($^1J(^{13}C-^{119}Sn)$ = 264 Hz, CH_2), 0.7 (CH_3), 68.1 (C_{cp}), 70.6 ($C_{cp-3,4}$), 72.9 ($C_{cp-2,5}$), 73.2 (C_{Cp-1}), 128.1 ($^3J(^{13}C-^{119}Sn)$ = 48 Hz, C_m), 128.4 (C_p), 136.7 ($^2J(^{13}C-^{119}Sn)$ = 38 Hz, C_o), 141.5 (C_i). Anal. Calcd for $C_{38}H_{44}Fe_2Si_2Sn$ (787.37): C, 58.0; H, 5.6. Found: C, 57.2; H, 5.4.

Synthesis of Bis{[(ferrocenyldimethylsilyl)methyl]diphenylstannyl}methane, $(FcMe_2SiCH_2SnPh_2)_2CH_2$ (4). $(Ph_2FSn)_2CH_2$[8e] (5.97 g, 10 mmol) was added in small portions to a magnetically stirred solution of $FcMe_2SiCH_2MgCl$ prepared from **1** (6.50 g, 22 mmol) and Mg (1.07 g, 44 mmol) in 100 mL of thf. The reaction mixture was heated at reflux overnight. After a workup procedure as described for compound **3**, 6.9 g (64%) of $(FcMe_2SiCH_2SnPh_2)_2CH_2$ (**4**) was obtained as a red crystalline solid, mp 96−100 °C. $^{119}Sn\{^1H\}$ NMR (CH_2Cl_2): δ −38.3 ($^2J(^{119}Sn-^{117}Sn)$ = 231 Hz). $^{29}Si\{^1H\}$ NMR (CH_2Cl_2): δ −1.4. ^1H NMR ($CDCl_3$): δ 0.06 (s, 12H, CH_3), 0.12 (s, $^2J(^1H-^{119/117}Sn)$ = 76/74 Hz, 4H, $SnCH_2Si$), 0.36 (s, $^2J(^1H-^{119}Sn)$ = 61 Hz, 2H, $SnCH_2Sn$), 3.92 (complex pattern, 4H, $H_{Cp-2,5}$), 4.05 (s, 10H, H_{Cp}), 4.27 (complex pattern, 4H, $H_{Cp-4,3}$), 7.20−7.40 (complex pattern, 20H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −13.9 ($^1J(^{13}C-^{119}Sn)$ = 275 Hz, $SnCH_2Sn$), −3.4 ($^1J(^{13}C-^{119}Sn)$ = 264 Hz, $SnCH_2Si$), 0.6 (CH_3), 68.0 (C_{cp}), 70.6 ($C_{cp-3,4}$), 72.9 ($C_{cp-2,5}$), 72.9 (C_{Cp-1}), 128.0 ($^3J(^{13}C-^{119}Sn)$ = 48 Hz, C_m), 128.4 (C_p), 136.6 ($^2J(^{13}C-^{119}Sn)$ = 38 Hz, C_o), 141.3 ($^1J(^{13}C-^{119/117}Sn)$ = 478/457 Hz, C_i). Anal. Calcd for $C_{51}H_{56}Fe_2Si_2Sn_2$ (1074.34): C, 57.0; H, 5.3. Found: C, 57.0; H, 5.3.

Synthesis of 1,1′-Bis{[(triphenylstannyl)methyl]dimethylsilyl}ferrocene, $fc(SiMe_2CH_2SnPh_3)_2$ (5). To a magnetically stirred solution of Ph_3SnCl (19.3 g, 50 mmol) in 100 mL of thf was added dropwise a solution of $fc(SiMe_2CH_2MgCl)_2$ prepared from **2** (10.0 g, 25 mmol) and excess Mg (2.44 g, 100 mmol) in 150 mL of thf. The reaction mixture was heated at reflux overnight, and two-thirds of the thf was distilled off, followed by addition of 100 mL of CH_2Cl_2. The reaction mixture was hydrolyzed under ice cooling with 100 mL of aqueous potassium fluoride solution. After filtration, the organic layer was separated, dried over Na_2SO_4, and filtered. The solvent was evaporated, and the resulting dark red residue was recrystallized from hexane to give 16.1 g (63%) of $fc(SiMe_2CH_2SnPh_3)_2$ (**5**) as an orange solid, mp 149 °C. $^{119}Sn\{^1H\}$ NMR (CH_2Cl_2): δ −91.1. $^{29}Si\{^1H\}$ NMR (CH_2Cl_2): δ −1.0 ($^2J(^{29}Si-^{119}Sn)$ = 21 Hz). ^1H NMR ($CDCl_3$): δ 0.11 (s, 12H, CH_3), 0.55 (s, $^2J(^1H-^{119}Sn)$ = 76 Hz, 4H, CH_2), 3.88 (complex pattern, 4H, $H_{Cp-2,5}$), 4.15 (complex pattern, 4H, $H_{Cp-3,4}$), 7.30−7.50 (complex pattern, 30H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −4.5 ($^1J(^{13}C-^{119}Sn)$ = 278 Hz, CH_2), 0.7 (CH_3), 71.1 ($C_{cp-3,4}$), 72.9 ($C_{cp-2,5}$, C_{Cp-1}), 128.3 ($^3J(^{13}C-^{119}Sn)$ = 50 Hz, C_m), 128.7 (C_p), 136.9 ($^2J(^{13}C-^{119}Sn)$ = 37 Hz, C_o), 139.6 ($^1J(^{13}C-^{119}Sn)$ = 504 Hz, C_i). Anal. Calcd for $C_{52}H_{54}Si_2Sn_2$ (1028.4): C, 60.7; H, 5.3. Found: C, 60.6; H, 5.3.

Synthesis of Bis{[(ferrocenyldimethylsilyl)methyl]phenylchlorostannyl}methane, $(FcMe_2SiCH_2SnClPh)_2CH_2$ (8). Iodine (294 mg, 1.2 mmol) was added under ice cooling in small portions to a solution of **4** (622 mg, 0.6 mmol) in 10 mL of CH_2Cl_2. The black reaction mixture was stirred overnight until the solution became orange. The solvent and iodobenzene were removed in vacuo, and the red oily residue of $(FcMe_2SiCH_2SnIPh)_2CH_2$ (**7**) ($^{119}Sn\{^1H\}$ NMR (CH_2Cl_2): δ −5.7; $^{29}Si\{^1H\}$ NMR (CH_2Cl_2): δ −1.6) was dissolved in 15 mL of CH_3CN/CH_2Cl_2 (1:1). Under exclusion of light silver chloride (672 mg, 4.6 mmol) was added and the mixture was stirred for 14 days until the ^{119}Sn NMR showed complete disappearance of **7**. The precipitate of AgI/AgCl was filtered off, and the solvent was removed in vacuo to give 512 mg (89%) of $(FcMe_2SiCH_2SnClPh)_2CH_2$ (**8**) as a reddish brown solid. $^{119}Sn\{^1H\}$ NMR (CH_2Cl_2): δ 91.2 ($^2J(^{119}Sn-^{117}Sn)$ = 245 Hz). $^{29}Si\{^1H\}$ NMR (CH_2Cl_2): δ −2.3. ^1H NMR ($CDCl_3$): δ 0.13 (s, 12H, CH_3), 0.46 (s, $^2J(^1H-^{119}Sn)$ = 85 Hz, 4H, $SnCH_2Si$), 0.71 (s, $^2J(^1H-^{119}Sn)$ = 61 Hz, 2H, $SnCH_2Sn$), 4.20−4.70 (complex pattern, 18H, H_{Cp}), 7.20−7.50 (complex pattern, 10H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 0.0 (CH_3), 3.6 ($^1J(^{13}C-^{119}Sn)$ = 294 Hz, $SnCH_2Si$), 5.6 ($^1J(^{13}C-^{119/117}Sn)$ = 301/289 Hz, $SnCH_2Si$), 70.9 (C_{Cp}), 73.6 ($C_{cp-3,4}$), 74.6 (C_{cp-1}), 75.8 ($C_{Cp-2,5}$), 128.5 ($^3J(^{13}C-^{119}Sn)$ = 61 Hz, C_m), 129.6 (C_p), 135.0 ($^2J(^{13}C-^{119}Sn)$ = 51 Hz, C_o), 141.1 ($^1J(^{13}C-^{119/117}Sn)$ = 574/574 Hz, C_i). Anal. Calcd for $C_{39}H_{46}Fe_2Cl_2Si_2Sn_2$ (991.04): C, 47.3; H, 4.7. Found: C, 46.0; H, 4.7.

Synthesis of Bis{[(ferrocenyldimethylsilyl)methyl]phenylfluorostannyl}methane, $(FcMe_2SiCH_2SnFPh)_2CH_2$ (9). Iodine (195 mg, 0.8 mmol) was added under ice cooling in small portions to a solution of **4** (413 mg, 0.4 mmol) in 10 mL of CH_2Cl_2. The black reaction mixture was stirred overnight until the solution became orange, followed by removal of the solvent and iodobenzene in vacuo. The oily residue was dissolved in 10 mL of diethyl ether and dropped under magnetic stirring into a solution of potassium fluoride (160 mg, 2.8 mmol) in 10 mL of water. The suspension was stirred for 3 days and the organic layer was separated and dried over Na_2SO_4. After filtration, the diethyl ether was evaporated to give 330 mg (89%) of $(FcMe_2SiCH_2SnFPh)_2CH_2$ (**9**) as an orange amorphous solid, mp 70−75 °C. $^{119}Sn\{^1H\}$ NMR (CH_2Cl_2): δ −44.6 ($w_{1/2} > 5500$ Hz). $^{29}Si\{^1H\}$ NMR (CH_2Cl_2): δ −1.6. Anal. Calcd for $C_{39}H_{46}F_2Fe_2Si_2Sn_2$ (958.036): C, 48.9; H, 4.8. Found: C, 48.8; H, 4.9. ESMS (*m/z* (%)): negative mode, 977 (60) $[M + F]^-$, 993 (100) $[M + Cl]^-$, 1009 (95) $[M - F + 2Cl]^-$, 1025 (40) $[M - 2F + 3Cl]^-$; positive mode, 937 (100) $[M - F]^+$, 980 (70) $[M + Na]^+$, 997 (50) $[M + K]^+$.

Synthesis of 1,1′-Bis{[(dimethylchlorostannyl)methyl]dimethylsilyl}ferrocene, $fc(SiMe_2CH_2SnClMe_2)_2$ (11). To a magnetically stirred solution of Me_3SnCl (4.4 g, 22 mmol) in 50 mL of hexane and 300 mL of liquid ammonia was added sodium (1.0 g, 44 mmol) in small quantities. The reaction mixture turned from blue to yellow. To this solution was added dropwise a solution of **2** (4.0 g, 10 mmol) in 50 mL of hexane at −78 °C. The reaction mixture was warmed to room temperature overnight. The reaction mixture was filtered and the sodium chloride washed with hexane. The solvent was evaporated to give 6.5 g (99%) of fc(SiMe$_2$CH$_2$SnMe$_3$)$_2$ (**6**) as an orange oil. ^{119}Sn{^{1}H} NMR (CHCl$_3$): δ 6.9.^{1}H NMR (CDCl$_3$): δ −0.06 (s, $^2J(^1\text{H}-^{119}\text{Sn}) = 70$ Hz, 4H, CH$_2$), 0.06 (s, $^2J(^1\text{H}-^{119}\text{Sn}) = 52$ Hz, 18H, SnCH$_3$), 0.25 (s, 12H, SiCH$_3$), 4.04 (complex pattern, 4H, H$_{\text{Cp}-2,5}$), 4.26 (complex pattern, 4H, H$_{\text{Cp}-3,4}$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ −7.9 ($^1J(^{13}\text{C}-^{119}\text{Sn}) = 332$ Hz, SnCH$_3$), −4.1 ($^1J(^{13}\text{C}-^{119}\text{Sn}) = 245$ Hz, CH$_2$), 0.9 (SiCH$_3$), 71.0 (C$_{\text{cp}-3,4}$), 72.8 (C$_{\text{cp}-2,5}$) 73.5 (C$_{\text{Cp}-1}$).

A mixture of **6** (5.6 g, 8.5 mmol) and Me$_2$SnCl$_2$ (3.7 g, 17 mmol) was stirred for 12 h at 60−70 °C. After sublimation of Me$_3$SnCl occurred, the residue was recrystallized from petroleum ether to afford 4.2 g (70%) of fc(SiMe$_2$CH$_2$SnClMe$_2$)$_2$ (**11**) as an orange solid, mp 98−100 °C. ^{119}Sn{^{1}H} NMR (CHCl$_3$): δ 167.6. ^{1}H NMR (CDCl$_3$): δ 0.34 (s, 12H, SiCH$_3$), 0.48 (s, $^2J(^1\text{H}-^{119}\text{Sn}) = 57$ Hz, 16H, SnCH$_3$ and SnCH$_2$), 4.07 (complex pattern, 4H, H$_{\text{Cp}-2,5}$), 4.32 (complex pattern, 4H, H$_{\text{Cp}-3,4}$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 0.1 ($^1J(^{13}\text{C}-^{119}\text{Sn}) = 370$ Hz, SnCH$_3$), 0.4 (SiCH$_3$), 5.2 ($^1J(^{13}\text{C}-^{119}\text{Sn}) = 267$ Hz, CH$_2$), 71.8 (C$_{\text{cp}-3,4}$), 72.1 (C$_{\text{cp}-1}$), 73.0 (C$_{\text{Cp}-2,5}$). Anal. Calcd for C$_{20}$H$_{36}$Cl$_2$FeSi$_2$Sn$_2$ (696.90): C, 34.5; H, 5.2. Found: C, 34.8; H, 5.4.

Synthesis of 1,1′-Bis{[(diphenylchlorostannyl)methyl]dimethylsilyl}ferrocene, fc(SiMe$_2$CH$_2$SnClPh$_2$)$_2$ (12). Iodine (5.1 g, 20 mmol) was added under ice cooling in small portions to a solution of **5** (10.3 g, 10 mmol) in 80 mL of CH$_2$Cl$_2$. The black reaction mixture was stirred overnight until the solution became orange. The solvent and iodobenzene were removed in vacuo and the red oily residue of fc(SiMe$_2$CH$_2$SnIPh$_2$)$_2$ (**10**) (^{119}Sn{^{1}H} NMR (CH$_2$Cl$_2$) δ −62.5) was dissolved in 80 mL of CH$_3$CN/CH$_2$Cl$_2$ (1:1). Under exclusion of light, silver chloride (4.8 g, 40 mmol) was added and the mixture was stirred for 11 days until the ^{119}Sn NMR showed complete disappearance of **10**. The precipitate of AgI/AgCl was filtered off, and the solvent was removed in vacuo to give 9.1 g (96%) of fc(SiMe$_2$CH$_2$SnClPh$_2$)$_2$ (**12**) as a reddish brown oil. ^{119}Sn{^{1}H} NMR (CH$_2$Cl$_2$): δ 26.7. ^{29}Si{^{1}H} NMR (CH$_2$Cl$_2$): δ −1.2 ($^2J(^{29}\text{Si}-^{119}\text{Sn}) = 24$ Hz). ^{1}H NMR (CDCl$_3$): δ 0.31 (s, 12H, CH$_3$), 0.85 (s, $^2J(\text{H}-^{119/117}\text{Sn}) = 84/81$ Hz, 4H, CH$_2$), 3.98 (complex pattern, 4H, H$_{\text{Cp}-2,5}$), 4.22 (complex pattern, 4H, H$_{\text{Cp}-3,4}$), 7.30−7.70 (complex pattern, 20H, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 0.5 (CH$_3$), 3.1 ($^1J(^{13}\text{C}-^{119/117}\text{Sn}) = 297/285$ Hz, CH$_2$), 71.5 (C$_{\text{cp}-3,4}$), 71.6 (C$_{\text{cp}-1}$), 73.0 (C$_{\text{Cp}-2,5}$), 128.7 ($^3J(^{13}\text{C}-^{119}\text{Sn}) = 62$ Hz, C$_\text{m}$), 129.9 ($^4J(^{13}\text{C}-^{119}\text{Sn}) = 13$ Hz, C$_\text{p}$), 135.5 ($^2J(^{13}\text{C}-^{119}\text{Sn}) = 50$ Hz, C$_\text{o}$), 139.5 ($^1J(^{13}\text{C}-^{119/117}\text{Sn}) = 578/553$ Hz, C$_\text{i}$). Anal. Calcd for C$_{40}$H$_{44}$Cl$_2$FeSi$_2$Sn$_2$ (945.11): C, 50.8,; H, 4.7. Found: C, 49.8.0; H, 4.6.

Synthesis of 1,1′-Bis{[(diphenylfluorostannyl)methyl]dimethylsilyl}ferrocene, fc(SiMe$_2$CH$_2$SnFPh$_2$)$_2$ (13). Iodine (415 mg, 1.6 mmol) was added under ice cooling in small portions to a solution of **5** (840 mg, 0.8 mmol) in 15 mL of CH$_2$Cl$_2$. The black reaction mixture was stirred overnight until the solution became orange, followed by removal in vacuo of the solvent and iodobenzene. The residue was dissolved in 10 mL of diethyl ether and dropped under magnetic stirring into a solution of potassium fluoride (300 mg, 5.2 mmol) in 10 mL of water. The suspension was stirred overnight, and the precipitate formed was filtered and washed with water and diethyl ether to give 730 mg (98%) of fc(SiMe$_2$CH$_2$SnFPh$_2$)$_2$ (**13**) as an orange amorphous solid, mp 213-216 °C. Anal. Calcd for C$_{40}$H$_{44}$F$_2$FeSi$_2$Sn$_2$ (912.18): C, 52.7; H, 4.9. Found: C, 53.0; H, 4.9.

Synthesis of 1,1′-Bis{[(((ferrocenyldimethylsilyl)methyl)diphenylstannyl)methyl]dimethylsilyl}ferrocene, fc(SiMe$_2$CH$_2$SnPh$_2$CH$_2$SiMe$_2$Fc)$_2$ (14). A solution of **12** (9.9 g, 10.5 mmol) in 50 mL of thf was added dropwise to a magnetically stirred solution of FcMe$_2$SiCH$_2$MgCl prepared from **1** (6.1 g, 22 mmol) and excess Mg (1.21 g, 50 mmol) in 70 mL of thf. The reaction mixture was heated at reflux for 2 h, and two-thirds of the thf was distilled off, followed by addition of 100 mL of CH$_2$Cl$_2$. The reaction mixture was hydrolyzed under ice cooling with 100 mL of water. After filtration the organic layer was separated, dried over Na$_2$SO$_4$, and filtered. The solvent was evaporated, and purification by size-exclusion chromatography (Sephadex LH20) afforded 11.3 g (77%) of fc(SiMe$_2$CH$_2$SnPh$_2$CH$_2$SiMe$_2$Fc)$_2$ (**14**) as a red oil. ^{119}Sn{^{1}H} NMR (CH$_2$Cl$_2$): δ −51.4.^{29}Si{^{1}H} NMR (CH$_2$Cl$_2$): δ −1.4 (1Si$_{(\text{I})}$), −1.6 (1Si$_{(\text{II})}$). ^{1}H NMR (CDCl$_3$): δ 0.06 (s, 12H, CH$_3$), 0.08 (s, 12H, CH$_3$), 0.23 (s, CH$_2$), 0.26 (s, CH$_2$), 3.86 (complex pattern, 4H, H$_{\text{Cp}-2,5}$), 3.94 (complex pattern, 4H, H$_{\text{Cp}-2,5}$), 4.08 (s, 10H, H$_\text{Cp}$), 4.14 (complex pattern, 4H, H$_{\text{Cp}-4,3}$), 4.26 (complex pattern, 4H, H$_{\text{Cp}-4,3}$), 7.10−7.40 (complex pattern, 20H, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$): δ −3.6 ($^1J(^{13}\text{C}-^{119}\text{Sn}) = 257$ Hz, CH$_2$), 0.45 (CH$_3$), 0.50 (CH$_3$), 67.9 (C$_\text{cp}$), 70.4 (C$_{\text{cp}-3,4}$), 70.9 (C$_{\text{Cp}-3,4}$), 72.5 (C$_{\text{cp}-2,5}$), 72.6 (C$_{\text{Cp}-2,5}$), 72.9 (C$_{\text{Cp}-1}$), 73.0 (C$_{\text{Cp}-1}$), 127.9 ($^3J(^{13}\text{C}-^{119}\text{Sn}) = 49$ Hz, C$_\text{m}$), 128.3 (C$_\text{p}$), 136.5 ($^2J(^{13}\text{C}-^{119}\text{Sn}) = 37$ Hz, C$_\text{o}$), 141.3 (C$_\text{i}$). Anal. Calcd for C$_{66}$H$_{78}$Fe$_3$Si$_4$Sn$_2$ (1388.66): C, 57.1; H, 5.7. Found: C, 56.2; H, 5.9.

Synthesis of 1,1,3,3,14,14,16,16,18,18,29,29-Dodecamethyl-3,14,18,29-tetrasila-1,16-distanna-[5,5]-ferrocenophane, fc(SiMe$_2$CH$_2$SnMe$_2$CH$_2$SiMe$_2$)$_2$fc (15). The synthesis of compound **15** has been described in a previous communication.[16] The ^{119}Sn NMR spectrum (CH$_2$Cl$_2$) of the crude reaction mixture obtained according to the procedure described in ref 16 displayed three signals at 7.3 (integral 3), 13.5 (integral 80), and 14.9 ppm (integral 15). From this mixture **15** (2.86 g, 60% yield) was isolated by size exclusion chromatography using Sephadex LH20. ^{119}Sn{^{1}H} NMR (CH$_2$Cl$_2$): δ 13.5. ^{29}Si{^{1}H} NMR (CDCl$_3$): δ 1.37 ($^2J(^{29}\text{Si}-^{117/119}\text{Sn}) = 21$ Hz). ^{1}H NMR (CDCl$_3$): δ −0.1 (s, $^2J(^1\text{H}-^{119}\text{Sn}) = 71$ Hz, 8H, CH$_2$), 0.05 (s, $^2J(^1\text{H}-^{119/117}\text{Sn}) = 52$ Hz, 12H, SnCH$_3$), 0.25 (s, 24H, SiCH$_3$) 4.02 (complex pattern, 8H, H$_{\text{Cp}-2,5}$), 4.25 (complex pattern, 8H, H$_{\text{Cp}-3,4}$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ −6.6 ($^1J(^{13}\text{C}-^{119/117}\text{Sn}) = 328/313$ Hz, SnCH$_3$), −2.8 ($^1J(^{13}\text{C}-^{119/117}\text{Sn}) = 240/229$ Hz, SnCH$_2$) 0.9 (SiCH$_3$), 71.1 (C$_{\text{cp}-3,4}$), 72.8 (C$_{\text{cp}-2,5}$), 73.5 (C$_{\text{Cp}-1}$). $\rho_\text{exptl} = 1.4635$ g/cm^3. Anal. Calcd for C$_{36}$H$_{60}$Fe$_2$Si$_4$Sn$_2$ (954.28): C, 45.3; H, 6.3. Found: C, 45.4; H, 6.4. ESMS (m/z (%)): positive mode, 954.5 [M$^+$].

Synthesis of 1,1,16,16-Tetraphenyl-3,3,14,14,18,18,29,29-octamethyl-3,14,18,29-tetrasila-1,16-distanna[5.5]-ferrocenophane, fc(SiMe$_2$CH$_2$SnPh$_2$CH$_2$SiMe$_2$)$_2$fc (16). A solution of **12** (7.4 g, 7.8 mmol) in 60 mL of thf and a solution of fc(SiMe$_2$CH$_2$MgCl)$_2$, prepared from **2** (3.47 g, 8.7 mmol) and excess Mg (845 mg, 34.8 mmol) in 60 mL of thf, were added dropwise and synchronously to magnetically stirred thf (300 mL). The reaction mixture was heated at reflux overnight, and two-thirds of the thf was distilled off, followed by addition of 100 mL of CH$_2$Cl$_2$. The reaction mixture was hydrolyzed under ice cooling with 100 mL of aqueous potassium fluoride solution. After filtration, the organic layer was separated, dried over Na$_2$SO$_4$, and filtered. The solvent was evaporated to give 7.5 g (80%) of an orange oil, the ^{119}Sn and ^{29}Si NMR spectra of which in CH$_2$Cl$_2$ showed two resonances at δ −51.4 (integral 1) and δ −51.5 (integral 3.5) and at δ −1.29 and −1.34, respectively, indicating the presence of at least two different species.

The oil was dissolved in diethyl ether and the solution left in the refrigerator to give **16** (3.5 g, 37%) as an orange crystalline solid, mp 188−190 °C. ^{119}Sn{^{1}H} NMR (CDCl$_3$): δ −51.6. ^{29}Si{^{1}H} NMR (CDCl$_3$): δ −1.0 ($^2J(^{29}\text{Si}-^{119/117}\text{Sn}) = 20/19$ Hz). ^{1}H NMR (CDCl$_3$): δ 0.08 (s, 24H, CH$_3$), 0.43 (s, $^2J(^1\text{H}-^{119/117}\text{Sn}) = 75/72$ Hz, 8H, CH$_2$), 4.06 (complex pattern, 8H, H$_{\text{Cp}-2,5}$), 4.29 (complex pattern, 8H, H$_{\text{Cp}-3,4}$), 7.30−7.50 (complex pattern, 20H, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$): δ −3.6 ($^1J(^{13}\text{C}-^{119/117}\text{Sn}) = 264/251$ Hz, CH$_2$), 1.0 (CH$_3$), 71.2 (C$_{\text{cp}-3,4}$), 73.0 (C$_{\text{cp}-2,5}$), 73.7 (C$_{\text{Cp}-1}$), 128.1 ($^3J(^{13}\text{C}-^{119}\text{Sn}) = 48$ Hz, C$_\text{m}$), 128.5 (C$_\text{p}$), 136.7 ($^2J(^{13}\text{C}-^{119}\text{Sn}) = 37$ Hz, C$_\text{o}$), 141.3 ($^1J(^{13}\text{C}-^{119/117}\text{Sn}) = 479/458$ Hz, C$_\text{i}$). Anal. Calcd for C$_{56}$H$_{68}$Fe$_2$Si$_4$Sn$_2$ (1202.62): C, 55.9; H, 5.7. Found: C, 55.8; H, 6.0. Molecular weight determination (CHCl$_3$, 36 °C): 1023.

Synthesis of 1,16-Diiodo-1,16-diphenyl-3,3,14,14,18,18,29,29-octamethyl-3,14,18,29-tetrasila-1,16-distanna[5.5]-ferrocenophane, fc(SiMe$_2$CH$_2$SnIPhCH$_2$SiMe$_2$)$_2$fc (17).

Table 5. Crystallographic Data for 4, 16, 17, 19, 20, 22, and 23

	4	**16**	**17**	**19**	**20**	**22**	**23**
formula	$C_{51}H_{58}Fe_2Si_2Sn_2$	$C_{56}H_{68}Fe_2Si_4Sn_2$	$C_{44}H_{58}Fe_2I_2Si_4Sn_2$	$C_{44}H_{58}Cl_2Fe_2Si_4Sn_2$	$C_{34}H_{54}Cl_2Fe_2Si_4Sn_2$	$[C_{34}H_{54}Cl_4Fe_2Si_4Sn_2]^{2-}2[C_{34}H_{30}NP_2]^{+}\cdot CH_2Cl_2$	$[C_{44}H_{58}Cl_4Fe_2Si_4Sn_2]^{2-}2[C_{34}H_{30}NP_2]^{+}\cdot CH_2Cl_2$
fw	1076.23	1202.54	1302.14	1119.24	995.11	2228.04	2352.17
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
cryst size, mm	0.40 × 0.35 × 0.35	0.25 × 0.20 × 0.20	0.25 × 0.10 × 0.10	0.25 × 0.20 × 0.20	0.40 × 0.20 × 0.08	0.15 × 0.10 × 0.10	0.30 × 0.10 × 0.10
space group	$P2/n$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$C2/c$
a, Å	18.109(1)	18.780(1)	13.502(1)	12.800(1)	13.141(5)	13.067(1)	23.775(1)
b, Å	11.122(1)	11.935(1)	14.043(1)	17.262(1)	13.527(8)	14.540(1)	30.498(1)
c, Å	24.979(1)	25.444(1)	14.243(1)	12.228(1)	13.252(7)	16.499(1)	15.927(1)
α, deg	90	90	106.742(1)	90	90	110.829(1)	95.695(1)
β, deg	105.389(1)	101.943(1)	97.322(1)	116.431(1)	118.18(4)	94.061(1)	
γ, deg	90(1)	90	99.619(1)	90	90	99.406(1)	
V, Å^3	4850.6(5)	5579.6(6)	2505.3(3)	2419.4(3)	2076.4(18)	2862.1(3)	11491.5(9)
Z	4	4	2	2	2	1	4
ρ_{calcd}, Mg/m^3	1.474	1.432	1.726	1.536	1.592	1.293	1.360
ρ_{measd}, Mg/m^3	1.437	1.421	1.684	not measd	not measd	not measd	1.459
μ, mm^{-1}	1.686	1.515	2.909	1.847	2.140	0.961	0.961
$F(000)$	2176	2448	1272	1128	1000	1142	4824
θ range, deg	2.94−25.68	2.75−24.11	3.44−23.34	4.09−25.65	3.01−27.49	3.46−25.43	3.42−25.02
index ranges	$-20 \leq h \leq 20$	$-21 \leq h \leq 21$	$-15 \leq h \leq 15$	$-15 \leq h \leq 13$	$-1 \leq h \leq 17$	$-15 \leq h \leq 15$	$-28 \leq h \leq 28$
$-13 \leq k \leq 13$	$-13 \leq k \leq 13$	$-15 \leq k \leq 15$	$-19 \leq k \leq 19$	$-1 \leq k \leq 17$	$-17 \leq k \leq 17$	$-36 \leq k \leq 36$	
$-30 \leq l \leq 29$	$-29 \leq l \leq 29$	$-14 \leq l \leq 14$	$-14 \leq l \leq 14$	$-17 \leq l \leq 15$	$-16 \leq l \leq 16$	$-17 \leq l \leq 17$	
no. of rflns collcd	66 602	64 221	15 638	32 775	5821	37 719	74 237
completeness to θ_{max}	97.9	100.0	79.6	98.4	99.8	91.9	97.8
no. of indep rflns/R_{int}	9059/0.045	8871/0.043	5747/0.046	4498/0.032	4763/0.0389	9726/0.033	9909/0.077
no. of rflns obsd with $I > 2\sigma(I)$	5306	5246	3023	3308	3308	5377	4357
abs cor	not measd	not measd	not measd	not measd	ψ-scan	not measd	not measd
T_{max}/T_{min}					1.000/0.687		
no. of refined params	516	587	489	250	206	593	630
GOF(F^2)	0.862	0.870	0.854	1.038	1.032	0.950	0.749
R1(F) ($I > 2\sigma(I)$)	0.0297	0.0315	0.0439	0.0270	0.0447	0.0471	0.0366
wR2(F^2) (all data)	0.0574	0.0614	0.0875	0.0592	0.1196	0.1386	0.0637
$(\Delta/\sigma)_{max}$	0.001	0.001	<0.001	0.001	<0.001	0.001	0.001
largest diff peak/hole, e/Å^3	0.271/−0.464	0.781/−0.305	1.368/−0.402	0.308/−0.372	0.909/−1.086	0.811/−0.301	0.291/−0.305

Iodine (455 mg, 1.8 mmol) was added under ice cooling in small portions to a solution of **16** (1.08 mg, 0.9 mmol) in 20 mL of CH_2Cl_2. The black reaction mixture was stirred overnight until the solution became orange. The solvent and iodobenzene were removed in vacuo, and the resulting dark red residue was recrystallized from hexane to give 1.16 g (99%) of fc($SiMe_2CH_2SnIPhCH_2SiMe_2$)$_2$fc (**17**) as a crystalline red solid, mp 171−174 °C. ^{119}Sn{^{1}H} NMR ($CDCl_3$): δ −13.1, −13.4. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ −1.3 ($^2J(^{29}Si-^{119}Sn) = 23$ Hz). ^{1}H NMR ($CDCl_3$): δ 0.18 (s, $w_{1/2} = 5.4$ Hz, 12H, CH_3), 0.37 (s, $w_{1/2} =$ 4.3 Hz, 12H, CH_3), 0.88 (complex pattern, $^2J(^1H-^{119}Sn) = 79$ Hz, 8H, CH_2), 4.05 (s, 4H, $H_{Cp-2,5}$), 4.10 (s, 4H, $H_{Cp-2,5}$), 4.32 (s, 8H, $H_{Cp-3,4}$), 7.20−7.50 (complex pattern, 10H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.60 (CH_3), 0.74 (CH_3), 0.84 (CH_3), 0.97 (CH_3), 4.32 ($^1J(^{13}C-^{119}Sn) = 250$ Hz, CH_2), 4.37 (CH_2), 71.41, 71.48, 71.55, 71.61, 72.73, 72.78, 72.86, 72.95, 73.05, 73.15 (C_{Cp}), 128.5 ($^3J(^{13}C-^{119}Sn) = 58$ Hz, C_m), 129.5 (C_p), 135.4 ($^2J(^{13}C-^{119}Sn) = 50$ Hz, C_o), 139.59 ($^1J(^{13}C-^{119}Sn) = 491$ Hz, C_i), 139.67 (C_i). Anal. Calcd for $C_{44}H_{58}Fe_2I_2Si_4Sn_2$ (1302.26): C, 40.6; H, 4.5. Found: C, 40.8; H, 4.6.

Synthesis of 1,16-Difluoro-1,16-diphenyl-3,3,14,14,18,18,29,29-octamethyl-3,14,18,19-tetrasila-1,16-distanna-[5.5]ferrocenophane, fc($SiMe_2CH_2SnFPhCH_2SiMe_2$)$_2$fc (18). Under exclusion of light, a solution of **17** (222 mg, 0.2 mmol) in 5 mL of diethyl ether was dropped into a magnetically stirred solution of potassium fluoride (100 mg, 1.7 mmol) in 5 mL of water. The suspension was stirred overnight and the precipitate filtered off and washed with water and diethyl ether to give 140 mg (76%) of fc($SiMe_2CH_2SnFPhCH_2SiMe_2$)$_2$fc (**18**) as a colorless amorphous solid, mp 126−128 °C. ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −209.7 ($^1J(^{19}F-^{119/117}Sn = 2357/2256$ Hz), −210.7 ($^1J(^{19}F-^{119/117}Sn = 2369/2266$ Hz); integral ratio 1:0.9. ^{1}H NMR ($CDCl_3$): δ 0.22 (s, 6H, CH_3), 0.23 (s, 6H, CH_3), 0.38 (s, 6H, CH_3), 0.39 (s, 6H, CH_3), 0.65 (complex pattern, $^2J(^1H-^{119}Sn) = 82$ Hz, 8H, CH_2), 4.09 (complex pattern, 8H, $H_{Cp-2,5}$), 4.32 (complex pattern, 8H, $H_{Cp-3,4}$), 7.30−7.50 (complex pattern, 10H, Ph). Anal. Calcd for $C_{44}H_{58}F_2Fe_2Si_4Sn_2$ (1086.45): C, 48.6; H, 5.4. Found: C, 47.5; H, 5.5. ESMS (m/z (%)): negative mode, 1105 (100) $[M + F]^-$; positive mode, 1067 (100) $[M - F]^+$, 1125 (70) $[M + K]^+$.

Synthesis of 1,16-Dichloro-1,16-diphenyl-3,3,14,14,18,18,29,29-octamethyl-3,14,18,19-tetrasila-1,16-distanna-[5.5]ferrocenophane, fc($SiMe_2CH_2SnClPhCH_2SiMe_2$)$_2$fc (19). Under exclusion of light, silver chloride (224 mg, 1.5 mmol) was added to a solution of **18** (503 mg, 0.39 mmol) in 20 mL of CH_2Cl_2/CH_3CN (1:1). The reaction mixture was stirred for 11 days until ^{119}Sn NMR showed the complete disappearance of **17**. The precipitate of AgI/AgCl was filtered and the solvent removed in vacuo. The resulting oily residue was dissolved in 10 mL of CH_2Cl_2, and 10 mL of hexane was added. Slow evaporation of the dichloromethane yielded 420 mg (97%) of fc($SiMe_2CH_2SnClPhCH_2SiMe_2$)$_2$fc (**19**) as an orange crystalline solid, mp 178−180 °C. ^{119}Sn{^{1}H} NMR (CD$_2$Cl$_2$): δ 95.4 ($w_{1/2}$ = 29 Hz). ^{29}Si{^{1}H} NMR (CD$_2$Cl$_2$): δ −1.6 ($^2J(^{29}$Si−^{119}Sn) = 22 Hz). ^{1}H NMR (CDCl$_3$): δ 0.20 (s, 12H, CH$_3$, $w_{1/2}$ = 12 Hz), 0.38 (s, 12H, CH$_3$, $w_{1/2}$ = 11 Hz), 0.70 (s, $^2J(^1$H−^{119}Sn) = 81 Hz, 8H, CH$_2$, $w_{1/2}$ = 8 Hz), 4.08 (complex pattern, 8H, H$_{\mathrm{Cp-2,5}}$), 4.33 (complex pattern, 8H, H$_{\mathrm{Cp-3,4}}$), 7.10−7.30 (complex pattern, 10H, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 0.7 (CH$_3$, $w_{1/2}$ = 20 Hz), 4.8 ($^1J(^{13}$C−$^{119/117}$Sn) = 279/266 Hz, CH$_2$), 71.6 (C$_{\mathrm{cp-3,4}}$), 72.8 (C$_{\mathrm{Cp-1}}$), 73.0 (C$_{\mathrm{cp-2,5}}$), 127.6 ($^3J(^{13}$C−^{119}Sn) = 61 Hz, C$_m$), 128.6 (C$_p$), 135.5 ($^2J(^{13}$C−^{119}Sn) = 51 Hz, C$_o$), 141.8 (C$_i$). Anal. Calcd for $C_{44}H_{58}Cl_2Fe_2Si_4Sn_2$ (1119.36): C, 47.2; H, 5.2. Found: C, 46.7; H, 5.2.

Synthesis of the 1:2 Chloride Complex {[fc(SiMe$_2$CH$_2$SnClMeCH$_2$SiMe$_2$)$_2$fc·2Cl]$^{2-}$2[(Ph$_3$P)$_2$N]$^+$} (22). Isolation of Single Crystals of *trans*-fc(SiMe$_2$CH$_2$SnClMeCH$_2$SiMe$_2$)$_2$fc (20). A mixture of **15**[16] (270 mg, 0.28 mmol) and Me$_2$SnCl$_2$ (124 mg, 0.57) was stirred for 2 days at 110 °C. Me$_2$SnCl$_2$ and the Me$_3$SnCl formed were removed in vacuo (5 × 10^{-3} Torr, 110 °C). The black residue was dissolved in 5 mL of CH$_2$Cl$_2$, the solution was filtered, and 5 mL of hexane was added. Slow evaporation of the CH$_2$Cl$_2$ yielded 130 mg of a red solid product mixture (^{119}Sn{^{1}H} (CH$_2$Cl$_2$) δ 168.8, 168.3, 167.3, 17.8, 17.7) from which two single crystals suitable for X-ray analysis of *trans*-fc(SiMe$_2$CH$_2$SnClMeCH$_2$SiMe$_2$)$_2$fc (**20**) (mp 156 °C) were isolated.

To a solution of the product mixture (113 mg) in 10 mL of CH$_2$Cl$_2$ was added (Ph$_3$P)$_2$NCl (130 mg, 0.2 mmol). After it was stirred for 1 h, the solution was filtered and 10 mL of hexane was added. Slow evaporation of the CH$_2$Cl$_2$ yielded 250 mg (62%) of {[fc(SiMe$_2$CH$_2$SnClMeCH$_2$SiMe$_2$)$_2$fc·2Cl]$^{2-}$2[(Ph$_3$P)$_2$N]$^+$} (**22**) as an orange solid, mp 230−231 °C. ^{119}Sn{^{1}H} NMR (CDCl$_3$): δ 62.1. ^{29}Si{^{1}H} NMR (CDCl$_3$): δ −2.2. ^{1}H NMR (CDCl$_3$): δ 0.31 (s, 24H, SiCH$_3$), 0.49 (s, $^2J(^1$H−^{119}Sn) = 60 Hz), 6H, SnCH$_3$), 0.62 (s, $^2J(^1$H−^{119}Sn) = 82 Hz, 8H, CH$_2$), 4.14 (complex pattern, 8H, H$_{\mathrm{Cp-2,5}}$), 4.31 (complex pattern, 8H, H$_{\mathrm{Cp-3,4}}$), 7.10−7.70 (complex pattern, 60H, PhP). ^{13}C{^{1}H} NMR (100.63 MHz, CDCl$_3$): δ 1.2 (SiCH$_3$), 5.8 (SnCH$_3$), 7.8 (CH$_2$), 70.8 (C$_{\mathrm{cp-3,4}}$), 73.0 (C$_{\mathrm{cp-2,5}}$), 73.7 (C$_{\mathrm{Cp-1}}$), 126.0−134.0 (4 signals with ^{31}P couplings, Ph$_3$P). Anal. Calcd for $C_{106}H_{114}Cl_4Fe_2N_2P_4Si_4Sn_2$ (2149.24): C, 59.4; H, 5.4; N, 1.2. Found: C, 59.2; H, 5.5; N, 1.3.

Synthesis of the 1:2 Chloride Complex {[fc(SiMe$_2$CH$_2$SnClPhCH$_2$SiMe$_2$)$_2$fc·2Cl]$^{2-}$2[(Ph$_3$P)$_2$N]$^+$} (23). To a solution of **19** (220 mg, 0.2 mmol) in 10 mL of CH$_2$Cl$_2$ was added (Ph$_3$P)$_2$NCl (226 mg, 0.4 mmol). After it was stirred for 1 h, the solution was filtered and 10 mL of hexane was added. Slow evaporation of the CH$_2$Cl$_2$ yielded 250 mg (56%) of {[fc(SiMe$_2$CH$_2$SnClPhCH$_2$SiMe$_2$)$_2$fc 2Cl]$^{2-}$2[(Ph$_3$P)$_2$N]$^+$} (**23**) as an orange crystalline solid, mp 203−208 °C. ^{119}Sn{^{1}H} NMR (CH$_2$Cl$_2$): δ −21.2. ^{29}Si{^{1}H} NMR (CH$_2$Cl$_2$): δ −2.1. ^{1}H NMR (CDCl$_3$): δ 0.14 (s, 24H, SiCH$_3$), 0.56 (s, 8H, CH$_2$), 4.38 (complex pattern, 8H, H$_{\mathrm{Cp-2,5}}$), 4.54 (complex pattern, 8H, H$_{\mathrm{Cp-3,4}}$), 7.10−7.80 (complex pattern, 70H, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 0.6 (SiCH$_3$), 7.3 (CH$_2$), 72.9 (C$_{\mathrm{cp-3,4}}$), 74.8 (C$_{\mathrm{cp-2,5}}$), 75.2 (C$_{\mathrm{Cp-1}}$), 126.0−134.0 (4 signals with ^{31}P couplings, Ph$_3$P), 127.1 (C$_m$), 128.3 (C$_p$), 135.6 (C$_o$), 144.0 (C$_i$). The crystal structure determination showed 1 molar equiv of dichloromethane in the unit cell. This was also confirmed by ^{1}H NMR (δ 5.27 (s, 2H, CH$_2$Cl$_2$)). Anal. Calcd for $C_{116}H_{118}Cl_4Fe_2N_2P_4Si_4Sn_2 \cdot CH_2Cl_2$ (2352.38): C, 59.7; H, 5.1; N, 1.2. Found: C, 59.9; H, 5.9; N, 1.2.

Crystallography. Intensity data for the red or orange crystals were collected on either a Nonius Mach3 (**22**) or KappaCCD (**4**, **16**, **17**, **19**, **22**, **23**) diffractometer with graphite-monochromated Mo Kα radiation at 291 K. Three standard reflections were recorded every 60 min (**21**), and an anisotropic intensity loss up to 6.7% (**20**) was detected during X-ray exposure. The data collections for **4**, **16**, **17**, **19**, **22**, and **23** covered the sphere of reciprocal space with 360 frames via ω rotation ($\Delta/\omega = 1°$) at 2 times 10 s (**4**, **16**, **17**, **19**, **23**) and 60 s (**22**) per frame. The crystal-to-detector distance was 2.7 cm (**4**, **16**, **17**, **19**), 2.8 cm (**22**), and 3.5 cm (**23**; detector-θ-offset 10°). Crystal decay was monitored by repeating the initial frames at the end of data collection. On analysis of the duplicate reflections, there was no indication for any decay. The structures were solved by direct methods (SHELXS86[25a]) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods (SHELXL93[25b]).

The H atoms were placed in geometrically calculated positions using a riding model and refined with common isotropic temperature factors for different C−H types (C$_{\mathrm{prim}}$−H = 0.96 Å, C−H$_{\mathrm{sec}}$ = 0.97 Å, U_{iso} = 0.109(3) (**4**), 0.104(3) (**16**), 0.088(6) (**17**), 0.114(3) (**19**), 0.083(5) (**20**), 0.125(6) (**22**), 0.096(4) Å^2 (**23**); H$_{\mathrm{aryl}}$ C−H = 0.93 Å, U_{iso} = 0.105(2) Å^2 (**4**), 0.069(2) (**16**), 0.052(5) (**17**), 0.079(3) (**19**), 0.061(6) (**20**), 0.093(4) (**22**), 0.077(2) (**23**) Å^2).

In **22** one anisotropically refined solvent molecule (CH$_2$Cl$_2$) and in **23** two isotropically refined disordered solvent molecules (CH$_2$Cl$_2$; C(81), C(82), Cl(5), Cl(6) (sof 0.5); Cl(3) (sof 0.2); Cl(4) (sof 0.3)) were found.

Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref 25c. Figures were created by SHELXTL-Plus.[25d] Crystallographic data are given in Table 5.

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Supporting Information Available: Tables of all coordinates, anisotropic displacement parameters, and geometric data for compounds **4**, **16**, **17**, **19**, **20**, **22**, and **23**, a detailed discussion of the complexation behavior of compounds **9**, **13**, and **18** toward fluoride ions in solution, including a table, and a detailed discussion of the electrochemistry, including a table. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) (a) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. (b) Sheldrick, G. M. University of Göttingen, 1997. (c) *International Tables for Crystallography*; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. C. (d) Sheldrick, G. M. SHELXTL-PLUS, Release 4.1; Siemens Analytical X-ray Instruments Inc., Madison, WI, 1991.