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Structure and Electrochemistry of Ferrocenyloligosilanes: α,ω-Bis(ferrocenyl)- and α,ω-(1,1′-Ferrocenediyl)oligosilanes

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Summary: The structures and electrochemical properties of 1,2-bis(ferrocenyl)-1,1,2,2-tetramethyldisilane ($Fc(SiMe_2)_nFc$, *n* = *2, Ib) and (1,1′-ferrocenediyl)tetramethyldisilane* ($(C_5H_4)_2(SiMe_2)_nFe$, *n* = *2, IIb), a ferrocenophane, are reported together with the electrochemical behavior of their analogs (n = 1 (a), 3 (c)). Complex Ib exhibited a Si–Si bond length of 2.340(2) Å and two distinctive reversible redox processes* (E_{ox} = *0.56 and 0.67 V,* E_{red} = *0.50 and 0.61 V). Complex IIb exhibited an elongated Si–Si bond length of 2.351(1) Å and an elongated* $C_{cyclopentadienyl}$*–Si bond length compared to Ib (1.881(3) versus 1.862(4) Å). These bond length elongations result in minimal cyclopentadienyl dihedral angle strain, 4.3°, in IIb. Electrochemically IIb exhibited a single oxidation process* (E_{ox} = *0.67 V,* E_{red} = *0.59 V). The ferrocenophane redox behavior disappeared after a few cycles because of decomposition. The monosilyl-bridged ferrocenophane IIa underwent decomposition upon electrochemical oxidation, while (1,1′-ferrocenediyl)heptamethyltrisilane (IIc) exhibited a completely reversible oxidation process. This trend reflects the capacity of the three bridges, Si,* Si_2 *and* Si_3*, to incorporate the increase in Fe–cyclopentadienyl ring distance upon oxidation. Electrochemical investigation of the* α,ω*-bis(ferrocenyl) complexes Ia–c, and complexes with n = 0 (biferrocene) and n = 6 (If), showed that the two redox systems are most separated when the two Fe atoms are adjacent (n = 0) and progressively become closer as the inter-ferrocene distance increases, until at n = 6 only a single process is observed. Complexes IIb,c did not undergo simple linear polymerization at temperatures below 350 °C, and above this temperature cross-linking polymerization occurred to produce insoluble materials. Both Ib and IIb undergo Si–Si bond cleavage upon photolysis in MeOH to produce the methoxysilane derivatives, and in the case of IIb the major product (>95%) was (1,1′-ferrocenediyl)tetramethyldisiloxane.*

The chemistry of new silicon-containing materials having transition-metal substituents is of growing interest since incorporation of the metal introduces new optical and electrical properties.[1] While introduction of the $(C_5H_5)Fe(CO)_2$ (Fp) group provides significant activation of the oligosilanes with respect to photochemical isomerizations and redistributions, the ferrocenyl group tends to deactivate the photochemical reactivity of the oligo- and polysilanes due to the capacity of the Fc unit to act as a triplet quenching agent.[1a,2] However, this latter group introduces a reversible redox center to the oligomer and polymer systems.[1b] We[3] and Manners[4] have independently reported that (1,1′-ferrocenediyl)dialkylsilanes are useful precursors to the linear polymers $[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4\text{-}SiR_2)-]_n$ in a manner reminiscent of that previously reported by Seyferth for the corresponding P and Sn ferrocenophanes.[5] The activity of the monosilylferrocenophanes is related to their strained structures, in which the two cyclopentadienyl groups have a dihedral angle of approximately 20°.[4,6] We wish to report on the structural, thermal, photochemical, and electrochemical properties of (1,1′-ferrocenediyl)tetramethyldisilane (IIb) and compare these to the same properties of the tetramethyldisilyl group when it bridges independent Fc units (Ib) and to extend the electrochemical study to the mono- and trisilyl analogs of both complexes, Ia–c and IIa–c and the hexasilyl analog If (Figure 1).

Experimental Section

The title complexes are readily prepared using literature procedures: I,[7] IIa,[8a] IIb,c.[8b] We describe the synthesis of complex Ic since the reported yield was 6%, whereas our yields were considerably greater.

Synthesis of 1,3-Bis(ferrocenyl)-1,1,2,2,3,3-hexamethyltrisilane (Ic). To a stirred solution of 1,3-dichlorohexamethyltrisilane (1.84 g, 7.5 mmol) in 30 mL of THF at −25 °C was added slowly a 60-mL solution of ferrocenyllithium obtained from 6.3 g (15 mmol) of chloromercurioferrocene and *n*-BuLi. The mixture was stirred for 30 min and then warmed to room temperature and stirred for a further 12 h. The solvent was removed in vacuo, and the orange residue was extracted into hexane (60 mL) and filtered. The filtrate was concentrated to 10 mL, the di-*n*-butylmercury removed by fractional distillation (61–62 °C/0.5 mmHg), and the residue twice recrystallized from hexane to yield 1.6 g (39%) of Ic. NMR (C_6D_6, ppm): ^{29}Si, −18.7, −48.6; ^{13}C, −6.1 ($SiMe_2$), −2.2 ($SiMe_2$), 68.4, 71.1, 72.4, 73.3 (Fc).

Using the same technique, $Fc(SiMe_2)_6Fc$ was synthesized in 39% yield. Anal. Calcd (found): C, 53.5 (53.9), H, 7.57 (7.85).

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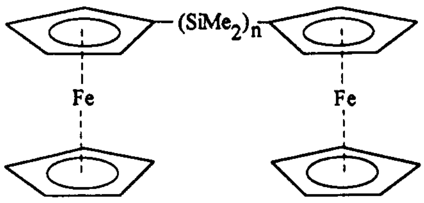
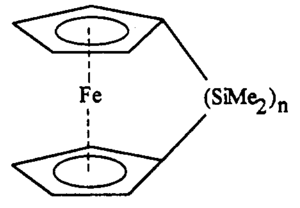


I (n = 1 (a), 2 (b), 3 (c), 6 (f))



II (n = 1 (a), 2 (b), 3 (c)); III (Si = C, n = 2)

Figure 1.

Mp: 121–122 °C. NMR (ppm): ^{1}H, 0.23, 0.24, 0.43 (SiMe$_2$), 3.97, 4.06 (s), 4.18 (Fc); ^{13}C, −5.1, −4.0, −2.1 (SiMe$_2$), 68.3, 71.1, 73.1 (Fc); ^{29}Si, −17.5, −38.9, −43.1.

The structural data were collected at room temperature on a Siemens R3m/V four-circle diffractometer using graphite-monochromated Mo Kα radiation. Details of the structure determinations are recorded in Table I; atomic coordinates are recorded in Table II, and the structures of Ib and IIb are illustrated in Figures 2 and 3, with relevant bond lengths and angles in Table III. Electrochemical studies were performed in 0.1 mM CH$_2$Cl$_2$ solution with tetraethylammonium tetrafluoroborate (0.1 M) as supporting electrolyte in a one-compartment cell equipped with a Pt-disk working electrode, a gold-wire counter electrode, and an Ag/AgCl (3.8 N KCl) double-junction reference electrode. The data are recorded in Table IV, and the data for complexes I are illustrated in Figure 4.

Photolysis of IIb. A 2-mL C$_6$D$_6$ solution of IIb (0.1 g, 3.3 mmol) was irradiated for 5 h under an argon atmosphere at a distance of 10 cm from a 450-W Hanovia medium-pressure mercury lamp. Analysis by ^{29}Si NMR indicated that no reaction had occurred. Replacement of the solvent by a 50/50 MeOH/C$_6$D$_6$ mixture gave the same result. Placement of this latter solution in a quartz tube and irradiation for 4 h under an O$_2$ atmosphere resulted in the formation of (1,1′-ferrocenediyl)tetramethyldisiloxane as the major product (>90%) and 1,1′-bis(methoxydimethylsilyl)ferrocene as a minor product as detected by ^{29}Si NMR and GC/mass spectrometry. Recrystallization of the products from hexane led to recovery of (1,1′-ferrocenediyl)tetramethylsiloxane: 55 mg, 60%; mp 86–87 °C, lit.[9d] mp 87–88 °C; mass spectrum m/e 300 (90), 285 (100%); ^{29}Si NMR (C$_6$D$_6$/MeOH) 1.2 ppm. We made no attempt to isolate bis(methoxyldimethylsilyl)ferrocene: mass spectrum m/e 362 (100), 332 (28%), ^{29}Si NMR (C$_6$D$_6$/MeOH) 13.0 ppm. Using GC/mass spectrometry to identify minor products from these reactions, i.e. a total yield of less than 3%, we observed FcSiMe$_2$OSiMe$_2$OMe, FcSiMe$_2$OMe, FcH, and trace amounts of ferrocene-free siloxanes (linear and cyclic). A similar, but much slower, reaction occurred when IIb was treated with a flow of O$_2$ in MeOH.

Thermolysis of IIb. A sample of IIb (1.0 g, 3.3 mmol) was placed in a sealed Pyrex tube (10^{-3} mmHg) and heated for 12 h to varying temperatures up to 350 °C. At all temperatures below 350 °C starting material was recovered. At 350 °C a dark red solid was obtained that was insoluble in all common solvents. Infrared analysis indicated the presence of cyclopentadienyl (Cp) groups[20] (KBr pellet, cm^{-1}; m = medium, s = strong) at 3087 (CH, m) 1161 (C–Si, m), 1034 (C–C, s), and 489 (Cp-Fe, m) and Me–Si groups as observed for polydimethylsilane[21] at 2952, 2888 (C–H stretch, m) and 1246 (CH$_3$–Si, s).

Results and Discussion

The Si–Si bond lengths in Ib and IIb are slightly but significantly different (bis(ferrocenyl)disilane Ib, 2.340(2) Å; ferrocenophane IIb, 2.351(1) Å). The normal Si–Si bond length in non-sterically-crowded organosilanes is 2.34 Å,[9] identical with that observed for Ib, which itself is almost identical with that reported for a bis(cyclopentadienyl)iron dicarbonyl complex, [(η^5-C$_5$H$_4$)Fe(CO)$_2$Me]$_2$Si$_2$Me$_4$, where the disilane fragment bridges the Fp units via the two cyclopentadienyl groups.[10] The Si–Si bond is susceptible to stretching and may be elongated up to 2.697(2) Å in hexa-*tert*-butyldisilane;[11] thus, the extension noted for IIb, while significant, is not great. The data also show that the C$_{\text{cyclopentadienyl}}$–Si bonds in IIb are significantly longer than their counterparts in Ib: Si1–C1 = 1.881(3) Å (Si2–C6 = 1.883(4) Å) in IIb; Si1–C1 = 1.862(4) Å in Ib. These two sets of bonds, Si–Si and Si–C, illustrate the manner in which the strain incurred upon bridging is accommodated by elongation rather than by significant twisting, since the dihedral angle between the two cyclopentadienyl rings in IIb is very low (4.3°). This is significantly less than that in monosilylferrocenophanes, where values of 19.2 and 20.3° are reported for the diphenyl- and dimethyl-substituted silyl groups respectively.[4,6] The value is also considerably less than the angle reported for the C analog of complex IIb, (1,1′-ferrocenediyl)tetramethylethane ((η^5-C$_5$H$_4$)$_2$Fe(C$_2$Me$_4$), III).[12] For III the two cyclopentadienyl rings are inclined at an angle of 23° (even larger than for the 1,1′-monosilyl complexes), denoting the smaller C$_{\text{cyclopentadienyl}}$–C$_{\text{exocyclic}}$ bond lengths compared to the related C–Si bond length, and the small C–C bridging bond versus the Si–Si bond of IIb. The angle between the cyclopentadienyl ring plane and the exocyclic silicon atoms in IIb is 11°, a value similar to that reported for the equivalent angle between the cyclopentadienyl plane and the exocyclic carbon atoms in III. Overall, the larger Si covalent radius, coupled with the greater flexibility of the Si–Si and Si–C$_{\text{cyclopentadienyl}}$ bonds, permits the energetically more favorable parallel nature of the cyclopentadienyl rings in ferrocene derivatives to dominate the structure. It is of interest that such a result was predicted by Kumada and co-workers 20 years ago from spectroscopic studies on IIb and a large array of other ferrocenylsilicon and -germanium complexes.[8b]

The conformations of Ib, IIb, and III are different when viewed along the Si–Si (C–C) bonds. The staggered conformation of I with the two bulky ferrocenyl groups in a trans arrangement is, as expected, the low-energy form with a dihedral angle between the adjacent Me–Si bonds of 59°. However, due to the gauche requirement of the two bridged cyclopentadienyl ligands with respect to the Si–Si bond in IIb, a more eclipsed conformation of the methyl and cyclopentadienyl groups is found with a dihedral angle of 7–8°. For complex III this dihedral angle is 25° and the C–C bridge bond length is elongated to 1.58 Å compared to the normal C–C value of 1.55 Å. This very

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Table I. Structure Determination Summary

	Ib	IIb
	Crystal Data	
empirical formula	$C_{12}H_{15}SiFe$	$C_{14}H_{20}FeSi_2$
color, habit	orange fragment	orange fragment
cryst size (mm)	0.8 × 0.4 × 0.4	0.48 × 0.20 × 0.50
cryst syst	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/n$
unit cell dimens		
a (Å)	11.205(3)	10.4330(10)
b (Å)	7.582(2)	8.7100(10)
c (Å)	14.366(4)	17.244(2)
β (deg)	107.62(2)	107.280(10)
V (Å^3)	1163.2(5)	1496.3(3)
Z	4	4
fw	243.2	300.3
density (calcd) (Mg/m^3)	1.389	1.333
abs coeff (mm^{-1})	1.356	1.142
F(000)	508	632
	Data Collection	
diffractometer used	Nicolet R3m/V	
radiation	Mo Kα (λ = 0.710 73 Å)	
temp (K)	298	
monochromator	highly oriented graphite cryst	
2θ range (deg)	3.5–45.0	
scan type	ω	
scan speed (deg/min)	variable; 3.00–15.00 in ω	variable; 3.00–20.00 in ω
scan range (ω) (deg)	1.20	1.50
bkgd measmt	stationary cryst and stationary counter at beginning and end of scan, each for 25.0% of total scan time	
std rflns	3 measd every 50 rflns	3 measd every 100 rflns
index ranges	$-3 \le h \le 12, 0 \le k \le 8, -15 \le l \le 14$	$0 \le h \le 11, -2 \le k \le 9, -18 \le l \le 17$
no. of rflns collected	1683	2916
no. of indep rflns	1398 (R_{int} = 0.70%)	1974 (R_{int} = 1.47%)
no. of obsd rflns	1252 ($F > 3.0\sigma$(F))	1557 ($F > 3.0\sigma(F)$)
abs cor	semiempirical	semiempirical
max/min transmissn	0.75/0.53	0.4577/0.6235
	Solution and Refinement	
system used	Nicolet SHELXTL PLUS (MicroVAX II)	
soln	direct methods	
refinement method	full-matrix least squares	
quantity minimized	$\sum w(F_o - F_c)^2$	
absolute confign	N/A	
extinction cor	$\chi = 0.0026(7)$, $F^* = F[1 + 0.002\chi F^2/\sin 2\theta]^{-1/4}$	$\chi = 0.0015(2)$
H atoms	riding model, fixed isotropic U	
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0001F^2$	$w^{-1} = \sigma^2(F) + 0.0009F^2$
final R indices (obsd data)	R = 3.40%, R_w = 3.96%	R = 3.09%, R_w = 3.99%
R indices (all data)	R = 3.97%, R_w = 3.99%	R = 4.44%, R_w = 4.37%
goodness of fit	2.70	1.00
largest and mean Δ/σ	1.174, 0.042	1.293, 0.376
data-to-param ratio	9.8:1	10.0:1
largest diff peak (e/Å^3)	0.25	0.22
largest diff hole (e/Å^3)	−0.28	−0.19

different stagger between methyl groups is another reflection of the greater covalent radius of Si compared to C, which permits a smaller eclipsed angle before the methyl group interactions become crucial. The various C_{methyl}–Si–C_{methyl} bond angles for Ib and IIb are larger than the $C_{cyclopentadienyl}$–Si–Si angles, reflecting the constraint within the bridging cycle.

The significantly less steric strain in IIb compared to that in the monosilyl- and monogermylferrocenophanes[13] is reflected in its thermal stability. The singly bridged complexes are readily ring opened at mild temperatures to form linear polymers, whereas IIb is stable up to 350 °C. Heating beyond this temperature resulted in a cross-linking polymerization that yielded a material that was insoluble in all common solvents and hence has not been well characterized. Furthermore, in contrast to (1,1′-ferrocenediyl)dialkylsilanes, which are also photochemically labile with respect to ring-opening polymerization,[14] IIb exhibited no change after 12-h irradiation of an inert hydrocarbon solution in a Pyrex or quartz tube. Adding MeOH to the solvent in the presence of O_2, and using a quartz tube, resulted in photochemical cleavage of the Si–Si bond and formation of 1,1′-bis(methoxydimethylsilyl)ferrocene (IV) and (1,1′-ferrocenediyl)tetramethyldisiloxane (V) (eq 1). This result is in accord with that

$$\mathrm{IIb} \rightarrow (\eta^5\text{-}C_5H_4SiMe_2OMe)_2Fe + (\eta^5\text{-}C_5H_4)_2Fe(\mu\text{-}SiMe_2OSiMe_2) \quad (1)$$

$$\mathrm{Ib} \rightarrow 2FcSiMe_2OMe \quad (2)$$

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Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)

	x	*y*	*z*	*U*(eq)[a]
		Compound Ib		
Fe	719(1)	222(1)	3197(1)	47(1)
Si	659(1)	496(1)	751(1)	53(1)
C1	131(3)	–496(4)	1746(3)	48(1)
C2	652(4)	–1955(5)	2357(2)	62(2)
C3	–36(5)	–2232(5)	3026(3)	74(2)
C4	–986(4)	–975(6)	2849(3)	68(2)
C5	–896(3)	86(5)	2071(3)	56(1)
C6	2136(4)	1989(6)	3409(3)	80(2)
C7	2507(4)	608(6)	4067(3)	81(2)
C8	1707(4)	536(6)	4630(3)	81(2)
C9	839(4)	1860(6)	4338(3)	80(2)
C10	1088(5)	2775(6)	3572(3)	85(2)
C11	559(4)	2955(5)	781(3)	76(2)
C12	2309(4)	–212(6)	915(3)	78(2)
		Compound IIb		
Fe	5347(1)	–5(1)	3378(1)	42(1)
Si1	5285(1)	937(1)	1501(1)	36(1)
Si2	3757(1)	–1056(1)	1483(1)	39(1)
C1	6128(3)	1232(4)	2617(2)	41(1)
C2	7123(3)	246(5)	3128(2)	56(2)
C3	7275(4)	646(6)	3949(2)	71(2)
C4	6404(5)	1854(6)	3964(2)	68(2)
C5	5694(4)	2228(5)	3150(2)	57(2)
C6	3878(3)	–1273(4)	2590(2)	43(1)
C7	4797(4)	–2246(5)	3164(3)	63(2)
C8	4781(5)	–1805(6)	3954(2)	73(2)
C9	3890(4)	–601(6)	3893(3)	68(2)
C10	3315(3)	–262(5)	3055(2)	54(2)
C11	4415(3)	2738(5)	1052(3)	60(2)
C12	6603(4)	430(5)	1010(2)	58(2)
C13	4274(4)	–2895(5)	1108(3)	70(2)
C14	1981(3)	–578(5)	908(2)	60(2)

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

obtained upon photolysis of Ib when (methoxydimethylsilyl)ferrocene was obtained upon photolysis under similar conditions (eq 2),[7] and the formation of V concurs with the results obtained by the Kumada group via oxidative acid methanolysis of IIb.[8c] From our study it was possible to see the gradual transformation of IV to V over time, and it appears that IV was the initial photoproduct and that the condensation to V was a thermal, not photochemical, transformation.

In the absence of methanol oxidative photochemistry of IIb in C_6D_6 led to low-efficiency transformation to V. Treatment of IIb with O_2 in methanol in the absence of photochemical irradiation led to the slow formation of V and $FcSiMe_2OSiMe_2OMe$.

The electrochemical properties of Ia–c (and the analogs with $n = 0$ (biferrocene) and 6 (If)) and IIa–c were studied via cyclic voltammetry, and the resulting data are recorded in Table IV and, for complexes I, illustrated in Figure 4. The bis(ferrocenyl) complexes I exhibited two discrete reversible oxidations for the complexes with silicon bridges containing zero, one, and two silicon atoms. The separation between the two distinct oxidation potentials becomes progressively smaller ($n = 0 > 1 > 2 > 3$), and for $n = 6$ it is possible to observe only a single oxidation process. This effect, due to the transmission of the electronic impact of a ferrocenium ion upon a neighboring Fc unit, has been observed for saturated carbon-bridged differocenes $Fc(CH_2)_nFc$, but only for the systems $n = 0, 1$, since for $n = 2$ only a single oxidation was observed; clearly the silicon chain is a superior bridge for the communication between the two Fc units.[16] When the carbon bridge contains an unsaturation, e.g. an acetylenic group, a separation between the two one-electron-oxidation potentials is noted;[17] thus, the present data are further examples that silicon atoms possess many electronic transmission characteristics of unsaturated alkene/alkyne fragments.[18] The ferrocenophane complexes II exhibit a

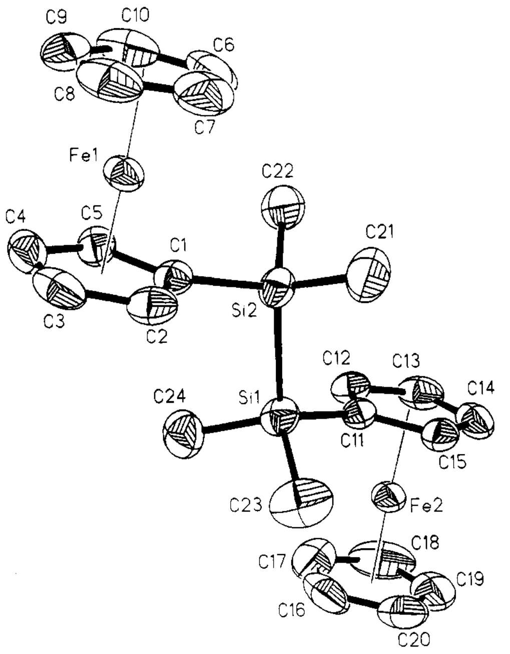

Figure 2. Structure of Ib.

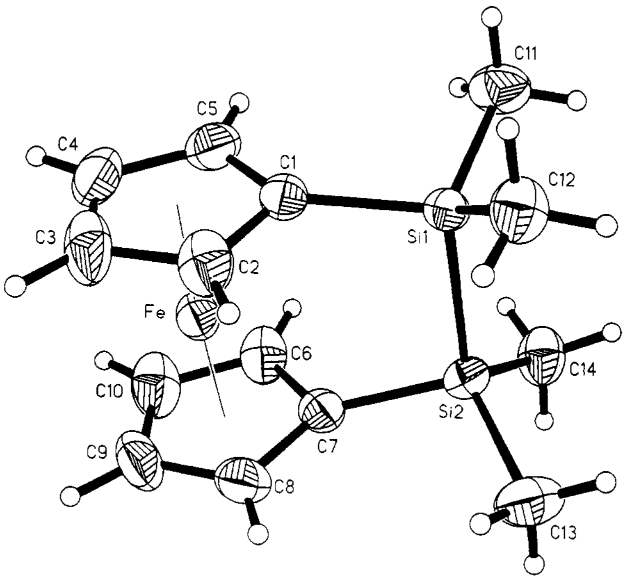

Figure 3. Structure of IIb.

Table III. Selected Bond Lengths (Å) and Angles (deg)

	Complex IIb		
Si1–Si2	2.351(1)	C6–Si2–Si1	102.7(2)
Si1–C1	1.881(3)	Si2–Si1–C1	102.9(2)
Si2–C6	1.883(4)	C13–Si2–C14	110.5(3)
Si1–C12	1.870(3)	C13–Si2–C6	109.0(3)
Si2–C13	1.867(4)	C12–Si1–Si2	114.0(2)
	Complex Ib		
Si1–Si1a	2.340(1)	C1–Si1–Si1a	108.7(1)
Si1–C1	1.862(4)	C11–Si1–C12	110.3(2)
Si1–C12	1.871(4)	C11–Si1–C1	110.5(2)

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Table IV. Oxidation Potentials (E_{pa}, V) and Difference of Potentials (ΔE_{pa}, V) for Complexes I and II

complex	$E_{pa}(1)$	$E_{pa}(2)$	ΔE_{pa}
biferrocene	0.46	0.80	0.34
Ia	0.58	0.73	0.15
Ib	0.56	0.67	0.11
Ic	0.54	0.62	0.08
If	0.58		0.00
ferrocene	0.60		
IIa	0.58		
IIb	0.67		
IIc	0.56		

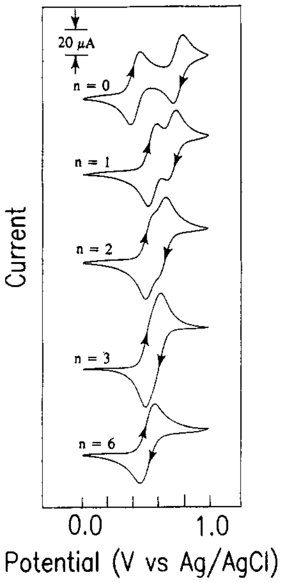

Figure 4. Electrochemical properties of complexes $Fc(SiMe_2)_nFc$ (I).

single oxidation; however, the reversibility was variable. For IIa with a single silicon atom bridging the two cyclopentadienyl rings the voltammogram was irreversible at the scan rates used in our study, whereas the two-silicon-atom bridge complex IIb was reversible, but only for a few cycles. This cycling resulted in a gradual decomposition that produced a transient uncharacterized species with E_{ox} = 0.74 V and E_{red} = 0.72 V. In contrast IIc, with a three-Si-atom bridge, exhibited a perfectly reversible redox at E_{ox} = 0.56 V and E_{red} = 0.50 V, which is stable upon recycling. The trend for the electrochemistry in the three systems with one, two, or three silicon atoms in the bridging unit result in nonreversibility (n = 1), partial reversibility on the cyclic voltammetric time scale (n = 2), or total reversibility (n = 3). Oxidation of the Fe atom in ferrocene increases the Fe–cyclopentadienyl ring center distance by approximately 0.04 Å,[15] thus placing a considerable structural strain upon the bridging unit which is insupportable by a small bridge. These results may be contrasted with those obtained from carbon-bridged ferrocenophanes, in which a two-carbon bridge could not support the distortions resulting upon oxidation and no reversibility was obtained.[19] The degree of reversibility noted for IIb reflects the greater bridging span of the disilyl group.

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Supplementary Material Available: Tables of all bond lengths and angles, anisotropic thermal parameters for non-hydrogen atoms, and positional and isotropic thermal parameters for hydrogen atoms for compounds Ib and IIb (8 pages). Ordering information is given on any current masthead page.

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(18) It was possible to observe the expected optical properties for the ferrocenium ions produced in the electrochemical study (λ_{max} in the range 628–680 nm). Furthermore, in certain cases a presumed intravalence band around 1500 nm was observed. A detailed study of this aspect of the complexes is currently in progress with Professor Paul Braterman, University of North Texas.

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