Synthesis, Spectroscopy, Electrochemical Characterization, and Nonlinear Optical Properties of Ferrocenyloligosilanes: $FcSi_nMe_{2n}(C_6H_5)$ (n = 1−6) and $FcSi_2Me_4(C_6H_4\text{-}X)$ (X = *m*-CF_3, *p*-Cl, *p*-Br, *p*-OMe, *p*-NMe_2, *p*-CH=C$(CN)_2$)

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New ferrocenyloligosilylene aryl complexes have been synthesized, $FcSi_nMe_{2n}C_6H_5$ (n = 1−6) and $FcSi_2Me_4\{C_6H_4\text{-}X\}$ (X = *m*-CF_3. *p*-Cl, *p*-Br, *p*-OMe, *p*-NMe_2, *p*-CH=C$(CN)_2$). The complexes have been evaluated with respect to their electrochemical redox and NLO hyperpolarizability properties. All complexes possess oxidation potentials that reflect, systematically but weakly, the various substituents on the aryl group, thereby indicating an aryl−ferrocenyl interaction via the silicon chains. However, hyperpolarizabilities of the complexes are generally similar to those of the corresponding substituted benzenes, with the exception of the most electron-withdrawing substituents, *p*-Cl and *p*-CH=C$(CN)_2$.

Introduction

There is current interest in the synthesis of new materials with large second-order optical nonlinearities, and organometallic compounds have been shown to be a useful general class of such materials.[1−4] For example, Marder et al. demonstrated that when the donor ferrocenyl group [(η^5-C_5H_4)Fe(C_5H_5)] (Fc) was connected by an ethylene linkage to the 1-methylpyridinium acceptor group, large powder SHG efficiencies (up to 200 times that of urea) were obtained.[1b] In a separate series of articles we reported that nonlinear optical properties were observed for oligosilanes and that the efficiency of such systems depended upon the number of silicon atoms in the chain.[5] We have also reported that ferrocenyl groups bridged via oligosilyl chains exhibit significant charge communication between the two Fc groups when the chain possesses one to four Si atoms.[6] On the basis of these data we have synthesized and studied a series of complexes in which the Fc group is separated from an acceptor group by an oligosilane chain: $FcSi_nMe_{2n}(C_6H_5)$ (n = 1−6 (**1**−**6**)) and $FcSi_2Me_4$-$(C_6H_4\text{-}X)$ (X = *m*-CF_3 (**2a**), *p*-Cl (**2b**), *p*-Br (**2c**), *p*-OMe (**2d**), *p*-NMe_2 (**2e**), *p*-CH=C$(CN)_2$) (**2g**))

Experimental Section

Synthetic manipulations were performed under an argon atmosphere using standard Schlenk techniques. The starting silicon compounds Me_2SiCl_2 and $PhSiMe_2Cl$ were purchased from Hüls America Inc., chloromercurioferrocene was obtained from Strem Chemicals, and malononitrile, 1,4-dichlorobenzene, 1,4-dibromobenzene, 4-bromoanisole, 3-bromobenzotrifluoride, 4-bromo-*N*,*N*-dimethylaniline, and piperidine were purchased from Aldrich Chemicals and were used as received. *N*,*N*-Dimethylformamide (Aldrich) was allowed to stand on 4 Å molecular sieves. NMR spectra were recorded on a Bruker NR 200 MHz spectrometer, IR spectra were recorded on a Perkin-Elmer 1600 FT IR spectrometer, and mass spectra were obtained on a 70 eV Hewlett-Packard 5890/5971 GC/mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc.

Ferrocenyloligosilanes $FcSi_nMe_{2n}(C_6H_5)$ (n = 1−6) and $FcSiMe_2SiMe_2(C_6H_4\text{-}X)$ (X = *p*-Cl, *p*-Br, *p*-OMe, *m*-CF_3) were synthesized by two general procedures. As typical examples the two syntheses of $FpSiMe_2SiMe_2Ph$ are described below.

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The spectroscopic and analytical data for the ferrocenyloligosilanes are recorded in Table 1.

Synthesis of $FcSiMe_2SiMe_2Ph$. Method A. FcLi + $ClSiMe_2SiMe_2Ph$ (2). To a stirred solution of l-chloro-2-phenyl-l,1,2,2-tetramethyldisilane[7] (6 g, 7.0 mmol) in 20 mL of THF at −25 °C was added slowly a 50 mL solution of ferrocenyllithium obtained from 2.95 g (7.0 mmol) of chloromercurioferrocene and *n*-BuLi.[8] 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, and the di-*n*-butylmercury was removed by distillation (61−62 °C/0.5 mmHg). The red liquid residue was purified by molecular distillation with a Kugelrohr (108−110 °C/0.03 mmHg) to yield 1.75 g (4.63 mmol, 66%) of the title complex.

Method B. $FcSiMe_2SiMe_2Cl$ + PhMgBr. (a) Synthesis of $FcSiMe_2SiMe_2Cl$. A solution of ferrocenyllithium was prepared from 6.3 g (15 mmol) of chloromercurioferrocene and *n*-butyllithium (15.8 mmol) in 60 mL of THF. After the solvent was removed in vacuo, 60 mL of degassed cyclohexane was added to the solid $[Fc]^-Li^+$. A solution of 1,2-dichlorotetramethyldisilane[7] (2.80 g, 15.0 mmol) in 60 mL of cyclohexane was added dropwise to the heterogeneous mixture at 0 °C. The reaction mixture was stirred vigorously for 2 h, and then the mixture was filtered through a sintered-glass frit and concentrated in vacuo to about 5 mL. Di-*n*-butylmercury was removed by fractional distillation (52−54 °C/0.1 mmHg), and $FcSiMe_2SiMe_2Cl$ was distilled at 108−110 °C/0.1 mmHg as a red liquid, yield 1.5 g (4.45 mmol, 30%).

(b) Reaction of $FcSiMe_2SiMe_2Cl$ with PhMgBr. To an ice-cooled solution of $FcSiMe_2SiMe_2Cl$ (0.62 g, 1.8 mmol) in 10 mL of THF was added dropwise over 45 min a solution of PhMgBr (prepared from 0.29 g (1.8 mmol) of bromobenzene and 0.04 mol of Mg). The mixture was stirred for 12 h at room temperature. At this time, THF was removed in vacuo, the residue was extracted with 30 mL of hexane, and the resulting mixture was filtered. The filtrate was concentrated to 5 mL and chromatographed on a silica gel column (20 × 2 cm). The orange band that developed with hexane was collected and upon evaporation of the solvent yielded $FcSiMe_2SiMe_2Ph$ as a red oil, yield 0.31 g (0.82 mmol, 45%).

Synthesis of $FcSiMe_2SiMe_2(C_6H_4$-*p*-$N(CH_3)_2)$. To a suspension of magnesium (0.64 mol) in 20 mL of THF was added a crystal of iodine followed by 5.0 g (26.7 mmol) of 1,2-dichlorotetramethyldisilane. To this mixture was added 5.3 g (26.5 mmol) of 4-bromo-*N*,*N*-dimethylaniline in 20 mL of THF slowly by syringe. The reaction mixture was stirred for 4 h at room temperature. To this in situ generated $ClSiMe_2SiMe_2$-C_6H_4-*p*-NMe_2 was added slowly, over 1 h at −25 °C, 100 mL of a THF solution of ferrocenyllithium (prepared from 10.0 g, 23.7 mmol, of chloromercurioferrocene). The mixture was stirred at low temperature for 1 h and then slowly warmed to room temperature and further stirred for 12 h. At this time, the solvent was removed on a rotary evaporator, the residue was extracted with 100 mL of hexane, and the extracts were filtered. The filtrate was concentrated to 10 mL, di-*n*-butylmercury was removed by fractional distillation (60−62 °C/0.5 mmHg), and the residue was chromatographed on a silica gel column (2.5 × 15 cm) developed with hexane. The orange band that developed with 90/10 hexane/methylene chloride mixture was collected and, after removal of the solvent, yielded $FcSiMe_2SiMe_2(C_6H_4$-*p*-$N(CH_3)_2)$ as an orange solid, which was recrystallized from hexane (2.5 g, 5.94 mmol, 25%).

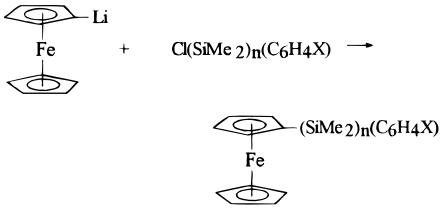
Synthesis of $FcSiMe_2SiMe_2(C_6H_4$-*p*-CHO). To a suspension of magnesium (0.19 mol) in 15 mL of THF was added a crystal of iodine. To this was added slowly a solution of 1-ferrocenyl-2-(4-bromophenyl)-1,1,2,2-tetramethyldisilane (3.7 g, 8.1 mmol) in 20 mL of THF. The mixture was refluxed for 17 h. This Grignard reagent was slowly cannulated into a solution of DMF (1.17 g, 16.0 mmol) in 10 mL of THF. The mixture was stirred for 20 h at room temperature. The reaction was quenched with 100 mL of 5% NaOH solution, and the resulting mixture was extracted with 100 mL of ethyl acetate. The organic layer was dried over $MgSO_4$, and the solvent was removed. Column chromatography on silica gel (hexane/methylene chloride, 90/10) yielded $FcSiMe_2SiMe_2(C_6H_4$-*p*-CHO) as a yellow powder, recrystallized from hexane (1.35 g, 3.32 mmol, 41%).

Synthesis of $FcSiMe_2SiMe_2(C_6H_4$-*p*-$CH{=}C(CN))$. To a solution of 0.86 g (2.1 mmol) of $FcSiMe_2SiMe_2(C_6H_4$-*p*-CHO) dissolved in a mixture of THF (3 mL) and ethanol (15 mL) was added 0.14 g (2.1 mmol) of solid malononitrile and a drop of piperidine. An immediate color change from yellow to dark red was observed. The mixture was stirred for 15 min, and then solvents were removed in vacuo. The red sticky residue was extracted with 5 mL of methylene chloride and passed through a silica gel column (25 × 2 cm), and a red band was eluted with methylene chloride. Evaporation of the solvent yielded the title complex as a red solid (0.63 g, 1.39 mmol, 66%).

Electrochemical and NLO Measurements. Materials and apparatus for electrochemistry and coupled UV−visible spectroscopy have been described elsewhere;[20] the data are recorded in Table 2. Hyperpolarizability (β) measurements were performed using the electric field induced second harmonic (EFISH) method.[10−14] The absorption maxima, dipole moments, and hyperpolarizabilities of the ferrocenyloligosilane complexes are listed in Table 3.

Results and Discussion

Synthesis and Spectroscopic Properties of Ferrocenyloligosilanes. The incorporation of the ferrocene unit into the oligosilane chains posed no significant synthetic problems and standard Grignard and salt-elimination chemistry was used (eq 1 and Scheme 1).



n = 1; X = H (**1**)
n = 2; X = H (**2**); *m*-CF_3 (**2a**); *p*-Cl (**2b**); *p*-Br (**2c**); *p*-OMe (**2d**); *p*-NMe_2 (**2e**)
n = 3; X = H (**3**)
n = 4, 5, 6; X = H (**4**, **5**, **6**)

The spectroscopic properties of the complexes are unremarkable. The ^{29}Si NMR data illustrate weak electronic effects of different substituents on the β-silicon in the series $FcSiMe_2SiMe_2(C_6H_4X)$. For example, compared to X = H, substitution of the benzene ring

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Table 1. Spectroscopic and Analytical Data for Ferrocenyloligosilanes[a]

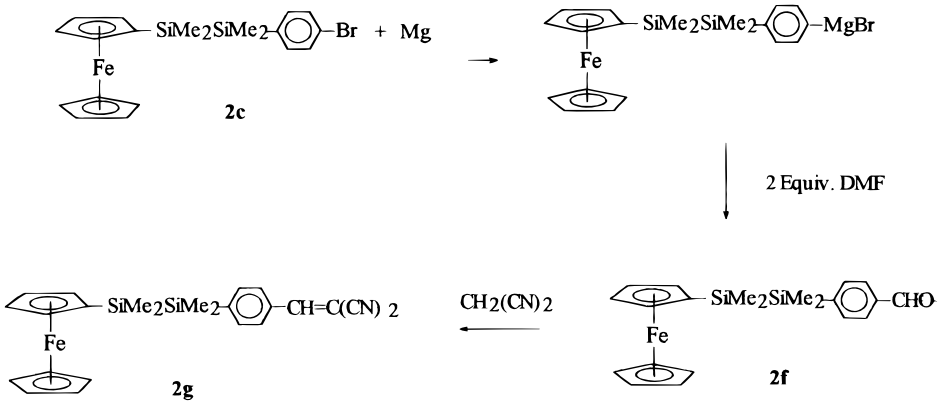
	$FcSiMe_2Ph$ (**1**)[b]
mp, °C	81−82
^1H NMR	0.47 (6H, s, $SiMe_2$); 3.97 (5H, s), 4.05 (t, 2H, J = 1.6 Hz), 4.20 (t, 2H, J = 1.6 Hz, Fc); 7.19, 7.55 (m, 5H, Ph)
^{13}C NMR	−1.45 ($SiMe_2$); 68.5, 69.9, 71.3, 73.7 (Fc); 129.1, 133.3, 134.0, 139.9 (Ph)
^{29}Si NMR	−7.22
MS, *m*/*e* (%)	320 (100); 305 (55); 289 (1); 255 (8); 183 (5); 121 (11); 56 (6)
	$FcSiMe_2SiMe_2Ph$ (**2**)
anal. calcd (found)	C, 63.47 (63.55); H, 6.92 (6.90)
^1H NMR	0.33 (6H, s), 0.34 (6H, s, $SiMe_2$); 3.92 (2H, t), 4.00 (5H, s), 4.17 (2H, t, Fc); 7.18, 7.45 (5H, m, Ph)
^{13}C NMR	−3.65, −2.91 ($SiMe_2$); 68.3, 71.0, 73.2 (Fc); 128.7, 134.2, 139.5 (Ph)
^{29}Si NMR	−22.59, −21.75
MS, *m*/*e* (%)	378 (35); 363 (1); 243 (100); 135 (7); 121 (5); 93 (5), 56 (2)
	$FcSiMe_2SiMe_2(C_6H_4$-*m*-$CF_3)$ (**2a**)
anal. calcd (found)	C, 56.49 (56.10); H, 5.64 (5.79)
^1H NMR	0.23, 0.26 (12H, s, $SiMe_2$); 3.83 (2H, t, J = 1.8 Hz), 4.01, (5H, s), 4.17 (2H, t, J = 1.8 Hz); 7.00, 7.36−7.39, 7.79 (4H, m, Ph)
^{13}C NMR	−4.09, −3.87 ($SiMe_2$); 68.2, 70.4, 71.2, 73.0 (Fc); 125.28, 125.34, 128.18, 130.46, 137.33, 141.39 (Ph and CF_3)
^{29}Si NMR	−21.79, −21.65
MS, *m*/*e* (%)	446 (32); 427 (2); 243 (100); 313 (9); 203 (12); 148 (5); 121 (11); 93 (8)
	$FcSiMe_2SiMe_2(C_6H_4$-*p*-Cl) (**2b**)
anal. calcd (found)	C, 58.18 (57.66); H, 6.10 (6.31)
^1H NMR	0.24, 0.28 (12H, $SiMe_2$); 3.85 (2H, t), 4.00 (5H, s), 4.16 (2H, 5, Fc); 7.16−7.17 (4B, m, Ph)
^{13}C NMR	−3.83, −3.15 ($SiMe_2$); 68.3, 70.7, 71.1, 73.1 (Fc); 128.2, 135.1, 135.5, 137.9 (Ph)
^{29}Si NMR	−22.27, −21.88
MS, *m*/*e* (%)	412 (20); 397 (1); 243 (100); 169 (7); 121 (6); 93 (5)
	$FcSiMe_2SiMe_2(C_6H_4$-*p*-Br) (**2c**)
anal. calcd (found)	C, 52.52 (52.63); H, 5.51 (5.55)
mp, °C	54−55
^1H NMR	0.36, 0.37 (12H, s, $SiMe_2$); 3.98 (2H, t, J = 1.6 Hz), 4.13 (5H, s), 4.29 (2H, t, J = 1.6 Hz), 7.19−7.23 (2H, d, J = 8 Hz), 7.45−7.49 (2H, d, J = 8 Hz, Ph)
^{13}C NMR	−3.89, −3.17 ($SiMe_2$); 68.3, 70.7, 71.1, 73.1 (Fc); 123.6, 131.1, 135.7, 138.4 (Ph)
^{29}Si NMR	−21.74, −21.48
MS, *m*/*e* (%)	458 (16); 243 (100); 213 (9); 121 (10); 93 (8), 73 (2)
	$FcSiMe_2SiMe_2(C_6H_4$-*p*-OMe) (**2d**)
anal. calcd (found)	C, 61.75 (61.70); H, 6.91 (6.33)
^1H NMR	0.363, 0.367 (12H, s, $SiMe_2$); 3.32 (3H, s, OMe); 3.95 (2H, t, J = 1.4 Hz), 4.01 (5H, s) 4.18 (2H, t, J = 1.4 Hz, Fc); 6.84−6.88 (2H, d, J = 8.4 Hz), 7.36−7.41 (2H, d, J = 8.4 Hz, Ph)
^{13}C NMR	−3.31, −2.81 ($SiMe_2$); 54.5 (OMe); 68.3, 71.0,71.2, 73.2 (Fc); 114.1, 128.5, 135.5, 160.7 (Ph)
^{29}Si NMR	−22.99, −21.89
MS, *m*/*e* (%)	408 (33); 393 (3); 243 (100); 213 (7); 165 (12); 121 (10); 93 (6); 73 (1)
	$FcSiMe_2SiMe(C_6H_4$-*p*-$NMe_2)$ (**2e**)
anal. calcd (found)	C, 62.69 (61.20); H, 7.41 (6.99); N, 3.33 (3.11)
mp, °C	80
^1H NMR	0.41, 0.43 (12H, s, $SiMe_2$); 2.52 (6H, s, $-NMe_2$); 3.97−4.03 (7H, s, t), 4.19 (2H, t), 6.64-6.68 (2H, d, J = 8.2 Hz), 7.44−7.48 (2H, d, J = 8.2 Hz, Ph)
^{13}C NMR	−3.1, −2.59 ($SiMe_2$); 39.88 ($-NMe_2$); 68.3, 70.9, 71.8, 73.3 (Fc); 112.6, 124.1, 135.2, 151.1 (Ph)
^{29}Si NMR	−23.54, −21.92
MS, *m*/*e* (%)	504 (20); 485 (2); 243 (100); 203 (9); 121 (10); 73 (11)
	$FcSiMe_2SiMe_2(C_6H_4$-*p*-CHO) (**2f**)
anal. calcd (found)	C, 62.05 (60.36); H, 6.44 (6.62)
mp, °C	94
^1H NMR	0.40, 0.41 (12H, s, $SiMe_2$); 3.98 (2H, t, J = 1.8 Hz), 4.13 (5H, s), 4.30 (2H, t, J = 1.8 Hz, Fc); 7.29, 7.71 (4H, dd, J = 8 Hz, Ph); 9.85 (−CHO)
^{13}C NMR	−4.12, −3.21 ($SiMe_2$); 68.3, 70.5, 71.1, 73.1 (Fc); 134.5, 138.9, 148.1 (Ph); 191.5 (C═O)
^{29}Si NMR	−21.41, −21.11
IR (hexane), cm^{-1}	1710 ν(C═O)
	$FcSiMe_2SiMe_2(C_6H_4$-*p*-CH═$C(CN)_2)$ (**2g**)
anal. calcd (found)	C, 63.42 (62.70); H, 5.76 (5.92)
mp, °C	84−85
^1H NMR	0.33, 0.35 (12H, s, $SiMe_2$); 3.92 (2H, t, J = 1.6 Hz), 4.08 (5H, s), 4.26 (2H, t, J = 1.6 Hz, Fc); 6.64 (1H, s, −CH═C); 7.25, 7.37−7.41 (4H, m, Ph)
^{13}C NMR	−4.24, −3.22 ($SiMe_2$); 68.4, 68.6, 71.2, 73.0 (Fc); 82.5 (−CH═$C(CN)_2$); 113.1, 114.1 (−CH═$C(CN)_2$); 129.3, 130.9, 134.6, 149.3 (Ph); 158.8 (−*CH*═C)
^{29}Si NMR	−21.0, −20.9
IR (hexane), cm^{-1}	2227 ν(CN), 1588 ν(C═C)
	$FcSiMe_2SiMe_2Cl$ (**2h**)
^1H NMR	0.37 (12H, s, $SiMe_2$); 3.95 (2H, t), 4.02 (5H, s), 4.17 (2H, t, Fc)
^{13}C NMR	−3.63 ($SiMe_2$); 2.27 ($SiMe_2Cl$); 68.9, 72.5, 73.3 (Fc)
^{29}Si NMR	21.28 ($SiMe_2Cl$), −21.39 ($SiMe_2Fc$)

Table 1 (Continued)

	$FcSiMe_2SiMe_2SiMe_2Ph$ (**3**)
anal. calcd (found)	C, 60.52 (60.52); H, 7.38 (7.51)
mp, °C	60
^{1}H NMR	0.14 (6H, s, $-SiMe_2-$), 0.32, 0.33 (12H, s, Fc-$SiMe_2$ & Ph$-SiMe_2$); 3.91 (2H, t, J = 1.6 Hz), 4.04 (5H, s), 4.18 (2H, t, J = 1.6 Hz, Fc); 7.16−7.20, 7.42−7.45 (5H, m, Ph)
^{13}C NMR	−6.30, −2.97, −2.54 ($SiMe_2$); 68.3. 71.0, 72.0. 73.1 (Fc); 128.5, 134.1, 139.9 (Ph)
^{29}Si NMR	−48.37 ($SiMe_2$); −18.65 (Fc-$SiMe_2$ & Ph-$SiMe_2$)
MS, *m/e* (%)	436 (25); 421 (0.5); 299 (1); 243 (100); 135 (12); 121 (5); 93 (6); 73 (7)
	$FcSiMeSiMe_2SiMe_2SiMe_2Ph$ (**4**)
anal. calcd (found)	C, 58.26 (58.03); H, 7.74 (7.64)
mp, °C	44
^{1}H NMR	0.11, 0.15 (12H, s, $-SiMe_2-SiMe_2-$), 0.37, 0.38 (12H, s, Fc$-SiMe_2$ & Ph$-SiMe_2$); 3.93 (2H, t, J = 1.6 Hz), 4.01 (5H, s), 4.18 (2H, t, J = 1.6 Hz, Fc); 7.16−7.19, 7.43 (5H, m, Ph)
^{13}C NMR	−5.34, −2.75, −2.28 ($SiMe_2$); 68.3, 71.0, 72.1, 73.1 (Fc); 128.5, 128.7, 134.1, 139.1 (Ph)
^{29}Si NMR	−44.72, −44.63, −18.15, −18.02
MS, *m/e* (%)	494 (24); 479 (0.5); 299 (3); 243 (100), 135 (12); 73 (8)
	$FcSiMe_2SiMe_2SiMe_2SiMe_2SiMe_2Ph$ (**5**)
anal. calcd (found)	C, 56.48 (55.95); H, 8.02 (8.19)
mp, °C	75−76
^{1}H NMR	0.15. 0.18. 0.21, 0.40, 0.41 (s, $SiMe_2$); 3.96 (2H, t), 4.06 (5H, s), 4.18 (2H, t, Fc); 7.16, 7.45−7.49 (5H, m, Ph)
^{13}C NMR	−5.09, −4.39, −2.79, −2.26 ($SiMe_2$); 68.3, 71.0, 72.2, 73.1 (Fc); 128.4, 134.0, 139.9 (Ph)
^{29}Si NMR	−43.12, −42.85, −40.03, −17.73, −17.54
MS, *m/e* (%)	552 (1); 343 (3); 299 (5); 285 (6); 243 (100); 177 (5); 135 (23); 73 (25)
	$FcSiMe_2SiMe_2SiMe_2SiMe_2SiMe_2SiMe_2Ph$ (**6**)
anal. calcd (found)	C, 55.03 (54.51); H, 8.24 (8.55)
^{1}H NMR	0.24, 0.26, 0.27, 0.29, 0.46, 0.48 ($SiMe_2$); 4.02 (2H, t), 4.11 (SiH, s), 4.24 (2H, t, Fc); 7.21−7.25, 7.51 (5H, m, Ph)
^{13}C NMR	−5.03, −4.08, −2.73. −2.20 ($SiMe_2$); 68.3, 71.0, 72.2, 73.1 (Fc); 128.7, 134.1, 139.2 (Ph)
^{29}Si NMR	−43.02, −42.74, −38.83, −38.61, −17.69, −17.47

[a] Samples with no melting point data are oils. NMR data (ppm) were recorded in C_6D_6. In ^{13}C NMR spectra, some resonances due to the phenyl group were masked by the solvent resonances. [b] See ref 9.

Scheme 1



with electron-releasing groups such as *p*-NMe_2 and *p*-OMe causes an ∼1 ppm high field shift of the *β*-silicon, whereas introduction of the electron-withdrawing groups *m*-CF_3, *p*-CH=C$(CN)_2$, and *p*-CHO onto the ring causes a 1 ppm low-field shift.

Electrochemical Studies. The electrochemical behavior of silicon-substituted ferrocenes,[6,15,16] polyferrocenes,[16a,c,d,17] and ferrocenyl and ferrocenylene polymers[18] is a routine characterization. Yellow-orange dichloromethane solutions of the complexes $FcSi_nMe_{2n}(C_6H_5)$ (n = 1−3) undergo the expected oxidation of the ferrocenyl unit through chemically reversible electron transfers, resulting in blue ferrocenium ion solutions (Table 2). Controlled-potential coulometry and appropriate cyclic voltammograms on the complexes with n = 1 and 3 signify transfer of one electron/molecule.[19] How-

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Table 2. Formal Electrode Potentials (V, vs SCE), Peak-to-Peak Separation (mV), Optical Properties (nm), and Relevant Hammett Substituent Constants for the Oxidation of Substituted Ferrocenes

complex	$E^{\circ\prime}_{0/+}$	E_p[a]	λ_{max}[b]	I_X[f]
$FcSiMe_3$	+0.42[c]	82	626	
	+0.40[d]	90		
$FcSiMe_2Ph$ (**1**)	+0.44[c]	84	631	
	+0.41[d]	81		
$FcSiMe_2SiMe_2Ph$ (**2**)	+0.42[c]	78	*e*	
	+0.38[d]	95		
$FcSiMe_2SiMe_2SiMe_2Ph$ (**3**)	+0.41[c]	80	684	
	+0.37[d]	86		
FcH	+0.43[c]	90	620	
	+0.39[d]	94		
$FcSiMe_2SiMe_2(C_6H_4$-*m*-$CF_3)$ (**2a**)	+0.42[c]	72	*e*	+0.43
	+0.40[d]	90		
$FcSiMe_2SiMe_2(C_6H_4$-*p*-Cl) (**2b**)	+0.43[c]	80		+0.24
	+0.40[d]	82		
$FcSiMe_2SiMe_2(C_6H_4$-*p*-OMe) (**2d**)	+0.41[c]	88		−0.28
	+0.37[d]	74	*e*	
$FcSiMe_2SiMe_2(C_6H_4$-*p*-$NMe_2)$ (**2e**)	+0.40[c]	75	*e*	−0.83
	+0.36[d]	78		
$FcSiMe_2SiMe_2(C_6H_4$-*p*-CHO) (**2f**)	+0.42[c]	84	*e*	+0.42
	+0.37[d]	72		
$FcSiMe_2SiMe_2(C_6H_4$-*p*-CH=$C(CN)_2$) (**2g**)	+0.43[c]	77	*e*	+0.54
	+0.40[d]	70		

[a] Measured at 0.2 V s^{-1}. [b] Referred to the ferrocenium cation. [c] Supporting electrolyte $[NBu_4]ClO_4$ (0.2 M). [d] Supporting electrolyte $[NBu_4]PF_6$ (0.2 M). [e] Coupled to chemical complications (see text). [f] From ref 21.

ever, similar studies on the disilane complexes $FcSiMe_2SiMe_2Ar$ indicate that a side reaction accompanies the electrogeneration of $[FcSiMe_2SiMe_2Ar]^+$ ($E^{\circ\prime}_{0/+} = +0.42$ V for Ar = Ph) and generates a new oxidizable species (E_{ox} is ~60 mV lower than that of $FcSiMe_2SiMe_2Ph$) which we have been unable to identify. The various aryl substituents have small, but predictable, effects on the redox potentials of the Fe center. Thus, changing from the most electron-donating substituent (NMe_2) to the most electron-withdrawing substituent ($CH{=}C(CN)_2$) causes a shift of 30 mV.

Nonlinear Optical Properties. In the oligosilane series $Fc(SiMe_2)_nPh$ ($n = 1-6$) moderate dipole moments and weak β_0 values are observed. Hyperpolarizabilities are 1 order of magnitude smaller than that of *p*-nitroaniline and are similar to those of monosubstituted benzenes. In the disilane series significant changes of dipole moment occur upon substituting electron-withdrawing or electron-accepting groups onto the phenyl ring of compound **2**. The largest increase is obtained for the vinyldicyano derivative **2g**, resulting in a value >2 times higher than that of (2,2-dicyanoethenyl)benzene.[22] The same behavior is observed for compound **2b**, where the β value is 5 times that of chlorobenzene.[10] However, both the dipole moment and the hyperpolarizability of these materials are similar to those of the trimethylsilyl analogues.[5b]

Table 3. Absorption Wavelengths (λ_{max}),[a] Dipole Moments (μ).[b] and Frequency-Independent Second-Order Polarizabilities (β_o[c]) for Ferrocenyl Oligosilanes

compd	λ_{max}[a]	μ, D	β_o, 10^{-30} esu
$FcSiMe_3$	448	1.26	0.5
1	456	4.5	0.5
2	455	1.75	−0.6
3	457	1.8	0.4
4	456	1.1	6.4
5	456	4.0	1.76
6	456	5.1	1.0
2a	457	3.15	2.2
2b	456	2.4	1.6
2d	456	1.1	−0.26
2e	455	2.4	3.5
2g	342	4.7	7

[a] Measured in chloroform. [b] Measured in dioxane.

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Supporting Information Available: Text giving NLO experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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