Synthesis, Structural Characterization, Electrochemical Properties and Polymerization Behaviour of the First Silicon-bridged [1.1]Ferrocenophane [{Fe(η-C_5H_4)$_2$SiMe$_2$}$_2$]†

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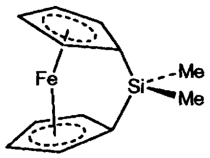
The first silicon-bridged [1.1]ferrocenophane, [{Fe(η-C_5H_4)$_2$SiMe$_2$}$_2$] **5**, was prepared in five steps starting from [Fe(η-C_5H_4Li)$_2$]·tmen (tmen = *N,N,N′,N′*-tetramethylethylenediamine). Reaction of [Fe(η-C_5H_4Li)$_2$]·tmen with $SiMe_2Cl(NEt_2)$ afforded [Fe{η-$C_5H_4SiMe_2(NEt_2)$}$_2$] **6** in high yield. Substitution of the silylamine groups of **6** for chlorine by reaction with acetyl chloride gave the dichloro species [Fe(η-$C_5H_4SiMe_2Cl$)$_2$] **7** also in high yield. Reaction of **7** with Li(C_5H_5) in tetrahydrofuran produced the intermediate [Fe{η-$C_5H_4SiMe_2(C_5H_5)$}$_2$], which was subsequently lithiated and treated with $FeCl_2$ to yield **5**, in moderate yield. A single crystal X-ray diffraction analysis of compound **5** revealed that the two ferrocene halves are in an *anti* conformation, with a Fe··· Fe distance of 5.171(9) Å. Cyclic voltammetric analysis of **5** in CH_2Cl_2 showed the presence of two reversible oxidation waves with a separation of 0.25 V consistent with an extensive interaction between the Fe centres. The room-temperature ^{57}Fe Mössbauer spectrum of **5** is similar to that of 1,1′-bis(trimethylsilyl)ferrocene with an isomer shift of 0.44(1) mm s^{-1} and a quadrupolar splitting value of 2.32(1) mm s^{-1}. Compound **5** was found to be resistant to thermal ring-opening polymerization and attempted copolymerization with the strained silicon-bridged [1]ferrocenophane [Fe(η-C_5H_4)$_2$SiMe$_2$] also proved unsuccessful.

The synthesis of high polymers containing skeletal transition-metal atoms is of current interest as a means of accessing processable materials with interesting physical, catalytic or preceramic properties.[1–4] Systems incorporating metallocene units represented some of the earliest targets of such studies. However, only recently have high molecular weight, well characterized materials been obtained with transition metals in close enough proximity to permit interactions.[2,5]

In 1992 we reported that strained, ring-tilted silicon-bridged [1]ferrocenophanes such as **1** undergo thermal ring-opening polymerization to yield high molecular weight poly(ferrocenylsilanes) (*e.g.* **2**).[6] Subsequent publications have focussed on the interesting properties of these polymers, such as their electrochemical characteristics which indicate that the iron atoms interact with one another,[7–11] and on the extension of the ring-opening polymerization route to related strained [1]- and [2]-metallocenophanes and thermal copolymerization reactions with other strained, cyclic species.[12–15] Recently we reported that in the presence of small quantities of initiators such as LiBu, living ring-opening polymerization is observed in solution.[16] This permits molecular weight control and also provides access to transition metal-based polymers with controlled architectures such as block copolymers.[16] In the presence of equimolar quantities of an anionic initiator linear oligo(ferrocenylsilanes) **3** are formed.[17] These function as valuable models with respect to the unusual electrochemical and conformational properties of the corresponding high polymers **2**.[17]

Cyclic oligomers might also function as useful models of poly(ferrocenylsilane) high polymers. Moreover, cyclic oligo(ferrocenylsilanes) have been detected as minor products in the ring-opening polymerization of strained [*n*]metallocenophanes by mass spectrometry but their role in these reactions is unclear.[12,18] In addition, we have described the formation of the unusual unsymmetrical dimer **4** as a by-product from the pyrolysis of poly(ferrocenylsilanes) at temperatures above 400 °C.[19] In contrast, formation of the symmetrical analogue **5** was not detected. In order to probe the role of cyclic oligo(ferrocenylsilane) species in the thermal ring-opening polymerization process and explore these species as models of poly(ferrocenylsilane) high polymers, we have initiated an effort to prepare and study the properties of these novel compounds. In this paper we report on the synthesis, properties and polymerization behaviour of the simplest cyclic oligo(ferrocenylsilane), the symmetrical [1.1]ferrocenophane **5**.



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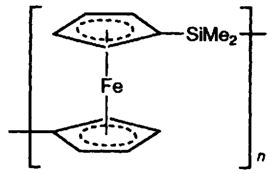

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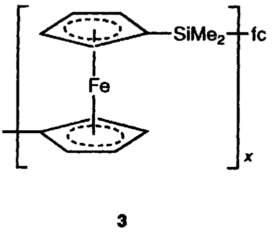

3

fc = (η-C_5H_5)Fe(η-C_5H_4)
x = 0–8

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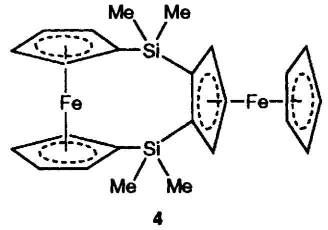
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



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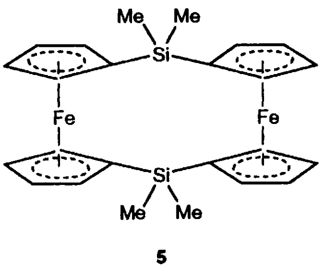
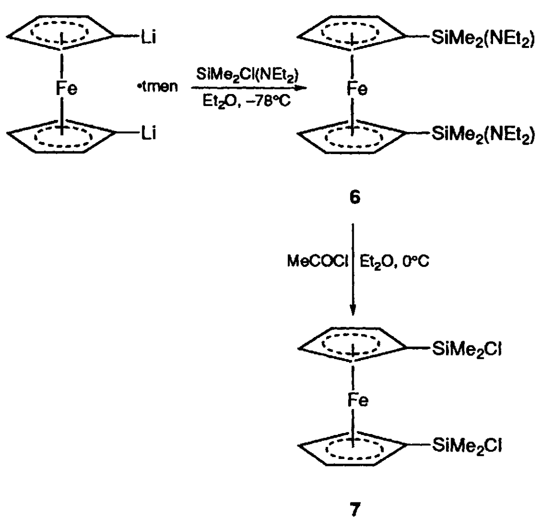


5

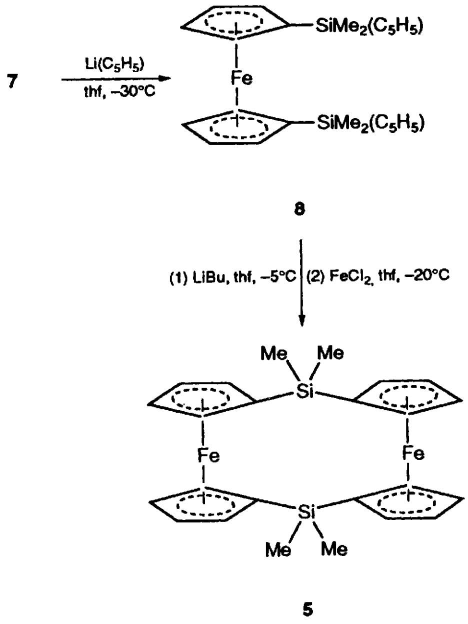
Results and Discussion

Synthesis of the [1.1]*Ferrocenophane* $[\{Fe(C_5H_4)_2SiMe_2\}_2]$ **5**.—1,1′-Disilylated ferrocenes, such as $[Fe(\eta\text{-}C_5H_4SiMe_3)_2]$, are commonly prepared from the reaction of $[Fe(\eta\text{-}C_5H_4Li)_2]$·tmen (tmen = *N,N,N′,N′*-tetramethylethylenediamine) with chlorotriorganosilanes (SiR_3Cl).[20] However, in our hands, the reactions of $[Fe(\eta\text{-}C_5H_4Li)_2]$·tmen with dichlorosilanes (SiR_2Cl_2) containing relatively small organic substitutents (*i.e.* R = Me) afford silicon-bridged [1]ferrocenophanes, $[Fe(\eta\text{-}C_5H_4)_2SiR_2]$ (*e.g.* **1**), rather than the bis(dialkylchlorosilyl)ferrocene products $[Fe(\eta\text{-}C_5H_4SiR_2Cl)_2]$, even in the presence of a large excess of the dichlorosilane.[18] We anticipated that 1,1′-bis(dialkylchlorosilyl)ferrocenes would be useful intermediates in the syntheses of novel [1.1]ferrocenophanes, and thus we have explored a strategy similar to that first reported by Schaaf and co-workers[21] to obtain these species in high yield. Prior to our work in this area, Pittman and co-workers[22] prepared the ferrocenylsilylamine $[Fe\{\eta\text{-}C_5H_4SiMe_2(NMe_2)\}_2]$ by reaction of $[Fe(\eta\text{-}C_5H_4Li)_2]$·tmen with $SiMe_2Cl(NMe_2)$. Schaaf and co-workers[21] reported the chlorination of the closely related ferrocenylsilylamine, $[Fe\{\eta\text{-}C_5H_4SiMe_2(NR_2)\}_2]$ (where NR_2 = 1-piperidyl), with a stoichiometric amount of HCl to yield the bis-chlorinated species $[Fe(\eta\text{-}C_5H_4SiMe_2Cl)_2]$.

Employing methodology similar to that of Schaaf and Pittman, we prepared $[Fe\{\eta\text{-}C_5H_4SiMe_2(NEt_2)\}_2]$ **6** and subsequently chlorinated this species to afford $[Fe(C_5H_4\text{-}SiMe_2Cl)_2]$ **7** (Scheme 1). Compound **6** was obtained as a viscous red liquid in 59% yield by reaction of $[Fe(\eta\text{-}C_5H_4Li)_2]$·tmen with a slight excess of $SiMe_2Cl(NEt_2)$. Crude **6** was purified by vacuum distillation after LiCl had been removed by filtration and its identity established by ^1H, ^{13}C and ^{29}Si NMR spectroscopy, and mass spectrometry. By employing $SiMe_2Cl(NEt_2)$ rather than $SiMe_2Cl(NMe_2)$ we were afforded the convenience of working with a liquid ($NHEt_2$) rather than gaseous ($NHMe_2$) amine in addition to realizing a considerable cost advantage. As Tamao *et al.*[23] have previously shown for other silylamines, we found that the amine groups of compound **6** can be easily exchanged for chlorine by reaction with excess acetyl chloride in diethyl ether at 0 °C to give the dichloro derivative **7**. High vacuum distillation of the reaction mixture, which first removed excess acetyl chloride and the acetylamide by-product, afforded **7** as a golden moisture-sensitive liquid in 82% yield. Upon cooling to room temperature, the distillate solidified to a golden yellow crystalline solid. While others have described the synthesis of compound **7**, minimal characterization data (^1H NMR) were reported.[21,24,25] Thus, we have further characterized this species by ^{29}Si and ^{13}C NMR spectroscopy and mass spectrometry.



Scheme 1



Scheme 2

Reaction of compound **7** with two equivalents of $Li(C_5H_5)$ in tetrahydrofuran (thf) at −30 °C (Scheme 2) yielded the intermediate, $[Fe\{\eta\text{-}C_5H_4SiMe_2(C_5H_5)\}_2]$ **8**, as a red oil which was characterized by ^1H, ^{13}C and ^{29}Si NMR spectroscopy, and mass spectrometry. The NMR data were consistent with the generation of **8** as a mixture of cyclopentadiene isomers.

Lithiation of the cyclopentadiene rings of **8** with LiBu in thf at −5 °C followed by isolation of the resulting salt $Li_2[Fe\{\eta\text{-}C_5H_4SiMe_2(C_5H_4)\}_2]$ and reaction with $FeCl_2$ in thf at −20 °C afforded a dark green-yellow reaction mixture. The solvent was removed *in vacuo* and the crude product extracted with hexane. The resulting suspension was filtered to remove LiCl and unreacted $FeCl_2$, and then concentrated *in vacuo*. Analysis of the crude yellow-orange residue by mass spectrometry revealed that it contained the desired [1.1]ferrocenophane $[\{Fe(\eta\text{-}C_5H_4)_2SiMe_2\}_2]$ **5**, but also higher cyclic oligo(ferrocenylsilanes). Recrystallization from hot hexanes afforded highly pure **5** in 35% yield. The identity of compound **5** was established by ^1H, ^{13}C and ^{29}Si NMR spectroscopy, mass

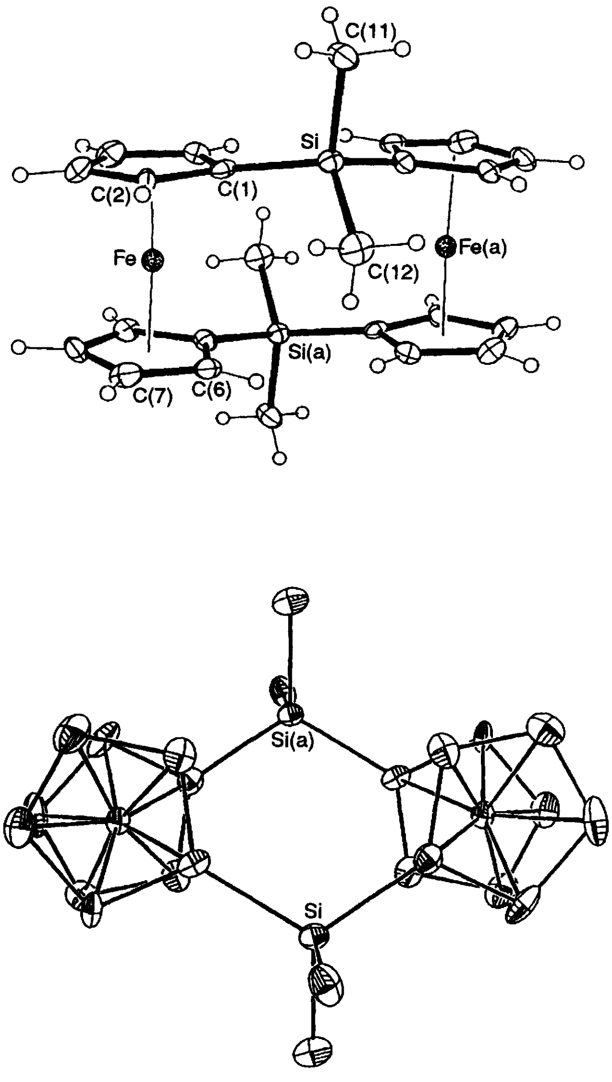


Fig. 1 Side and top ORTEP views of $[\{Fe(\eta\text{-}C_5H_4)_2SiMe_2\}_2]$ **5**

spectrometry, elemental analysis and finally by X-ray crystallography (see below).

The single resonance in the ^{29}Si NMR spectrum of **5** exhibits a chemical shift (δ −6.5) similar to those of the internal silicon atoms of the linear oligo(ferrocenylsilanes) **3** and poly(ferrocenylsilane) **2** (δ *ca.* −6.4). The *ipso*-C_5H_4 carbon ^{13}C NMR resonance of **5** is found at δ 71.4, similar to those reported for both $[Fe(\eta\text{-}C_5H_4SiMe_3)_2]$ (δ 72.0)[26] and **2** (δ 71.9).[6] In comparison, the *ipso*-C_5H_4 carbon resonance for the silicon-bridged [1]ferrocenophane **1** is located at δ 33.5, reflecting the strained, ring-tilted structure of this species.[6,27] Both the ^{29}Si and the ^{13}C NMR *ipso*-C_5H_4 carbon chemical shifts of **5** suggest that this species is relatively unstrained. Slow recrystallization of **5** from pentanes afforded orange crystals suitable for a single crystal X-ray diffraction study.

Crystal Structure of the [1.1]*Ferrocenophane* **5**.—Fig. 1 shows two alternative views of the molecular structure of compound **5**, Table 1 gives a summary of cell constants and data collection parameters, Table 2 gives fractional coordinates and Table 3 lists important bond lengths and bond angles.

Table 1 Crystallographic data for $[\{Fe(\eta\text{-}C_5H_4)_2SiMe_2\}_2]$ **5**

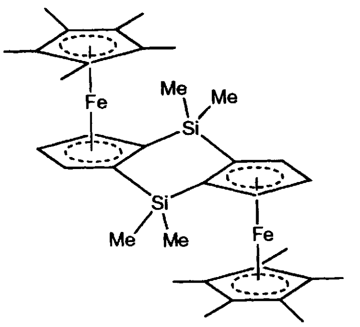
Formula	$C_{24}H_{28}Fe_2Si_2$
M	484.3
Crystal system	Monoclinic
Crystal habit	Orange plate
T/K	228
Crystal dimensions/mm	0.42 × 0.40 × 0.23
Space group	$P2_1/n$
a/Å	8.699(2)
b/Å	12.099(2)
c/Å	10.310(2)
β/°	90.55(1)
U/Å^3	1088(1)
Z	2
D_c/g cm^{-3}	1.478
(Mo-Kα)/cm^{-1}	14.51
T(max.)/T(min.)	0.339/0.303
Diffractometer	Siemens P4
Monochromator	Graphite
Radiation	Mo-Kα (λ = 0.710 73 Å)
2θ scan range	4.0–50.0
Data collected (h, k, l)	±10, +14, +12
Reflections collected	2006
Independent reflections	1899
Independent reflections [$F_o \geqslant 5\sigma(F_o)$]	1515
R	0.0759
R'	0.1398
Δ/σ(max.)	0.001
$\Delta\rho$/e Å^{-3}	1.81
N_o/N_v	11.9
Goodness-of-fit	1.55

Quantity minimized = $\Sigma w\Delta^2$; $R = \Sigma\Delta/\Sigma(F_o)$; $R' = \Sigma\Delta w^{\frac{1}{2}}/\Sigma(F_o \cdot w^{\frac{1}{2}})$, $\Delta = |(F_o - F_c)|$.

Table 2 Atomic coordinates (× 10^4) for the non-hydrogen atoms of compound **5** with estimated standard deviations in parentheses

Atom	x	y	z
Si	1 576(3)	−48(2)	−2 052(2)
Fe	2 095(1)	1 170(1)	1 147(1)
C(1)	2 005(11)	1 072(7)	−859(8)
C(2)	3 555(11)	1 354(8)	−410(8)
C(3)	3 416(12)	2 363(8)	321(10)
C(4)	1 888(14)	2 698(9)	354(11)
C(5)	1 001(12)	1 909(8)	−384(9)
C(6)	1 829(10)	−355(8)	1 989(9)
C(7)	3 182(12)	159(9)	2 476(11)
C(8)	2 761(13)	1 160(10)	3 035(10)
C(9)	1 058(14)	1 276(8)	2 924(9)
C(10)	514(11)	323(8)	2 246(8)
C(11)	2 251(11)	432(10)	−3 664(9)
C(12)	2 634(13)	−1 355(9)	−1 628(11)

The molecular structure of compound **5** consists of two ferrocene units linked in a [1.1] manner through two dimethylsilyl ($SiMe_2$) bridges. It possesses a centre of inversion and is found in an *anti* conformation, crystallizing in the space group $P2_1/n$. The bond lengths and angles of this relatively unstrained molecule are not unusual and are comparable to those of structurally characterized linear oligo(ferrocenylsilanes) **3** (x = 1 or 3).[17,28] The iron–carbon bond distances in the ferrocene moieties are essentially equal and are similar to analogous distances in other disubstituted ferrocenes. The C_5H_4 rings of each ferrocene unit are tilted slightly [4.9(3)°], in a manner opposite to that found in silicon-bridged [1]ferrocenophanes, such that the greatest C_5H_4–C_5H_4 separation is between the *ipso*-carbon atoms. The centroid(1)–Fe–centroid(2) angle of 176.9(2)° in **5** reflects the small degree of ring-tilting in this species. The C_5H_4 rings of the ferrocene units are staggered by 13.2(5)° with respect to each other, as defined by the torsion angle C(1)–centroid(1)–centroid(2)–C(10). Similarly, the $SiMe_2$ bridges are staggered by −41.6(6)°, as defined by the torsion angle C(1)–Si–Si(a)–C(10). The Fe ••• Fe distance of 5.171(9) Å is noteably shorter



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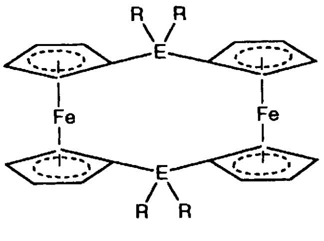

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Table 3 Selected bond lengths (Å) and angles (°) for **5** with estimated standard deviations in parentheses

Si–C(1)	1.865(9)	Fe–C(10)	2.063(9)
Si–C(11)	1.861(10)	C(1)–C(2)	1.462(13)
Si–C(12)	1.879(11)	C(1)–C(5)	1.427(13)
Si–C(10a)	1.858(10)	C(2)–C(3)	1.441(14)
Fe–C(1)	2.073(9)	C(3)–C(4)	1.391(16)
Fe–C(2)	2.068(9)	C(4)–C(5)	1.441(15)
Fe–C(3)	2.036(10)	C(6)–C(7)	1.419(14)
Fe–C(4)	2.029(11)	C(6)–C(10)	1.434(13)
Fe–C(5)	2.042(10)	C(7)–C(8)	1.391(15)
Fe–C(6)	2.053(10)	C(8)–C(9)	1.491(17)
Fe–C(7)	2.059(11)	C(9)–C(10)	1.426(13)
Fe–C(8)	2.026(11)	C(10)–Si(a)	1.858(10)
Fe–C(9)	2.054(10)		
C(1)–Si–C(11)	107.4(5)	C(12)–Si–C(10a)	110.5(5)
C(1)–Si–C(12)	111.3(4)	Si–C(1)–C(2)	123.8(7)
C(11)–Si–C(12)	108.2(5)	Si–C(1)–C(5)	128.5(7)
C(1)–Si–C(10a)	113.0(4)	C(6)–C(10)–Si(a)	131.2(7)
C(11)–Si–C(10a)	106.1(4)	C(9)–C(10)–Si(a)	121.2(7)

in comparison to the distance of 6.913(5) Å found for the interior Fe atoms of **3** (x = 3).[17]

The related silicon-bridged biferrocenes **4**[19] and **9**[29] have been previously structurally characterized. Both biferrocenes possess considerably longer Fe ··· Fe distances [**4** 5.820(5) Å, **9** 6.009(3) Å] in comparison to **5**. To our knowledge, the only symmetrically Group 14 substituted [1.1]ferrocenophanes that have been structurally characterized are the methylene-bridged [1.1]ferrocenophane **10** (E = C, R = H)[30] and the dibutyltin-bridged [1.1]ferrocenophane[31] **10** (E = Sn, R = Bu^n). The methylene-bridged C_5H_4 rings of **10** (E = C, R = H) are twisted by 13.3° with respect to each other, with the molecule crystallizing in a *syn* conformation. The Fe ··· Fe distance of 4.816(2) Å in this compound is, as expected, shorter (0.35 Å) than in **5**. The angles between the centroids of the C_5H_4 rings and the Fe centre of the two ferrocene moieties are essentially 180°. Conversely, the dibutyltin-bridged [1.1]ferrocenophane **10** (E = Sn, R = Bu^n) is found, like **5**, in an *anti* conformation to relieve steric interactions. The Fe ··· Fe distance of 5.50 Å in the former compound is substantially longer (0.33 Å) in comparison to **5** as a result of the longer Sn–C bridging bonds [C–Sn (average) 2.19 *vs.* C–Si (average) 1.86 Å].[31]

Electronic Properties of Compound **5**.—*Cyclic voltammetry*. In order to examine the extent of electronic communication between the two Fe centres in **5**, a cyclic voltammetry study was performed. Previous electrochemical studies of [1.1]ferrocenophanes,[32] linear oligoferrocenes[17,33,34] and poly(ferrocenes)[7] suggest that substantial through bond interactions between neighbouring Fe centres exist when the group(s) linking the metallocene units are not insulating. The cyclic voltammogram of **5** (Fig. 2) shows two well resolved oxidation waves at −0.01 and 0.24 V *vs.* the ferrocene–ferrocenium couple, respectively. The separation (0.25 V) of these waves, $\Delta E_{\frac{1}{2}}$, provides a measure of the interaction between the two Fe centres. For comparison purposes, Table 4 lists $\Delta E_{\frac{1}{2}}$ values obtained from previous studies of linked oligo(ferrocene) species. It is clear from the data in Table 4 that a greater Fe ··· Fe interaction exists in **5** than in the linear $SiMe_2$-bridged biferrocene **3** (x = 0).[17,35] Longer oligo(ferrocenylsilanes) (**3**, $x > 5$) as well as poly(ferrocenylsilane) **2** show similar differences in $\Delta E_{\frac{1}{2}}$ (≈ 0.24 V).[7,17] The bis-$SiMe_2$-bridged species **4**[36] and **9**[29] show $\Delta E_{\frac{1}{2}}$ values similar to that of **5** even though there are significant structural differences among the three compounds. These results suggest that the physical distance between the metal centres is less important for electronic communication in comparison to the number and type of bridge(s) linking the two metal centres.

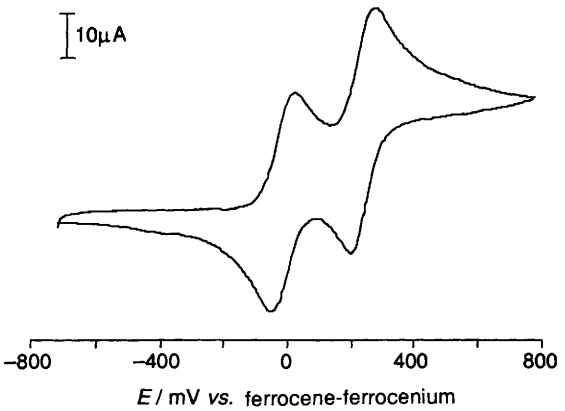

Fig. 2 Cyclic voltammogram of a 10^{-3} mol dm^{-3} CH_2Cl_2 solution of compound **5** which was also 0.1 mol dm^{-3} in NBu_4PF_6 supporting electrolyte obtained at a scan rate of 25 mV s^{-1} at 22 °C

Table 4 Redox couplings and intramolecular Fe ··· Fe distances for [1.1]ferrocenophanes

Compound	E	R	$\Delta E_{\frac{1}{2}}$*/V	Fe ··· Fe/Å	Ref.
3 (x = 0)	Si	Me	0.15	—	17, 35
3 (x = 1)	Si	Me	0.20	6.188(1)	17
3 (x = 3)	Si	Me	0.23	6.913(5)	17
4	Si	Me	0.26	5.820(5)	19, 36
5	Si	Me	0.25	5.171(9)	This work
9	Si	Me	0.27	6.009(3)	29
10	C	H	0.20	4.816(2)	32
10	Sn	Bu^n	0.20	5.50	38
10	Pb	Ph	0.28	—	37

* All values reported were obtained by analysis of CH_2Cl_2 solutions of the analyte.

The $\Delta E_{\frac{1}{2}}$ value for compound **5** can also be compared to the values reported for the other [1.1]ferrocenophanes compiled in Table 4. Müller-Westerhoff and co-workers[30] found a $\Delta E_{\frac{1}{2}}$ value of 0.20 V for the methylene-bridged [1.1]ferrocenophane **10** (E = C, R = H), which is significantly smaller than that found for silicon-bridged **5** even though the Fe $\cdots$ Fe distance is considerably (*ca.* 0.36 Å) shorter in the former compound. More efficient through bond communication is probably responsible for the larger $\Delta E_{\frac{1}{2}}$ observed for **5**. Conversely, the diphenyllead-bridged [1.1]ferrocenophane **10** (E = Pb, R = Ph) shows a somewhat larger $\Delta E_{\frac{1}{2}}$ value than **5** suggesting that electronic communication in this Pb-bridged species is as efficient as in Si-bridged **5**.[37] The presumably longer Fe $\cdots$ Fe distance in the former compound lends further support to the importance of through bond electronic communication in these species.

Mössbauer spectroscopy. The electronic environment of the Fe centre in **5** was also probed by room-temperature ^{57}Fe Mössbauer spectroscopy. The isomer shift values (δ) and, in particular, the small quadrupolar splitting values (ΔE_q) (< 2.0 mm s^{-1}) obtained from Mössbauer analysis of silicon-bridged [1]ferrocenophanes (*e.g.* **1**) have been attributed to Fe–Si dative interactions in these compounds. Conversely, the isomer shift of 0.44(1) mm s^{-1} and ΔE_q value of 2.32(1) mm s^{-1} found for **5** are similar to the Mössbauer data reported for [Fe(η-$C_5H_4SiMe_3)_2$] (77 K, δ = 0.52 mm s^{-1}, ΔE_q = 2.30 mm s^{-1})[26] and nearly identical to those of poly(ferrocenylsilane) **2** [77 K, δ = 0.41(1) mm s^{-1}, ΔE_q = 2.35(10) mm s^{-1}].[39] Similarities in the electrochemical and Mössbauer properties suggest similar Fe electronic environments in **5** and **2**.

Thermal Polymerization Behaviour.—The thermal behaviour of **5** was investigated in order to determine if this compound would undergo thermal ring-opening polymerization or copolymerize with the strained, silicon-bridged [1]ferrocenophane **1**. When compound **5** was heated in a sealed evacuated Pyrex tube for 15 h at 250 °C no change in melt viscosity was detected. Analysis of the tube contents by ^{1}H NMR spectroscopy showed only resonances attributable to **5**. An attempt to copolymerize **5** with **1** was likewise unsuccessful. In this attempted melt copolymerization, equimolar quantities of **1** and **5** were sealed in an evacuated Pyrex tube, heated slowly to 100 °C in order to dissolve **5** in molten **1**, and then further heated at 150 °C. After several minutes at 150 °C, the tube contents became immobile. The tube was maintained at this temperature for 1 h to ensure complete reaction. The tube contents were then dissolved in toluene and precipitated into hexanes. Analysis of the yellow precipitate by ^{1}H NMR spectroscopy showed only resonances consistent with poly(ferrocenylsilane) **2**. Gel-permeation chromatography (GPC) of the polymer showed it to be monomodal and of high molecular weight ($M_w = 4.5 \times 10^5$, $M_n = 3.1 \times 10^5$). The orange hexanes solution was concentrated and a highly crystalline residue recovered. Analysis of the residue by ^{1}H NMR spectroscopy identified it as **5** (95% recovered yield). It is clear from these experiments that compound **5** is both thermally stable and inert toward copolymerization with **1**. These results suggest that **5** is not a reactive intermediate in the thermal ring-opening polymerization of **1**.[2]

Conclusion

We have prepared and crystallographically characterized the first silicon-bridged [1.1]ferrocenophane **5** utilizing a five-step synthesis. Its electrochemical properties were found to be similar to those for the poly(ferrocenylsilane) **2**. In addition, a comparison of the cyclic voltammetric data for **5** with those of other known biferrocenes and [1.1]ferrocenophanes suggest that the degree of electronic communication between the two iron centres is dependent on the distance between them but also depends on the number and nature of the bridge(s) present. Studies of the thermal polymerization behaviour of **5** showed it to be unreactive under the same conditions which induce the thermal ring-opening polymerization of the strained [1]ferrocenophane monomer **1**.

Experimental

All reactions and manipulations were performed under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove-box (Vacuum Atmospheres), except for polymer manipulations which were carried out in air. Solvents were dried by standard methods. Melting points were obtained with a Perkin-Elmer DSC 7 differential scanning calorimeter under N_2. Proton NMR spectra were recorded either on a Varian Gemini 200 or Varian Unity 400 XL spectrometer (200 or 400 MHz) and referenced to residual protonated C_6D_6 at δ 7.15. The ^{13}C NMR spectra (50.3 or 100.5 MHz) were recorded either on a Varian Gemini 200 or Varian Unity 400 spectrometer and referenced to residual protonated C_6D_6 at δ 128.0 ppm. The ^{29}Si NMR spectra (79.5 MHz) were recorded on a Varian Gemini 400 instrument utilizing a proton-decoupled DEPT pulse sequence and were referenced externally to $SiMe_4$. Room-temperature ^{57}Fe Mössbauer spectra were obtained using a Ranger Scientific Vt-1200 instrument using a MS-1200 digital channel analyser. The γ-source was a 6 mCi ^{57}Co sample supplied by Amersham. The data were collected in a −15.8 to +15.8 mm s^{-1} range and referenced to Fe foil. Mass spectra were obtained with the use of a VG 70-250S mass spectrometer operating in either an electron impact (EI) or fast atom bombardment (FAB) mode. Molecular weights were estimated by gel-permeation chromatography using a Waters Associates liquid chomatograph equipped with a model U6K injector, and Ultrastyragel columns differential refractometer. A flow rate of 1.0 cm^3 min^{-1} was used, and the eluent was a solution of 0.1% tetra-*n*-butylammonium bromide in thf. Polystyrene standards were used for calibration purposes. Elemental analyses were performed by Quantitative Technologies, Whitehouse, NJ.

Preparations.—$SiMe_2Cl(NEt_2)$. Chloro(diethylamino)dimethylsilane was prepared in 80% yield according to the method of Tamao *et al.*[23] and gave similar ^{1}H NMR data. Additional data for $SiMe_2Cl(NEt_2)$: ^{29}Si NMR (C_6D_6): δ 11.5; ^{13}C NMR (C_6D_6): δ 40.1 (NCH_2CH_3), 15.4 (NCH_2CH_3), 2.00 ($SiCH_3$).

[Fe{η-$C_5H_4SiMe_2(NEt_2)\}_2$] **6**. A modification of the methods reported by Pittman[22] and Schaaf[21] and co-workers for other ferrocenyldimethylsilylamines was employed to prepare **6**. To [Fe(η-$C_5H_4Li)_2$]·tmen (18.5 g, 58.8 mmol) in diethyl ether (150 cm^3) at −78 °C was added a cooled (−78 °C) solution of $SiMe_2Cl(NEt_2)$ (21.4 g, 129 mmol) in diethyl ether (25 cm^3) over 10 min. The reaction mixture was allowed to warm slowly to 25 °C and was then stirred overnight. The reaction mixture was then filtered and the solvents removed *in vacuo*. The crude dark liquid was then distilled to yield 15.4 g (59%) of **6** as a red liquid (b.p. 100 °C, 0.005 mmHg): ^{29}Si NMR (C_6D_6): δ − 0.67; ^{13}C NMR (C_6D_6): δ 73.6 (C_5H_4), 71.8 (C_5H_4), 68.7 (*ipso*-C_5H_4), 40.6 (NCH_2CH_3), 16.1 (NCH_2CH_3), −0.56 ($SiCH_3$); ^{1}H NMR (C_6D_6): δ 4.21 (t, *J* 1.6, 4 H, C_5H_4), 4.05 (t, *J* 1.6, 4 H, C_5H_4), 2.78 (q, *J* 7.0, 8 H, NCH_2CH_3), 0.92 (t, *J* 7.0 Hz, 12 H, NCH_2CH_3), 0.39 (s, 6 H, $SiCH_3$); high resolution mass spectrum: calc. for $C_{22}H_{40}{}^{56}FeSi_2N_2$ *m/z* 444.2079, found 444.2079.

[Fe(η-$C_5H_4SiMe_2Cl)_2$] **7**. To a chilled (−78 °C) solution of **6** (3.2 g, 10.2 mmol) in diethyl ether (150 cm^3) was added dropwise a cooled solution (−78 °C) of acetyl chloride (1.79 g, 10.2 mmol) in diethyl ether (25 cm^3). After stirring for 3 h, the mixture was concentrated *in vacuo* and the crude product then distilled at high vacuum to afford 3.1 g (82%) of **7** as a golden liquid (b.p. 175 °C, 0.005 mmHg). Upon cooling, the liquid solidified affording a yellow-orange crystalline solid, m.p. 89 °C; ^{29}Si NMR (C_6D_6): δ 22.8; ^{13}C NMR (C_6D_6): δ 73.6

(C_5H_4), 72.8 (C_5H_4), 69.6 (*ipso*-C_5H_4), 2.98 (CH_3); ^1H NMR (C_6D_6): δ 4.17 (t, *J* 1.6, 4 H, C_5H_4), 4.01 (t, *J* 1.6 Hz, 4 H, C_5H_4), 0.46 (s, 12 H, CH_3); high resolution mass spectrum: calc. for $C_{14}H_{20}{}^{56}FeSi_2{}^{35}Cl_2$ *m/z* 369.9830, found 369.9850, calc. for $C_{14}H_{20}{}^{56}FeSi_2{}^{35}Cl^{37}Cl$ *m/z* 371.9801, found 371.9850.

[Fe{η-$C_5H_4SiMe(C_5H_5)$}$_2$] **8**. Cold (−20 °C) thf was added to a mixture of **7** (3.8 g, 10.2 mmol) and Li (C_5H_5) (1.5 g, 20.8 mmol). After stirring the mixture overnight at −30 °C the solvent was removed *in vacuo* and then replaced with hexanes. Lithium chloride was removed by filtration and the hexanes were removed *in vacuo* to yield 3.5 g (80%) of **8** as a dark red oil: ^{29}Si NMR (C_6D_6): δ −2.25, 0.90; ^{13}C NMR (C_6D_6): 133.5 (C_5H_5), 130.7 (C_5H_5), 73.5 (C_5H_4), 71.9 (C_5H_4), 70.8 (*ipso*-C_5H_4), 53.7 (*ipso*-C_5H_5), −3.6 (CH_3); ^1H NMR (C_6D_6): δ 6.67 (br s, 4 H, C_5H_5), 6.57 (br s, 4 H, C_5H_5), 4.16 (t, *J* 1.6, 4 H, C_5H_4), 3.96 (t, *J* 1.6 Hz, 4 H, C_5H_4), 3.45 (br s, 2 H, *ipso*-C_5H_5), 0.10 (s, 12 H, CH_3); high resolution mass spectrum: calc. for $C_{24}H_{30}{}^{56}FeSi_2$ *m/z* 430.1235, found 430.1236.

[{Fe(η-C_5H_4)$_2$SiMe$_2$}$_2$] **5**. Butyllithium (12.1 cm^3, 1.6 mol dm^{-3} in hexanes) was added dropwise to a cold (−5 °C) solution of **8** (3.4 g, 7.9 mmol) in thf (150 cm^3). After stirring overnight, the solvent was removed *in vacuo* and replaced with hexanes. The pale yellow salt was collected by filtration, washed with hexanes (3 × 25 cm^3), and then dried *in vacuo* to afford 2.8 g (80%) of Li_2[Fe{η-$C_5H_4SiMe_2(C_5H_4)$}$_2$] as a canary yellow solid. Cold (−5 °C) thf (100 cm^3) was added to a mixture of Li_2[Fe{η-$C_5H_4SiMe_2(C_5H_4)$}$_2$] (0.85 g, 1.9 mmol) and $FeCl_2$ (0.24 g, 1.9 mmol). The resulting mixture was stirred at −20 °C overnight and then the solvent was removed *in vacuo* and replaced with hexanes. The solution was filtered and solvent was again removed *in vacuo*. Recrystallization of the resulting residue from hot hexanes afforded 0.33 g (35%) of **5** as an orange-red powder, m.p. 235 °C; ^{29}Si NMR (C_6D_6): δ −6.52; ^{13}C NMR (C_6D_6): δ 73.9 (C_5H_4), 71.4 (*ipso*-C_5H_4), 70.9 (C_5H_4), 2.19 (CH_3); ^1H NMR (C_6D_6): δ 4.31 (t, *J* 1.6, 8 H, C_5H_4), 4.25 (t, *J* 1.6 Hz, 8 H, C_5H_4), 0.40 (s, 12 H, CH_3); high-resolution mass spectrum: calc. for $C_{24}H_{28}{}^{56}Fe_2Si_2$ *m/z* 484.0428, found 484.0420 (Found: C, 59.90; H, 5.95. Calc. for $C_{24}H_{28}Fe_2Si_2$: C, 59.50; H, 5.85%).

Polymerization Studies of Compound **5**.—*Thermal polymerization behaviour.* Compound **5** (30 mg) was placed in an evacuated Pyrex tube and sealed under vacuum. The tube was then heated to 250 °C, which brought the contents into the melt. Heating was continued for 15 h, after which the tube contents were cooled to room temperature. Analysis of the highly crystalline product by ^1H NMR spectroscopy revealed that it was unreacted **5**.

Attempted thermal copolymerization of **5** *with the* [1]*ferrocenophane* **1**. Equimolar quantities of compounds **1** and **5** were placed in a sealed, evacuated Pyrex tube. The tube contents were brought into the melt by heating the mixture to 100 °C. The mixture was then heated further to 150 °C and the tube contents became immobile after several minutes. The tube was heated for an additional 1 h at this temperature and the tube contents precipitated into a large excess of hexanes. The polymer was analysed by ^1H NMR spectroscopy and showed resonances consistent with previously reported values for **2**. GPC revealed it to be of high molecular weight. Analysis of the recovered hexanes residues by ^1H NMR spectroscopy showed it to consist of only unreacted **5**.

Crystal Structure Determination.—Crystal, data collection and refinement parameters are given in Table 1. A suitable crystal was selected and mounted with epoxy cement to a glass fibre. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($20 \leqslant 2\theta \leqslant 25°$).

The systematic absences in the diffraction data were uniquely consistent for the space group $P2_1/n$. The structure was solved using direct methods, completed by subsequent Fourier-difference syntheses and refined by full-matrix least-squares procedures. A semi-empirical ellipsoid absorption correction was applied to the data set. The compound molecule was located at an inversion centre. Several large peaks (max. = 1.81 e Å^{-3}) in the difference map were observed after all the atoms were assigned. The consistent and gradual decrease in peak height (0.1–0.2 e Å^{-3}) for consecutive peaks and the chemically unrecognizable positions of these peaks identify them as noise peaks which were ignored. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in either the SHELXTL (5.1) or the SHELXTL PLUS (4.2) program libraries.[40] Fig. 1 was drawn using ORTEP.[41]

Acknowledgements

We thank the donors of the Petroleum Research Fund (PRF), administered by the American Chemical Society, for financial support of this work. D. L. Z. is grateful to the Natural Science and Engineering Research Council of Canada (NSERC) for a summer fellowship. I. M. is grateful to the Alfred P. Sloan Foundation for a Research Fellowship. We also thank Derek Gates for his assistance with the manipulation of the crystallography data, Professor Geoff Ozin for the use of his Mössbauer spectrometer and Professor Robert Morris for the use of his electrochemical equipment.

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Received 10*th January* 1995; *Paper* 5/00153F