Ring-opening addition of hydrogen chloride to monocyclic and spirocyclic [1]ferrocenophanes: a convenient and controlled route to ferrocenylchlorosilanes and germanes†

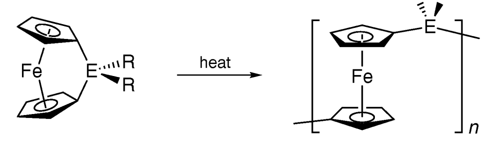
Mark J. MacLachlan, Madlen Ginzburg, Juan Zheng, Oliver Knöll, Alan J. Lough and Ian Manners*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6 Canada

The ring-opening addition of HCl to [1]ferrocenophanes has been shown to provide a general method for the preparation of chlorosilanes and germanes with ferrocenyl substituents. Reaction of HCl with dimethyl[1]silaferrocenophane, $fcSiMe_2$ (**1a**) [fc = $Fe(\eta\text{-}C_5H_4)_2$], affords chlorodimethylferrocenylsilane, $FcMe_2SiCl$ (**3a**) [Fc = $(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$], in 68% yield. Trichloroferrocenylsilane, $FcSiCl_3$ (**3b**), and chlorodimethylferrocenylgermane, $FcMe_2GeCl$ (**3c**), were prepared by an analogous route from ferrocenophanes $fcSiCl_2$ (**1b**) and $fcGeMe_2$ (**1c**). Ring-opening addition of HCl to the spirocyclic [1]ferrocenophane, $fcSi(CH_2)_3$ (**4**), leads to cleavage of the Si—C bond of the strained ferrocenophane, giving the silacyclobutane $FcSiCl(CH_2)_3$ (**5**) in 84% yield. Moreover, treatment of the spirocyclic [1]silaferrocenophane fc_2Si (**6**) with HCl affords orange crystals of dichlorodiferrocenylsilane, Fc_2SiCl_2 (**7**), in 88% yield. Hydrolysis of **7** in the presence of triethylamine generated diferrocenylsilanediol, $Fc_2Si(OH)_2$ (**8**), in 90% yield. A single crystal X-ray diffraction study combined with spectroscopic identification confirmed that **8** crystallizes in a new bead-and-chain motif.

A thriving fundamental scientific and industrial enterprise has been built on the preparation of chlorosilanes R_xSiCl_{4-x} ($0 \leqslant x \leqslant 3$), organometallic compounds that find utility as CVD precursors, surface and electrode derivatization agents, sol–gel precursors, and in the preparation of polymers (polysilanes, polysiloxanes, polycarbosilanes), silsesquioxanes, and reactive synthetic intermediates.[1,2] Silica surfaces treated with organochlorosilanes are found in applications as diverse as chromatography and tribology.[3] In addition, new classes of high-molecular weight poly(ferrocenes) have recently been prepared from the ring-opening polymerization (ROP) of [1]ferrocenophanes (Scheme 1), monomers synthesized from chlorosilanes and chlorogermanes.[4,5] Thus, in view of their widespread utility, convenient and controlled routes to novel substituted organochlorosilanes and germanes are of considerable interest.

Unfortunately, the preparation of pure ferrocenylchlorosilanes by the reaction of monolithioferrocene [FcLi, Fc = $(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$] with chlorosilanes ($R_xSiCl_{4-x}$, $0 \leqslant x \leqslant 3$) is often frustrated by three factors: FcLi is difficult to prepare in high yields {usually it is obtained in combination with a substantial amount of dilithioferrocene, $fcLi_2$ [fc = $Fe(\eta\text{-}C_5H_4)_2$]}, a mixture of products with different degrees of chloride substitution is obtained, and the products and by-products are very moisture sensitive.[6] For these reasons, few examples of chlorosilanes or chlorogermanes containing ferrocenyl substituents have been reported and even fewer have been prepared in high yield.



1a (E = Si; R = CH_3)
1b (E = Si; R = Cl)
1c (E = Ge; R = CH_3)

2a (E = Si; R = CH_3)
2b (E = Si; R = Cl)
2c (E = Ge; R = CH_3)

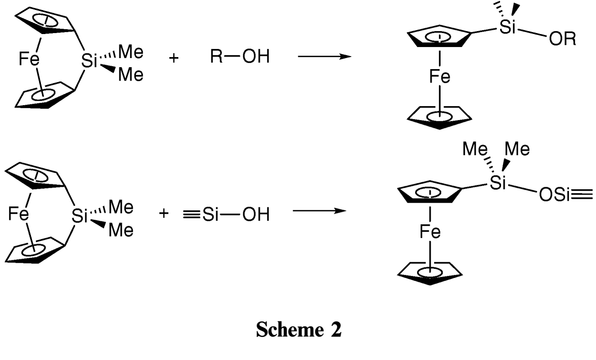
Scheme 1

Silicon-bridged [1]ferrocenophanes are known to react with water, methanol and silanol groups to generate ring-opened ferrocenylsilane species with Si—O bond formation, relieving the ring strain in the process (Scheme 2).[7] The reaction with silanol groups has been used to derivatize the surface of mesoporous silica and as a route to novel magnetic nanostructures.[7,8] In this paper we report a new, convenient synthesis of chlorinated ferrocenylsilanes and germanes *via* the ring-opening addition of HCl to monocyclic and spirocyclic [1]ferrocenophanes.

Results and Discussion

HCl addition to monocyclic [1]ferrocenophanes

As a demonstration of the synthetic application of HCl addition across the Si—C or Ge—C bond of [1]ferrocenophanes, **1a–c** were chosen as representative precursors to ferrocenylsilanes and germanes. The reactions are illustrated in Scheme 3. With the slow addition of an ethereal solution of



Scheme 2

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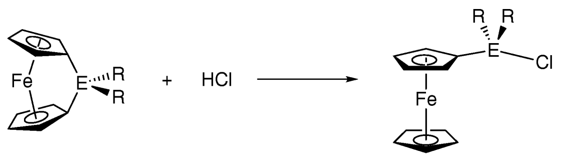
† Non-SI units employed: 1 Torr ≈ 133 Pa.



1a (E = Si; R = CH_3)
1b (E = Si; R = Cl)
1c (E = Ge; R = CH_3)

3a (E = Si; R = CH_3)
3b (E = Si; R = Cl)
3c (E = Ge; R = CH_3)

Scheme 3

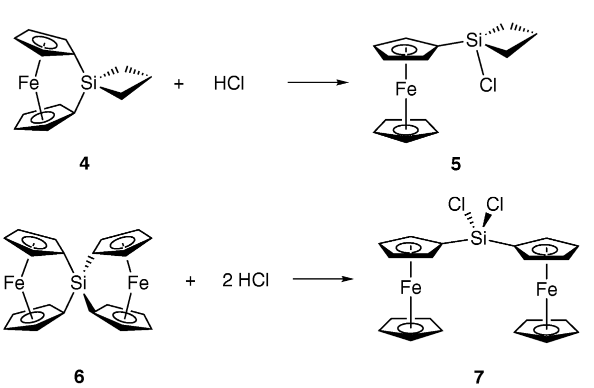
HCl, the red solution of **1a** slowly turned yellow. Subsequent workup afforded orange crystals of chlorodimethylferrocenylsilane (**3a**) in 68% yield. The trichloroferrocenylsilane **3b** and chlorodimethylferrocenylgermane **3c** were similarly prepared in 77% and 74% yields, respectively, by an analogous procedure. The mass spectra and ^1H, ^{13}C, and ^{29}Si NMR spectra of compounds **3a–c** were consistent with their proposed structures. In the UV/VIS spectrum, **3a** shows a shift in its absorption maximum from 483 nm (CH_2Cl_2) in **1a** to 446 nm in **3a**. This blue shift is consistent with the ring-opening of the [1]ferrocenophane and is also observed in the preparation of **3b,c**.[4b]

Compounds **3a–c** are difficult to prepare by other means and may be useful synthetic intermediates; **3a** and **3b** have already been used as reagents in the preparation of ferrocenylsilane oligomers, and for silica and electrode derivatization.[7–9] Previously, the chloroferrocenylsilane **3a** was prepared from FcLi and dichlorodimethylsilane.[9a,10] Not surprisingly, this route, though reproducible, consistently gave very low yields of *ca.* 10%. Improvements in the yield to 78% by transmetallation with chloromercurioferrocene were reported and a dark red oil with bp of 98–100 °C/0.5 Torr was obtained.[9a] In our laboratory, **3a** is an orange crystalline compound melting at 47–49 °C. Trichloroferrocenylsilane **3b** has also been reported, though it was also isolated in only 25% yield.[9c] Chlorodimethylferrocenylgermane (**3c**), however, has not been previously described.

Wrighton and coworkers explored the addition of OH groups to [1]silaferrocenophanes, but the mechanistic details of these reactions were not discussed.[7a] As HCl addition results in the rapid ring-opening of the [1]ferrocenophanes and tetraphenylphosphonium chloride does not react with the ferrocenophane **6** even after 1 h at room temperature, we propose that the initial step does not involve nucleophilic attack at silicon. The reaction may proceed by σ-bond metathesis or electrophilic addition of a proton to the *ipso*-carbon atom. It should be noted that ring-opening addition of HCl to the Si—C bond of strained carbosilane rings is also known.[11]

HCl addition to spirocyclic [1]ferrocenophanes

We recently reported practical preparations of the spirocyclic [1]ferrocenophanes **4** and **6**.[12] As we have observed HCl addition to [1]silaferrocenophanes and HCl addition to silacyclobutanes is known, we were curious as to which strained ring in the spirocycle **4** would ring-open first. When 1 equiv. of HCl was added to a solution of **4**, only compound **5** was isolated from distillation of the crude reaction mixture (Scheme 4). With an isolated yield of 84% for pure **5**, it appears that HCl addition occurs preferentially and virtually exclusively to the strained ferrocenophane ring of **4**. This is surprising in light of the fact that the endocyclic Si—C bonds of silacyclobutanes can be cleaved by the electrophilic addition of acids and water. In both the ferrocenophane and the silacyclobutane moieties, the high strain and the presence of the $Si^+—C^-$ dipole would be expected to be the driving force for ring-opening reactions.



Scheme 4

In the ^{13}C NMR spectrum of **5** (in C_6D_6), four peaks consistent with a ferrocenyl group and two peaks attributed to the methylene groups of the silacyclobutane ring are observed [Fig. 1(*a*)]. The resonance assigned to the *ipso*-carbon atom has shifted from 31.9 ppm in ferrocenophane **4** to 65.9 ppm in **5**, consistent with ring-opening of the strained [1]ferrocenophane. As well, the ^{29}Si NMR spectrum of **5** shows only a single peak at 25.7 ppm, downfield from the resonance observed at 3.6 ppm for **4**. In the ^1H NMR spectrum, however, there are only two resonances due to the Cp ligands and four peaks assigned to the methylene groups [Fig. 1(*b*)]. There appears to be a fortuitous coincidence of the chemical shifts of the protons on the Cp ligand attached to Si as deduced by the integrated intensity of the two peaks near 4 ppm. To explain the four methylene resonances, the protons on each of the methylene carbon atoms of the puckered silacyclobutane ring become inequivalent upon ring-opening of the ferrocenophane and they show extensive coupling.

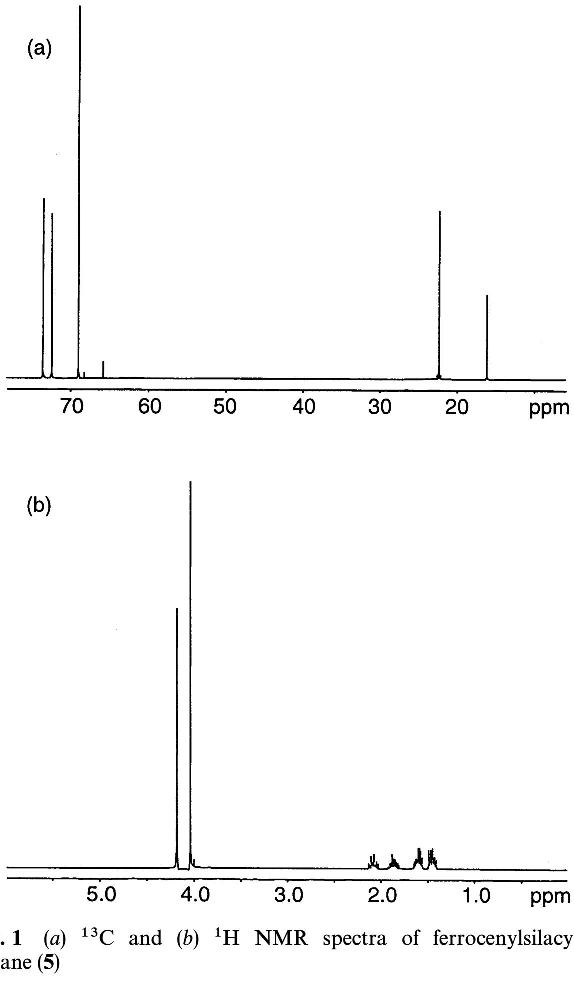


Fig. 1 (*a*) ^{13}C and (*b*) ^1H NMR spectra of ferrocenylsilacyclobutane (**5**)

Table 1 Infrared and Raman bands of **8**

Infrared[a]	Raman	Assignment[b]
3579(w)		ν O—H (free)
3455(s,br)		ν O—H (H-bonded)
3404(s,br)		ν O—H (H-bonded)
3287(s,br)		ν O—H (H-bonded)
3097(m)	3108(m)	ν C—H (sym.)
3080(m)	3086(m)	ν C—H
1780(w,br)		
1706(w,br)		
1653(w,br)		
1423(m)	1423(w)	ν C—C (sym.)
1411(w)	1411(w)	ν C—C (sym.)
1383(w)	1384(w)	ν C—C
1367(m)	1367(w)	ν C—C
1353(w)	1354(w)	ν C—C
1174(s)	1170(m)	δ C—H$_{ip}$
1105(s)	1107(s)	asym. ring breath
1066(w)	1064(m)	δ C—H$_{oop}$
	1055(vw)	
1039(s)	1040(w)	δ C—H$_{ip}$
1024(m)	1025(vw)	δ C—H$_{ip}$
1001(m)	999(vw)	δ C—H$_{ip}$
924(s)		ν Si—O
899(m)	892(vw)	ring distortion
877(s)		
851(w)		δ C—H$_{oop}$
841(w)		
811(s)	819(vw)	δ C—H$_{oop}$
775(s)	776(vw)	
658(w)		
	642(vw)	
631(m)	629(vw)	
	597(vw)	δ C—C$_{oop}$
550(m)	549(vw)	Cp—Fe—Cp deform.
497(s)	502(vw)	
492(w)		
486(w)		
474(s)		
469(s)		
464(w)		
461(w)		
456(m)		
452(w)		
	435(w)	
	404(w)	
	394(m)	ring tilt (sym.)
	343(vw)	
	317(s)	ν Fe—Cp (sym.)
	295(vw)	
	253(vw)	
	218(w)	
	197(vw)	

[a] Nujol mull. [b] ν = stretch; δ = bend; ip = in-plane; oop = out-of-plane

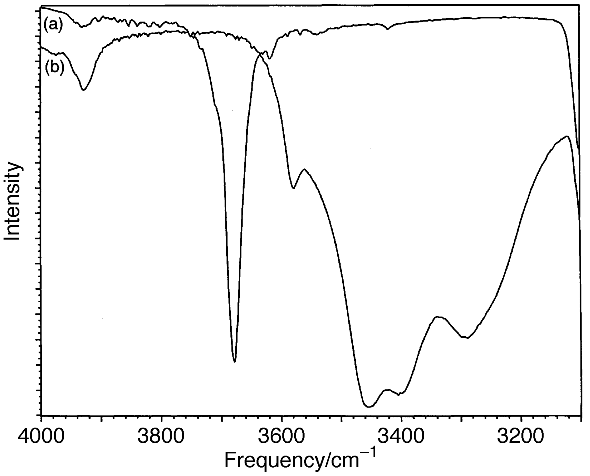


Fig. 2 IR spectrum (4000–3100 cm^{-1}) of **8** obtained as a (*a*) dilute solution in CCl_4 and (*b*) Nujol mull

Addition of 2 equiv. of HCl to the spirocyclic [1]silaferrocenophane **6** resulted in the formation of an amber solution. Following workup and recrystallization, compound **7** was obtained as pure yellow-orange crystals in 88% yield. Spectroscopic data were consistent with the ring-opened ferrocene derivative **7**, showing two triplets for the protons on the Cp ring bound to Si and a singlet for the free Cp ring in the ^{1}H NMR spectrum. In the ^{13}C NMR spectrum of **7**, four peaks attributed to Cp resonances are evident, including a resonance attributed to the *ipso*-carbon at 67.6 ppm. This resonance is shifted downfield from the resonance at 31.1 ppm observed for **6**. In addition, the ^{29}Si NMR spectrum of **7** shows a singlet at 15.2 ppm, which represents a significant downfield shift from the resonance observed at −16.6 ppm for **6**. The UV/VIS absorption maximum in **7** was present at 448 nm, a substantial blue shift from the absorption maximum observed in **6** (483 nm in CH_2Cl_2).

In 1979, Wrighton and coworkers isolated compound **7** in 8% yield from the crude reaction mixture (containing mostly ferrocene and Fc_xSiCl_{4-x}, $0 \leqslant x \leqslant 4$, species) by fractional sublimation.[13] Interestingly, their product, a yellow-orange solid, had a broad melting range (5 °C) and a melting point 30 °C lower than we measured, although mass spectrometry indicated the molecular ion and its elemental analysis as satisfactory. It is probably difficult to isolate a substantial yield of pure **7** from monolithioferrocene and $SiCl_4$.

During the reactions, the addition of HCl to the Si—C bond of the [1]ferrocenophanes is favoured over oxidation of the iron. Near the end of the reaction a small amount of oxidation is evident in the form of a green precipitate that is insoluble in non-polar solvents. It may be possible to eliminate oxidation of the metal completely by quantifying the concentration of the HCl by titration of the solution used.

The ring-opening addition reactions are expected to be a general synthetic procedure that may be applied to a wide variety of [1]ferrocenophanes and various anions other than chloride. Indeed, we have observed the ring-opening addition of HOTf to [1]silaferrocenophanes.[14] Since many symmetrically and unsymmetrically substituted [1]ferrocenophanes are now readily available,[15] ferrocenylchlorosilanes and germanes that were previously unreported or obtained in low yield by other means should be readily accessible by our method.

Synthesis and characterization of diferrocenylsilanediol (8)

Silanols are structurally analogous to alcohols, but are much more acidic and reactive.[16] Thus, these intermediates from the hydrolysis of chlorosilanes in the preparation of silicones are generally unstable but can be isolated as solids only under very stringent conditions or where the other substituents at Si are large. The close proximity of the OH groups in silanediols often leads to interesting, unpredictable hydrogen-bonded structures. We thought it would be interesting to examine the structure of a silanediol with two bulky ferrocenyl substituents, which was expected to be readily accessible by using the new method described above for making the chlorinated precursor.

We prepared diferrocenylsilanediol (**8**) in 90% yield from the hydrolysis of compound **7** in the presence of an excess of triethylamine. The product was isolated as an orange powder melting at 159–160 °C. Both ^{13}C NMR and ^{1}H NMR spectra are consistent with the proposed structure. The ^{29}Si NMR spectrum of **8** shows a single resonance at −25.1 ppm, a significant upfield shift from the ^{29}Si resonance in compound **7** (15.2 ppm). Interestingly, the resonance attributed to the hydroxyl group, which appears at 6.21 ppm in DMSO-d_6, appears to be independent of concentration. The mass spectrum of **8** indicated M^+ ($m/z = 432$) as the dominant species.

Diferrocenylsilanediol (**8**) was reported in the late 1960s, but was prepared in only 4% yield as a by-product in the Friedel–

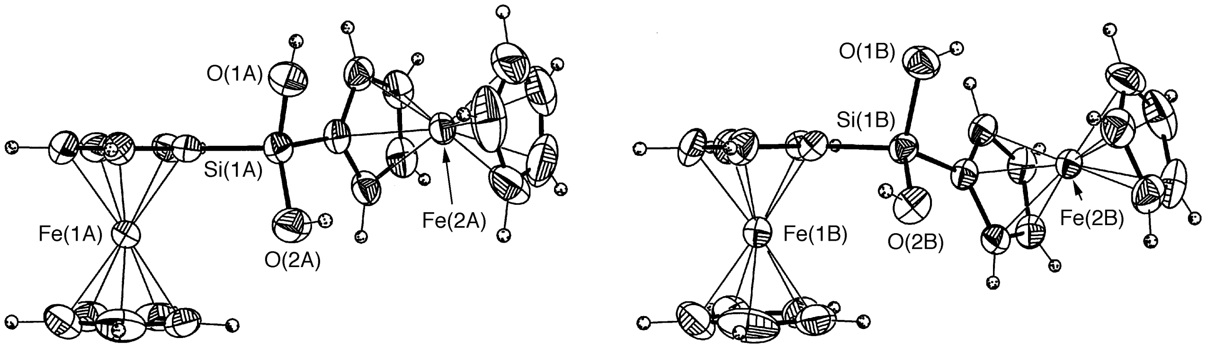


Fig. 3 The molecular structure of diferrocenylsilanediol (**8**). Both molecules that crystallize in the asymmetric unit are shown at the 50% probability level

Crafts silylation of ferrocene.[17] Interestingly, the reported product was recrystallized from heptanes, whereas in our laboratory **8** is insoluble in heptanes.

We investigated the vibrational spectroscopy of **8** by Raman and infrared (IR) spectroscopies. Table 1 lists the peaks observed in the IR (Nujol mull) and Raman spectra of **8** with their relative intensities. Fig. 2 shows the IR spectra of the O—H stretching region for **8** in the solid state and in solution. In the solid state, four vibrations attributed to O—H stretching are observed between 3800 and 3100 cm^{-1}. The first peak (3579 cm^{-1}) is sharp and is due to the stretching of free O—H groups in the stucture. The other three peaks observed between 3460–3280 cm^{-1} are consistent with O—H stretching frequencies expected for hydrogen-bonded silanol groups. In CCl_4, however, only a free O—H stretching mode is observed at 3679 cm^{-1}. The Si—O stretch is observed at 924 cm^{-1}. C—H stretching modes are observed near 3100 cm^{-1} as observed in other ferrocene derivatives. Other peaks consistent with the vibrations of the ferrocenyl substituent are identified in Table 1.[18]

Table 2 Crystal data for silanediol **8**

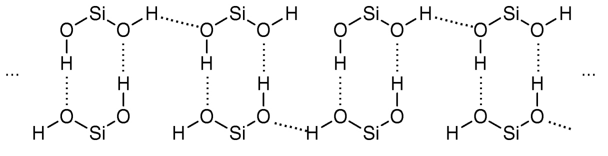
	8
Empirical formula	$C_{20}H_{20}Fe_2O_2Si$
M_r	432.15
T/K	293(2)
λ/Å	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	12.066(1)
b/Å	12.085(1)
c/Å	12.747(1)
α/deg	97.81(1)
β/deg	106.75(1)
γ/deg	91.08(1)
U/Å^3	1759.9(6)
Z	4
D_{calc}/g cm^{-3}	1.631
μ(Mo Kα)/mm^{-1}	1.727
F(000)	888
Crystal size/mm	0.16 × 0.17 × 0.18
θ range collected/deg	4.10–26.47
Total no. of reflect.	30089
No. of unique reflect.	7107
R_{int}	0.046
Absorption correction	Denzo-SMN (multi-scan)
wR_2 (all data)	0.0966
R_1 [$I > 2\sigma(I)$]	0.0318
GOF	1.067
$(\Delta/\sigma)_{max}$ in last cycle	
No. of params.	460
Residual electron density/e Å^{-3}	0.467 and −0.550
Ex. coeff.	0.0075(9)

To investigate the structure of diferrocenylsilanediol (**8**), single crystals suitable for X-ray diffraction were grown from warm $CDCl_3$. The compound crystallizes in the triclinic space group $P\bar{1}$ with two different molecules (A and B) in the asymmetric unit. Fig. 3 shows the molecular structure of both molecules of diol **8**. Crystal data and collection parameters are listed in Table 2 and selected bond lengths, angles, and intermolecular distances are collected in Table 3. The cyclopentadienyl rings in the ferrocenyl substituents are essentially planar, although the ferrocenyl substituents exhibit a small ring tilt of 2.6(2)° and 2.9(2)° in molecule A and 0.7(2)° and 3.4(2)° in molecule B. In molecules A and B, the ferrocenyl groups are oriented at 89.8(2)° and 73.5(2)° to one another (using the Si—Cp plane as a reference), respectively. Furthermore, the Fe···Fe separations in the molecules are 6.452(1) and 6.173(1) Å in molecules A and B, respectively. The silicon atoms are nearly tetrahedral with C—Si—C bond angles of 109.5(1)° and 110.2(1)° and O—Si—O bond angles of 107.0(1)° and 108.2(1)° for the two distinct molecules in the asymmetric unit.

In the solid state, compound **8** crystallizes in an extended network of hydrogen-bonded chains as illustrated in Scheme 5. Hydrogen-bonded dimers form 8-membered rings that are joined by a single hydrogen bond to neighbouring dimers in

Table 3 Selected bond lengths (Å), intermolecular distances (Å), and bond angles (°) for silanediol **8**

Si(1A)—O(1A)	1.644(2)	Si(1B)—O(1B)	1.659(2)
Si(1A)—O(2A)	1.623(2)	Si(1B)—O(2B)	1.644(2)
Si(1A)—C(1A)	1.849(3)	Si(1B)—C(1B)	1.840(3)
Si(1A)—C(11A)	1.839(3)	Si(1B)—C(11B)	1.837(3)
O(1A)···O(2A)	2.799(3)	O(1A)···O(2B)	2.930(3)
O(1B)···O(2B)	2.908(3)		
C(1A)—Si(1A)—C(11A)	109.52(12)	C(1B)—Si(1B)—C(11B)	110.23(12)
C(1A)—Si(1A)—O(1A)	108.71(11)	C(1B)—Si(1B)—O(1B)	105.35(11)
C(1A)—Si(1A)—O(2A)	107.62(11)	C(1B)—Si(1B)—O(2B)	113.01(11)
C(11A)—Si(1A)—O(1A)	111.04(11)	C(11B)—Si(1B)—O(1B)	110.40(11)
C(11A)—Si(1A)—O(2A)	112.81(12)	C(11B)—Si(1B)—O(2B)	109.51(11)
O(1A)—Si(1A)—O(2A)	107.00(11)	O(1B)—Si(1B)—O(2B)	108.25(11)



Scheme 5

the chain. These chains, which run parallel to the *c* axis, have a repeat distance of 12.747(1) Å and are separated from adjacent chains by 12.066(1) Å along the *a* axis and by 12.085(1) Å along the *b* axis. Interestingly, one O—H from every other diol does not take part in hydrogen-bonding. This is consistent with the IR spectrum of crystalline **8** where, in addition to three broad peaks from hydrogen-bonded O—H groups, a free O—H stretch is observed at 3579 cm^{-1}.

In the hydrogen-bonded silanediol chain, two distinct hydrogen-bonded rings are formed. The first ring, which has two hydrogen substituents that do not participate in hydrogen-bonding, lies nearly parallel to the *ac* plane while the other is nearly in the *bc* plane. The intermolecular O···O distances between the diols in the two rings are 2.799(3) and 2.908(3) Å, respectively. Moreover, the nearest O···O separation between adjacent rings, spanned by a hydrogen bond [O(1A)···O(2B)], is 2.930(3) Å. Fig. 4 shows the molecular structure of the chain. To the best of our knowledge, this is the first observation of a bead-and-chain motif in silanediols. Very bulky substituents usually lead to ladder chains, as observed in $R_2Si(OH)_2$ (R = Pr^i, Bu^t, c-C_6H_{11}, *o*-tolyl), though hexameric, tetrameric, or even dimeric structures may form with extremely bulky ligands [*e.g.*, R = C(SiMe$_3$)$_3$].[16a] Silanediol **8** is thermally stable to its melting point of 159–160 °C and was observed to even sublime under vacuum.

Summary

A new and convenient methodology for the preparation of ferrocenylchlorosilanes and germanes has been discovered. Thus, addition of HCl to [1]silaferrocenophanes gives chloroferrocenylsilanes in good yields. Using this route, chloroferrocenylsilanes and germanes **3a–c**, **5**, and **7** were prepared and characterized. The stable silanediol with two ferrocenyl substituents, (**8**), was prepared by hydrolysis of dichlorodiferrocenylsilane (**7**) in the presence of triethylamine. Characterization by single crystal X-ray diffraction, vibrational spectroscopy, and multinuclear NMR confirmed the structure of **8**. The hydrogen-bonded bead-and-chain structure of **8** is a new motif for silanediols.

Experimental

Materials and equipment

Triethylamine was purchased from Aldrich and distilled from Na prior to use. Anhydrous 1 M HCl in diethyl ether and tetraphenylphosphonium chloride were purchased from Aldrich and used as received. The ferrocenophanes **1a–c**, **4**, and **6** were prepared by literature methods.[12,15b,19]

All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (Innovative Technologies) unless otherwise noted. Solvents were dried by standard methods, distilled, and stored under nitrogen. 400 MHz ^{1}H NMR spectra and 100.5 MHz ^{13}C NMR spectra were recorded on a Varian Unity 400 spectrometer. 79.5 MHz ^{29}Si NMR spectra were recorded on a Varian Unity 400 spectrometer using either a normal or a DEPT pulse sequence and were referenced externally to TMS. UV/VIS spectra were obtained in CH_2Cl_2 (*ca.* 5 × 10^{-4} M) on a Perkin–Elmer Lambda 900 UV/VIS-Near IR spectrometer using a 1 cm quartz cuvette. IR spectra were obtained as Nujol mulls or CCl_4 solutions with a Nicolet Magna-IR 550 spectrometer. FT-Raman spectra were collected on a Bomems MB-157 FT spectrometer with a Spectra Physics diode pumped Nd:YLF laser (1064 nm, 350 kHz repetition rate). The instrument was configured in 180° back-scattering mode using sealed glass capillary tubes to hold the neat, crystalline samples. Electron impact (EI) mass spectra were obtained with a VG 70-250S mass spectrometer. Elemental analyses were performed by Quantitative Technologies, Inc. (Whitehouse, NJ).

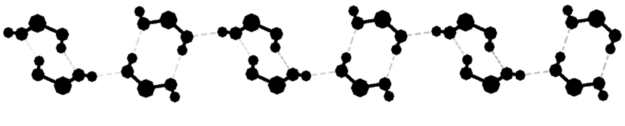


Fig. 4 Molecular structure of the hydrogen-bonded network in the silanediol **8** (ferrocenyl substituents have been omitted for clarity)

Syntheses

Chlorodimethylferrocenylsilane (3a). Hydrogen chloride (1.0 M in diethyl ether; 4.2 mL, 4.2 mmol) was added dropwise to a stirred solution of **1a** (0.908 g, 3.75 mmol) in *ca.* 50 mL of diethyl ether at room temperature. The solution turned from red to yellow and a small amount of green precipitate formed. After stirring for 8 min, the solution was filtered and pumped dry to give yellow crystals. Recrystallization from hexanes followed by two room-temperature vacuum sublimations gave 0.71 g (2.5 mmol; 68%) of yellow-orange crystals. ^{13}C NMR (100.5 MHz, C_6D_6) δ = 73.2 (SiCp), 71.9 (SiCp), 68.9 (Cp), 68.6 (*ipso*-Cp), 2.8 (CH_3). ^{1}H NMR (400 MHz, C_6D_6) δ = 4.14 (t, $^3J_{HH}$ = 1.8 Hz, 2H, Cp), 4.03 (t, $^3J_{HH}$ = 1.65 Hz, 2H, Cp), 3.95 (s, 5H, Cp), 0.49 (s, 6H, CH_3). ^{29}Si NMR (79.5 MHz, C_6D_6): δ = 22.3. UV/VIS (CH_2Cl_2): λ_{max} = 446 nm (ε = 121 L mol^{-1} cm^{-1}), 326 nm (ε = 94 L mol^{-1} cm^{-1}). MS (EI, 70 eV): *m*/*z* (%) = 278 (100, M$^+$). HRMS: Calcd for $C_{12}H_{15}Cl^{56}FeSi$: 277.998096. Found: 277.997957. Mp 47–49 °C (lit. bp 98–100 °C/0.5 Torr[9a] and 135–138 °C/1.5 Torr[10]).

Trichloroferrocenylsilane (3b). Hydrogen chloride (1.0 M in diethyl ether; 18.7 mL, 18.7 mmol) was added dropwise to a stirred solution of 4.73 g (17.0 mmol) **1b** in *ca.* 300 mL of hexanes at room temperature. The colour immediately changed from red to yellow-orange. After stirring for 10 min, the solution was filtered through a glass frit and the solvent was removed under vacuum. The yellow residue was recrystallized from hexanes then sublimed to afford 4.18 g (13.1 mmol; 77%) of yellow crystals of **3b**. ^{13}C NMR (100.5 MHz, C_6D_6) δ = 73.5 (SiCp), 73.1 (SiCp), 70.1 (Cp), 69.8 (*ipso*-Cp). ^{1}H NMR (400 MHz, C_6D_6) δ = 4.14 (t, $^3J_{HH}$ = 1.85 Hz, 2H, Cp), 4.04 (t, $^3J_{HH}$ = 1.85 Hz, 2H, Cp), 3.97 (s, 5H, Cp). ^{29}Si NMR (79.5 MHz, C_6D_6): δ = 2.5. UV/VIS (CH_2Cl_2): λ_{max} = 444 nm (ε = 156 L mol^{-1} cm^{-1}), 331 nm (ε = 285 L mol^{-1} cm^{-1}). MS (EI, 70 eV): *m*/*z* (%) = 186 (100, FcH$^+$), 318 (90, M$^+$), 253 (18, M$^+$ − C_5H_5), 283 (7, M$^+$ − Cl). HRMS: Calcd for $C_{10}H_9Cl_2{}^{37}Cl^{56}FeSi$: 319.885901. Found: 319.885898. Mp 82–83 °C. (lit.[9c] mp 75–77 °C).

Chlorodimethylferrocenylgermane (3c). Hydrogen chloride (1.0 M in diethyl ether; 1.05 mL, 1.05 mmol) was added dropwise to a stirred solution of **1c** (0.300 g; 1.05 mmol) in *ca.* 50 mL of diethyl ether at 0 °C. After stirring for 5 min, the solution was filtered under nitrogen and the solvent was removed under vacuum. Room-temperature vacuum sublimation followed by recrystallization from hexanes at −40 °C afforded 0.251 g (0.777 mmol; 74%) of **3c** as large orange crystals. ^{13}C NMR (100.5 MHz, C_6D_6) δ = 72.4 (*ipso*-Cp), 72.3 (GeCp), 71.4 (GeCp), 68.8 (Cp), 4.0 (CH_3). ^{1}H NMR (400 MHz, C_6D_6) δ = 4.11 (s, 2H, Cp), 4.02 (s, 2H, Cp), 3.92 (s, 5H, Cp), 0.66 (s, 6H, CH_3). UV/VIS (CH_2Cl_2): λ_{max} = 444 nm (ε = 143 L mol^{-1} cm^{-1}), 331 nm (ε = 233 L mol^{-1} cm^{-1}). MS (EI, 70 eV): *m*/*z* (%) = 324 (100, M$^+$), 259 (37, M$^+$ − Cp). HRMS:

Calcd for $C_{12}H_{15}Cl^{56}Fe^{74}Ge$: 323.942346. Found: 323.942077. Mp 61–62 °C.

Chloroferrocenylsilacyclobutane (5). Anhydrous hydrogen chloride (1.0 M in diethyl ether; 15.8 mL, 15.8 mmol) was added dropwise to a stirred solution of 4.027 g (15.8 mmol) of [1]silaferrocenophane **4** in *ca.* 50 mL of hexanes cooled to 0 °C, the colour changing immediately from red to orange to yellow. The solvent was removed under vacuum to leave a red oil. Fractional distillation of the crude mixture was performed under dynamic vacuum (10^{-2} Torr), keeping the fraction that distilled between 90–95 °C. Compound **5** was isolated as a pure, red oil in 84% yield (3.84 g; 13.3 mmol). ^{13}C NMR (100.5 MHz, C_6D_6) $\delta = 73.6$ (SiCp), 72.4 (SiCp), 69.0 (Cp), 65.9 (*ipso*-Cp), 22.4 ($SiCH_2$, $^1J_{CSi} = 23.4$ Hz), 16.1 (CH_2). ^1H NMR (400 MHz, C_6D_6) $\delta = 4.18$ (s, 4H, Cp), 4.04 (s, 5H, Cp), 2.1 (m, 1H, $CH_2CH_2CH_2$), 1.9 (m, 1H, $CH_2CH_2CH_2$), 1.6 (m, 2H, $SiCH_2$), 1.45 (m, 2H, $SiCH_2$). ^{29}Si NMR (79.5 MHz, C_6D_6): $\delta = 25.7$. MS (EI, 70 eV): *m/z* (%) = 186 (100, FcH^+), 290 (67, M^+), 262 (57, $M^+ - C_2H_4$), 121 (50, $CpFe^+$). HRMS: Calcd for $C_{13}H_{15}Cl^{56}FeSi$: 289.998096. Found: 289.997295.

Dichlorodiferrocenylsilane (7). Hydrogen chloride (1.0 M in diethyl ether; 10.8 mL, 10.8 mmol) was added dropwise to a suspension of **6** (2.145 g, 5.41 mmol) in *ca.* 40 mL of CH_2Cl_2. The colour changed from bright orange to amber and all of the solid dissolved during the addition. After removing all of the solvent under vacuum, the crude product was extracted with *ca.* 4 × 50 mL of warm hexanes (60 °C). Following filtration, the solvent was removed until a saturated solution of **7** in hexanes was present. After recrystallizing at −55 °C, the solvent was decanted and the product was dried under vacuum. Large yellow needles were obtained with a yield of 88% (2.235 g, 4.76 mmol). ^{13}C NMR (100.5 MHz, C_6D_6) $\delta = 73.8$ (SiCp), 72.4 (SiCp), 69.8 (Cp), 67.6 (*ipso*-Cp). ^1H NMR (400 MHz, C_6D_6) $\delta = 4.32$ (t, $^3J_{HH} = 1.77$ Hz, 4H, Cp), 4.15 (t, $^3J_{HH} = 1.77$ Hz, 4H, Cp), 4.10 (s, 10H, Cp). ^{29}Si NMR (79.5 MHz, $CDCl_3$) $\delta = 15.2$. UV/VIS (CH_2Cl_2): $\lambda_{max} = 448$ nm ($\varepsilon = 250$ L mol^{-1} cm^{-1}). MS (EI, 70 eV): *m/z* (%) = 468 (100, M^+), 403 (28, $M^+ - C_5H_5$), 312 (28, $M^+ - C_5H_5FeCl$), 277 (26, $M^+ - C_5H_5FeCl_2$), 156 (26, $M^+ - FcH - FeCl_2$), 247 (19, $M^+ - FcH - Cl$). Mp 112–114 °C (lit.[13] mp 80–85 °C). Anal. calcd: C, 51.21; H, 3.87; N, 0.00%. Found: C, 51.74; H, 3.84; N, <0.05%.

Diferrocenylsilanediol (8). A solution of **7** (0.500 g, 1.07 mmol) in 50 mL of diethyl ether was added dropwise *via* cannula to a stirred solution of 0.37 mL triethylamine (2.67 mmol), 0.04 mL water (2.2 mmol), and 50 mL of diethyl ether. During the addition, the solution became cloudy and remained yellow. The reaction mixture was stirred for an additional 10 min, then filtered through a Buchner funnel to remove insoluble triethylamine hydrochloride. Solvent was removed from the filtrate by rotary evaporation to afford a yellow solid. Recrystallization from ether gave orange crystals of **8** (0.416 g, 0.963 mmol, 90%). ^{13}C NMR (100.5 MHz, DMSO-d_6) $\delta = 72.9$ (SiCp), 70.2 (*ipso*-Cp), 70.0 (SiCp), 68.2 (Cp). ^1H NMR (400 MHz, DMSO-d_6) $\delta = 6.21$ (s, 2H, OH), 4.29 (t, $^3J_{HH} = 1.7$ Hz, 4H, Cp), 4.18 (t, $^3J_{HH} = 1.75$ Hz, 4H, Cp), 4.11 (s, 10H, Cp). ^{29}Si NMR (79.5 MHz, DMSO-d_6) $\delta = -25.1$. UV/VIS (CH_2Cl_2): $\lambda_{max} = 447$ nm ($\varepsilon = 277$ L mol^{-1} cm^{-1}). MS (EI, 70 eV): *m/z* (%) = 432 (100, M^+), 186 (29, FcH^+), 367 (28, $M^+ - C_5H_5$), 301 (16, $M^+ - 2C_5H_5$). Mp 159–160 °C (lit.[17] mp 164–165.5 °C). Anal. calcd: C, 55.59; H, 4.66; N, 0.00%. Found: C, 55.44; H, 4.61; N, <0.05%.

Attempted reaction of 6 with tetraphenylphosphonium chloride

Spirocyclic [1]silaferrocenophane **6** (53 mg; 0.13 mmol) was dissolved in 10 mL of dichloromethane and cooled to 0 °C, giving a clear, red solution. Tetraphenylphosphonium chloride (100 mg; 0.268 mmol), dissolved in 1.5 mL of dichloromethane, was added dropwise to the solution of **6**. Once the addition was complete, the reaction mixture was warmed to room temperature and stirred for 1 h. The solution, still red in colour, was pumped dry under vacuum. A ^1H NMR spectrum of the mixture in $CDCl_3$ showed only unreacted **6** and tetraphenylphosphonium chloride.

X-Ray structure determination

A summary of selected crystallographic data for **8** is given in Table 2. Selected inter- and intramolecular distances and bond angles are provided in Table 3. Data were collected at room temperature on a Nonius Kappa-CCD diffractometer using graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The data from 180 × 1° phi scans were integrated and scaled using the Denzo-SMN package.[20] The structure was solved and refined using the SHELXTL/PC package.[21] Refinement was by full-matrix least-squares on F^2 using all data (negative intensities included). The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0552P)^2 + 0.57P]$ where $P = (F_o^2 + 2F_c^2)/3$. All hydrogen atoms were included in calculated positions and treated as riding atoms except for the silanol hydrogens, which were refined with isotropic thermal parameters. CCDC reference number 440/073.

Acknowledgements

M. J. M. thanks the Natural Sciences and Engineering Research Council of Canada (NSERC) for a Postgraduate Scholarship (1995–1999). I. M. thanks the Alfred P. Sloan Foundation for a Research Fellowship (1994–1998), NSERC for an E. W. R. Steacie Fellowship (1997–1999), and the University of Toronto for a McLean Fellowship (1997–2003).

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Received in New Haven, CT, USA, 28th July 1998;
Paper 8/06682E