

Vinylsilylferrocenes and Ethynyl(vinyl)silylferrocenes. Synthesis, Multinuclear Magnetic Resonance Study and DFT Calculations

Bernd Wrackmeyer and Elena V. Klimkina

Anorganische Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany

Reprint requests to Prof. Dr. B. Wrackmeyer. E-mail: b.wrack@uni-bayreuth.de

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Ferrocenylsilanes with various functions at silicon (chlorine, vinyl, ethynyl) were prepared and studied by multinuclear magnetic resonance methods (^1H , ^{13}C , ^{29}Si NMR spectroscopy). The gas-phase geometries of the silanes were optimized by calculations at the B3LYP/6-311+G(d,p) level of theory, and NMR parameters (chemical shifts $\delta^{13}\text{C}$, $\delta^{29}\text{Si}$, spin-spin coupling constants) were calculated at the same level of theory.

Key words: Ferrocenylsilanes, ^{13}C , ^{29}Si NMR, Coupling Constants, DFT Calculations

Introduction

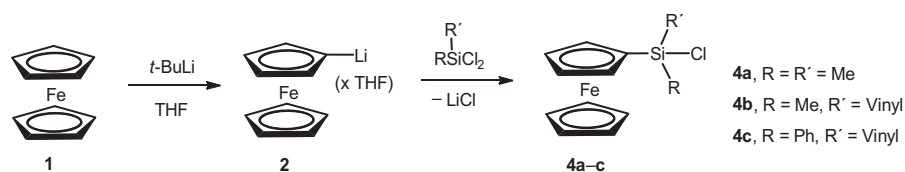
Ferrocene derivatives have received considerable attention in applications ranging from material sciences [1–5] to pharmacy [5–10]. The attractive properties of the ferrocene unit can be combined in numerous ways with that of other organometallic functions. In this context, ferrocenylsilanes are of interest. Although many of these compounds are already known [11–26], their NMR spectroscopic characterization is far from complete. In the present work we have prepared some ferrocenylsilanes bearing different functionalities at silicon (methyl, vinyl, phenyl, chlorine, and ethynyl), some of which invite to further synthetic transformations, measured their ^{13}C and ^{29}Si NMR data, and optimized their gas-phase geometries by DFT calculations at the B3LYP/6-311+G(d,p) level of theory. For further studies it seemed important to find out about the performance of the theoretical models for the calculation of NMR parameters, chemical shifts $\delta^{13}\text{C}$, $\delta^{29}\text{Si}$ and various spin-spin coupling constants.

Results and Discussion

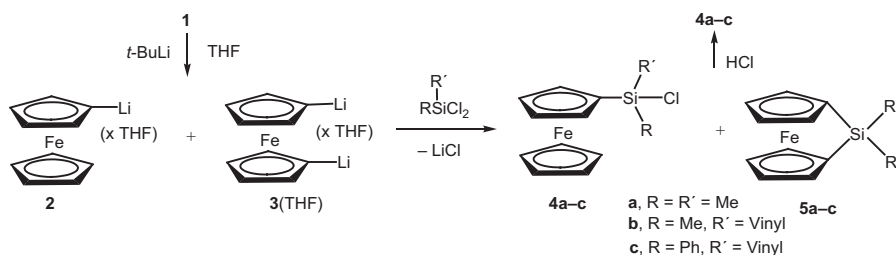
Synthesis

At present, one of the most versatile routes for derivatization of ferrocene takes advantage of the mono-lithiation of ferrocene **1**, leading to FcLi **2**, followed by reactions with electrophiles (Scheme 1), which in this work are chlorosilanes. Whereas **4a** is known [18, 27], **4b** and **4c** have not been described as yet. The chlorides **4** or the corresponding hydrides are potential precursors of ferrocene stabilized silylium cations, some of which have recently been characterized by ^{29}Si NMR spectroscopy and quantum-chemical analyses [24–26].

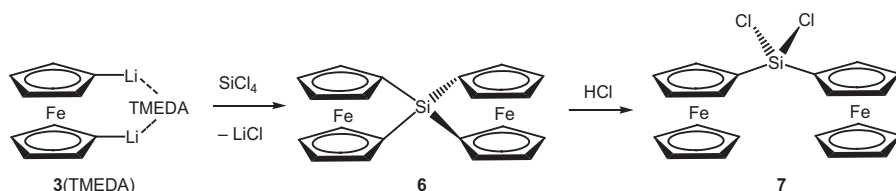
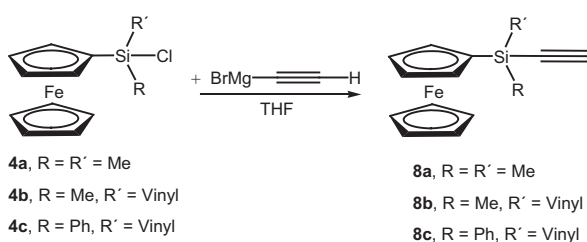
Since the mono-lithiation may also afford some dilithiated ferrocene FcLi_2 , **3**(THF) (Scheme 2), in particular in large-scale syntheses, the desired products **4** may have to be separated from the sila[1]ferrocenophanes **5** (**5a** [17] and **5b** [28] are known). As shown in Scheme 2, treatment of the mixture of **4** and **5** with HCl affords cleanly the products **4**.



Scheme 1. Mono-lithiation of ferrocene, followed by reaction with dichlorosilanes.



Scheme 2. Large-scale synthesis of ferrocenyl(chloro)silanes.

Scheme 3. Synthesis of the ferrocenophane **6**, followed by ring-opening.

Scheme 4. Synthesis of ethynyl(ferrocenyl)silanes.

In a similar way, another useful chlorosilane **7** has been prepared [29], starting from **3**(TMEDA) via the strained spiro-compound **6** [30] (Scheme 3). For both **6** and **7** numerous NMR data, in particular spin-spin coupling constants, are missing, and both compounds are of interest to test the validity of theoretical calculations.

Although the Si–C≡C–H moiety can serve for many useful purposes, ethynyl(ferrocenyl)silanes have not been reported as yet. We found that the chlorosilanes **4** are readily converted into the ethynylsilanes **8** (Scheme 4). By contrast, under the same conditions, **7** does not react with the Grignard reagent BrMg–C≡CH.

NMR spectroscopy

^{13}C and ^{29}Si NMR data (experimental and calculated) of the compounds **4–8** are given in Table 1, together with some other data for comparison. The assignment of ^{13}C NMR signals of the cy-

clopentaadienyl groups is based on their relative intensity (C_5H_5 ; C-1), on the absence or presence of ^{29}Si satellites for $^1J(^{29}Si, ^{13}C)$, and on coupling constants $^1J(^{13}C(1)^{13}C(2))$ and $^1J(^{13}C(2), ^{13}C(3))$ [31]. In turn, the assignment of the 1H NMR signals follows from two-dimensional (2D) $^1H/^{13}C$ shift correlations, confirmed by appropriate 1H - 1H NOE difference experiments. Expectedly, the presence of the silicon atom as a chiral center causes non-equivalence of the $^{13}C(^1H)^{2,5}$ as well as of the $^{13}C(^1H)^{3,4}$ nuclei. In most cases, the coupling constants $^nJ(^{29}Si, ^{13}C)$ ($n = 1, 2, 3$) can also be measured from the ^{13}C satellites in the ^{29}Si NMR spectra, confirming the data $^{2,3}J(^{29}Si, ^{13}C)$ (Fig. 1). Compound **8b** serves as an instructive example to demonstrate the expected increase in the magnitude of $|^1J(^{29}Si, ^{13}C)|$ for tetraorganosilanes, when the formal hybridization of carbon is changed from sp^3 to sp [$^1J(^{29}Si, ^{13}C) = 60.3$ Hz (Me), 74.7 Hz (vinyl), 83.2 Hz (Fc), and 87.8 Hz ($C\equiv$)] (Fig. 2). The polar Si–C≡ bond is responsible for the relatively small increase in $|^1J(^{29}Si, ^{13}C_{C\equiv})|$, a trend which is much more pronounced for the heavy and more electropositive congeners of group-14 nuclei (^{119}Sn , ^{207}Pb [32]).

Apparently, the magnitude of $^2J(^{57}Fe, ^{29}Si)$ is very small (< 1.5 Hz), because ^{57}Fe satellites were not observed in the ^{29}Si NMR spectra. However, some ^{13}C NMR signals are accompanied by ^{57}Fe satellites for $^1J(^{57}Fe, ^{13}C)$ in the usual range (≈ 5 Hz) [17]. Representative ^{13}C and ^{29}Si NMR spectra are shown in Figs. 1–3.

Table 1. ^{13}C and ^{29}Si NMR data^a of compounds 4–8.

No. Compound	Solvent	^{29}Si	Cp	C ¹	C ^{2,5}	C ^{3,4}	R	R'	$^{-}\text{C}\equiv\text{CH}$
Fe-SiMe ₃ ^b	CDCl ₃	-3.6 ^c	68.1	72.0	72.7	70.6	-0.1	-	-
Fe-SiMe ₃ (calcd.)		-2.8	70.4	76.0	75.5	72.8	-3.0	-	-
4a Fe-SiMe ₂ Cl	C ₆ D ₆	22.6 (84.3) (60.0) (6.7) (5.4)	69.4	[+39.5] (-66.1) [+48.1]	[+39.5] (-5.9) [+48.1]	72.5 (+48.1)	3.4 (60.5)	-	-
Fe-SiMe ₂ Cl (calcd.)		32.1	70.5	72.8 (-79.1)	75.8 (-6.9)	74.0 (-5.1)	-0.2 (-54.1)	-	-
4b Fe-SiMe(vinyl)Cl	C ₆ D ₆	10.5 (87.0) (78.2) (62.6)	69.1	66.9 (87.0)	73.6 (6.6) 73.8 (7.0)	72.35 (5.4) 72.36 (5.4)	1.4 (62.6)	= CH ₂ : 134.9 (<2) = CH-: 135.8 (78.4)	-
Fe-SiMe(vinyl)Cl (calcd.)		21.7	70.5	71.8 (-81.8)	76.4 (-7.4)	74.2 (-5.3)	-0.4 (-55.8)	= CH ₂ : 140.8 (-0.9) = CH-: 139.3 (-87.8)	-
4c Fe-SiPh(vinyl)Cl	CD ₂ Cl ₂	2.1 (88.9) (81.4) (80.2) (5-7)	69.4	65.2 (88.9)	C ² : 74.1 (6.3) C ⁵ : 74.2 (7.3)	72.44 (5.4) 72.47 (5.4)	C _m : 128.4 (6.3) C _p : 130.8 (<2) C _o : 134.6 (5.2) C _i : 134.7 (81.4)	= CH-: 133.8 (80.2) = CH ₂ : 137.1 (<2)	-
Fe-SiPh(vinyl)Cl (calcd.)		12.6	71.2	72.1 (84.6)	76.9 (-7.1)	73.8 (-5.3)	130.8 (-6.1) 133.5 (+1.2) 139.7 (-5.5) 134.1 (-76.7)	= CH-: 142.7 (-74.2) = CH ₂ : 136.5 (-3.6)	-
5a Fe(SiMe ₂) ^d (in a mixture with 4a) Fe(SiMe ₂) (calcd.)	C ₆ D ₆	-4.8 -4.4	-	33.5 (57.8) 35.8	75.8 (5.2)	77.9	-2.9 (53.3)	-	-
5b Fe[SiMe(vinyl)] (in a mixture with 4b)	C ₆ D ₆	-2.6	-	28.8	75.5, 75.9	77.7, 77.8	-2.9	= CH ₂ : 135.0 = CH-: 135.8	-
5c Fe[SiPh(vinyl)] (in a mixture with 4c)	CD ₂ Cl ₂	-10.3	-	30.9	76.4, 76.6	78.1, 78.2	C _m : 128.7 C _p : 130.6 C _o : 134.9 C _i : n. o.	= CH-: n. o. = CH ₂ : 136.3	-

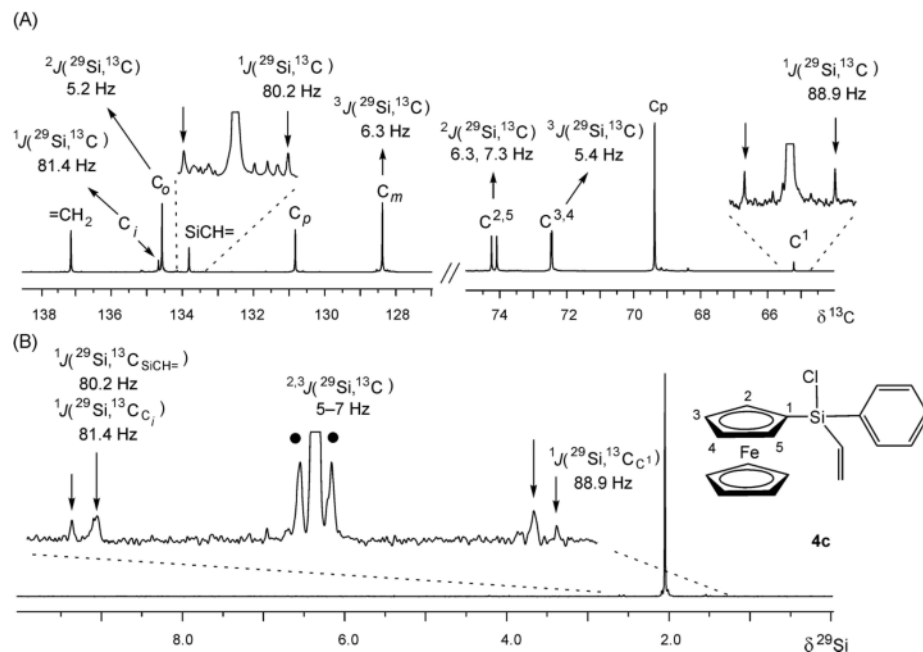


Fig. 1. Chloro(phenyl)(vinyl)silyl-ferrocene (**4c**). (A) 100.5 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (in CD_2Cl_2 , at 23°C). (B) 79.4 MHz $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (refocused INEPT [36, 37]) (in CD_2Cl_2 , at 23°C). The ^{13}C satellites for $^1J(^{29}\text{Si}, ^{13}\text{C})$ are marked by arrows, for $^{2,3}J(^{29}\text{Si}, ^{13}\text{C})$ by filled circles.

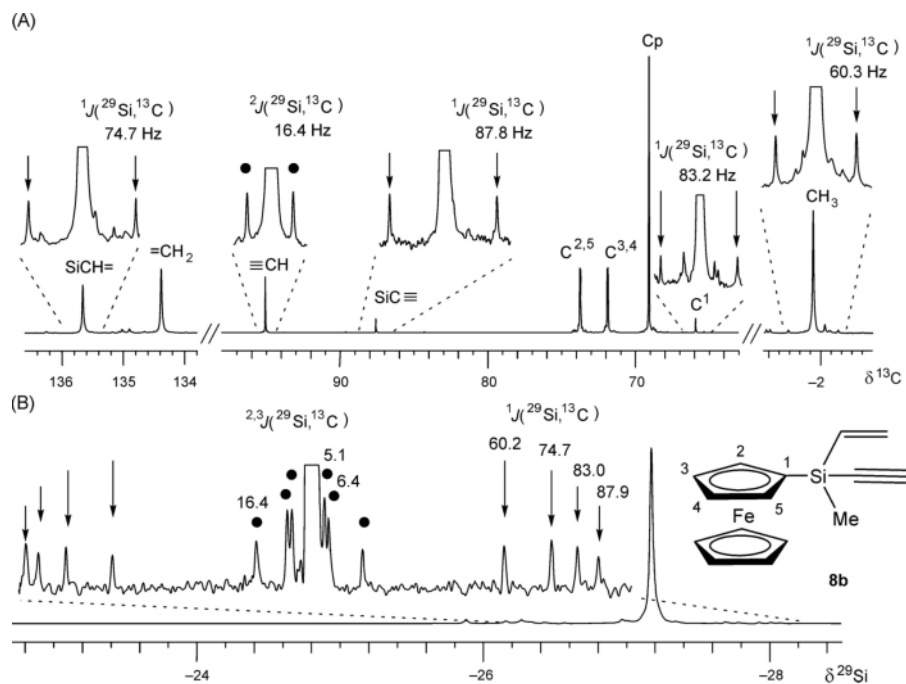


Fig. 2. Ethynyl(methyl)(vinyl)silyl-ferrocene (**8b**). (A) 62.9 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (in CD_2Cl_2 , at 23°C). (B) 49.7 MHz $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (refocused INEPT [36, 37]) (in CD_2Cl_2 , at 23°C). The ^{13}C satellites for $^1J(^{29}\text{Si}, ^{13}\text{C})$ are marked by arrows, for $^{2,3}J(^{29}\text{Si}, ^{13}\text{C})$ by filled circles (all coupling constants are given in Hz).

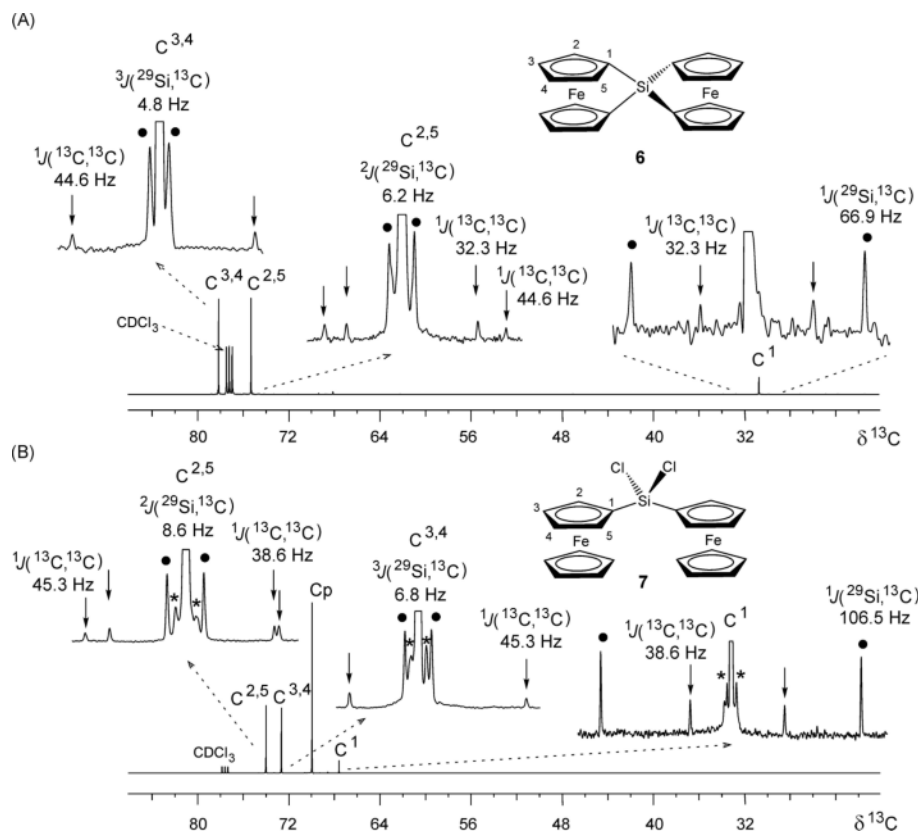


Fig. 3. (A) 125.8 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6** (in CDCl_3 , 23 °C). The ^{29}Si satellites for $^nJ(^{29}\text{Si},^{13}\text{C})$ are marked by filled circles; the ^{13}C satellites for $^1J(^{13}\text{C},^{13}\text{C})$ are marked by arrows. (B) 125.8 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7** (in CDCl_3 , 23 °C). The ^{29}Si satellites for $^nJ(^{29}\text{Si},^{13}\text{C})$ are marked by filled circles; the ^{13}C satellites for $^1J(^{13}\text{C},^{13}\text{C})$ are marked by arrows, the ^{57}Fe satellites for $^nJ(^{57}\text{Fe},^{13}\text{C})$ are marked by asterisks.

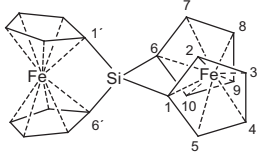
DFT calculations

All gas-phase structures of the ferrocene derivatives studied were optimized at the B3LYP/6-311+G(d,p) level of theory [38–42], and NMR parameters [chemical shifts $\delta^{13}\text{C}$ and $\delta^{29}\text{Si}$ [43], and spin-spin coupling constants $^nJ(^{29}\text{Si},^{13}\text{C})$ ($n = 1–4$) and $^1J(^{13}\text{C},^{13}\text{C})$] [44–46] were calculated at the same level. The expected structures show the cyclopentadienyl rings in eclipsed conformation; a comparison of experimental [30] and calculated structural data for the [1]ferrocenophane **6** reveals reasonable agreement (Table 2).

Most calculated NMR parameters (Table 1) correspond closely to the experimental data. The influence of the Si–Cl function on calculated $\delta^{29}\text{Si}$ values is not well reproduced (see **4a**, **4b**, **4c**, **7**). The calculated

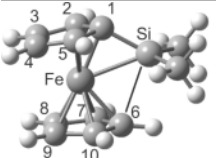
magnitude as well as the sign of coupling constants $^nJ(^{29}\text{Si},^{13}\text{C})$ appear to be fairly accurate for $n > 1$. Frequently for $n = 1$, the calculated magnitude is too small, which has been noted before [48]. For the Si–CH=CH₂ function $^2J(^{29}\text{Si},^{13}\text{C})$ could not be measured because of its small magnitude, supported by the calculations. The calculated data $^1J(^{13}\text{C},^{13}\text{C})$ are in good agreement with experimental data, and this is also true for $^1J(^{57}\text{Fe},^{13}\text{C})$, where it could be determined. All calculated $J(^{57}\text{Fe},^{29}\text{Si})$ data are small (< 2 Hz) which explains that they could not be observed experimentally. Even in the [1]ferrocenophane **6**, where Fe and Si are only 270 pm apart, the calculated value $J(^{57}\text{Fe},^{29}\text{Si}) = +1.8$ Hz is small.

A recent experimental NMR study together with quantum-chemical analyses of ferrocenylsilylium cations has provided evidence for multicenter bonding

Table 2. Selected bond lengths (pm) and angles (deg)^a of the [1]ferrocenophane **6** (1' corresponds to 6) and **6** (calcd.).


	6 ^b	6 (calcd.)
Fe–Si(1)	265.72(5)	270.0
Fe–C(1), Fe–C(6)	201.7(3), 201.9(3)	202.5
Fe–C(2), Fe–C(7)	203.2(3), 202.8(3)	205.5
Fe–C(3), Fe–C(8)	208.4(3), 206.8(3)	211.8
Fe–C(4), Fe–C(9)	207.5(3), 207.7(3)	211.9
Fe–C(5), Fe–C(10)	202.7(3), 203.1(3)	205.4
Si–C(1), Si–C(6)	187.4(3), 187.1(3)	189.2
C(1)–Si–C(6)	98.48(12)	96.9
C(1)–Si–C(1')	113.85 (13)	116.1
Fe...Fe	531.4(1)	540.4
C ₅ /C ₅ (α)	19.4(2)	18.0
C ₅ /Si (β)	37.0(6)	40.0
C ₅ /C ₅ (twist) (τ)	1.1	0

^a The definition of the angles α, β, and τ is given in ref. [47];
^b ref. [30].

Table 3. NMR parameters of the ferrocenyl(dimethyl)silylium and ferrocenyldihydrosilylium cations **9**, **10**.


	[Fc–SiMe ₂] ⁺ 9 exp. [24]	[Fc–SiMe ₂] ⁺ 9 ^a calcd. ^c <i>d</i> _{Fe–Si} = 257.5 pm	[Fc–SiMe ₂] ⁺ 9 ^b calcd. ^c <i>d</i> _{Fe–Si} = 246.2 pm	[Fc–SiH ₂] ⁺ 10 ^a calcd. ^c <i>d</i> _{Fe–Si} = 245.8 pm
NMR parameter				
δ ²⁹ Si (<i>J</i> (⁵⁷ Fe, ²⁹ Si))	111.0	149.1 (+0.9)	109.1 (–0.1)	74.6 (+0.6)
δ ¹³ C(1) (¹ <i>J</i> (²⁹ Si, ¹³ C))	d	64.8 (–48.6)	65.0 (–51.4)	70.7 (–48.5)
[¹ <i>J</i> (¹³ C(1), ¹³ C(2))]		[+35.8]	[+35.2]	[+35.2]
δ ¹³ C(2,5) (² <i>J</i> (²⁹ Si, ¹³ C))	d	81.3 (–4.7)	79.2 (–4.7)	83.2 (–4.5)
[¹ <i>J</i> (¹³ C(2), ¹³ C(3))]		[+48.4]	[+47.9]	[+48.2]
δ ¹³ C(3,4) (³ <i>J</i> (²⁹ Si, ¹³ C))	d	91.9 (–5.9)	95.1 (–5.9)	92.7 (–6.1)
δ ¹³ C(6) (<i>J</i> (²⁹ Si, ¹³ C))	d	62.7 (+0.5)	60.8 (+2.3)	58.7 (+0.6)
[¹ <i>J</i> (¹³ C(6), ¹³ C(7))]		[+45.9]	[+45.8]	[+45.2]
δ ¹³ C(7,10) (<i>J</i> (²⁹ Si, ¹³ C))	d	72.6 (+0.8)	74.4 (+0.8)	74.0 (+1.1)
[¹ <i>J</i> (¹³ C(7), ¹³ C(8))]		[+48.3]	[+47.9]	[+48.2]
δ ¹³ C(8,9) (<i>J</i> (²⁹ Si, ¹³ C))	d	85.5 (–0.3)	83.4 (–0.4)	88.2 (–0.5)
δ ¹³ C(SiMe)	–1.6	–1.8	–3.0	–
(¹ <i>J</i> (²⁹ Si, ¹³ C))		(–49.3)	(–52.1)	

^a Gas-phase geometry optimized at the B3LYP/6-311+G(d,p) level of theory; ^b geometry from PBE0-D3/def2-TZVPP calculations, as given in ref. [24]; ^c calcd. NMR parameters at the B3LYP/6-311+G(d,p) level of theory; ^d δ¹³C values given as 66.4, 74.4, 80.3, 86.8 ppm without assignment [24].

involving Si, Fe and the unsubstituted cyclopentadienyl ring [24]. This is confirmed by the calculated coupling constants (experimental data are missing) given in Table 3. Although ¹*J*(⁵⁷Fe, ²⁹Si) is rather small (magnitude and sign depending on geometry), the interaction between Si and the unsubstituted cyclopentadienyl ring is again reflected by small calculated coupling constants *J*(²⁹Si, ¹³C), which however, are significantly larger than in "normal" ferrocenylsilanes. Similarly, calculations indicate spin-spin coupling interactions between ²⁹Si and the ¹H nuclei of the unsubstituted cyclopentadienyl ring in the ferrocenylsilylium ion, which are negligible in ferrocenylsilanes.

Conclusion

Ferrocenylsilanes bearing various functional groups at silicon are readily available. Their characterization in solution by NMR methods is straightforward.

These measurements are conveniently complemented by quantum-chemical calculations of structure and NMR parameters. The latter appear to be particularly helpful for the discussion of extreme bonding situations.

Experimental Section

All syntheses and the handling of the samples were carried out observing necessary precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. CD_2Cl_2 and CDCl_3 were distilled over CaH_2 in an atmosphere of argon. All other solvents were distilled from Na metal in an atmosphere of argon. Silicon halides, ethynylmagnesium bromide (0.5 M in THF), *t*-BuLi (1.7 M in pentane), hydrogen chloride (1.0 M in Et_2O), were commercial products and were used as received. FcLi [18] and $\text{FcLi}_2(\text{TMEDA})$ [18] were prepared following literature procedures. NMR measurements: Bruker ARX 250, DRX 500: ^1H , ^{13}C , and ^{29}Si NMR [refocused INEPT [36, 37] based on $^{2,3}J(^{29}\text{Si}, ^1\text{H}) = 25$ Hz (Si-vinyl), 7 Hz (Si-Me) or 4–5 Hz (Si-Ph)]; Varian INOVA 400: ^1H , ^{13}C , ^{29}Si NMR; chemical shifts are given in ppm relative to Me_4Si [$\delta(^1\text{H}(\text{CHCl}_3)) = 7.24$, ($\text{C}_6\text{D}_5\text{H}) = 7.15$, (CHDCl_2) = 5.31, ($\text{C}_6\text{D}_5\text{CD}_2\text{H}) = 2.08$ (± 0.01); $\delta(^{13}\text{C}$ (C_6D_6) = 128.2, (CDCl_3) = 77.2, (CD_2Cl_2) = 53.8, ($\text{C}_6\text{D}_5\text{CD}_3$) = 20.4 (± 0.1); $\delta(^{29}\text{Si}) = 0$ (± 0.1) for $\Xi(^{29}\text{Si}) = 19.867184$ MHz]. The assignments of ^1H and ^{13}C NMR signals are based on ^1H - ^1H NOE difference [49], and 2D $^1\text{H}/^{13}\text{C}$ gHSQC experiments [50]. EI-MS spectra: Finnigan MAT 8500 spectrometer (ionisation energy 70 eV) with direct inlet. The m/z data refer to the isotopes ^1H , ^{12}C , ^{28}Si , ^{35}Cl , and ^{56}Fe .

All quantum-chemical calculations were carried out using the GAUSSIAN 09 program package [51]. Geometries were optimized at the B3LYP/6-311+G(d,p) level of theory, and nuclear shieldings were calculated [43] at the same level. The nuclear shielding constants were converted into chemical shifts $\delta(^{13}\text{C})$ and $\delta(^{29}\text{Si})$, using the calculated shielding constants for SiMe_4 with $\sigma(^{13}\text{C}) = 181.0$ and $\sigma(^{29}\text{Si}) = 340.1$, respectively.

Chloro(R)(R')silyl-ferrocene, Fc-SiR(R')(Cl) (4a-c)

Method A

Chlorodimethylsilyl-ferrocene, Fc-SiMe₂(Cl) (4a) [18]: ^1H NMR (400 MHz, C_6D_6 , 23 °C): $\delta = 0.49$ (s, 6H, SiMe_2), 4.00 (s, 5H, Cp), 4.04 (m, 2H, $\text{H}^{2,5}$), 4.17 (m, 2H, $\text{H}^{3,4}$).

Chloro(methyl)(vinyl)silyl-ferrocene, Fc-SiMe(vinyl)(Cl) (4b)

A solution of freshly prepared FcLi (769 mg, 4.01 mmol) in THF (20 mL) was cooled to -30 °C and dropwise added

to a solution of Me(vinyl)SiCl_2 (2.26 g, 2.1 mL, 16 mmol) in THF (15 mL). This mixture was allowed to reach ambient temperature and kept stirring for 20 h. The volatile materials were removed in vacuum, and the oily residue was dissolved in hexane (25 mL). Insoluble materials were filtered off, and hexane was removed in vacuum to give the chloroferrocene **4b** together with ferrocene. The product was heated to 45 °C in vacuum (8×10^{-3} Torr) for 1–2 h to sublime off the impurities of ferrocene. The remaining brown oil of **4b** (yield 488 mg, 42%) can be used directly for further reactions. – ^1H NMR (400 MHz, C_6D_6 , 23 °C): $\delta = 0.57$ [s, 3H, SiMe , $^2J(^{29}\text{Si}, ^1\text{H}) = 7.0$ Hz], 4.00 (s, 5H, Cp), 4.07, 4.09 (m, m, 1H, 1H, H^2 , H^5), 4.18 (m, 2H, $\text{H}^{3,4}$), 5.90 [dd, 1H, = CH_2 -*trans*, $^3J(\text{H}, \text{H}) = 19.7$ Hz, $^2J(\text{H}, \text{H}) = 3.4$ Hz], 5.93 [dd, 1H, = CH_2 -*cis*, $^3J(\text{H}, \text{H}) = 14.9$ Hz, $^2J(\text{H}, \text{H}) = 3.4$ Hz], 6.24 [dd, 1H, = CH -, $^3J(\text{H}, \text{H}) = 19.7$ Hz, $^3J(\text{H}, \text{H}) = 14.9$ Hz]. – EI-MS (70 eV) for $\text{C}_{13}\text{H}_{15}\text{ClSiFe}$ (290.64): $m/z(\%) = 290$ (100) $[\text{M}]^+$, 275 (10) $[\text{M}-\text{CH}_3]^+$, 263 (5) $[\text{M}-\text{C}_2\text{H}_3]^+$, 255 (3) $[\text{M}-\text{Cl}]^+$, 225 (10) $[\text{M}-\text{C}_5\text{H}_5]^+$, 199 (15) $[\text{M}-\text{C}_5\text{H}_5-\text{C}_2\text{H}_2]^+$.

Chloro(phenyl)(vinyl)silyl-ferrocene, Fc-SiPh(vinyl)(Cl) (4c)

The synthesis was carried out as described for **4b**, starting from 850 mg (4.42 mmol) of FcLi in THF (30 mL) and a solution of Ph(vinyl)SiCl_2 (1.80 mg, 1.50 mL, 8.86 mmol) in THF (10 mL). The residue was heated to 30–40 °C in vacuum (8×10^{-3} Torr) for 1–2 h to remove the impurities of ferrocene and Ph(vinyl)SiCl_2 . The oily residue was distilled (130–150 °C, 8×10^{-3} Torr) to give **4c** as a dark-brown oil (yield 869 mg, 56%). – ^1H NMR (400 MHz, CD_2Cl_2 , 23 °C): $\delta = 4.26$ (s, 5H, Cp), 4.36 (m, 1H, H^5), 4.39 (m, 1H, H^2), 4.57 (m, 2H, $\text{H}^{3,4}$), 6.19 [dd, 1H, = CH_2 -*trans*, $^3J(\text{H}, \text{H}) = 19.9$ Hz, $^2J(\text{H}, \text{H}) = 3.5$ Hz], 6.41 [dd, 1H, = CH_2 -*cis*, $^3J(\text{H}, \text{H}) = 14.7$ Hz, $^2J(\text{H}, \text{H}) = 3.5$ Hz], 6.64 [dd, 1H, = CH -, $^3J(\text{H}, \text{H}) = 19.9$ Hz, $^3J(\text{H}, \text{H}) = 14.7$ Hz], 7.52 (m, 3H, H_m , H_p), 7.82 (m, 2H, H_o). – EI-MS (70 eV) for $\text{C}_{18}\text{H}_{17}\text{ClSiFe}$ (352.71): $m/z(\%) = 352$ (100) $[\text{M}]^+$, 225 (5) $[\text{M}-\text{C}_2\text{H}_3]^+$, 287 (5) $[\text{M}-\text{C}_5\text{H}_5]^+$, 261 (10) $[\text{M}-\text{C}_5\text{H}_5-\text{C}_2\text{H}_2]^+$, 252 (5) $[\text{M}-\text{C}_5\text{H}_5-\text{Cl}]^+$, 212 (5), 195 (5).

Method B

Chlorodimethylsilyl-ferrocene, Fc-SiMe₂(Cl) (4a)

A solution of ferrocene **1** (6.694 g, 35.98 mmol) in THF (35 mL) was cooled to 0 °C, *t*-BuLi (21.1 mL of a 1.7 M solution in hexane, 36.0 mmol) was added dropwise, and the solution was kept stirring for 15 min. Hexane (40 mL) was added, the suspension was cooled to -78 °C and kept at complete rest for 30 min. The supernatant liquid phase was carefully decanted *via* a cannula. THF (30 mL) was added at -78 °C to the orange precipitate, and this cold suspension was added dropwise to a solution of Me_2SiCl_2 (9.29 g,

8.8 mL, 72 mmol) in THF (10 mL) at -40°C . The mixture was allowed to reach ambient temperature and kept stirring for 20 h. The volatile materials were removed in vacuum, and the oily residue was dissolved in hexane (50 mL). Insoluble materials were filtered off, and hexane was removed in vacuum to give the mixture of **4a** (ca. 60%) together with **5a** (ca. 10%) and ferrocene (ca. 30%). The product was heated at 40°C in vacuum (8×10^{-3} Torr) for 2–3 h to sublime off impurities of ferrocene. The residue was dissolved in hexane (30 mL), and HCl (5 mL, 1.0 M in Et₂O) was added dropwise at 0°C . The solution was kept stirring for 1 h. The solvent was removed in vacuum, and the oily residue was dissolved in hexane (30 mL). Insoluble materials were filtered off, and hexane was removed in vacuum to give the chlorosilylferrocene **4a** (5.053 g, 50% calculated on ferrocene **1**).

Chloro(methyl)(vinyl)silyl-ferrocene, Fc-SiMe(vinyl)(Cl)
(**4b**)

The synthesis was carried out as described for **4a**, starting from ferrocene **1** (5.426 g, 29.16 mmol), *t*-BuLi (17.1 mL of a 1.7 M solution in hexane, 29.0 mmol) and Me(vinyl)SiCl₂ (8.22 mg, 7.6 mL, 58.3 mmol). The oily residue was heated to $50-60^{\circ}\text{C}$ in vacuum (8×10^{-3} Torr) for 2–3 h to sublime off impurities of ferrocene. The residue was dissolved in hexane (30 mL), insoluble materials were filtered off, and hexane was removed in vacuum to give the chlorosilylferrocene **4b** (3.517 g, 42% calculated on ferrocene **1**).

Chloro(phenyl)(vinyl)silyl-ferrocene, Fc-SiPh(vinyl)(Cl)
(**4c**)

The synthesis was carried out as described for **4a**, starting from ferrocene **1** (5.306 g, 28.52 mmol), *t*-BuLi (16.8 mL of a 1.7 M solution in hexane, 28.5 mmol) and Ph(vinyl)SiCl₂ (5.79 mg, 4.8 mL, 28.5 mmol). The mixture contained **4c** (80%), **5c** (20%) together with Ph(vinyl)SiCl₂ and ferrocene. This oily residue was heated to $30-50^{\circ}\text{C}$ in vacuum (8×10^{-3} Torr) for 2–3 h to separate from impurities of ferrocene and Ph(vinyl)SiCl₂. The oil was dissolved in hexane (20 mL), and HCl (4 mL, 1.0 M in Et₂O) was added dropwise at 0°C , and the solution was kept stirring for 1 h. The solvent was removed in vacuum, and the oily residue was dissolved in hexane (30 mL). Insoluble materials were filtered off, and hexane was removed in vacuum to give **4c** (5.029 g, 50% calculated on ferrocene **1**).

Spirocyclic [1]silaferrocenophane (6) [30]: $-\text{}^1\text{H NMR}$ (400 MHz, CDCl₃, 23°C): $\delta = 4.48$ (m, 8H, H^{2,5}), 4.63 (m, 8H, H^{3,4}).

Dichloro(diferrocenyl)silane (7) [29]: $-\text{}^1\text{H NMR}$ (400 MHz, CDCl₃, 23°C): $\delta = 4.26$ (s, 10H, Cp), 4.42 (m, 4H, H^{2,5}), 4.51 (m, 4H, H^{3,4}).

Ethynyldimethylsilyl-ferrocene, Fc-SiMe₂(C≡CH) (8a)

A solution of ethynylmagnesium bromide (1.86 mL of a 0.5 M solution in THF) was added dropwise to a solution of **4a** (259 mg, 0.93 mmol) in THF (5 mL) at 0°C . The progress of the reaction was monitored by ^1H and ^{29}Si NMR spectroscopy. The reaction mixture was stirred for 20 h at r.t. The solvent was removed in vacuum, the residue was dissolved in hexane (30 mL), and insoluble materials were filtered off. Hexane was removed in vacuum to give **8a** as an orange-brown oil (235 mg, 94%). $-\text{}^1\text{H NMR}$ (400 MHz, CD₂Cl₂, 23°C): $\delta = 0.41$ (s, 6H, SiMe₂), 2.53 [s, 1H, $\equiv\text{CH}$, $^1J(^{13}\text{C}, ^1\text{H}) = 236.8$ Hz], 4.18 (s, 5H, Cp), 4.19 (m, 2H, H^{2,5}), 4.39 (m, 2H, H^{3,4}).

Ethynyl(methyl)(vinyl)silyl-ferrocene, Fc-SiMe(vinyl)(C≡CH) (8b)

A solution of ethynylmagnesium bromide (3.32 mL of a 0.5 M solution in THF) was added dropwise to a solution of **4b** (483 mg, 1.66 mmol) in THF (5 mL) at 0°C . The reaction mixture was stirred for 4 d at r.t. The progress of the reaction was monitored by ^1H and ^{29}Si NMR spectroscopy. The solvent was removed in vacuum, the residue was dissolved in hexane (100 mL), and insoluble materials were filtered off. Hexane was removed in vacuum to give **8b** as a brown oil (385 mg, 83%). $-\text{}^1\text{H NMR}$ (250.1 MHz, CD₂Cl₂, 23°C): $\delta = 0.41$ [s, 3H, SiMe, $^2J(^{29}\text{Si}, ^1\text{H}) = 7.0$ Hz], 2.13 [s, 1H, $\equiv\text{CH}$, $^1J(^{13}\text{C}, ^1\text{H}) = 238.0$ Hz], 4.06 (s, 5H, Cp), 4.07, 4.12 (m, m, 1H, 1H, H², H⁵), 4.17 (m, 2H, H^{3,4}), 5.95 [d, 1H, =CH₂-*trans*, $^3J(\text{H},\text{H}) = 23.0$ Hz], 5.97 [d, 1H, =CH₂-*cis*, $^3J(\text{H},\text{H}) = 11.1$ Hz], 6.22 [dd, 1H, =CH-, $^3J(\text{H},\text{H}) = 23.0$ Hz, $^3J(\text{H},\text{H}) = 11.1$ Hz]. $-\text{EI-MS}$ (70 eV) for C₁₅H₁₆SiFe (280.21): $m/z(\%) = 280$ (100) [M]⁺, 265 (25) [M-CH₃]⁺, 253 (10) [M-C₂H₃]⁺, 189 (15), 186 (5).

Ethynyl(phenyl)(vinyl)silyl-ferrocene, Fc-SiPh(vinyl)(C≡CH) (8c)

A solution of ethynylmagnesium bromide (3.24 mL of a 0.5 M solution in THF) was added dropwise to a solution of **4c** (572 mg, 1.62 mmol) in THF (10 mL) at 0°C . The reaction mixture was stirred for 4 d at r.t. The progress of the reaction was monitored by ^1H and ^{29}Si NMR spectroscopy. The solvent was removed in vacuum, the residue was dissolved in hexane (120 mL), and insoluble materials were filtered off. Hexane was removed in vacuum to give **8c** as a brown oil (468 mg, 84%). $-\text{}^1\text{H NMR}$ (250.1 MHz, CD₂Cl₂, 23°C): $\delta = 2.80$ [s, 1H, $\equiv\text{CH}$, $^1J(^{13}\text{C}, ^1\text{H}) = 238.7$ Hz], 4.18 (s, 5H, Cp), 4.26 (m, 2H, H^{2,5}), 4.45 (m, 2H, H^{3,4}), 6.07 [dd, 1H, =CH₂-*trans*, $^3J(\text{H},\text{H}) = 19.7$ Hz, $^2J(\text{H},\text{H}) = 4.1$ Hz], 6.26 [dd, 1H, =CH₂-*cis*, $^3J(\text{H},\text{H}) = 14.5$ Hz, $^2J(\text{H},\text{H}) = 4.1$ Hz], 6.46 [dd, 1H, =CH-, $^3J(\text{H},\text{H}) = 19.7$ Hz, $^3J(\text{H},\text{H}) = 14.5$ Hz],

7.40 (m, 3H, Ph), 7.69 (m, 2H, Ph). – EI-MS (70 eV) for $C_{20}H_{18}SiFe$ (342.29): $m/z(\%) = 342$ (100) $[M]^+$, 315 (5) $[M-C_2H_3]^+$, 277 (5) $[M-C_5H_5]^+$, 251 (10) $[M-C_5H_5-C_2H_2]^+$, 225 (4).

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