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Complexes with sterically demanding ligands

VII *. Crystal structure and dynamic solution behavior of 1,1′,3,3′-tetrakis(trimethylsilyl)ferrocene

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Abstract

A single-crystal X-ray diffraction study of 1,1′,3,3′-tetrakis(trimethylsilyl)ferrocene $Fe[(1,3\text{-}SiMe_3)_2\text{-}\eta^5\text{-}C_5H_3]_2$ has revealed a conformation of C_2 symmetry in which the trimethylsilyl groups are arranged in a staggered fashion, with the five-membered rings nearly eclipsed. From variable-temperature ^1H NMR spectroscopic study a barrier to ring rotation of $\Delta G^{\neq}$ 11.0 kcal mol^{-1} can be estimated.

Introduction

The 1,3-bis(trimethylsilyl)cyclopentadienyl ligand $1,3\text{-}(SiMe_3)_2C_5H_3(Si_2Cp)$ is gaining importance as an ancillary ligand with properties complementary to those of the parent cyclopentadienyl (Cp) and the pentamethylcyclopentadienyl ligand (C_5Me_5). Lappert et al. have utilized the steric bulk and the high lipophilicity of Si_2Cp for the successful synthesis of a series of novel *f*-element complexes, [2] and both Jutzi et al. [3] and Raston et al. [4] have described the preparation and structural characterization of Si_2Cp complexes of various main group elements. On the other hand, relatively little is known on transition metal complexes bearing this ligand [5–8]. We report here the X-ray structure and dynamic solution behavior of the prototypical ferrocene derivative $Fe(Si_2Cp)_2$ [5,7].

Results and discussion

The title compound is straightforwardly prepared by the reaction of $FeCl_2 \cdot 1.5$ THF with $Li(Si_2Cp)$ in THF. As was observed in the case of the bulkier Si_3Cp

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* For Part VI see ref. 1.

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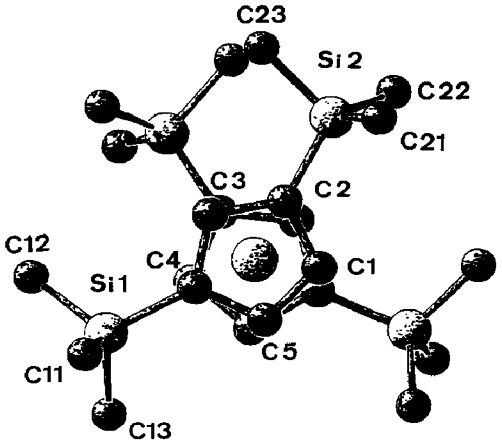

Fig. 1. Top view of the title compound.

system (Si_3Cp = 1,2,4-$(SiMe_3)_3$-η^5-C_5H_2 [9,10], a thermally labile intermediate having just one five-membered ring is formed first at lower temperatures and can be trapped, e.g. with CO to give orange-red dicarbonyl $(Si_2Cp)Fe(CO)_2Cl$ albeit in low yield [11*]. $Fe(Si_2Cp)_2$ is isolated as sublimable, pentane-soluble orange crystals in yields of 50–60%, substantially higher than these of $Fe(Si_3Cp)_2$ [10].

The title compound crystallizes from methanol at −30 °C as orange platelets. The monoclinic lattice contains discrete well-separated molecules on a crystallographic C_2 symmetry axis. Figure 1 shows the molecular geometry and the crystallographic numbering scheme. Table 1 lists the final atomic coordinates and Table 2 selected bond lengths and angles. The observed structure of this sandwich molecule

Table 1

Final positional parameters of the title compound (including estimated standard deviations)

Atom	*x*	*y*	*z*	$B_{eq.}$ (Å^2) [a]
Fe	0	0.39879(5)	0.25	3.51(2)
Si(1)	0.2630(1)	0.4734(1)	0.2660(1)	5.45(4)
Si(2)	0.0039(1)	0.2598(1)	0.4540(1)	6.01(4)
C(1)	0.0060(4)	0.4144(3)	0.4126(3)	4.5(1)
C(2)	0.0473(4)	0.3442(3)	0.3966(3)	4.1(1)
C(3)	0.1369(4)	0.3555(3)	0.3424(3)	3.9(1)
C(4)	0.1551(4)	0.4294(3)	0.3255(3)	3.8(1)
C(5)	0.0716(4)	0.4655(3)	0.3706(4)	4.6(1)
C(11)	0.3770(5)	0.4993(4)	0.3776(5)	8.1(2)
C(12)	0.3182(5)	0.4106(4)	0.1741(5)	9.0(2)
C(13)	0.2115(5)	0.5541(4)	0.1911(5)	9.4(2)
C(21)	0.0260(10)	0.2670(5)	0.5986(6)	21.3(4)
C(22)	−0.1366(6)	0.2330(4)	0.4019(6)	10.3(2)
C(23)	0.0930(6)	0.1858(4)	0.4206(7)	12.5(3)
Cp	0.0833	0.4018	0.3695	

[a] The equivalent isotropic parameters are defined as $B_{eq.} = \frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ac\cos\beta B_{13}]$. Cp denotes the center of the Si_3Cp ligand.

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* Reference number with asterisk indicates a note in the list of references.

Table 2

Interatomic distances (Å) and angles (deg) and their standard deviations

Bond lengths			
Fe–C(1)	2.047(2)	Si(1)–C(4)	1.848(2)
Fe–C(2)	2.092(2)	Si(2)–C(2)	1.861(2)
Fe–C(3)	2.045(2)	C(1)–C(2)	1.442(3)
Fe–C(4)	2.071(2)	C(1)–C(5)	1.422(3)
Fe–C(5)	2.038(2)	C(2)–C(3)	1.424(3)
		C(3)–C(4)	1.429(3)
		C(4)–C(5)	1.441(3)
Fe–Cp	1.660		
Bond angles			
C(2)–C(1)–C(5)	108.7(2)	Si(2)–C(2)–C(1)	126.0(2)
C(1)–C(2)–C(3)	105.2(2)	Si(2)–C(2)–C(3)	128.3(2)
C(2)–C(3)–C(4)	112.0(2)	Si(1)–C(4)–C(1)	129.9(2)
C(3)–C(4)–C(5)	104.6(2)	Si(1)–C(4)–C(5)	125.4(2)
C(1)–C(5)–C(4)	109.5(2)		

is apparently dictated by the 'interlocking' of the four bulky trimethylsilyl groups. Thus, the virtually planar five-membered rings adopt a nearly eclipsed conformation with a slight tilt (dihedral angle 6°). The Fe–C(ring) bond distances of Si-substituted carbon atoms C(2) and C(4) exceed the iron–carbon bond distances for the unsubstituted carbon atoms C(1), C(3), and C(5), indicating significant interannular repulsion between the Si$_2$Cp rings. The average Fe–C(ring) bond length of 2.059(2) Å is comparable to that in ferrocene and its derivatives (triclinic ferrocene [12]: 2.052(2), orthorhombic ferrocene [13]: 2.045(1), decamethylferrocene [14]: 2.050(2), 1,1′,3,3′-tetra(t-butyl)ferrocene [15]: 2.05 Å), as are the C–C bond distances (average 1.456(2) Å) within the five-membered ring. The trimethylsilyl groups are bent away from the metal center (average 8°) each Me$_3$Si(2) group interacts more strongly with two other Me$_3$Si groups, than the Me$_3$Si(1) groups.

The ^{1}H NMR spectrum of Fe(Si$_2$Cp)$_2$ at room temperature consists of a sharp high field singlet of relative integral 18, assignable to the protons of the trimethylsilyl groups, and a doublet of relative integral 2 next to a triplet of integral 1 due to the ring protons. While this spectrum is consistent with C_{2v} or C_{2h} symmetry, reflecting free rotation of the Si$_2$Cp ligands, cooling brings about a major change, as shown in Fig. 2. The high field singlet decoalesces at $-50\,^\circ$C and the doublet at $-45\,^\circ$C. At $-80\,^\circ$C both resonances are clearly separated into two signals and the spectrum allows deduction of a conformation of C_2 symmetry in which the two trimethylsilyl groups as well as the two vicinal ring protons within the same ring have become inequivalent. The free activation enthalpy for the observed dynamic process can be estimated to $\Delta G^{\neq}$ 11.0 ± 0.5 kcal mol^{-1} from the above data. In Fig. 3 a qualitative energy profile is shown in which all possible 10 rotamers are placed according to their approximate energy contents as deduced on the simplistic assumption that interannular repulsions of the trimethylsilyl groups in a rigid sandwich molecule are solely responsible for a certain conformation [10]. For each rotamer its is shown whether the five-membered rings are eclipsed (e) or staggered (s). The sum of repulsions is given by a subscript, staggered interaction of two trimethylsilyl groups in different rings being counted as 0.25 and a fully staggered

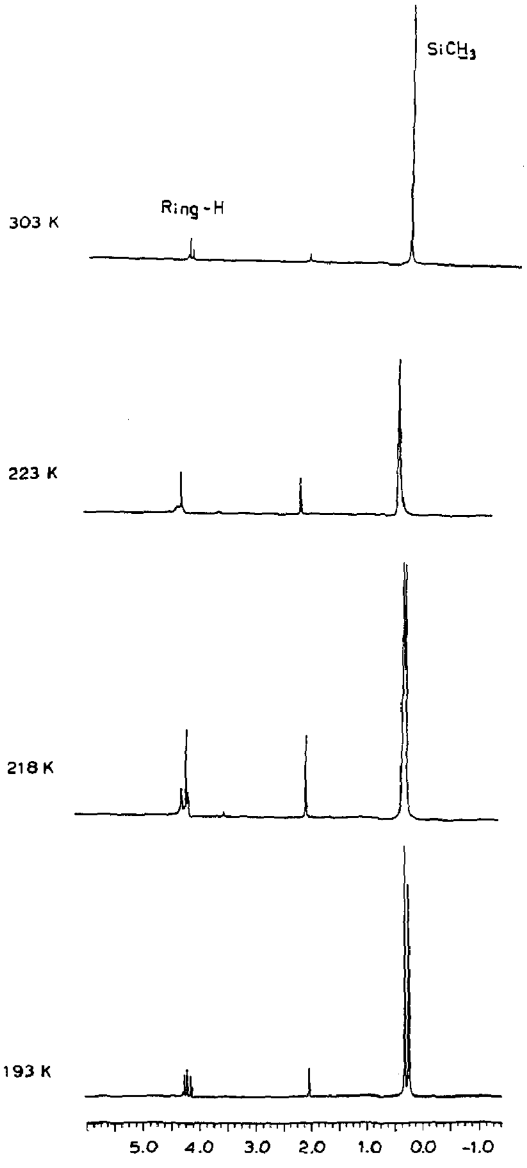

Fig. 2. Variable temperature ^{1}H NMR spectra ($C_6D_5CD_3$; 400 MHz).

one as 0.5. The ground state e_0 (or its enantiomer e_0') obviously corresponds to the solid state structure with the four substituents in a fully staggered arrangement, also in agreement with the low-temperature-limit spectrum indicating C_2 symmetry. Rotamers e_2 and s_1 are of higher energy, and their populations at temperatures above the coalescence temperatures would account for the apparent C_{2v} or C_{2h} symmetry. The barrier to rotation can then be related to the energy difference $E(e_2) - E(e_0)$.

An entirely analogous feature has been observed for 1,1′,3,3′-tetra-t-butylferrocene. While the X-ray structure shows a conformation roughly described as $s_{1/2}$ [15], the value of $\Delta G^{\neq}$ estimated from the ^{1}H NMR spectroscopic data is 13.1 kcal

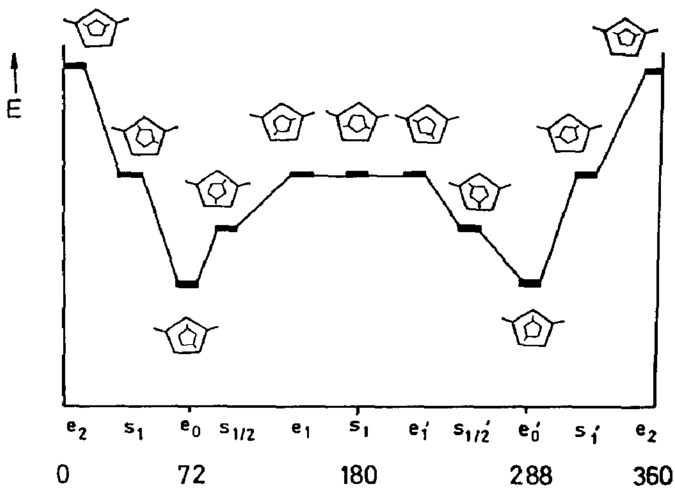

Fig. 3. Qualitative energy profile for the internal rotation. See text for details.

mol^{-1} [16]. The somewhat higher rotational barrier can be accounted for in terms of the fact that t-butyl groups are slightly more compact than the trimethylsilyl groups, leading to an increased steric congestion. Recently, we have also determined the rotational barrier of the five-membered rings in $Fe(Si_3Cp)_2$ ($\Delta G^{\neq}$ 11.1 kcal mol^{-1} [10]) and $Fe(BuSi_2Cp)_2$ ($BuSi_2Cp = 1,2,4\text{-}(CMe_3)(SiMe_3)_2\text{-}\eta^5\text{-}C_5H_2$; $\Delta G^{\neq}$ 9.7 kcal mol^{-1} [1]) and noted the peculiarity that the value for $\Delta G^{\neq}$ in these apparently even more sterically crowded ferrocenes is about the same as for $Fe(Si_2Cp)_2$.

Experimental

Preparation of 1,1′3,3′-tetrakis(trimethylsilyl)ferrocene

To a solution of $FeCl_2 \cdot 1.5$ THF (470 mg, 2 mmol) in THF (50 ml) was added a THF solution of bis(trimethylsilyl)cyclopentadienyllithium, prepared from bis(trimethylsilyl)cyclopentadiene (4 mmol) and 1.6 *M* n-butyllithium in hexane (4 mmol). The mixture was allowed to warm to room temperature and stirred for 16 h. After removal of the solvent, the residue was extracted with pentane (3 × 15 ml) and the extracts filtered through kieselguhr. The solvent was pumped off and the crude product recrystallized from pentane to give orange platelets. Yield 500 mg (1.1 mmol; 53%). M.p. 157 °C (Lit. [5]: 164 °C). ^1H NMR ($C_6D_5CD_3$; 25 °C): 0.24 (s, 18H, $SiCH_3$), 4.13 (t, $^4J(H,H)$ 1.2 Hz, 1H, C_5H), 4.23 (d, $^4J(H,H)$ 1.2 Hz, 2H, C_5H_2). ^1H NMR ($C_6D_5CD_3$; −80 °C): 0.24, 0.31 (s, 9H, $SiCH_3$), 4.14 (s, 1H, C_5H_2), 4.21 (s, 1H, C_5H), 4.27 (s, 1H, C_5H_2). ^{13}C NMR ($C_6D_5CD_3$; 25 °C): 0.61 (q, $J(CH)$ 119 Hz, $SiCH_3$), 75.18 (s, CSi), 76.11 (dt, $^1J(CH)$ 173 Hz; $^3J(CH)$ 7 Hz, C_5H_2), 79.15 (dt, $^1J(CH)$ 172 Hz, $^3J(CH)$ 9 Hz, C_5H). IR (KBr): 2958m, 1268sh, 1248s, 1092ms, 835vs, 755m cm^{-1}. EI MS: $m/e = 474$ (M^+, 100%), 402 ($M^+ - SiMe_3$, 23%). Anal. Found: C, 55.47; H, 8.82. $C_{22}H_{42}FeSi_4$ (474.75) calcd.: C, 55.65; H, 8.92%.

Structure determination

An orange platelet was obtained by recrystallization from methanol at −40 °C and mounted on a Enraf–Nonius CAD4 diffractometer. Mo-K_α radiation was used.

Table 3

Summary of crystallographic data

Formula	$C_{22}H_{42}Si_4Fe$
Formula weight	474.87
Space group	$C2/c$ (No. 15)
Cell constants	a 12.454(2) Å
	b 18.782(3) Å
	c 12.533(2) Å
	β 100.57(1)°
	V 2882 Å^3
	$Z = 4$
Calcd. density	1.094 g cm^{-3}
Absorption μ(Mo-K_α)	6.91 cm^{-1}
θ range	$2° \leq \theta \leq 25°$
No. of reflections measured	1683
No. of data used [$I > 1\sigma(I)$]	1275
No of parameters refined	123
$R = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.045
$R_w = [\Sigma_w(\|F_o\| - \|F_c\|)^2/\Sigma_w\|F_o\|^2]^{1/2}$	0.045

The compound crystallizes in the monoclinic space group $C2/c$ (No. 15). Intensities were collected by the ω-scan technique. No correction for absorption was made. The structure was solved by Patterson and direct methods. All hydrogen atoms were refined isotropically at calculated positions. The crystal showed slight twinning, axes a and c being interchanged. The program used was STRUX-II [17]. Relevant crystallographic data are listed in Table 3. For further details see ref. 18*.

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