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X-ray structural study of a bulky iron-substituted trisilane

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Abstract

The structure of (η^5-C_5H_5)Fe(CO)$_2$Si(Ph)(SiMe$_3$)$_2$, **1** has been studied by X-ray diffraction; **1** crystallizes in the $P\bar{1}$ space group with a 8.767(1), b 15.782(3), c 16.543(3) Å, α 87.84(1), β 86.28(1), and γ 85.47(1)°. There are two independent molecules in the asymmetric unit. Both conformers are staggered and related by a 120° rotation. The Fe–Si bond lengths are 2.366(1) and 2.355(1) Å. A steric argument is used to discuss the discrepancy in the Fe–Si distances.

Introduction

Transition metal substituted disilenes are still unknown. A recent report from these laboratories described the generation of an iron-substituted silylene from the thermolysis of a dimethylacetylenedicarboxylate adduct of a (7-methyl-7-silanorbornadienyl)(η^5-C_5H_5)Fe(CO)$_2$ complex [1]. Hence it is plausible to envisage the formation of a metal-substituted disilene from dimerization of a metal-containing silylene, L_nMRSi:, which in turn can be generated by the photolysis of a transition metal substituted trisilane.

$$L_nM(R)Si(SiMe_3)_2 \xrightarrow[-(Me_3Si)_2]{h\nu} [L_nM(R)Si:] \xrightarrow{2\times} L_nM(R)Si{=}Si(R)ML_n$$

$$L_nM = (\eta^5\text{-}C_5H_5)Fe(CO)_2,\ R = Ph$$

Scheme 1

In this paper, we present the X-ray crystal structure of such a trisilane, CpFe(CO)$_2$Si(Ph)(SiMe$_3$)$_2$, **1**.

Experimental

Complex **1** was prepared according to the literature method [1,2] and crystallized as orange prisms from a saturated toluene solution at −20 °C.

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X-ray diffraction study of 1

A single crystal of **1**, of dimensions 0.2mm × 0.2mm × 0.2mm, was mounted on a glass fiber and coated with epoxy cement. The initial orientation matrix was calculated from 12 machine-centered reflections obtained from a rotation photograph. These data were used to determine the crystal system. Final unit cell parameters were subsequently determined from the least-squares fit of the angular settings of 25 reflections ($25° < 2\theta < 30°$). Crystal data: $C_{16}H_{28}O_2Si_3Fe$, M = 428.53, triclinic, space group $P\bar{1}$ (No.2), a 8.767(1), b 15.782(3), c 16.543(3) Å, α 87.84(1), β 86.28(1), γ 85.47(1)°, V 2276(1) Å^3, D_c 1.251 g cm^{-3}, λ (Mo-K_α) 0.71073 Å, μ(Mo-K_α) 0.83 mm^{-1}. Totals of 10305 unique reflections were collected on a Syntex–Nicolet $P\bar{1}$ diffractometer at 25°C in the range $3.5° \leq 2\theta \leq 54.9°$. The data were processed by using the SHELXTL PLUS software package on a MicroVAX II. Lorentz polarization corrections were applied to the data set. No absorption or decay correction was needed. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares using 5192 reflections with $I > 3.0\sigma(I)$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions (C–H = 0.96 Å; H–C–H = 109.5°), and allowed to ride with the carbons to which they are attached. The final residuals were $R = 0.0443$ and $R_w = 0.0427$, using the weighting scheme $1/w = \sigma^2(F) + 0.000148F^2$. The final difference Fourier map at this stage was featureless. Final atomic coordinates are listed in Table 1.

Complete tables of bond lengths and angles, thermal parameters, hydrogen-atom coordinates, and listings of structure factors are available from the authors.

Discussion

Structural data on polysilyl complexes of iron are still relatively scarce. The structures of two $CpFe(CO)_2$ derivatives of cyclic silylcyclopentasilane have been

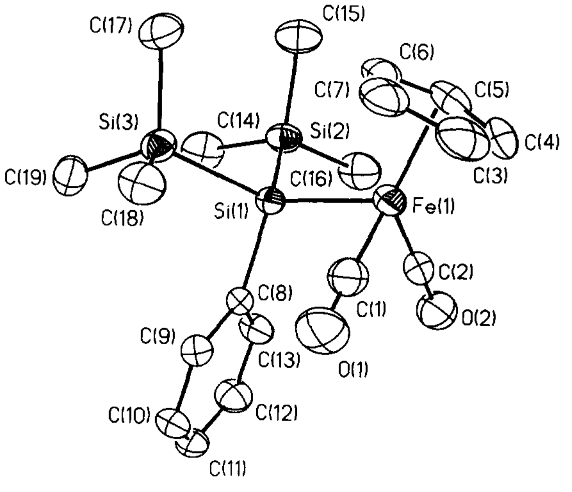

Fig. 1. Molecular structure of conformer (A) of **1**. Important bond lengths (Å) and angles (°): Fe(1)–Si(1) 2.366(1), Si(1)–Si(2) 2.379(2), Si(1)–Si(3) 2.369(2), Fe(1)–Si(1)–Si(2) 112.8(1), Fe(1)–Si(1)–Si(3) 112.1(1), Si(2)–Si(1)–Si(3) 108.9(1), Fe(1)–Si(1)–C(8) 111.4(1).

Table 1

Atomic coordinates (e.s.d.'s in parentheses) of **1**

	x	*y*	*z*
Fe(1)	3369(1)	8793(1)	4386(1)
C(1)	4239(5)	8120(3)	5100(3)
O(1)	4830(4)	7707(2)	5595(2)
C(2)	4998(6)	8745(3)	3716(3)
O(2)	6083(4)	8721(2)	3295(2)
C(3)	2568(8)	9739(4)	5200(4)
C(4)	2966(7)	10117(3)	4462(5)
C(5)	2061(6)	9820(3)	3877(4)
C(6)	1093(5)	9263(3)	4277(3)
C(7)	1404(6)	9201(3)	5091(4)
Si(1)	2733(1)	7573(1)	3732(1)
C(8)	4463(4)	6766(2)	3592(2)
C(9)	4894(4)	6202(2)	4217(2)
C(10)	6129(5)	5600(2)	4125(3)
C(11)	6952(5)	5536(3)	3398(3)
C(12)	6578(5)	6084(3)	2773(3)
C(13)	5357(4)	6691(3)	2868(3)
Si(2)	1855(1)	7894(1)	2416(1)
C(14)	1568(5)	6877(3)	1917(3)
C(15)	−15(5)	8544(3)	2409(3)
C(16)	3213(5)	8505(3)	1753(3)
Si(3)	864(1)	6832(1)	4505(1)
C(17)	−1119(4)	7358(3)	4453(3)
C(18)	1269(5)	6699(3)	5608(2)
C(19)	853(5)	5741(3)	4096(3)
Fe(2)	2932(1)	3470(1)	2358(1)
C(20)	2340(5)	2695(3)	3045(3)
O(3)	1999(4)	2184(2)	3532(2)
C(21)	1098(6)	3901(3)	2186(3)
O(4)	−129(4)	4205(3)	2091(3)
C(22)	4262(6)	4406(3)	1814(3)
C(23)	5145(5)	3627(3)	1842(3)
C(24)	3810(6)	4620(3)	2618(4)
C(25)	4399(6)	3985(3)	3125(3)
C(26)	5218(5)	3368(3)	2653(3)
Si(4)	2712(1)	2515(1)	1319(1)
C(27)	4257(4)	1595(2)	1357(2)
C(28)	4982(5)	1257(3)	663(3)
C(29)	6056(5)	562(3)	694(3)
C(30)	6431(5)	190(3)	1411(4)
C(31)	5762(6)	517(3)	2097(4)
C(32)	4686(5)	1205(3)	2076(3)
Si(5)	397(1)	1829(1)	1340(1)
C(33)	782(6)	813(3)	801(4)
C(34)	−443(6)	1574(4)	2372(3)
C(35)	−1136(5)	2477(3)	833(3)
Si(6)	2924(1)	3185(1)	15(1)
C(36)	2401(5)	2465(3)	−787(3)
C(37)	1593(6)	4166(3)	−26(3)
C(38)	4895(5)	3506(3)	−295(3)

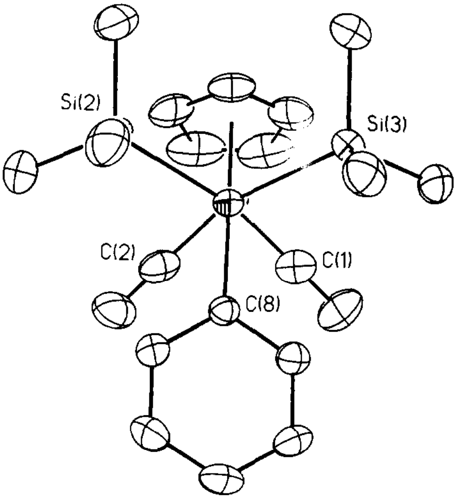

Fig. 2. Newman projection down the Fe(1)-Si(1) bond of (**A**). Torsion angles (°): C(8)-Si(1)-Fe(1)-C(1) −48.2, C(8)-Si(1)-Fe(1)-C(2) 45.2, C(8)-Si(1)-Fe(1)-Cp(centroid) 179.5, Si(2)-Si(1)-Fe(1)-C(1) −167.6, Si(2)-Si(1)-Fe(1)-C(2) −74.2, Si(2)-Si(1)-Fe(1)-Cp(centroid) 60.1, Si(3)-Si(1)-Fe(1)-C(1) 69.1, Si(3)-Si(1)-Fe(1)-C(2) 162.5, Si(3)-Si(1)-Fe(1)-Cp(centroid) −63.2.

previously studied in these laboratories [3], while Pannell et al. have reported structural data on $CpFe(CO)_2SiMe_2SiPh_3$ [4], and more recently on two complexes with disilyl groups bridging two Fp systems, $[CpFe(CO)_2]_2Si_2Me_4$, and $Si_2Me_4[(\eta^5\text{-}C_5H_4)Fe(CO)_2CH_3]_2$ [5]. While Fink has recently described the structure of $(dcpe)Pt[SiPh(SiMe_3)_2]Cl$ [6], **1** represents the first iron-substituted trisilane to be

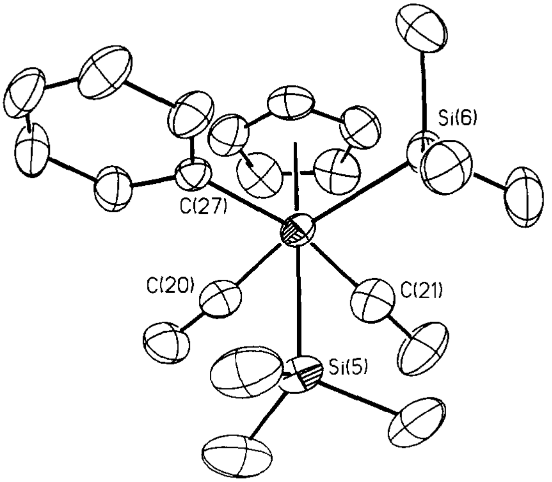

Fig. 3. Newman projection down the Fe(2)-Si(4) bond of (**B**). Important bond lengths (Å) and angles (°): Fe(2)-Si(4) 2.355(1), Si(4)-Si(5) 2.372(2), Si(4)-Si(6) 2.369(2), Fe(2)-Si(4)-Si(5) 116.7(1), Fe(2)-Si(4)-Si(6) 112.1(1), Si(5)-Si(4)-Si(6) 104.5 (1), Fe(2)-Si(4)-C(27) 111.1(1), C(27)-Si(4)-Fe(2)-C(20) −69.6, C(27)-Si(4)-Fe(2)-C(21) −164.7, C(27)-Si(4)-Fe(2)-Cp(centroid) 61.1, Si(5)-Si(4)-Fe(2)-C(20) 48.9, Si(5)-Si(4)-Fe(2)-C(21) −46.2, Si(5)-Si(4)-Fe(2)-Cp(centroid) 179.5, Si(6)-Si(4)-Fe(2)-C(20) 169.4, Si(6)-Si(4)-Fe(2)-C(21) 74.4, Si(6)-Si(4)-Fe(2)-Cp(centroid) −59.9.

structurally characterized. The most interesting structural feature is the presence of two independent molecules in the asymmetric unit. One molecule (**A**) adopts a symmetric, perfectly staggered conformation about the Fe(1)–Si(1) bond (Figs. 1 and 2) which reflects steric hindrance between the phenyl and the two $SiMe_3$ substituents (see torsion angles, Fig. 2). The Cp ligand and phenyl group are *anti* to one another (Cp(centroid)–Fe(1)–Si(1)–C(8) torsion angle = 179.5°), while the two $SiMe_3$ groups are in a *gauche* relationship with the Cp ligand and are near mirror images of one another (Si(2)–Si(1)–Fe(1)–Cp(centroid) and Si(3)–Si(1)–Fe(1)–Cp (centroid) torsion angles are 60.1° and −63.2°, respectively). The other molecule (**B**) is also staggered (Fig. 3) and has the Fe–Si bond rotated by 120° such that one of the $SiMe_3$ groups is now *anti* to the Cp ligand (Si(5)–Si(4)–Fe(2)–Cp(centroid) torsion angle = 179.5°). Consequently, only one *gauche* interaction exists between the Cp ligand and the other $SiMe_3$ group.

This difference in conformation results in a shortening of the Fe–Si bond length from 2.366(1) Å in (**A**) to 2.355(1) Å in (**B**). The peripheral Si–Si bond lengths are however, nearly identical in both conformers. Hence, the discrepancy in the Fe–Si distances is probably due to steric rather than electronic effects: notwithstanding packing considerations (vide infra) the extra *gauche* interaction between the Cp ligand and the $SiMe_3$ group in (**A**) relative to (**B**) is presumably responsible for the lengthening of the Fe–Si bond by about 0.11 Å. It is also noteworthy that the Si–Si–Si angle in (**B**) (104.5(1)°) is more acute than that in (**A**) (108.9(1)°), suggestive of considerably more *s* character concentrated in the Fe–Si bond in (**B**). This would result in a shorter Fe–Si bond and this is indeed observed. Furthermore, the Si–Si–Si angles for both conformers are smaller than those of previously published trisilanes [7] (114°) which probably reflects the steric bulk of the metal moiety.

Figure 4 shows the packing of the two conformers in the crystal lattice of **1**. While no short intermolecular distances were observed, the molecules are sufficiently close to one another in the asymmetric unit that their different conforma-

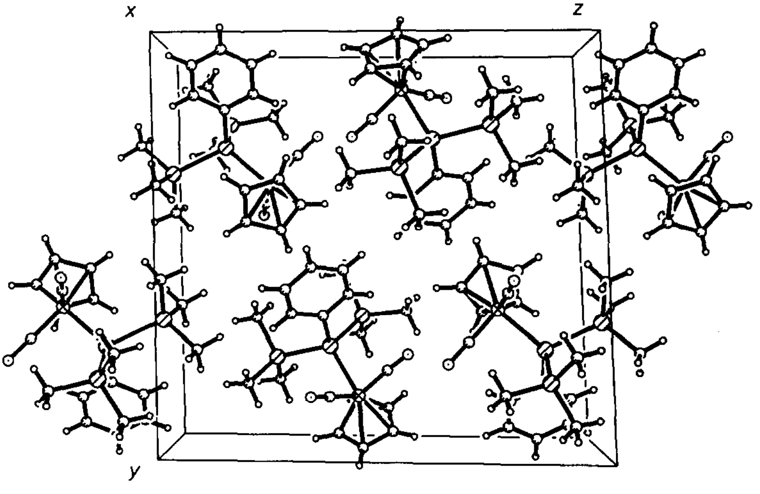

Fig. 4. Molecular packing in the crystal of 1.

tions may be influenced by packing forces. Due to the close packing of the molecules in the unit cell of **1**, it is possible that rotation about the Fe–Si is impaired thus giving rise to the two different conformations.

Acknowledgements

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