

ORGANOMETALLOIDAL DERIVATIVES OF THE TRANSITION METALS

IX *. SYNTHESIS AND THE CRYSTAL STRUCTURE OF $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiMe}_2\text{-SiPh}_3$

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Summary

Reaction of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeNa}$ with $\text{ClSiMe}_2\text{-SiPh}_3$ yields $(\eta^5\text{-C}_5\text{H}_5)\text{-Fe}(\text{CO})_2\text{SiMe}_2\text{-SiPh}_3$. The crystal structure of the compound has been determined by X-ray diffraction. The Si–Si bond distance is 2.374(1) Å, which is longer by 0.018 Å than that in $\text{Me}_3\text{Si-SiPh}_3$. This difference is in agreement with spectroscopic data, and is presumably due to the σ -donor property of the silyl group. The Si–Fe bond length is 2.346(1) Å.

Introduction

Previous studies on complexes of the general type $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{R}$, M = transition metal, R = silyl, polysilyl, silylmethyl and alkyl, have shown that the Si–M or Si–C–M linkage is less reactive than the C–M bond [1,2]. A combined Mössbauer and IR spectral investigation on these systems (M = Fe) have suggested that the enhanced s -electron density at the iron nucleus for the silyl derivatives is due to the superior σ -donation by the silyl group as compared with the alkyl group rather than to iron–silicon retrodonative π -bonding [3]. A recent ^{29}Si NMR study has shown that a rather pronounced σ inductive effect is operating, which does not involve d -orbital participation by the silicon atom [4].

Although the physical and chemical properties of these compounds have been widely studied few structural data are available. The crystal structures of two

* For part VIII see ref. 4.

permethylated cyclopentasilane derivatives have been published [5]. The crystal structure determination of the title compound was undertaken to reveal the structural differences between the $\text{Ph}_3\text{Si-SiMe}_2$ ligand and the $\text{Ph}_3\text{Si-SiMe}_3$ molecule [6].

Experimental

Synthesis

A tetrahydrofuran solution of 0.01 mol of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeNa}$ was stirred with 0.01 mol of $\text{ClSi}(\text{CH}_3)_2\text{Si}(\text{C}_6\text{H}_5)_3$ for 30 min. The solvent was rapidly removed at $25^\circ/10$ mmHg, and the residue extracted twice with 100 ml of a 10% (v/v) methylene chloride/hexane mixture. The extract was filtered and the solvent removed at $25^\circ\text{C}/10$ mmHg. The residue was chromatographed on a 2×40 cm alumina column with elution by 10% (v/v) methylene chloride/hexane. A yellow band was collected and the solvent was removed at $25^\circ\text{C}/10$ mmHg, to give a 60% yield of the title compound, which was recrystallized from the same solvent mixture (m.p. 155°C). ^{13}C , ^{29}Si NMR data in C_6D_6 with respect to TMS and ^1H NMR in CDCl_3 are as follows ($\delta(\text{ppm})$): ^{13}C : C_5H_5 83.56, $(\text{CO})_2$ 216.23, $\text{Si}(\text{CH}_3)_2$ 6.18, $(\text{C}_6\text{H}_5)_3\text{Si}$ 136.95, 137.74, 128.56, 129.41; ^{29}Si : $\text{Si}(\text{C}_6\text{H}_5)_3$ 15.42, $\text{Si}(\text{CH}_3)_2$ -16.79; ^1H : $(\text{CH}_3)_2\text{Si}$ 0.58, C_5H_5 4.49, $(\text{C}_6\text{H}_5)_3\text{Si}$ 7.5.

Intensity data, solution and refinement of the structure

Intensity data were collected on an Enraf-Nonius CAD-4 computer controlled four-circle diffractometer with graphite monochromated Mo-K_α -radiation (λ 0.71073 Å). Crystal data and data collection parameters are summarized in Table 1.

The structure was solved by direct methods (MULTAN program [7], $288 E \geq 1.93$) and Fourier techniques. After the solution of the structure 543 reflections having zero intensity were eliminated from the data set.

3175 reflections ($F_o^2 \geq 3.0\sigma(F_o^2)$) were used in the least-squares refinement. At the end of the isotropic refinement ($R = 0.08$) atomic coordinates were calculated

TABLE 1
CRYSTAL DATA AND DATA COLLECTION PARAMETERS

Empirical formula	$\text{C}_{27}\text{H}_{25}\text{O}_2\text{Si}_2\text{Fe}$ Formula weight 493.5
Cell constants ^a	a 8.665(2), b 35.078(7), c 8.192(2) Å, β 96.60(2)°, V 2473.5(1.8) Å ³
Space group	$P2_1/c$, $Z = 4$
d_x (g cm^{-3})	1.325
$\mu(\text{Mo-K}_\alpha)$ (cm^{-1})	7.43
Approx. crystal size (mm)	0.25 × 0.25 × 0.25 (cube-shaped)
2θ -range	$3.0 \leq 2\theta \leq 50.0^\circ$
Scan width (°)	$0.35 + 0.35 \tan \theta$
Max. scan time (min)	1.0
Number of refl.	4336
Number of reflections with zero intensity	543

^a Obtained by least-squares from the setting angles of 25 carefully centered reflections.

TABLE 2

FINAL POSITIONAL PARAMETERS ($\times 10^4$) AND B_{eq} a (\AA^2) VALUES FOR THE NON-HYDROGEN ATOMS

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Fe	7557.9(4)	504.9(1)	2343.2(5)	3.17(5)
Si(1)	10297.9(9)	1445.7(2)	2909.2(9)	3.07(10)
Si(2)	9102.3(9)	958.7(2)	1193.6(9)	3.14(10)
O(1)	6947(3)	230(1)	-996(3)	7.1(5)
O(2)	10274(3)	35(1)	3067(3)	6.2(4)
C(1)	8865(3)	1740(1)	3923(3)	3.4(4)
C(2)	7526(3)	1888(1)	3025(4)	4.1(4)
C(3)	6448(4)	2096(1)	3758(4)	4.8(5)
C(4)	6693(4)	2177(1)	5402(5)	5.3(5)
C(5)	8005(4)	2045(1)	6336(4)	5.1(5)
C(6)	9080(4)	1823(1)	5605(4)	4.2(4)
C(7)	11318(3)	1763(1)	1515(3)	3.4(4)
C(8)	10686(4)	2105(1)	871(4)	4.5(5)
C(9)	11402(5)	2317(1)	-229(5)	5.7(6)
C(10)	12786(4)	2203(1)	-726(4)	5.8(6)
C(11)	13450(4)	1870(1)	-113(5)	5.7(5)
C(12)	12723(4)	1653(1)	986(4)	4.9(5)
C(13)	11798(3)	1253(1)	4536(3)	3.3(4)
C(14)	13118(4)	1463(1)	5120(4)	4.5(4)
C(15)	14221(4)	1318(1)	6317(4)	5.1(5)
C(16)	14030(4)	963(1)	6962(4)	4.7(5)
C(17)	12740(4)	750(1)	6433(4)	4.7(5)
C(18)	11648(3)	894(1)	5219(4)	4.1(4)
C(19)	10761(4)	731(1)	256(4)	5.2(5)
C(20)	7958(5)	1220(1)	-565(4)	5.9(6)
C(21)	6202(4)	941(1)	3179(5)	6.3(5)
C(22)	5254(4)	657(1)	2491(5)	6.0(5)
C(23)	5580(4)	322(1)	3383(4)	5.1(5)
C(24)	6755(4)	403(1)	4619(5)	6.3(6)
C(25)	7149(4)	795(1)	4476(5)	6.9(5)
C(26)	7210(4)	337(1)	342(4)	4.5(4)
C(27)	9217(3)	226(1)	2775(4)	3.8(4)

 a B_{eq} is defined as $4/3$ trace (bg) where b is the thermal motion tensor and g is the direct metric tensor.

TABLE 3

CALCULATED ATOMIC COORDINATES ($\times 10^3$) FOR THE HYDROGEN ATOMS a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
H(2)	735	184	181	H(17)	1259	49	692
H(3)	548	219	309	H(18)	1072	73	482
H(4)	592	233	592	H(19a)	1035	52	-49
H(5)	819	211	754	H(19b)	1128	93	-38
H(6)	1002	172	629	H(19c)	1152	63	115
H(8)	968	220	122	H(20a)	742	103	-134
H(9)	1091	256	-68	H(20b)	717	139	-12
H(10)	1330	236	-153	H(20c)	868	138	-115
H(11)	1446	178	-46	H(21)	620	121	280
H(12)	1322	141	141	H(22)	446	69	151
H(14)	1327	172	466	H(23)	506	7	317
H(15)	1516	147	671	H(24)	724	22	546
H(16)	1484	86	782	H(25)	797	94	519

 a Isotropic temperature factors for the hydrogen atoms were derived from B_{eq} of the carbon atom to which they are bonded. $B(\text{H}) = B_{\text{eq}}(\text{C}) + 1.0$ (\AA^2).

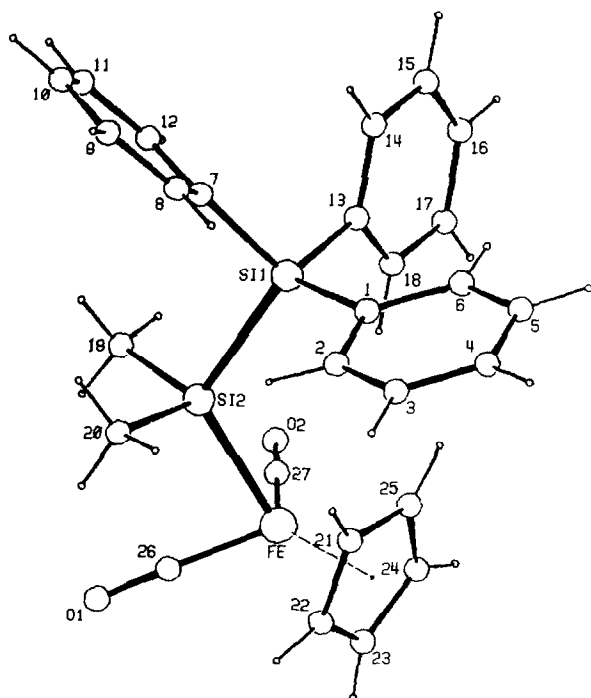


Fig. 1. Molecular diagram with the numbering of atoms. Numbers are for carbon atoms unless indicated otherwise.

for each hydrogen atom (trigonal arrangements were assumed for the phenyl and cyclopentadiene hydrogens and a regular staggered tetrahedral geometry for the methyl hydrogen atoms, C-H 1.0 Å). Anisotropic least-squares refinement reduced R_0 to 0.035 ($R_w = 0.051$) for the observed and R_T to 0.048 for all (3793) reflections. The weighting scheme applied was identical to that in ref. 8. Atomic scattering factors and anomalous dispersion coefficients were taken from ref. 9. No absorption correction was applied. The final atomic parameters are given in Tables 2 and 3*.

Discussion

A molecular diagram with the numbering of the atoms is shown in Fig. 1, and the relevant bond lengths and angles are listed in Table 4.

Comparison of the ^{29}Si NMR data for the title compound to those of $\text{Me}_3\text{SiSiPh}_3$ reveals a shift of +33.8 ppm for the SiMe_2 group and +3.6 ppm for the SiPh_3 group. This type of shift is in agreement with the results of the recent ^{29}Si NMR study [4] carried out on complexes with methyl substituted ligands, i.e. the silyl group acts as a σ -donor towards Fe.

The Si-Si bond distance in the complex (2.373(1) Å) is 0.018 Å longer than that

* Lists of structure factors and anisotropic thermal parameters may be obtained from L.P. (Budapest).

TABLE 4

RELEVANT BOND LENGTHS AND ANGLES WITH THEIR E.S.D.'S

Bond lengths (Å)					
Fe–Si(2)	2.346(1)	Fe–C(27)	1.741(3)	O(1)–C(26)	1.156(4)
Fe–C(21)	2.091(4)	Si(1)–Si(2)	2.373(1)	O(2)–C(27)	1.138(4)
Fe–C(22)	2.083(4)	Si(1)–C(1)	1.880(3)	C(21)–C(22)	1.371(5)
Fe–C(23)	2.100(4)	Si(1)–C(7)	1.886(3)	C(21)–C(25)	1.365(5)
Fe–C(24)	2.094(4)	Si(1)–C(13)	1.877(3)	C(22)–C(23)	1.395(5)
Fe–C(25)	2.087(4)	Si(2)–C(19)	1.883(3)	C(23)–C(24)	1.380(5)
Fe–C(26)	1.735(3)	Si(2)–C(20)	1.890(3)	C(24)–C(25)	1.425(5)

Bond angles (°)			
Si(2)–Fe–C(26)	84.0(2)	Fe–Si(2)–C(20)	111.2(2)
Si(2)–Fe–C(27)	88.1(2)	Si(1)–Si(2)–C(19)	104.2(2)
C(26)–Fe–C(27)	92.9(2)	Si(1)–Si(2)–C(20)	104.9(2)
Si(2)–Si(1)–C(1)	113.0(2)	C(19)–Si(2)–C(20)	104.7(3)
Si(2)–Si(1)–C(7)	105.6(2)	C(22)–C(21)–C(25)	109.0(6)
Si(2)–Si(1)–C(13)	112.4(2)	C(21)–C(22)–C(23)	108.7(5)
C(1)–Si(1)–C(7)	108.8(2)	C(22)–C(23)–C(24)	107.4(5)
C(1)–Si(1)–C(13)	108.8(2)	C(23)–C(24)–C(25)	107.6(5)
C(7)–Si(1)–C(13)	107.9(2)	C(21)–C(25)–C(24)	107.3(5)
Fe–Si(2)–Si(1)	118.8(1)	Fe–C(26)–O(1)	178.4(5)
Fe–Si(2)–C(19)	111.9(2)	Fe–C(27)–O(2)	178.0(5)

in 1,1,1-trimethyltriphenyl-disilane [6] (2.355(1) Å), but similar to that in cyclo-Si₅Me₉SiMe₂[Fe(CO)₂(η⁵-C₅H₅)] (2.371(1) Å) [5]. An exocyclic and an endocyclic (Fe)Si–Si bond is present (in a Fe–Si(1)–Si(2)–Si(3)–Fe system) in the complex cyclo-Si₅Me₈[Fe(CO)₂(η⁵-C₅H₅)]–SiMe₂[Fe(CO)₂(η⁵-C₅H₅)], the structure of which was also elucidated by X-ray diffraction [5]. The exocyclic Si(1)–Si(2) bond length is 2.362(1) Å while the endocyclic one (Si(2)–Si(3)) is 2.376(1) Å, longer than any other Si–Si bond in this ring.

The Ph₃Si–SiMe₂Fe part of the molecule is closer to the regular staggered conformation than is the Ph₃Si–SiMe₃ molecule, as shown by the Newman projections in Fig. 2.

The Si–Fe bond distance (2.346(1) Å) is slightly shorter than that in cyclo-Si₅Me₉SiMe₂[Fe(CO)₂(η⁵-C₅H₅)] (2.350(1) Å) and cyclo-Si₅Me₈[Fe(CO)₂(η⁵-

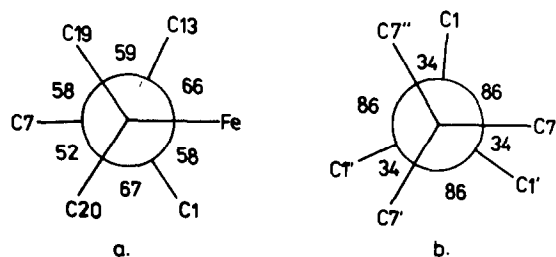


Fig. 2. Newman projections along the Si–Si bond axis for the title compound (a) and Me₃Si–SiPh₃ (b).

C_5H_5)]-SiMe₂[Fe(CO)₂(η^5 -C₅H₅)] (2.350(1) and 2.363(1) Å). The geometry of the [Fe(CO)₂(η^5 -C₅H₅)] moiety is normal.

An analysis of intermolecular distances revealed no close contacts, and so the effect of packing forces on the molecular structure is presumably minimal.

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References

- 1 C.S. Cundy, B.M. Kingston and M.F. Lappert, *Adv. Organometallic Chem.*, 11 (1973) 253.
- 2 K.H. Pannell and J.R. Rice, *J. Organomet. Chem.*, 78 (1974) C35.
- 3 K.H. Pannell, C.C. Wu and G.J. Long, *J. Organomet. Chem.*, 186 (1980) 85.
- 4 K.H. Pannell and A.R. Bassindale, *J. Organomet. Chem.*, 229 (1982) 1.
- 5 T.J. Drahnak, R. West and J.C. Calabrese, *J. Organomet. Chem.*, 198 (1980) 55.
- 6 L. Párkányi and E. Hengge, *J. Organomet. Chem.*, 235 (1982) 273.
- 7 P. Main (principal author), S.E. Hull, L. Lessinger, G. Germain, J-P. Declercq, M.M. Woosfson, MULTAN 78, A System of Computer Programmes for the Automatic Solution of Crystal Structures from X-ray Diffraction data.
- 8 L. Párkányi, P. Hencsei and L. Bihátsi, *J. Organomet. Chem.*, 232 (1982) 315.
- 9 J.A. Ibers and W.C. Hamilton (Eds.), *International Tables for X-ray Crystallography*, Vol. 4. Kynoch Press, Birmingham, England, 1974.