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Synthesis and characterization of $Fe(1\text{-}Me_3Si\text{-}3\text{-}CH_3C_5H_5)_2$, an open ferrocene derived from an unsymmetric pentadienyl ligand

Wimonrat Trakarnpruk, Atta M. Arif, Richard D. Ernst *

Department of Chemistry, University of Utah, Salt Lake City, UT 84112, USA

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Abstract

The reaction of $FeCl_2$ with two equivalents of $K(1\text{-}Me_3Si\text{-}3\text{-}CH_3C_5H_5)$ leads to $Fe(1\text{-}Me_3Si\text{-}3\text{-}CH_3C_5H_5)_2$. Although this product could exist as two diastereomers, only one has been observed spectroscopically, and its structure confirmed by X-ray diffraction.

Keywords: Ferrocenes; Pentadienyl complexes; Open ferrocenes

1. Introduction

Although metal pentadienyl compounds have been the focus of significant attention in recent years [1], the majority of the pentadienyl ligands employed in these studies have been symmetric, such as C_5H_7, $3\text{-}C_6H_9$, $2,4\text{-}C_7H_{11}$, $1,5\text{-}(C_6H_5)_2C_5H_5$ [2], $2,4\text{-}(^tC_4H_9)_2C_5H_5$ [3], $2,4\text{-}(CF_3)_2C_5H_5$ [4], $2,3,4\text{-}C_8H_{13}$ [5] or $1,5\text{-}(Me_3Si)_2C_5H_5$ [6] (C_6H_9 = methylpentadienyl; C_7H_{11} = dimethylpentadienyl; C_8H_{13} = trimethylpentadienyl). While some complexes have been prepared with asymmetric pentadienyl ligands such as $1\text{-}C_6H_9$, $2\text{-}C_6H_9$ or $2,3\text{-}C_7H_{11}$ [7], few structural studies on such η^5-bound species have been reported [7,8].

There are a number of attractive features that various asymmetric pentadienyl ligands can impart to their metal complexes. Such ligands can readily lead to either geometric or optical isomers and probably would be more useful than their symmetric counterparts in synthetic applications. Using the previously reported $1\text{-}Me_3Si\text{-}3\text{-}CH_3C_5H_5$ anion [9], we have prepared and characterized the open ferrocene $Fe(1\text{-}Me_3Si\text{-}3\text{-}CH_3C_5H_5)_2$, whose nature and structure are now described.

2. Experimental details

All operations involving organometallics were carried out under a pre-purified nitrogen atmosphere using Schlenk techniques, or in a glove-box. Hydrocarbon, aromatic and ethereal solvents were purified by distillation from benzophenone ketyl under nitrogen. NMR spectroscopic studies were carried out on a Varian XL-300 spectrometer (75.4 MHz for ^{13}C spectra), while mass spectra were obtained on a Finnigan MAT 95 instrument. $K(1\text{-}Me_3Si\text{-}3\text{-}CH_3C_5H_5)$ was prepared as previously described [9], while $FeCl_2$ was prepared by a reported procedure [10].

2.1. *Bis(1-trimethylsilyl-3-methylpentadienyl)iron* ($Fe(1\text{-}Me_3Si\text{-}3\text{-}CH_3C_5H_5)_2$)

A slurry of 0.59 g (4.6 mmol) of ferrous chloride in 30 ml of tetrahydrofuran (THF) was cooled to −78°C under a nitrogen atmosphere, and a solution of 1.77 g (9.2 mmol) of the potassium salt of the 1-trimethylsilyl-3-methylpentadienyl anion in THF was slowly added. The mixture was slowly warmed to room temperature and stirred overnight by which time a red–brown solution had resulted. The solvent was then removed in vacuo, the residue was extracted with 3 × 20 ml of pentane and filtered. The product was obtained with a 40–45% yield by cooling the concentrated filtrate to

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* Corresponding author.

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−30°C, at which temperature it separated as dark-red crystals (melting point, 71–72°C), which were finally sublimed at 80°C under vacuum.

^{1}H NMR (benzene-d_6, ambient): δ 4.16 (d, 1H, H-2, $J = 12$ Hz), 3.72 (t, 1H, H-4, $J = 9$ Hz), 1.72 (d, 1H, H$_x$-5, $J = 8.6$ Hz), 1.65 (s, CH_3), 1.21 (d, 1H, H$_n$-1, J = 12 Hz), 0.44 (s, 9H, $Si(CH_3)_3$), −0.85 (d, 1H, H$_n$-5, $J = 10$ Hz).

^{13}C NMR (benzene-d_6, ambient): δ 99.6 (d, C-4, $J = 159$ Hz), 99.1 (s, C-3), 91.2 (d, C-2, $J = 159$ Hz), 53.9 (d, C-1, $J = 143$ Hz), 49.1 (t, C-5, $J = 157$ Hz), 22.3 (q, CH_3, $J = 128$ Hz), 1.5 (q, $Si(CH_3)_3$, $J = 120$ Hz).

IR (Nujol mull): ν 1629(w), 1578(m), 1244(s), 1192(s), 1083 (w, br), 978(s), 862(ms), 834(s), 724(m) cm^{-1}.

Mass spectroscopy (electron impact, 17 eV) m/z (relative intensity): 363(24), 362(80), 307(20), 306(61), 233(16), 210(37), 208(26), 192(60), 154(27), 153(22), 139(41), 138(48), 137(35), 125(21), 123(62), 75(26), 74(63), 73(100), 59(47).

High resolution mass spectroscopy: calc., 362.1548; found, 362.1568.

2.2. X-ray diffraction study of $Fe(1\text{-}Me_3Si\text{-}3\text{-}CH_3C_5H_5)_2$

Single crystals of the compound were grown by slow vacuum sublimation at about 80°C and thereafter mounted in glass capillaries under nitrogen. They were then transferred to an Enraf–Nonius CAD 4 rotating-anode diffractometer, on which unit-cell determination and data collection were carried out. All calculations and refinements employed the SDP crystallographic programs. Direct methods were used to locate the non-hydrogen atoms, which were then subjected to refinement. Most of the hydrogen atoms could then also be located from a difference Fourier map and were placed in idealized positions. The positional parameters for the five hydrogen atoms attached to the pentadienyl skeleton were refined successfully. Pertinent unit-cell, data collection and refinement information are presented in Table 1, while atomic coordinates are listed in Table 2, and bond distances and angles are provided in Table 3. Additional bonding parameters and the structure factor tables may be obtained from the authors.

3. Results and discussion

The reaction of $FeCl_2$ with two equivalents of $K(1\text{-}Me_3Si\text{-}3\text{-}CH_3C_5H_5)$ in THF at −78°C leads to the formation of the desired open ferrocene with a reasonable yield. The product may first be isolated by low temperature crystallization from hydrocarbon solvents, after which sublimation can be used to isolate pure crystalline material. By analogy to other open ferrocene complexes incorporating unsymmetric ligands (e.g. $Fe(2\text{-}C_6H_9)_2$ and $Fe(2,3\text{-}C_7H_{11})_2$), this complex can be expected to exist in two isomeric forms **I** and **II**,

Table 1
Crystallographic data for $Fe(1\text{-}Me_3Si\text{-}3\text{-}CH_3C_5H_5)_2$

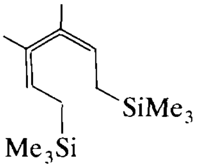
Crystal parameters	
Formula	$C_{18}H_{34}Si_2Fe$
Formula weight	362.491
Crystal system	Monoclinic
Space group	*I2/a*
a (Å)	12.608(2)
b (Å)	9.637(1)
c (Å)	17.695(4)
β (°)	107.01(2)
V (Å^3)	2055.88
Z	4
D_{calc} (g cm^{-3})	1.171
T (K)	293
Color	Red
Size (mm)	0.24 × 0.19 × 0.19
Data collection	
Diffractometer	Enraf–Nonius CAD 4
Radiation	Mo Kα
λ (Å)	0.70930
Scan range (°)	4–50
μ (Mo Kα) (cm^{-1})	8.41
Independent reflections	1927
Independent observed reflections	1277
Transmission factors (relative)	0.930–1.000
Refinement	
$R(F)$	0.052
$R_w(F)$	0.064
N_o/N_v	11.5
ρ (electrons Å^{-3})	0.82

Table 2
Positional parameters for the refined atoms in $Fe(1\text{-}Me_3Si\text{-}3\text{-}CH_3C_5H_5)_2$

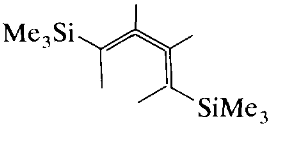
Atom	x	y	z	B (Å^2)
Fe	0.250	0.2795(2)	0.000	3.58(3)
S(i)	0.3160(1)	0.5468(2)	0.1489(1)	4.28(4)
C(1)	0.3550(5)	0.4147(7)	0.0857(3)	4.0(1)
C(2)	0.3681(5)	0.2742(8)	0.1089(3)	4.3(1)
C(3)	0.3834(5)	0.1560(8)	0.0649(3)	4.4(2)
C(4)	0.3805(5)	0.1653(8)	−0.0148(4)	4.9(2)
C(5)	0.3780(5)	0.2906(9)	−0.0551(3)	4.8(2)
C(6)	0.3870(6)	0.0133(9)	0.1013(4)	6.0(2)
C(7)	0.2874(7)	0.4680(9)	0.2380(4)	6.6(2)
C(8)	0.1927(7)	0.6527(9)	0.0957(5)	6.9(2)
C(9)	0.4360(6)	0.6651(9)	0.1864(4)	5.7(2)
H(1)	0.404(5)	0.454(7)	0.066(4)	4.0 [a]
H(2)	0.345(5)	0.248(7)	0.152(4)	4.0 [a]
H(3)	0.363(5)	0.060(7)	−0.044(4)	4.0 [a]
H(4)	0.430(5)	0.376(7)	−0.033(3)	4.0 [a]
H(5)	0.350(5)	0.288(8)	−0.110(4)	4.0 [a]

[a] fixed.

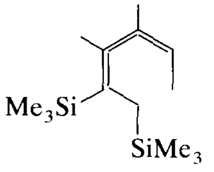
each of which can be expected to interconvert between the two possible *gauche*-eclipsed forms depicted below.



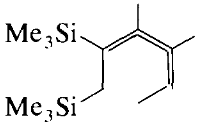
Ia



Ib



IIa



IIb

Since the steric effect of the Me$_3$Si groups can be expected to be dominant, and these groups are located on terminal carbon atoms, for which the *exo* substituents generally display the greatest tilting out of the pentadienyl plane toward the metal atom, it would appear that isomer **Ia**, which possesses C_2 symmetry (as does diastereomeric form **Ib**), should be especially favorable. Isomers **IIa** and **IIb**, which are enantiomers having no non-trivial symmetry elements, would appear more sterically congested. As was the case for Fe(2-C_6H_9)$_2$ and Fe(2,3-C_7H_{11})$_2$, one can expect the variable temperature behavior of the two species to differ. The symmetric enantiomers **Ia** and **Ib** are energetically non-equivalent, and hence no interconversion or VT behavior need be expected, leading to a ^{1}H NMR spectrum composed of seven resonances. For asymmetric enantiomers **IIa** and **IIb**, VT changes can be expected such that, at temperatures low enough to render ligand oscillation slow on the ^{1}H NMR time scale, the asymmetric ground state structure, with 14 resonances, should be apparent while, at higher temperatures, broadening and eventually coalescence to a seven-line pattern would occur, as a result of a rapid interconversion between **IIa** and **IIb**. It is notable, then, that the isolated product displays in its ^{1}H NMR spectrum only a simple seven-line pattern which is essentially invariant with temperature. This establishes the product as **I** (presumably **Ia**) [11].

Table 3
Pertinent bonding distances (Å) and angles (°) for Fe(1-Me$_3$Si-3-CH$_3$C$_5$H$_5$)$_2$

Bond distances			
Fe–C(1)	2.139(6)	Si–C(8)	1.868(8)
Fe–C(2)	2.063(5)	Si–C(9)	1.855(7)
Fe–C(3)	2.106(6)	C(1)–C(2)	1.411(9)
Fe–C(4)	2.060(6)	C(2)–C(3)	1.424(9)
Fe–C(5)	2.119(6)	C(3)–C(4)	1.403(8)
Si–C(1)	1.855(7)	C(3)–C(6)	1.514(10)
Si–C(7)	1.877(7)	C(4)–C(5)	1.399(10)
Bond angles			
C(1)–Si–C(7)	112.3(3)	Si–C(1)–C(2)	120.8(4)
C(2)–Si–C(8)	113.5(3)	C(1)–C(2)–C(3)	129.1(5)
C(1)–Si–C(9)	107.7(3)	C(2)–C(3)–C(4)	122.1(6)
C(7)–Si–C(8)	108.0(4)	C(2)–C(3)–C(6)	119.0(5)
C(7)–Si–C(9)	106.6(3)	C(4)–C(3)–C(6)	118.3(6)
C(8)–Si–C(9)	108.4(4)	C(3)–C(4)–C(5)	123.9(7)

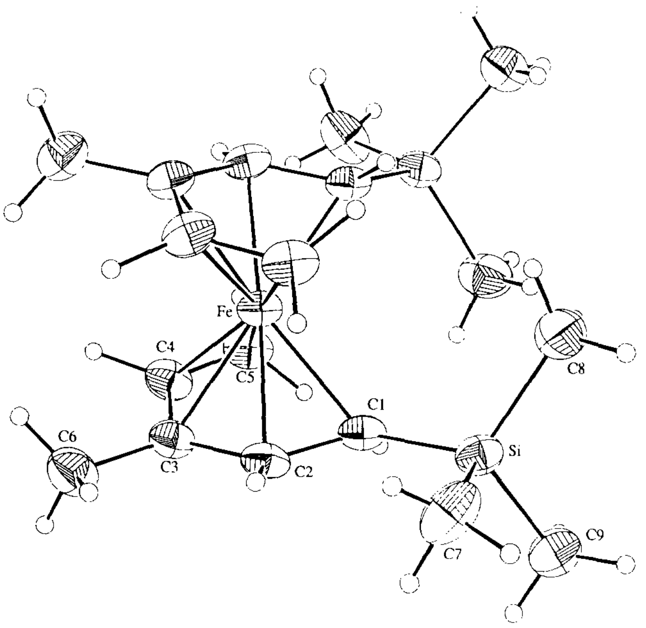


Fig. 1. Perspective view and numbering scheme for Fe(1-Me$_3$Si-3-CH$_3$C$_5$H$_5$)$_2$.

A structural determination was undertaken to confirm the product formulation as **Ia**. As can be seen in Figs. 1 and 2, the solid state structure indeed corresponds to **Ia**, which would seem to allow the Me$_3$Si groups more room to tilt down toward the metal atom, as *exo*-oriented terminal substituents are prone to do (see below). A crystallographic C_2 axis of symmetry is imposed on the molecule. The conformation appears reasonably close to being *gauche* eclipsed, as can be seen from the two nearly overlapping butadiene fragments (C(2)–C(5)). However, the conformation angle χ [12] is found to be 45.4°, significantly less than the ideal 60° for the usual *gauche*-eclipsed form [13]. This can be traced to some extent to the greater C–C–C angle about C(2) compared with C(4), 129.1(5)° vs. 123.9(7)°, which pulls the midpoint between C(1) and C(5) more towards the silyl-substituted side of the ligand (without by itself affecting the C(2)–C(5) placements), yielding an apparently smaller conformation angle.

Despite the asymmetric nature of the ligand, the Fe–C bonds are fairly regular, with average [14] Fe–C(1,5), Fe–C(2,4) and Fe–C(3) lengths of 2.129(4), 2.062(4) and 2.106(6) Å respectively and an overall average Fe–C bond distance of 2.097(3) Å. The trend is similar to that found for Fe(2,4-C_7H_{11})$_2$, for which

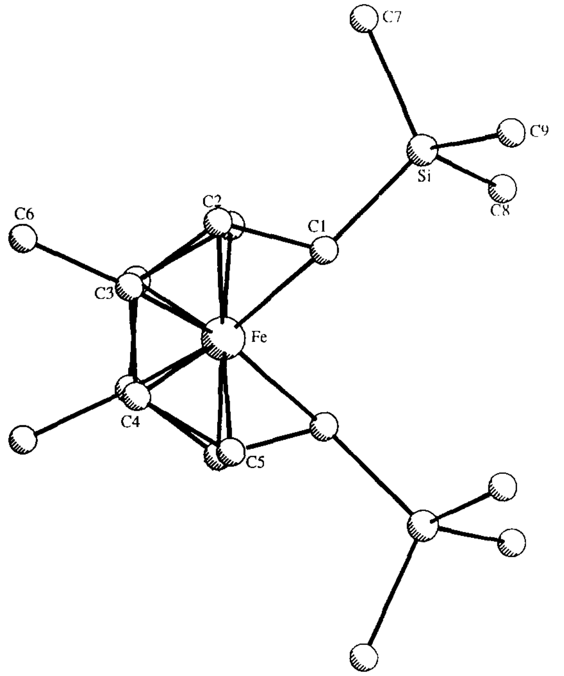


Fig. 2. Alternative view of Fe(1-Me_3Si-3-$CH_3C_5H_5)_2$, approximately perpendicular to the dienyl ligand planes.

an average Fe–C bond distance of 2.089(1) Å was found. The delocalized C–C distances are essentially equal, averaging 1.409(5) Å. The presence of a methyl group on C(3) causes the C(2)–C(3)–C(4) angle (122.1(6)°) to be smaller than those about C(2) and C(4) (129.1(5)° and 123.9(7)° respectively). As noted earlier, the C(1)–C(2)–C(3) angle seems particularly large, which appears to reflect an attempt to minimize the interligand Me_3Si–$SiMe_3$ interactions and also leads to the unusually small conformation angle.

As is normal for such complexes, the pentadienyl substituents tend to tilt significantly out of the plane [15]. The H(1,5) *endo* tilts occur away from the metal atom, by respective values of 47.0° and 50.8°, averaging 48.9°. The H(2,4) tilts of 18.7° and 22.4° average 20.6°, a surprisingly large tilt given the fact that in Fe(2,4-$C_7H_{11})_2$ the methyl group tilts average only 9.5° [15] (actually occurring in two types, 5.5° and 13.6°), which is reasonably typical for a wide variety of related complexes. As the tilt seems to occur in order to improve overlap between the p orbitals of the attached pentadienyl carbon atom and the metal d orbitals (as in **III**) [16], this serves to emphasize the fact that these ligands are in general very large relative to the size of most metal centers and must deform themselves significantly to optimize their bonding interactions. It would appear there is also a sizeable dependence of the degree of tilting on the size of the substituent, which is not unreasonable given the steric crowding that generally occurs in these complexes. This may also be seen from the respective deformations of H(5)*exo* and Si(1) towards the metal, 24.1° and 10.1°. The former deformation actually appears slightly greater than usual, perhaps a response to the small degree of tilting that Si(1) could undergo. One explanation for the deformations of terminal CH_2 groups in metal-bound π systems invokes a rehybridization of the carbon-based orbitals [17], and it would seem possible that, if rehybridization at one side were inhibited, an enhancement might occur at the other end. Finally, a relatively small tilt of the methyl group by 2.2° towards the iron atom is observed. It has often been observed that substituents in the 3 position do not tend to tilt so much, and in Fe(2,3,4-$C_8H_{13})_2$ the tilt actually is in the other direction, by 3.2°. There is a tilt of 12.8° between the two dienyl ligand planes.

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[11] It is possible that some **II** is also formed but perhaps was too soluble to crystallize from the hydrocarbon solutions owing to its lower symmetry. The fact that no **II** is observed in the sublimed samples indicates either that **II** is far less stable thermodynamically or (more probably) that the interconversion rate is extremely slow. An interconversion would seem to require conversion of one ligand to an η^1-bound form.

[12] The conformation angle is defined as the angle between two ligand related planes, each derived from the metal atom, the respective C(3) atom, and the midpoint between C(1) and C(5).

[13] The *gauche*-eclipsed conformation is twisted 60° from the *syn*-eclipsed form, and has a pseudo-octahedral arrangement of the formally charged (C(1), C(3) and C(5)) carbon atoms. A second *gauche*-eclipsed form occurs with a 120° twist but has not been observed, presumably since the charged positions define a trigonal prism.

[14] The standard deviations accompanying average values reflect the uncertainties in the average values, but not necessarily the distributions of the individual values.

[15] The sine of the tilt angle is defined as the deviation of the substituent below the dienyl plane divided by the bond length between the substituent and the attached carbon atom.

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