Kurzmitteilung/Short Communication

Complexes with Sterically Demanding Ligands, XVI[1)]

An Unexpected Coupling of Trimethylsilyl-Substituted Cyclopentadienide Anion by Ferric Chloride

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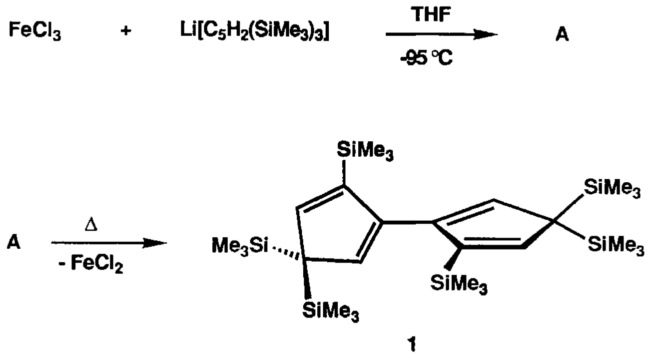
Reaction of 1,2,4-tris(trimethylsilyl)cyclopentadienyllithium with ferric chloride in THF at −95°C leads to the formation of a thermally sensitive iron(III) complex which decomposes to the new dihydrofulvalene derivative 3,7-dihydro-1,3,3,5,7,7-hexakis(trimethylsilyl)fulvalene (**1**).

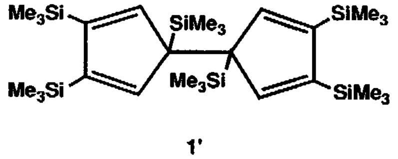
In 1951 Pauson attempted to oxidatively couple the cyclopentadienide anion equivalent MgCpBr (Cp = η^5-C_5H_5) by using ferric chloride with the aim of synthesizing fulvalene, but instead isolated ferrocene $FeCp_2$[2)]. Subsequently it was found that cyclopentadienide anions invariably yield ferrocene derivatives when treated with ferric chloride which is presumably reduced to iron(II) prior to nucleophilic substitution[3)]. In order to achieve an oxidative coupling of the cyclopentadienide anion to dihydrofulvalene[4a)], mild oxidants such as iodine[4b)] and cupric chloride[4c)] have to be used. We report here that tris(trimethylsilyl)cyclopentadienyllithium Li(Si$_3$Cp) [Si$_3$Cp = 1,2,4-$(SiMe_3)_3C_5H_2$][5)] gives with ferric chloride an intermediate iron(III) complex which decomposes to form the new substituted dihydrofulvalene **1** in a remarkably selective coupling reaction with concomitant migration of one trimethylsilyl group.

When Li(Si$_3$Cp) is treated with a stoichiometric amount of ferric chloride in THF at −95°C an intensely turquoise-colored solution is formed immediately. Upon warming to −40°C the green color faints and a white precipitate of $FeCl_2(THF)_{1.5}$ is deposited. From the supernatant hydrocarbon-soluble, sublimable, colorless crystals of **1** are isolated in 85% yield. Analytical and spectroscopic data indicate that air-stable and thermally robust **1** is a new dihydrofulvalene derivative, but not the symmetrically coupled isomer **1'**.

The unexpected structure of **1** was confirmed by a single-crystal X-ray structural analysis. As can be seen from Figure 1 the molecule has a crystallographically imposed C_2 symmetry. The virtually planar five-membered rings are connected by a C−C bond with a distance of 1.500(3) Å. The dihedral angle amounts to 108.3°. The bond distances within the five-membered rings show the expected variation between double and single bonds. Selected bond distances and angles are listed in Table 1.



1



1'

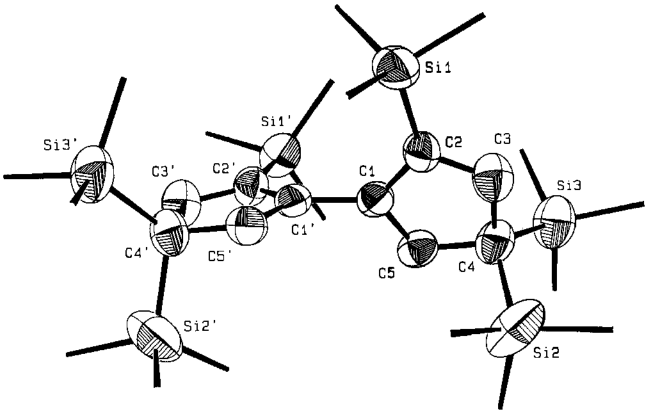


Figure 1. ORTEP diagram of **1** (50% probability ellipsoids). Methyl groups of the trimethylsilyl substituents have been omitted for the sake of clarity

Attempts to isolate the initial product were hampered by the extreme thermal instability. Rapid workup of the reaction mixture by evaporation, pentane extraction, and filtration below −40°C,

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however, led to the isolation of paramagnetic, dark blue crystals of **A** for which the elemental analysis gave a composition in agreement with the formulation $Fe(Si_3Cp)Cl_2$. We tentatively assign a dimeric structure by analogy with complexes of the extensively studied series $[(\eta^5\text{-}C_5H_5)MCl_2]_2$[7]. It was secured that **A** is *not* $[(Fe(Si_3Cp)_2]\text{-}FeCl_4$ which has the same stoichiometry and a similar blue color. The latter was prepared by treating $Fe(Si_3Cp)_2$[6] with ferric chloride and shown to be thermally stable and unable to decompose to give $FeCl_2$ and **1** under the above conditions[1]. We are continuing to further characterize the nature of the reactive intermediate **A** and clarify the course of this unusual coupling reaction.

Table 1. Selected bond lengths [Å] and angles [°] of **1**. Atoms related by the symmetry operation $(-x, y, 0.5 - z)$ are marked with ′

Si1-C2	1.853(2)	Si2-C4	1.906(2)
Si3-C4	1.898(2)	Si1-C11	1.861(2)
Si2-C21	1.869(3)	Si3-C31	1.847(2)
Si1-C12	1.876(2)	Si2-C22	1.880(3)
Si3-C32	1.855(2)	Si1-C13	1.859(2)
Si2-C23	1.869(3)	Si3-C33	1.827(2)
C1-C1'	1.500(3)	C1-C2	1.458(2)
C2-C3	1.368(2)	C3-C4	1.484(2)
C4-C5	1.482(3)	C5-C1	1.361(1)
C1'-C1-C2	126.1(2)	C1-C2-Si1	130.1(1)
C1'-C1-C5	123.8(2)	C3-C2-Si1	123.9(1)
C2-C1-C5	109.6(1)	C1-C2-C3	106.0(1)
C3-C4-Si2	107.1(1)	C3-C4-Si3	110.1(1)
C5-C4-Si2	104.0(1)	C5-C4-Si3	114.3(1)
Si2-C4-Si3	118.6(1)		

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Experimental

All experiments were carried out under dry nitrogen or argon by using standard Schlenk-technique. Solvents were purified, dried, and distilled under nitrogen. – ^1H and ^{13}C NMR: Jeol JNM-GX 270 or 400. – IR: Nicolet FT-5-DX. – UV: Perkin-Elmer Lambda 2 Spectrometer. – MS: Varian 311. – Melting points were determined in sealed capillaries.

3,7-Dihydro-1,3,3,5,7,7-hexakis(trimethylsilyl)fulvalene (**1**): To a suspension of $FeCl_3$ (1.62 g, 10.0 mmol) in 50 ml of THF was added dropwise a solution of tris(trimethylsilyl)cyclopentadienyllithium (2.89 g, 10.0 mmol) in 100 ml of THF at −95°C. The mixture immediately turned turquoise and was stirred at −78°C for 1 h. It was then allowed to slowly warm up to −40°C during which time the off-white precipitate of $FeCl_2$ started to deposit and the green color completely disappeared. The solvent was removed in vacuo, the residue extracted with 3 × 20 ml of pentane, and after filtration of $FeCl_2$ the filtrate was concentrated until incipient crystallization. The solution was cooled to −78°C to afford colorless crystals; yield 2.39 g (85%), m.p. 132°C. – ^1H NMR ($CDCl_3$, 25°C): $\delta = -0.05$ (s, 18H, $SiCH_3$), -0.02 (s, 9H, $SiCH_3$), 6.15 [d, $^4J(HH) = 2.2$ Hz, 1H, ring H], 6.66 [d, $^4J(HH) = 2.2$ Hz, 1H, ring H]. – ^{13}C NMR ($CDCl_3$, 25°C): $\delta = -0.29$ [q, $^1J(CH) = 119$ Hz, $SiCH_3$], 0.59 [q, $^1J(CH) = 119$ Hz, $SiCH_3$], 58.56 (s, C-9,10), 134.55 [d, $^1J(CH) = 164$ Hz, C-4,8], 144.45 (s, C-3,7), 146.28 [d, $^1J(CH) = 164$ Hz, C-2,6], 148.05 (s, C-1,5). – IR (KBr): $\tilde{\nu} = 3053\ cm^{-1}$ w, 2954 s, 2900 mw, 1496 m, 1252 s, 990 s, 910 s, 852 vs, 756 s, 687 ms, 632 ms, 439 m. – UV (*n*-hexane): λ (lg ε) = 202 nm (4.491), 262 (3.643). – EI MS: m/z (%) = 562 (50) [M^+], 547 (5) [$M^+ - Me$], 475 (10) [$M^+ - SiMe_3 - Me$], 387 (15) [$M^+ - 2\ SiMe_3 - 2\ Me$], 313 (10), [$M^+ - 3\ SiMe_3 - 2\ Me$], 73 (100) [$SiMe_3$].

$C_{14}H_{29}Si_3$ (281.6)	Calcd.	C 59.71	H 10.38
	Found	C 59.77	H 10.34

X-ray Structural Analysis of **1**: Large crystals of **1** were obtained by slow evaporation of an *n*-pentane solution. By using a polarization microscope an isometric fragment of dimensions 0.40 × 0.50 × 0.50 mm was cut. Cell dimensions and intensity data were obtained with an Enraf-Nonius CAD-4 diffractometer by using following parameters: Cu-K_α radiation, graphite monochromator, $\lambda = 1.54184$ Å, $1.0° \le \Theta \le 60°$, $T = 23$°C. Orthorhombic space group *Pbcn* (IT No. 60); $a = 10.927(2)$, $b = 18.617(6)$, $c = 18.914(7)$ Å, $V = 3848$ Å^3, $d_{calcd.} = 0.972\ g\ cm^{-3}$, $Z = 4$, $M = 563.3$, $F(000) = 1240$. 2486 independent reflections of which 1964 were assigned observed [$I > 3.0\sigma(I)$]. The structure was solved by direct methods and difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated at their idealized positions, but were not included in the refinement. Data manipulation and refinements were performed with STRUX II[8]. $R = 0.054$ [$R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$], $R_w = 0.051$ $\{[\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}\}$[9]. Temperature-dependent Guinier photographs indicate a reversible phase transition at −2.5°C[10]. Atomic coordinates are listed in Table 2.

Table 2. Fractional atomic coordinates and thermal parameters of **1** ($B_{equiv} = 4/3\ [a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33}]$)

Atom	x/a	y/b	z/c	B_{equiv}
Si1	0.21053(10)	0.20053(6)	0.32901(5)	5.62(3)
Si2	0.25944(14)	-0.02177(7)	0.16805(6)	8.54(4)
Si3	0.23754(11)	0.11235(7)	0.05709(6)	6.77(3)
C1	0.0585(3)	0.1118(2)	0.2293(2)	3.85(8)
C2	0.1745(3)	0.1431(2)	0.2517(2)	4.30(8)
C3	0.2595(3)	0.1208(2)	0.2033(2)	5.40(9)
C4	0.2063(3)	0.0736(2)	0.1481(2)	4.96(9)
C5	0.0755(3)	0.0736(2)	0.1687(2)	4.26(8)
C11	0.2093(4)	0.1469(2)	0.4121(2)	8.4(1)
C12	0.3673(4)	0.2396(2)	0.3169(2)	8.5(1)
C13	0.0995(4)	0.2760(2)	0.3345(2)	7.9(1)
C21	0.2276(5)	-0.0423(2)	0.2630(2)	9.7(1)
C22	0.1728(7)	-0.0889(2)	0.1132(3)	14.8(2)
C23	0.4268(5)	-0.0324(3)	0.1503(3)	17.2(2)
C31	0.1689(6)	0.0573(3)	-0.0138(2)	13.4(2)
C32	0.4038(5)	0.1215(4)	0.0395(3)	15.8(2)
C33	0.1697(5)	0.2019(3)	0.0524(2)	13.2(2)

CAS Registry Numbers

1: 133670-94-7 / $Li[C_5H_2(SiMe_3)_3]$: 97535-99-4 / $FeCl_3$: 7705-08-0

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[10] W. Massa, unpublished results.

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