

Novel π -complexes of divalent silicon: mixed substituted neutral sandwich compounds and the half-sandwich cation ($i\text{Pr}_5\text{C}_5$)Si $^{+\dagger}$

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Received (in Cambridge, UK) 22nd May 2006, Accepted 23rd June 2006

First published as an Advance Article on the web 11th July 2006

DOI: 10.1039/b607236d

The pentamethylcyclopentadienylsilicon(II) cation, $\text{Me}_5\text{C}_5\text{Si}^+$, opens up access to novel silicocene derivatives; the penta-*iso*-propylcyclopentadienylsilicon(II) cation, $i\text{Pr}_5\text{C}_5\text{Si}^+$, is obtained by reaction of the mixed silicocene ($i\text{Pr}_5\text{C}_5$)(Me_5C_5)Si with $\text{H}(\text{OEt})_2^+\text{Al}[\text{OC}(\text{CF}_3)_3]_4^-$.

π -Complexes of divalent silicon that are stable under ordinary conditions of temperature and pressure are still rather rare.^{1–3} More detailed reactivity studies have been performed only with the sandwich compound bis(pentamethylcyclopentadienyl)silicon(II), (Me_5C_5)₂Si (decamethylsilicocene) (**1**),⁴ which was first synthesized two decades ago.¹

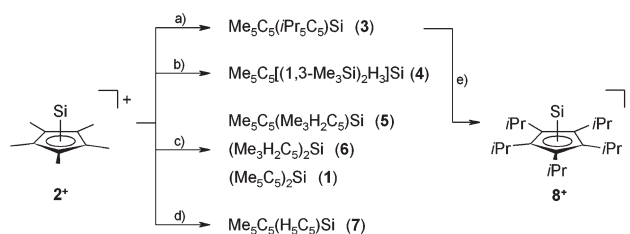
In the strategy so far applied to the synthesis of π -cyclopentadienylsilicon(II) compounds, peralkylation of the cyclopentadienyl rings was necessary to avoid unwanted sigma-tropic rearrangements within the σ -bonded cyclopentadienyl substituents of the tetravalent silicon precursors.⁴ This restriction has become obsolete with the recently published synthesis of stable compound (Me_5C_5)Si $^+$ B(C₆F₅)₄ $^-$ (**2**), containing the half-sandwich (pentamethylcyclopentadienyl)silicon(II) cation (**2** $^+$).³ The cation **2** $^+$ is highly electrophilic and can, in principle, react with many types of nucleophilic reagents. In this communication, we report on the reactions of **2** with differently substituted lithium cyclopentadienides, which have led to the formation of novel stable silicocene derivatives. Furthermore, we report on the synthesis of a further substituted cyclopentadienylsilicon(II) cation.

Lithium penta-*iso*-propylcyclopentadienide⁵ reacts with **2** in dimethoxyethane (DME) solvent to give, in nearly quantitative yield, the silicocene pentamethylcyclopentadienyl[(penta-*iso*-propyl)cyclopentadienyl]silicon(II) (**3**), a moderately air-sensitive colourless compound, stable at room temperature (see Scheme 1). \ddagger

Compound **3** was structurally characterized by NMR spectroscopic methods and by X-ray diffraction. The solid state structure of **3** (one enantiomer) is presented in Fig. 1.⁶ The silicocene **3** shows nearly parallel cyclopentadienyl ring planes (179.7°), arranged in a staggered conformation in order to minimize contacts between the methyl and *iso*-propyl groups. The five *iso*-propyl groups in the $i\text{Pr}_5\text{C}_5$ ring are oriented in the same direction. This “paddle-wheel” type arrangement generates planar chirality and creates a pair of enantiomers.

The metallocenic chirality arises from the fact that all the methyl C–H groups are pointing either clockwise or counter clockwise

around the ring, comparable to the situation in $\text{Me}_5\text{C}_5(i\text{Pr}_5\text{C}_5)\text{M}^+$ cations (M = Co, Rh).⁷ The enantiomers present in the crystal cause disorder to the positions of the ring carbon atoms and to the methine carbons of the *iso*-propyl groups within the $i\text{Pr}_5\text{C}_5$ unit. Due to steric constraints, the $\text{C}_{\text{pcentroid}}\text{–Si}$ distances (2.18 and 2.19 Å) are greater than those in the decamethylsilicocene conformer with parallel-arranged Cp* rings (2.11 Å).¹



a) $i\text{Pr}_5\text{C}_5\text{Li}$; b) $(\text{Me}_3\text{Si})_2\text{H}_3\text{C}_5\text{Li}$; c) $\text{Me}_3\text{H}_2\text{C}_5\text{Li}$; d) $\text{H}_5\text{C}_5\text{Li}$
e) $\text{H}(\text{OEt})_2^+\text{Al}[\text{OC}(\text{CF}_3)_3]_4^-$

Scheme 1

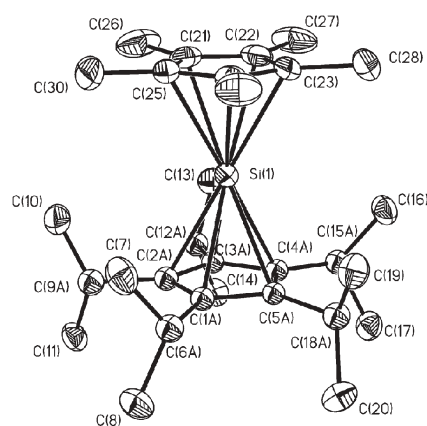


Fig. 1 ORTEP plot of the molecular structure of one enantiomer of **3**. The ellipsoids are at the 50% probability level. Due to the existence of enantiomers, the positions C(1A)–C(5A), C(6A), C(9A), C(12A), C(15A) and C(18A) are disordered and have been isotropically refined. Hydrogens are omitted for clarity. Selected bond lengths (Å): C(21)–C(22) 1.410(3), C(21)–C(25) 1.412(5), C(22)–C(23) 1.423(5), C(23)–C(24) 1.418(4), C(24)–C(25) 1.411(4), C(21)–C(26) 1.516(5), C(22)–C(27) 1.506(5), C(23)–C(28) 1.502(4), C(24)–C(29) 1.510(5), C(25)–C(30) 1.501(4), and $\text{C}_{\text{pcentroid}}\text{–Si}(1)$ 2.18 and 2.19. Selected bond angles (°): C(21)–C(22)–C(23) 107.7(3), C(22)–C(23)–C(24) 107.7(3), C(23)–C(24)–C(25) 108.3(3), C(21)–C(25)–C(24) 107.8(3), C(22)–C(21)–C(25) 108.6(3) and $\text{C}_{\text{pcentroid}}\text{–Si}(1)\text{–C}_{\text{pcentroid}}$ 179.7.

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\ddagger Electronic supplementary information (ESI) available: Complete assignment of the NMR data of compounds **4–6**. See DOI: 10.1039/b607236d

Presumably, for the same reason, the C–Me and the C–Pr bonds are significantly bent out of the Cp ring planes.

According to the NMR data, the structure of **3** in solution is comparable to that found in the solid state. In the ^1H and ^{13}C NMR spectra, only one set of signals is obtained both for the corresponding substituents and for the ring carbon atoms of each Cp ring. This indicates that both Cp rings in **3** are bonded to the central silicon atom in a π -type fashion, exhibiting five chemically equivalent methyl groups in the Me_5C_5 ring and five chemically equivalent *iso*-propyl groups in the $^i\text{Pr}_5\text{C}_5$ unit. The methyl groups of the *iso*-propyl units are found to be chemically non-equivalent due to their fixation in *endo* and *exo* positions, and hence two sets of signals are observed in the NMR spectra. At room temperature on the NMR timescale, no interconversion of the enantiomers is observed.

Lithium 1,3-bis(trimethylsilyl)cyclopentadienide⁸ reacts with **2** in DME in nearly quantitative yield to give the silicocene pentamethylcyclopentadienyl(1,3-bis(trimethylsilyl)cyclopentadienyl)silicon(II) (**4**), a colourless, thermally stable but rather air-sensitive compound (see Scheme 1).[‡] The structure assignment to this π -complex is based on 1D and 2D NMR experiments (2D experiments: see ESI[†]), and on MS and analytical data. The reaction of **2** with lithium 1,2,4-(trimethyl)cyclopentadienide⁹ leads to the formation of three π -complexes, namely to pentamethylcyclopentadienyl(1,2,4-trimethylcyclopentadienyl)silicon(II) (**5**), bis(1,2,4-trimethylcyclopentadienyl)silicon(II) (**6**) and decamethylsilicocene (**1**) in a roughly 8 : 1 : 1 ratio (see Scheme 1).[‡] Obviously, exchange of the cyclopentadienyl ligands amongst the products cannot be avoided under the chosen reaction conditions.¹⁰ A separation by fractional crystallization was unsuccessful. However, these silicocenes are unambiguously characterized by their NMR data. Application of heteronuclear multiple bond correlation (HMBC) techniques allowed the assignment of all ^1H , ^{13}C and ^{29}Si resonances to the related silicocenes in the mixture (complete assignments are given in the ESI[†]).

In order to explore the stability frontiers of mixed silicocenes bearing one Me_5C_5 ligand, we envisaged the synthesis of cyclopentadienyl(pentamethylcyclopentadienyl)silicon(II) (**7**). In this context, compound **2** was reacted with lithium cyclopentadienide at $-50\text{ }^\circ\text{C}$ in DME-*d*₁₀ in a specially designed two-chamber NMR tube, which allows the merging of two components within the probe of an NMR spectrometer at low temperature, enabling reactions to be followed directly by NMR.¹¹ Compound **7** is quantitatively formed in this reaction.[‡] The π -complex structure is documented by the appearance of singlets for the Cp–H and Cp–Me groups, respectively, by proton NMR, and by one ^{13}C signal for the ring carbon atoms of each Cp system and for the methyl groups in the Me_5C_5 unit (see Scheme 2). This “half-parent” silicocene is rather thermolabile, obviously due to the lack of steric protection. It decomposes markedly at temperatures above $-30\text{ }^\circ\text{C}$.

	δ_{H} [ppm]	δ_{C} [ppm]
Si:	2.09 (Me_5C_5)	10.4 (Me_5C_5)
7	5.97 (H_5C_5)	111.2 (H_5C_5)
		119.1 (Me_5C_5)

Scheme 2

The silicocenes **3** and **4** have been reacted in CH_2Cl_2 solvent with the oxonium salt $\text{H}(\text{OEt}_2)_2^+ \text{Al}[\text{OC}(\text{CF}_3)_3]_4^{-12}$ (a proton transfer agent) with the intention of synthesizing salt-like compounds containing novel half-sandwich cyclopentadienylsilicon(II) cations. In the reaction with **4**, the known (pentamethylcyclopentadienyl)silicon(II) cation **2**⁺ is formed, whereas the reaction of **3** yields quantitatively the extremely air- and moisture-sensitive, but thermally stable pale-yellow compound **8**, containing the novel (penta-*iso*-propylcyclopentadienyl)silicon(II) cation **8**⁺ (see Scheme 1). Compound **8** has been characterized by NMR spectroscopy and elemental analysis.[‡]

The NMR data indicate the existence of a π -structure in the cation **8**⁺ in solution (see graphical abstract). In the ^{13}C NMR spectrum, a single resonance is observed for all Cp ring carbon atoms. The equivalence of all five *iso*-propyl substituents is documented by the appearance of one set of signals in the ^{13}C and ^1H NMR spectra. Similar to the silicocene **3**, the methyl groups within the *iso*-propyl units are chemically inequivalent due to their fixed *exo* and *endo* orientation, a consequence of the mutual steric hindrance. The NMR data for the aluminate anion do not differ from that of the oxonium salt, as expected for only a weakly interacting counterion.

Compound **8** has also been investigated by X-ray diffraction,⁶ but due to the poor quality of the crystal and disorder, the data do not allow exact structural parameters to be determined. However, a pentagonal-pyramidal structure for the cationic unit can be unambiguously assigned.

The central atoms in π -complexes of main group elements exhibit pronounced high-field NMR shifts and thus are useful diagnostic probes.¹³ Table 1 presents the ^{29}Si NMR chemical shift data for silicon complexes **1–8**. All resonances appear extremely upfield-shifted, characteristic of the presence of π -complexes. Substitution of alkyl groups in the cyclopentadienyl periphery by trimethylsilyl groups or hydrogen atoms causes an appreciable downfield shift, as documented by the resonances for π -complexes **4–6**. It is worth mentioning that the ^{29}Si resonance in the cationic species is not downfield-shifted compared to those of neutral silicocenes.

The described synthetic method is a novel versatile route to mixed substituted silicocenes. It allows the use of a wide range of cyclopentadienyl ligands, even with hydrogen atoms as substituents. Such complexes are not accessible *via* the classical reductive elimination route.⁴ The half-parent silicocene **7** seems to mark the

Table 1 ^{29}Si NMR chemical shifts of **1–8**

Compound	1 ^a	2 ^b	3 ^a	4 ^a	5 ^a	6 ^a	7 ^c	8 ^b
δ/ppm	–392.6	–400.2	–420.0	–337.3	–333.0	–311.4	–335.8	–397.4

^a Solvent C_6D_6 . ^b Solvent CD_2Cl_2 . ^c Solvent DME-*d*₁₀.

limit of kinetic stabilization in pentamethylcyclopentadienyl substituted silocenes. In the reaction of silocene derivatives with proton transfer agents containing weak coordinating anions, the thermodynamic stability of the resulting silicon cation is the most important parameter and not the π -basicity of the cyclopentadienyl ligand in the respective silocene.

This work was supported by the Deutsche Forschungsgemeinschaft and by the University of Bielefeld.

Notes and references

† **Experimental section:** All manipulations were carried out under an inert atmosphere of argon using standard Schlenk techniques. High resolution NMR data were collected on Bruker DRX 500 and Bruker Avance 600 instruments.

Silocenes **3–6** (general procedure): 0.36 mmol of (pentamethylcyclopentadienyl)silicon(II) tetrakis(pentafluorophenyl)borate (**2**), dissolved in 2 ml of DME, was added dropwise to a solution of 0.36 mmol of the corresponding lithium cyclopentadienide in 2 ml of DME, pre-cooled to $-55\text{ }^{\circ}\text{C}$. After stirring for 2 h, the solution was warmed to rt and the solvent removed *in vacuo*. After the addition of 10 ml of hexane, the lithium salt was separated by filtration and all volatile components were removed *in vacuo*. The corresponding silocenes were isolated as colourless, air- and moisture-sensitive solids.

3: ^1H NMR (600.13 MHz, C_6D_6 , δ/ppm): 1.23 and 1.24 (2 d, $^3J_{\text{HH}} = 7.3$ Hz, 30 H, $\text{CH}(\text{CH}_3)_2\text{C}_5$), 1.91 (s, 15 H, Me_5C_5) and 2.99 (sept., $^3J_{\text{HH}} = 7.3$ Hz, 5 H, $\text{CH}(\text{CH}_3)_2\text{C}_5$); $^{13}\text{C}\{^1\text{H}\}$ NMR (150.92 MHz, C_6D_6 , δ/ppm): 10.4 (Me_5C_5), 23.2 and 24.9 ($\text{CH}(\text{CH}_3)_2\text{C}_5$), 26.0 ($\text{CH}(\text{CH}_3)_2\text{C}_5$), 118.4 (Me_5C_5) and 129.2 ($\text{CH}(\text{CH}_3)_2\text{C}_5$); $^{29}\text{Si}\{^1\text{H}\}$ NMR (119.20 MHz, C_6D_6 , δ/ppm): -420.0 .

4: ^1H NMR (499.89 MHz, C_6D_6 , δ/ppm): 0.31 (s, 18 H, $\text{H}_3(\text{SiMe}_3)_2$), 1.71 (s, 15 H, Me_5C_5), 5.87 (d, $^4J_{\text{HH}} = 1.4$ Hz, 2 H, $\text{H}_3(\text{SiMe}_3)_2\text{C}_5$) and 6.56 (t, $^4J_{\text{HH}} = 1.4$ Hz, 1 H, $\text{H}_3(\text{SiMe}_3)_2\text{C}_5$); $^{13}\text{C}\{^1\text{H}\}$ NMR (150.92 MHz, C_6D_6 , δ/ppm): 0.9 ($\text{H}_3(\text{SiMe}_3)_2\text{C}_5$) and 119.4 (Me_5C_5); $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.29 MHz, C_6D_6 , δ/ppm): -337.3 and -10.3 . MS (EI, m/z), 237 ($\text{H}_3(\text{SiMe}_3)_2\text{C}_5\text{Si}^+$, 163 ($\text{Me}_5\text{C}_5\text{Si}^+$). $\text{C}_{21}\text{H}_{35}\text{Si}_3$ requires C 67.66, H 9.73; found C 66.52, H 8.94%.

5: ^1H NMR (600.13 MHz, C_6D_6 , δ/ppm): 1.84 (s, 15 H, Me_5C_5), 1.99 (s, 6 H, $\text{Me}_3\text{H}_2\text{C}_5$), 2.08 (s, 3 H, $\text{Me}_3\text{H}_2\text{C}_5$) and 5.44 (s, 2 H, $\text{Me}_3\text{H}_2\text{C}_5$); $^{13}\text{C}\{^1\text{H}\}$ NMR (150.92 MHz, C_6D_6 , δ/ppm): 10.4 (Me_5C_5), 12.6 and 14.4 ($\text{H}_2\text{Me}_3\text{C}_5$), 111.2, 119.1 and 124.4 ($\text{H}_2\text{Me}_3\text{C}_5$) and 119.4 (Me_5C_5); $^{29}\text{Si}\{^1\text{H}\}$ NMR (119.20 MHz, C_6D_6 , δ/ppm): -333.0 .

6: ^1H NMR (600.13 MHz, C_6D_6 , δ/ppm): 1.93 (s, 12 H, $\text{H}_2\text{Me}_3\text{C}_5$), 2.02 (s, 6 H, $\text{H}_2\text{Me}_3\text{C}_5$) and 5.38 (s, 4 H, $\text{H}_2\text{Me}_3\text{C}_5$); $^{13}\text{C}\{^1\text{H}\}$ NMR (150.92 MHz, C_6D_6 , δ/ppm): 12.4 and 14.2 ($\text{H}_2\text{Me}_3\text{C}_5$), and 112.0, 120.6 and 124.6 ($\text{H}_2\text{Me}_3\text{C}_5$); $^{29}\text{Si}\{^1\text{H}\}$ NMR (119.20 MHz, C_6D_6 , δ/ppm): -311.4 .

1: ^1H NMR (600.13 MHz, C_6D_6 , δ/ppm): 1.88 (s, 30 H, Me_5C_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (150.92 MHz, C_6D_6 , δ/ppm): 10.4 (Me_5C_5) and 119.4 (Me_5C_5); $^{29}\text{Si}\{^1\text{H}\}$ NMR (119.20 MHz, C_6D_6 , δ/ppm): -392.6 .

7: In a special two-chamber coaxial NMR tube,¹¹ 83.0 mg of (pentamethylcyclopentadienyl)silicon(II) tetrakis(pentafluorophenyl)borate (**2**) in 0.5 ml of DME- d_{10} were reacted at $-50\text{ }^{\circ}\text{C}$ directly in the probe of an NMR instrument with 7.10 mg of $\text{H}_5\text{C}_5\text{Li}$ dissolved in 0.25 ml of DME- d_{10} , giving quantitatively the silocene $(\text{C}_5\text{H}_5)(\text{C}_5\text{Me}_5)\text{Si}$ (**7**) and $\text{Li}(\text{C}_6\text{F}_5)_4$. ^1H NMR (600.13 MHz, DME- d_{10} , $-50\text{ }^{\circ}\text{C}$, δ/ppm): 2.09 (s, 15 H, Me_5C_5) and 5.97 (s, 5 H, H_5C_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (150.92 MHz,

DME- d_{10} , $-50\text{ }^{\circ}\text{C}$, δ/ppm): 10.4 (Me_5C_5), 111.2, (H_5C_5) and 119.1 (Me_5C_5); $^{29}\text{Si}\{^1\text{H}\}$ NMR (119.20 MHz, DME- d_{10} , $-50\text{ }^{\circ}\text{C}$, δ/ppm): -335.8 .

8: A solution of 202 mg (180 mmol) of $\text{H}(\text{OEt})_2^+\text{Al}[\text{OC}(\text{CF}_3)_3]_4^-$ in 2 ml of CH_2Cl_2 was added dropwise to a solution of 102 mg (201 mmol) of penta-*iso*-propylcyclopentadienyl(pentamethylcyclopentadienyl)silicon(II) (**3**) in 4 ml of CH_2Cl_2 at $-50\text{ }^{\circ}\text{C}$. After warming to rt, the reaction mixture was stirred for an additional 30 min. After removing the solvent, the residue was washed three times with 5 ml portions of hexane and dried *in vacuo*. **8** was obtained as pale yellow solid in quantitative yield. ^1H NMR (600.13 MHz, CD_2Cl_2 , δ/ppm): 1.42 and 1.43 (2 d, $^3J_{\text{HH}} = 5.3$ Hz, 30 H, $((\text{CH}_3)_2\text{CH})_5\text{C}_5$) and 3.38 (sept., $^3J_{\text{HH}} = 5.3$ Hz, 5 H, $((\text{CH}_3)_2\text{CH})_5\text{C}_5$); $^{13}\text{C}\{^1\text{H}\}$ NMR (150.92 MHz, CD_2Cl_2 , δ/ppm): 19.9 and 25.2 ($((\text{CH}_3)_2\text{CH})_5\text{C}_5$), 25.8 ($((\text{CH}_3)_2\text{CH})_5\text{C}_5$), 121.7 (q, $^1J_{\text{CF}} = 292.8$ Hz, $\text{C}(\text{CF}_3)_3$) and 132.7 ($((\text{CH}_3)_2\text{CH})_5\text{C}_5$); ^{19}F NMR (470.65 MHz, CD_2Cl_2 , δ/ppm): -75.7 ; $^{29}\text{Si}\{^1\text{H}\}$ NMR (119.20 MHz, CD_2Cl_2 , δ/ppm): -397.4 . $\text{C}_{36}\text{H}_{35}\text{AlF}_{36}\text{O}_4\text{Si}$ requires C 34.02, H 2.78; found C 33.49, H 2.35%.

- P. Jutzi, D. Kanne and C. Krüger, *Angew. Chem.*, 1986, **98**, 163.
- (a) P. Jutzi and E. A. Bunte, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1605; (b) T. Müller, P. Jutzi and T. Kühler, *Organometallics*, 2001, **20**, 5619.
- P. Jutzi, A. Mix, B. Rummel, W. W. Schoeller, B. Neumann and H. G. Stammer, *Science*, 2004, **305**, 849.
- T. Kühler and P. Jutzi, *Adv. Organomet. Chem.*, 2003, **49**, 1.
- T. Dezember and H. Sitzmann, *Z. Naturforsch., B: Chem. Sci.*, 1997, **52**, 911.
- (a) X-Ray data were collected on a Nonius KappaCCD instrument equipped with graphite-monochromatized Mo- $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Crystals of the silocene **3** for X-ray diffraction studies were obtained from a hexane solution. Crystal structure data of $\text{C}_{30}\text{H}_{50}\text{Si}_2\text{O}_5$ at 100 K: $M_r = 481.88$, triclinic $\bar{P}1$, $a = 9.8950(10)$, $b = 9.9430(8)$, $c = 18.0340(18)\text{ \AA}$, $\alpha = 105.747(5)$, $\beta = 93.344(4)$, $\gamma = 110.354(5)^\circ$, $V = 1578.0(3)\text{ \AA}^3$, $Z = 2$, $\rho_{\text{calc}} = 1.014\text{ g cm}^{-3}$, $R_F = 0.0689$ for 5509 reflections with $I_0 > 2\sigma(I_0)$, $wR_{F2} = 0.1738$ for all data. The structure was solved by direct methods. CCDC 603837. Crystals of **8** were obtained from a dichloromethane solution. Crystal structure data of $\text{C}_{36}\text{H}_{35}\text{AlF}_{36}\text{O}_4\text{Si}$ at 100 K: $M_r = 1270.71$, triclinic $\bar{P}1$, $a = 10.2390(14)$, $b = 15.481(5)$, $c = 15.9790(17)\text{ \AA}$, $\alpha = 92.105(18)$, $\beta = 90.523(11)$, $\gamma = 102.87(2)^\circ$, $V = 2467.1(9)\text{ \AA}^3$, $Z = 2$, $\rho_{\text{calc}} = 1.711\text{ g cm}^{-3}$, $R_F = 0.1006$ for 4746 reflections with $I_0 > 2\sigma(I_0)$, $wR_{F2} = 0.2790$ for all data. The structure was solved by direct methods. Due to poor quality and disorder, structural details are not discussed. CCDC 611465. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607236d.
- D. Buchholz, B. Gloaguen, J.-L. Fillaut, M. Cotrait and D. Astruc, *Chem.-Eur. J.*, 1995, **1**, 347.
- P. Jutzi, W. Leffers, S. Pohl and W. Saak, *Chem. Ber.*, 1989, **122**, 1449.
- Lithium-1,3,4-trimethylcyclopentadienide: P. Jutzi, S. Pilotek, B. Neumann and H.-G. Stammer, *J. Organomet. Chem.*, 1998, **552**, 1–2, 221.
- Cp group exchange can happen *via* a cationic triple-decker-type Cp_3Si_2^+ cation or *via* an anionic Cp_3Si^- intermediate.
- P. Jutzi, A. Mix, B. Rummel, B. Neumann, H. G. Stammer, A. Rozhenko and W. W. Schoeller, in *Organosilicon Chemistry VI: From Molecules to Materials*, ed. N. Auner, J. Weis, Wiley-VCH, 2005, vol. **1**, pp. 69–73.
- I. Krossing and A. Reisinger, *Eur. J. Inorg. Chem.*, 2005, **10**, 1979.
- P. Jutzi and N. Burford, *Chem. Rev.*, 1999, **99**, 969.