

The addition-reaction product of 1,1,1,4,4,4-hexachloro-1,4-disilabutane with *N*-methylimidazole

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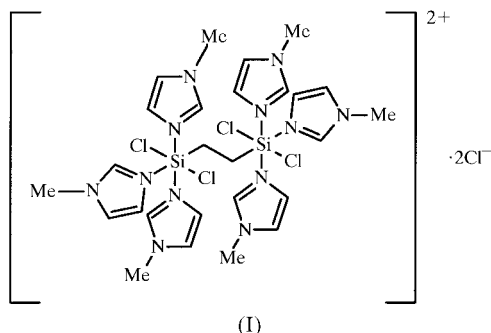
Received 7 June 2000

Accepted 29 June 2000

The product of the addition reaction of 1,1,1,4,4,4-hexachloro-1,4-disilabutane with *N*-methylimidazole is μ -ethylene- $C^1:C^2$ -bis[dichlorotris(1-methylimidazole- N^3)silicon(IV)] dichloride, $C_{26}H_{40}Cl_4N_{12}Si_2^{2+} \cdot 2Cl^-$. Two of the six Cl atoms are replaced by aromatic nitrogen bases and the coordination sphere of silicon is extended from four to six. The molecule is located on a crystallographic centre of inversion. The environment around the Si atom can be described as a slightly distorted octahedron with the Cl atoms occupying axial positions and the three *N*-methylimidazole ligands and the ethylene bridge in the equatorial plane.

Comment

In recent years, the extension of the coordination sphere of silicon in complexes with organic nitrogen bases has been the subject of numerous studies (Bechstein *et al.*, 1990; Chuit *et al.*, 1993; Kane *et al.*, 1998; Hensen, Kettner *et al.*, 1998; Hensen, Mayr-Stein, Stumpf *et al.*, 2000). Several complexes of silicon halides are already known, but little is known about the adducts of compounds containing more than one silicon



centre. We present here the product of the addition reaction of 1,1,1,4,4,4-hexachloro-1,4-disilabutane with *N*-methylimid-

azole, namely μ -ethylene- $C^1:C^2$ -bis[dichlorotris(1-methylimidazole- N^3)silicon(IV)] dichloride, (I).

Only two of the six Cl atoms are replaced by aromatic nitrogen bases, but the coordination sphere of silicon is extended from four to six. The reaction product is a dication (located on a crystallographic centre of inversion) crystallizing with two chloride ions. Compared with other hexacoordinated complexes of halogen silanes with tertiary nitrogen bases, the current product shows a remarkable new feature, *i.e.* it bears two silicon centres that both carry a formal charge of +1. In contrast, until now, only neutral addition complexes, *e.g.* dichlorobis(pyridine)silane (Hensen, Stumpf *et al.*, 1998), tetrachlorobis(4-methylpyridine)silicon (Hensen, Mayr-Stein, Spangenberg & Bolte, 2000) and tetrachlorobis(3,4-dimethylpyridine)silicon (Hensen, Mayr-Stein, Spangenberg, Bolte & Rühl, 2000), or dicationic complexes, *e.g.* $SiHCl(N\text{-methylimidazole})_4^{2+}$ (Hensen, Kettner *et al.*, 1998), $SiCl_2(N\text{-methylimidazole})_4^{2+}$ with different counter-ions and solvent molecules (Hensen, Mayr-Stein, Stumpf *et al.*, 2000), and bis(2,2'-bipyridyl- N,N')dichlorosilicon (Hensen, Mayr-Stein, Rühl & Bolte, 2000), have been obtained. The current structure is the first example of a hexacoordinated silicon centre where only one halogen atom is removed from the coordination sphere of the starting material, thus the ratio of removed halogen ligands to newly added base ligands of 1:3 is observed for the first time. The silicon centres appear in a nearly ideal octahedral environment, where the two remaining chlorine ligands occupy axial positions. The three *N*-methylimidazole groups and the ethylene bridge lie in the equatorial plane. There are only minor deviations from perfect octahedral coordination: all bond angles involving C1 are bigger than 90° ; whereas the two Si–N bonds *trans* to each other are of nearly the same length, the Si–N bond *trans* to C1 is slightly shorter than the other two; the two Si–Cl bonds differ by approximately 0.05 Å. Compared with the free Lewis acid 1,1,1,4,4,4-hexachloro-1,4-disilabutane (Mitzel *et al.*, 1997), in which the Si–Cl bond lengths range from 2.0225 (6) to

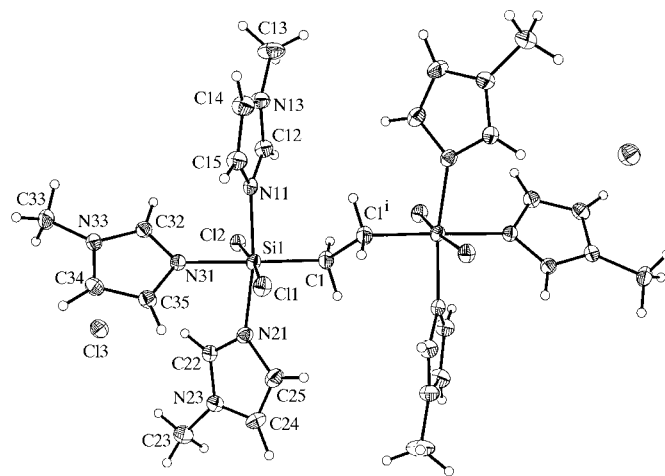


Figure 1

Perspective view of (I) with the atomic numbering scheme; displacement ellipsoids are at the 50% probability level. The symmetry code is as in Table 1.

2.0283 (6) Å, those in the current structure are considerably longer. For comparison, a search of the Cambridge Structural Database (Version 5.19, April 2000; Allen & Kennard, 1993) yielded 39 Si—Cl fragments (hexacoordinated Si, mono-coordinated Cl) with a mean Si—Cl bond length of 2.20 (5) Å. Furthermore, it is remarkable that the Si—C—C angle is widened to nearly 120°, a fact that can be attributed to the bulky substituents at the silicon centres. The C—C bond length, on the other hand, shows a normal value. The crystal packing is stabilized by short contacts between the Cl[−] ion and various H atoms (Table 2).

Experimental

To 1,1,1,4,4,4-hexachloro-1,4-disilabutane (5 ml) in chloroform (25 ml) was added *N*-methylimidazole and the reaction was monitored by measuring the temperature. After approximately 2 h, the precipitated solid was isolated, washed and dried. Crystals of (I) were obtained by subliming the powder in an evacuated glass ampoule for several days at 315 K.

Crystal data

C ₂₆ H ₄₀ Cl ₄ N ₁₂ Si ₂ ²⁺ ·2Cl [−]	<i>D_x</i> = 1.452 Mg m ^{−3}
<i>M_r</i> = 789.58	Mo <i>K</i> α radiation
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Cell parameters from 5816 reflections
<i>a</i> = 13.8976 (1) Å	<i>θ</i> = 1–25°
<i>b</i> = 7.5553 (1) Å	<i>μ</i> = 0.581 mm ^{−1}
<i>c</i> = 17.3704 (2) Å	<i>T</i> = 133 K
<i>β</i> = 97.947 (1)°	Block, colourless
<i>V</i> = 1806.39 (3) Å ³	0.30 × 0.20 × 0.20 mm
<i>Z</i> = 2	

Data collection

Siemens CCD three-circle diffractometer	<i>R</i> _{int} = 0.057
<i>ω</i> scans	<i>θ</i> _{max} = 26.41°
Absorption correction: empirical (<i>SADABS</i> ; Sheldrick, 1996)	<i>h</i> = −17 → 17
<i>T</i> _{min} = 0.84, <i>T</i> _{max} = 0.90	<i>k</i> = −9 → 9
22 213 measured reflections	<i>l</i> = −21 → 21
3679 independent reflections	274 standard reflections
2894 reflections with <i>I</i> > 2σ(<i>I</i>)	frequency: 900 min
	intensity decay: none

Table 1

Selected geometric parameters (Å, °).

Si1—C1	1.921 (2)	Si1—Cl1	2.2351 (9)
Si1—N31	1.938 (2)	Si1—Cl2	2.2840 (8)
Si1—N11	1.953 (2)	C1—Cl ⁱ	1.531 (5)
Si1—N21	1.954 (2)		
C1—Si1—N31	177.81 (10)	N11—Si1—Cl1	91.68 (6)
C1—Si1—N11	93.10 (9)	N21—Si1—Cl1	89.11 (6)
N31—Si1—N11	85.97 (8)	C1—Si1—Cl2	90.73 (8)
C1—Si1—N21	95.67 (10)	N31—Si1—Cl2	87.29 (6)
N31—Si1—N21	85.20 (8)	N11—Si1—Cl2	90.01 (6)
N11—Si1—N21	171.10 (9)	N21—Si1—Cl2	88.41 (6)
C1—Si1—Cl1	94.45 (8)	Cl1—Si1—Cl2	174.46 (4)
N31—Si1—Cl1	87.56 (6)	Cl ⁱ —C1—Si1	119.1 (2)

Symmetry code: (i) 2 − *x*, 1 − *y*, 1 − *z*.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C34—H34...Cl3 ⁱ	0.95	2.61	3.450 (3)	148
C33—H33A...Cl3 ⁱⁱ	0.98	2.61	3.540 (3)	159
C22—H22...Cl3	0.95	2.68	3.524 (3)	149

Symmetry code: (i) 1 − *x*, −*y*, 1 − *z*; (ii) 1 − *x*, 1 − *y*, 1 − *z*.

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0273 <i>P</i>) ²
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.041	+ 1.7731 <i>P</i>
<i>wR</i> (<i>F</i> ²) = 0.085	where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>S</i> = 1.078	(Δ/σ) _{max} = 0.002
3679 reflections	Δρ _{max} = 0.34 e Å ^{−3}
211 parameters	Δρ _{min} = −0.29 e Å ^{−3}
H-atom parameters constrained	

All H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [*U*(H) = 1.5*U*_{eq}(C_{methyl}) or *U*(H) = 1.2*U*_{eq}(C)] using a riding model with C—H(aromatic) = 0.95 Å, C—H(secondary) = 0.99 Å or C—H(methyl) = 0.98 Å. The methyl groups were allowed to rotate about their local threefold axis.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1418). Services for accessing these data are described at the back of the journal.

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