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Bromo(hydrido)methylbis(4-methylpyridine-*N*)silicon Bromide at 173 K

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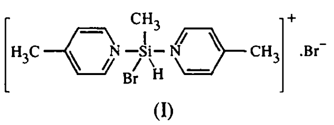
Abstract

Dibromomethylsilane, $HSiMeBr_2$, and 4-methylpyridine in aprotic solvents form a crystalline 1:2 compound stable at room temperature. X-ray structure analysis shows a $[HSiMeBr(4\text{-methylpyridine})_2]^+$ complex, $C_{13}H_{18}BrN_2Si^+.Br^-$, with one bromide ion removed to the second area of coordination. The ligands bound directly to the silicon centre exhibit an almost trigonal-bipyramidal geometry.

Comment

The reaction between halogensilanes and heterocyclic nitrogen bases [pyridine (Hensen *et al.*, 1983), methylpyridine (Hensen *et al.*, 1992), dimethylpyridine (Hensen & Wagner, 1993), *N*-methylimidazole (Burger *et al.*, 1995) and *N*-(trimethylsilyl)imidazole (Hensen, Müller & Pickel, 1988)] leads to Lewis acid–base adducts with dative Si—N bonds. It is very difficult to assess the geometry of these complexes in advance. The central Si atom can have the coordination numbers 4, 5 or 6 and the complexes can be neutral, monocationic or dicationic. The structure of the title compound, (I), shows a pentacoordinated Si atom (Fig. 1).



(I)

One of the bromides is displaced from the first coordination sphere by the reaction of the dihalogenalkylsilane with 4-methylpyridine. The result is a monocationic complex. The distance between the Si atom and the displaced bromide ion Br2, 3.765 (1) Å, is shorter than in other cationic halogensilane–base complexes and also shorter than the sum of the van der Waals radii of Si and Br (3.8 Å; Bondi, 1964). To our knowledge, this is the first such dihalogenalkyl–amine complex where only one halogen is moved to the second area of coordination by the reaction with the Lewis base. In all previously known complexes of this kind, both halogen atoms are displaced, resulting in dicationic complexes (Hensen *et al.*, 1997; Burger *et al.*, 1995; Fleischer *et al.*, 1996).

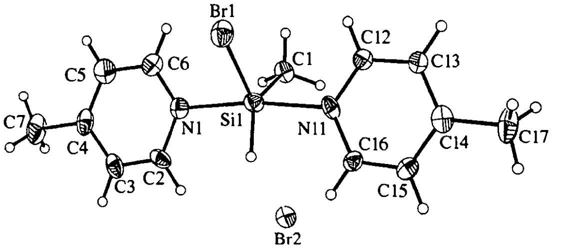


Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level.

The distances of the dative Si—N bonds in the complex are almost identical (Table 1). This corresponds well with other complexes containing pentacoordinated silicon. The geometry is a distorted trigonal bipyramid common to pentacoordinated Si complexes (Hensen, Zengerly *et al.*, 1988). The N1—Si1—N11 angle is 171.3 (1)°, whereas the H1—Si1—C1, H1—Si1—Br1 and C1—Si1—Br1 angles are 134 (1), 113 (1) and 113.4 (1)°, respectively. A least-squares plane through atoms Si1, H1, C1 and Br1 (r.m.s. deviation = 0.002 Å) encloses an angle of 89.5 (2)° with the plane of the pyridine ring formed by atoms N1 and C2–C6, and an angle of 87.9 (2)° with the plane of the pyridine ring formed by atoms N11 and C12–C16. The planes of the two pyridine rings are almost coplanar [dihedral angle 1.75 (5)°].

Experimental

To a solution of dibromomethylsilane (5.16 mmol) in hexane (25 ml), 3.5 equivalents of 4-methylpyridine were added dropwise under an atmosphere of dry argon. The mixture was stirred for 2 h at room temperature. The solvent was removed by filtration and the precipitate was dried *in vacuo*. Colourless moisture-sensitive single crystals of the title compound were obtained by sublimation *in vacuo*.

Crystal data

$C_{13}H_{18}BrN_2Si^+.Br^-$
$M_r = 390.20$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Orthorhombic
$P2_12_12_1$
$a = 9.3972\,(1)$ Å
$b = 12.3917\,(1)$ Å
$c = 13.7857\,(2)$ Å
$V = 1605.31\,(3)$ Å^3
$Z = 4$
$D_x = 1.615$ Mg m^{-3}
D_m not measured

Cell parameters from 5772 reflections
$\theta = 1\text{–}25°$
$\mu = 5.111$ mm^{-1}
$T = 173$ K
Block
0.30 × 0.10 × 0.10 mm
Colourless, transparent

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996*a*)
$T_{\min} = 0.383$, $T_{\max} = 0.600$
17 926 measured reflections
2950 independent reflections

2576 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.055$
$\theta_{\max} = 26.02°$
$h = -11 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$
305 standard reflections frequency: 840 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.043$
$S = 1.001$
2950 reflections
169 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0135P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.266$ e Å^{-3}
$\Delta\rho_{\min} = -0.399$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.003 (8)

Table 1. *Selected geometric parameters (Å, °)*

Si1—H1	1.37 (3)	Si1—N11	2.021 (2)
Si1—C1	1.870 (3)	Si1—Br1	2.2797 (9)
Si1—N1	2.018 (3)		
H1—Si1—C1	133.6 (11)	N1—Si1—N11	171.27 (11)
H1—Si1—N1	85.7 (11)	H1—Si1—Br1	112.9 (11)
C1—Si1—N1	92.81 (12)	C1—Si1—Br1	113.44 (10)
H1—Si1—N11	85.6 (11)	N1—Si1—Br1	92.35 (8)
C1—Si1—N11	93.35 (12)	N11—Si1—Br1	90.87 (8)

The data collection nominally covered a sphere of reciprocal space, by a combination of eight sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 6.0 cm. Coverage of the unique set was over 99% complete to at least 25° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. All H atoms could be located by difference Fourier synthesis. Whereas the H atom bonded to silicon was refined isotropically, the others were refined with fixed individual displacement parameters [$U(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$ or $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$] using a riding model with C—H$_{\text{methyl}}$ = 0.98 or C—H$_{\text{aromatic}}$ = 0.95 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: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996*b*). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1258). Services for accessing these data are described at the back of the journal.

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1,10-Phenanthrolin-1-ium Chloride Bis(1,10-phenanthroline) Solvate at 143 K

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Abstract

The crystal and molecular structure of the title compound, $C_{12}H_9N_2^+.Cl^-.2C_{12}H_8N_2$, has been determined at 143 K. It consists of three phenanthroline units and one