Crystal data

$C_{11}H_{10}O$
$M_r = 158.19$
Monoclinic
$P2_1/c$
$a = 17.104\,(1)$ Å
$b = 6.012\,(1)$ Å
$c = 8.110\,(1)$ Å
$\beta = 95.46\,(1)°$
$V = 830.16\,(18)$ Å^3
$Z = 4$
$D_x = 1.266$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8192 reflections
$\theta = 1–25°$
$\mu = 0.080$ mm^{-1}
$T = 173\,(2)$ K
Plate
0.80 × 0.65 × 0.20 mm
Colourless

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: *SADABS* (Sheldrick, 1996)
$T_{\min} = 0.939$, $T_{\max} = 0.984$
15 038 measured reflections
2075 independent reflections
1734 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.018$
$\theta_{\max} = 28.95°$
$h = -22 \rightarrow 22$
$k = -7 \rightarrow 8$
$l = -10 \rightarrow 10$
1310 standard reflections frequency: 1320 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.112$
$S = 1.072$
2075 reflections
109 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 0.1403P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.266$ e Å^{-3}
$\Delta\rho_{\min} = -0.212$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C2—O2	1.3749 (11)	O2—C21	1.4250 (14)
O2—C2—C1	125.18 (9)	C1—C2—C3	120.80 (9)
O2—C2—C3	114.01 (8)	C2—O2—C21	117.22 (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 5.8 cm. Coverage of the unique set is complete to at least 26° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [$U({\rm H}) = 1.5U_{\rm eq}({\rm C_{methyl}})$ or $U({\rm H}) = 1.2U_{\rm eq}({\rm C})$], using a riding model with C—H(methyl) = 0.98 or C—H(aromatic) = 0.95 Å.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *PLUTON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1220). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1863–1865

Bromo(ethyl)hydridobis(3,4-dimethylpyridine-*N*)silicon Bromide at 173 K

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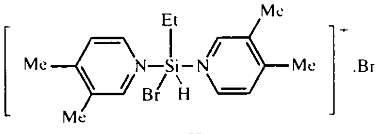
Abstract

In aprotic solvents, dibromoethylsilane ($\rm HSiEtBr_2$) and 3,4-dimethylpyridine form a stable 1:2 crystalline complex. X-ray structure analysis reveals an $\rm [HSiEtBr(3,4\text{-dimethylpyridine})_2]^+$ ($\rm C_{16}H_{24}BrN_2Si^+.Br^-$) complex, with one $\rm Br^-$ ion in the outer coordination sphere. The ligands bound directly to the Si centre exhibit almost trigonal-bipyramidal geometry. The geometry of the title compound compares well with that of bromo(hydrido)methylbis(4-methylpyridine-*N*)silicon bromide.

Comment

Recently, we described the X-ray analysis of the complex $[HSiMeBr(4\text{-methylpyridine})_2]^+.Br^-$, (I) (Hensen *et al.*, 1998). This was the first such complex in which only one of the halogen atoms was removed from the primary coordination sphere of Si as a result of the reaction with a Lewis base. In all previously known dihalogenalkylamine complexes, both halogens had always been displaced, resulting in dicationic complexes (Hensen *et al.*, 1997; Burger *et al.*, 1995; Fleischer *et al.*, 1996). The complex described in this paper, $[HSiEtBr(3,4\text{-dimethylpyridine})_2]^+.Br^-$, (II), is a second example of a monocationic product.



(II)

The title compound contains a pentacoordinate Si atom (Fig. 1), with only one of the two halogen atoms having been displaced from the primary coordination sphere around Si by the reaction of dibromoethylsilane with 3,4-methylpyridine. The distance between the Si atom and the displaced Br2 ion is shorter [3.747 (1) Å] than in other cationic halogenosilane base complexes, and lies just within the sum of the van der Waals radii of Si and Br (3.8 Å; Bondi, 1964).

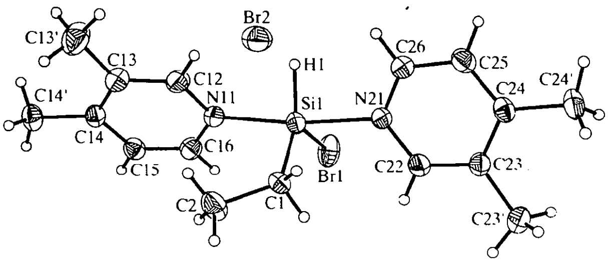


Fig. 1. Perspective view of the title complex, (II), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Although the lengths of the two dative Si—N bonds correspond closely with those found in other complexes containing pentacoordinate Si, they show a slight but significant difference (see Table 1). The geometry about Si can be described as distorted trigonal bipyramidal, in common with previously known pentacoordinate Si complexes (Hensen *et al.*, 1988). The N11—Si1—N21 angle [172.6 (1)°] is significantly non-linear. At first sight it might seem astonishing that the H1—Si1—C1 angle is larger than the angles at Si involving Br1, but this can be explained by taking the steric influence of Br2 into account. This atom deviates by only 0.36 (3) Å from the plane of Si1, H1, C1 and Br1, and the line Si1–Br2 intersects the H1—Si1—C1 angle. These geometric parameters are in good agreement with those of the previously determined structure of (I), but there are some significant differences between these two structures: whereas both aromatic rings in (I) are nearly coplanar [dihedral angle 1.75 (5)°], the dihedral angle between the aromatic rings in the title compound is 33.8 (2)°. This difference can also be expressed by the dihedral angles formed by the least-squares mean plane through Si1, H1, C1 and Br1 (r.m.s. deviation 0.02 Å) and the two aromatic rings. Whereas the N21-containing ring encloses an angle of 87.2 (2)° with the plane through Si1, H1, C1 and Br1, the N11-containing ring forms a smaller angle with that plane [81.7 (2)°]. In (I), these two angles differ by only 1.6°. We attribute these geometric differences to the exchange of the methyl group in (I) by the more sterically demanding ethyl group in (II). A least-squares fit (r.m.s. deviation of fitted atoms = 0.045 Å) of (I) and (II) is shown in Fig. 2.

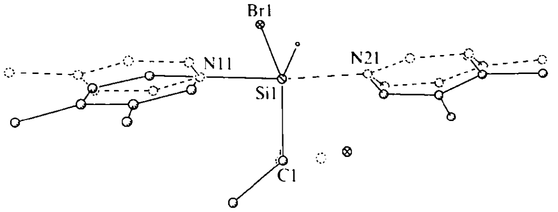


Fig. 2. Least-squares fit of (I) (dashed lines) with (II) (solid bonds and atoms); only the fitted atoms are labelled.

Experimental

To a solution of dibromoethylsilane (5.40 mmol) in hexane (20 ml), 3,4-dimethylpyridine (2.5 equivalents) was 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 dried *in vacuo*. Moisture-sensitive single crystals of the title compound were obtained by sublimation *in vacuo*. Elemental analysis: $C_{16}H_{24}Br_2N_2Si$ requires C 44.5, H 5.6, N 6.5, Br 37.0%; found C 45.6, H 5.7, N 6.8, Br 35.8%. ^1H NMR (270 MHz, $CDCl_3$, TMS): δ = 0.89 (*t*, 3H), 1.33 (*q*, 2H), 2.26 (*s*, 12H), 5.68 (*s*, 1H), 7.20 (*d*, 2H), 8.50 (*m*, 4H). ^{29}Si NMR (400 MHz, $CDCl_3$, TMS): $\delta = -53.92$, $^1J(^{29}Si-^1H) = 317.3$ Hz.

Crystal data

$C_{16}H_{24}BrN_2Si^+.Br^-$
$M_r = 432.28$
Monoclinic
$C2/c$
$a = 33.756\ (2)$ Å
$b = 7.3910\ (4)$ Å
$c = 17.087\ (1)$ Å
$\beta = 118.420\ (1)°$
$V = 3749.3\ (4)$ Å^3
$Z = 8$
$D_x = 1.532$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 6224 reflections
$\theta = 1–25°$
$\mu = 4.384$ mm^{-1}
$T = 173$ K
Block
0.3 × 0.2 × 0.2 mm
Colourless

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.262$, $T_{\max} = 0.416$
25 065 measured reflections
3781 independent reflections
2809 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.062$
$\theta_{\max} = 26.39°$
$h = -42 \rightarrow 41$
$k = -9 \rightarrow 9$
$l = -21 \rightarrow 20$
283 standard reflections
frequency: 20 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.082$
$S = 1.052$
3781 reflections
198 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0303P)^2 + 8.9146P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.451$ e Å^{-3}
$\Delta\rho_{\min} = -0.523$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Si1—H1	1.39 (3)	Si1—N21	2.043 (3)
Si1—C1	1.868 (3)	Si1—Br1	2.2722 (10)
Si1—N11	2.011 (3)		
H1—Si1—C1	132.2 (11)	N11—Si1—N21	172.64 (12)
H1—Si1—N11	86.1 (11)	H1—Si1—Br1	112.0 (11)
C1—Si1—N11	95.34 (14)	C1—Si1—Br1	115.60 (12)
H1—Si1—N21	86.5 (11)	N11—Si1—Br1	93.27 (9)
C1—Si1—N21	89.21 (13)	N21—Si1—Br1	89.96 (9)

The data collection nominally covered a sphere of reciprocal space by a combination of seven 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. The absence of crystal decay was established 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 Si was refined isotropically, the others were refined using a riding model with C—H(methylene) = 0.99, C—H(methyl) = 0.98 or C—H(aromatic) = 0.95 Å, and $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where $x = 1.5$ for methyl H atoms and $x = 1.2$ for others. The methyl groups attached to the aromatic rings 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*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991).

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2,3-Dihydronaphto[2,3-*b*][1,4]dioxine

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Abstract

In the title compound, $C_{12}H_{10}O_2$, the molecules are stacked and form layers parallel to the (101) planes. Each molecule consists of three six-membered rings which are not strictly coplanar. The dioxine ring adopts a half-chair conformation with an angle of 55.2 (4)° between the (O1, C12, C11) and (C12, C11, O2) planes. The crystal arrangement is stabilized by van der Waals forces.

Commentaire

Au cours de nos recherches sur les polyéthers cycliques, nous avons été amenés à réaliser la synthèse de la 2,3-dihydronaphto[2,3-*b*]-1,4-dioxine (I). La dioxine (I) a été précédemment obtenue par Heertjes (Heertjes *et al.*, 1954). Dans notre laboratoire, nous l'avons préparée selon la synthèse de Williamson (Pedersen, 1967). L'arrangement cristallin du composé (I) est

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1278). Services for accessing these data are described at the back of the journal.

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