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Halogen exchange and expulsion: ligand stabilized dihalogen silicon dications

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The first ligand stabilized $SiCl_2^{2+}$ dications were synthesized using *N*-methylimidazole as co-ordinating ligand. The compounds $SiCl_4$, $SiBr_2Cl_2$, and SiH_2Cl_2 form six-co-ordinated dicationic compounds of almost octahedral symmetry with similar structures which were investigated by single crystal X-ray analysis and density functional calculations. The structures exhibit particularly short dative Si–N bonds of about 1.90 Å. Complexes crystallized from the same solvent are isostructural. A different solvent, though, leads to geometrical variations. It was also discovered that the halogen exchange process among mixed silicon tetrahalides occurs under much milder conditions than previously thought and proceeds with considerable speed even without a catalyst.

Introduction

The extension of silicon's co-ordination sphere in compounds formed from silicon halides and organic nitrogen bases has been of scientific interest over a long period of time.[1–10] Neutral adducts as well as cationic complexes have been characterized. Most known ionic complexes contain charge stabilizing alkyl ligands bound to the silicon centre. Only recently, the first ligand stabilized SiH_2^{2+} dications were found.[11,12] Silylium ions have played an important part in recent research efforts in the area of silicon chemistry.[13–16] Here, the importance of alkyl substituents as a charge stabilizing factor was underscored. Cationic bipyridine complexes of silicon halides have been characterized spectroscopically.[17] In this work we have investigated the formation of ionic compounds from silicon tetrahalides by using the unidentate ligand *N*-methylimidazole (NMI). To study the effects of different halides as leaving groups we decided upon $SiCl_4$ as well as $SiBr_2Cl_2$ as starting materials. By using the mixed silicon halide $SiBr_2Cl_2$, halogen exchange processes had to be taken into account: silicon halides are known to exchange ligands at high temperatures and pressures,[18] and it has been postulated that pyridine or comparable co-ordinating ligands catalyse halogen exchange reactions on silicon halides by loosening the silicon–halogen bonds.[19] This, however, implies that apart from the Lewis acid–base reaction a simultaneous base catalysed dismutation of the mixed halide could lead to a mixture of co-ordination compounds. Ligand exchange in various silicon halides has been the subject of several investigations.[20–23] Also, mixtures of products have previously been observed when silicon halides are treated with amines.[24,25] Base catalysed halogen exchange in silicon tetrahalides has been studied extensively by gas chromatography. This led to the conclusion that the dismutation of silicon bromide chlorides which occurs readily at high temperatures (700 °C) requires the presence of a catalyst to proceed at or somewhat above room temperature (50 °C) as it is kinetically impaired at these lower temperatures.[3,20] Nevertheless, on the basis of NMR experiments, equilibration reactions in the absence of a catalyst at lower temperatures have been reported for mixed trihalogen silanes.[26]

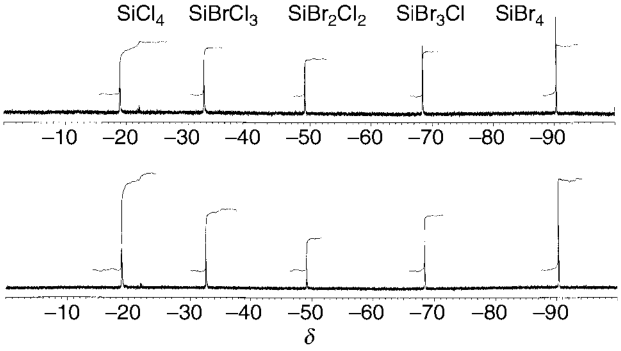

Fig. 1 The ^{29}Si NMR spectra (79.49 MHz) of a 40 h old mixture of $SiCl_4$ and $SiBr_4$ in $CDCl_3$ at 25 °C (below) and of the same sample (above) 53 h later under the same conditions. The sealed NMR tube was kept at 25 °C at all times.

Results and discussion

Halogen exchange reactions

To synthesize $SiBr_2Cl_2$, equal amounts of $SiCl_4$ and $SiBr_4$ were allowed to equilibrate to yield a mixture of $SiCl_4$, $SiBrCl_3$, $SiBr_2Cl_2$, $SiBr_3Cl$, and $SiBr_4$. Contrary to previously published results,[18,20] we found that this reaction requires neither high temperatures nor the presence of a catalyst but proceeds close to the equilibrium values at room temperature within one week as characterized by ^{29}Si NMR experiments (Fig. 1). Separation of the various silicon halides by repeated fractional distillation was possible, as shown by ^{29}Si spectra.[27] Further to explore this matter, we have kept pure samples of these mixed silicon halides at room temperature. Subsequent ^{29}Si measurements revealed observable dismutation within hours and the equilibrium was nearly reached after a few weeks. The absence of catalytic amounts of any co-ordinating base was ensured using no other chemicals than freshly distilled $SiCl_4$ and $SiBr_4$ in the synthesis of the other silicon halides as well as by ^1H NMR experiments. No dismutation was detected after long-time storage (>6 months) at temperatures below the respective melting points.

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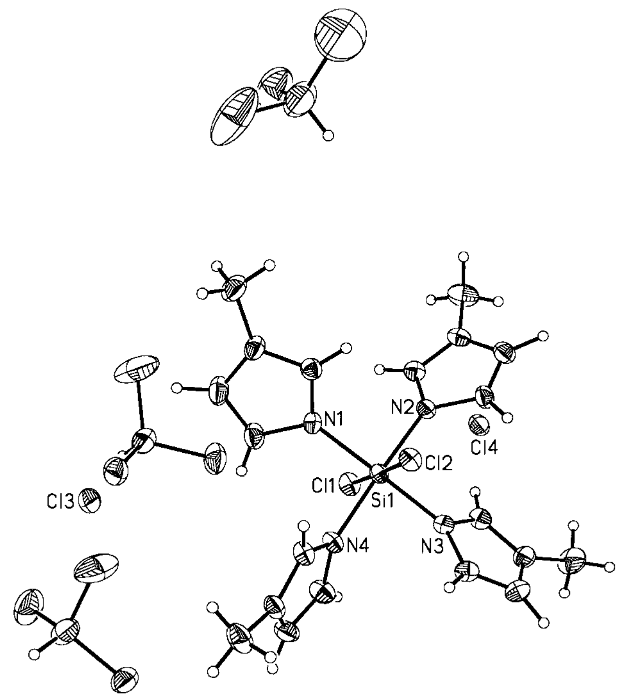

Fig. 2 An ORTEP[28] diagram of compound **1**. Displacement ellipsoids are at the 50% probability level in all the crystal structures.

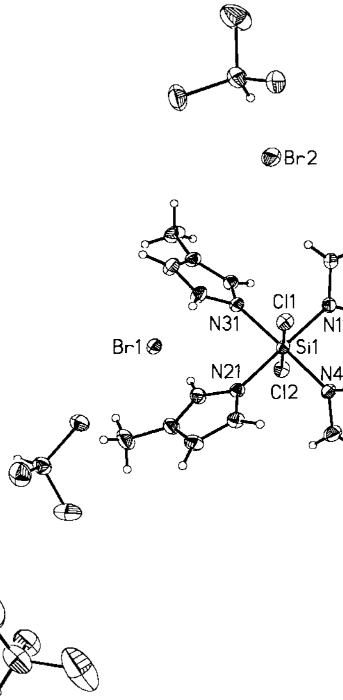

Fig. 3 An ORTEP diagram of compound **2a**.

Table 1 Selected bond lengths [Å] for compounds **1**–**3**

	1	**2a**	**2b**	**3**
Si–N1	1.894(3)	1.889(2)	1.901(4)	1.926(3)
Si–N2	1.890(3)	1.900(2)	1.927(4)	
Si–N3	1.876(3)	1.901(2)		1.922(3)
Si–N4	1.893(3)	1.904(2)		
Si–Cl1	2.184(1)	2.207(1)	2.184(1)	
Si–Cl2	2.191(1)	2.205(1)		
Si–H				1.56(4)

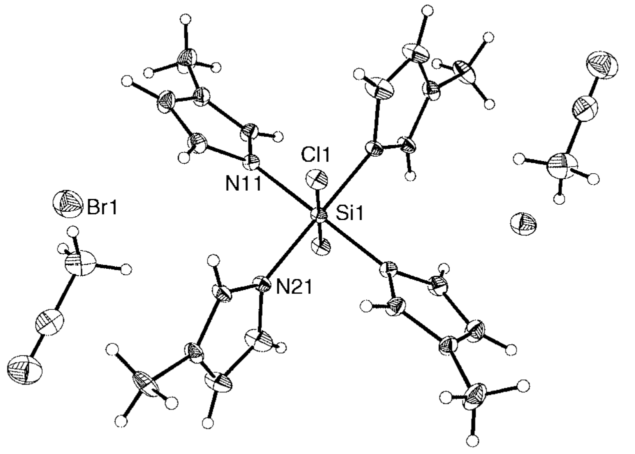

Fig. 4 An ORTEP diagram of compound **2b**.

$$SiCl_4 + NMI \xrightarrow{\text{hexane, 25 °C}} SiCl_4{\cdot}6NMI \xrightarrow{CHCl_3,\ NMI} \mathbf{1}$$

Scheme 1

The first $SiCl_2^{2+}$ dications

The reaction of *N*-methylimidazole (NMI) with silicon tetrachloride yields $[SiCl_2(NMI)_4]Cl_2{\cdot}3CHCl_3$ **1** according to Scheme 1. The structure of compound **1** was determined by single crystal X-ray analysis. It shows a six-co-ordinated silicon centre, surrounded by four nitrogen and two chlorine atoms with a virtually octahedral geometry. The maximum deviation from ideal octahedron angles is 2.1° (Fig. 2). Compound **1** represents the first known structure of a ligand stabilized dihalogen silicon dication. The crystal structure is stabilized by hydrogen bonds from three chloroform molecules. If the compound is prepared in hexane this stabilization is apparently achieved by incorporating two NMI molecules, which explains the existence of the intermediate $SiCl_4{\cdot}6NMI$ in Scheme 1. The compound $[SiCl_2(NMI)_4]Br_2{\cdot}3CHCl_3$ **2a** results from the reaction of NMI with silicon dibromide dichloride. It is isostructural to **1** and represents the first known structure derived from a mixed silicon tetrahalide (Fig. 3). The Si···Cl distances to the outer chlorine atoms in **1** are 5.038 and 5.710 Å; Si···Br distances in **2a** are 5.157 and 5.668 Å. These are significantly longer than the sum of the van der Waals radii of the involved atoms which are 3.80 and 3.68 Å respectively.[29] Further important bond lengths are listed in Table 1. The ionic character of the compounds is thereby confirmed. The different anions apparently do not affect the geometry of the complexes, and they also do not have differing effects on the positioning of the molecules within the crystal.

In both structures the anions are stabilized by short H···Cl or H···Br distances (<3Å) to $CHCl_3$ and NMI. Notably, the two anions in each structure are in a different environment: one is surrounded by hydrogen atoms of NMI only, the other by two hydrogen atoms of $CHCl_3$ and two of NMI.

Differing molecular geometry in another solvent

When $SiBr_2Cl_2$ was allowed to react with NMI in acetonitrile we were able to isolate a few small crystals of $[SiCl_2(NMI)_4]Br_2{\cdot}2CH_3CN$ **2b** (Fig. 4) that were extraordinarily susceptible to hydrolysis, along with much $SiBr_2Cl_2{\cdot}4NMI$. Even though the geometry of the first co-ordination sphere of silicon in **2b** is mostly identical with that of **2a**, the different solvents not only cause a varying arrangement of the molecules within the crystal but also lead to a different orientation of the NMI rings within the molecules. This is clearly shown in Fig. 5, where $[SiCl_2(NMI)_4]^{2+}$ from **2a** and **2b** are projected over each other. The bromide ions in **2b** are close to one hydrogen atom of CH_3CN as well as to three more hydrogen atoms of NMI.

Further experiments

The reaction of dichlorosilane with NMI yields $[SiH_2(NMI)_4]$-

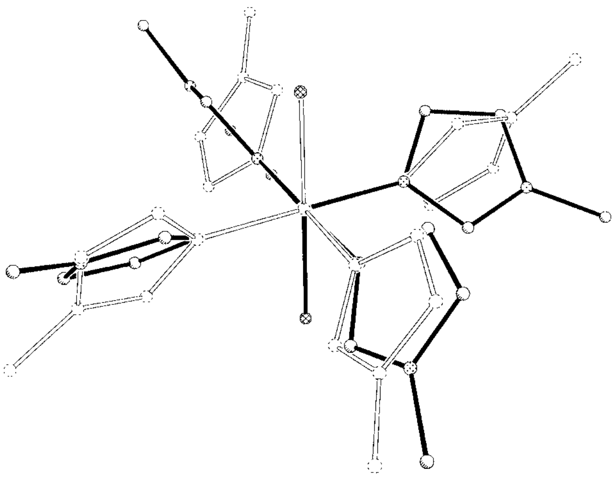

Fig. 5 The dications of $[SiCl_2(NMI)_4]Br_2{\cdot}3CHCl_3$ (dark bonds) and of $[SiCl_2(NMI)_4]Br_2{\cdot}2CH_3CN$ (clear bonds).

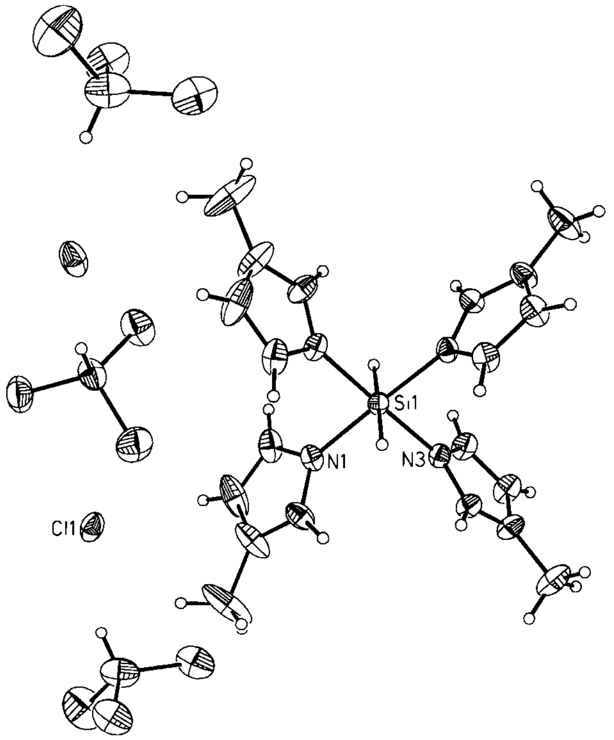

Fig. 6 An ORTEP diagram of compound **3**.

$$SiH_2Cl_2 + NMI \xrightarrow{\text{hexane, } -78\,^{\circ}\text{C}} SiH_2Cl_2{\cdot}5NMI \xrightarrow{CHCl_3,\ NMI} \mathbf{3}$$

Scheme 2

$Cl_2{\cdot}3CHCl_3$ **3** (Fig. 6) according to Scheme 2. The ^1H NMR spectra of **2a** and **2b** show NMI signals that differ significantly in chemical shift from those of non-co-ordinated NMI, indicating that the six-co-ordinated silicon dications known from the solid state structures also exist in chloroform solution. Proton 2 of the free NMI ring exhibits a chemical shift of δ 7.41 that appears at δ 9.51 when bound in the complex. The signal intensities in the spectrum of **3** show a SiH_2^{2+}:NMI ratio of 1:4, further supporting this conclusion. The low solubility of the complexes did not allow heteronuclear NMR experiments in solution.

Density functional calculations

By geometry optimization of $[SiX_2(Him)_4]^{2+}$ (C_{2h}, X = H or Cl, Him = imidazole) using density functional methods (B3LYP/6-31G(d)),[30,31] we have investigated the structures of the isolated dications and compared them to those obtained from the crystal structures. Singlet as well as triplet states of $SiCl_2^{2+}$ were investigated. The former (linear, $D_{\infty h}$, Si–Cl 1.91 Å) proved to be of lower energy than the latter (bent, C_{2v}, Si–Cl 2.06 Å). The Si–N bonds of the isolated species ($[SiH_2(Him)_4]^{2+}$, 1.981; $[SiCl_2(Him)_4]^{2+}$, 1.982 Å) are nearly equal, *i.e.* H and Cl have about the same impact. The calculated Si–N bonds are longer than those in the crystal, a common observation with dative bonds.[12,32] The Si–Cl bond in $[SiCl_2(Him)_4]^{2+}$ (2.182 Å), however, is close to the experimental results for **1**, but significantly longer than in $SiCl_2^{2+}$.

Table 2 B3LYP/6-31G* Geometry of the $[SiH_2(Him)_4]^{2+}$ and the $[SiCl_2(Him)_4]^{2+}$ complex, compared to isolated imidazole. Bond lengths in Å, angles in °

	$[SiH_2(Him)_4]^{2+}$	$[SiCl_2(Him)_4]^{2+}$	Him
N1–C2	1.3324	1.3419	1.3147
C2–N3	1.3451	1.3392	1.3675
N3–C4	1.3800	1.3793	1.3809
C4–C5	1.3659	1.3620	1.3726
C5–N1	1.3862	1.3966	1.3783
Si–N	1.9812	1.9816	
C2–N1–C5	106.99	106.26	105.23
N3–C2–N1	109.59	109.74	111.78
C4–N3–C2	108.85	109.17	107.15
C5–C4–N3	105.74	105.83	105.02
N1–C5–C4	108.84	108.99	110.82

Comparing the geometrical parameters of imidazole and $[SiH_2(Him)_4]^{2+}$, it is evident that complexation does not have much impact on the structure of the imidazole molecule (Table 2). Imidazole behaves thus similarly to pyridine, whose structure is not changed much by complexation of $[SiH_2]^{2+}$.[12] The Si–N bond in $[SiH_2(Him)_4]^{2+}$ is slightly shorter than in $[SiH_2(py)_4]^{2+}$ (2.0165 Å). Thermochemical calculations show that the formation of $[SiH_2(Him)_4]^{2+}$ is of course endothermic and endergonic ($\Delta H = +918.1$ kJ mol^{-1}, $\Delta G = +1051.6$ kJ mol^{-1}), but by much less than the formation of $[SiH_2(py)_4]^{2+}$ ($\Delta H = +1028.9$ kJ mol^{-1}, $\Delta G = +1163.2$ kJ mol^{-1}).[12] These results reflect the experimentally found enhanced complexation ability/Lewis basicity of NMI compared to pyridine and its methyl derivatives. This may give an explanation as to why NMI forms ionic complexes whereas pyridine simply yields $SiCl_4{\cdot}2py$.

Conclusion

The nitrogen ligand *N*-methylimidazole stabilizes $SiCl_2^{2+}$ by formation of $[SiCl_2(NMI)_4]^{2+}$. The solid state structures of these complexes are virtually independent of the nature of the anions investigated yet susceptible to the nature of solvent molecules that are incorporated into the crystal structure. The complexes also exist in solution. The compounds $SiBrCl_3$, $SiBr_2Cl_2$, and $SiBr_3Cl$ are thermodynamically and kinetically unstable at room temperature with respect to dismutation reactions, as is a mixture of $SiBr_4$ and $SiCl_4$ with respect to comproportionation.

Experimental

General remarks

Silicon halides as well as the complexes derived from these compounds are highly susceptible to hydrolysis. Therefore, all operations were carried out under an inert atmosphere of nitrogen or argon gas in carefully dried vessels.

Preparations

$SiBr_2Cl_2$. This compound was prepared by equilibrating $SiBr_4$ (125.5 ml, 1 mol) and $SiCl_4$ (114.6 ml, 1 mol) as they were stirred for 3 d at room temperature with no solvent. The

$SiBr_2Cl_2$ was then separated by repeated fractional distillation at ambient pressure (bp 103–106 °C), immediately frozen, and stored in evacuated glass vials at −75 °C to protect the substance from dismutation. It was identified by ^{29}Si NMR (79.49 MHz, $CDCl_3$, −20 °C, TMS): δ −49.94 (s); lit.[25] (11.92 MHz, C_6F_6, TMS) δ −50.7. Percentage yield 16.0% from an equilibrium content of 31.6% $SiBr_2Cl_2$ as determined by NMR. Total yield 5.1%.

$[SiCl_2(NMI)_4]Cl_2{\cdot}3CHCl_3$ 1. *N*-Methylimidazole (4.80 ml, 60.0 mmol) was added dropwise to silicon tetrachloride (1.15 ml, 15.0 mmol; dissolved in 50 ml *n*-hexane). A white precipitate, $SiCl_4{\cdot}6NMI$, was isolated. Quantitative yield. Calc. for $C_{24}H_{36}Cl_4N_{12}Si$: C, 43.5; H, 5.4; Cl, 21.4; N, 25.4. Found: C, 43.3; H, 5.6; Cl, 20.6; N, 25.6%. The compound $SiCl_4{\cdot}6NMI$ (100 mg, 0.151 mmol) was dissolved in 5 ml chloroform and a few drops of NMI then cooled to 4 °C. Crystals of **1** grew within 4–5 d. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS): δ 3.88 (s, 12 H, NCH_3), 6.90 (s, 4 H, H^5), 7.16 (s, 4 H, H^4) and 8.94 (s, 4 H, H^2).

$[SiCl_2(NMI)_4]Br_2{\cdot}3CHCl_3$ 2a and $[SiCl_2(NMI)_4]Br_2{\cdot}2CH_3CN$ 2b. *N*-Methylimidazole (1.8 ml, 22.6 mmol) was added dropwise to 5 mmol (129.4 g) $SiBr_2Cl_2$ in 25 ml solvent. In $CHCl_3$ crystals of compound **2a** grew after 12 h at room temperature. In CH_3CN the same conditions led to only very few crystals of **2b** together with much $SiBr_2Cl_2{\cdot}4NMI$. Quantitative yield. Calc. for $SiCl_2Br_2{\cdot}4NMI$, $C_{16}H_{24}Br_2Cl_2N_8Si$: C, 32.7; H, 4.1; Br, 27.2; Cl, 12.1; N, 19.1. Found: C, 32.1; H, 4.3; Br, 25.9; Cl, 11.5; N, 18.7%. ^{1}H NMR of $SiBr_2Cl_2{\cdot}4NMI$ (250 MHz, $CDCl_3$, 25 °C, TMS): δ 4.03 (s, 12 H, NCH_3), 7.07 (s, 4 H, H^5), 7.31 (s, 4 H, H^4) and 9.51 (s, 4 H, H^2).

$[SiH_2(NMI)_4]Cl_2{\cdot}3CHCl_3$ 3. *N*-Methylimidazole (2.40 ml, 30 mmol) was added to a solution of dichlorosilane (1.0 ml, 15.0 mmol) in 50 ml *n*-hexane at −78 °C. The compound $SiH_2Cl_2{\cdot}5\,NMI$ was filtered off, washed, and dried. Quantitative yield. Calc. for $C_{20}H_{32}Cl_2N_{10}Si$: C, 47.0; H, 6.3; Cl, 13.9; N, 27.4. Found: C, 46.8; H, 6.5; Cl, 13.5; N, 27.2%. It (100 mg, 0.196 mmol) was then dissolved in 5 ml chloroform and an excess of NMI. The solution was cooled to 4 °C and crystals of **3** appeared within 4 d. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS): δ 3.27 (s, 12 H, NCH_3), 6.54 (s, 4 H, H^5), 6.69 (s, 4 H, H^4), 8.69 (s, 4 H, H^2) and 5.23 (s, 2 H, H_2Si).

X-Ray crystallographic studies

Crystal data. **1**, $C_{19}H_{27}Cl_{13}N_8Si$, $M = 856.43$, triclinic, space group $P\bar{1}$, $a = 9.568(1)$, $b = 12.333(1)$, $c = 15.507(2)$ Å, $\alpha = 91.70(1)$, $\beta = 95.32(1)$, $\gamma = 100.31(1)°$, $Z = 2$, $V = 1790.6(3)$ Å^3, $\mu = 1.063$ mm^{-1}, $T = 150$ K, reflections 5942 measured, 5568 independent ($R_{int} = 0.023$), $R = 0.0618$, $wR2 = 0.1109$.

2a, $C_{19}H_{27}Br_2Cl_{11}N_8Si$, $M = 945.35$, triclinic, space group $P\bar{1}$, $a = 9.653(1)$, $b = 12.550(1)$, $c = 15.709(2)$ Å, $\alpha = 92.37(1)$, $\beta = 94.74(1)$, $\gamma = 99.17(1)°$, $Z = 2$, $V = 1869.4(3)$ Å^3, $\mu = 3.013$ mm^{-1}, $T = 173$ K, reflections 45112 measured, 11710 independent ($R_{int} = 0.025$), $R = 0.0526$, $wR2 = 0.0798$.

2b, $C_{20}H_{30}Br_2Cl_2N_{10}Si$, $M = 669.35$, monoclinic, space group $P2_1/c$, $a = 7.978(1)$, $b = 18.955(1)$, $c = 9.585(3)$ Å, $\beta = 100.39(1)$; $Z = 2$, $V = 1425.7(2)$ Å^3, $\mu = 3.102$ mm^{-1}, $T = 173$ K, reflections 22781 measured, 3278 independent ($R_{int} = 0.106$), $R = 0.102$, $wR2 = 0.146$.

3, $C_{19}H_{29}Cl_{11}N_8Si$, $M = 787.54$, orthorhombic, space group $Pbcn$, $a = 25.308(1)$, $b = 12.229(1)$, $c = 11.336(3)$ Å, $Z = 4$, $V = 3508.4(4)$ Å^3, $\mu = 0.930$ mm^{-1}, $T = 130$ K, reflections 3415 measured, 2874 independent ($R_{int} = 0.057$), $R = 0.081$, $wR2 = 0.140$.

CCDC reference number 186/1774.

See http://www.rsc.org/suppdata/dt/a9/a908134h/ for crystallographic files in .cif format.

Density functional calculations

All calculations were performed on the UNIX cluster of the Zentrum für Datenverarbeitung, Johannes Gutenberg Universität Mainz, using the GAUSSIAN 94 program package.[30] The geometries of SiX_2Cl_2 (C_{2v} and T_d), SiX_2^{2+} (D_∞), $[SiX_2(Him)_4]^{2+}$ (C_{2h}) (X = H or Cl), and imidazole (C_s) were, starting from standard bond lengths, angles, and dihedral angles, successively optimized with the following models: Hartree Fock (HF) level, using a full electron double zeta basis set including polarization functions (HF/3-21G*); Hartree Fock level, using an improved basis set of the double zeta plus polarization type (HF/6-31G*); density functional theory (DFT), employing a combination of local, gradient-corrected, and exact exchange functionals according to the prescription of Becke and the gradient-corrected correlation functional of Lee *et al.*[31] together with the improved basis set (B3LYP/6-31G*). All stationary points except for $[SiCl_2(Him)_4]^{2+}$ were characterized as true minima of the potential energy surface by vibrational frequencies derived from analytic second derivatives of the potential energy. Single point energy calculations of the geometries, representing stationary points on the potential energy surface, and thermochemical calculations followed the geometry optimizations. Only those geometries and thermochemical data resulting from the B3LYP/6-31G* model are given in the present paper.

Acknowledgements

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References

1 K. Hensen, T. Zengerly, P. Pickel and G. Klebe, *Angew. Chem.*, 1983, **95**, 739.

2 K. Hensen, T. Zengerly, P. Pickel and T. Müller, *Z. Anorg. Allg. Chem.*, 1988, **558**, 21.

3 O. Bechstein, B. Ziemer, D. Hass, S. I. Trojanov, V. B. Rybakov and G. N. Maso, *Z. Anorg. Allg. Chem.*, 1990, **582**, 211.

4 V. O. Atwood, D. A. Atwood, A. H. Cowley and S. Trofimenko, *Polyhedron*, 1992, **11**, 711.

5 C. Chuit, R. J. P. Corriu, C. Reye and J. C. Young, *Chem. Rev.*, 1993, **93**, 1371.

6 K. Hensen, F. Gebhardt and M. Bolte, *Z. Anorg. Allg. Chem.*, 1997, **623**, 633.

7 B. Pfrommer and R. Tacke, *Eur. J. Inorg. Chem.*, 1998, 415.

8 K. M. Kane, C. R. Lorenz, D. M. Heilman and F. R. Lemke, *Inorg. Chem.*, 1998, **37**, 669.

9 J. Belzner, U. Dehnert, H. Ihmels, M. Hübner, P. Müller and I. Usón, *Chem. Eur. J.*, 1998, **4**, 852.

10 J. Belzner, V. Ronneberger, D. Schär, C. Brönnecke, R. Herbst-Irmer and M. Noltemeyer, *J. Organomet. Chem.*, 1999, **577**, 330.

11 H. Fleischer, K. Hensen and T. Stumpf, *Chem. Ber.*, 1996, **129**, 765.

12 K. Hensen, T. Stumpf, M. Bolte, C. Näther and H. Fleischer, *J. Am. Chem. Soc.*, 1998, **120**, 10402.

13 J. Belzner, *Angew. Chem.*, 1997, **109**, 1331.

14 C. A. Reed, *Acc. Chem. Res.*, 1998, **31**, 325.

15 C. Maerker and P. v. Ragué Schleyer, in *The Chemistry of Organic Silicon Compounds*, eds. Z. Rappoport and Y. Apeloig, Wiley, New York, 1998, vol. 2, ch. 10, pp. 513–555.

16 P. D. Lickiss, in *The Chemistry of Organic Silicon Compounds*, eds. Z. Rappoport and Y. Apeloig, Wiley, New York, 1998, vol. 2, ch. 11, pp. 557–594.

17 D. Kummer and T. Seshadri, *Z. Anorg. Allg. Chem.*, 1977, **428**, 129.

18 G. S. Forbes and H. H. Anderson, *J. Am. Chem. Soc.*, 1944, **66**, 931.

19 U. Wannagat, R. Schwarz, H. Voss and K. G. Knauff, *Z. Anorg. Allg. Chem.*, 1954, **227**, 73.

20 D. Hass and O. Bechstein, *Z. Anorg. Allg. Chem.*, 1981, **483**, 140; D. Hass, O. Bechstein and M. Hentschel, *Z. Anorg. Allg. Chem.*, 1989, **576**, 131; O. Bechstein, M. Feist and D. Hass, *Z. Chem.*, 1989, **29**, 343; O. Bechstein and D. Hass, *Z. Anorg. Allg. Chem.*, 1991, **594**, 202.

21 A. R. Bassindale, J. C. Lau and P. G. Taylor, *J. Organomet. Chem*, 1995, **490**, 75.

22 U. Herzog, R. Richter, E. Brendler and G. Roewer, *J. Organomet. Chem.*, 1996, **507**, 221.

23 D. Kost, I. Kalikhman and M. Raban, *J. Am. Chem. Soc.*, 1995, **117**, 11512.

24 P. Boudjouk, S. D. Kloos, B.-K. Kim, M. Page and D. Thweatt, *J. Chem. Soc.*, *Dalton Trans.* 1998, 877.

25 H. J. Campbell-Ferguson and E. A. V. Ebsworth, *J. Chem. Soc. A*, 1966, 1508.

26 E. Hengge and F. Höfler, *Z. Naturforsch.*, *Teil A*, 1971, **26**, 768.

27 For ^{29}Si chemical shift data on the mixed halides of silicon, see: U. Niemann and H. C. Marsmann, *Z. Naturforsch.*, *Teil B*, 1975, **30**, 202.

28 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

29 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

30 GAUSSIAN 94, Revision E.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.

31 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

32 K. R. Leopold, M. Canagaratna and J. A. Phillips, *Acc. Chem. Res.*, 1997, **30**, 57; A. Haaland, *Angew. Chem.*, 1989, **101**, 1017.

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