Two different co-ordination modes of hydrazide ligands in silicon and germanium compounds †

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The compounds $SiCl_4$ and $GeCl_4$ reacted with $Me_2NNMeLi$ in hexane to form dichlorobis(trimethylhydrazido)-silane, $SiCl_2(NMeNMe_2)_2$ **1** and tetrakis(trimethylhydrazido)germane, $Ge(NMeNMe_2)_4$ **2** in 51 and 50% yield, respectively. The liquid **1** (m.p. 6 °C) and solid **2** (m.p. 73 °C) decompose at temperatures greater than 100 and 140 °C, respectively. Both compounds can be slowly vaporised at ambient temperature in high vacuum. They have been characterised by spectroscopic techniques including NMR (^1H, ^{13}C, ^{29}Si), IR, mass and high-resolution mass spectrometry. Evidence for higher co-ordination of the silicon atom occurs from the ^{29}Si chemical shift ($\delta -44.0$). The crystal structure of **1** shows the N_β atoms of the hydrazide ligands interacting with the silicon atom resulting in a 4 + 2 co-ordination, whereas no $N_\beta \cdots Ge$ interactions are detectable in the structure of **2**. While the geometry at the N_α atom in **1** is completely planar, that of the corresponding atom in **2** is slightly pyramidal. *Ab initio* calculations have been carried out for the model systems $SiCl_2(N_2H_3)_2$ **1a**, $GeCl_2(N_2H_3)_2$ **1b** (both C_{2v}), and $Si(N_2H_3)_4$ **2a** and $Ge(N_2H_3)_4$ **2b** (both S_4) up to the MP2/6-31G* level of theory. The results lead to the prediction that the germanium compound analogous to **1** should have $N_\beta \cdots Ge$ interactions which are even stronger than the $N_\beta \cdots Si$ ones in **1**.

Hydrazide derivatives of many transition-metal elements have been reported in the literature, mainly in the context of nitrogen fixation.[1] In almost all of these compounds the hydrazide ligands are bound to the metals in an η^2-type of co-ordination, *i.e.* they act as β-donor ligands.

Compared with the large number of such transition-metal hydrazides,[2] the number of main-group element hydrazides is small. Recent structural investigations for alkali-metal hydrazides[3,4] showed the variety of structural possibilities. Most of the known hydrazide species of p-block elements (except carbon) are silylated hydrazines,[5,6] which have been studied because of their interesting structural chemistry and their applications in synthesis. Hydrazide compounds of germanium are comparatively rare. In almost all cases known to date the geometry around the Si- and Ge-bonded nitrogen atoms in these classes of compounds is completely planar. Very recently, some gallium hydrazides have been prepared and tested as single-source precursors for thin films of GaN.[7] Homoleptic hydrazides of p-block elements are limited to a few phosphorus[8] and beryllium[9] hydrazides, and just two homoleptic hydrazides of silicon, $Si(NHNMe_2)_4$[10] and $Si(NHNEt_2)_4$[11] (and a few related heteroleptic derivatives[11]). However, almost nothing is known about the co-ordination type of the hydrazide ligands in these compounds, and co-ordination of the β-nitrogen atom has never been observed in these species.

Here we report two examples of hydrazide compounds of silicon and germanium, dichlorobis(trimethylhydrazido)silane **1** and tetrakis(trimethylhydrazido)germane **2**, which were prepared in the course of the search for volatile hydrazides and hydroxylamines and in order to explore the co-ordination properties of simple β-donor ligands towards main-group elements.

Results and Discussion

Silicon tetrachloride reacts in the presence of a four-fold molar quantity of a suspension of $Me_2NNMeLi$ in hexane at -20 °C to give solutions of $SiCl_2(NMeNMe_2)_2$ **1** and LiCl [equation (1)]. Despite this excess of lithium trimethylhydrazide applied

$$2 Me_2NNMeLi + SiCl_4 \longrightarrow$$
$$2 LiCl + SiCl_2(NMeNMe_2)_2 \quad (1)$$
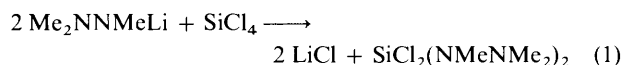
in the preparation, the doubly substituted species **2** is the dominant product. Carrying out the reaction at elevated temperatures does not lead to a different product distribution. The compound $Si(NMeNMe_2)_4$ can be found in traces, besides other products, and identified by high-resolution mass spectrometry of the raw product (Found: m/z 320.28368. Calc. for $C_{12}H_{36}N_8Si$: 320.28322). The liquid **1** (m.p. 6 °C) can be separated from the mixture by repeated crystallisation at low temperature yielding 51% of **1**. Attempts to distil the raw product mixture led to decomposition as indicated by gas evolution and growing complexity of ^1H NMR spectra. The pure compound shows decomposition at temperatures greater than 100 °C.

The analogous reaction with $GeCl_4$ carried out under similar conditions leads to a complete exchange of the chloro substituents resulting in the formation of $Ge(NMeNMe_2)_4$ **2** [equation (2)]. The reaction proceeds much more uniformly,

$$4 Me_2NNMeLi + GeCl_4 \longrightarrow$$
$$4 LiCl + Ge(NMeNMe_2)_4 \quad (2)$$
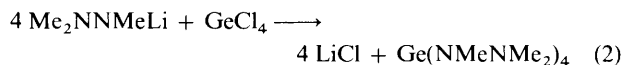
but after the purification procedures yields are also moderate (50%). Compound **2** is preferably isolated by crystallisation from hexane. Careful distillation (0.05 mbar, 80 °C) is possible, but **2** is thermally unstable (as is **1**) and some decomposition cannot be avoided. On heating above 140 °C **2** releases a rapid stream of nitrogen.

A possible explanation for the incomplete substitution of all four Cl substituents in $SiCl_4$ as compared with $GeCl_4$ may be seen in the lower covalent radius of Si. However, it should be noted that $Si(NHNMe_2)_4$ can be prepared[10] by complete substitution of chlorine in $SiCl_4$ using H_2NNMe_2 without need to use the lithium hydrazide.

The pure compounds **1** and **2** vaporise slowly at ambient temperature under a pressure of *ca.* 10^{-3} mbar. They are sensitive to moisture being hydrolysed to give the corresponding trimethylhydrazine.

The ^{1}H NMR spectrum of each of compounds **1** and **2** shows two singlets with their integrals being 1:2, as expected for a N(CH$_3$)N(CH$_3$)$_2$ group. The resonances for the N$_\beta$-CH$_3$ protons appear at δ 2.26 for **1** and 2.52 for **2**, those of the N$_\alpha$-CH$_3$ groups at δ 2.46 for **1** and 2.76 for **2**, *i.e.* there is about 0.3 ppm difference in both cases. The ^{13}C NMR chemical shifts for the carbon atoms bound to N$_\beta$ in **1** and **2** are very similar (δ 42.9 and 43.4, respectively) but differ by 3.4 ppm for the carbon atoms attached to N$_\alpha$ (**1**, δ 22.1; **2**, 25.5). The chemical shift of the ^{29}Si nucleus in **1** deserves some attention since the resonance is found at δ −44.0, a much lower frequency than the resonances for Si(NMe$_2$)$_4$ (δ −28.6) and SiCl$_4$ (δ −18.3). This value provides some evidence for higher co-ordination at the silicon atom in solution,[12] which could occur by inter- or intramolecular interactions with the N$_\beta$ atoms of the hydrazide ligands.

Crystal structures of compounds 1 and 2

A single crystal of compound **1** was produced by zone refinement of the polycrystalline material slightly below the melting temperature in an *in situ* experiment. X-Ray diffraction analysis of this crystal showed **1** to be present as monomeric molecules which possess no crystallographically imposed symmetry (Fig. 1). The Si–N bonds are as short as 1.666(5) and 1.672(4) Å (Table 1), which is probably caused by the electron-withdrawing properties of the chlorine substituents. Similar

short Si–N distances are also observed in the gas-phase structures of SiClH$_2$(NMe$_2$) [1.681(4) Å][13] and SiCl$_3$(NMe$_2$) [1.657(12) Å].[14] The most intriguing structural feature of **1** is the extreme deviation of the co-ordination sphere of silicon from a regular tetrahedral environment. The silicon atom is best described as 4 + 2 co-ordinated. The Si–N(10)–N(11) angle is
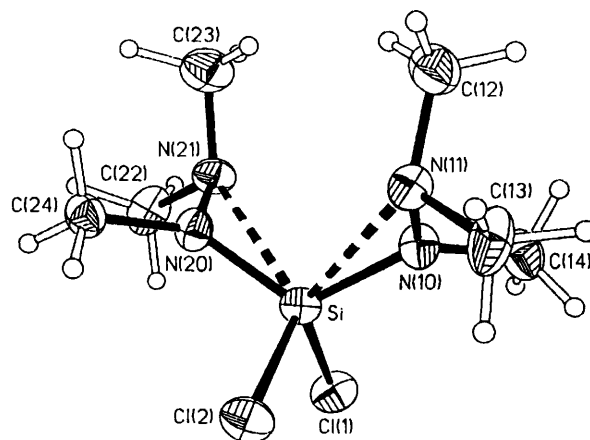

Fig. 1 Molecular structure of compound **1** showing the 4 + 2 co-ordination at the silicon atom

Table 1 Structural parameters (distances in Å, angles in °) for compounds **1** and **2**

	SiCl$_2$(NMeNMe$_2$)$_2$ **1**	Ge(NMeNMe$_2$)$_4$ **2**
E–N(10)	1.672(4)	1.834(2)
E–N(20)	1.666(5)	1.828(2)
Si–Cl(1)	2.057(2)	
Si–Cl(2)	2.069(2)	
N(10)–N(11)	1.438(5)	1.435(3)
N(10)–C(14)	1.449(6)	1.460(3)
N(11)–C(12)	1.457(6)	1.457(3)
N(11)–C(13)	1.477(6)	1.460(3)
N(20)–C(21)	1.440(5)	1.434(3)
N(20)–C(24)	1.468(6)	1.459(3)
N(21)–C(22)	1.473(6)	1.460(3)
N(21)–C(23)	1.448(7)	1.453(4)
N(20)–E–N(10)	118.9(2)	113.4(1)
N(10a)–Ge–N(10)		101.8(1)
N(10)–Ge–N(20a)		101.4(1)
Cl(1)–Si–Cl(2)	105.4(1)	
N(20)–Si–Cl(1)	111.3(2)	
N(10)–Si–Cl(1)	104.8(2)	
N(20)–Si–Cl(2)	104.3(2)	
N(10)–Si–Cl(2)	111.6(2)	
N(11)–N(10)–C(14)	119.6(4)	116.7(2)
N(11)–N(10)–E	107.7(3)	114.0(1)
C(14)–N(10)–E	131.8(4)	119.8(2)
N(10)–N(11)–C(12)	112.2(4)	110.3(2)
N(10)–N(11)–C(13)	110.7(4)	113.6(2)
C(12)–N(11)–C(13)	111.3(5)	111.3(2)
N(21)–N(20)–C(24)	118.2(4)	116.9(2)
N(21)–N(20)–E	109.6(3)	114.5(2)
C(24)–N(20)–E	132.2(4)	119.9(2)
N(20)–N(21)–C(23)	113.0(4)	113.5(2)
N(20)–N(21)–C(22)	111.1(4)	109.6(2)
C(23)–N(21)–C(22)	111.0(5)	111.1(2)
E···N(11)	2.514(4)	2.750(3)
E···N(21)	2.514(4)	2.753(3)
E–N(11)–l.p.(11)	68.2	73.6
E–N(21)–l.p.(21)	69.0	73.7
l.p.(11)–N(11)–N(10)–E	4.6	27.8
l.p.(21)–N(21)–N(20)–E	3.0	25.7
l.p.(11)–N(11)–N(10)–l.p.(10)	90.4	78.6
l.p.(21)–N(21)–N(20)–l.p.(20)	88.1	80.1

The lone pairs l.p. are defined to enclose equal angles to all nitrogen substituents.

compressed to only 107.7(3)° and the resulting Si ⋯ N(11) distance is 2.514(4) Å, which is in the range established for donor Si–N bonds in six-co-ordinate silicon compounds (2.50–2.81 Å).[15] The absence of a characteristic lengthening of the co-valent Si–Cl and Si–N bonds as compared to standard bond lengths indicates the weakness of the Si ⋯ N interaction and it is difficult to distinguish clearly between weak donor bonds and strong coulombic interactions in this case. The space required by the NMe$_2$ groups of 1 causes compression of the Cl(1)–Si–Cl(2) angle to 105.4(1)°, but widening of the N(10)–Si–N(20) angle to 118.9(2)°. The Si ⋯ N interactions also distort the geometry of the N$_\alpha$ atoms: they are planar as expected, but the Si–N(10)–C(14) angle is extremely large [131.8(4)°] compared with the mean Ge–N–C angle of 119.9° in compound 2, which bears undistorted trimethylhydrazido groups (see below).

Compound 2 crystallises by slowly cooling a concentrated hexane solution to −30 °C. Its crystal structure consists of discrete molecules as shown in Fig. 2; there is a crystallographic two-fold axis passing through the germanium atom, relating two pairs of trimethylhydrazido groups. The Ge–N bond distances are 1.834(2) and 1.828(2) Å, which is within the established range for this parameter. In contrast to 1, no expansion of the co-ordination sphere is detectable for 2. The angle Ge–N(10)–N(11) [114.0(1)°] and the relatively long Ge ⋯ N(11) and Ge ⋯ N(21) distances of 2.750(3) and 2.753(3) Å indicate the absence of an attractive Ge ⋯ N$_\beta$ interaction, as the difference to the corresponding values for 1 (difference between mean values: 0.238 Å) is much larger than the difference in covalent radii of silicon and germanium (0.05 Å).[16] The bond length Si–N in 1 is about 0.16 Å shorter than the values of Ge–N in 2. This can be attributed to the electron-withdrawing effect of the Cl atoms in 1, which is also a possible contribution to the observed differences between the Si ⋯ N$_\beta$ and Ge ⋯ N$_\beta$ distances.

The germanium atom in compound 2 exhibits a markedly distorted tetrahedral co-ordination. In contrast to other structurally characterised open-chain systems, which contain a Ge–N–N skeleton and completely planar α-nitrogen atoms (Cambridge Crystallographic Database), the nitrogen atoms bound to the germanium atom in 2 are shallow pyramids [Σ angles at N(10), 350.5°; at N(20), 351.3°]. The conform-ations of the hydrazide ligands can be understood in terms of lone-pair repulsion: as in 1, the nitrogen lone pairs of 2 are orthogonal to each other corresponding to the minimum-energy conformation.

In order to analyse the crystallographic data for compounds 1 and 2 in more detail, we calculated the idealised positions of the nitrogen lone pairs (l.p.) such that they define equal angles to the three atoms bound to the nitrogen atoms (see Fig. 3). With the aid of this construction we calculated the angles between the vectors N$_\beta$–l.p. and Si ⋯ N$_\beta$ for 1 and N$_\beta$–l.p. and Ge ⋯ N$_\beta$ for 2. The mean value of this angle for 1 is 68.6°, and about 5° wider in the case of 2 (73.7°), being markedly different and subsequently consistent with our interpretation in terms of a Si ⋯ N$_\beta$ interaction. This point is confirmed even more clearly by the set of torsion angles E–N–N–l.p. which indicate to what degree the lone pairs are pointing towards the central atom E (Si or Ge). The mean value for this parameter is 3.8° for 1, corresponding to an almost ideal orientation of the lone pair towards the silicon atom, but 26.7° in the case of 2, indicating that secondary interaction is not of great importance and is not maximised.

Ab initio calculations on model systems

Since compounds 1 and 2 differ both in the central atom and in the number of hydrazide ligands, it is not possible to ascertain the causes of structural differences. We have therefore performed ab initio calculations on model systems. Details are
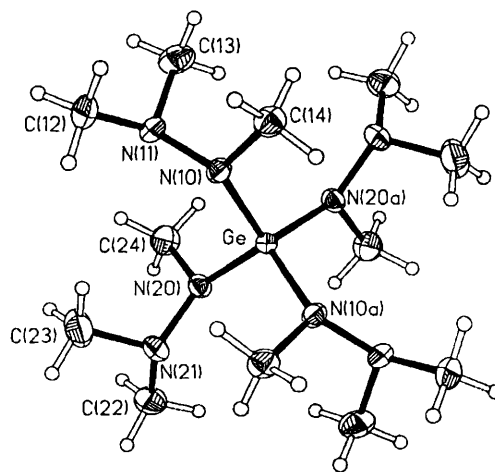

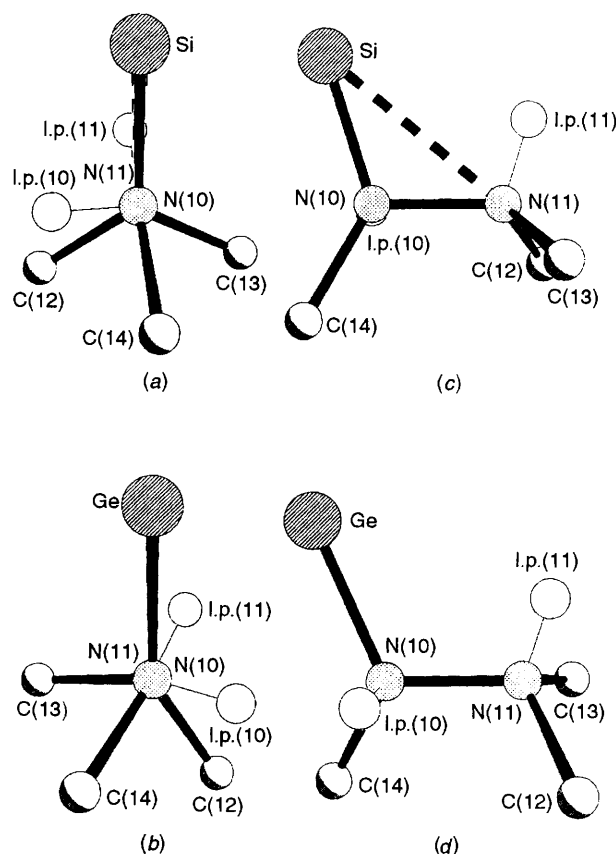**Fig. 2** Molecular structure of compound 2 shown in a view along the crystallographic C_2 axis

(a)   *(c)*

(b)   *(d)*

Fig. 3 Views of the E–N(C)–NC$_2$ parts of the molecular structures of compounds 1 (a) and 2 (b) along the N–N bonds with the idealised positions of the lone pairs at the nitrogen atoms; (c) and (d) show the different geometries of the hydrazide ligands in 1 and 2

given in the Experimental section. For reasons of the size of the calculations we decided to neglect the effects caused by the methyl groups and replaced them by hydrogen atoms. Optimised geometries of the following four compounds were calculated at the SCF/3-21G*, SCF/6-31G* and MP2/6-31G* level of theory to gauge the effects on geometrical parameters as the sophistication of the theory is improved: SiCl$_2$(N$_2$H$_3$)$_2$ 1a, GeCl$_2$(N$_2$H$_3$)$_2$ 1b, which both proved to exhibit C_{2v} symmetry, and Si(N$_2$H$_3$)$_4$ 2a and Ge(N$_2$H$_3$)$_4$ 2b both having S_4 symmetry. The calculated parameters are listed in Table 2 and the geometries are shown in Fig. 4.

In general, improvements in the theoretical method were found to have a modest effect upon bond lengths and angles. Most of the predicted bond lengths differ within a range of 0.03

Table 2 Calculated geometrical parameters for model compounds **1a**, **1b**, **2a** and **2b** at the MP2/6-31G* level of theory (values calculated at the levels SCF/3-21G* and SCF/6-31G* in parentheses)

	1a $SiCl_2(N_2H_3)_2$	**1b** $GeCl_2(N_2H_3)_2$	**2a** $Si(N_2H_3)_4$	**2b** $Ge(N_2H_3)_4$
	C_{2v}	C_{2v}	S_4	S_4
E–N	(1.691/1.698) 1.709	(1.777/1.790) 1.803	(1.710/1.720) 1.731	(1.801/1.820) 1.841
E–Cl	(2.045/2.058) 2.053	(2.166/2.147) 2.149		
N–N	(1.441/1.400) 1.419	(1.435/1.397) 1.416	(1.455/1.412) 1.437	(1.448/1.415) 1.447
E–N–N	(115.0/119.0) 116.9	(115.8/117.4) 114.5	(123.2/125.4) 123.7	(123.9/121.1) 117.0
N–E–N'	(107.4/106.1) 105.3	(108.0/107.9) 108.3	(113.6/118.7) 121.1	(113.9/117.7) 119.1
N–E–N"			(107.5/105.1) 104.0	(107.3/105.5) 104.9
Cl–E–Cl	(106.0/105.2) 105.1	(105.8/104.5) 103.9		
Cl–E–N	(110.9/111.4) 111.5	(110.8/111.1) 111.2		
E···N	(2.645/2.674) 2.669	(2.727/2.731) 2.715	(2.786/2.786) 2.797	(2.872/2.824) 2.811
Σ angles at N_α	359.1	360.0	353.3	341.8
l.p.–N–N–l.p.	90.0	90.0	90.0	92.2
l.p.–N_β···E	74.6	72.1	140.4	143.3
E–N_α–N_β–l.p.	0.0	0.0	163.5	158.0

Atom N' is generated from N by a C_2 operation, N" by a $S_4{}^1$ operation.
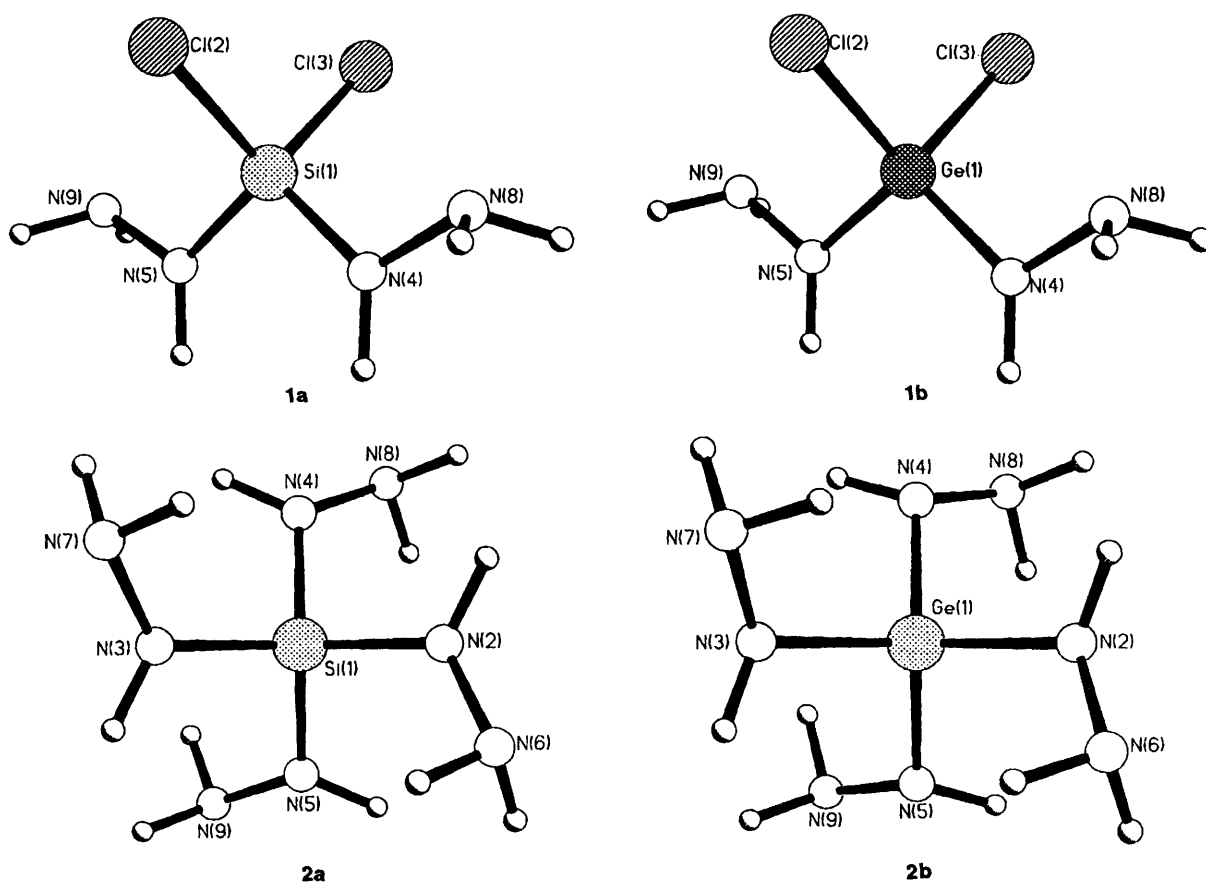
Fig. 4 *Ab initio* geometries of the molecules **1a**, **1b**, **2a** and **2b** calculated at the MP2/6-31G* level of theory

Å of each other. Corresponding deviations in angles were up to 7°, but generally less than 4°. Larger deviations occur in those parts of the molecules involving N–N bonds. This is not surprising, as it is well established that bonds between electronegative elements are poorly described when electron correlation is not taken into account.[17]

Comparison of the crystal structure of compound **1** with that calculated for **1a** shows the bond lengths to have similar magnitudes. For **1a** the calculated Si–N distance at the highest level of theory (1.709 Å) is longer, but the N–N distance (1.419 Å) is shorter than the corresponding distance in **1** (mean values 1.669 and 1.439 Å, respectively). The angles Cl–Si–Cl of **1a**

(105.1°) and **1** (105.4°) compare well, but large differences between the model system and parent compound occur for the bond angles N–Si–N (**1a**, 105.3; **1**, 118.9°) and Si–N–N (**1a**, 116.9; **1**, mean 108.7°), resulting in a markedly longer Si···N_β distance in **1a** (2.669 Å) compared with **1** (2.514 Å). If steric effects are strongly operative in these systems the reverse order for the model compound and parent system would be expected for the values of the Si–N–N angles. A contribution to this difference can be attributed to the higher basicity of a β-NMe_2 group as compared with a β-NH_2 group. The sum of angles at the N_α atom in **1a** is 359.1° corresponding to a virtually planar configuration.

The differences between the skeletal geometries of the parent compound **1** and the model **1a** suggest that some care needs to be taken when comparisons between these structures are made. However, a qualitative understanding should be obtainable by comparing the four calculated model compounds. The interaction E $\cdots$ N$_\beta$, is stronger for E $=$ Ge than for Si, as can be seen from the corresponding values for the angles E–N–N for **1a** and **1b** (which is more acute in the germanium case) and the distances E $\cdots$ N$_\beta$, which are almost identical despite the different covalent radii of Ge and Si (1.22 and 1.17 Å). It is currently not clear why the secondary interaction between the N$_\beta$ atom and germanium is apparently stronger than that to silicon. It may be the result of decreased steric repulsion in the case of the germanium compound **1b** or the larger positive charge of the Ge atom in this molecule. The calculated Mulliken charges are $+1.37$ e for **1b** and $+1.30$ e for **1a** at the SCF/6-31G* level of theory.

Whereas both models **1a** and **1b** (as well as **1**) exhibit conformations with the lone pairs at the N$_\beta$ atoms oriented towards the central atom, this is clearly not the case for **2a** and **2b**. The conformation of the hydrazide ligands, which is dominated by lone-pair repulsions in these compounds (see above) is such that the nitrogen lone pairs are orthogonal to one another, but, in contrast to **2**, pointing completely away from the central atom, as indicated by the E–N$_\alpha$–N$_\beta$–l.p. torsion angles of 163.5° for **2a** and 158.0° for **2b**. This strong conformational preference for the ECl$_2$(NRNR$_2$)$_2$ compounds **1**, **1a** and **1b** is further evidence for secondary interactions of the E $\cdots$ N$_\beta$ type, while the absence of this effect in the group of compounds E(NRNR$_2$)$_4$ **2**, **2a** and **2b** allows two conformational possibilities, one verified in the crystals of **2**, the other predicted for **2a** and **2b** by the calculations. The conformation of the model system **2b** cannot be realised in the parent compound **2** because of the steric demand of the N$_\beta$ methyl substituents.

The calculated system **2b** and the crystal structure for **2** compare much better than the two compounds **1** and **1a** discussed above. As Table 2 shows, the Ge–N and N–N bond lengths for the model system **2b** are predicted to be quite similar to values observed for **2**. The angles Ge–N–N (117.0°) and N–Ge–N (119.1 and 104.9°) predicted for **2b** are not perfectly akin to those observed in **2** (114.3, 113.4, 101.6°) but compare better than those of **1a** and **1**. The unexpected non-planar configuration of the N$_\alpha$ atoms observed in **2** is also predicted for the model systems **2a** and **2b**.

As for the pair **1a**/**1**, the E–N–N angle in the model compound **2b** has been predicted to be larger than that in the parent compound **2**. In general, the silicon model compounds **1a** and **2a** have wider E–N–N angles than the corresponding germanium analogues **1b** and **2b**. The E $\cdots$ N$_\beta$ distances are similar within both pairs of model systems ECl$_2$(N$_2$H$_3$)$_2$ and E(N$_2$H$_3$)$_4$. As the germanium compounds always have the narrower E–N–N angles, our comparison of the Si–N–N angle in **1** with the Ge–N–N angle in **2** seems to underestimate the effect of E $\cdots$ N$_\beta$ interactions in **1** rather than being unrealistic.

Conclusion

Whereas β-donor ligand activity (η^2 co-ordination) is well documented for transition-metal complexes it is much rarer in main-group chemistry. The effect appears to be absent for Ge(NMeNMe$_2$)$_4$, but for the compound SiCl$_2$(NMeNMe$_2$)$_2$ we have demonstrated for the first time that hydrazide ligands are able to co-ordinate to main-group elements through their N$_\beta$ atoms. Although calculations of the simpler model systems with N$_2$H$_3$ ligands appear to deviate slightly in some respects from the trimethylhydrazide systems these differences are to be expected. The calculations support our conclusions about the existence of N$_\beta$ $\cdots$ Si interactions and predict such interactions

to be even stronger for corresponding germanium compounds. While the N$_\beta$ $\cdots$ Si interaction is predictably weak, recent results in this laboratory suggest that the co-ordination sphere is expanded even further in the related hydroxylamide compound Si(ONMe$_2$)$_4$.[18]

Experimental

Synthesis of SiCl$_2$(NMeNMe$_2$)$_2$ 1

Trimethylhydrazine (9.0 cm^3, 92 mmol) was dissolved in hexane (100 cm^3) and butyllithium solution (2.5 mol dm^{-3} in hexane, 36.6 cm^3) was added dropwise at -78 °C. The mixture was allowed to warm to ambient temperature and stirred for 1 h. The resulting suspension of lithium trimethylhydrazide was cooled to -40 °C and silicon tetrachloride (2.6 cm^3, 22 mmol) dissolved in hexane (10 cm^3) was added dropwise. The mixture was allowed to warm to ambient temperature and stirred for 2 h. A clear solution resulted, from which LiCl precipitated slowly. The solvent was removed under reduced pressure and the residue extracted with pentane (50 cm^3), then filtered and the pentane distilled off under reduced pressure. The remaining oily liquid was diluted with pentane (*ca.* 1 cm^3) and slowly cooled to -78 °C with formation of a crystalline precipitate. The liquid was removed by a cannula at this temperature, and the residue recrystallised in the same way giving 1.93 g compound **1** (51% yield); m.p. 6 °C. NMR (C$_6$D$_6$): ^{1}H (250.13 MHz), δ 2.26 [s, 6 H, (H$_3$C)$_2$N] and 2.46 (s, 3 H, H$_3$CN); ^{13}C-{^{1}H} (62.90 MHz), δ 22.1 (s, CN) and 42.9 (s, C$_2$N). ^{29}Si-{^{1}H} (29.76 MHz), δ -44.0. IR (film, KBr): ṽ/cm^{-1} 2991m, 2949vs, 2859s, 2773m, 1454m, 1274m, 1157w, 1097m, 1014w, 862s, 845s, 655w (vSiN), 551s, 508s. Mass spectrum: [electron impact (EI), 70 eV] m/z 244, 229, 214, 208, 199, 171, 127 and 73; (high resolution) m/z 244.06782 (Calc. for C$_6$H$_{18}$Cl$_2$N$_4$Si: 244.06778).

Synthesis of Ge(NMeNMe$_2$)$_4$ 2

Trimethylhydrazine (12.0 cm^3, 122 mmol) was dissolved in hexane (100 cm^3) cooled to -78 °C and butyllithium (48.8 cm^3, 2.5 mol dm^{-3} solution in hexane) added dropwise. After allowing to warm to ambient temperature, stirring for 1 h and cooling to -40 °C, a solution of germanium tetrachloride (3.5 cm^3) was added dropwise. The mixture was allowed to reach ambient temperature, stirred for 2 h and filtered. Removal of the solvent under reduced pressure caused further precipitation of LiCl, which was filtered off. The residue was diluted with pentane (4 cm^3), crystallised at -78 °C and the liquid impurities removed. After recrystallisation, 5.64 g (50%) of compound **2** were obtained, m.p. 73 °C. NMR (C$_6$D$_6$): ^{1}H (200.13 MHz), δ 2.52 [s, 24 H, (H$_3$C)$_2$N] and 2.76 (s, 12 H, H$_3$CN); ^{13}C-{^{1}H} (62.90 MHz), δ 25.5 (s, CN) and 43.4 (s, C$_2$N). IR (film): ṽ/cm^{-1} 2977s, 2934s, 2644vs, 2764s, 1466m, 1460m, 1447m, 1452m, 1447m, 1432m, 1260vw, 1235vw, 1205w, 1174w, 1148m, 1084m, 1070s, 1010m, 970m, 961 m, 823s and 608m. Mass spectrum: (EI, 70 eV) m/z 366, 337, 321, 308, 293, 277, 253, 220, 219, 205, 190, 163, 147 and 73; (high resolution) m/z 366.22820 (Calc. for C$_{12}$H$_{36}$GeN$_8$: 366.22819).

X-Ray crystallography

Compound 1. A cylindrical crystal (0.25 mm diameter, 0.8 mm long) was grown from a melt in a sealed capillary by *in situ* methods on a Stoe Stadi-4 four-circle diffractometer fitted with an Oxford Cryosystems low-temperature device.[19]

Crystal data. $C_6H_{18}Cl_2N_4Si$, $M = 245.23$, orthorhombic, space group *Pbca*, $a = 11.4469(9)$, $b = 13.2330(12)$, $c = 16.8921(13)$ Å; $U = 2558.8(4)$ Å^3, $Z = 8$, $D_c = 1.273$ g cm^{-3}, $T = 143$ K; $\lambda = 0.710\,73$ Å, $\mu(\text{Mo-K}\alpha) = 0.570$ mm^{-1}, $F(000) = 1040$.

The structure was solved by direct methods[20] and refined[21] with 133 parameters on F^2 (all non-H atoms anisotropic, hydrogen atoms were introduced in calculated positions, all angles fixed to the ideal tetrahedral angles and one common C–H bond length was refined for each CH_3 group with the isotropic thermal parameters tied to that of the adjacent carbon atom by a factor of 1.5) to give $R1 = 0.0634$ [based on 1134 observations with $F \geqslant 4\sigma(F)$] and $wR2 = 0.1204$ for all 2242 unique data, residual electron density (minimum, maximum) $-0.4, 0.39$ e Å^{-3}. Weighting scheme employed: $w = [\sigma^2(F_o^2) + (0.0358P)^2 + 0.8971P]^{-1}$, where $P = 0.3333(F_o^2 + 2F_c^2)$.

Compound 2. A crystal ($0.65 \times 0.55 \times 0.10$ mm) was transferred under nitrogen into inert oil (RS3000) and mounted on a glass fibre.

Crystal data. $C_{12}H_{36}GeN_8$, $M = 365.06$, monoclinic, space group *C2/c*, $a = 17.994(5)$, $b = 7.175(3)$, $c = 16.610(6)$ Å, $\beta = 116.73(3)°$, $U = 1915.3(12)$ Å^3, $Z = 4$, $D_c = 1.266$ g cm^{-3}, $T = 150$ K, $\lambda = 0.710\,73$ Å, $\mu(\text{Mo-K}\alpha) = 1.608$ mm^{-1}, absorption correction by ψ scans (T_{min}, $T_{\text{max}} = 0.784$, 1.000), $F(000) = 784$.

Stoe Stadi-4 four-circle diffractometer. The structure was solved by direct methods[22] and refined[21] with 102 parameters on F^2 (all non-H atoms anisotropic, hydrogen atoms were introduced in calculated positions, all angles fixed to the ideal tetrahedral angles and one common C–H bond length was refined for each CH_3 group with the isotropic thermal parameters tied to that of the adjacent carbon atom by a factor of 1.5) to give $R1 = 0.0293$ [based on 1503 observations with $F \geqslant 4\sigma(F)$] and $wR2 = 0.0686$ for all 1691 unique data (2485 data collected, $R_{\text{int}} = 0.026\%$), residual electron density (minimum, maximum) -0.42, 0.32 e Å^{-3}. Weighting scheme employed: $w = [\sigma^2(F_o^2) + (0.0498P)^2 + 1.346P]^{-1}$, where $P = 0.3333(F_o^2 + 2F_c^2)$.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/25.

Theoretical methods

All *ab initio* molecular orbital calculations were performed on a DEC Alpha APX 1000 computer using the GAUSSIAN 92 program.[23] Geometry optimisations were performed at the self-consistent field (SCF) level of theory using the standard 3-21G*[24–26] and 6-31G*[27–29] basis sets, while the larger of these two was used for optimisations at the second-order Møller–Plesset perturbation (MP2) level of theory. Vibrational-frequency calculations were based on analytic second derivatives at the SCF level using the 3-21G* basis set to determine the nature of all located stationary points and verify that the calculated structures represent local minima on the potential-energy surface.

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