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Facile central-element exchange in neutral hexacoordinate germanium and silicon complexes; synthesis and characterization of germanium complexes†

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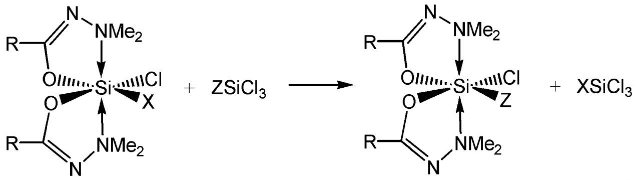
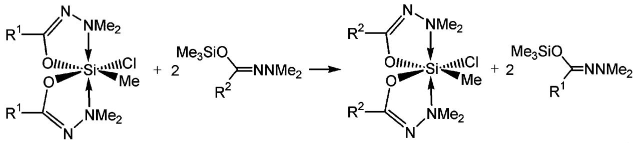
Neutral hexacoordinate germanium complexes with hydrazido chelating ligands have been synthesized and characterized. Facile exchange of central element between silicon and germanium in these complexes is demonstrated, following given selectivity constraints.

We have recently shown that complete and rapid exchange of ligands takes place between neutral hexacoordinate silicon complexes and their differently substituted precursors:[1,2] formal exchange of monodentate ligands between a complex and a trichlorosilane (eqn (1)), following a well defined "priority list"; exchange of bidentate chelating ligands between complexes and a trimethylsilyl-hydrazide precursor (eqn (2)) as well as between differently substituted complexes (eqn (3)).



(1)



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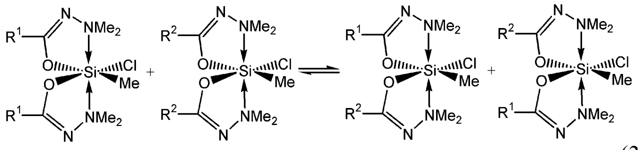
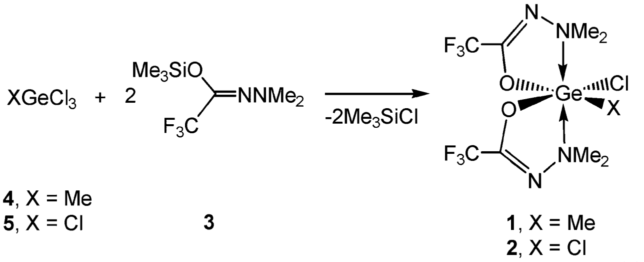


(3)

We now find that even the central element in these complexes can readily be replaced by a different one, namely the silicon is replaced by germanium and germanium by silicon, obeying certain selectivity constraints. This is quite a remarkable observation in view of the many bonds which must be cleaved, and others which are formed during the exchange.

Hexacoordinate germanium complexes[3] (**1** and **2**) were prepared like their silicon analogues, from the *O*-trimethylsilylated hydrazide (**3**) and methylgermanium trichloride (**4**) and germanium tetrachloride (**5**), respectively (eqn (4)).[4] Products **1** and **2** were characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis and by single crystal X-ray diffraction analysis. The molecular structures of **1** and **2** in the solid state are depicted in Fig. 1 and 2, respectively, and selected bond lengths and angles are listed in Table 1.



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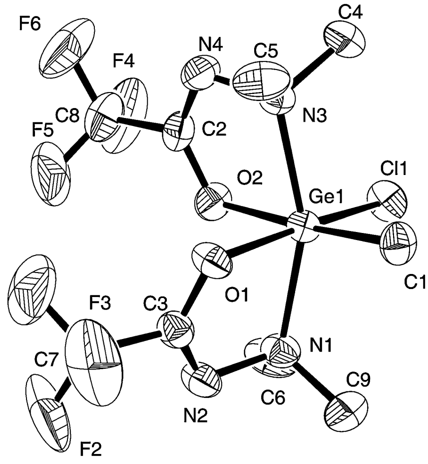

Fig. 1 ORTEP representation of the molecular structure of **1**, depicted at the 50% probability level and omitting hydrogen atoms.

From Fig. 1 and 2, and the data in Table 1, it is evident that the germanium complexes are hexacoordinate and their geometry around the central atom is a distorted octahedron. Like in the silicon analogues,[2f,2g] the nitrogen ligands in **1** and **2** are positioned *trans* to each other, while the oxygen pair, as well as the pair of monodentate ligands, possess *cis* positions. Further examination of the data in Table 1 reveals substantial similarity between the dichloro-germanium (**2**) and -silicon (**6**) complexes: all of the bonds to germanium are, as one might expect, slightly longer than the corresponding bonds in the silicon complex (**2** *vs.* **6**). It may be worth noting that while the Ge–N and Ge–Cl bonds are *ca.* 0.08 Å longer than those to silicon, the corresponding Ge–O bond elongation (0.15 Å), relative to Si–O, is almost twice as large. This is undoubtedly a manifestation of the special strength of the Si–O bond, relative to the Ge–O bond.[6]

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† CCDC reference numbers 780239 and 780240. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00625d

Table 1 Selected crystallographic bond lengths and angles for **1** and **2**, and for the silicon analogue **6** for comparison

1		**2**		**6**[a]	
CCDC No. 780239		CCDC No. 780240		CCDC No. SOJQAJ	
Bond lengths/Å					
Ge–N	2.141(3)	Ge–N	2.085(5)	Si–N	2.011(2)
Ge–N	2.147(3)	Ge–N	2.106(5)	Si–N	2.013(2)
Ge–Cl	2.2899(9)	Ge–Cl	2.2234(19)	Si–Cl	2.141(1)
Ge–C	1.975(3)	Ge–Cl	2.2226(19)	Si–Cl	2.142(1)
Ge–O	1.977(2)	Ge–O	1.934(4)	Si–O	1.775(1)
Ge–O	1.952(2)	Ge–O	1.928(4)	Si–O	1.777(1)
Bond angles (°)					
N–Ge–N	158.50(12)	N–Ge–N	164.5(2)	N–Si–N	168.73(7)
Cl–Ge–N	98.23(8); 93.06(8)	Cl–Ge–N	92.20(15); 98.29(15)	Cl–Si–N	92.16(5); 94.09(5)
C–Ge–N	95.88(13); 101.31(13)		92.31(15); 98.31(16)		90.84(5); 98.28(5)
O–Ge–N	86.99(10); 78.93(10)	O–Ge–N	87.7(2); 81.17(19)	O–Si–N	87.37(7);83.22(7)
	79.10(10); 83.40(10)		80.9(2); 87.4(2)		82.91(6); 90.60(7)
O–Ge–O	84.24(10)	O–Ge–O	85.9(2)	O–Si–O	88.28(7)
Cl–Ge–O	87.38(8); 169.11(7)	Cl–Ge–O	90.14(15); 172.49(14)	Cl–Si–O	89.53(5); 174.95(5)
C–Ge–O	93.94(13); 174.57(12)		90.19(15); 172.26(14)		90.40(6); 173.64(5)

[a] Taken from ref. 5; data for only one of two unique molecules are cited.

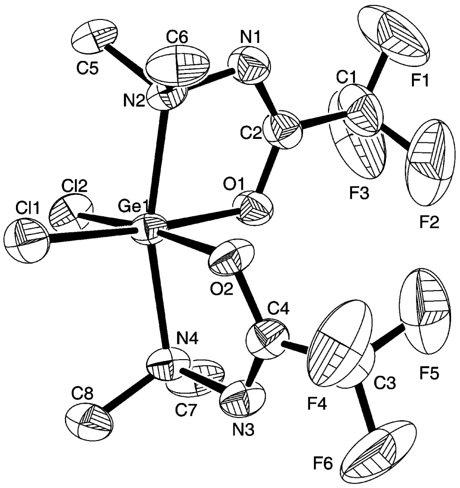
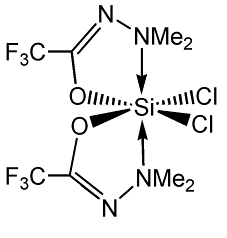
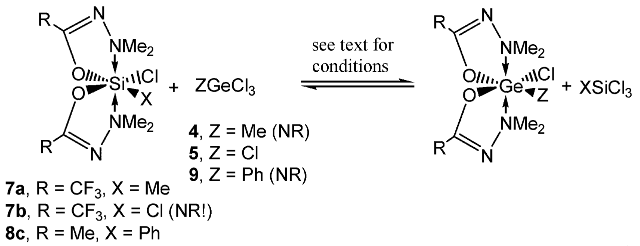


Fig. 2 ORTEP representation of the molecular structure of **2**, depicted at the 50% probability level and omitting hydrogen atoms.



6

When a silicon complex (**7**, **8**) is allowed to react with excess $GeCl_4$ (**5**) in chloroform solution for 1 h at boiling temperature, or for two days at room temperature, nearly all of the silicon complex has disappeared, and a new compound, identified as the germanium complex, is formed (eqn (5)). This is evident from the disappearance of the high-field signal characteristic of the hexacoordinate silicon compound (–124.4 ppm) in the reaction of **7a** with **5**, and its conversion to the signal (12.6 ppm) assigned to $MeSiCl_3$ in the ^{29}Si NMR spectrum. Likewise, in the ^1H NMR spectrum (Fig. 3) the Si–Me singlet of **7a** at 0.64 ppm is converted to the $MeSiCl_3$ signal at 1.11 ppm, and the NMe resonances at 2.75 and 2.94 ppm are transformed to those of **2**, at 3.04 and 3.15 ppm.



(5)

When methyltrichlorogermane (**4**) is used instead of **5**, no exchange takes place. The ability of germanium to replace silicon in its complex depends on the electronegativity of the ligands attached to germanium, and to those attached to silicon, in analogy with the "ligand priority list" reported previously for the exchange reaction shown in eqn (1).[1] Thus, $GeCl_4$ produces dichloro-complexes, which take priority over the monodentate ligands in the starting silicon complex: Me and Cl in **7a**, or Ph and Cl in **8c**. As a result, the lower-priority ligands *with the attached central silicon* are replaced by the chloro-ligands and germanium.

In line with this observation, when equally substituted silicon and germanium are concerned, *i.e.*, when the two monodentate ligands attached to the silicon complex are the same as the ones that would enter the expected germanium complex, if exchange took place (Z = X in eqn (5)), no intermolecular exchange is observed. In other words, when equally substituted, and in the absence of any ligand priority driving force, silicon takes priority over germanium, and is not replaced from its complex. Conversely, germanium is readily and quantitatively replaced by silicon in the reverse reaction, when both are equally substituted (Z = X in eqn (5), reverse direction), confirming again the priority of silicon over germanium in the formation of these neutral hexacoordinate complexes. Thus, $SiCl_4$ replaces germanium in any one of its

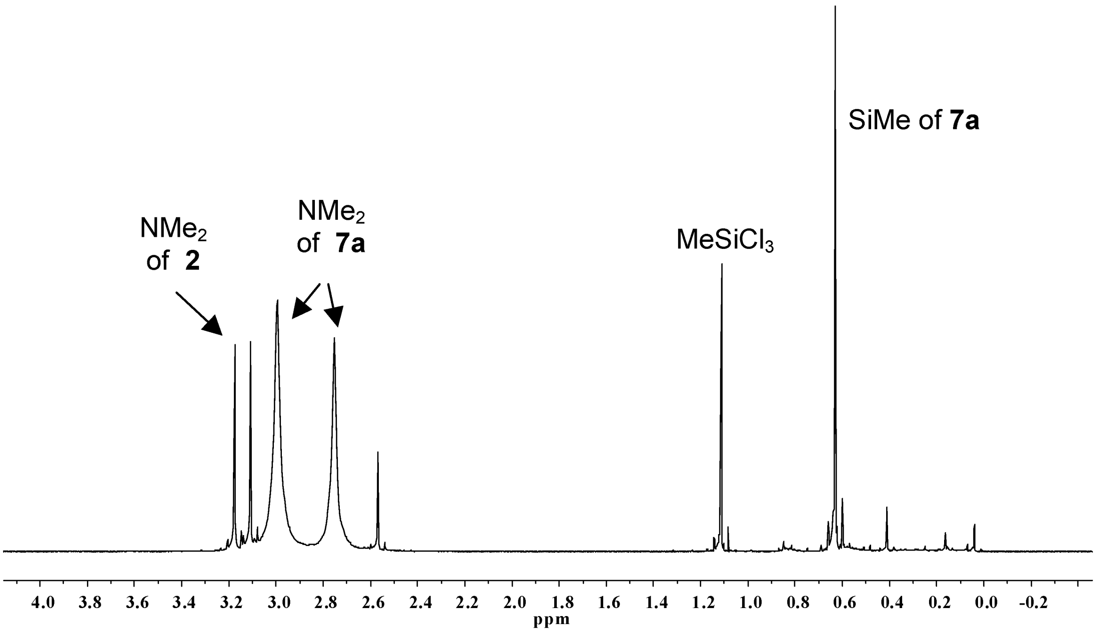


Fig. 3 ^1H NMR spectrum of the reaction (eqn (5)) between **7a** and $GeCl_4$ (**5**) in $CDCl_3$ solution, after partial conversion, featuring both silicon and germanium complexes. The signal at 2.58 ppm belongs to residual **3**.

complexes, any ligand Z (reverse eqn (5)), and similarly $XSiCl_3$ replaces germanium as long as Z = X.

It is evident that the ligand electronegativities play a major role in the exchange of silicon and germanium. The extent to which silicon takes intrinsic priority over germanium can only be partly assessed: silicon replaces germanium as long as they are equally substituted. Can a less electronegative ligand X be attached to silicon, without loss of its power to replace germanium? When $PhSiCl_3$ (X = Ph) was allowed to react with **2**, so that the germanium ligands (two chloro ligands) have priority over the silicon ligands (chloro and phenyl), no trace of exchange could be detected (reverse eqn (5)). Likewise, $HSiCl_3$ caused no central-element exchange with the dichloro-germanium complex (**2**, Z = Cl, X = H in reverse eqn (5)). This means that ligand priority dominates the reaction, and hence that the central-element priority is of lesser importance.

The limits of priority were further probed in the forward reaction: germanium replacing silicon. It takes $GeCl_4$ to replace silicon substituted by Me, Cl (Z = Cl, eqn (5)). An attempt to lower the ligand priority, by using $PhGeCl_3$ (**9**) to replace SiMeCl from **7a**, led to no exchange, despite the fact that the germanium ligand priorities (Ph, Cl in **9**) were greater than the silicon ligand priorities (Me, Cl in **7a**).

From the results presented in this paper, combined with previous results on ligand exchange in silicon compounds,[1] it appears that the mechanism of central-element exchange is similar to that of the ligand exchange reaction. This is supported by the observation that silicon-germanium exchange is essentially dominated by the same ligand priority order, just as the ligand exchange reactions described previously. Apparently the bidentate, chelate forming ligands, are capable of rapid bond cleavage and transfer from one central element to the other, thereby effecting complete exchange between complexes. It is likely that the dative N → Si bonds are first to cleave and attack a neighboring "heavy" element (silicon or germanium), followed by O–Si cleavage and complete transport of the bidentate ligand from silicon to the neighboring element. This initial process is then followed by cleavage and transfer of all the bidentate ligands from one molecule to its neighbor and *vice versa*. At no point along this exchange is a silicon carbon or germanium carbon bond ever cleaved.

Acknowledgements

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References

1 S. Sergani, I. Kalikhman, S. Yakubovich and D. Kost, *Organometallics*, 2007, **26**, 5799–5802.

2 For selected reviews on hypercoordinate silicon compounds see: (*a*) M. A. Brook, in *Silicon in Orgsanic, Organometallic and Polymer Chemistry*, Wiley, New York, 2000 pp. 97–115; (*b*) A. R. Bassindale, S. J. Glynn and P. G. Taylor, in *The Chemistry of Organic Silicon Compounds*, ed. Z. Rappoport, and Y. Apeloig, Wiley: Chichester, U.K, 1998, Vol. 2, Part 1, pp. 495–511; (*c*) C. Chuit, R. J. P. Corriu and C. Reyé, in *The Chemistry of Hypervalent Compounds*, ed. Kin-ya Akiba, Wiley-VCH: Weinheim, Germany 1999, pp. 81–146; (*d*) M. Kira and L.-C. Zhang, in *The Chemistry of Hypervalent Compounds*, ed. Kin-ya Akiba, Wiley-VCH: Weinheim, Germany, 1999, pp. 147–169; (*e*) R. Tacke, M. Pülm and B. Wagner, *Adv. Organomet. Chem.*, 1999, **44**, 221–273; (*f*) D. Kost and I. Kalikhman, *Adv. Organomet. Chem.*, 2004, **50**, 1–106; (*g*) D. Kost and I. Kalikhman, in *The Chemistry of Organic Silicon Compounds*, ed. Z. Rappoport and Y. Apeloig, Wiley, Chichester, U.K, 1998, Vol. 2, Part 2, pp. 1339–1445; (*h*) V. Pestunovich, S. Kirpichenko and M. Voronkov, in *The Chemistry of Organic Silicon Compounds*, ed. Z. Rappoport and Y. Apeloig, Wiley, Chichester, U.K, 1998, Vol. 2, Part 2, pp. 1447–1537; (*i*) V. V. Negrebetsky, S. N. Tandura and Yu. I. Baukov, *Uspekhi Khimii*, 2009, **78**, 24–55 English translation: V. V. Negrebetsky, S. N. Tandura and Yu. I. Baukov, *Russ. Chem. Rev.*, 2009, **78**, 21–51; (*j*) D. Kost and I. Kalikhman, *Acc. Chem. Res.*, 2009, **42**, 303–314.

3 For different hexacoordinate germanium compounds see: (*a*) S. D. Pastor, V. Huang, D. NabiRahni, S. A. Koch and H.-F. Hsu, *Inorg.*

Chem., 1997, **36**, 5966–5968; (*b*) A. Biller, C. Burschka, M. Penka and R. Tacke, *Inorg. Chem.*, 2002, **41**, 3901–3908; (*c*) S. N. Tandura, A. N. Shumsky, B. I. Ugrak, V. V. Negrebetsky, S. Yu. Bylikin and S. P. Kolesnikov, *Organometallics*, 2005, **24**, 5227–5240; (*d*) I. I. Seifullina, N. V. Shmatkova and E. E. Martsinko, *Koord. Khim.*, 2004, **30**, 228–234, English translation: I. I. Seifullina, N. V. Shmatkova and E. E. Martsinko, *Russ. J. Coord. Chem.*, 2004, **30**, 214–220.

4 Synthesis: **Bis(*N*-(dimethylamino)trifluoroacetimidato-*N*,*O*)chloro-(methyl)germanium(IV)** (**1**): A mixture of 0.70 g (3.1 mmol) of **3** and 0.31 g (1.6 mmol) of **4** in 5 mL of chloroform was stirred at room temperature for 30 min. The volatiles were removed under reduced pressure (0.1 mmHg) and the residue was washed with 5 mL of n-hexane. A single crystal for X-ray analysis was grown from n-hexane. Yield: 0.65 g (94%). Mp, 105 °C (dec). ^{1}H NMR ($CDCl_3$, 300 K): δ 1.26 (s, 3H, $GeCH_3$), 2.87, 2.89, 2.97, 3.09 (4 s, 12H, NCH_3). ^{13}C NMR ($CDCl_3$, 300 K): δ 18.2 ($GeCH_3$), 48.9, 49.4, 49.7, 50.6 (NCH_3), 117.3 (q, $^{1}J_{(F-C)}$ = 278 Hz, CF_3), 117.4 (q, $^{1}J_{(F-C)}$ = 280 Hz, CF_3), 157.4 (q, $^{2}J_{(F-C)}$ = 36.5 Hz, C=N), 158.2 (q, $^{2}J_{(F-C)}$ = 36.5 Hz, C=N). Anal. calcd. for $C_9H_{15}ClF_6GeN_4O_2$: C, 24.95; H, 3.49; N, 12.93. Found: C, 25.20; H, 3.39; N, 12.81. **Bis(*N*-(dimethylamino)trifluoroacetimidato-*N*,*O*)dichlorogermanium(IV)** (**2**): **2** was prepared as described for **1**, using **5** instead of **4**. Yield: 0.63 g, 95%. Mp: 118 °C (dec). ^{1}H NMR ($CDCl_3$, 300 K): δ 3.11, 3.17 (2 s, 12H, $N(CH_3)$). ^{13}C NMR ($CDCl_3$, 300 K): δ 50.6, 50.7 (NCH_3), 117.0 (q, $^{1}J_{(F-C)}$ = 278 Hz, CF_3), 157.1 (q, $^{2}J_{(F-C)}$ = 38 Hz, C=N). Anal. calcd. for $C_8H_{12}Cl_2F_6GeN_4O_2$: C, 21.18; H, 2.67; N, 12.35. Found: C, 21.37; H, 2.82; N, 12.17.

5 D. Kost, I. Kalikhman, S. Krivonos, D. Stalke and T. Kottke, *J. Am. Chem. Soc.*, 1998, **120**, 4209–4214.

6 T. L. Cottrell, *The Strengths of Chemical Bonds*, 2nd ed., Butterworths, London, 1958.