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SILYLAMIDES OF GROUP IVA AND IVB ELEMENTS WITH SPIROBICYCLOHEPTANE STRUCTURE

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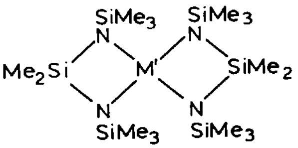
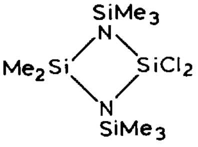
Summary

Spirocyclic metal silylamides with spiro[3.3]heptane structure, M′ = Si, Ge, Sn, Ti, Zr and Hf, have been prepared. Except for the Si derivative, the synthesis involved the reaction of the appropriate tetrachloride M′Cl$_4$ with Me$_3$SiN(M)SiMe$_2$N(M)SiMe$_3$, M = Li, Na. The M′ = Si derivative was obtained via reaction of IIIb with NH$_3$, subsequent treatment with butyllithium and Me$_3$SiCl, and then ring closure with Me$_2$SiCl$_2$. The new compounds have been characterized by analyses, NMR, IR, Raman and mass spectra. The metallaspiranes are thermally stable to > 200°C, are very volatile, and do not form complexes with ether.




(IIIb)

Introduction

Mono- and bidentate amido ligands with silyl substituents have been successfully used for the stabilization of metals with low coordination numbers [1]. Monocyclic and spirobicyclic amides in which Main Group elements and transition metals are incorporated into five- and six-membered rings have been described [2]. Spirobicycloheptane derivatives B, R = R′ = alkyl, of Si, Sn and the transition metals Ti and Zr have been reported [2,3] and some of them have been characterized by X-ray structure determinations.

Closer analogy to amides with bis(silylamido) ligands, M–N(SiR$_3$)$_2$, should be shown by derivatives of trisiladiazanes, such as the well-known Me$_3$SiNHSiMe$_2$NHSiMe$_3$ (I), which can be activated by metallation with LiC$_4$H$_9$, NaNH$_2$ etc. [4].

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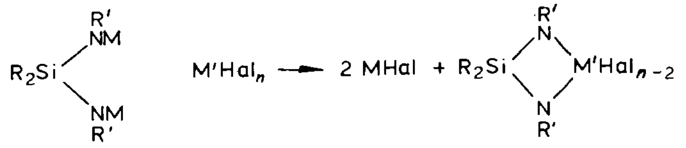
We describe below the synthesis and properties of Group IVa and IVb element derivatives of this particular ligand with spirobicycloheptane structure **B**, R′ = $SiMe_3$.

The synthesis of the titanaspirane XI was first achieved in our laboratory by Seifert [5] and later confirmed during an investigation of titanacyclobutane derivatives [6]. To our knowledge, none of the other compounds IV to XIII has previously been reported.

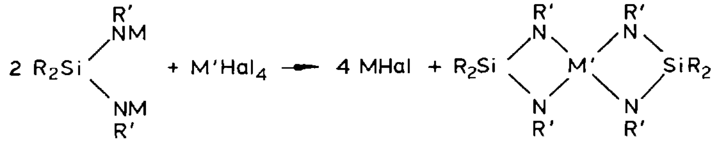
Synthesis

Transmetallation of alkali metal substituted bis(amido)silanes $R_2Si[N(M)R']_2$, R = methyl, phenyl (Me, Ph), R′ = alkyl, Me_3Si, M = Li, Na, with metal halides has been used extensively in the synthesis of mono- and spirobicyclic metal amides (eqs. 1, 2):



(A)

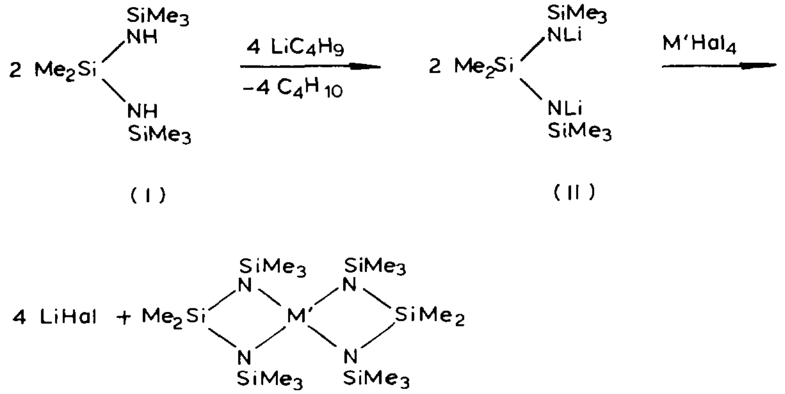
(1)



(B)

(2)

The ease of reaction 2 indicated that the reaction sequence (eq. 3) would provide a facile route to Group IVa and IVb spirobicycloheptane derivatives of I:



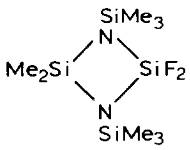
(I) (II)

(3)

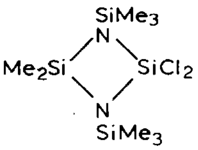
M′ = Si	Ge	Sn	Ti	Zr	Hf
VI	IX	X	XI	XII	XIII

However, it turned out that only X to XIII could be prepared in reasonable yields, i.e. 60 to 80%, by this route. Attempts to synthesize VI from SiF_4, $SiCl_4$ or

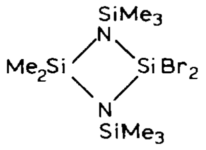
$SiBr_4$ and II or the corresponding disodio derivative [4] gave only the type A cyclobutane derivatives IIIa to IIIc along with oligomeric material which did not show the characteristic spectroscopic features of VI (Raman, IR, NMR, MS) with significant intensity.



(IIIa)

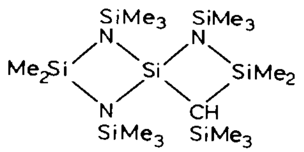


(IIIb)

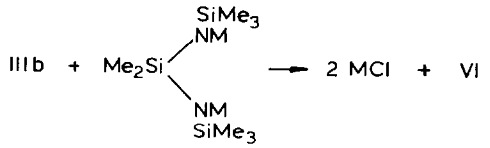


(IIIc)

The difficulties encountered in the synthesis of VI were at first unexplainable. The preparation of the surprisingly stable compound C rather than $Si[N(SiMe_3)_2]_4$ from $SiCl_4$ with $NaN(SiMe_3)_2$ at 200°C [7] as well as the ease with which other trisilatetraazaspiro[3,3]heptanes had been obtained [8,9] suggested that the one-pot route (eq. 3) was inadequate for the synthesis of VI. The crucial step in the synthesis is obviously the formation of the spirane, as in eq. 4, from IIIb, which has previously been obtained from dimetallated I and $SiCl_4$ in high yield [10].



(C)



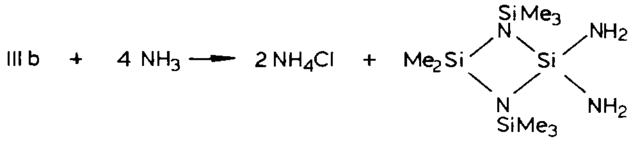
$$\text{IIIb} + Me_2Si(NMSiMe_3)_2 \longrightarrow 2\,MCl + \text{VI} \qquad (4)$$

(M = Li, Na)

Compounds IIIb and II react very slowly at room temperature, and formation of LiCl is incomplete even at elevated temperature. Under forcing conditions, CH activation, which led to the formation of compound C and which is also revealed by the molecular structure of $Me_2Si[N(Na)SiMe_3]_2$ in the solid state [4], obviously causes various side reactions to take place rather than formation of VI. When the larger Sn, Ti, Zr and Hf atoms are present the reaction is apparently more facile, the spiranes X to XIII being formed at low temperature and in good yields.

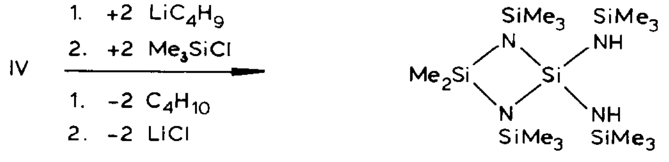
Treatment of the disodio-derivative of I with IIIb in the absence of a solvent at

200°C for several days afforded an inhomogeneous product, from which on one occasion a small amount of a high-melting, volatile material was isolated by sublimation in vacuo. This had the approximate composition $Si[(NSiMe_3)_2SiMe_2]_{1.9}Cl_{0.2}$, showed peaks at m/e 492 and 477 (M^+ and $M - CH_3^+$ for VI) in the mass spectrum and was inert towards CH_3OH, but it could not be obtained analytically pure. However, these promising indications were not further followed up because of an alternative synthesis found. This involved a three step synthesis (eqs. 5–7) starting from IIIb, which afforded VI in a (not optimized) overall yield of 35%.



(5)

(IV)



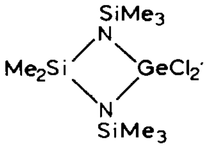
(6)

(V)

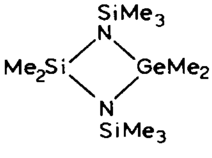
$$V \xrightarrow[\substack{1.\ -2\ C_4H_{10}\\ 2.\ -2\ LiCl}]{\substack{1.\ +2\ LiC_4H_9/THF\\ 2.\ +Me_2SiCl_2}} VI \qquad (7)$$

The bis(amino)silane IV is sufficiently stable towards condensation to allow distillation at reduced pressure. It reacts quantitatively and selectively to yield the N,N'-dilithio derivative, which forms V exothermically upon treatment with Me_3SiCl at 0°C (eq. 6). Treatment of V with butyllithium in hexane solution led only to quantitative recovery of V, but in the presence of THF, the bis(lithio) derivative of V was formed. This reacted with Me_2SiCl_2 to form the spirane VI, which was isolated in 75% yield.

The synthesis of the germa-spirane IX was made from $GeCl_4$ and II in a 1/2 ratio by the reaction shown in eq. 3. The formation of LiCl was essentially complete at room temperature, and in order to avoid side reactions, e.g. CH substitution or SiN cleavage, the temperature was not raised. The work-up by sublimation in vacuo causes further loss of material because by-products of comparable volatility, such as VII, depress the melting point, impede crystallization and necessitate repeated resublimation. The final yield, 15%, was unsatisfactory, and therefore we attempted to improve the synthesis of IX by use of a two-step route similar to eq. 4, with VII as an intermediate.



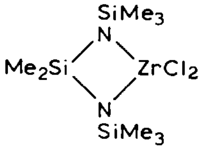
(VII)



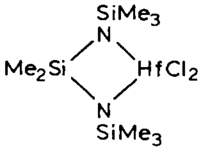
(VIII)

VII was isolated in ~ 70% yield from a reaction analogous to eq. 1. In order to test the reactivity of VII, it was treated with CH_3MgI in ether, and the germa analogue VIII of the well-known bis(trimethylsilyl)-tetramethylcyclodisiladiazane [10] was isolated in a yield of ~ 70%. The reaction of VII with II analogous to eq. 4 afforded only a mixture of IX and unreacted VII, the yield of IX as determined by ^1H NMR spectroscopy being 25%. Therefore the two-step route offers no real advantage over the straightforward synthesis.

With increasing size of M′, reaction 3 becomes more and more specific, the yield of isolated spirane exceeding 80% for XIII. This increase in selectivity may be related to a change of the properties of the monocyclic dichlorides A. While the derivatives of Si (IIIb), Ge (VII) and Ti [6] are apparently molecular in nature, (e.g. they are monomeric in solution, volatile, and soluble in nonpolar solvents, have IR absorptions indicative of terminal M′Cl bonds, and are unable to form complexes with ether), the Zr and Hf dichlorides XIV and XV separate out as amorphous polymers which, according to their IR spectra, are chlorine-bridged, with structures probably similar to Et_2NTiCl_3 [11], and form soluble and stable 1/1 complexes with diethyl ether (XIVa, XVa). Essentially quantitative yields of XIV and XV are obtained by cleavage of XII and XIII with equimolar amounts of $ZrCl_4$ and $HfCl_4$, respectively.



(XIV)



(XV)

Properties

The physical properties of the compounds III to XIII are listed in Table 1. All the compounds are colourless, though XI requires careful purification to remove traces of yellow contaminants. XIII is probably also colourless, though our material was very slightly and inhomogeneously brownish, the intensity of the colour decreasing progressively upon repeated sublimation and recrystallization. We believe that the HfO_2 contained an unidentified impurity which is responsible for this colour, and essentially complete removal of this impurity was accompanied by substantial loss of material. Compounds III to XIII are soluble in aromatic hydrocarbons, petrol ether and ether, the solubility of the spirane increasing with the amount of impurities present. Even small amounts depress the melting point of the spiranes below room

TABLE 1

PHYSICAL PROPERTIES AND NMR CHEMICAL SHIFTS

Compound	M.p. (°C)	B.p./subl.p. (°C)	^{1}H NMR (δ, ppm)			^{29}Si NMR (δ, ppm)				^{13}C NMR (δ, ppm)		
			$\mathrm{Si}(\mathrm{C}H_3)_2$	$\mathrm{Si}(\mathrm{C}H_3)_3$	$\mathrm{NHSi}(\mathrm{C}H_3)_3$ $\mathrm{Ge}(\mathrm{C}H_3)_2$	$Si\mathrm{C}_2$	$Si\mathrm{C}_3$	$\mathrm{NH}Si\mathrm{C}_3$	$Si\mathrm{N}_4$	$\mathrm{Si}C_2$	$\mathrm{Si}C_3$	$\mathrm{NHSi}C_3$
IIIa[a]	~ 0	70/10	0.32	0.08	–							
IIIc	39	15/0.1	0.21	0.12	–							
IV	17	64/1	0.24	0.14	–	−10.09	−10.09	–	−50.63	4.31	2.44	–
V	97	$45/10^{-3}$ 115/1	0.28	0.18	0.18	−10.09	−10.09	3.42	−53.89	4.57	2.68	2.68
VI	> 250	$35/10^{-3}$	0.32	0.19	–	−8.58	−9.38	–	−62.91	4.47	2.81	–
VII	43–44	$30/10^{-3}$	0.20	0.13	–	5.71	−3.12	–	–	4.15	2.03	–
VIII	41–42	$30/10^{-3}$	0.29	0.06	0.49							
IX	> 250	$40/10^{-3}$	0.31	0.20	–	5.31	−2.04	–	–	4.73	2.84	–
X	171	$60/10^{-2}$	0.50	0.37	–	1.17	8.28	–	–			
XI[b]	194	$70/5\times10^{-2}$	0.51	0.42	–	−38.7	−4.4	–	–			
XII	206	$70/10^{-2}$	0.54	0.31	–	−34.35	−7.18	–	–			
XIII	203	$70/10^{-2}$	0.60	0.39	–	−35.14	−5.71	–	–			
XIVa[c]			0.49	0.40	–							
XVa[d]			0.51	0.42	–							

[a] $\delta(^{19}\mathrm{F})$ −132.7 ppm. [b] Ref. 6, 18. [c] δ (^{1}H) OCH 3.33 (q), CCH 1.05 ppm (t). [d] δ (^{1}H) OCH 3.37 (q), CCH 1.08 ppm (t).

temperature, purified samples of VI and IX to XIII melting near 200°C. The insolubility of XIV and XV due to association has already been mentioned. The halides and the spiranes IX to XIII are sensitive to hydrolysis, generally giving I under basic conditions. By far the most stable species is VI, which can be recrystallized from boiling methanol or isopropanol without decomposition. In a sealed tube it sublimes at 250°C without melting or decomposition. It shares these unusual properties with the closely related species **C**.

Spectra

The ^{1}H NMR spectra of III to XIII are listed in Table 1. XIV and XV are not sufficiently soluble to permit determination the NMR spectra. ^{13}C, ^{19}F and ^{29}Si spectra were also recorded in relevant cases. The NMR spectra, which are very simple, confirm the constitution and purity of the compounds in question. The large ^{29}Si chemical shifts of the "inorganic" Si atom in IV–VI should be noted, as well as the dissimilarity of the shifts for the endocyclic $\mathit{Si}\mathrm{Me}_2$ and exocyclic $\mathit{Si}\mathrm{Me}_3$ atoms in XII and XIII, particularly in comparison with VI.

Typically the $[M-\mathrm{CH}_3{}^+]$ fragment is the base peak in the mass spectra (see Experimental); the M^+ ion appears with substantial intensity and its isotope pattern confirms the suggested constitution. The mass spectra are listed in the order of decreasing intensity.

Selected features of the IR and Raman spectra are given in Table 2, and an assignment is suggested. Figure 1 shows the spectrum of IX in the region < 1300 cm^{-1} as a typical example. The spectra are dominated by the group vibrations of the $\mathrm{Me_2Si}$ and $\mathrm{Me_3Si}$ fragments [12], but several bands attributable to vibrations of the substituents and the $\mathrm{M'N_4}$ [13] and $\mathrm{Si(NSi)_2M'}$ fragment [14] appear with considerable intensity, and are suitable for diagnostic purposes. In general, the spectra of the spiranes are quite insensitive to the nature of M′, and this may be expected from the orthogonality of the four-membered rings and the damping of vibrational motions by the heavy spiro center. Thus the comparison with the six skeletal stretching vibrations ω_1 to ω_6 of $\mathrm{Me_3Si(NSiMe_2)_2SiMe_3}$ [14] appears to be adequate, the doubling of the highest "SiN" stretching vibration in the spiranes being particularly remarkable. The Raman line near 1100 cm^{-1} ω_1, which is due to a "pseudo-asymmetric" exocyclic SiN stretching vibration, appears in a region which is unusually high for a SiN mode, but any other assignment can be ruled out. The intense Raman

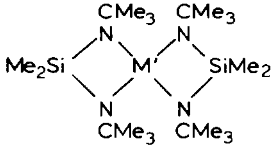
TABLE 2

DIAGNOSTIC SKELETAL VIBRATIONS OF SPIROCYCLIC GROUP IV ELEMENT AMIDES (cm^{-1})

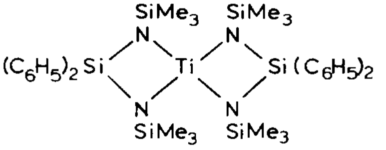
VI	IX	X	XI	XII	XIII	Assignment [c]
382 –/vs [a]	377 –/vs	370 –/vs	377 –/vs	372 –/vs	374 –/vs	ω_5
418 m/–	395 w/–	380 s/–	410 m/–	400 m/w	400 s/w	ω_6
520 m/–		425 –/w		429 m/m	431 w/–	ω_4
910 vs/–	884 sh/–	[b]	[b]	[b]	[b]	ω_2
1020 vs/–	991 vs/–	983 vs/–	990 vs/–	980 vs/–	980 vs/–	ω_1'
1120 vw/w	1095 –/m	1069 –/m	1070 –/m	1069 –/m	...	ω_1

[a] Relative intensities IR/Raman. [b] Blended by $\mathrm{SiCH_3}$ rocking vibration. [c] See text.

line near 375 cm^{-1} is probably associated with a symmetric breathing of the entire molecule. Some assignments for the monocyclic species are given in the experimental section.



M' = Sn(D), Ti(E), Zr(F)



(G)

Previous single crystal structural investigations of the related compounds **D** [15],

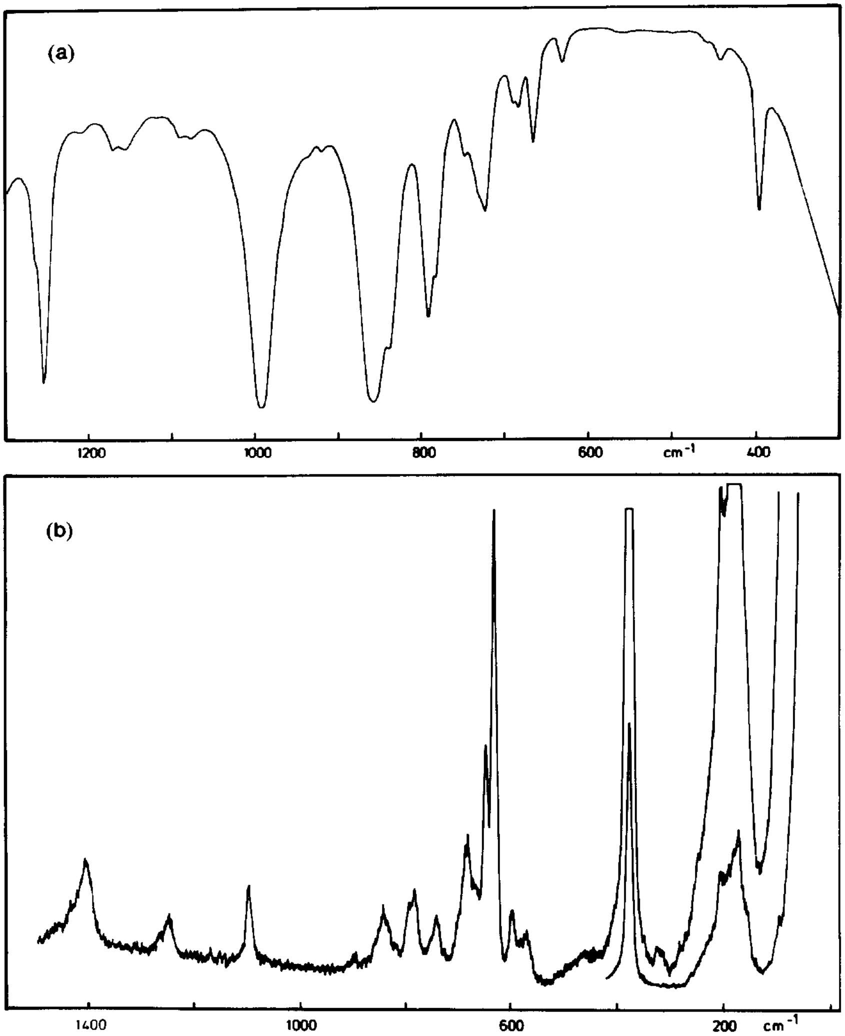


Fig. 1. Infrared (a) and Raman spectrum (b) of compound IX.

E, F [3] and G [16] revealed essentially D_{2d} symmetry for the spiroheptane fragment, the ring atoms in G deviating most (0.03 Å) from planarity. The NM′N angles, 76.4(2) (D), 83.4(2) (E), 77.9(1) (F) and 83.4(1)° (G) are the smallest ones within the four-membered rings, and apparently decrease with increasing M′N bond length. It is to be expected that, due to the short SiN distance and a NSiN bond angle close to 90°, the Me_3Si substituents of the orthogonal four-membered rings are close and build up a nearly spherical molecule with a methyl surface. The main properties of VI are easily understood in terms of the shape of the molecule, and it is not surprising that even compounds XI–XIII do not coordinate ether; this contrasts with the less perfectly shielded $M'C_2N_2$ fragment in the tricyclic $[(Me_3Si)_2NM'(CHSiMe_2)NSiMe_3]_2$, M′ = Zr, Hf, which adds one molecule pyridine per M′ atom [17].

Experimental

Synthesis

Compound I was prepared according to ref. 18 and metallated with LiBu [19] and $NaNH_2$ [4] respectively. The dilithio derivative II was preferentially used in solution. Compound IIIb was prepared according to ref. 10. The analytical data are given in Table 3.

1,3-Bis(trimethylsilyl)-2,2-difluoro-4,4-dimethyl-1,3-diaza-2,4-disila-cyclobutane (IIIa). 54 mmol SiF_4 are condensed into a solution of 10 g (36 mmol) disodiooctamethyltrisiladiazane in 150 ml petroleum ether in a stainless steel cylinder and the mixture heated at 100°C for several hours. The precipitate (Na_2SiF_6) is filtered off, the solvent removed in vacuo and the residue fractionally distilled; yield 40%.

1,3-Bis(trimethylsilyl)-2,2-dibromo-4,4-dimethyl-1,3-diaza-2,4-disila-cyclobutane (IIIc) was obtained as described for IIIb from II and $SiBr_4$ in a 2/1 ratio; yield 40%.

1,3-Bis(trimethylsilyl)-2,2-diamino-4,4-dimethyl-1,3-diaza-2,4-disila-cyclobutane (IV). A solution of 15.7 g (47 mmol) IIIb in 300 ml petroleum ether was treated at 0°C with dry gaseous NH_3. The NH_4Cl was filtered off and washed with petroleum ether. The solvent was removed from the combined filtrate and washings, and the residue fractionally distilled; yield 72%, n_D^{25} 1.4462.

MS: $m/e = 130\ (Me_2SiNSiMe_2)^+$, 43 $(MeSi)^+$, 277 $(M-15)^+$, 73 $(Me_3Si)^+$.

IR: 3500s ($\nu_{as}(NH_2)$), 3420s ($\nu_s\ (NH_2)$), 2955vs, 2899s, 1538s ($\delta(NH_2)$), 1440m, 1303m, 1252vs, 1035vs (ω_1), 935vs (ω_2), 865vs, 860s, 835s, 795vs, 782vs, 751m, 685vs, 640m, 505m (ω_4), 444s (ω_6).

1,3-Bis(trimethylsilyl)-2,2-bis(trimethylsilylamino)-4,4-dimethyl-1,3-diaza-2,4-disila-cyclobutane (V). A solution of 14.8 g (50 mmol) IV in 100 ml n-hexane is treated at 0°C with 100 mmol LiBu in n-hexane. Subsequently 10.9 g (100 mmol) Me_3SiCl is added. After several hours stirring, LiCl is filtered off (or separated with a centrifuge), the solvent removed in vacuo, and V isolated from the residue by sublimation in vacuo, yield 64%.

MS: $m/e = 421\ (M-15)^+$, 333 $(M - 2 \times 15 - Me_3Si)^+$, 275 $(M - (Me_3Si)_2NH)^+$, 436 M^+, 73 $(Me_3Si)^+$.

IR: 3379m ($\nu(NH)$), 2959vs, 2900m, 1440w, 1410w, 1252vs, 1211vs ($\delta(NH)$), 1025vs (ω_1), 969/945m (ν_{as} (SiNHSi)), 901vs (ω_2), 835vs, 781s, 750w, 682s, 641m, 607m, 588m (ν_s (SiNHSi)), 518m (ω_4), 452m (ω_6), 375m.

1,3,5,7-Tetrakis(trimethylsilyl)-2,2,6,6-tetramethyl-1,3,5,7-tetraaza-2,4,6-trisila-spiro-[3.3]heptane (VI). A mixture of 2.0 g (45 mmol) V in 40 ml THF with 90 mmol LiBu in n-hexane is heated under reflux for 4 h, then 0.59 g (45 mmol) Me_2SiCl_2 is added. After refluxing for 1 h the solvent is removed in vacuo, 50 ml petroleum ether are added, and the LiCl removed by centrifugation. The solvent is evaporated off in vacuo, and VI isolated from the residue by sublimation in vacuo, yield 75%.

MS: $m/e = 477$ $(M-15)^+$, 231 $(M-2\times15)^{2+}$, 462 $(M-2\times15)^+$, 492 M^+, 447 $(M-3\times15)^+$.

1,3-Bis(trimethylsilyl)-2,2-dichloro-4,4-dimethyl-1,3-diaza-2-germa-4-sila-cyclobutane (VII). Made as described for IIIb [10] from I, LiBu and $GeCl_4$, and isolated by sublimation in vacuo, yield 68%.

MS: m/e (^{74}Ge,^{35}Cl): 361 $(M-15)^+$, 341 $(M-Cl)^+$, 73 $(Me_3Si)^+$, 376 M^+.

IR: 1256vs, 988vs (ω_1), 890vs (ω_2), 851vs, 797s, 752m, 691m, 663m, 633w, 462m, 425vs (ν_{as} ($GeCl_2$)).

TABLE 3

ELEMENTAL ANALYSES

	Molecular formula	Analyses (Found (calcd.) (%))				
		C	H	N		
IIIa	$C_8H_{24}F_2N_2Si_4$	31.47	8.00	9.38		
		(32.18)	(8.10)	(9.38)		
IIIc	$C_8H_{24}Br_2N_2Si_4$	22.22	5.79	6.60	Br 37.23	
		(22.85)	(5.75)	(6.66)	(38.00)	
IV	$C_8H_{28}N_4Si_4$	32.40	9.51	18.99		
		(32.83)	(9.64)	(19.14)		
V	$C_{14}H_{44}N_4Si_6$	38.60	10.17	12.65		
		(38.48)	(10.15)	(12.82)		
VI	$C_{16}H_{48}N_4Si_7$	38.19	9.78	11.18		
		(38.97)	(9.81)	(11.36)		
VII	$C_8H_{24}Cl_2GeN_2Si_3$	25.46	6.43	7.46	Cl 18.79	
		(25.55)	(6.43)	(7.45)	(18.85)	
VIII	$C_{10}H_{30}GeN_2Si_3$			8.45		
				(8.36)		
IX	$C_{16}H_{48}GeN_4Si_6$	36.21	9.06	10.04		
		(35.74)	(9.00)	(10.42)		
X	$C_{16}H_{48}N_4Si_6Sn$			9.60	Sn 19.89	
				(9.60)	(20.33)	
XII	$C_{16}H_{48}N_4Si_6Zr$	34.03	8.56	10.07	Zr 16.18	
		(34.54)	(8.70)	(10.07)	(16.40)	
XIII	$C_{16}H_{48}HfN_4Si_6$			8.64	Hf 27.02	
				(8.71)	(27.73)	
XIV	$C_8H_{24}Cl_2N_2Si_3Zr$	24.11	6.15	6.57	Zr 23.00	Cl 17.94
		(24.35)	(6.13)	(7.10)	(23.11)	(17.97)
XIVa	$C_{12}H_{34}Cl_2N_2OSi_3Zr$			5.90	Zr 19.02	Cl 15.10
				(5.97)	(19.46)	(15.12)
XV	$C_8H_{24}Cl_2HfN_2Si_3$			6.05	Cl 14.65	
				(5.81)	(14.71)	
XVa	$C_{12}H_{34}Cl_2HfN_2OSi_3$			5.00	Cl 12.48	
				(5.04)	(12.75)	

1,3-Bis(trimethylsilyl)-2,2,4,4-tetramethyl-1,3-diaza-2-germa-4-sila-cyclobutane (VIII). To a solution prepared from 0.65 g (27 mmol) Mg and 1.89 g (27 mmol) MeI in 70 ml Et_2O, are added 5 g (13.3 mmol) VII. Work up gives a 71% yield.

MS: m/e (^{74}Ge): 130 $(Me_2SiNSiMe_2)^+$, 321 $(M-15)^+$.

IR: 1249vs, 1005vs (ω_1), 881vs (ω_2), 845 vs, 791vs, 749w, 682s, 652s, 608m, 581w (ν(GeC)), 396s (ω_6).

1,3,5,7-Tetrakis(trimethylsilyl)-2,2,6,6-tetramethyl-1,3,5,7-tetraaza-2,6-disila-4-germa-spiro[3.3]heptane (IX). 4 g (17 mmol) I in 100 ml petroleum ether and 50 ml THF was metallated with LiBu. The solution was treated with 1.82 g (8.5 mmol) $GeCl_4$ in 50 ml petroleum ether, and the mixture was refluxed for 1 h. After filtration, the solvent was removed in vacuo and the residue fractionally sublimed in vacuo, yield 14%.

MS: m/e (^{74}Ge) 523 $(M-15)^+$, 130 $(Me_2SiNSiMe_2)^+$, 538 M^+.

Analogous: 1,3,5,7-Tetrakis(trimethylsilyl)-2,2,6,6-tetramethyl-1,3,5,7-tetraaza-2,6-disila-4-stanna-spiro[3.3]heptane (X). Yield 60%. MS: m/e (^{120}Sn) 569 $(M-15)^+$, 130 $(Me_2SiNSiMe_2)^+$, 73 $(Me_3Si)^+$, 584 M^+.

1,3,5,7-Tetrakis(trimethylsilyl)-2,2,6,6-tetramethyl-1,3,5,7-tetraaza-2,6-disila-4-zircona-spiro[3.3] heptane (XII). Yield 77%.

MS: m/e (^{90}Zr): 524 $(M-2\times15)^+$, 539 $(M-15)^+$, 130 $(Me_2SiNSiMe_2)^+$, 73 $(Me_3Si)^+$, 554 M^+.

1,3,5,7-Tetrakis(trimethylsilyl)-2,2,6,6-tetramethyl-1,3,5,7-tetraaza-2,6-disila-4-hafna-spiro[3.3]heptane (XIII). Yield 82%.

1,3-Bis(trimethylsilyl)-2,2-dichloro-4,4-dimethyl-1,3-diaza-2-zircona-4-sila-cyclobutane (XIV). An equimolar amount of XII is added to $ZrCl_4$ dissolved in 10/1 toluene/Et_2O. The solvent is removed in vacuo; quantitative yield.

MS: m/e (^{90}Zr, ^{35}Cl): 377 $(M-15)^+$, 130 $(Me_2SiNSiMe_2)^+$, 73 $(Me_3Si)^+$, 392 M^+ (rel. intensity 5% of 377 peak).

Analogous: 1,3-Bis(trimethylsilyl)-2,2-dichloro-4,4-dimethyl-1,3-diaza-2-hafna-4-sila-cyclobutane (XV).

Diethyletherates $XIV\cdot Et_2O$ (XIVa) and $XV\cdot Et_2O$ (XVa). XIV and XV are dissolved in Et_2O and the solvent removed in vacuo. The 1/1 adducts are obtained in quantitative yield.

Spectra

^{1}H NMR: Varian EM 390, 90 MHz, ≤ 20% in C_6D_6, TMS as internal standard. ^{19}F NMR: Varian EM 390, 84.67 MHz, ≤ 20% in C_6D_6, $CFCl_3$ as internal standard. ^{13}C NMR: Varian FT 80, 20.0 MHz, C_6D_6 as solvent and internal standard, δ 127.96 ppm. ^{29}Si NMR: Varian FT 80, 15.80 MHz, ≤ 50% in C_6D_6, internal standard TMS.

IR: Nujol mulls or neat, 300–4000 cm^{-1}, Perkin–Elmer 580 B. Raman: Crystalline material in 1 mm o. d. capillaries, Cary 82, Kr^+ 6471 Å excitation.

MS: Varian MAT 311, EI, 70 eV.

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