Synthesis and Characterization of Group 14 1-Haloazametallatranes

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The reaction between $MHal_4$ (M = Ge, Sn; Hal = Cl, Br) and $N(CH_2CH_2NRLi)_3$ (R = Me, $SiMe_3$) yields 1-haloazametallatranes **1**–**8**, $N(CH_2CH_2NR)_3M$–Hal (**1**, M = Ge, Hal = Cl, R = Me; **2**, M = Ge, Hal = Br, R = Me; **3**, M = Ge, Hal = Cl, R = $SiMe_3$; **4**, M = Ge, Hal = Br, R = $SiMe_3$; **5**, M = Sn, Hal = Cl, R = Me; **6**, M = Sn, Hal = Br, R = Me; **7**, M = Sn, Hal = Cl, R = $SiMe_3$; **8**, M = Sn, Hal = Br, R = $SiMe_3$). The composition and structures of the new compounds were established by elemental analyses, ^1H and ^{13}C NMR spectroscopy and mass spectrometry. Single crystal structures of **1** and **3** were determined by X-ray diffraction studies: both compounds show transannular Ge–N_{ax} interactions.
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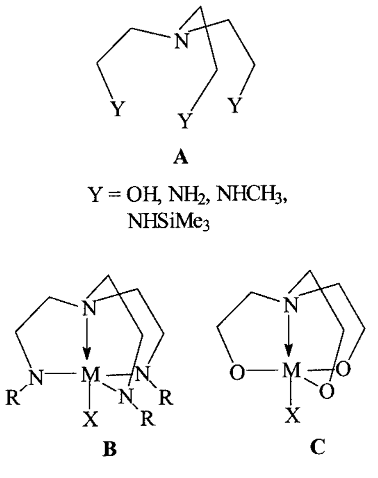
Introduction

The chemistry of pentacoordinate complexes of the group 14 elements has attracted much attention, mostly from a theoretical point of view, with the nature of the intramolecular interaction the main subject of interest.[1−4] In addition, these species are ideal models for the investigation of nucleophilic substitution pathways in group 14 element chemistry.[5] During the last decade we have focussed our research interests on metallatranes containing symmetrical tripodal ligands of type **A** (Scheme 1).[4,6−10]



Scheme 1

Metal derivatives of tripodal amines — azametallatranes (type **B**) — have greater chemical and structural flexibility than the "usual" metallatranes (type **C**) due to the influence of various substituents R (for example, R = H, Me, $SiAlk_3$, C_6F_5 etc.) on the structure and the chemical properties of these derivatives. Although azasilatranes have been known for some twenty years,[2] azagermatranes and azastannatranes are compounds which have been very little studied.[11−19]

Compounds containing an $SiAlk_3$ group apart from the equatorial nitrogen atoms (N_{eq}) of the azatrane skeleton are the subject of special interest among the group 14 element azametallatranes (**B**). Due to the extremely long Si−N_{ax} distance in the only structurally characterized example $[N(CH_2CH_2NSiMe_3)_3Si-CH_3]$[20] Verkade et al. coined the term "*quasi-azasilatranes*" for these rare silicon species.[2] The corresponding azastannatranes (**B**, R = $SiMe_3$) are as yet unknown and for germanium only $N(CH_2CH_2NSiMe_3)_3Ge$−allyl has been reported amongst the $N(CH_2CH_2NSiMe_3)_3Ge$−X derivatives prior to this work.[12]

In this paper we report on the synthesis of 1-haloazametallatranes (M = Ge, Sn) by metathetical exchange reactions between $MHal_4$ (M = Ge, Sn; Hal = Cl, Br) and the trilithium salts of the parent amines $N(CH_2CH_2NHMe)_3$ (Me_3-tren) and $N(CH_2CH_2NHSiMe_3)_3$ (TMS_3-tren). Details of the X-ray crystal and molecular structures of $N(CH_2CH_2NMe)_3GeCl$ (**1**) and $N(CH_2CH_2NSiMe_3)_3GeCl$ (**3**) are also described.

Results and Discussion

Our aim was to obtain 1-haloazametallatranes as precursors for further synthetic applications and to find a new

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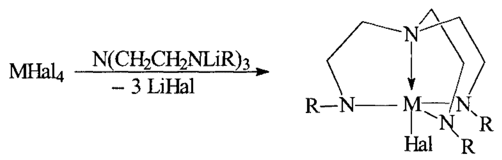
improved method of preparation for azametallatranes of group 14 elements. 1-Haloazatranes of group 14 elements are those bearing reactive apical groups which have the possibility for further derivatization at the metal centre. Verkade et al. reported only a relatively complicated multistep procedure involving $N(CH_2CH_2NMe)_3Si{-}H$ and $N(CH_2CH_2NMe)_3Sn{-}NMe_2$ as intermediate products leading finally to 1-chloro-*N*,*N′*,*N′′*-trimethylazasilatranes and 1-chloro(bromo)-*N*,*N′*,*N′′*-trimethylazastannatranes.[16,21] We prepared azagermatranes **1** and **2** by transamination reactions of $HalGe(NMe_2)_3$ with Me_3-tren.[13]

Another method for building the main group element azatrane framework was previously only used for transition metals.[22] Tetrahalides (Hal = Cl, Br) of germanium and tin react readily with the trilithium salts of Me_3-tren and TMS_3-tren (in toluene at room temperature) to give 1-haloazametallatranes **1**−**8** in high yield (Scheme 2). The derivatives with Me_3-tren were purified by recrystallization from toluene/*n*-pentane while those of TMS_3-tren were purified by recrystallization from *n*-pentane. Lithium salts of Me_3-tren and TMS_3-tren are conveniently generated in situ by treatment of Me_3-tren or TMS_3-tren with the equivalent amount of *n*BuLi.



M = Ge; **1**, R = Me, Hal = Cl; **2**, R = Me, Hal = Br
3, R = $SiMe_3$, Hal = Cl; **4**, R = $SiMe_3$, Hal = Br
M = Sn; **5**, R = Me, Hal = Cl; **6**, R = Me, Hal = Br
7, R = $SiMe_3$, Hal = Cl; **8**, R = $SiMe_3$, Hal = Br

Scheme 2

The structures of **1**−**8** were confirmed by ^1H and ^{13}C NMR spectroscopy. In the ^1H NMR spectra of **1**−**8** the signals of the methylene protons of the azatrane skeleton appear as a set of two pseudo-triplets, forming an AA′BB′ spin system. This pattern is a general feature of the "atrane" framework for a variety of metallatranes.[1,2,4]

The reaction of silicon derivatives ($SiCl_4$, $SiBr_4$) with lithium salts of Me_3-tren and TMS_3-tren resulted in unidentifiable polymeric products.

To the best of our knowledge, compounds **1** and **3** (Figure 1 and 2, respectively) are the first structurally characterized azagermatranes. Molecules of **1** lie on a crystallographic threefold axis, while molecules of **3** possess approximate C_3 symmetry. The coordination polyhedron of the germanium atom in both compounds is a distorted trigonal bipyramid with the N(4) [for compound **3**; N(1) for compound **1**] and Cl atoms in the axial positions and the three nitrogen atoms in equatorial sites. The germanium atoms are displaced by 0.25 Å (for **3**) and by 0.22 Å (for **1**) from a plane defined by the three equatorial nitrogen atoms towards the chlorine substituent. The $N_{ax}{-}Ge{-}Cl$ angles are exactly 180° for **1** and 179.53(7)° for **3**. The Ge−Cl distances observed in **3** [2.2727(8) Å] and in **1** [2.2968(9) Å] are significantly longer than in the closely related 1-chlorogermatrane $N(CH_2CH_2O)_3Ge{-}Cl$ (**9**) [2.209(1) Å].[23] The $Ge{-}N_{ax}$ bonds [2.278(2) Å for **3** and 2.167(4) Å for **1**] are also longer than in **9** [2.096(3) Å]. Thus, a formal substitution of the oxygen atom in molecule **9** by a NCH_3 group (molecule **1**) results in a simultaneous increase of the Ge−Cl and $Ge{-}N_{ax}$ distances by 0.088 Å and 0.051 Å, respectively. With the same formal substitution in silatranes this leads to the opposite change in the Si−X and $Si{-}N_{ax}$ bond lengths, as found previously for the compounds $N(CH_2CH_2O)_3Si{-}OEt$ [$d(Si{-}O_{ax})$ = 1.699(2) Å, $d(Si{-}N_{ax})$ = 2.135(2) Å] and $N(CH_2CH_2NMe)_3Si{-}OEt$

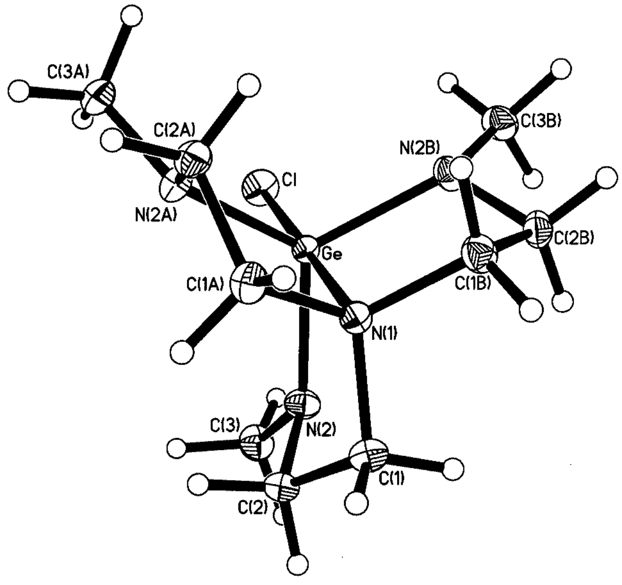


Figure 1. Molecular structure of compound **1**

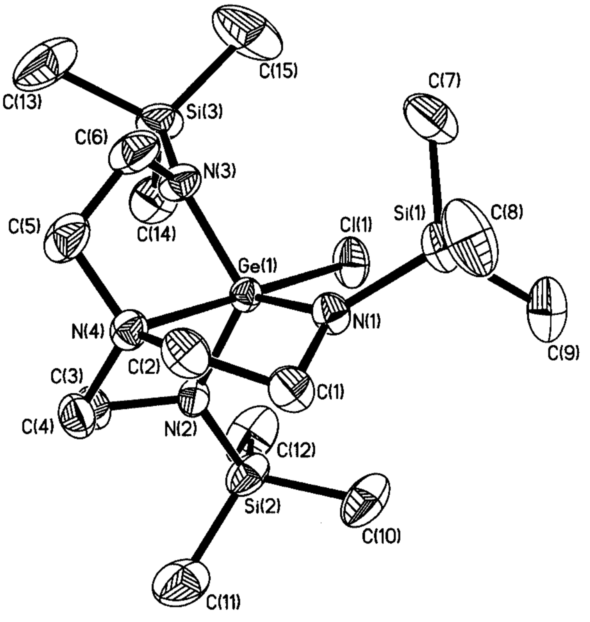


Figure 2. Molecular structure of compound **3**; hydrogen atoms have been omitted for clarity

[d(Si−O_{ax}) = 1.658 Å, d(Si−N_{ax}) = 2.152 Å (averaged for two independent molecules)].[24,25] The Ge−N_{ax} distance in **3** [2.278(2) Å] lies within the typical range for germatranes [2.081(5)−2.32(1) Å][26,27] and clearly verifies the existence of a Ge−N transannular bond in **3**. In contrast, the Si analogue of **3**, $N(CH_2CH_2NSiMe_3)_3Si-CH_3$, possesses an extremely long Si−N_{ax} bond [2.775(7) Å].[20] The Ge−N_{ax} bond length in **1** [2.167(4) Å] is noticeably shorter than that in **3** [2.278(2) Å]; the Ge−N_{eq} distances are 1.837(2) Å, 1.838(2) Å and 1.838(2) Å for **3** and 1.858(1) Å for **1**.

The environment at the N_{ax} atoms is approximately tetrahedral with C−N_{ax}−C and C−N_{ax}−Ge angles ranging between 104.1(2)° and 114.4(3)° for **3** and 106.3(2)° and 112.5(2)° for **1**. The axial nitrogen atoms are displaced by 0.37 Å (for **3**) and by 0.42 Å (for **1**) from a plane defined by the three carbon atoms towards germanium.

All five-membered rings of the atrane skeleton in **1** and **3** adopt an "envelope"-like conformation; for both **1** and **3** all carbon atoms in the positions β to the N_{ax} atom occupy "flap" sites, while the C-α atoms form the base of an envelope plane, the latter being unusual for germatranes without C-β substituents.[9]

Conclusion

In summary, metathetical exchange reactions between $MHal_4$ (M = Ge, Sn; Hal = Cl, Br) and the lithiated parent amines afford compounds **1**−**8** in good yields. The presence of a transannular Ge←N interaction in **1** and **3** was confirmed by X-ray diffraction analyses. Further studies on the application of this reaction for the synthesis of main group element azametallatranes and an investigation of their chemical behaviour are in progress.

Experimental Section

General Remarks: All manipulations were performed under dry, oxygen-free argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. $MHal_4$ (M = Si, Ge, Sn; Hal = Cl, Br) (Aldrich) were used as supplied. Starting materials Me_3-tren[28] and TMS_3-tren[12] were prepared according to the literature. C_6D_6 was obtained from Deutero GmbH and dried over sodium. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC200 spectrometer. ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University and by that of the Fachbereich Chemie of the Philipps-University of Marburg (Heraeus-Rapid-Analyser). Mass spectra (EI-MS) were recorded on a VARIAN CH-7a device using electron impact ionization at 70 eV; mass spectra (FD-MS) were recorded on a HP-5989B device; all assignments were made with reference to the most abundant isotopes.

1-Chloro-*N*,*N*′,*N*′′-trimethylazagermatrane (1): A 1.6 M *n*BuLi solution (4.88 mL, 7.8 mmol) in hexane at room temperature was added dropwise to a stirred solution of Me_3-tren (0.48 g, 2.6 mmol) in 40 mL of toluene. The reaction mixture was stirred for 5 h and a solution of $GeCl_4$ (0.55 g, 2.6 mmol) in 10 mL of toluene was added dropwise at room temperature. After stirring for a further 24 h a white precipitate of LiCl was filtered off. Most of the volatiles were then evaporated in vacuo and 10 mL of *n*-pentane was added. A white crystalline solid was separated by filtration, washed with cold *n*-pentane (3 × 5 mL) and dried in vacuo. Yield: 0.50 g (65%). ^1H NMR and ^{13}C NMR spectroscopic data were consistent with those already reported.[13]

1-Bromo-*N*,*N*′,*N*′′-trimethylazagermatrane (2): Following the same experimental procedure as above for **1** using Me_3-tren (0.50 g, 2.7 mmol), a 1.6 M *n*BuLi solution in hexane (5.06 mL, 8.1 mmol) and $GeBr_4$ (1.04 g, 2.7 mmol), colourless crystals (0.63 g, 69%) were obtained. ^1H NMR, ^{13}C NMR and EI MS data were consistent with those already reported.[13]

1-Chloro-*N*,*N*′,*N*′′-tris(trimethylsilyl)azagermatrane (3): A 1.6 M *n*BuLi solution in hexane (4.67 mL, 7.5 mmol) at room temperature was added dropwise to a stirred solution of TMS_3-tren (0.90 g, 2.5 mmol) in 40 mL of toluene. The reaction mixture was stirred for 5 h and a solution of $GeCl_4$ (0.53 g, 2.5 mmol) in 10 mL of toluene was added dropwise at room temperature. The mixture was stirred for another 24 h. Removal of all volatiles in vacuo followed by extraction of the residue with 20 mL of *n*-pentane gave a yellowish extract. The solution was reduced in volume by 50% and stored at −30 °C to obtain colourless crystals **3** (0.81 g, 70%). ^1H NMR (C_6D_6, 200.13 MHz): δ = 0.40 (s, 27 H, $SiCH_3$), 1.81 (t, ^1J = 6 Hz, 6 H, CH_2N), 2.59 (t, ^1J = 6 Hz, 6 H, CH_2NSi) ppm. ^{13}C NMR (C_6D_6, 50.32 MHz): δ = 2.41 ($SiCH_3$), 41.03 (CH_2N), 58.79 (CH_2NSi) ppm. EI MS: m/z (%) = 468 (13) [M^+], 453 (21) [$M^+ - CH_3$], 433 (7) [M^+ − Cl], 367 (100) [$M^+ - Me_3SiNCH_2$], 353 (17) [$M^+ - Me_3SiNCH_2CH_2$]. $C_{15}H_{39}ClGeN_4Si_3$ (467.8): calcd. C 38.51, H 8.40, N 11.98; found C 38.21, H 8.63, N 11.73.

1-Bromo-*N*,*N*′,*N*′′-tris(trimethylsilyl)azagermatrane (4): Using the same experimental procedure as above for **3** employing TMS_3-tren (1.85 g, 5.1 mmol), 9.56 mL of a 1.6 M *n*BuLi solution (15.3 mmol) in hexane and $GeBr_4$ (2.00 g, 5.1 mmol), colourless crystals **4** (1.72 g, 66%) were obtained from an *n*-pentane solution at −30 °C. ^1H NMR (C_6D_6, 200.13 MHz): δ = 0.43 (s, 27 H, $SiCH_3$), 1.82 (t, ^1J = 6 Hz, 6 H, CH_2N), 2.59 (t, ^1J = 6 Hz, 6 H, CH_2NSi) ppm. ^{13}C NMR (C_6D_6, 50.32 MHz): δ = 2.63 ($SiCH_3$), 41.34 (CH_2N), 59.14 (CH_2NSi). FD-MS: m/z (%) = 512 (21) [M^+], 433 (100) [M^+ − Br]. $C_{15}H_{39}BrGeN_4Si_3$ (512.3): calcd. C 35.17, H 7.67, N 10.94; found C 35.43, H 7.49, N 11.15.

1-Chloro-*N*,*N*′,*N*′′-trimethylazastannatrane (5): The procedure was analogous to that for **1**: reaction of Me_3-tren (1.06 g, 5.6 mmol) with 10.56 mL of a 1.6 M *n*BuLi solution (16.9 mmol) in hexane and then with $SnCl_4$ (1.46 g, 5.60 mmol) gave **5** as a white crystalline solid. Yield: 1.31 g (69%). ^1H NMR and ^{13}C NMR spectroscopic data were consistent with those already reported.[16]

1-Bromo-*N*,*N*′,*N*′′-trimethylazastannatrane (6): The procedure was analogous to that for **1**: reaction of Me_3-tren (1.77 g, 9.4 mmol) with 17.63 mL of a 1.6 M *n*BuLi solution (28.2 mmol) in hexane and then with $SnBr_4$ (4.12 g, 9.4 mmol) gave **6** as a white crystalline solid. Yield: 2.58 g (71%). ^1H NMR and ^{13}C NMR spectroscopic data were consistent with those already reported.[16]

1-Chloro-*N*,*N*′,*N*′′-tris(trimethylsilyl)azastannatrane (7): The procedure was analogous to that for **3**: reaction of TMS_3-tren (0.93 g, 2.6 mmol) with 4.81 mL of a 1.6 M *n*BuLi solution (7.7 mmol) in hexane and then with $SnCl_4$ (0.68 g, 2.6 mmol) gave **7** as a white crystalline solid. Yield: 0.84 g (63%). ^1H NMR (C_6D_6, 200.13 MHz): δ = 0.38 (s, 27 H, $SiCH_3$), 1.81 (t, ^1J = 6 Hz, 6 H, CH_2N), 2.71 (t, ^1J = 6 Hz, 6 H, CH_2NSi) ppm. ^{13}C NMR (C_6D_6,

Table 1. Crystal data, data collection, structure solution and refinement parameters for **1** and **3**

Compound	**1**	**3**
Empirical formula	$C_9H_{21}Cl_1Ge_1N_4$	$C_{15}H_{39}Cl_1Ge_1N_4Si_3$
Molecular weight	293.34	467.81
Colour, habit	Colorless block	Colorless prism
Crystal size [mm]	0.60 × 0.30 × 0.30	0.36 × 0.24 × 0.18
Crystal system	Trigonal	Monoclinic
Space group	$R3c$	$P2_1/c$
a [Å]	11.2754(2)	16.341(1)
b [Å]		10.081(1)
c [Å]	16.5461(4)	15.144(1)
β [°]		93.76(1)
Volume [Å^3]	1821.75(6)	2489.4(3)
Z	6	4
Density (calcd.)[g·cm^{-3}]	1.604	1.248
Absorption coefficient [mm^{-1}]	2.718	1.488
F(000)	912	992
Diffractometer	Bruker SMART CCD	Enraf Nonius CAD4
Temperature [K]	100.0(2)	203(2)
Radiation [λ/Å]	graphite-monochromated Mo-K_α (0.71073)	
θ range [°]	3.23 to 27.49	2.38 to 24.99
Index ranges	$-14 \le h \le 14$ $-14 \le k \le 14$ $-21 \le l \le 21$	$-19 \le h \le 0$ $-11 \le k \le 0$ $-17 \le l \le 18$
Reflections collected	6253	4401
Independent reflections	934 [R_{int} = 0.0316]	3994 [R_{int} = 0.0500]
Data reduction	Bruker SAINT[29]	XCAD4[30]
Absorption correction type	Empirical	Empirical
Min. and Max. transmission	0.2028 and 0.3508	0.6163 and 0.7755
Solution method	Direct methods (SHELXS-97)[31]	
Refinement method	Full-matrix least-squares on F^2 (SHELXL-97)[32]	
Hydrogen treatment	Isotropic refinement	Riding model
Data/restraints/parameters	934/1/75	3994/0/227
Reflections with $I > 2\sigma(I)$	906	3301
Goodness-of-fit on F^2	1.033	1.018
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0135$, $wR2 = 0.0358$	$R1 = 0.0338$, $wR2 = 0.0797$
R indices (all data)	$R1 = 0.0142$, $wR2 = 0.0364$	$R1 = 0.0468$, $wR2 = 0.0858$
Absolute structure parameter	−0.005(8)	−
Extinction coefficient	0.0007(2)	0.0004(2)
Largest diff. peak and hole [e Å^{-3}]	0.382 and −0.183	0.303 and −0.465

50.32 MHz): δ = 2.57 ($SiCH_3$), 41.17 (CH_2N), 59.27 (CH_2NSi) ppm. $C_{15}H_{39}ClN_4Si_3Sn$ (513.9): calcd. C 35.06, H 7.65, N 10.90; found C 35.27, H 7.94, N 10.79.

1-Bromo-*N*,*N*′,*N*′′-tris(trimethylsilyl)azastannatrane (8): The procedure was analogous to that for **3**: reaction of TMS_3-tren (2.65 g, 7.3 mmol) with 13.70 mL of a 1.6 M *n*BuLi solution (21.9 mmol) in hexane and then with $SnBr_4$ (3.21 g, 7.3 mmol) gave **8** as a white crystalline solid. Yield: 2.81 g (69%). ^1H NMR (C_6D_6, 300.13 MHz): δ = 0.40 (s, 27 H, $SiCH_3$), 1.83 (t, ^1J = 6 Hz, 6 H, CH_2N), 2.71 (t, ^1J = 6 Hz, 6 H, CH_2NSi) ppm. ^{13}C NMR (C_6D_6, 50.32 MHz): δ = 2.83 ($SiCH_3$), 41.39 (CH_2N), 59.76 (CH_2NSi) ppm. EI MS: *m*/*z* (%) = 479 (1.03) [$M^+ - Br$], 443 (4.30) [$M^+ - Me_3SiNCH_2CH_2$], 364 (7.15) [$M^+ - Br - Me_3SiNCH_2CH_2$]. $C_{15}H_{39}BrN_4Si_3Sn$ (558.4): calcd. C 32.27, H 7.04, N 10.03; found C 31.85, H 7.26, N 9.82.

Attempted Syntheses of $N(CH_2CHNR)_3Si-Hal$: Reactions of trilithium salts of Me_3-tren and TMS_3-tren with $SiCl_4$ and $SiBr_4$ were carried out as for **1** and **3**, respectively, resulting (according to ^1H NMR spectra) in a complex mixture of products which were difficult to separate and to identify.

X-ray Crystallographic Study: Crystal data, data collection, structure solution and refinement parameters for compounds **1** and **3** are presented in Table 1.

CCDC-178804 (**1**) and -184337 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] M. G. Voronkov, V. M. D'yakov, S. V. Kirpichenko, *J. Organomet. Chem.* **1982**, *233*, 1−147.
[2] J. G. Verkade, *Coord. Chem. Rev.* **1994**, *137*, 233−295.

[3] V. Pestunovich, S. Kirpichenko, M. Voronkov, in *The Chemistry of Organic Silicon Compounds* (Ed.: Z. Rappoport, Y. Apeloig), John Wiley & Sons, **1998**, volume 2, part 1, chapter 24.
[4] S. S. Karlov, G. S. Zaitseva, *Chem. Heterocycl. Comp.* **2001**, *37*, 1325−1357.
[5] C. Chuit, R. J. P. Corriu, C. Reye, J. C. Young, *Chem. Rev.* **1993**, *93*, 1371−1448.
[6] M. Nasim, L. I. Livantsova, G. S. Zaitseva, J. Lorberth, *J. Organomet. Chem.* **1991**, *403*, 85−91.
[7] G. S. Zaitseva, L. I. Livantsova, M. Nasim, S. S. Karlov, A. V. Churakov, J. A. K. Howard, E. V. Avtomonov, J. Lorberth, *Chem. Ber./Recueil* **1997**, *130*, 739−746.
[8] G. S. Zaitseva, S. S. Karlov, A. V. Churakov, J. A. K. Howard, E. V. Avtomonov, J. Lorberth, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1144−1150.
[9] G. S. Zaitseva, S. S. Karlov, B. A. Siggelkow, E. V. Avtomonov, A. V. Churakov, J. A. K. Howard, J. Lorberth, *Z. Naturforsch., Teil B* **1998**, *53*, 1247−1254.
[10] G. S. Zaitseva, S. S. Karlov, G. V. Pen'kovoy, A. V. Churakov, J. A. K. Howard, B. A. Siggelkow, E. V. Avtomonov, J. Lorberth, *Z. Anorg. Allg. Chem.* **1999**, *625*, 655−660.
[11] Y. Wan, J. G. Verkade, *Inorg. Chem.* **1993**, *32*, 79−81.
[12] G. S. Zaitseva, B. A. Siggelkow, S. S. Karlov, G. V. Pen'kovoy, J. Lorberth, *Z. Naturforsch., Teil B* **1998**, *53*, 1255−1258.
[13] P. L. Shutov, S. S. Karlov, J. Lorberth, G. S. Zaitseva, *Z. Naturforsch., Teil B* **2001**, *56*, 137−140.
[14] A. Tzschach, K. Jurkschat, C. Mugge, *Z. Anorg. Allg. Chem.* **1982**, *492*, 135−138.
[15] W. Plass, J. G. Verkade, *Inorg. Chem.* **1993**, *32*, 5145−5152.
[16] W. Plass, J. G. Verkade, *Inorg. Chem.* **1993**, *32*, 5153−5159.
[17] W. Plass, J. Pinkas, J. G. Verkade, *Inorg. Chem.* **1997**, *36*, 1973−1978.
[18] W. Plass, J. G. Verkade, *J. Am. Chem. Soc.* **1992**, *114*, 2275−2276.
[19] W. Plass, J. G. Verkade, *Inorg. Chem.* **1993**, *32*, 3762−3765.
[20] D. Gudat, L. M. Daniels, J. G. Verkade, *J. Am. Chem. Soc.* **1989**, *111*, 8520−8522.
[21] Y. Wan, J. G. Verkade, *J. Am. Chem. Soc.* **1995**, *117*, 141−156.
[22] R. R. Schrock, *Acc. Chem. Res.* **1997**, *30*, 9−16.
[23] R. Eujen, E. Petrauskas, A. Roth, D. J. Brauer, *J. Organomet. Chem.* **2000**, *613*, 86−92.
[24] R. J. Garant, L. M. Daniels, S. K. Das, M. N. Janakiraman, R. A. Jacobson, J. G. Verkade, *J. Am. Chem. Soc.* **1991**, *113*, 5728−5735.
[25] D. Gudat, J. G. Verkade, *Organometallics* **1989**, *8*, 2772−2779.
[26] S. P. Narula, S. Soni, R. Shankar, R. K. Chadha, *J. Chem. Soc., Dalton Trans.* **1992**, 3055−3056.
[27] S. N. Gurkova, S. N. Tandura, A. V. Kisin, A. I. Gusev, N. V. Alekseev, T. K. Gar, N. Yu. Khromova, I. R. Segel'man, *Zh. Strukt. Khim.* **1982**, *23*, 101−106.
[28] H. Schmidt, C. Lensink, S. K. Xi, J. G. Verkade, *Z. Anorg. Allg. Chem.* **1989**, *578*, 75−80.
[29] *SAINT Version 5.0.,* Bruker AXS Inc., Madison, Wisconsin, USA, **1997**.
[30] K. Harms, *XCAD4, Program for the Lp-Correction of Nonius CAD4 Data*, Marburg, Germany, **1997**.
[31] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.
[32] G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

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