

Hexa(1-alkynyl)disilanes. Synthesis, structure and 1,1-ethylboration

Bernd Wrackmeyer*, Wolfgang Milius, Amin Badshah¹

Laboratorium für Anorganische Chemie II, Universität Bayreuth, Universitätsstr. 30, NW 1, D-95440 Bayreuth, Germany

Received 26 February 2002; accepted 9 April 2002

Abstract

The reaction of hexachlorodisilane, Si_2Cl_6 , with six equivalents of lithium alkynides, $\text{Li}-\text{C}\equiv\text{C}-\text{R}$ ($\text{R} = \text{Bu}$, SiMe_3) led to hexa(1-alkynyl)disilanes $\text{Si}_2(\text{C}\equiv\text{C}-\text{R})_6$ [$\text{R} = \text{Bu}$ (**1**), Me_3Si (**2**)], whereas the reaction with the propynide $\text{Li}-\text{C}\equiv\text{C}-\text{Me}$, under analogous conditions, afforded only tetra(1-propynyl)silane, $\text{Si}(\text{C}\equiv\text{C}-\text{Me})_4$ **3**. The molecular structures of **2** and **3** were determined by X-ray analysis. Surprisingly, in the course of 1,1-ethylboration of the disilanes **1** and **2** the Si–Si bond is cleaved and finally monosilanes such as the substituted 5-silaspiro[4.4]nona-2,4,6,8-tetraenes **4** and **5**, respectively, were obtained, compounds analogous to **6** which previously have been shown to result from 1,1-ethylboration of tetra(1-alkynyl)silanes $\text{Si}(\text{C}\equiv\text{C}-\text{R})_4$ such as **3** ($\text{R} = \text{Me}$). In the case of the reaction of **2** with triethylborane, it proved possible to detect an intermediate **7**, in which the disilane structure is still retained and, according to NMR data (^1H , ^{11}B , ^{13}C , ^{29}Si -NMR), only two of the six $\text{C}\equiv\text{C}-\text{SiMe}_3$ moieties have reacted. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Disilanes; Silanes; Boron; Organoboration; NMR multinuclear; X-ray

1. Introduction

Alkynylsilanes are attractive reagents in 1,1-organoboration reactions [1–4]. This is also true for 1,2-bis(1-alkynyl)disilanes [5,6]. Although such disilanes are readily available by conventional synthetic methods [7], disilanes containing three, four, five or six 1-alkynyl groups have received little attention or are not known at all. Considering the synthetic potential of the previously unknown hexa(1-alkynyl)disilanes, $\text{Si}_2(\text{C}\equiv\text{C}-\text{R})_6$, we have attempted to prepare such compounds and to study their reactivity in 1,1-ethylboration reactions. The substituents $\text{R} = \text{Me}$, Bu , Me_3Si were selected since the corresponding monosilanes $\text{Si}(\text{C}\equiv\text{C}-\text{R})_4$ are known, and their reactivity in 1,1-ethylboration has been studied [8,9].

2. Results and discussion

2.1. Reactions of hexachlorodisilane Si_2Cl_6 with lithium alkynides $\text{LiC}\equiv\text{C}-\text{R}'$

The results of the reactions of Si_2Cl_6 with six equivalents of three different lithium alkynides are shown in Scheme 1. With $\text{Li}-\text{C}\equiv\text{C}-\text{Bu}$ and $\text{Li}-\text{C}\equiv\text{C}-\text{SiMe}_3$ the desired new disilanes **1** and **2** were readily accessible, whereas with $\text{Li}-\text{C}\equiv\text{C}-\text{Me}$ the tetra(1-propynyl)silane **3** was obtained instead. The identity of **2** and **3** was proved by the NMR data in solution and by X-ray structural analysis in the solid state. The identity of **1** as the disilane follows from consistent NMR data which do not agree with those of an authentic sample of tetra(1-hexynyl)silane [9]. The oily compound **1** contains a small amount (< 5%) of the monosilane $\text{Si}(\text{C}\equiv\text{C}-\text{Bu})_4$.

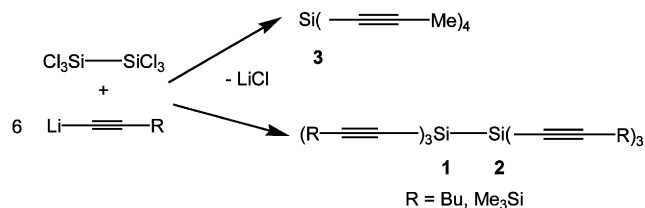
2.2. 1,1-Ethylboration of the hexa(1-alkynyl)disilanes **1** and **2**

Intermolecular 1,1-organoboration reactions of 1-alkynylsilanes proceed by cleavage of the Si–C \equiv bond, formation of a borate-like zwitterionic intermediate, and

* Corresponding author. Tel.: +49-921-552542; fax: +49-921-552157

E-mail address: b.wrack@uni-bayreuth.de (B. Wrackmeyer).

¹ On leave from the Department of Chemistry, Gomal University, D.I. Khan, N.W.F.P., Pakistan.



Scheme 1.

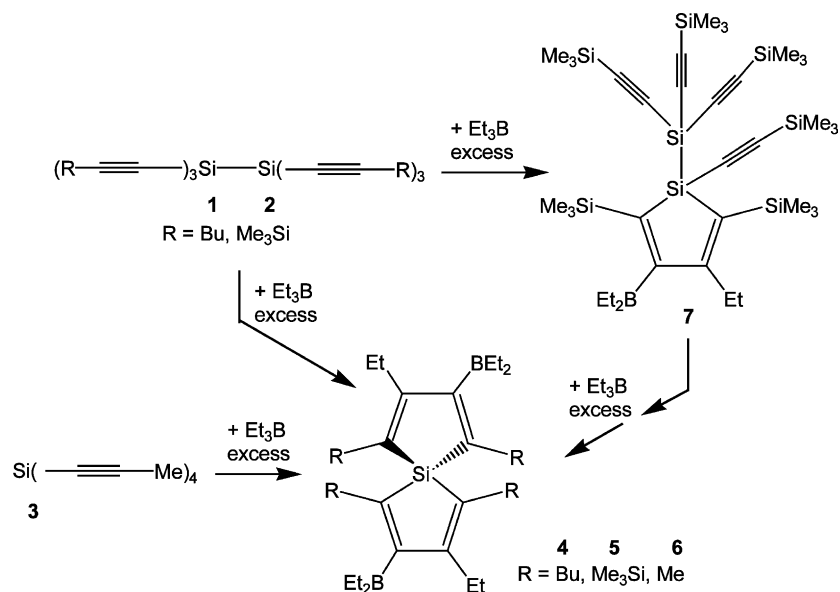
formation of a new C–Si and C–C bond to give an organometallic-substituted alkene derivative [1]. If there are additional Si–C≡ bond(s), intramolecular 1,1-organoboration may take place, in general under much milder conditions than for the intermolecular reaction. In the case of 1,2-bis(1-alkynyl)-tetramethyldisilanes seven-membered rings, substituted 1,2-dihydro-1,2,5-disilaborepines, were isolated as the final 1,1-organoboration products [5,6]. Products containing such structural units were not formed at all in the reaction of **1** or **2** with an excess of triethylborane. When the reaction mixtures were heated at ca. 100 °C for several days until all of **1** or **2** was consumed, only the monosilanes **4** and **5** were present (Scheme 2). Although the ¹H, ¹³C and ²⁹Si-NMR spectra showed numerous very small and rather broad signals, all sharp and prominent signals could be assigned to **4** and **5**. The 1,1-ethylboration of **3** was reproduced to give **6**, of which NMR data, chemistry and structure are known [8], and which corresponds to the products **4** and **5**. Therefore, in the course of the 1,1-ethylboration of **1** and **2** the Si–Si bond must be cleaved, to give a monosilane. The second product, left after cleavage of the Si–Si bond, a silylene or compounds formed by its decomposition or by further reactions could not be identified so far. Trapping of such silylenes with alkynes may be difficult because the siloles formed

either as intermediates or as final products can also react with various alkynes [10,11].

In the case of the reaction of **2** with triethylborane, the reaction was monitored by ²⁹Si-NMR, focusing on changes in the typical region of ²⁹Si(SiMe₃) resonances. This can be done most conveniently by INEPT experiments [12], even for diluted reaction solutions. After 2 h at reflux in boiling triethylborane as a solvent, there are prominent ²⁹Si(SiMe₃) signals for a new compound **7**, a smaller signal for the starting material **2**, and even less intense signals for the final product **5**. After removing the excess of triethylborane, and dissolving the residue in C₆D₆, the pattern in the ²⁹Si-NMR spectrum (INEPT) remained unchanged. The ¹H coupled single pulse ²⁹Si-NMR spectrum of the same sample displayed the expected multiplets for the Me₃Si groups, a sharp singlet for the ²⁹Si resonance of the central silicon atoms in **2** and two sharp singlets for the ²⁹Si resonance signals of the disilane unit in **7**. Together with a consistent set of ¹³C-NMR data, we propose that the structure of **7** possesses a disilane unit, in which one silicon atom ($\delta^{29}\text{Si} -100.1$) bears three C≡C–SiMe₃ groups and the other one ($\delta^{29}\text{Si} -32.5$) is part of a sila-2,4-cyclopentadiene ring and bears only one C≡C–SiMe₃ group (see Scheme 3). This leads to the conclusion that cleavage of the Si–Si bond does not take place in the initial steps of the 1,1-ethylboration.

2.3. X-Ray structural analysis of the disilane **2** and of the monosilane **3**

The molecular structures of **2** and **3** are shown in the Figs. 1 and 2, together with selected bond lengths and angles. Compound **2** crystallises rhombohedrally, and there is a centre of inversion on the middle of the Si–Si



Scheme 2.

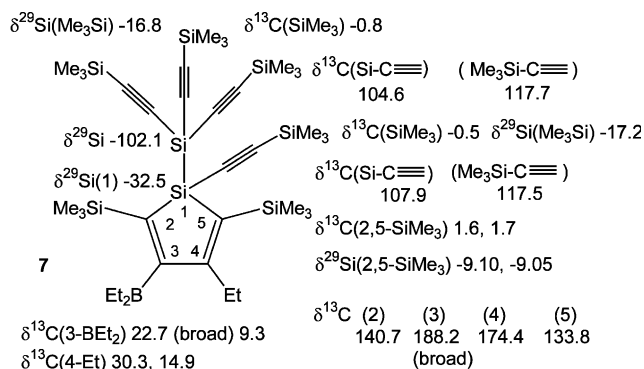
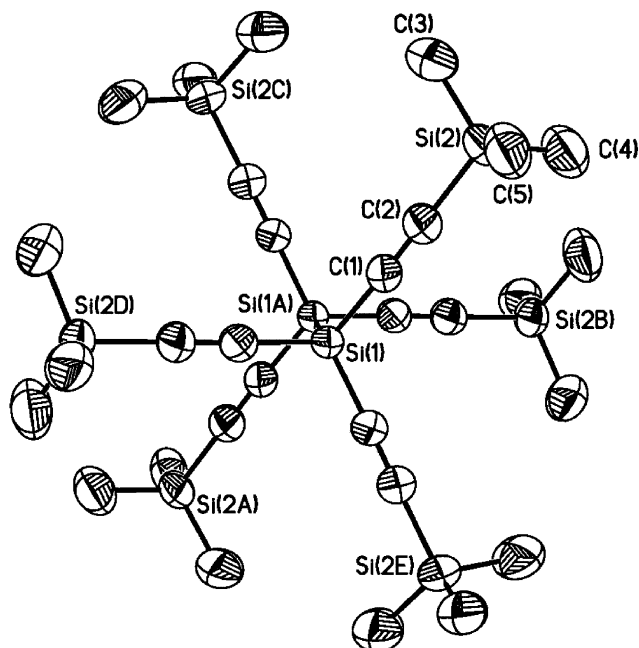
Scheme 3. ^{13}C and ^{29}Si chemical shifts of the intermediate **7**.

Fig. 1. ORTEP view (50% probability level) of the molecular structure of hexakis(trimethylsilyl)ethynyl)disilane **2**. Selected bond lengths (pm) and angles (degrees): Si(1)–Si(2) 231.7(3), Si(1)–C(1) 182.4(3), Si(2)–C(2) 185.4(4), Si(2)–C(5) 184.6(5), C(1)–C(2) 119.8(4); C–Si(1)–C 111.23(11), C(1)–Si(1)–Si(1A) 107.65(12).

axis. All bond lengths and angles are in the normal range, well comparable with the data for $\text{Si}(\text{C}\equiv\text{C}-\text{SiMe}_3)_4$ [13]. The tetrahedral surroundings of the central silicon atoms are slightly distorted owing to the wider bond angles C–Si–C ($111.23(11)^\circ$) as compared with the angles C–Si–Si ($107.65(12)^\circ$).

Tetra(1-propynyl)silane **3** crystallises in a tetragonal structure with a large unit cell which contains 16 molecules, different from the solid-state structures of $\text{Si}(\text{C}\equiv\text{C}-\text{SiMe}_3)_4$ [13] and $\text{Si}(\text{C}\equiv\text{C}-t\text{Bu})_4$ [14] (both orthorhombic with space group *Pnma* and *Z* = 4). In the molecular structure of **3**, all four propynyl groups are crystallographic slightly different; however, as expected, the tetrahedral surroundings of the silicon

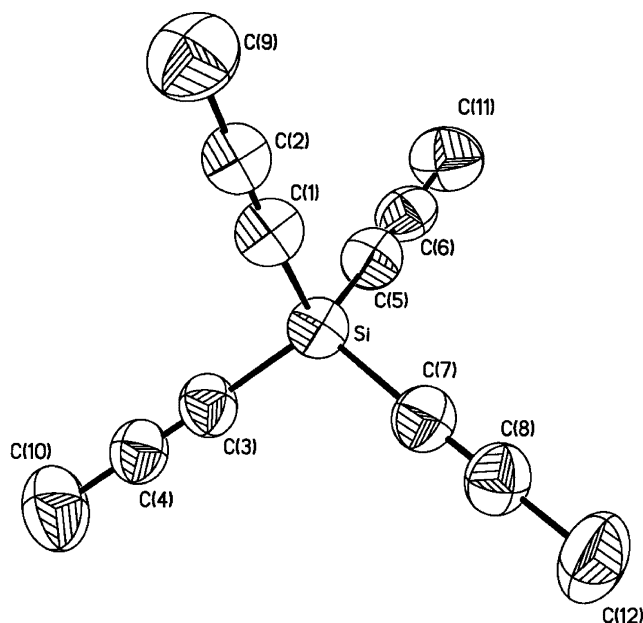


Fig. 2. ORTEP view (50% probability level) of the molecular structure of tetra(1-propynyl)silane (**3**). Selected bond lengths (pm) and angles (degrees): Si–C(1) 181.2(5), Si–C(3) 181.8(5), Si–C(5) 180.2(5), Si–C(7) 181.6(5), C(1)–C(2) 118.4(5), C(3)–C(4) 117.2(6), C(7)–C(8) 117.4(6), C(2)–C(9) 147.5(6), C(4)–C(10) 147.3(7), C(6)–C(11) 147.3(6), C(8)–C(12) 146.4(6); C(1)–Si–C(3) 109.4(2), C(1)–Si–C(5) 110.5(2), C(3)–Si–C(7) 109.4(2), C(2)–C(1)–Si 176.5(4), C(1)–C(2)–C(9) 179.0(4).

atom is hardly disturbed. As in other *tetra*(1-alkynyl)silanes [13,14], there are no intermolecular contacts.

3. Conclusions

Hexa(1-alkynyl)silanes can be prepared from the reaction of Si_2Cl_6 with lithium alkynides as shown for the compounds **1** and **2**. However, the failure in the case of the propynide, when the monosilane **3** was obtained instead, indicates that a generally valid procedure is still not available. The finding that 1,1-ethylboration of **1** and **2** at some stage of the reaction leads to cleavage of the Si–Si bond is noteworthy. Clearly, more work is necessary since the fate of a silylene-like fragment formed from potential intermediates such as **7** is not obvious as yet.

4. Experimental

4.1. Starting materials and measurements

All preparations and handling of samples were carried out under an inert atmosphere (Ar or N_2), and carefully dried glass ware and dry solvents were used. Hexachlorodisilane, BuLi (1.6 M) in hexane, the alkynes and Et_3B

were commercial products, and were used without further purification.

NMR spectra were recorded by using ARX 250 and DRX 500 instruments, equipped with multinuclear units. Samples dissolved in C_6D_6 (5–10%) in 5 mm (o.d.) tubes were measured at 23 ± 1 °C. Chemical shifts are given with respect to solvent signals [δ^1H (C_6D_5H) = 7.15; δ^{13C} (C_6D_6) = 128.0; and external references [δ^{11B} (BF_3OEt_2) = 0, $\Xi(^{11B})$ = 32.083971 MHz; δ^{29Si} (Me_4Si) = 0, $\Xi(^{29Si})$ = 19.867184 MHz]. 29Si -NMR spectra [15] were measured using either INEPT pulse sequences [12,15] [based on $^2J(^{29Si}, ^1H_{Me})$ (ca. 7 Hz) or $^nJ(^{29Si}, ^1H)$ ca. 1 Hz for the central Si in **1–3**] or for 1H coupled spectra single pulse techniques with a 30° pulse for 29Si .

IR spectra: Perkin–Elmer, Spectrum 2000 FTIR. EIMS: Finnigan MAT 8500 (ionisation energy 70 eV; direct inlet); the m/z data refer to the isotopes 1H , 11B , 12C , 28Si . Melting points (uncorrected): Büchi 510 melting point apparatus.

4.2. Hexa(1-alkynyl)disilanes **1** and **2**

1-Hexyne (10 ml, 86.6 mmol) or ethynyltrimethylsilane (5 ml, 35.4 mmol) were dissolved in hexane (200 ml) and cooled to -78 °C. After adding dropwise a solution of BuLi in hexane (54.1 ml or 22.1 ml, 1.6 M) within 1 h, the mixtures were warmed up to room temperature (r.t.), and then a solution of Si_2Cl_6 (2.49 or 1.02 ml, 14.43 or 5.9 mmol) was added slowly, followed by heating at reflux for 12 h. The colour of the reaction solutions changes first to brown and then to yellow. After filtering off insoluble material, the solvent was removed in vacuo and 6.25 g (80%) of a colourless oil (**1**) or 3.5 g of a colourless solid (**2**) was left. Compound **1** contains a small amount (<5%) of the monosilane $Si(C\equiv C-Bu)_4$. Compound **2** was recrystallised from ether–acetone to give 3.1 g (82%) of a colourless crystalline material (m.p. 176 °C).

1: 1H -NMR (250 MHz; C_6D_6): δ = 0.78 (t, 18H), 1.32 (m, 24H), 2.03 (t, 12H)— 13C -NMR (62.9 MHz, C_6D_6) δ [$J(^{29Si}, ^{13C})$] = 111.1 [21.3, 3.0] ($\equiv C$), 77.4 [108.0, 9.4] ($SiC\equiv$), 20.2 [1.9], 30.6, 22.1, 13.6 (Bu)— 29Si -NMR (49.7 MHz; C_6D_6): δ = -83.2 —EIMS: m/z (%) = 542 [M]⁺ (**2**), 352 (**8**), 309 (**56**) 295 (**57**), 271 [$M/2$]⁺ (**100**), 228 (**43**).

2: 1H -NMR (250 MHz; C_6D_6): δ = 0.15 (s, 54H, $SiMe_3$)— 13C -NMR (62.9 MHz, C_6D_6) δ [$J(^{29Si}, ^{13C})$] = 102.7 [100.0, 12.1, 8.2] ($SiSiC\equiv$), 120.1 [75.0, 16.3] ($\equiv C-Si$), -0.5 [56.6] ($SiMe_3$)— 29Si -NMR (49.7 MHz; C_6D_6): δ = -85.7 —IR: $\nu(C\equiv C)$ = 2108 cm^{-1} —EIMS: m/z (%) = 638 [M]⁺ (**4**), 416 (**47**), 401 (**63**) 343 (**18**), 313 (**82**), 73 [Me_3Si]⁺ (**100**).

4.3. Tetra(1-propynyl)silane (**3**)

The same procedure as described for **1** and **2** afforded pure tetra(1-propynyl)silane (**3**) as a colourless solid (m.p. 171–172 °C) which was recrystallised from toluene–hexane. 1H -NMR (250 MHz; C_6D_6): δ^1H = 1.42 (s, 12H, Me)— 13C -NMR (62.9 MHz; C_6D_6): δ [$J(^{29Si}, ^{13C})$] = 78.6 [127.0] ($Si-C\equiv$), 104.7 [26.5] ($\equiv C$), 4.5 [1.5] (Me)— 29Si -NMR (49.7 MHz; C_6D_6): δ = -95.1 —EIMS: m/z (%) = 184 [M]⁺ (**16**), 178 (**28**), 175 (**25**) 169 (**16**), 145 (**100**).

4.4. 1,1-Ethylboration of **1–3**

A five fold molar excess of triethylborane was added to the compounds **1–3** and the mixture was heated at reflux for 48 h (**1** and **3**) or 24 h (**2**). After removing the excess of triethylborane yellow oils were left which were studied by 1H , 11B , 13C and 29Si -NMR spectroscopy. This revealed their identity with the known [8,9] 5-silaspiro[4.4]nona-1,3,6,8-tetraenes with diethylboryl groups in 2,7-positions, ethyl groups in 3,8-positions and groups R [$R = Bu$ (**4**), Me_3Si (**5**) and Me (**6**)] in 1,4,6,9-positions.

In the case of the reaction of **2** with triethylborane, samples were taken at various intervals and 29Si -NMR spectra were measured. After 90 min. at reflux, a dominant species **7** was present (ca. 60%) together with starting material **2** (20%), the final product **5** (ca. 15%) and small amounts of unidentified products.

4.5. Crystal structures of hexakis(trimethylsilyl)ethynyl-disilane (**2**) and tetra(1-propynyl)silane (**3**)

Intensity data collections were carried out at r.t. on a Siemens P4 diffractometer with Mo- K_α -radiation ($\lambda = 71.073$ pm, graphite monochromator). (**2**) colourless plate of dimensions 0.22 × 0.16 × 0.08 mm, crystallises rhombohedrally, space group $R\bar{3}$; $a = 13.9107(10)$, $c = 1977.9(2)$ pm, $Z = 3$, $\mu = 0.320$ mm^{-1} ; 15256 reflections collected in the range 2–27.5° in θ , 1654 reflections independent, 876 reflections assigned to be observed ($I > 2\sigma(I)$); full-matrix least-squares refinement on F^2 with 59 parameters, R_1/wR_2 -values 0.0625/0.1800, no absorption correction; max./min. residual electron density 0.489/–0.246 $e \cdot 10^{-6}$ pm^{-3} . (**3**) colourless prism of dimensions 0.18 × 0.15 × 0.12 mm, crystallises tetragonally, space group $I4_1/a$; $a = 1566.9(14)$, $c = 1955.9(2)$ pm, $Z = 16$, $\mu = 0.209$ mm^{-1} ; 2763 reflections collected in the range 2–24.99° in θ , 2092 reflections independent, 975 reflections assigned to be observed ($I > 2\sigma(I)$); full-matrix least-squares refinement on F^2 with 118 parameters, R_1/wR_2 -values 0.0731/0.1691, no absorption correction, max./min. residual electron density 0.158/–0.184 $e \cdot 10^{-6}$ pm^{-3} .

5. Supplementary information

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-181619 (2) and CCDC-181620 (3). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:<http://www.ccdc.cam.ac.uk>).

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft, Volkswagen-Stiftung, and the Fonds der Chemischen Industrie. We are grateful to the government of Pakistan for a post-doctoral fellowship (A.B.).

References

- [1] B. Wrackmeyer, *Coord. Chem. Rev.* 145 (1995) 125.
- [2] R. Köster, G. Seidel, R. Boese, B. Wrackmeyer, *Chem. Ber.* 120 (1987) 669.
- [3] R. Köster, G. Seidel, J. Süß, B. Wrackmeyer, *Chem. Ber.* 126 (1993) 1107.
- [4] B. Wrackmeyer, G. Kehr, J. Süß, E. Molla, *J. Organomet. Chem.* 562 (1998) 207.
- [5] B. Wrackmeyer, *J. Chem. Soc. Chem. Commun.* (1988) 1624.
- [6] (a) B. Wrackmeyer, H.E. Maisel, W. Milius, *Chem. Ber./Recl.* 130 (1997) 1349;
(b) B. Wrackmeyer, W. Milius, E.V. Klimkina, Y.N. Bubnov, *Chem. Eur. J.* 7 (2001) 775.
- [7] W.E. Davidsohn, M.C. Henry, *Chem. Rev.* 67 (1967) 73.
- [8] R. Köster, G. Seidel, I. Klopp, C. Krüger, G. Kehr, J. Süß, B. Wrackmeyer, *Chem. Ber.* 126 (1993) 1385.
- [9] B. Wrackmeyer, S. Bayer, manuscript in preparation.
- [10] J. Dubac, A. Laporterie, G. Manuel, *Chem. Rev.* 90 (1990) 215.
- [11] (a) H. Appler, L.W. Gross, B. Mayer, W.P. Neumann, *J. Organomet. Chem.* 291 (1985) 9;
(b) S.I. Kirin, D. Vikić-Topić, E. Mestrovic, B. Kaitner, M. Eckert-Maksic, *J. Organomet. Chem.* 566 (1998) 85.
- [12] (a) G.A. Morris, R. Freeman, *J. Am. Chem. Soc.* 101 (1979) 760;
(b) G.A. Morris, *J. Am. Chem. Soc.* 102 (1980) 428;
(c) G.A. Morris, *J. Magn. Reson.* 41 (1980) 185;
(d) D.P. Burum, R.R. Ernst, *J. Magn. Reson.* 39 (1980) 163.
- [13] H. Schmidbaur, J. Ebenhöch, G. Müller, *Z. Naturforsch Teil B* 43 (1988) 49.
- [14] B. Wrackmeyer, H.E. Maisel, J. Süß, W. Milius, *Z. Naturforsch Teil B* 51 (1996) 1320.
- [15] J. Schraml, in: Z. Rappoport, Y. Apeloig (Eds.), *The Chemistry of Organic Silicon Compounds*, vol. 3 (Chapter 3), Wiley, Chichester, 2001, pp. 223–339.