1,1-Ethylboration of Trimethyl(methoxypropargyl)- and Chloro(dimethyl)methoxypropargylsilane. A Novel 1,2,5-Oxasilaborolane

Bernd Wrackmeyer, Elena V. Klimkina,
Tomas Kupcik, and Ruth Lohwasser

Anorganische Chemie II, Universität Bayreuth,
95440 Bayreuth, Germany

Reprint requests to Prof. Dr. B. Wrackmeyer.
E-mail: b.wrack@uni-bayreuth.de

Z. Naturforsch. **2011**, *66b,* 98 – 102;
received September 13, 2010

Triethylborane reacts with trimethyl(methoxypropargyl)silane *via* 1,1-ethylboration to give quantitatively a 90 : 10 mixture of (*E*)- and (*Z*)-3-diethylboryl-2-trimethylsilyl-pent-2-yl-methyl ethers. In contrast, the reaction of triethylborane with chloro(dimethyl)methoxypropargylsilane affords the novel 1,2,5-oxasilaborolane [2,2-dimethyl-5-ethyl-3-(1-ethylpropylidenyl)-1-oxa-2-sila-5-boracyclopentane] by 1,1-ethylboration, rearrangement and ether cleavage.

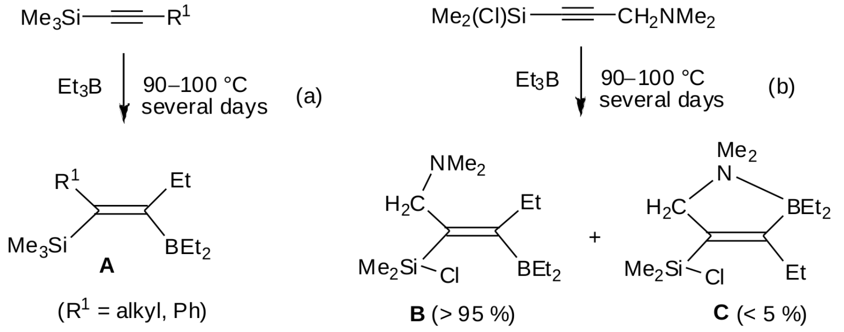
Key words: Organoboration, Methoxypropargylsilanes, Heterocycles, NMR

Numerous monoalkynylsilanes can be transformed *via* 1,1-organoboration [1] into alkenes bearing silyl and dialkylboryl groups in *cis*-positions at the C=C bond (Scheme 1a). This reaction proceeds slowly at about 100 °C and gives selectively the (*E*)-isomer of type **A** in most cases studied. For the reaction thermally robust trialkylboranes such as triethylborane, BEt$_3$, are required. Noticeable exceptions can in principle be expected if the subsutituent R contains a Lewis-basic center which may give rise to ring closure in the final product by adduct formation with the Lewis-acidic boryl group. This has been found in the case of the reaction of chloro(dimethyl)dimethyaminopropargylsilane with BEt$_3$, when the products **B** and **C** were identified (Scheme 1b) [2, 3].

We have now studied the behavior of two silylpropargyl ethers **1** and **2** towards BEt$_3$. In the case of the trimethylsilyl derivative **1**, it was of interest to compare the result of the 1,1-ethylboration with that of the reaction of the alkynylborate Na[Et$_3$BC≡CSiMe$_3$] [4, 5] with the electrophile ClCH$_2$OMe [5]. In the case of the chloro(dimethyl)silyl derivative **2**, the 1,1-ethylboration may be accompanied by rearrangements and further reactions due to the reactive Si–Cl bond. This has already been observed for **C** and related derivatives [2, 3], although some of the numerous products could not be identified.

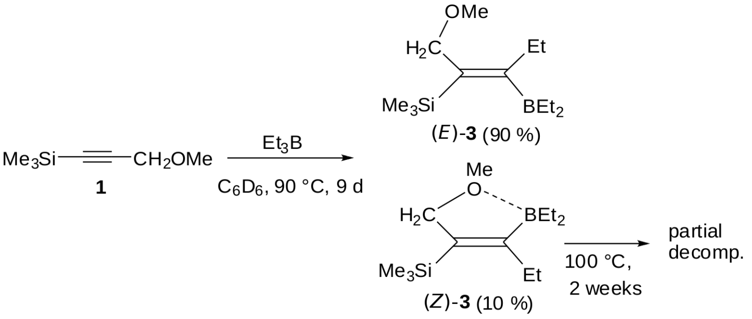
The alkynylsilanes **1** and **2** are readily obtained from the reaction of the respective chlorosilane with the alkynyllithium reagent, as has been described previously [6, 7] (Scheme 2).

The 1,1-ethylboration of **1** (Scheme 3) affords quantitatively a mixture of the two alkene derivatives **3** in approximately the same ratio as reported previously, using the route *via* the alkynylborate [5]. A conclusive set of NMR data (Experimental Section and Table 1) supports the proposed structures. The intramolecular adduct formation, indicated for (*Z*)-**3**, follows from its ^{11}B NMR signal, typical of four-coordinate boron [8], shifted by 60.3 ppm to low frequency when compared

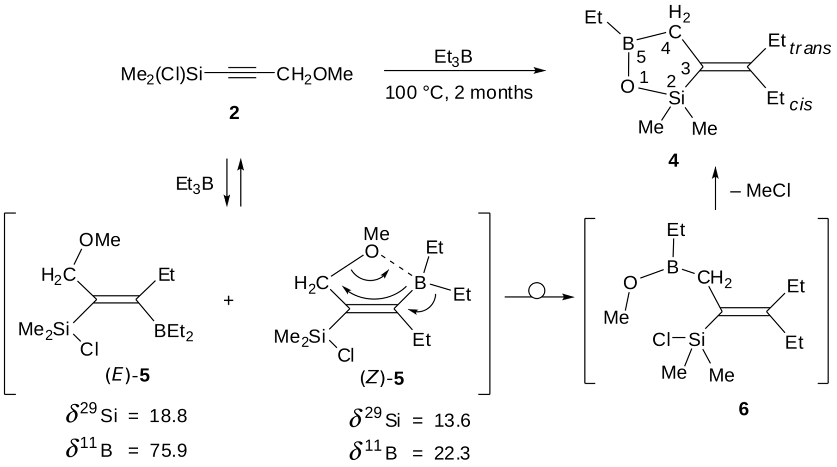


Scheme 1. (a) Typical results of 1,1-ethylboration for monoalkynylsilanes; (b) results for monoalkynylsilanes bearing a functional group at the C≡C bond and/or at the silicon atom.

Scheme 2. Synthesis of the silylprogargyl ethers.



Scheme 3. 1,1-Ethylboration of trimethylsilylpropargyl methyl ether.



Scheme 4. 1,1-Ethylboration of chloro(dimethyl)silylpropargyl methyl ether.

Table 1. ^{13}C, ^{29}Si and ^{11}B data[a] of the compounds (*E*)-**3**, (*Z*)-**3** and **4**.

	(*E*)-**3**	(*Z*)-**3**	**4**
	C_6D_6	C_6D_6	$[D_8]$toluene
$\delta^{13}C(SiMe)$	0.5 [51.2]	0.3 [51.2]	0.9 [57.8]
$\delta^{13}C(={C}Si)$	134.4 [69.9]	125.7 [68.2]	131.0 [76.0]
$\delta^{13}C(C{=}CSi)$	164.4 (br.)	174.0 (br.)	154.4 [7.1]
$\delta^{13}C(CH_2C{=})$	72.2 [3.7]	86.7 [13.1]	24.5 (br., BCH_2[b])
$\delta^{13}C(BEt)$	9.5 (CH_3) 21.1 (br., BCH_2)	10.2 (CH_3) 19.8 (br., BCH_2)	8.0 (CH_3) 13.3 (br., BCH_2[c])
$\delta^{13}C(EtC{=})$	14.0 (CH_3) 22.5 [7.8] (CH_2)	14.4 (CH_3) 26.5 (CH_2)	12.3 (CH_3(*trans*)), 14.0 (CH_3(*cis*)), 25.1 [6.0] (CH_2(*trans*)), 31.5 [5.3] (CH_2(*cis*))
$\delta^{13}C(OCH_3)$	57.7	56.1	–
$\delta^{11}B$	82.5 /440/	22.2 /180/	58.3 /440/
$\delta^{29}Si$	−5.8 [69.8] [51.2] [7.6][6.9]	−13.9 [68.2] [51.4][13.1]	24.1 [76.0][57.6]

[a] $^nJ(^{29}Si,^{13}C)$ coupling constants [±0.5 Hz] are given in brackets; line width $h_{1/2}$ (±20 Hz) of ^{11}B NMR signals are given in / /; [b] $h_{1/2} = 32 \pm 5$ Hz; [c] $h_{1/2} = 45 \pm 5$ Hz.

with that of (*E*)-**3**. Heating of this mixture for prolonged periods of time at 100 °C leads to partial decomposition, by which the amount of (*Z*)-**3** appears to be reduced. However, the resulting mixture is too complex to allow for structural assignments of the new products.

The 1,1-ethylboration of **2** in BEt_3 as the solvent (Scheme 4) proceeds even more slowly than that of **1**. Monitoring of the reaction by ^{11}B and ^{29}Si NMR spectroscopy showed the formation of two intermediates, for which the structures (*E*)-**5** and (*Z*)-**5** can be assigned in analogy to the results for **1**. After several weeks, the signals arising from **2** and the proposed (*E*)-**5** and (*Z*)-**5** decrease in intensity, and new ^{11}B and ^{29}Si NMR signals are growing together with a ^1H NMR signal for MeCl. Finally, after 2 months, the conversion of **2** into the new heterocycle **4** is essentially complete ($>$ 90 %) without appreciable amounts of side products.

It is known that 1,1-organoboration reactions are reversible [1]. Thus, the rearrangement of (*Z*)-**5** into **6**, followed by ether cleavage and irreversible formation of **4**, drives the 1,1-ethylboration until all of **2** is consumed. The migration of an ethyl group from boron to carbon in alkenyl(diethyl)boranes can be induced

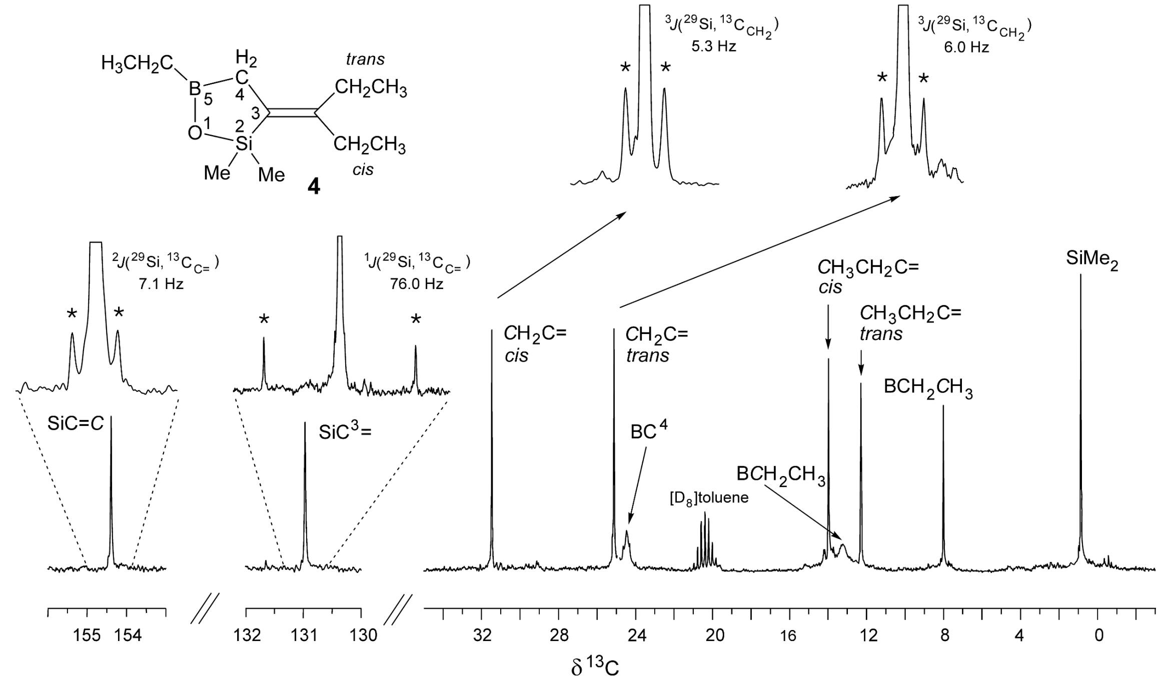


Fig. 1. 62.9 MHz $^{13}C\{^1H\}$ NMR spectrum of **4** (in $[D_8]$toluene, at 23 °C). The ^{29}Si satellites for $^nJ(^{29}Si,^{13}C)$ are marked by asterisks.

in some cases by treatment with methanol [9] or trialkyltin alkoxides [10], and the intermediacy of a borane adduct prior to the rearrangement is conceivable. In the case of (*Z*)-**5**, this adduct is present. The solution state structure of **4** follows conclusively from the ^1H (Experimental Section), ^{11}B, ^{13}C (Fig. 1) and ^{29}Si NMR data (Table 1). The mutual assignment of ^1H and ^{13}C NMR signals was confirmed by 2D $^1H/^{13}C$ HSQC and $^1H/^{13}C$ HMBC experiments. Furthermore, the gas-phase geometry of **4** was optimized [B3LYP/6-311+G(d,p) level of theory], and chemical shifts and coupling constants [$J(^{29}Si,^{13}C)$ and $^1J(^{13}C,^{11}B)$] were calculated at the same level of theory. The calculated NMR data are in good agreement with the experimental results. As for many other examples [11], the calculated values $^1J(^{29}Si,^{13}C)$ are smaller in magnitude by 10–15% than the experimental data [*e. g.* $^1J(^{29}Si,^{13}C^3) = -69.1$ (calcd.) and 76.0 Hz (exp.)], whereas the two- or three-bond couplings are well reproduced [$^2J(^{29}Si,^{13}C) = -7.3$ (calcd.) and 7.1 Hz (exp.), or $^3J(^{29}Si,^{13}C_{trans}) = -5.7$ (calcd.) and 6.0 Hz (exp.), $^3J(^{29}Si,^{13}C_{cis}) = -5.2$ (calcd.) and 5.3 Hz (exp.)]. Usually, the calculation of coupling constants $^1J(^{13}C,^{11}B)$ at this level of theory gives data in close agreement with experimental measurements [12, 13]. It is therefore noteworthy, that the coupling constant $^1J(^{13}C,^{11}B)$ is significantly larger for the exocyclic B–C bond (calcd.: +61.4 Hz; calcd. from exp. line widths [13]: 64 ± 2 Hz) when compared with that for the endocyclic B–C bond (calcd.: +51.1 Hz; calcd. from exp. line widths [13]: 54 ± 2 Hz). This can be attributed to the smaller endocyclic bond angle OBC^4 (calcd.: 114.1°), when compared with the exocyclic one OBC(Et) (calcd.: 119.1°) The difference in the magnitude of the coupling constants $^1J(^{13}C,^{11}B)$ is mirrored by the somewhat smaller line width of the $^{13}C(BC^4)$ NMR signal [13] (see Table 1).

Conclusion

A straightforward "one-pot" synthesis of a 1,2,5-oxasilaborolane **4** in high yield using readily available starting materials is reported. This compound is thermally stable and at the same time highly sensitive towards moisture. Therefore, **4** is an attractive material to convert a boric acid derivative with a siloxane unit by hydrolysis into polymers. The combination of polysiloxanes with boroxanes is of interest for various applications [14, 15], *e. g.* in materials for protective coatings [16, 17].

Experimental Section

All syntheses and the handling of the samples were carried out observing necessary precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. All solvents were distilled from Na metal in an atmosphere of argon. Silicon halides, methyl propargyl ether, and ^{n}BuLi (1.6 M in hexane) were commercial products and were used as received. NMR measurements (in C_6D_6 at 23 °C, if not mentioned otherwise): Bruker ARX 250, DRX 500, Varian INOVA 300 and Varian INOVA 400: ^{1}H, ^{11}B, ^{13}C (HSQC, HMBC [18]), and ^{29}Si NMR (refocused INEPT [19] based on $^2J(^{29}\text{Si}^1\text{H}_{Me})$ = 7 Hz; chemical shifts are given relative to Me_4Si [$\delta^1\text{H}(C_6D_5H)$ = 7.15, ($C_6D_5CD_2H$) = 2.08 (± 0.01); $\delta^{13}\text{C}$ (C_6D_6) = 128.2, ($C_6D_5CD_3$) = 20.4 (± 0.1); $\delta^{29}\text{Si}$ = 0 (± 0.1) for $\Xi(^{29}\text{Si})$ = 19.867184 MHz]; and to Et_2O-BF_3 ($\delta^{11}\text{B}$ = 0 with $\Xi(^{11}\text{B})$ = 32.083971 MHz).

For all quantum chemical calculations the GAUSSIAN 03 program package [20] was used. The geometry of **4** was optimized at the B3LYP/6-311+G(d,p) level of theory, and NMR parameters (nuclear shielding and spin-spin coupling constants) were calculated at the same level.

*(3-Methoxy-1-propyn-1-yl)trimethylsilane (**1**)*

A freshly prepared suspension of 3-methoxy-1-propyn-1-yllithium (59.2 mmol) in a mixture of hexane (40 mL) and THF (120 mL) was cooled to −78 °C, and Me_3SiCl (25.7 g, 237 mmol) was added dropwise. The reaction mixture was stirred overnight at r. t., and then the solvents and the excesss of Me_3SiCl were evaporated (20 Torr). The residue was extracted with portions of hexane (60 mL). After filtration the solvent was removed *in vacuo* (20 Torr), and fractional distillation afforded **1** as a colorless liquid (b. p. 74 °C/10 Torr; 3.74 g, 45 %). – ^{1}H NMR (300 MHz): δ = 0.14 (s, 9H, Si-CH_3), 3.13 (s, 3H, OCH_3), 3.86 (s, 2H, CH_2). – ^{13}C NMR (75.4 MHz): δ [$J(^{29}\text{Si},^{13}\text{C})$] = −0.1 [56.6] ($SiMe_3$), 57.1 (OMe), 60.3 ($CH_2O$), 91.1 [84.1] (SiC≡), 102.7 [15.4] (≡CCH_2). – ^{29}Si NMR (59.6 MHz): δ = −18.4 [83.9] [56.5].

*(3-Methoxy-1-propyn-1-yl)chloro(dimethyl)silane (**2**)*

The synthesis was carried out as described for **1**, starting from 3-methoxy-1-propyn-1-yllithium (59.2 mmol) and Me_2SiCl_2 (30.6 g, 237 mmol). The fractional distillation of the oily residue gave **2** (b. p. 60 – 62 °C/10 Torr; 3.0 g, 30 %) as a colorless liquid, and a second fraction consisting of bis(3-methoxy-1-propyn-1-yl)dimethylsilane as a colorless liquid (b. p. 45 – 47 °C/0.8 Torr; 2.6 g, 45 %).

2: ^{1}H NMR (300 MHz): δ = 0.34 (s, 6H, Si-CH_3), 3.04 (s, 3H, OCH_3), 3.74 (s, 2H, CH_2). – ^{13}C NMR (75.4 MHz): δ [$J(^{29}\text{Si},^{13}\text{C})$] = 3.4 [65.7] ($SiMe_2$), 57.3 (OMe), 60.0 ($CH_2O$), 87.4 [101.8] (SiC≡), 104.8 [20.0] (≡CCH_2). – ^{29}Si NMR (59.6 MHz): δ = −0.3 [102.0] [65.5].

Bis(3-methoxy-1-propyn-1-yl)dimethylsilane: ^{1}H NMR (300 MHz): δ = 0.02 (s, 6H, Si-CH_3), 2.86 (s, 6H, OCH_3), 3.57 (s, 4H, CH_2). – ^{13}C NMR (75.4 MHz): δ [$J(^{29}\text{Si},^{13}\text{C})$] = 0.0 [62.4] ($SiMe_2$), 57.0 (OMe), 60.0 ($CH_2O$), 87.7 [96.4] (SiC≡), 103.5 [18.5] (≡CCH_2). – ^{29}Si NMR (59.6 MHz): δ = −40.2.

*(E)- and (Z)-3-Diethylboryl-2-trimethylsilyl-pent-2-yl-methyl ether ((E)-**3** and (Z)-**3**)*

1 (100 mg, 0.7 mmol) was dissolved in C_6D_6 (1 mL), and BEt_3 (0.20 mL, 1.4 mmol) was added. The mixture was given into an NMR tube which was sealed. This mixture was heated at 100 °C (oil bath) for 9 d. The solution thus obtained contained (*E*)-**3** (90 %), (*Z*)-**3** (10 %) and BEt_3 (^{1}H, ^{11}B, ^{29}Si and ^{13}C NMR).

(*E*)-**3**: ^{1}H NMR (500.1 MHz): δ = 0.07 (s, 9H, $SiCH_3$), 0.86 (t, 3H, CH_3 from Et), 0.97 (t, 6H, CH_3 from BEt_2), 1.12 (q, 4H, BCH_2), 1.90 (q, 2H, CH_2 from Et), 3.14 (s, 3H, OCH_3), 4.04 (s, 2H, CH_2O).

(*Z*)-**3**: ^{1}H NMR (500.1 MHz): δ = 0.10 (s, 9H, $SiCH_3$), 0.76 (t, 6H, CH_3 from BEt_2), 1.05 (t, 3H, CH_3 from Et), 2.23 (q, 2H, CH_2 from Et), 3.01 (s, 3H, OCH_3), 4.15 (s, 2H, CH_2O).

*2,2-Dimethyl-5-ethyl-3-(1-ethylpropylidenyl)-1-oxa-2-sila-5-boracyclopentane (**4**)*

BEt_3 (0.35 mL, 2.4 mmol) was added to **2** (100 mg, 0.62 mmol), and the mixture was given into an NMR tube which was sealed. The mixture was heated at 100 °C (oil bath) for 2 months. The mixture thus obtained contained BEt_3, **4**, and CH_3Cl. Volatile materials were removed *in vacuo*, and the oily colorless residue was purified by distillation to give a colorless, extremely air- and moisture-sensitive liquid (b. p. 45 – 50 °C/10^{-2} Torr), containing about 95 % of **4** (^{1}H, ^{11}B, ^{29}Si and ^{13}C NMR). – ^{1}H NMR (500.1 MHz, [D_8]toluene, 23 °C): δ = 0.27 (s, 6H, $SiCH_3$), 0.96 (m, 8H, 2 CH_3 from =CEt_2, BCH_2 from Et), 1.03 (t, 3H, CH_3 from BEt), 1.72 (s, 2H, BC^4H_2), 2.00 (q, 2H, =CCH_2(*cis*)), 2.07 (q, 2H, =CCH_2(*trans*)).

Acknowledgement

Support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

[1] B. Wrackmeyer, *Coord. Chem. Rev.* **1995**, *145*, 125.

[2] B. Wrackmeyer, K. Shahid, S. Ali, *Appl. Organomet. Chem.* **2005**, *19*, 377.

[3] B. Wrackmeyer, T. Kupcik, O. L. Tok, K. Shahid, R. Kempe, *Appl. Organomet. Chem.* **2007**, *21*, 676.

[4] L. A. Hagelee, R. Köster, *Syn. React. Inorg. Metal.-Org. Chem.* **1977**, *7*, 53.

[5] R. Köster, L. A. Hagelee, *Synthesis* **1976**, 118.

[6] a) W. E. Davidsohn, M. C. Henry, *Chem. Rev.* **1967**, *67*, 73; b) L. Brandsma, *Preparative Acetylenic Chemistry* (2nd ed.), Elsevier, Amsterdam, **1988**; c) L. Brandsma, *Synthesis of Acetylenes, Allenes, and Cumulenes – Methods and Techniques*, Elsevier, Amsterdam, **2004**.

[7] H. Hopf, E. Naujoks, *Tetrahedron Lett.* **1988**, *29*, 609.

[8] H. Nöth, B. Wrackmeyer, *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds* in *NMR – Basic Principles and Progress* (Eds.: P. Diehl, E. Fluck, R. Kosfeld), Vol. 14, Springer, Berlin, **1978**.

[9] P. Binger, R. Köster, *Synthesis* **1973**, 309.

[10] B. Wrackmeyer, U. Klaus, W. Milius, *Chem. Ber.* **1995**, *128*, 679.

[11] B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.* **2006**, *57*, 1.

[12] T. Onak, J. Jaballas, M. Barfield, *J. Am. Chem. Soc.* **1999**, *121*, 2850.

[13] B. Wrackmeyer, O. L. Tok, *Z. Naturforsch.* **2005**, *60b*, 259; b) B. Wrackmeyer, E. V. Klimkina, *Z. Naturforsch.* **2008**, *63b,* 923.

[14] G. D. Soraru, F. Babonneau, C. Gervais, N. Dallabona, *J. Sol-Gel Sci. Techn.* **2000**, *18*, 11.

[15] E. Lesniak, Z. Michalska, J. Chojnowski, *Patent Application: PL* 98-324956 19980220 (Poland) **2005**.

[16] a) W. J. Bobear, *Patent Application: US* 69-849279 19690805 (USA) **1970**; b) S. Yajima, K. Okamura, T. Shishido, Y. Hasegawa, *Patent Application: DE* 79-2918549 19790508 (Germany) **1979**.

[17] S. Hoshii, A. Kojima, S. Otani, *J. Mat. Sci. Lett.* **2000**, *19*, 169.

[18] T. Parella, *J. Magn. Reson.* **2004**, *167*, 266, and refs. cited therein.

[19] G. A. Morris, R. Freeman, *J. Am. Chem. Soc.* **1979**, *101*, 760.

[20] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, GAUSSIAN03 (revision B.02), Gaussian, Inc., Pittsburgh, PA (USA) **2003**.