other hand, the higher ammonia concentration at the surface favors the fast addition of ammonia to the aldehyde-type intermediates, and suppresses the reaction of the alcoholic OH group with the intermediate or product amines that leads to dimerization products. That is, the weaker basicity of ammonia, relative to the product amines, is partly compensated by its higher concentration at the surface. All these effects can contribute to the remarkable enhancements in the overall amination selectivities (Figures 1–3).

In conclusion we can state that the application of scNH_3 as a solvent and reactant in the amination of simple alkanediols and aminoalcohol affords significant improvement in selectivities to primary diamines, relative to the procedure at subcritical pressure. Most of the changes in selectivities occur in a narrow pressure range in the near critical region of the medium. The selectivity improvement is attributed to the higher concentration of ammonia at the surface, which favors the amination with ammonia and suppresses the hydrogenolysis-type (degradation) side reactions. It seems that the phenomenon is not limited to a specific catalyst or reactant, though the final selectivity is a function of the structure of the reactant aminoalcohol or diol. We are presently working on the extension to other amination reactions where the low reactivity of ammonia relative to the product amine prevents the efficient synthesis of primary amines.

Experimental Section

The Co–Fe catalyst was prepared by co-precipitation. Aqueous solutions of cobalt nitrate, iron nitrate, and ammonium carbonate were mixed at room temperature and the pH adjusted to 7. The precipitate was filtered off, dried at 120 °C in a vacuum, and calcined at 400 °C for 4 h. The BET surface area was 8 $m^2 g^{-1}$ and the pore volume 0.1 $cm^3 g^{-1}$.

The commercial Ni catalyst (Engelhard No. 6458) contained 56 wt% of pre-reduced Ni. The BET surface area was 180 $m^2 g^{-1}$ and the pore volume 0.3 $cm^3 g^{-1}$.

The amination experiments were carried out isothermally in a continuous tubular reactor with an inner diameter of 13 mm. The reactor was loaded with crushed and sieved catalyst particles of 140 to 400 μm. The liquid ammonia and 1,3-propanediol or the solution of 2,2-dimethyl-1,3-propanediol in ammonia were dosed into the reactor by ISCO D500 syringe pumps. The total pressure in the reaction system was set by a TESCOM back-pressure regulator. Details of the reaction conditions are indicated in the figure captions. The liquid product was separated from the gas and analyzed on an HP 5890 gas chromatograph (HP 1701 column). The products were identified by GC-MS analysis.

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[1] M. G. Turcotte, T. A. Johnson, *Kirk-Othmer, Encycl. Chem. Technol., Vol. 2*, Wiley, New York, **1992**, p. 369.
[2] G. C. Carter, A. R. Doumaux, S. W. Kaiser, P. R. Umberger, *Kirk-Othmer, Encycl. Chem. Technol., Vol. 8*, Wiley, New York, **1992**, p. 74.
[3] D. M. Roundhill, *Chem. Rev.* **1992**, *92*, 1.
[4] A. Baiker in *Catalysis of Organic Reactions* (Eds.: J. R. Kosak, T. A. Johnson), Marcel Dekker, New York, **1994**, p. 91.
[5] A. Fischer, T. Mallat, A. Baiker, *Catal. Today* **1997**, *37*, 167.
[6] T. Mallat, A. Baiker in *Handbook of Heterogeneous Catalysis, Vol. 5* (Eds.: G. Ertl, H. Knözinger, J. Weitkamp), WILEY-VCH, Weinheim, **1997**, p. 2334.
[7] R. E. Vultier, A. Baiker, A. Wokaun, *Appl. Catal.* **1987**, *30*, 167.
[8] J. Kijenski, P. J. Niedezielski, A. Baiker, *Appl. Catal.* **1989**, *53*, 107.
[9] A. Baiker, J. Kijenski, *Catal. Rev. Sci. Eng.* **1985**, *27*, 653.
[10] J. Kijenski, J. Burger, A. Baiker, *Appl. Catal.* **1984**, *11*, 295.
[11] R. J. Card, J. L. Schmitt, *J. Org. Chem.* **1981**, *46*, 754.
[12] G. Sirokmán, A. Molnár, M. Bartok, *J. Mol. Catal.* **1983**, *19*, 35.
[13] Á. Molnár, G. Sirokman, M. Bartok, *J. Mol. Catal.* **1983**, *19*, 25.
[14] J. Runeberg, A. Baiker, J. Kijenski, *Appl. Catal.* **1985**, *17*, 309.
[15] R. Becker, V. Menger, W. Reif, A. Henne (BASF AG), US-A 5608113, **1997**, [*Chem. Abstr.* **1996**, *124*, 316502].
[16] C. A. Gibson, J. R. Winters (Union Carbide), US-A 4400539, **1983**, [*Chem. Abstr.* **1983**, *99*, 21938w].
[17] A. Moriya (Nippon Shokubai Co.), EP-B 0652207, **1994**, [*Chem. Abstr.* **1995**, *123*, 9064].
[18] T. Hironaka, N. Nagasaka, Y. Hara (Tosoh Corp.), EP-B 0526851, **1992**, [*Chem. Abstr.* **1993**, *118*, 212475].
[19] F. Merger, A. Segnitz (BASF AG), US-A 4158017, **1979**.
[20] *Encyclopedie de Gaz*, Elsevier, **1976**, p. 951.
[21] H. Feichtinger, H. Aschmann, H. Birnkraut (Ruhrchemie AG), US-A 4078003, **1978**, [*Chem. Abstr.* **1975**, *83*, 78566x].
[22] E. Brunner, *J. Chem. Thermodynamics* **1988**, *20*, 1397.
[23] E. Brunner, *J. Chem. Thermodynamics* **1988**, *20*, 273.
[24] J. C. Giddings, M. N. Myers, L. McLaren, R. A. Keller, *Science* **1968**, *162*, 67.
[25] S. Borman, *Sci. Technol.* **1995**, 33.
[26] A. Baiker, *Chem. Rev.* **1999**, in press.
[27] C. Eckert, B. L. Knutson, P. G. Debenedetti, *Nature* **1996**, *383*, 313.
[28] P. E. Savage, S. Gopalan, T. I. Mizan, C. J. Martino, E. E. Brock, *AIChE J.* **1995**, *41*, 1723.
[29] T. Tacke, S. Wielander, P. Panster in *High Pressure Chemical Engineering, Vol. 12* (Eds.: R. von Rohr, C. Trepp), Elsevier, Zurich, Switzerland, **1996**, p. 17.
[30] P. N. Rylander, *Catalytic Hydrogenation over Platinium Metals*, Academic Press, New York, **1967**.
[31] P. Rylander, *Catalytic Hydrogenation in Organic Synthesis*, Academic Press, New York, **1979**.
[32] M. Freifelder, *Practical Catalytic Hydrogenation—Techniques and Applications*, Wiley-Interscience, New York, **1971**.

Calcium, Strontium, and Barium Acetylides—New Evidence for Bending in the Structures of Heavy Alkaline Earth Metal Derivatives[**]

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Since their development in the early 1900s, Grignard reagents have proven to be immensely useful in synthetic chemistry and are among the most common organometallic reagents.[1, 2] In contrast, information about beryllium, calcium, strontium, and barium analogues is scarce.[1c, 2, 3] Organo-

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metallic compounds of the heavy alkaline earth metals are more difficult to access due to enhanced reactivity and decreased kinetic stability.[1c, 2a,b, 3a,b] The high electropositive character and large ionic radii of the heavy alkaline earth metals result in a chemistry that is mostly governed by electrostatic and steric requirements. Consequently, the formation of polymeric, insoluble solids is frequently observed.[1c, 2, 3]

Well characterized organometallic calcium, strontium, and barium derivatives are mainly limited to compounds exhibiting metal–π interactions, such as cyclopentadienyl compounds,[3a,b] fluorenyl and indenyl complexes,[4] and a few others.[5] In contrast, there are still very few σ-bound organometallic compounds and these are often only characterized by the products of their reactions with electrophiles.[1c] Structurally characterized σ-bound alkaline earth metal compounds include $[Ca\{CH(SiMe_3)_2\}_2(1,4\text{-dioxane})_2]$,[6] $[Ca\{C(SiMe_3)_3\}_2]$,[7] and $[\{[(C_3H_7)_4C_5H]Ca(\mu\text{-}C{\equiv}CPh)(thf)\}_2]$;[8] no well characterized compounds displaying σ-bound Sr–C or Ba–C moieties have been reported. This lack of data[9] is contradicted by the recent use of, for example, allylbarium reagents in the α-selective and stereospecific allylation of carbonyls or imines,[10] the utilization of organobarium derivatives as effective polymerization initiators,[11] and the employment of organocalcium reagents in the synthesis of functionalized polymers.[12]

We present here a family of calcium, strontium, and barium triphenylsilylethynyl derivatives $[M([18]crown\text{-}6)(CCSiPh_3)_2]$ (M = Ca (**1a**), Sr (**1b**), and Ba (**1c**)), which were synthesized by treatment of alkaline earth metal amides with triphenylsilylethyne in the presence of [18]crown-6 [Eq. (1); M = Ca, Sr, Ba]. The compounds crystallize as colorless solids that can be stored indefinitely under inert gas. They are extremely sensitive to oxygen and moisture; contact with water results in immediate decomposition under formation of $[M([18]crown\text{-}6)(OSiPh_3)_2]$ and acetylene [Eq (2)].[13]

$$[M\{N(SiMe_3)_2\}_2(thf)_2] + 2\,HCCSiPh_3 + [18]crown\text{-}6 \longrightarrow [M([18]crown\text{-}6)(CCSiPh_3)_2] + 2\,HN(SiMe_3)_2 \quad (1)$$

$$[M([18]crown\text{-}6)(CCSiPh_3)_2] + 2\,H_2O \longrightarrow [M([18]crown\text{-}6)(OSiPh_3)_2] + 2\,HCCH \quad (2)$$

Compounds **1a**–**c** were characterized by NMR and IR spectroscopy, and their structures elucidated by X-ray crystallography. The IR frequencies at 1980 (**1a**), 1969 (**1b**), and 1955 cm^{-1} (**1c**) for the C≡C bond as compared to those for the neutral precursor $HCCSiPh_3$ (2036 cm^{-1}) clearly indicate the presence of the ethynyl derivative, and are also in accord with those observed in $[\{[(C_3H_7)_4C_5H)Ca(\mu\text{-}CCR)(thf)\}_2]$[8] and a series of polymeric derivatives $[\{M(CCPh)_2\}_n]$ (M = Ca, Sr, Ba).[14] A decrease in ethynyl stretching frequency was also observed upon descending Group 1.[15]

Compounds **1a**–**c** crystallize as monomeric molecules in which the metal atom lies in the center of the crown and the ethynyl ligands are arranged *trans* to each other (C-M-C 168.7(2) (**1a**), 166.0(1) (**1b**; Figure 1), and 162.7(1)° (**1c**; Figure 2)). The M–C distances are 2.523(7) and 2.558(7) Å (**1a**), 2.692(4) and 2.723(4) Å (**1b**), and 2.852(3) and 2.853(3) Å (**1c**). The C≡C distances are 1.229(8) and 1.234(8) Å (**1a**), 1.201(5) and 1.222(5) Å (**1b**), and 1.223(4) and 1.236(5) Å (**1c**). Interestingly, the ethynyl ligand is not bound linearly to the metal center, and the M-C-C angles are 162.4(5) and 164.0(5)° (**1a**), 158.9(3) and 159.7(3)° (**1b**), and 126.6(3) and 141.3(3)° (**1c**).

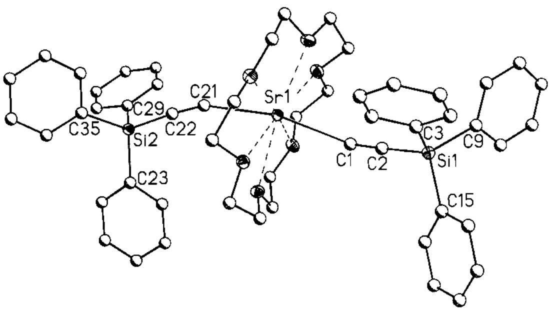

Figure 1. Structure of **1b** in the crystal (anisotropic displacement parameters depicting 30% probability). All hydrogen atoms have been omitted for clarity.

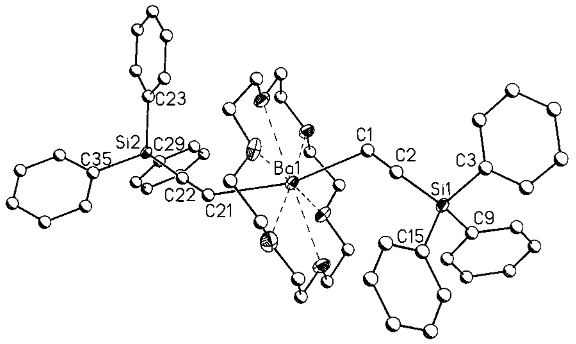

Figure 2. Structure of **1c** in the crystal (anisotropic displacement parameters depicting 30% probability). All hydrogen atoms have been omitted for clarity.

The Ca–C distances in **1a**, in which the Ca atom is eight-coordinate, compare well with those in $[Ca\{CH(SiMe_3)_2\}_2(1,4\text{-dioxane})_2]$ (2.483(5) Å)[6] and $[Ca(C(SiMe_3)_3)_2]$ (2.459(9) Å),[7] in which the Ca atom is four-coordinate and two-coordinate, respectively. The good agreement of the bond lengths despite the increased coordination number at the metal in **1a** can be explained by the sp hybridization of the ligand carbon atom, resulting in a decreased effective ionic radius. No σ-bonded organostrontium or -barium compounds are available for structural comparison with **1b** and **1c** which display a smooth increase in metal–carbon distance as compared to **1a** (effective ionic radii for a coordination number 8: 1.12 (Ca), 1.26 (Sr), and 1.42 Å (Ba)).[16]

Two main structural trends are observed in **1a**–**c** upon descending Group 2: a decrease in the C-M-C and the M-C-C angles. The decrease in C-M-C angle is in agreement with results of calculations which indicated low energy barriers between linear and bent structures.[17] The small degree of bending observed in **1a**–**c** might be explained by steric repulsion between the crown ether and the ligand.

More unusual are the M-C-C angles in **1a**–**c**. Angles close to 160° are observed for **1a** and **1b,** those for **1c** are considerably narrower with 126.6(3) and 141.3(3)°. This finding does not correlate well with literature values; terminal acetylide groups generally display angles close to 180° as observed in $[Mg(tmeda)_2(CCR)_2]$ (R = Ph,[18] *t*Bu[19]) or $[U(C_5H_5)_3(CCPh)]$.[20] The unusual geometry in **1c** can be explained by the high s-character of the sp-hybridized carbon atom of the ethynyl group causing a low directionality of the ligand orbitals. The resulting very low energy barrier is responsible for the bending at the C atom.[21] Moreover, the large ionic radius of barium and the small size of the ligand allow for extensive structural flexibility in the ligand orientation, accounting for the large variation observed in the ethynyl ligation. The smaller degree of bending for **1a** and **1b** might be due to space limitations resulting in reduced structural flexibility. The low energy barrier for the bending might also allow for packing effects. If one considers the unusual Ba-C-C angles on the basis of metal–ligand π interactions, as discussed in various alkali metal acetylide derivatives,[22] or in $[Be(NMe_3)(CCMe)_2]_2$,[23] the bending in **1c** can also be explained by a partial side-on orientation of the ligand resulting in a π interaction.

Experimental Section

All reactions were performed under vigorous exclusion of water and oxygen. The compounds $[M\{N(SiMe_3)_2\}_2(thf)_2]$ (M = Ca, Sr, Ba) were prepared by treating the alkaline earth metal iodides with potassium amide.[24] All reagents and solvents were purified by standard procedures.

1a–c: To a 100 mL Schlenk flask was added $[Ca\{N(SiMe_3)_2\}_2(thf)_2]$ (0.25 g, 0.5 mmol), $[Sr\{N(SiMe_3)_2\}_2(thf)_2]$ (0.28 g, 0.5 mmol), or $[Ba\{N(SiMe_3)_2\}_2(thf)_2]$, [18]crown-6 (0.13 g, 0.5 mmol), and THF (15 mL). In a second flask $HCCSiPh_3$ (0.28 g, 1.0 mmol) was dissolved in THF (10 mL). Both flasks were cooled to −80 °C and the contents combined at −80 °C and stirred. The colorless solutions were filtered, and the resulting clear solutions were stored at −20 °C. Colorless crystals formed overnight.

1a: M.p. 261 °C; yield: 0.15 g (34.4 %); ^1H NMR (300 MHz, 25 °C, C_6D_6): $\delta = 3.31$ (s, 24 H, [18]crown-6), 7.21(m, 18 H, Ph_3Si), 8.10 (m, 12 H, Ph_3Si); IR (Nujol): $\tilde{\nu} = 3854$ s, 3822 s, 3752 s, 3736 s, 3712 s, 3691 s, 3676 s, 3650 s, 3630 s, 3620 s, 3568 s, 3062 s, 3042 s, 2922 s, 1980 s, 1831 w/m, 1564 w/m, 1481 s, 1427 s, 1351 s, 1284 m, 1261 m, 1249 s, 1185 m, 1107 s, 1029 m, 997 m, 972 s, 846 m, 744 s, 705 s, 656 s, 617 m, 544 cm^{-1} w/m.

1b: M.p. 269 °C; yield: 0.14 g (30.0 %); ^1H NMR (300 MHz, 25 °C, C_6D_6): $\delta = 3.22$ (s, 24 H, [18]crown-6), 7.21 (m, 18 H, Ph_3Si), 8.12 (m, 12 H, Ph_3Si); IR (Nujol): $\tilde{\nu} = 3853$ m, 3750 m, 3675 m, 3648 m, 2284 w, 1969 m, 1829 w, 1772 w, 1733 w, 1716 w, 1698 w, 1684 w, 1670 w, 1636 w, 1616 w, 1558 w, 1540 w, 1521 w, 1506 w, 1427 m, 1350 m, 1285 w, 1248 w, 1186 w, 1101 s, 1039 w, 1020 w, 997 w, 969 m, 843 w, 746 w, 703 s, 654 w, 618 cm^{-1} w.

1c · 2 THF: M.p. 232 °C; yield: 0.26 g (54.7 %); ^1H NMR (300 MHz, 25 °C, C_6D_6): $\delta = 1.43$ (m, 8 H, THF), 3.09 (s, 24 H, [18]crown-6), 3.58 (m, 8 H, THF), 7.19 (m, 18 H, Ph_3Si), 8.11 (m, 12 H, Ph_3Si); IR (Nujol): $\tilde{\nu} = 2930$ s, 1955 s, 1830 s, 1773 s, 1566 s, 1426 s, 1346 s, 1305 m/s, 1283 s, 1261 s, 1245 s, 1185 s, 1092 s, 1063 s, 1028 s, 997 m/s, 961 s, 911 s, 859 m, 828 s, 745 s, 703 s, 652 s, 617 cm^{-1} m.

Crystal data for **1a**: $C_{52}H_{54}CaO_6Si_2$, $M_r = 871.21$, monoclinic, space group $P2_1/n$, $a = 15.9096(5)$, $b = 17.0207(6)$, $c = 18.6612(7)$ Å, $\beta = 114.924(1)°$, $V = 4582.7(3)$ Å^3, T (K) = 120, Z = 4, $\mu = 0.239$ mm^{-1}($Mo_{K\alpha}$); colorless rods $0.15 \times 0.15 \times 0.40$ mm^3; 4865 independent reflections ($3.4 \leq 2\theta \leq 42.00°$); $R_1 = 0.0713$ for 3013 data $I > 2\sigma(I)$ and $wR_2 = 0.1426$ for all data. **1b**: $C_{52}H_{54}O_6Si_2Sr$, $M_r = 918.75$, monoclinic, space group $P2_1/n$, a = 15.9659(1), b = 17.1540(2), c = 18.5590(1) Å, $\beta = 115.13(1)°$, $V = 4601.81(6)$ Å^3, T (K) = 90, $Z = 4$, $\mu = 1.273$ mm^{-1}($Mo_{K\alpha}$). Colorless plates of dimensions $0.30 \times 0.18 \times 0.12$ mm^3, 10456 independent reflections ($3.4 \leq 2\theta \leq 57.00°$). $R_1 = 0.0723$ for 7537 data $I > 2\sigma(I)$ and $wR_2 = 0.1157$ for all data. **1c** · 2 THF: $C_{60}H_{70}BaO_8Si_2$, $M_r = 1112.68$, triclinic, space group $P\bar{1}$, $a = 11.5909(1)$, $b = 15.9312(2)$, $c = 16.8368(2)$ Å, $\alpha = 70.912(1)$, $\beta = 89.602(1)$, $\gamma = 74.824(1)°$, $V = 2825.06(5)$ Å^3, T (K) = 90, $Z = 2$, $\mu = 0.797$ mm^{-1} ($Mo_{K\alpha}$). Colorless rods of dimensions $0.64 \times 0.10 \times 0.10$ mm^3, 12906 independent reflections ($3.1 \leq 2\theta \leq 57.00°$). $R_1 = 0.0471$ for 11048 data $I > 2\sigma(I)$ and $wR_2 = 0.1185$ for all data. The crystals were mounted on the diffractometer as described previously.[25] The data were collected utilizing a Siemens SMART system, complete with 3-circle goniometer and CCD detector as described earlier.[26] The crystal structures of **1a** and **1b** were solved with direct methods, **1c** by Patterson synthesis. All structures were refined by full-matrix least-squares refinement on F^2.[27] All non-hydrogen atoms were refined anisotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-102521 – CCDC-102523. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] a) P. R. Markies, O. S. Ackerman, F. Bickelhaupt, W. J. J. Smeets, A. L. Spek, *Adv. Organomet. Chem.* **1991**, *32*, 147; b) F. Bickelhaupt, *J. Organomet. Chem.* **1994**, *475*; c) W. E. Lindsell in *Comprehensive Organometallic Chemistry* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, **1982**.

[2] a) G. E. Coates, M. L. H. Green, K. Wade, *Organometallic Compounds*, *Vol. 1*, Methuen, London, **1969**; b) S. T. Ioffe, A. N. Nesmeyanov, *The Organo Compounds of Magnesium, Beryllium, Calcium, Strontium, and Barium*, North Holland, Amsterdam, **1967**.

[3] a) T. P. Hanusa, *Acc. Chem. Res.* **1993**, *93*, 1023; b) T. P. Hanusa, *Polyhedron* **1990**, *9*, 1345; c) N. A. Bell in *Comprehensive Organometallic Chemistry* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, **1982**.

[4] See for example: a) K. A. Allen, B. G. Gowenlock, W. E. Lindsell, *J. Organomet. Chem.* **1974**, *65*, 1; b) J. S. Overby, T. P. Hanusa, *Organometallics* **1996**, *15*, 2205; c) G. Mösges, F. Hampel, P. von R. Schleyer, *Organometallics* **1992**, 11, 1769.

[5] a) K. Mashima, H. Sugiyama, N. Kamehisa, Y. Kai, H. Yasuda, N. Nakamura, *J. Am. Chem. Soc.* **1994**, *116*, 6977; b) A. Nakamura, K. Mashima, *J. Organomet. Chem.* **1995**, *500*, 261; c) J. S. Overby, T. P. Hanusa, *Angew. Chem.* **1994**, *106*, 2300; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2191; d) S. Harder, M. Lutz, *Organometallics* **1997** *16*, 225.

[6] F. G. Cloke, P. B. Hitchcock, M. F. Lappert, G. A. Lawless, B. Royo, *J. Chem. Soc. Chem. Commun.* **1991**, 724.

[7] C. Eaborn, S. A. Hawkes, P. B. Hitchcock, J. D. Smith, *Chem. Commun.* **1997**, 1961.

[8] D. Burkey, T. P. Hanusa, *Organometallics* **1996**, 15, 4971.

[9] C. Elschenbroich, A. Salzer, *Organometallics*, 2nd ed., VCH, New York, **1992**.

[10] a) A. Yanagisawa, S. Habaue, K. Ysaue, H. Yamamoto, *J. Am. Chem. Soc.* **1994**,*116*, 6130; b) A. Yanagisawa, K. Ogasawara, K. Yasue, H. Yamamoto, *Chem. Commun.* **1996**, 367, and references therein.

[11] a) L. C. Tang, C. Mathis, B. Francois, *J. Organomet. Chem.* **1983**, *243*, 359; b) B. De Groof, M. Van Beulen, M. Szwarc, *Macromolecules* **1975**, *8*, 396; c) B. De Groof, W. Morteier, M. Van Beulen, M. Szwarc, *Macromolecules* **1977**, *10*, 598.

[12] R. A. O'Brien, T. Chen, R. D. Rieke, *J. Org. Chem.* **1992**, *57*, 2667.

[13] The compounds $M([18]crown\text{-}6)(OSiPh_3)_2$ (M = Ca, Sr, Ba) have been identified by X-ray crystallography and IR spectroscopy.

[14] M. A. Coles, F. A. Hart, *J. Organomet. Chem.* **1971**, *32*, 279.

[15] R. Nast, J. Gremm, *Z. Anorg. Allg. Chem.* **1963**, *325*, 62.

[16] R. D. Shannon, *Acta Crystallogr. A* **1976**, *32*, 751.

[17] a) M. Kaupp, P. von R. Schleyer, H. Stoll, H. Preuss, *J. Chem. Phys.* **1991**, *94*, 1360; b) M. Kaupp, P. von R. Schleyer, H. Stoll, H. Preuss, *J. Am. Chem. Soc.* **1991**, *113*, 6012; c) L. Seijo, Z. Brandiarán, S. Huzinaga, *J. Chem. Phys.* **1991**, *94*, 3762; d) M. Hargittai, M. Kolonits, D. Knausz, I. Hargittai, *J. Chem. Phys.* **1992**, *96*, 8990; e) M. Kaupp, P. von R. Schleyer, *J. Am. Chem. Soc.* **1992**, *114*, 491.

[18] B. Schubert, U. Behrens, E. Weiss, *Chem. Ber.* **1981**, *114*, 2640.

[19] M. Geissler, J. Kopf, E. Weiss, *Chem. Ber.* **1989**, *122*, 1395.

[20] J. L. Atwood, C. F. Hains, *J. Chem. Soc. Chem. Commun.* **1973**, 452.

[21] D. M. Root, C. R. Landis, T. Cleveland, *J. Am. Chem. Soc.* **1993**, *115*, 4201.

[22] B. Goldfus, P. von R. Schleyer, F. Hampel, *J. Am. Chem. Soc.* **1997**, *119*, 1072, and references therein.
[23] N. A. Bell, I. W. Nowell, H. M. M. Shearer, *J. Chem. Soc. Chem. Commun.* **1982**, 147.
[24] D. C. Green, K. Ruhlandt-Senge, unpublished results.
[25] H. Hope, *Progr. Inorg. Chem.* **1994**, *41*, 1.
[26] S. Chadwick, K. Ruhlandt-Senge, *Chem. Eur. J.* **1998**, *4*, 1768.
[27] G. M. Sheldrick, SHELXTL Version 5, Siemens Analytical X-ray Instruments, Madison, WI, **1994**.

$Ce_{16}Si_{15}O_6N_{32}$—An Oxonitridosilicate with Silicon Octahedrally Coordinated by Nitrogen[**]

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Octahedrally coordinated silicon is a peculiarity in silicate chemistry because the vast majority of natural and synthetic oxosilicates contain SiO_4 tetrahedra as typical structural building units.[1] However, there are only a small number of silicates, in which the coordination number of silicon is larger than four.[1–3] Most of the known examples are high-pressure phases like the rutile-type SiO_2 modification stishovite, the perovskite-analogous (Mg,Fe)SiO_3, which is found in the deeper crust of the earth, or hollandite-analogous $CaAl_2Si_2O_8$.[2] At lower pressure several silicates are accessible that contain SiO_6 octahedra and SiO_4 tetrahedra (e.g. $K_2Si_4O_9$,[4] $BaSi_4O_9$,[5] and $Na_{1.8}Ca_{1.1}Si_6O_{14}$[6]). Furthermore there are a small number of silicon phosphates that have been obtained at ambient pressure and these contain polymeric network structures of SiO_6 octahedra and PO_4 tetrahedra (e.g. SiP_2O_7 (form I),[7] $Rb_2SiP_4O_{13}$,[8] $(NH_4)_2SiP_4O_{13}$[9]). Owing to its enhanced basicity Si rather than P prefers the octahedral coordination in these compounds.[8]

A formal exchange of oxygen by nitrogen leads from the oxosilicates to the nitridosilicates. Yet all known representatives are constructed from SiN_4 tetrahedra. Unlike their oxidic analogues, more varied possibilities for the linkage of the SiX_4 building units (X = N, O) occur in the nitridosilicates.[10]

The compounds in the Si-Al-O-N and Si-O-N systems ("sialons" and "sions", respectively) have gained significant importance in materials science because of their outstanding thermal, chemical, and mechanical stability.[11] These compounds may be viewed as a link between oxidic silicates and aluminosilicates on one hand and the nitridosilicates and nitridoaluminosilicates on the other.[12, 13] Among the hitherto known crystalline nitridosilicates,[10] oxonitridosilicates, and oxonitridoaluminosilicates[11–13] as well as all the glassy phases that have been investigated in the systems Si-O-N and Si-Al-O-N[11, 14] no experimental evidence for the occurence of octahedrally coordinated silicon has yet been found.

With $Ce_{16}Si_{15}O_6N_{32}$ we have now synthesized the first oxonitridosilicate containing SiN_6 octahedra.[15] This new sion has been obtained by the reaction of stoichiometric amounts of cerium metal with silicon diimide and silicon dioxide in a radio frequency (rf) furnace under nitrogen atmosphere (ambient pressure) [Eq. (a)].

$$30\,Ce + 8\,SiO_2 + 27\,Si(NH)_2 + 6\,N_2 \xrightarrow[\text{rf furnace}]{1000-1540\,^{\circ}C,\ N_2} Ce_{16}Si_{15}O_6N_{32} + 2\,Ce_3Si_6N_{11} + 2\,Ce_4Si_4O_5N_6 + 27\,H_2 \quad (a)$$

Despite varying all experimental parameters (stoichiometry, reaction temperature, reaction time) we have not yet succeeded in synthesizing single-phase $Ce_{16}Si_{15}O_6N_{32}$. Under optimized conditions (see Experimental Section) coarsely crystalline $Ce_{16}Si_{15}O_6N_{32}$ was obtained as ruby-red single crystals in a yield of approximately 20% among yellow $Ce_3Si_6N_{11}$[16] and yellow-orange $Ce_4Si_4O_5N_6$.[17] All three phases are easily distinguishable in the reaction product due to their crystal habitus and their color, and they are obtained in the ratio given in Equation (a). Similar to all other highly condensed nitridosilicates, $Ce_{16}Si_{15}O_6N_{32}$ is stable up to 1600 °C and insensitive to hot acids and alkalis.

The X-ray structural analysis using diffraction data obtained on a four-circle diffractometer initially yielded a simple perovskite-type structure with a cubic lattice constant a = 385.1 pm. However neither a plausible composition of the compound nor a sufficient anisotropic refinement of the crystal structure could be performed based on this unit cell. A complete set of precession photographs revealed a 4 × 4 × 4 superstructure with a cubic lattice constant a' = 1540.36(9) pm. Accordingly the volume of the unit cell is 64 times as large as that of the simple perovskite structure type. In order to record even the weak superstructure reflections the data collection was performed by using the Stoe-IPDS image plate diffraction system.

According to the single-crystal X-ray structure determination,[18] the solid contains a three-dimensional network of corner-sharing SiN_6 octahedra and $Si(O,N)_4$ tetrahedra[15] (Figure 1). The structure may be viewed as a distorted defect variant $Ce_{16}(Si_{15}\square_1)O_6N_{32}\square_{10}$ of a 4 × 4 × 4 superstructure derived from the perovskite type (ABX_3). From a total of 64 octahedra per unit cell only four remain unchanged, four have been eliminated, and 56 have been replaced by tetrahedra (Figure 2).

A partial replacement of octahedra by tetrahedra in the perovskite structure type under formation of a superstructure has been reported, for example, for $Sr_3Al_2O_6$,[19] in which every fourth octahedron remains unchanged. A nearly complete substitution of 15 from 16 octahedra, as occurs in $Ce_{16}Si_{15}O_6N_{32}$, is to our knowledge unprecedented. However the few remaining SiN_6 octahedra in $Ce_{16}Si_{15}O_6N_{32}$ are nearly regular and they are only slightly tilted from their ideal

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