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Silylene, the Most Stable Form of Silicon in Aromatic Compounds

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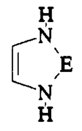
Abstract: Relative stability of the silylene-type cyclic compound $(HNSi)_3$ over $(HSiN)_3$ has been demonstrated by using correlated ab initio calculations. Aromaticity of both compounds has been revealed by using homodesmic reactions, indicating that Si^{II}—N building blocks can be used in constructing aromatic species instead of using normal double-bonded (Si^{IV}=N) systems. Although aromatic stabilization is somewhat smaller for the silylenes than for the Si^{IV}—N double-bonded systems according to the homodesmic reactions, the total energy of the silylenic compound $(HNSi)_3$ is lower than that of the silane $(HSiN)_3$. The stabilization for one silylene unit is the largest for the aromatic cyclic compound $(HNSi)_3$ among the substituted silylenes.

Introduction

Silylenes, the most intensively investigated[1] low-valent silicon species, are generally reactive and unstable molecules. It has been shown, however, that an NH_2 substituent[2] has a substantial (22.3 kcal/mol) stabilizing effect; thus the double-bonded H_2Si=NH is less stable by 18 kcal/mol[2] than HSi—NH_2, its silylene isomer. Stabilization by other groups such as OH[2] or SH[3] has been shown to be somewhat less effective. By the recent synthesis of the stable Arduengo's carbene[4] (**a**), the possibility of stable heavy atom analogues became apparent, and the corresponding germylene[5] and silylene[6] have been synthesized. Aromaticity—thought to be an important factor in the stabilization[6]—has been concluded from their NMR spectra as well as from ab initio quantum chemical calculations (comparing the heat of hydrogenation of Wanzlik- (**b**) and Arduengo- (**a**) type carbenes). Aromaticity of other (three- and four-membered ring) silylenes was concluded from low-level quantum chemical calculations as well,[7] but (apart from the Arduengo-type silylene) none of them has been isolated yet. Aromaticity of compounds containing σ^3,λ^4-silicon has been discussed in detail (see refs 1 and 8 and references cited therein), concluding a decreased aromaticity compared to the corresponding carbon analogues. These compounds, however, were detected as short-lived species only,[1] in contrast to their stable analogues containing σ^2,λ^3-phosphorus (—P=C bond), reported to have aromaticity similar to that of the corresponding C=C bonded compounds.[9]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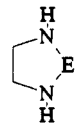
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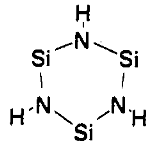
E:C. Si, Ge

In this work we want to point out, using quantum chemical calculations, that the Si^{II}—N building block can generally be an alternative to the double-bonded Si—N π-systems in building up aromatic structures and predict that, similarly to the "Arduengo-type silylene" (**a**), other stable aromatic silylenes might be isolated. A suitable target compound for our investigation is the six-membered ring $(HNSi)_3$ (**c**), which having six π-electrons and three σ^2,λ^2-silicon atoms can form an aromatic ring, together with its isomer $(HSiN)_3$ (**d**), which is the σ^3,λ^4-silicon-containing analogue of the well-known aromatic *s*-triazine.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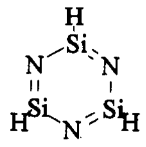
d

Calculations

Quantum chemical calculations were carried out using the GAUSSIAN 92[10] suite of programs. The structures of the compounds investigated were optimized at the HF/6-31G* and MP2/6-31G* levels of theory. In the text—unless otherwise stated—the MP2/6-31G* results are discussed. The stationary points obtained have been characterized by second derivative calculations, and real minima were found (no imaginary frequencies) unless otherwise stated. In certain cases (see text), to test the reliability of the calculations, a larger basis set (6-311G**) and higher levels of sophistication (CCSD) were used.

In order to test the adequacy of the single-determinant wave function, CISD and CASSCF calculations were carried out for $(HNSi)_3$ (**c**) and H_2NSiH. For H_2NSiH, the CASSCF active space consisted of four

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(1) Apeloig, Y. Theoretical aspects of organosilicon compounds. In *The Chemistry of Organic Silicon Compounds*; Patai. S.. Rappoport. Z., Eds.: John Wiley: Chichester, UK, 1989.

(2) Luke, B. T.: Pople, J. A.; Krogh-Jespersen. M.-B.; Apeloig, Y.; Karni. M.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 270. Truong. T. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 1775.

(3) Nyulászi, L.; Belghazi, A.; Kis-Szétsi, S.; Veszprémi, T.: Heinicke, J. *J. Mol. Struct.* (*THEOCHEM*). in press.

(4) Arduengo, A. J.; Harlow. R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**. *113*. 361.

(5) Hermann, W. A.: Denk, M.: Behm, J.; Scherer, W.; Klingan, F.-R.: Bock, H.: Wagner, M. *Angew. Chem.* **1992**, *104*. 1489.

(6) Denk, M.; West, R. Scientific Program and Abstracts of the 1st JOM Conference, Munich, Nov 4–5, 1993; p 21. Heinemann. C.: Thiel, W. Scientific Program and Abstracts of the 1st JOM Conference, Munich, Nov 4–5, 1993; p 44. Denk, M.; Lennon, R.; West, R.; Kiprof. P.: Wagner, M.; Haaland, A. Abstracts of lectures and oral at poster contributions of 10th International Symposium on Organometallic Chemistry, Poznan, Sept 15–20, 1993.

(7) Jemmis, E. D.; Prasad, B. V.; Tsuzuki, S.; Tanabe, K. *J. Phys. Chem.* **1990**. *94*. 5530. Frenking, G.; Remington, R. B.; Schaefer, H. F. *J. Am. Chem. Soc.* **1986**, *108*, 2169. Holmes, T. A.; Gordon, M. S. *Organometallics* **1984**, *3*, 399. Chandrasekhar, J.; Schleyer, P. v. R. *J. Organomet. Chem.* **1985**, *289*. 51. Gordon, M. S.; Boudjouk, P. *J. Am. Chem. Soc.* **1985**. *107*, 1439.

(8) (a) Baldridge. K. K.; Gordon. M. S. *J. Am. Chem. Soc.* **1988**, *110*. 4204. (b) Nagase, S. *Polyhedron* **1991**, *10*, 1299.

(9) Nyulászi, L.: Veszprémi, T.: Réffy, J. *J. Phys. Chem.* **1993**. *97*. 4011.

(10) Frish, M. J.; Trucks, G. W.: Head-Gordon. M.; Gill, P. M. W.: Wong, W.: Foresman, J. B.: Johnson. B. G.: Schlegel, H. B.: Robb. M. A.; Repolgle, E. S.; Gomperts, M.; Andrews. J. A.; Ragchavachari, K.; Binkley, J. S.; Gonzalez, C.: Martin, R. L.; Fox, D. J.; Defrees, J.: Baker, J.: Stewart, J. P.: Pople. J. A. GAUSSIAN 92. Revision C: Gaussian. Inc.: Pittsburgh. PA. 1992.

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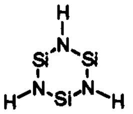
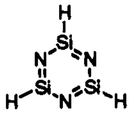
Table 1. Geometrical Parameters and Energies of c and d at Different Levels of Theory

									
	SiN	SiNSi	NSiN	$-E_{tot}$	SiN	SiNSi	NSiN	$-E_{tot}$	ΔE
HF/1[a]	1.740	129.21	110.70	1031.944 60	1.635	118.44	121.56	1031.898 12	23.84
MP2/1	1.756	129.57	110.43	1032.701 32	1.665	116.98	123.02	1032.666 81	16.30
CASSCF/1	1.744	129.25	110.75	1031.984 52	1.642	118.40	121.60	1031.943 19	20.57
CCSD/1[b]	1.756	129.57	110.43	1032.699 00	1.665	116.98	123.02	1032.642 54	30.05
MP2/2	1.751	129.74	110.26	1033.248 62	1.659	117.31	122.69	1033.207 31	20.56

[a] 1 denotes 6-31G*, 2 6-311G** basis set. [b] CCSD/6-31G*//MP2/6-31G*. Geometrical Data are given in angstroms and degrees. E_{tot}, total energy in atomic units. ΔE, the energy difference between structures **c** and **d** in kcal/mol, including ZPE.

electrons and four orbitals (4,4). In contrast to H_2Si,[11] the configuration characterizable by the σ–π^* double excitation did not have a significant weight (the 0.03 CI coefficient was the fourth largest in the CASSCF wave function). As for the CISD calculation of $(HNSi)_3$ (**c**), no determinant other than the HF had a CI coefficient larger than 0.02 in the wave function.

Based on the above results, CASSCF calculations for the two isomeric rings (**c** and **d**) were carried out on the π-orbital (6,6) space (the silicon nonbonding orbitals situated in the molecular plane of **c**, having little importance, have not been included). Again, similarly to the previous observations, no reference configuration other than the HF had significant weight.

Zero-point energies (ZPEs) used in the isodesmic reactions were calculated at the MP2/6-31G* level of theory for energy differences calculated at correlated levels, while HF/6-31G* ZPEs were used for energy differences obtained at the HF level of theory. MP2/6-311G** ZPEs, calculated for a few compounds only, were nearly the same as the MP2/6-31G* values.

Results and Discussion

The calculated geometries and energies of **c** and **d** at different levels of theory are shown in Table 1. Second derivative calculations reveal that both structures are real minima on the potential energy surface, at both the MP2/6-31G* and the HF/6-31G* levels of theory. The structures are planar; however, the out-of-plane motions of hydrogens are characterized by rather low harmonic frequencies (151, 133 and 210, 180 cm^{-1} at the HF and MP2 levels for **c** and **d**, respectively), according to the second derivative calculations (cf. the nonplanar minimum for hexasilabenzene[1,8b]). The Si–N bond length shows no alternation either for **c** or for **d**, as is usual for aromatic compounds. The Si–N distances, however, are considerably longer in the case of **c** than those for **d** at any level of theory used here. This feature alone would indicate that **d** has stronger bonds and thus is the more stable of the two compounds. From Table 1, however, it is apparent that structure **c** is more stable by at least 16 kcal/mol. A larger basis set and a higher level of electron correlation stabilize structure **c** relative to **d** (Table 1). Considering the relative energies of the silylimine–aminosilylene pair, the above contradiction becomes understandable. At the MP2/6-31G*//MP2/6-31G*+ZPE level of theory, aminosilylene is more stable by 12.22 kcal/mol (cf. 18 kcal/mol[2]), although the Si–N bond length is longer by 0.102 Å (1.719 vs 1.617 Å), thus the longer bond in the more stable **c** is understandable. The larger bond length is well-known in the case of silylenes and is explained by the large p character in the bonding MO.[1,2] The larger stability of **c** is in accordance with the difference between the strengths of the N–H and Si–H bonds. As concluded from the bond dissociation energies of SiH_4[12] and NH_3,[13] the N–H bond is more stable than the Si–H by about 16 kcal/mol. (As a consequence, replacement of hydrogens with bulky protecting groups might alter the relative stabilities of **c** and **d**.)

The bond angles (Table 1) in **d** are near 120°, while for **c** larger alternation is shown, where NSiN and SiNSi are near to 110 and 130°, respectively. Considering the bond angles in H_2NSiNH_2 and HSiNHSiH (in cis,cis form), the bonding angles are somewhat different (99.87° and 136.84°, respectively). Calculating the MP2/6-31G* energies of H_2NSiNH_2 and HSiNHSiH at NSiN and SiNSi angles, fixed at the values obtained for the ring at the same level of theory (all other parameters optimized), 2.62 and 0.93 kcal/mol increases were obtained. As **c** consists of three nitrogen and silicon atoms, a ring strain of 3(2.62 ± 0.93), about 10 kcal/mol, can be estimated.

In order to elucidate how large the contribution of the aromatic character in the stabilization of the two compounds is, the following conventional bond separation (1), homodesmic (2), and superhomodesmic (3) reactions have been investigated. (Henceforth, for the reactions, the results of MP2/6-31G*//MP2/6-31G*+ZPE calculations are given, with the HF/6-31G*//HF/6-31G*+ZPE values in parentheses. For reactions 1 and 2, MP2/6-31G**//MP2/6-311G**+ZPE energies were calculated as well but differed by less than 1 kcal/mol from the MP2/6-31G* results.)

$$\mathbf{c} + 3NH_3 + 3SiH_3 = 6HSi\text{—}NH_2 \qquad E = -17.94\ (-11.17) \quad (1c)$$

$$\mathbf{c} + 3HSi\text{—}NH_2 = 3HSi\text{—}NH\text{—}Si\text{—}NH_2 \qquad \Delta E = +5.95\ (+6.45) \quad (2c)$$

$$\mathbf{c} + 3HSi\text{—}NH\text{—}Si\text{—}NH_2 = 3HSi\text{—}NH\text{—}Si\text{—}NH\text{—}Si\text{—}NH_2 \qquad \Delta E = +3.10\ (+5.84) \quad (3c)$$

$$\mathbf{d} + 3NH_3 + 3SiH_4 = 3HN{=}SiH_2 + 3H_2N\text{—}SiH_3 \qquad \Delta E = +68.40\ (+75.21) \quad (1d)$$

$$\mathbf{d} + 3HN{=}SiH_2 = 3H_2Si{=}N\text{—}SiH{=}NH \qquad \Delta E = +19.57\ (+12.15) \quad (2d)$$

$$\mathbf{d} + 3H_2Si{=}N\text{—}SiH{=}NH = 3H_2Si{=}N\text{—}SiH{=}N\text{—}SiH{=}NH \qquad \Delta E = +9.27\ (-1.55) \quad (3d)$$

As for the fragments used in homodesmic reactions 2 and 3, several conformers are conceivable. All of them were optimized at the HF/6-31G* level of theory, and those having the lowest energies were reoptimized at the MP2/6-31G* level of theory. The energies of the different conformers did not show larger scatter than 1.5 kcal/mol. Second derivatives have been calculated at both levels. The four- and six-membered chains

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[11] Meadows, J. H.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1976**, *98*, 4383. Banschlider, C. W.; Schaefer, H. F., III; Bagus, P. S. *J. Am. Chem. Soc.* **1977**, *99*, 7106.

[12] Walsh, R. Thermochemistry. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, UK, 1989.

[13] *CRC Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, Ann Arbor, Boston, 1990.

with tetravalent silicon (in reactions **2d** and **3d**) were found as saddle points but not minima in their planar forms at both the HF and MP2 levels of theory. The real minima were found at slightly (1–2 kcal/mol) lower energies, with the hydrogens on silicon occupying an out-of-plane position. The $H_2Si{=}NSi{\sim}$ part of the chain has been found to be linear, similarly to $H_2Si{=}NSiH_3$,[14] for both the four- and six-membered compounds. All the chains containing divalent silicon are planar according to the second derivative calculations.

For **d**, bond separation (**1d**), homodesmic (**2d**), and superhomodesmic (**3d**) reactions have energies similar to—although somewhat smaller than—those for benzene,[8a] and the largest reaction energy, in accordance with expectations, is exhibited by the bond separation reaction. Comparing the HF and the MP2 reaction energies, the values obtained at the correlated level are somewhat larger, as usual. All these facts suggest that **d** is a normal aromatic molecule. As the optimized structure of **d** was found to be planar, but the four- and six-membered chains have slightly nonplanar minima, it is reasonable to conclude that the planar structure for **d** is stabilized by aromaticity.

As for **c**, bond separation energy is negative; thus seemingly no stabilization, compared to the Si^{II}–N building block, is achieved. Investigating the energies of homodesmic and superhomodesmic reactions, however, the stabilization energy for ring cyclization is considerably larger, having a positive value. Inclusion of electron correlation decreases somewhat the stabilization energy. It is well-known that homodesmic reactions are much better measures of aromaticity[8a] than bond separation reactions, as the stabilization present in the dimeric (trimeric) units is not included; however, both types of these reactions used to show stabilization for aromatic compounds. The obvious reason for the destabilization in the isodesmic reaction (**1c**) is shown in the isodesmic reaction 4,

$$HSi{-}NH{-}Si{-}NH_2 + NH_3 + SiH_2 = 3HSi{-}NH_2 \qquad \Delta E = -7.87\ (-5.88) \tag{4}$$

where the dimeric silylene compound ($HSi{-}NH{-}Si{-}NH_2$) shows *destabilization* compared to the three monomeric units, explaining the difference between energies of bond separation and homodesmic reactions. The endothermicity of this reaction means that the stabilization achieved by the formation of the SiN bond in the "monomeric" $HSiNH_2$ is larger than that at the formation of the new Si–N bond between two aminosilylenes.

The destabilization can be detected on the bond lengths of the "dimer" ($HSiNHSiNH_2$), too, as each bond length is larger than the corresponding one in $HSiNH_2$. The increase is the largest in case of the central Si–N bond, resulting in similar bond length distribution as for butadiene. The length of this bond (1.779 Å at the MP2/6-31G* level) is larger, while the peripheral bond lengths (1.723 and 1.744 Å) are shorter than those in ring **c**, (cf. the cases of butadiene and benzene).

In order to understand this behavior, the stabilization of the silylene by the amino substituent has to be investigated. In case of H_2NSiH, this stabilization has been explained by the interaction of the amino group lone pair and the silylenic LUMO and has been measured by isodesmic reaction 5 to be 22.3 kcal/mol at the MP4/6-31G*//HF/3-21G(*) level of theory.[2] (At the level of theory used in this work, this value is somewhat smaller.)

$$H_2N{-}SiH + SiH_4 = H_2N{-}SiH_3 + SiH_2 \qquad \Delta E = 21.96\ (16.42) \tag{5}$$

Although this reaction is not strictly isodesmic, as the Si^{II}–N or the Si^{II}–H bond should obviously be different from the Si^{IV}–N and Si^{IV}–H bonds, respectively (cf., for example, the Si–H bond lengths of SiH_4 and SiH_2), its energy is close to the rotation barrier of H_2NSiH (26.74 kcal/mol at the MP2/6-31G*//MP2/6-31G*+ZPE level of theory). (Note that in the case of the rotated form of H_2NSiH, the repulsion of the amino and silylene "lone pairs" causes further destabilization; thus the 26.74 kcal/mol destabilization is not entirely due to the loss of amino group lone pair–silylene empty orbital interaction.)

The stabilization exerted by a second amino group on silylene is, however, smaller than that caused by the first amino group, as is shown by the exothermicity of reaction 6. Rotating one of

$$NH_2{-}Si{-}NH_2 + SiH_2 = 2HSi{-}NH_2 \qquad \Delta E = -6.74\ (-3.52) \tag{6}$$

the amino groups by 90° in order to avoid the stabilizing interaction, a destabilization of 12.40 kcal/mol was obtained. This value (at the MP2/6-31G*//MP2/6-31G* level of theory) is 14.34 kcal/mol smaller than the one obtained for $HSiNH_2$ (cf. the exothermicity of reaction **6**). The subsequent rotation of the second amino group resulted in similar destabilization (28.20 kcal/mol), as in the case of $HSiNH_2$. A similar phenomenon has already been shown by investigating the rotation of the amino groups in diaminogermylene,[5] with 12 and 24 kcal/mol destabilization upon the subsequent rotation of the first and then the second amino groups, respectively.[5] Similar conclusions were obtainable from reaction 7 (and the corresponding rotational barriers as well), showing that the stabilization of the amino group is less effective on the second silylene center.

$$SiHNHSiH + NH_3 = 2HSiNH_2 \qquad \Delta E = -6.97\ (-6.19) \tag{7}$$

From the above reactions, the perplexing result obtained from the homodesmic reaction **1c** becomes understandable: the stabilization on a silylene that has already been stabilized is smaller than that for the unsubstituted parent compound. Nevertheless, the presence of a second amino group results in further stabilization. In case of H_2NSiNH_2, for example, the stabilization is 2(21.96 – 6.74) (from reactions 5 and 6, respectively) = 37.18 kcal/mol. The sum of the barriers for the two subsequent NH_2 group rotations is 40.60 (12.40 + 28.20) kcal/mol, in good agreement with the above value. The average stabilization for the two silylenes (one singly and one doubly amino-substituted) in $HSiNHSiNH_2$ is 29.01 kcal/mol using the relative destabilization compared to three aminosilylenes in reaction 4. For ring **c**, the stabilization of one silylene unit is 37.94 kcal/mol (using reaction 1c and the stabilization of NH_2SiH from reaction 5). The stabilization for the silylenes can be seen in Figure 1, showing that it is the largest for cyclic **c** among the compounds investigated here. The homodesmic reaction energies of 2c and 3c indicating aromaticity of **c**, reflect again the same stabilization.

Conclusions

The investigations of the two isomeric silicon–nitrogen cycles **c** and **d** showed that both compounds are real minima on the potential energy surface, **c**, built up from silylenes (σ^2,λ^2-silicon atoms), being the more stable by 30.05 kcal/mol (CCSD/6-31G*//MP2-631G* level of theory). This stability is at least partly due to the strength of the N–H bond (compared to the Si–H bond).

According to homodesmic reaction energies, both compounds are aromatic, with the larger stabilization obtained for **d**. The energy of the superhomodesmic reaction for **c**, however, is of similar value, as for pyrrole or furan,[8a] thus **c**—containing σ^2,λ^2-silicon—has aromatic character. Taking into account the ring stain (estimated as about 10 kcal/mol) for **c**, a strong aromatic stabilization for this bonding structure can be concluded.

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(14) Schleyer, P. v. R.; Stout, P. *J. Chem. Soc., Chem. Commun.* **1986**, 1373. Walter, S.; Klingebiel, U.; Schmidt-Bäse, D. *J. Organomet. Chem.* **1991**, *412*, 319.

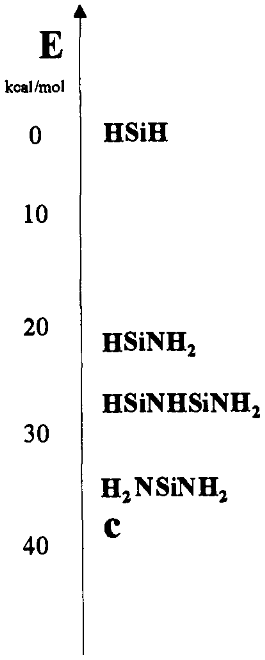

Figure 1. Stabilization energies exerted by different substituents on silylene.

The bond separation energy for **c**—unprecedented among aromatic compounds—shows destabilization. This fact, however, is the consequence of the smaller stabilization obtained when the *second* Si^{II}–N bond is formed with silicon, as shown by the bond separation reaction energy for $HSiNHSiNH_2$ and NH_2SiNH_2.

Due to aromaticity, the thermodynamic stabilization for one silylene in **c** is even larger than that achieved by two amino groups on silylene, as is shown in Figure 1. As a highly strained four-membered ring, diaminosilylene has already been reported to be stable up to 77 K,[15] there is good hope that the aromatic **c** (presumeably with bulky protecting substituents on nitrogen) is a synthesizeable compound. More generally, the silylenic building block -Si—NH- can alternatively used instead of -HSi═N- in constructing aromatic systems, and Arduengo's silylene (**a**) was the first but not the last synthesized example of stable aromatic silylenes.

Acknowledgment. Financial support from OTKA 642 and 754 is gratefully acknowledged. Suggestions of one of the referees about the impact of the SiH vs NH bond strength on the relative stabilities of structures **c** and **d** are acknowledged.

Note Added in Proof: During the refereeing process, the following paper about the "Arduengo silylene" (cf. ref 6) appeared in print. Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc* **1994**, *116*, 2691.

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(15) Veith, M.; Werle. E.; Lisowsky, R.: Köppe. R.: Schnöckel, H. *Chem. Ber.* **1992**, *125*. 1375.