First Evidence of Unhindered Silanimines Obtained by Flash Vacuum Thermolysis and Vacuum Gas-Solid Reaction

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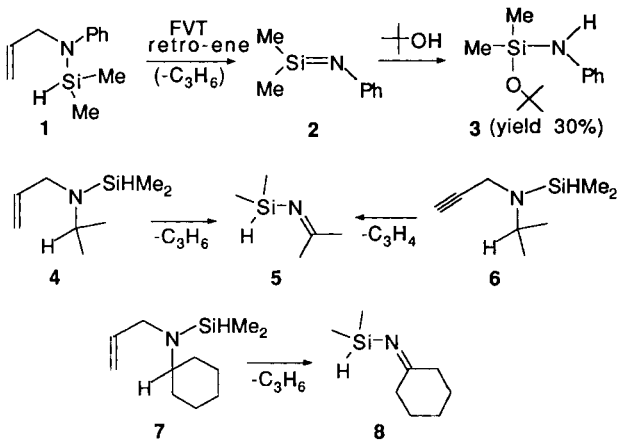
The unhindered silanimines 1,1-dimethyl-*N*-phenylsilanimine (**2**) and *N*-isopropyl-1,1-dimethylsilanimine (**10**) have been generated by flash vacuum thermolysis of the *N*-allylsilanamine **1** and vacuum gas-solid reaction of the 1-chlorosilanamine **9**, respectively. The silanimines **2** and **10** have been characterized by MS as well as by chemical trapping to yield **3** or dimerization to the cyclodisilazane **11**.

The chemistry of silicon-nitrogen double-bonded compounds has recently culminated in the isolation of two kinetically stabilized silanimines[1]. The scarcity of such isolated compounds can be explained by their extreme instability: silanimines substituted by sterically demanding substituents polymerize rapidly in solution even at low temperature[2]. Attempts to synthesize silanimines by thermal elimination of lithium fluoride from lithium salts of fluorosilanamines generally led to the corresponding cyclodisilazanes[3]. If a silanimine can be effectively formed as a reactive intermediate in this process, a bimolecular two-step cyclodisilazane formation cannot however be excluded[4]. The aminosilylene $HSi-NH_2$ has been observed, instead of the unsubstituted silanimine $H_2Si=NH$, by the 254-nm photolysis of silyl azide isolated in an argon matrix at 12 K[5]. Transient *N*-*p*-tolyl- and *N*-phenyl-1,1-dimethylsilanimines, characterized by their dimers or addition products, have been obtained by mild thermal [2 + 3] cycloreversion of a siladihydrotriazole at +50°C[6,7], cothermolysis of dimethylsilacyclobutane and *N*-phenylbenzaldimine[8], and photolysis of dimethylphenylsilyl azide[9]. We report here on the first direct spectrometric evidence of the formation of two unhindered silanimines using respectively the retro-ene reaction of an *N*-allylsilanamine under flash vacuum thermolysis (FVT) conditions, and the dehydrochlorination of an 1-chlorosilanamine by vacuum gas solid reaction (VGSR)[10].

The FVT of allyl dimethylsilyl ether has been shown to lead to dimethylsilanone by a retro-ene decomposition[11] and therefore, we anticipated the silanamine **1** as a precursor of the *N*-phenyldimethylsilanimine **2**. Compound **1** was prepared from allylphenylamine and chlorodimethylsilane by the slightly modified general procedure[12] (see Experimental). In fact, the FVT of **1** at 900°C/10^{-4} hPa led mainly to the expected products, propene and silanimine **2**. The formation of **2** was unambiguously demonstrated by injection of *tert*-butyl alcohol, an efficient trapping agent of reactive silanimines[2,9], into the oven exit during the time of thermolysis. The expected addition product **3** was thus obtained in ca. 30% yield (determined by GC) and identified by comparison (NMR, GC/MS) with an authentic sample[13].

Direct evidence of the presence of **2** in the FVT of precursor **1** has been obtained by coupling the oven with a high-resolution mass spectrometer, as previously described[14]. All the species produced by FVT of compound **1** at 900°C have been characterized in this way in real time by MS. In particular, the spectrum shows the disappearance of the molecular (*m/z* 191) and base peak (*m/z* 59, $[(CH_3)_2SiH]^+$) of the precursor **1**. At the same time, a new peak at *m/z* 149.067 (30%) appears, corresponding to that expected for silanimine **2** ($C_8H_{11}NSi$, calcd. 149.0661), as confirmed by its MS/MS analysis showing fragments at *m/z* 134 (− CH_3), and 91 ($[Ph-N]^+$) resulting from the cleavage of the Si=N double bond.



The FVT of precursors **4**, **6**, **7** was undertaken under similar conditions. The energetically favored, competitive retro-ene process leading to the *N*-(dimethylsilyl)imines **5** and **8** was however predominant, and no silanimine was observed. The imines **5** and **8**, obtained in ca. 30% yield (GC), were characterized by IR [Si−H: 2080 (**5**) or 2095 cm^{-1} (**8**), C=N: 1670 cm^{-1} (**5** and **8**)], in good agreement with the values reported for similar compounds[15], as

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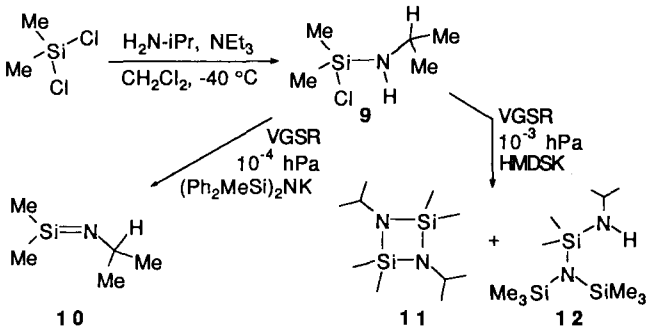
well as by MS. The mass spectra of imines **5** and **8** exhibit the respective $M^{+\bullet}$ peaks at *m/z* 115.082 and 155.113 [calcd. $C_5H_{13}NSi$ (**5**) 115.0817; $C_8H_{17}NSi$ (**8**) 155.1130]. The *N*-silylimine structure is obvious in both compounds, owing to their important fragment ion at *m/z* 59 ($[(CH_3)_2SiH]^+$, rel. int. 87% for **5** or 28% for **8**) resulting from the cleavage of the Si–N single bond.

On the other hand, the dehydrochlorination under VGSR conditions of the chlorosilanamine **9**, synthesized by condensation of isopropylamine with dichlorodimethylsilane in the presence of triethylamine, gave the expected *N*-isopropyldimethylsilanimine **10**. The VGSR apparatus has previously been described[10]. When potassium bis(trimethylsilyl)amide (HMDSK)[16] was used as a solid base, 2,4-diisopropyl-1,1,3,3-tetramethylcyclodisilazane (**11**) and *N'*-isopropyl-1,1-dimethyl-*N,N*-bis(trimethylsilyl)silanediamine (**12**) were formed in a 7:3 molar ratio, accompanied by hexamethyldisilazane. These compounds have been characterized by ^1H NMR, GC, and HRMS. The data for cyclodisilazane **11** are consistent with those of an authentic sample[12]. It is likely that silanediamine **12** resulted from a substitution reaction. Due to the fact that dehydrochlorination occurred under high dilution conditions (10^{-3} hPa), the cyclodisilazane ring formation can be explained only by dimerization of the unstable silanimine **10** in the cold trap.



The presence of the intermediate **10** was unambiguously confirmed by direct analysis of the gaseous flow. In the recently described device[14] the VGSR reactor is connected with the ion source of the mass spectrometer. In order to increase the selectivity of the reaction, potassium bis(methyldiphenylsilyl)amide[16] was used as a more hindered solid base of low nucleophilicity. Products resulting from the vaporization of chlorosilanamine **9** on this solid base were identified by real-time MS analysis. The mass spectrum obtained [$C_5H_{13}NSi$ calcd. 115.0817, found 115.082, fragmentations at *m/z* 114, 100 (– $^{\bullet}CH_3$), 72 (– $^{\bullet}CH(CH_3)_2$)] showed clearly the formation of the silanimine **10**, the isomeric *N*-silylimine structure **5** being precluded by the absence of the characteristic ion at *m/z* 59.

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Experimental

Preparation of Silanamines **1**, **4**, **6**, **7**: The corresponding secondary amine (10 mmol), triethylamine (1.1 g, 11 mmol), and dichloromethane (10 ml) were placed in a thoroughly dried, nitrogen-flushed two-necked flask (allylphenyl- and allylcyclohexylamine were purchased from Aldrich, allylisopropyl- and isopropylpropargylamine were prepared according to ref.[17]). The mixture was cooled to –40 °C and chlorodimethylsilane (1.2 g, 13 mmol) was added dropwise with stirring. After stirring at –40 °C for 1 h, then at room temp. for 2 h, 10 ml of pentane was added. After filtration of triethylamine hydrochloride under nitrogen and evaporation of solvents under vacuum, another 30 ml of pentane was added to the residue and the mixture again filtered and concentrated. The crude silanamines thus obtained were distilled under vacuum and stored under nitrogen in a Schlenk tube.

N-Allyl-1,1-dimethyl-N-phenylsilanamine (**1**): B.p. 105 °C/15 hPa, yield 96%. – HRMS: $C_{11}H_{17}NSi$ calcd. 191.1130, found 191.113. – MS: *m/z* (%) = 191 (75), 190 (24.7), 176 (37.5), 174 (12.1), 164 (66.2), 150 (28.5), 149 (14.5), 135 (22.9), 133 (24), 132 (17), 130 (13.5), 120 (14.5), 106 (25.4), 104 (16.7), 93 (5.8), 86 (18.5), 77 (20.5), 66 (8.6), 59 (100), 51 (8.1), 45 (6.3), 43 (6.7), 39 (10), 28 (8.3). – IR (film): $\tilde{\nu}$ = 3080 cm^{-1} (=C–H), 2130 (Si–H), 1625 (C=C), 1235 (Si–C), 900 (br., Si–N). – ^1H NMR ($CDCl_3$): δ = 0.34 [d, *J* = 3 Hz, 6H, $Si(CH_3)_2$], 3.86–4.00 (m, 2H, $CH_2CH=CH_2$), 4.80 (sept, *J* = 3 Hz, 1H, HSi), 4.93–5.30 (m, 2H, $CH_2CH=CH_2$), 5.58–6.20 (m, 1H, $CH_2CH=CH_2$), 6.53–7.33 (m, 5H, Ph). – ^{13}C NMR ($CDCl_3$): δ = –1.6 [2 C, $Si(CH_3)_2$], 50.3 ($CH_2CH=CH_2$), 115.0 ($CH_2CH=CH_2$), 117.4 (2 C, Ph), 118.7 (Ph), 128.8 (2 C, Ph), 136.5 ($CH_2CH=CH_2$), 149.3 (Ph). – ^{29}Si NMR ($CDCl_3$): δ = –4.5.

N-Allyl-N-isopropyl-1,1-dimethylsilanamine (**4**): B.p. 36 °C/15 hPa, yield 56%. – HRMS: $C_8H_{19}NSi$ calcd. 157.1287, found 157.129. – MS: *m/z* (%) = 157 (10.9), 142 (100), 133 (1.5), 130 (6.3), 100 (24.4), 98 (7.9), 88 (5.3), 86 (13.4), 84 (6.5), 73 (6.8), 59 (58.4), 56 (3.9), 45 (5.8), 43 (7.6), 41 (19.1), 39 (7.3), 28 (11.6), 27 (8.3). – IR (film): $\tilde{\nu}$ = 3070 cm^{-1} (=C–H), 2120 (Si–H), 1630 (C=C), 1245 (Si–C), 895 (br., Si–N). – ^1H NMR ($CDCl_3$): δ = 0.13 [d, *J* = 3 Hz, 6H, $Si(CH_3)_2$], 1.08 [d, *J* = 6 Hz, 6H, $CH(CH_3)_2$], 3.15 [sept, *J* = 6 Hz, 1H, $CH(CH_3)_2$], 3.28–3.40 (m, 2H, $CH_2CH=CH_2$), 4.47 (sept, *J* = 3 Hz, 1H, HSi), 4.83–5.27 (m, 2H, $CH_2CH=CH_2$), 5.50–6.13 (m, 1H, $CH_2CH=CH_2$). – ^{13}C NMR ($CDCl_3$): δ = –0.6 [2 C, $Si(CH_3)_2$], 23.2 [2 C, $CH(CH_3)_2$], 47.8 ($CH_2CH=CH_2$), 49.1 [$CH(CH_3)_2$], 113.6 ($CH_2CH=CH_2$), 141.1 ($CH_2CH=CH_2$). – ^{29}Si NMR ($CDCl_3$): δ = –10.2.

N-Isopropyl-1,1-dimethyl-N-propargylsilanamine (**6**): B.p. 46 °C/60 hPa, yield 65%. – HRMS: $C_8H_{17}NSi$ calcd. 155.1130, found 155.113. – MS: *m/z* (%) = 155 (2.4), 154 (1.2), 140 (87.4), 100 (35.6), 98 (10.8), 86 (20.2), 83 (12.4), 82 (20.9), 73 (23.8), 59 (100), 56 (13.5), 45 (9.8), 43 (29.3), 41 (17.5), 39 (28.8), 28 (20.7), 27 (18). – IR (film): $\tilde{\nu}$ = 3310 cm^{-1} (≡C–H), 2120 (Si–H and C≡C), 1245 (Si–C), 895 (br., Si–N). – ^1H NMR ($CDCl_3$): δ = 0.20 [d, *J* = 3 Hz, 6H, $Si(CH_3)_2$], 1.13 [d, *J* = 6 Hz, 6H, $CH(CH_3)_2$], 2.10 (t, *J* = 2.5 Hz, 1H, C≡CH), 3.23 [sept, *J* = 6 Hz, 1H, $CH(CH_3)_2$], 3.47 (d, *J* = 2.5 Hz, 2H, $CH_2C\equiv C$), 4.42 (sept, *J* = 3 Hz, 1H, HSi). – ^{13}C NMR ($CDCl_3$): δ = –1.1 [2 C, $Si(CH_3)_2$], 22.7 [2 C, $CH(CH_3)_2$], 33.5 ($CH_2C\equiv CH$), 49.4 [$CH(CH_3)_2$], 69.4 ($CH_2C\equiv CH$), 85.8 ($CH_2C\equiv CH$). – ^{29}Si NMR ($CDCl_3$): δ = –4.7.

N-Allyl-N-cyclohexyl-1,1-dimethylsilanamine (**7**): B.p. 96 °C/15 hPa, yield 85%. – HRMS: $C_{11}H_{23}NSi$ calcd. 197.1600, found 197.160. – MS: *m/z* (%) = 197 (16.8), 182 (6), 170 (3.1), 156 (14.3), 154 (80.1), 141 (27.9), 140 (19.6), 139 (13.9), 128 (3.9), 126 (28.3), 112 (23.1), 100 (13.5), 99 (13), 96 (100), 86 (36.8), 83 (12), 73 (5.6), 68 (20.8), 59 (84), 55 (21.3), 54 (15), 45 (4.4), 43 (10.2), 41 (64.1), 39 (29.1), 28 (19.2), 27 (19.9). – IR (film): $\tilde{\nu}$ = 3080 cm^{-1} (=C–H), 2125 (Si–H), 1640 (C=C), 1245 (Si–C), 900 (br., Si–N). – ^1H NMR ($CDCl_3$): δ = 0.13 [d, *J* = 3 Hz, 6H, $Si(CH_3)_2$], 0.9–1.9 (m, 10H, cyclohexyl CH_2), 2.20–2.76 (m, 1H, cyclohexyl CH), 3.27–3.43 (m, 2H, $CH_2CH=CH_2$), 4.45 (sept, *J* = 3 Hz, 1H, HSi), 4.76–5.25 (m, 2H, $CH_2CH=CH_2$), 5.46–6.16 (m, 1H, $CH_2CH=CH_2$). – ^{13}C NMR ($CDCl_3$): δ = –0.4 [2 C, $Si(CH_3)_2$], 26.1 (cyclohexyl CH_2), 26.7 (2 C, cyclohexyl CH_2), 34.2 (2 C, cyclohexyl CH_2), 48.7 ($CH_2CH=CH_2$), 58.4 (cyclohexyl CH), 113.5 ($CH_2CH=CH_2$), 141.1 ($CH_2CH=CH_2$). – ^{29}Si NMR ($CDCl_3$): δ = –10.1.

1-Chloro-N-isopropyl-1,1-dimethylsilanamine (**9**): B.p. 52°C/60 hPa, yield 85%. – HRMS: $C_5H_{14}ClNSi$ calcd. 151.0584, found 151.057. – MS: *m/z* (%) = 138 (33), 136 (100), 116 (30), 115 (9), 113 (14), 100 (26), 95 (19), 93 (53), 59 (11), 44 (9). – IR (film): $\tilde{\nu}$ = 3370 cm^{-1} (NH), 1260 (Si–C), 890 (br., Si–N), 650 (Si–Cl). – ^1H NMR ($CDCl_3$): δ = 0.43 [s, 6H, $Si(CH_3)_2$], 1.11 [d, *J* = 7 Hz, 6H, $CH(CH_3)_2$], 1.37 (1H, NH), 3.20 [sept, *J* = 7 Hz, 1H, $CH(CH_3)_2$]. – ^{29}Si NMR ($CDCl_3$): δ = 9.1.

FVT of Silanamines **1**, **4**, **6**, **7**: Thermolysis was performed at 900°C/10^{-4} hPa (oven dimensions: *l* = 10 cm, i.d. = 14 mm). The oven was coupled either to an IR cryostat, allowing direct recording of spectra under vacuum between −196 and +50°C, or to a high resolution mass spectrometer. Chemical trapping experiments yielding *tert*-butoxysilanamine **3** were performed by gas phase co-injection of *tert*-butyl alcohol (1.5 equivalents) into the oven exit during the thermolysis of silanamine **1**.

1,1-Dimethyl-N-phenylsilanimine (**2**): HRMS: $C_8H_{11}NSi$ calcd. 149.0661, found 149.067. – MS: *m/z* (%) = 149 (31.1), 148 (15.9), 136 (12.2), 134 (17.2), 132 (12.6), 120 (3.4), 104 (8), 93 (12), 91 (100), 78 (7), 67 (24), 65 (12.6), 56 (8), 55 (9.2), 54 (16.7), 43 (6.7), 41 (67.7), 39 (33.3), 28 (15.8), 27 (15.8); MS/MS of *m/z* 149: 148, 146, 134, 132, 119, 105, 91, 37, 28.

N-Isopropylidene-1,1-dimethylsilanamine (**5**): HRMS: $C_5H_{13}NSi$ calcd. 115.0817, found 115.082. – MS: *m/z* (%) = 115 (7.3), 114 (2.5), 102 (3.6), 100 (34), 86 (5.3), 84 (1.8), 73 (7.6), 59 (86.9), 57 (11.3), 55 (3.6), 45 (11), 43 (15), 42 (100), 41 (97.1), 39 (50.3), 28 (30.7), 27 (32.5); MS/MS of *m/z* 115: 114, 113, 112, 100, 28.

N-Cyclohexylidene-1,1-dimethylsilanamine (**8**): HRMS: $C_8H_{17}NSi$ calcd. 155.1130, found 155.113. – MS: *m/z* (%) = 155 (9.3), 154 (4.2), 141 (2), 140 (1.9), 126 (14.4), 112 (33.5), 100 (3.3), 99 (7.8), 97 (9.5), 78 (5.1), 72 (7.8), 69 (11.4), 67 (10.9), 59 (27.8), 58 (11.5), 54 (24.2), 43 (4.9), 42 (60.4), 41 (100), 39 (63.4), 28 (30.6), 27 (32.2).

Dehydrochlorination of Chlorosilanamine **9** *on Potassium Bis(trimethylsilyl)amide (HMDSK):* The VGSR reactor was filled in half-section with HMDSK (60 g, 0.3 mol), then heated and degassed at 60°C during 5 h. Chlorosilanamine **9** was slowly vaporized on the surface of the solid base, products were trapped on a cold finger, and further analysis was carried out at room temp. (^1H NMR, GC, MS). The mixture consisted of *hexamethyldisilazane* [$C_5H_{16}NSi_2$ ($M^{+\cdot}$ – CH_3) calcd. 146.0821, found 146.082 (MS). – ^1H NMR ($CDCl_3$): δ = 0.10 ($SiCH_3$)], *2,4-diisopropyl-1,1,3,3-tetramethylcyclodisilazane* (**11**) {$C_{10}H_{26}N_2Si_2$ calcd. 230.1634, found 230.163 (MS). – ^1H NMR ($CDCl_3$): δ = 0.10 (s, 12H, $SiCH_3$); 1.103 [d, *J* = 6.3 Hz, 12H, $CH(CH_3)_2$], 3.21 [sept, *J* = 6.3 Hz, 2H, $CH(CH_3)_2$]}, and *N'-isopropyl-1,1-dimethyl-N,N-bis(trimethylsilyl)silanediamine* (**12**) {$C_{11}H_{32}N_2Si_3$ calcd. 276.1873, found 276.185 (MS). – ^1H NMR ($CDCl_3$): δ = 0.10 (24H, $SiCH_3$), 1.09 [d, *J* = 6.2 Hz, 6H, $CH(CH_3)_2$], 3.12 [sept, *J* = 6.2 Hz, 1H, $CH(CH_3)_2$]} Cyclodisilazane **11** and silanediamine **12** were obtained in a 7:3 molar ratio.

Dehydrochlorination of **9**, *VGSR/MS Sequence:* The VGSR reactor, filled in half-section with $(Ph_2MeSi)_2NK$ (3 g, 6.8 mmol), was connected to the mass spectrometer and then heated at 60°C and degassed (10^{-4} hPa) for 2 h. Products formed when chlorosilanamine **9** was slowly vaporized on the surface of the solid base heated at 60°C. They were characterized by real-time MS analysis, the hydrogen chloride elimination being shown not to occur in the ion source of the mass spectrometer.

N-Isopropyl-1,1-dimethylsilanimine (**10**): HRMS: $C_5H_{13}NSi$ calcd. 115.0817, found 115.082. – MS: *m/z* (%) = 115 (5), 114 (11), 100 (17), 73 (7), 72 (46), 71 (31), 58 (8), 52 (9), 51 (6), 50 (6), 44 (77), 43 (18), 42 (100), 41 (37), 40 (9), 39 (14).

[1] [1a] N. Wiberg, K. Schurz, G. Reber, G. Müller, *J. Chem. Soc., Chem. Commun.* **1986**, 591. – [1b] N. Wiberg, K. Schurz, *Chem. Ber.* **121** (1988) 581. – [1c] M. Hesse, U. Klingebiel, *Angew. Chem., Int. Ed. Engl.* **25** (1986) 649.

[2] [2a] S. S. Zigler, R. West, J. Michl, *Chem. Lett.* **1986**, 1025. – [2b] S. S. Zigler, L. M. Johnson, R. West, *J. Organomet. Chem.* **341** (1988) 187. – [2c] A. Sekiguchi, W. Ando, K. Honda, *Chem. Lett.* **1986**, 1029.

[3] [3a] U. Klingebiel, A. Meller, *Chem. Ber.* **109** (1976) 2430. – [3b] W. Clegg, U. Klingebiel, G. M. Sheldrick, N. Vater, *Z. Anorg. Allg. Chem.* **482** (1981) 88.

[4] [4a] N. Wiberg, *J. Organomet. Chem.* **273** (1984) 141. – [4b] G. Raabe, J. Michl, *Chem. Rev.* **85** (1985) 419. – [4c] G. Raabe, J. Michl in *The Chemistry of Organic Silicon Compounds* (S. Patai, Z. Rappoport, Eds.), p. 1015, J. Wiley, New York 1989.

[5] G. Maier, J. Glatthaar, H. P. Reisenauer, *Chem. Ber.* **122** (1989) 2403.

[6] N. Wiberg, P. Karampatses, Chung-Kyun Kim, *Chem. Ber.* **120** (1987) 1203.

[7] N. Wiberg, G. Preiner, P. Karampatses, Chung-Kyun Kim, K. Schurz, *Chem. Ber.* **120** (1987) 1357.

[8] C. M. Golino, R. D. Bush, L. H. Sommer, *J. Am. Chem. Soc.* **96** (1974) 614.

[9] D. R. Parker, L. H. Sommer, *J. Am. Chem. Soc.* **98** (1976) 618.

[10] For VGSR sequences see e.g., [10a] J. C. Guillemin, J. M. Denis, *Tetrahedron* **44** (1988) 4431. – [10b] B. Pellerin, P. Guenot, J. M. Denis, *Tetrahedron Lett.* **28** (1987) 5811.

[11] T. J. Barton, S. Bain, *Organometallics* **7** (1988) 528.

[12] G. H. Wiseman, D. R. Wheeler, D. Seyferth, *Organometallics* **5** (1986) 146.

[13] J. Pikies, W. Wojnowski, *Z. Anorg. Allg. Chem.* **503** (1983) 224.

[14] L. Wazneh, J. C. Guillemin, P. Guenot, Y. Vallée, J. M. Denis, *Tetrahedron Lett.* **29** (1988) 5899.

[15] J. C. Guillemin, L. Ammi, J. M. Denis, *Tetrahedron Lett.* **29** (1988) 1287.

[16] Potassium amides were prepared according to the described method: C. A. Brown, *Synthesis* **1974**, 427; *J. Org. Chem.* **39** (1974) 3913.

[17] J. J. D'Amico, M. W. Harman, R. H. Cooper, *J. Am. Chem. Soc.* **79** (1957) 5270.

[12/92]

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1: 139976-64-0 / **2**: 59239-77-9 / **3**: 86936-22-3 / **4**: 139976-65-1 / **5**: 139976-66-2 / **6**: 139976-67-3 / **7**: 139976-68-4 / **8**: 139976-69-5 / **9**: 6026-03-5 / **10**: 139976-70-8 / **11**: 98689-74-8 / **12**: 139976-71-9 / HMDSK: 40949-94-8 / $PhNHCH_2CH=CH_2$: 589-09-3 / $iPrNHCH_2CH=CH_2$: 35000-22-7 / $iPrNHCH_2C\equiv CH$: 6943-48-2 / $(Ph_2MeSi)_2NK$: 139976-72-0 / allylcyclohexylamine: 6628-00-8