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Control of N- or C-Bridging Mode in Dimeric Butylmagnesium Silylamides

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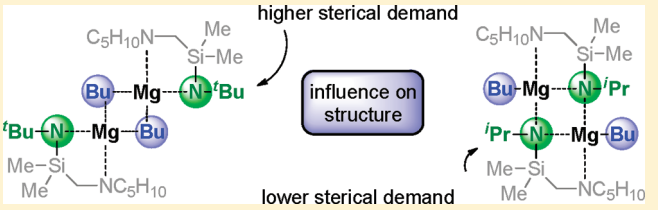
Supporting Information

ABSTRACT: The simple approach to cleave 4,5-dihydro-2-furyl with lithiated primary amines yields a wide range of *N*-alkyl-substituted (aminomethyl)silazanes. These are easily deprotonated by dibutylmagnesium, resulting in either magnesium disilylamides or butylmagnesium silylamides upon variation of the stochiometric ratios and reaction temperatures. The obtained dimeric butylmagnesium silylamide compounds $[\{(CH_3)_2Si(CH_2NC_5H_{10})(NR)\}Mg(n\text{-}Bu)]_2$ (R = *t*-Bu, *i*-Pr), examined by single-crystal X-ray diffraction analysis, exhibit different bridging modes Mg−El−Mg (El = C, N) according to the steric demand of the ligand. This observation has been studied using theoretical methods.

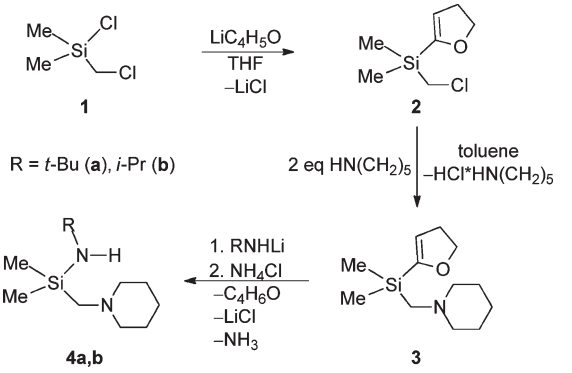


INTRODUCTION

The N−H bond of silazanes is easily deprotonated by metal alkyl reagents, resulting in new compounds, for example, metal *bisamides* or mixed *alkyl*metal *amides*. Alkylmetal amides are suitable as alkylation or deprotonation reagents in organic synthesis, and metal bisamides are of interest as molecular precursors for new materials or lactide polymerization catalysts.[1−4] To enhance their reactivity, a precoordination of the metal is achieved by a side arm with a coordinating donor atom as for example in (aminomethyl) silazanes.[5] Additionally, the chelating aminomethyl moiety already occupies one coordination site of the metal atom, providing ample stability to prevent oligomerization. Thereby the creation of small volatile molecules suitable for chemical vapor deposition (CVD) applications is possible.[6] Considering dibutylmagnesium as a deprotonation reagent for these silazanes, either just one or both butyl groups are expected to be substituted by the ligand. Until now, only a few small intermediates with similar bidentate nitrogen ligands still bearing a butyl group and thereby maintaining one functionality are known.[2,7] As shown by Chong and co-workers these intermediates possess interesting applicabilities, e.g., as enantioselective alkylation reagents for aldehydes.[2] The deprotonation of two amines containing an additional side arm with another coordinating amine function yields small four-coordinate magnesium compounds, which are potential CVD precursors.[6,8] Starting from the same ligand, the selective synthesis of either an intermediate still bearing one functionality or the 2-fold deprotonation product would be desirable. This simplifies the large-scale preparation of similar compounds.

We herein report a general three-step synthetic route for silazanes such as **4a,b,c**, which exhibit different alkyl substituents at the amine moieties. With this preparation method, more varied silazanes can easily be designed to suit a specific purpose. These silazane ligands were successfully used for the selective synthesis of magnesium disilylamides **5a,b,c** and butylmagnesium silylamides **6a,b** by deprotonation with dibutylmagnesium. We obtained new magnesium silylamide compounds displaying interesting structural features. Controlled by the sterical demand of the silazane ligand, two different bridging modes for the dimeric alkylmagnesium silylamide species are formed. Due to these unexpected structural features, these compounds may potentially be used as alkylation reagents in organic synthesis.

Scheme 1. Synthesis of (Piperidinomethyl)silazanes



RESULTS AND DISCUSSION

Synthesis of Silazanes with Different Alkyl Substituents at the Amine Moieties. The introduction of the protecting group 4,5-dihydro-2-furyl at the silicon center marks the first step of this synthesis with a simplified experimental procedure already developed by Chan and co-workers.[9] In the following reaction step, the amination of the chloromethyl group with a secondary amine, in this case piperidine, yields compound **3**. In this synthesis

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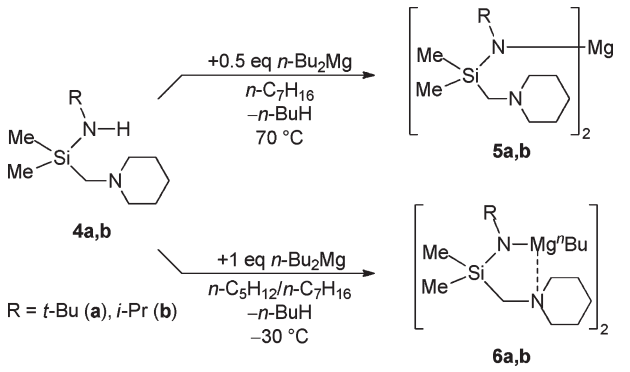
Scheme 2. Syntheses of Butylmagnesium Silylamides and Magnesium Disilylamides



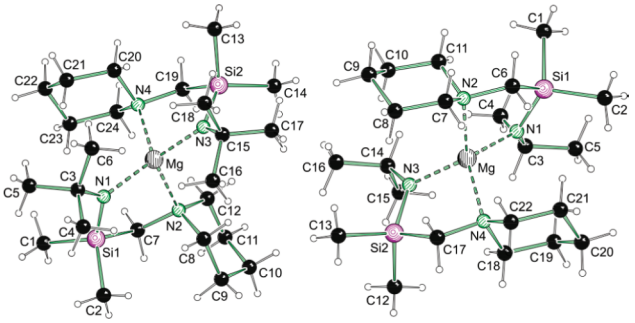


Figure 1. Molecular structure of compounds **5a** (left) and **5b** (right). Selected bond lengths (Å) and angles (deg) of **5a**: Mg−N2 2.252(2), Mg−N4 2.219(2), Mg−N1 2.030(2), Mg−N3 2.033(2), Si1−N1 1.689(2), Si2−N3 1.691(2), N1−C3 1.479(3), N3−C15 1.476(3), N1−Mg−N2 93.06(7), N1−Mg−N3 137.60(8), N1−Mg−N4 110.53(7), N2−Mg−N3 116.01(7), N2−Mg−N4 103.61(7), N3−Mg−N4 92.71(7); **5b**: Mg−N2 2.223(1), Mg−N4 2.250(1), Mg−N1 2.004(1), Mg−N3 2.014(1), Si1−N1 1.692(1), Si2−N3 1.683(1), C3−N1 1.469(2), C14−N3 1.475(2), N1−Mg−N2 92.57(5), N1−Mg−N3 126.18(5), N1−Mg−N4 116.30(5), N2−Mg−N3 119.04(5), N2−Mg−N4 111.37(5), N3−Mg−N4 92.66(5).

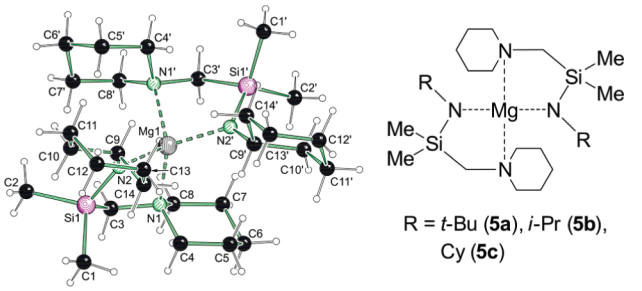


Figure 2. Molecular structure of compound **5c** (left) and schematic display of compounds **5a,b,c** (right). Selected bond lengths (Å) and angles (deg) (symmetry operation: $-x+3/2$, y, $-z+1/2$): Mg−N2 2.014(2), Mg−N1 2.232(2), Si1−N2 1.689(2), N2−C9 1.455(3), N1−Mg−N2 92.30(6), N2−Mg−N2′130.25(10), N1−Mg−N1′ 110.07(10), N2−Mg−N1′ 116.23(6).

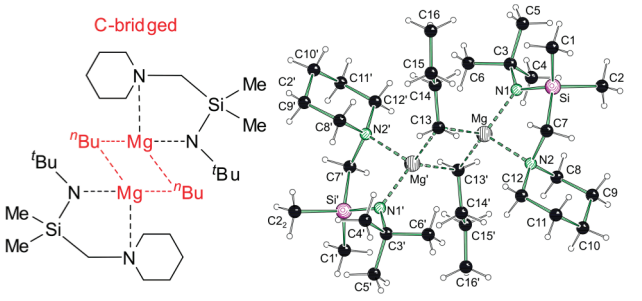


Figure 3. Molecular structure and schematic display of compound **6a**. Selected bond lengths (Å) and angles (deg) (symmetry operation: $-x+1$, $-y+2$, $-z+1$): Mg−N1 2.000(2), Mg−N2 2.185(2), Mg−C13 2.276(3), Mg−C13′ 2.260(3), Si−N1 1.688(2), N1−C3 1.468(3), Mg−C13−Mg′ 75.28(9), C13−Mg−C13′ 104.72(9), N1−Mg−N2 92.17(7), N1−Mg−C13 119.04(9), N1−Mg−C13′ 121.91(9), C13−Mg−N2 106.61(8), C13′−Mg−N2 110.72(9).

two equivalents of amine are necessary to bind the generated hydrochloric acid. Finally, the protection group is removed via reaction with 1 equiv of lithiated primary amine [*tert*-butylamine (**a**), isopropylamine (**b**), and cyclohexylamine (**c**)]. As stated by Chan and co-workers, lithiated reagents are necessary to cleave the Si−C bond of the protecting 4,5-dihydro-2-furyl moiety. Subsequent addition of ammonium chloride, as a nonhydrolytic protonation reagent, yields the desired silazane ligands **4a,b,c** (Scheme 1). This proves to be a remarkably simple reaction pathway with an overall yield of 52%.

Selective Syntheses of Magnesium Disilylamide or Alternatively Butylmagnesium Silylamide Compounds. Treatment of compound **4a** with 1 equiv of commercially available dibutylmagnesium solution in heptane at −20 °C and subsequent storage at room temperature for 12 h results in the formation of not only the butylmagnesium silylamide compound **6a** (intermediate) but a crystalline mixture of both the magnesium disilylamide and butylmagnesium silylamide **5a** and **6a**. Both compounds could be distinguished by their differing crystal shape, small elongated blocks for **6a** and large square blocks for compound **5a**. The selective synthesis of compounds **6a, b**, however, was achieved by slowly adding a solution of the silazane ligand in pentane to dibutylmagnesium at −10 °C and subsequent storage at −30 °C. These butylmagnesium silylamide complexes **6a,b** could be isolated as colorless crystals with yields of 42% and 91%, respectively. The reaction of 0.5 equiv of dibutylmagnesium with **4a,b,c** and subsequent storage at room temperature (**5a,b**) or 0 °C (**5c**) results in colorless crystals of compounds **5a,b,c** exclusively, with a minimum yield of 63% (Scheme 2). With the exception of compound **5c**, which required dilution of the silazane ligand in pentane, no additional solvent was added in both the butylmagnesium silylamide and magnesium disilylamide syntheses to obtain the crystalline products.

Compounds **5a,b,c** crystallize in the monoclinic crystal system, space group $P2_1/n$ (**a**), $P2_1/c$ (**b**), and $P2/n$ (**c**). The central magnesium atom exhibits contacts to both nitrogen atoms of two ligand molecules, resulting in a four-coordinate magnesium center. The dative Mg−N bonds of the intramolecularly coordinated piperidinomethyl substituents are considerably longer (approximately 0.2 Å) than the Mg−N bonds to the silicon-bonded nitrogen atom with a largely electrostatic attraction. Deprotonation of the silazane leads to strongly shortened Si−N bond lengths [1.683(1)−1.694(1) Å] due to an increase of

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ionic bond character. The ideal tetrahedral environment at the magnesium center is strongly distorted by the sterically demanding *tert*-butyl (**a**), isopropyl (**b**), and cyclohexyl (**c**) substituents as well as the five-membered ring formed by chelation of the aminomethyl side arm (Figures 1 and 2). The observed structural parameters are

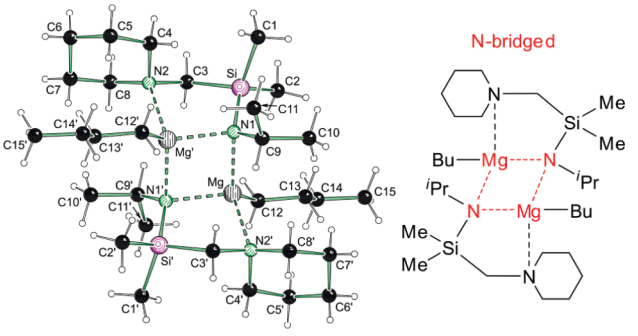


Figure 4. Molecular structure and schematic display of compound **6b**. Selected bond lengths (Å) and angles (deg) (symmetry operation: $-x$, $-y+2$, $-z+1$): Mg−N1 2.184(2), Mg−N1′ 2.151(2), Mg−N2′ 2.298(2), Mg−C12 2.148(2), Si−N1 1.728(2), C9−N1 1.491(2), C12−Mg−N1′ 121.36(7), C12−Mg−N1 120.95(8), N1′−Mg−N1 92.19(6), C12−Mg−N2′ 110.45(8), N1′−Mg−N2′ 93.02(6), N1−Mg−N2′ 114.84(6), C9−N1−Si 119.40(12), C9−N1−Mg′ 115.35(11), Si−N1−Mg′ 108.49(8), C9−N1−Mg 104.90(11), Si−N1−Mg 116.77(8), Mg′−N1−Mg 87.81(6).

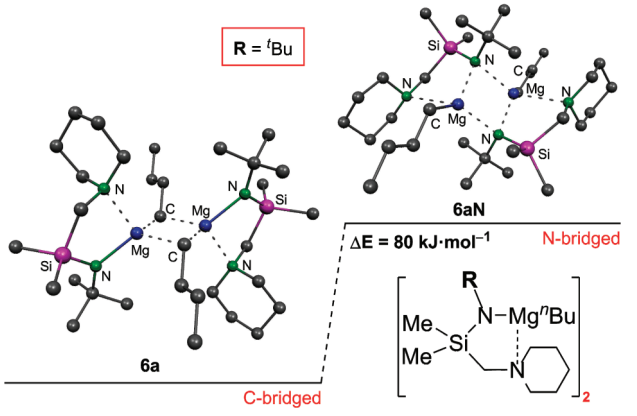
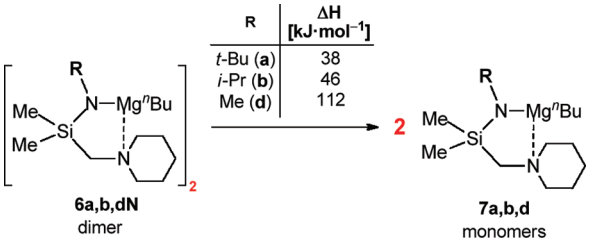


Figure 5. Relative difference in energy for optimized structures [B3LYP/6-31+G(d)] of *tert*-butyl-substituted compounds with C-bridging (**6a**) and N-bridging modes (**6aN**) (hydrogens omitted for clarity).

similar to comparable published magnesium disilylamides bearing an additional donor function, for example, $Mg[\{(CH_3)_3Si\}N(CH_2)_3N(CH_3)_2]_2$.[6,8c,10] While compounds **5a**,**b** are well soluble in noncoordinating solvents (benzene-d_6), compound **5c** displays a considerably reduced solubility. Therefore the characterization of **5c** via ^{29}Si and ^{13}C NMR could be achieved only by correlation methods. Additionally, signals of the starting material, the silazane, which is formed by decomposition of the magnesium amide bond become more dominant after a prolonged measurement time. The *n*-butyl-bearing compounds **6a**,**b** show no solubility in benzene or toluene at all. Since the use of coordinating solvents (thf) results in the formation of a complex mixture of thf adducts, the NMR characterization of compounds **6a**,**b** was not possible.[11]

The molecular structures of compounds **6a**,**b** are both those of strictly centrosymmetric dimers, which crystallized in the triclinic crystal system, space group $P\bar{1}$. Their most salient difference is their bridging mode. The central four-membered ring comprises two carbon and two magnesium atoms for compound **6a** (C-bridge) and two nitrogen and two magnesium atoms for compound **6b** (N-bridge) (Figure 3 and Figure 4). The bridging moiety changes from the *n*-butyl group in compound **6a** to the silylamide in compound **6b**. As expected, the Mg−N1/Mg−N1′ bond lengths of the bridging, four-coordinate amide nitrogens in compound **6b** are slightly larger compared to the Mg−N1 bond length of compound **6a**, in which the silicon-bonded nitrogen centers are still three-coordinate. Still, the magnesium amide bonds are shorter than the dative Mg−N2 and Mg−N2′ bonds of the chelating piperidinomethyl arm. At 2.276(3) and 2.260(3) Å, the bridging Mg−C13 bond in **6a** is quite long compared to the sum of the covalent radii [2.17 Å] of magnesium and carbon and the nonbridging Mg−C12 bond of compound **6b**. To the author's knowledge, there are no directly comparable systems with bridging alkyl groups known, but dimeric structures with the

Scheme 3. Energy Needed to Break Dimers into Monomers



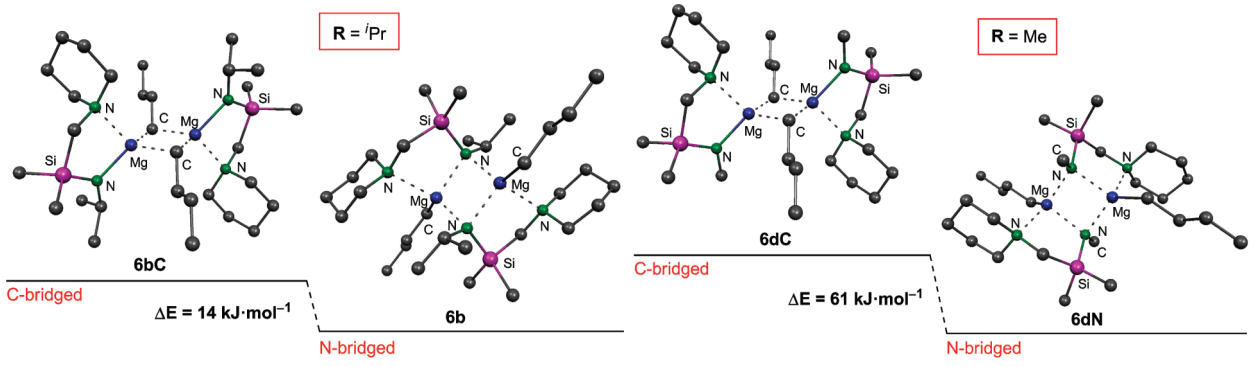


Figure 6. Relative difference in energy for optimized structures [B3LYP/6-31+G(d)] of isopropyl- (left) and methyl-substituted (right) compounds with C-bridging (**6bC** and **6dC**) and N-bridging modes (**6b** and **6dN**) (hydrogens omitted for clarity).

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Table 1. Crystal Data and Structure Refinement Parameters for 5a,b,c and 6a,b

	5a	5b	5c	6a	6b
formula	$C_{24}H_{54}MgN_4Si_2$	$C_{22}H_{50}MgN_4Si_2$	$C_{28}H_{58}MgN_4Si_2$	$C_{32}H_{72}Mg_2N_4Si_2$	$C_{30}H_{68}Mg_2N_4Si_2$
fw [g·mol^{-1}]	479.20	451.15	531.27	617.74	589.68
T [K]	173(2)	193(2)	173(2)	173(2)	173(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P2/n$	$P\bar{1}$	$P\bar{1}$
Z	4	4	4	1	1
a [Å]	9.8598(12)	16.189(4)	15.5428(6)	9.121(2)	8.5742(14)
b [Å]	17.856(2)	10.5506(13)	10.1316(4)	10.235(2)	10.2417(17)
c [Å]	17.272(2)	16.739(3)	20.2967(10)	10.943(2)	10.7960(18)
α [deg]	90	90	90	97.28(4)	83.090(3)
β [deg]	106.098(2)	101.37(2)	102.192(4)	102.20(4)	88.234(3)
γ [deg]	90	90	90	92.947(4)	74.707(3)
V [Å^3]	2921.6(6)	2803.1(9)	3124.1(2)	987.2(4)	907.8(3)
ρ_{calc} [g·cm^{-3}]	1.089	1.069	1.130	1.039	1.079
μ [mm^{-1}]	0.161	0.164	0.156	0.146	0.156
θ range [deg]	2.16−26.00	2.29−27.00	2.26−26.00	1.92−26.00	1.90−27.00
no. of reflns	15 169	28 963	33 942	8729	9322
no. of indep reflns/R_{int}	5735/0.0428	6069/0.0454	6143/0.0497	3823/0.0318	3863/0.0258
params	290	270	321	195	185
R_1/wR_2 indices [$I > 2\sigma(I)$]	0.0521/0.1170	0.0519/0.1419	0.0412/0.0855	0.0507/0.1302	0.0503/0.1281
R_1/wR_2 for all reflns	0.0769/0.1319	0.0560/0.1464	0.0815/0.0892	0.0656/0.1436	0.0628/0.1388
GooF on F^2	1.069	1.054	1.025	1.020	1.069
largest diff peak/hole [e·Å^{-3}]	0.313/−0.202	0.287/−0.397	0.281/−0.531	0.337/−0.194	0.397/−0.192

β-diketiminato ligand, which displays a different electronic structure, show similar Mg−C bond lengths.[12] The Si−N bond length for compound **6a** [1.688(2) Å] is comparable to those of compounds **5a,b,c**, whereas the length of the Si−N bond in **6b** is slightly longer [1.728(2) Å] as a result of the dimerization via the amide nitrogen bridge. Due to the restricting cyclic structures and sterically demanding *tert*-butyl and isopropyl groups, the ideal tetrahedral arrangements at the magnesium atoms are strongly distorted.

To determine the relative difference in energy concerning these two possible bridging modes for the *tert*-butyl- as well as the isopropyl-substituted compounds, DFT calculations were performed at the B3LYP/6-31+G(d) level.[13]

Due to the strong sterical demand of a *tert*-butyl group, the unusual carbon bridge (**6a**) is highly favored [80 kJ·mol^{-1}] compared to a nitrogen bridge (**6aN**) (Figure 5). This is in agreement with the determined crystal structure of **6a**, although most dimeric magnesium compounds found in the literature usually prefer the most electronegative atom as the bridging unit.[2,6,14] An energy difference of 14 kJ·mol^{-1} was calculated for the carbon-bridged compound **6bC** and the favored nitrogen-bridged compound **6b**. This is consistent with the experimental result of a dimerization via the nitrogen atom observed in the crystal structure (Figure 6). Additionally, this rather small value might indicate that the sterical restriction is still quite significant. To verify the steric influence on the bridging mode, the model structures **6dC** (C-bridge) and **6dN** (N-bridge), which feature a small methyl group [R = Me] instead of the sterically demanding *tert*-butyl or isopropyl groups, were calculated at the same level. As expected, these model structures without sterically demanding groups also favor a nitrogen bridge (**6dN**) with a difference of 61 kJ·mol^{-1} compared to the C-bridged compound (**6dC**) (Figure 6).

The sterical restrictions of both the calculated structures and the corresponding synthesized compounds **6a,b** indicate enhanced energy levels compared to sterically undemanding structures. This should result in an enhancement of reactivity of **6a,b** compared to less sterically clustered structures. To evaluate the reactivity of these compounds, the energy consumed by splitting the dimers into monomers was calculated using their energetically most stable dimeric structures (**6a,b**) and the dimeric methyl-substituted model structure **6dN** (Scheme 3). These calculations revealed that the sterically unrestricted structure **6dN** needs 112 kJ·mol^{-1} to be separated into monomers. The dimeric compounds **6a** and **6b**, however, are split at the cost of 38 kJ·mol^{-1} (**a**) and 46 kJ·mol^{-1} (**b**), respectively. These calculations are in accordance with the proposed higher reactivities for those compounds, especially the carbon-bridged *tert*-butyl-substituted dimer **6a**.

CONCLUSION

The synthesis of more varied (aminomethyl)silazanes, which exhibit different alkyl substituents at the amine moieties, has been a preparative challenge in organosilicon chemistry. Chan and coworkers have demonstrated that the protecting group 4,5-dihydro-2-furyl is easily cleaved using alkyl lithium reagents. This method was applied and extended to the synthesis of (aminomethyl)silazanes. By cleaving this protecting group with lithiated primary amines, a wide range of *N*-alkyl-substituted (aminomethyl)silazanes is now accessible. Since previous research demonstrates an extensive practical potential of metal

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amides and mixed alkylmetal amides, the prepared (aminomethyl)silazanes were deprotonated by the 2-fold base dibutylmagnesium. This reaction yields either magnesium disilylamides (**5a,b,c**) or butylmagnesium silylamides (**6a,b**) selectively upon variation of the stochiometric ratios and reaction temperatures. The examination of the obtained dimeric butylmagnesium silylamide compounds by single-crystal X-ray diffraction analysis reveals different bridging modes. According to the steric demand of the ligand, either a carbon- or nitrogen-bridged dimer is formed. In consequence, by changing the substituent of the (aminomethyl)silazane from isobutyl to *tert*-butyl the mode of aggregation can be controlled. While sterically undemanding substituents lead to a nitrogen-bridged dimer, commonly observed in similar magnesium complexes, sterically demanding substituents form an unusual carbon-bridged dimer. The calculated energy difference of 80 kJ·mol^{-1} between the two possible bridging modes of compound **6a** featuring *tert*-butyl groups illustrates the impact of steric effects, which control the aggregation mode.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under argon using a standard Schlenk line. All solvents were dried by standard methods. NMR spectra were recorded on Bruker Avance-500, Bruker DRX 500, Bruker Avance-400, Bruker DRX 400, Bruker DPX 300, and Varian Inova 500 spectrometers. ^{1}H NMR spectra are referenced to the internal standards C_6D_5H at 7.16 ppm or $CHCl_3$ at 7.27 ppm, and ^{13}C NMR spectra are referenced to C_6D_5H at 128.39 ppm or $CHCl_3$ at 77.00 ppm (external standard: TMS). The ^{29}Si NMR spectra are referenced to the external standard TMS. The GC-MS spectra were measured with the gas chromatography column HP 6890 [J. & W. Scientific; 25 m length, i.d. 0.2 mm, helium gas, 2.06 bar; temperature progam: 50 °C (1 min) to 40 °C/min to 300 °C (5 min)] and a HP mass selective detector 5973 (EI(+)-MS, 70 eV). The elemental analysis was conducted on a Leco CHNS-932/O VTF-900 analyzer. All chemicals were used as purchased with the exception of ammonium chloride, which was purified and dried by sublimation prior to use.

Crystal Structure Determination of Compounds 5a,b,c and 6a,b. The crystals of all compounds were mounted in an inert oil (perfluoropolyalkyl ether) at −60 °C (N_2 stream), using the X-TEMP 2 device.[15] **5a and 6a,b**: Bruker Apex CCD diffractometer; programs used for data collection, cell determination, and cell refinement: Smart V. 5622 (Bruker AXS, 2001), integration: SaintPlus V. 6.02 (Bruker AXS, 1999), empirical absorption correction: Sadabs V. 2.01 (Bruker AXS, 1999). **5b**: Stoe IPDS diffratometer; data collection: Expose in IPDS (Stoe & Cie, 1999), cell determination and refinement: Cell in IPDS (Stoe & Cie, 1999), integration: Integrate in IPDS (Stoe & Cie, 1999), numerical absorption correction: Faceit in IPDS (Stoe & Cie, 1999). **5c**: Oxford Diffraction Xcalibur S, programs used for data collection, cell determination, and cell refinement: CrysAlis (Oxford, 2008); CrysAlis RED (Oxford, 2008), empirical absorption correction: Scale3 Abspack (Oxford, 2008). The structures were solved using direct methods (SHELXS90); structural refinement was done with SHELXL97.

Synthesis of (Chloromethyl)(4,5-dihydrofuran-2-yl)dimethylsilane (2). The synthesis was carried out using a simplified procedure developed by Chan and co-workers. Analytical data are identical and not listed here.[9] A 5.5 mL (5.1 g, 73 mmol) sample of 2,3-dihydrofuran was disssolved in 60 mL of thf and cooled to −60 °C. After addition of 29.0 mL (72.5 mmol, 2.5 M in hexane) of *n*-BuLi the reaction mixture was stirred for 1 h and warmed to 0 °C. This reaction mixture was added to a solution of 9.2 g (64 mmol) of (chloromethyl) dimethylchlorosilane in 30 mL of thf cooled to −60 °C. After stirring for 1 h and warming to 0 °C the reaction was quenched with 70 mL of water and afterward extracted with diethyl ether (5 × 50 mL). After drying the combined organic fractions over Na_2SO_4 the solvent was removed and the oily residue distilled in vacuo to give 10.2 g (58 mmol, 90%) of a colorless liquid (36 °C, 1 × 10^{-2} mbar).

Synthesis of (4,5-Dihydrofuran-2-yl)(piperidinomethyl) dimethylsilane (3). A 9.0 g (51 mmol) portion of **2** was dissolved in 50 mL of toluene, and 10.1 mL (8.7 g, 102 mmol) of piperidine was added. The reaction mixture was stirred under reflux for 55 h. The precipitation was removed via filtration and washed with 100 mL of pentane. After removal of the solvent the oily residue was distilled *in vacuo* to give 10.3 g (46 mmol, 90%) of a colorless liquid (60 °C, 1 × 10^{-2} mbar). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.21 [s, 6H; Si(CH_3)$_2$], 1.33−1.40 [m, 2H; NCH$_2$CH$_2$$CH_2$], 1.51−1.58 [m, 4H; NCH$_2$$CH_2$-CH$_2$], 2.03 [s, 2H; Si$CH_2$N], 2.32−2.36 [m, 4H; NC$H_2CH_2CH_2$], 2.59 [td, 2H, $^3J_{HH}$ = 9.6 Hz, $^3J_{HH}$ = 2.6 Hz; SiCCHCH_2CH$_2$O], 4.27 [t, 2H, $^3J_{HH}$ = 9.6 Hz; SiCCHCH$_2$CH_2O], 5.26 [t, 1H, $^3J_{HH}$ = 2.6 Hz; SiCCH-CH$_2$CH$_2$O]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ −3.6 [Si(CH_3)$_2$], 23.7 [NCH$_2$CH$_2$CH$_2$], 26.2 [NCH$_2$CH$_2$CH$_2$], 30.7 [SiCCHCH_2CH$_2$O], 49.2 [SiCH_2N], 58.2 [NCH_2CH$_2$CH$_2$], 70.3 [SiCCHCH$_2$$CH_2$O], 111.8 [SiCCHCH$_2CH_2$O], 161.3 [SiCCHCH$_2CH_2$O]. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ −13.0. GC-EI(+)MS, t_R = 4.98 min, m/z [%]: 225 (3) [M$^+$], 98 (100) [(CH$_2$NC$_5$H$_{10}$)$^+$]. Anal. Calcd: C, 63.94; H, 10.28; N, 6.21. Found: C, 64.0; H, 10.1; N, 6.1.

Synthesis of (*tert*-Butylamino)(piperidinomethyl)dimethylsilane (4a). A 9.3 mL (15 mmol, 1.6 M in hexane) amount of *n*-BuLi was added to a solution of 3.4 mL (2.2 g, 30 mmol) of *tert*-butylamine in 50 mL of thf at −50 °C. The mixture was allowed to warm to 0 °C before adding 2.5 g (11 mmol) of **3**. The reaction mixture was stirred for 30 min at 0 °C, and then 0.8 g (15 mmol) of ammonium chloride was added. After removal of the solvent the residue was dissolved in pentane. The solid was filtered off under argon. Afterward the solvent of the filtrate was removed and the residual oil purified via bulb-to-bulb distillation (65 °C, 4.2 × 10^{-2} mbar) to give 1.8 g (8 mmol, 71%) of a colorless liquid. ^{1}H NMR (300.1 MHz, C_6D_6): δ 0.20 [s, 6H; Si(CH_3)$_2$], 0.96 [br, 1H; SiNHC(CH_3)$_3$], 1.16 [s, 9H; SiNHC(CH_3)$_3$], 1.28−1.36 [m, 2H; NCCCH_2], 1.51−1.58 [m, 4H; NCCH_2C], 1.84 [s, 2H; SiCH_2N], 2.36 [br, 4H; NCH_2CC]. ^{13}C NMR (75.5 MHz, C_6D_6): δ 2.7 [Si(CH_3)$_2$], 24.8 [NCCCH_2], 27.3 [NCCH_2C], 34.3 [SiNC-(CH_3)$_3$], 49.6 [SiNC(CH_3)$_3$], 52.9 [SiCH_2N], 59.1 [NCH_2CC]. ^{29}Si NMR (59.6 MHz, C_6D_6): δ −6.0. Anal. Calcd: C, 63.09; H, 12.35; N, 12.26. Found: C, 62.0; H, 12.1; N, 12.0.

Synthesis of (Isopropylamino)(piperidinomethyl)dimethylsilane (4b). The synthetic approach was identical to the procedure described above: 20.0 mL (32 mmol, 1.6 M in hexane) of *n*-BuLi, 5.6 mL (3.8 g, 65 mmol) of isopropylamine in 50 mL thf, 4.5 g (20 mmol) of **3**, 2.0 g (37 mmol) of ammonium chloride. Bulb-to-bulb distillation at 60 °C and 5 × 10^{-2} mbar gave 3.0 g (14 mmol, 70%). ^{1}H NMR (300.1 MHz, C_6D_6): δ 0.15 [s, 6H; Si(CH_3)$_2$], 0.34 [br, 1H; SiNHCH-(CH_3)$_2$], 1.01 [d, 6H, $^3J_{HH}$ = 6.3 Hz; SiNHCH(CH_3)$_2$], 1.28−1.36 [m, 2H; NCCCH_2], 1.51−1.59 [m, 4H; NCCH_2C], 1.85 [s, 2H; SiCH_2N], 2.36 [br, 4H; NCH_2CC], 3.01 [septd, 1H, $^3J_{HH}$ = 6.3 Hz, $^3J_{HH}$ = 10.2 Hz; SiNHCH(CH_3)$_2$]. ^{13}C NMR (75.5 MHz, C_6D_6): δ 0.1 [Si(CH_3)$_2$], 24.8 [NCCCH_2], 27.3 [NCCH_2C], 28.6 [SiNCH(CH_3)$_2$], 43.7 [SiNCH(CH_3)$_2$], 52.2 [SiCH_2N], 59.3 [NCH_2CC]. ^{29}Si NMR (59.6 MHz, C_6D_6): δ −2.4. Anal. Calcd: C, 61.62; H, 12.22; N, 13.06. Found: C, 61.2; H, 12.0; N, 13.1.

Synthesis of (Cyclohexylamino)(piperidinomethyl)dimethylsilane (4c). The synthetic approach was identical to the procedure described above: 17.5 mL (28 mmol, 1.6 M in hexane) of *n*-BuLi, 4.0 mL (3.5 g, 35 mmol) of cyclohexylamine in 50 mL of thf, 4.3 g (19 mmol) of **3**, 1.6 g (30 mmol) of ammonium chloride. Bulb-to-bulb distillation at 90 °C and 1.4 × 10^{-2} mbar gave 2.8 g (11 mmol, 59%). ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.18 [s, 6H; Si(CH_3)$_2$], 0.51 [d, 1H, $^3J_{HH}$ = 8.0 Hz; SiNHCHC$_6$H$_{10}$], 0.94−1.09 [m, 3H; SiNHCHC$_6$$H_{10}$],

1.16−1.25 [m, 2H; SiNHCHC$_6H_{10}$], 1.30−1.35 [m, 2H; NCCCH_2], 1.46−1.51 [m, 1H; SiNHCHC$_6H_{10}$], 1.54−1.58 [m, 4H; NCCH_2C], 1.60−1.66 [m, 2H; SiNHCHC$_6H_{10}$], 1.88 [s, 2H; SiCH_2N], 2.38 [br, 4H; NCH_2CC], 2.61−2.68 [m, 1H; SiNHCHC$_6$H$_{10}$]. ^{13}C NMR (125.8 MHz, C$_6$D$_6$): δ 0.3 [Si(CH$_3$)$_2$], 24.8 [NCCCH$_2$], 26.3 [SiNHCHCCH$_2$C], 26.6 [SiNHCHCCCH$_2$], 27.3 [NCCH$_2$C], 39.5 [SiNHCHCH$_2$CC], 51.2 [SiNHCHCH$_2$CC], 52.3 [SiCH$_2$N], 59.3 [NCH$_2$CC]. ^{29}Si NMR (59.6 MHz, C$_6$D$_6$): δ −2.3. Anal. Calcd: C, 66.07; H, 11.88; N, 11.01. Found: C, 65.7; H, 11.6; N, 10.8.

Synthesis of Magnesium Disilylamide 5a. To 131 mg (0.57 mmol) of **4a** cooled to −60 °C was added 0.29 mL (0.30 mmol, 1.0 M in heptane) of *n*-Bu$_2$Mg, and the mixture was allowed to warm to room temperature. Storage for 20 h yields 86 mg (0.18 mmol, 63%) of colorless crystals of **5a** suitable for X-ray analysis. ^{1}H NMR (300.1 MHz, C$_6$D$_6$): δ 0.27 + 0.40 [s, 12H; Si(CH$_3$)$_2$], 1.15−1.57 [m, 12H; NCH$_2$CH$_2$CH$_2$], 1.59 [s, 18H; NC(CH$_3$)$_3$], 1.67 + 2.05 [AB-system, 4H, $^2J_{HH}$ = 14.3 Hz; SiCH$_2$N], 2.18−2.25 [m, 2H; NCH$_2$CH$_2$CH$_2$], 2.74−2.87 [m, 4H; NCH$_2$CH$_2$CH$_2$], 3.14−3.23 [m, 2H; NCH$_2$CH$_2$CH$_2$]. ^{13}C NMR (100.6 MHz, C$_6$D$_6$): δ 6.8 + 7.5 [Si(CH$_3$)$_2$], 20.1 [NCH$_2$CH$_2$CH$_2$], 20.6 [NCH$_2$CH$_2$CH$_2$], 24.7 [NCH$_2$CH$_2$CH$_2$], 38.3 [NC(CH$_3$)$_3$], 47.0 [SiCH$_2$N], 52.4 [NC(CH$_3$)$_3$], 54.6 [NCH$_2$CH$_2$CH$_2$], 58.6 [NCH$_2$CH$_2$CH$_2$]. ^{29}Si NMR (59.6 MHz, C$_6$D$_6$): δ −16.9. Anal. Calcd: C, 60.16; H, 11.36; N, 11.69. Found: C, 59.5; H, 11.4; N, 11.5.

Synthesis of Magnesium Disilylamide 5b. To 160 mg (0.75 mmol) of **4b** cooled to −60 °C was added 0.38 mL (0.40 mmol, 1.0 M in heptane) of *n*-Bu$_2$Mg, and the reaction mixture was allowed to warm to room temperature. Storage for 20 h yielded 128 mg (0.28 mmol, 75%) of colorless crystals of **5b** suitable for X-ray analysis. ^{1}H NMR (400.1 MHz, C$_6$D$_6$): δ 0.24 + 0.42 [s, 12H; Si(CH$_3$)$_2$], 1.01−1.14 [m, 2H; NCH$_2$CH$_2$CH$_2$], 1.53−1.60 [m, 2H; NCH$_2$CH$_2$CH$_2$], 1.47 + 1.49 [d, 12H, $^3J_{HH}$ = 6.3 Hz; NCH(CH$_3$)$_2$], 1.65−1.71 [m, 2H; NCH$_2$CH$_2$CH$_2$], 1.63 + 1.75 [AB-system, 4H, $^2J_{HH}$ = 14.2 Hz; SiCH$_2$N], 1.84−2.00 [m, 6H; NCH$_2$CH$_2$CH$_2$], 2.58−2.64 [m, 2H; NCH$_2$CH$_2$CH$_2$], 3.40−3.44 [m, 2H; NCH$_2$CH$_2$CH$_2$], 3.73 [sept, 2H, $^3J_{HH}$ = 6.2 Hz; NCH(CH$_3$)$_2$]. ^{13}C NMR (100.6 MHz, C$_6$D$_6$): δ 5.5 + 6.5 [Si(CH$_3$)$_2$], 22.8 [NCH$_2$CH$_2$CH$_2$], 24.0 [NCH$_2$CH$_2$CH$_2$], 24.3 [NCH$_2$CH$_2$CH$_2$], 31.6 [NCH(CH$_3$)$_2$], 32.0 [NCH(CH$_3$)$_2$], 48.5 [NCH(CH$_3$)$_2$], 52.2 [SiCH$_2$N], 56.2 [NCH$_2$CH$_2$CH$_2$], 60.7 [NCH$_2$CH$_2$CH$_2$]. ^{29}Si NMR (59.6 MHz, C$_6$D$_6$): δ −15.7. Anal. Calcd: C, 58.57; H, 11.17; N, 12.42. Found: C, 58.0; H, 11.0; N, 12.3.

Synthesis of Magnesium Disilylamide 5c. To a solution of 67 mg (0.26 mmol) of **4c** in 5 mL of pentane cooled to −60 °C was added 0.13 mL (0.13 mmol, 1.0 M in heptane) of *n*-Bu$_2$Mg, and the reaction mixture was allowed to warm to 0 °C. After 20 h 47 mg (0.09 mmol, 69%) of colorless crystals of **5c** suitable for X-ray analysis was obtained. ^{1}H NMR (300.1 MHz, C$_6$D$_6$): δ 0.26, 0.43 [s, 12H; Si(CH$_3$)$_2$], 0.88−1.93 [m, 14H; NCH$_2$CH$_2$CH$_2$, SiNCHC$_6H_{10}$], 1.60 + 1.78 [AB-system, $^2J_{HH}$ = 14.3 Hz, 4H; SiCH$_2$N], 2.14 [br, 2H; NCH$_2$CH$_2$CH$_2$], 2.60 [br, 1H; SiNCHC$_6$H$_{10}$], 3.07 [br, 1H; NCH$_2$CH$_2$CH$_2$], 3.48−3.53 [m, 1H; NCH$_2$CH$_2$CH$_2$]. ^{13}C NMR (125.8 MHz, C$_6$D$_6$): δ 5.9, 6.7 [Si(CH$_3$)$_2$], 23.1−30.7 [NCH$_2$CH$_2$CH$_2$, NCHCH$_2$CH$_2$CH$_2$], 42.5 [NCHCH$_2$CH$_2$CH$_2$], 52.9 [SiCH$_2$N], 56.6 [NCH$_2$CH$_2$CH$_2$], 58.1 [NCHCH$_2$CH$_2$CH$_2$], 61.1 [NCH$_2$CH$_2$CH$_2$]. ^{29}Si NMR (59.6 MHz, C$_6$D$_6$): δ −16.0. Anal. Calcd: C, 63.30; H, 11.00; N, 10.55. Found: C, 62.8; H, 11.2; N, 10.3.

Synthesis of Butylmagnesium Silylamide 6a. A 0.44 mL (0.44 mmol, 1.0 M in heptane) amount of *n*-Bu$_2$Mg was diluted in 5 mL of pentane and cooled to −60 °C. Retaining the temperature, a solution of 101 mg of **4a** (0.44 mmol) in 5 mL of pentane was added slowly, while the reaction mixture was warmed to −30 °C. Storage at −30 °C for 20 h yielded 57 mg (0.09 mmol, 42%) of colorless crystals of **6a** suitable for X-ray analysis. Anal. Calcd: C, 62.22; H, 11.75; N, 9.07. Found: C, 61.3; H, 11.5; N, 8.6.

Synthesis of Butylmagnesium Silylamide 6b. A 0.76 mL (0.76 mmol, 1.0 M in heptane) sample of *n*-Bu$_2$Mg was diluted in 5 mL of pentane and cooled to −60 °C. Retaining the temperature, a solution of 164 mg of **4b** (0.76 mmol) in 5 mL of pentane was added slowly, while the reaction mixture was warmed to −30 °C. Storage at −30 °C for 20 h yielded 207 mg (0.35 mmol, 92%) of colorless crystals of **6a** suitable for X-ray analysis. Anal. Calcd: C, 61.11; H, 11.62; N, 9.50. Found: C, 59.8; H, 11.6; N, 9.5.

■ ASSOCIATED CONTENT

Supporting Information. Crystallographic data in CIF format and figures giving thermal ellipsoid plots of **5a**,**b**,**c** and **6a**,**b**. Total energies and Cartesian coordinates for all computed structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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