A New Type of Anionic Rearrangement in Metalated Benzylhydrazines

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Metalation of *N*,*N*-dibenzyl-*N*′-(trimethylsilyl)hydrazine with organyllithium and -magnesium compounds led to the migration of the benzyl group, and the deprotonation of Si–Me groups was observed. The syntheses and crystal structures of $Bzl_2N–NH_2$, $[Bzl(Li)N–N(SiMe_3)Bzl]_2$, and $[Mg\text{-}[BzlN–N(SiMe_2CH_2)Bzl]_2$ are presented.

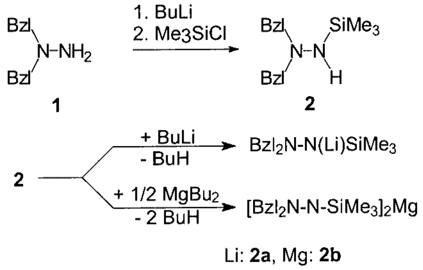
Introduction

Precursors of lithium−, magnesium−, and aluminium−nitrogen compounds with low aggregation degrees are highly desired for their use in the synthesis of nitridic ceramic composite materials[1] by CVD techniques. Different ligand systems have been investigated in order to obtain low-coordinated, volatile precursors.[2] The structural chemistry of amides of group-1, -2, and -13 metals has already been widely explored and indicates the formation of oligomeric or polymeric ring and cage structures.[3−5]

Hydrazines are interesting ligands, and metalated hydrazines exhibit a different coordination chemistry due to an additional donor atom in the α-position. Some recent aspects of the coordination chemistry of alkali metal hydrazides have been reported in the past,[6−8] and the syntheses of aluminium and gallium hydrazides were also studied as possible precursors for AlN[9] and GaN.[10,11] The structural chemistry of group-2 metal hydrazides is rather unexplored, and therefore we studied the synthesis and reactivity of alkaline earth metal hydrazides in order to compare them with the corresponding hydrazides of group-1 and -13 elements.[6−8]

Results and Discussion

In this report, the properties of *N*,*N*-dibenzyl-*N*′-(trimethylsilyl)hydrazine (**2**), prepared by silylation of *N*,*N*-dibenzylhydrazine (**1**), were characterized with respect to the coordination to lithium and magnesium atoms. The aim was to achieve the corresponding lithium and magnesium hydrazides **2a** and **2b**, respectively, in a straightforward reaction involving hydrazine **2** and organolithium or -magnesium compounds according to Scheme 1. The reactions were carried out in hexane to avoid additional coordination of donor solvent molecules at the metal atoms.



Scheme 1

Molecular Structures in the Solid State

In the course of this study, the solid-state structure of the starting material *N*,*N*-dibenzylhydrazine (**1**) was characterized. Single crystals suitable for X-ray structure determination could be obtained from freshly distilled *N*,*N*-dibenzylhydrazine by cooling at 4 °C.

The molecular structure is depicted in Figure 1. The crystals belong to the monoclinic system and the space group $P2_1/c$. The N−N bond length is 1.450(2) Å, the N−C distances are 1.467(2) Å [N(1)−C(7)] and 1.476(2) Å [N(1)−C(27)]. The nitrogen atom N(1) is threefold coordinated and shows sp^3-type bonding, as indicated by the sum of the bonding angles (330°).

The individual molecule is chiral in the solid state, but is linked to the corresponding enantiomer by hydrogen bonds via the $-NH_2$ groups. The N···H distance of the hydrogen bonds is 2.433 Å. This leads to a fourfold coordination of the nitrogen atom N(2), with N−N−H angles ranging from 103.4° to 108.9°, and a chain-like arrangement of the individual isomers in the crystal. It is interesting that the nitrogen atom N(2) of the hydrazide unit does not participate in the bonding via hydrogen bonds.

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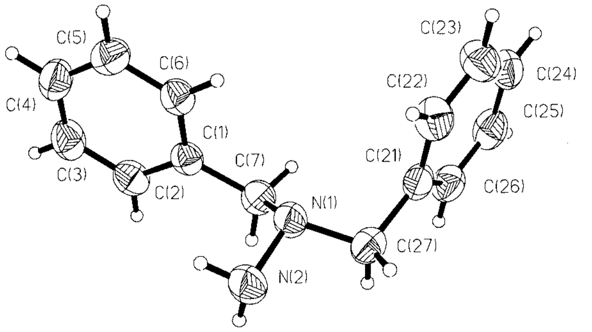

Figure 1. Molecular structure of *N*,*N*-dibenzylhydrazine (**1**); thermal ellipsoids are shown at a 50% probability level; selected bond lengths [Å] and bond angles [°]: N(1)−N(2) 1.4498(15), N(1)−C(7) 1.4672(18), N(1)−C(27) 1.4761(18), C(1)−C(7) 1.5184(19), C(21)−C(27) 1.5099(19); N(2)−N(1)−C(7) 111.37(10), N(2)−N(1)−C(27) 107.00(10), C(7)−N(1)−C(27) 111.42(11)

Light yellow crystals suitable for X-ray single-crystal structure determination could be obtained from the lithiation reaction in hexane (Scheme 1).[12] The molecular structure of the obtained product is depicted in Figure 2. It is a dimeric isomer of the anticipated product **2a**, *N*,*N'*-dibenzyl-*N'*-(trimethylsilyl)hydrazide (**3**), indicating the migration of a benzyl group.

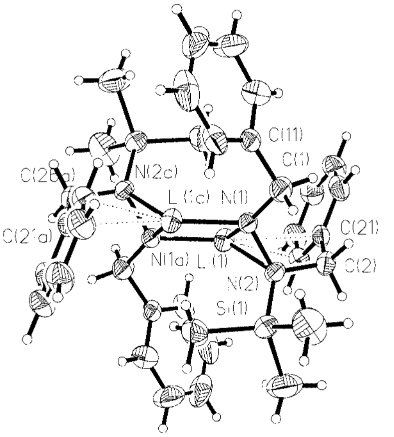

Figure 2. Molecular structure of dimeric lithium *N*,*N'*-dibenzyl-*N'*-(trimethylsilyl)hydrazide (**3**); thermal ellipsoids are shown at a 25% probability level and hydrogen atoms are omitted for clarity; selected atom distances [Å] and bond angles [°]: N(1)−N(2) 1.482(4), N(1)−C(1) 1.460(5), N(1)−Li(1) 1.924(8), N(1)−Li(1a) 1.954(7), C(1)−C(11) 1.483(6), Si(1)−N(2) 1.729(3), N(2)−C(2) 1.482(5), N(2)−Li(1) 2.091(8), C(2)−C(21) 1.489(6), C(21)−Li(1) 2.647(8),C(26)−Li(1) 2.678(8), Li(1)−Li(1a) 2.288(13); C(1)−N(1)−N(2) 111.4(3), C(1)−N(1)−Li(1) 150.6(4), N(2)−N(1)−Li(1) 74.5(3), C(1)−N(1)−Li(1a) 122.0(3), N(2)−N(1)−Li(1a) 120.0(3), Li(1)−N(1)−Li(1a) 72.3(3), N(1)−C(1)−C(11) 110.5(3), N(1)−N(2)−C(2) 113.9(3), N(1)−N(2)−Si(1) 115.5(2), C(2)−N(2)−Si(1) 119.2(3), N(1)−N(2)−Li(1) 62.4(2), C(2)−N(2)−Li(1) 103.9(3), Si(1)−N(2)−Li(1) 129.2(3), N(1)−Li(1)−N(1a) 107.7(3), N(1)−Li(1)−N(2) 43.08(19), N(1)a−Li(1)−N(2) 129.3(4)

The crystal belongs to the triclinic system and space group $P\bar{1}$ and contains two independent dimers of **3** per unit cell. The bonding parameters of the individual molecules are very similar.

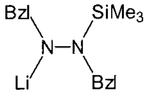

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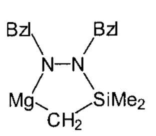
Figure 2 represents one centrosymmetric dimer with an Li_2N_4 core structure of two three-membered LiN_2 rings and a central four-membered Li_2N_2 ring. The observed Li_2N_4 core structure results from aggregation of two side-on-coordinated hydrazide units, a structural feature which has been observed for other dimeric lithiated silylhydrazides.[7,8]

In $(\mathbf{3})_2$, the nitrogen atoms of the hydrazide ligand show fourfold coordination, whereas the lithium atoms are threefold coordinated by two amide-type nitrogen atoms and one amine-type nitrogen atom.

The N−N bond length of the hydrazide unit is 1.482(4) Å. The Li−N distances of the four-membered Li_2N_2 ring [N(1)−Li(1) 1.924(8) Å, N(1)−Li(1a) 1.954(7) Å] are shorter than the distance between the coordinating α-nitrogen atom N(2) and the hydrazide ligand [N(2)−Li(1) 2.091(8) Å]. The distance between the lithium atoms Li(1)−Li(1a) is 2.288(13) Å; similar distances have been observed in other dimeric lithium silylhydrazides.[6−9]

Additional steric shielding of the lithium atoms results from interaction between the lithium atoms and the *ortho*-C−H position of the aromatic ring system of the benzyl groups of the hydrazide ligand [C(21)−Li(1) 2.647(8) Å, C(26)−Li(1) 2.678(8) Å]. Comparable Li−C distances were reported for lithiated hydrazides with aryl substituents.[7,8]

In a similar reaction of 2 equiv. of **2** with dibutylmagnesium according to Scheme 1, colourless single crystals suitable for X-ray structure determination were obtained from a hexane solution. The X-ray structure determination reveals the formation of a twofold deprotonated derivative **4** (1,2-dibenzyl-3,3-dimethyl-1,2-diaza-3-sila-5-magnesacyclopentane), instead of the anticipated hydrazide **2b**.



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The crystal belongs to the triclinic system and space group $P\bar{1}$. The crystal structure of the hydrazide **4** is depicted in Figure 3.

The isolated product **4** is dimeric in the solid state. The magnesium atoms are coordinated by four nitrogen atoms and one carbon atom of the deprotonated trimethylsilyl group. This leads to an Mg_2N_4 core derived from side-on-coordinated MgN_2 rings. The Si−C bond length of the methylene group [Si(1)−C(15), 1.827 Å] is significantly shorter than the Si−C distances of the methyl groups (1.884 and 1.856 Å), due to the carbanionic nature of C(15).

Furthermore, there is a weak interaction between the magnesium atom and the π-electrons of the phenyl ring

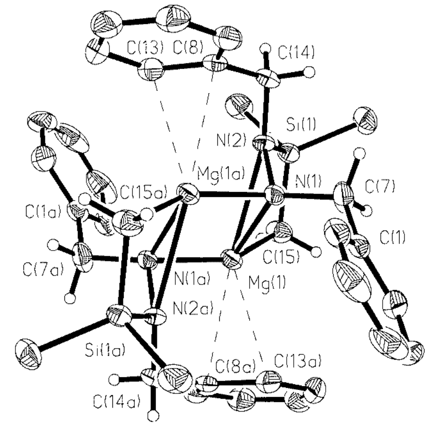


Figure 3. Molecular structure of **4**; thermal ellipsoids are shown at a 25% probability level and hydrogen atoms of aryl and methyl groups are omitted for clarity; selected bond lengths [Å] and bond angles [°]: N(1)−N(2) 1.491(4), Mg(1)−N(1) 2.121(3), Mg(1)−N(2) 2.596(3), Mg(1)−Mg(1a) 2.883(3), N(1)−Mg(1a) 2.044(3), N(2)−Mg(1a) 2.763(3), C(13)−Mg(1a) 2.789(4), C(8)−Mg(1a) 2.721(3), N(2)−C(14) 1.475(4), N(1)−C(7) 1.466(5), Si(1)−C(15) 1.827(4), Si(1)−C(16) 1.884(4), Si(1)−C(17) 1.856(4), Mg(1)−C(15) 2.129(4), Mg(1)−Mg(1a) 2.883(4); N(1a)−Mg(1)−N(1) 92.43(12), N(2)−Mg(1)−N(2a) 114.98(7), N(1)−Mg(1)−N(2) 35.05(10), N(2)−N(1)−Mg(1a) 101.65(19), N(2)−N(1)−Mg(1) 90.13(18), C(7)−N(1)−Mg(1a) 134.3(3), C(7)−N(1)−N(2) 110.1(2)

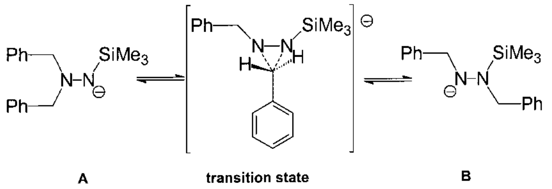
system. The C−Mg distances C(8)−Mg(1a) and C(13)−Mg(1a) range between 2.721 Å and 2.789 Å, and are shorter than the distance Mg(1a)−N(2) [2.763 Å]. When this interaction is considered as part of the coordination sphere, the magnesium atoms exhibit a sixfold coordination.

Both nitrogen atoms of the hydrazine ligand are involved in the coordination and the sum of the bond angles at the deprotonated nitrogen atom N(1) involving the surrounding atoms C(7), N(2), Mg(1) and Mg(1a) is 334.5° and 346.1°, respectively. Thus, the coordination geometry at the nitrogen centre N(1) is not planar, but resembles a distorted tetrahedral coordination. The C−N bond lengths (1.475 Å and 1.466 Å) are in the range of C−N single bonds (1.470 Å). The N−N bond length (1.491 Å) is slightly larger than that in *N*,*N*-dibenzylhydrazine (**1**) (1.450 Å).

The N−N bond lengths in the metalated species **3** and **4** are longer than that in **1**, due to the additional negative charge at the nitrogen atom. The C−N bond lengths of the benzylic groups are not significantly affected by the metalation. A comparable increase in the N−N bond length is reported for the structures of alkali metal organyl- and silylhydrazides.[6−9]

Discussion

The crystal structures of **3** and **4** both indicate the formation of an *N*,*N′*-dibenzylhydrazide isomer. Although *N*,*N*-dibenzyl-*N′*-(trimethylsilyl)hydrazine (**2**) was used as the starting material, migration of the benzyl group occurred during metalation with butyllithium and dibutylmagnesium according to Scheme 2, finally leading to compounds **3** and **4**. Thus, the rearrangement must have taken place during the reaction from the structural unit **A** to **B**, by migration of a benzyl group.



Scheme 2

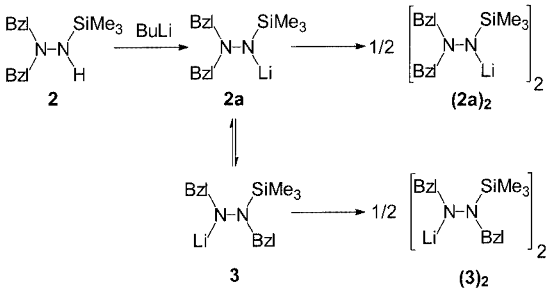
The starting material consists of the pure isomer *N*,*N*-dibenzyl-*N′*-(trimethylsilyl)hydrazine (**2**), as indicated by the NMR spectroscopic data. The ^{29}Si NMR spectrum of **2** reveals a single resonance at δ = 2.23 and the ^{13}C NMR spectrum exhibits only one set of signals for the benzyl ligands (δ = 65.01, 126.96, 127.93, 129.85, and 138.01). The *N*,*N′* isomer would have given rise to 10 resonances for the benzyl groups in the ^{13}C NMR spectrum, assuming free rotation of the ligands.

In the chemistry of silylated hydrazines, the migration of silyl groups is a common feature and has already been reported.[13,14] However, this is the first time that a similar rearrangement of benzyl groups is observed. Steric overcrowding cannot be considered to be responsible for this type of rearrangement, as indicated by the crystal structure of the unsubstituted hydrazine **1** (Figure 1), nor for the free rotation of the benzyl groups in solution of the hydrazines **1** and **2**, as indicated by the ^{13}C NMR spectroscopic data of these compounds. A stabilising effect of the negative charge by an aromatic system[7] is also not possible in this case. The migration of the benzyl group can be explained by an intramolecular S_N-type reaction caused by the increased nucleophilic character of the deprotonated hydrazide nitrogen atom in **A**, although stabilisation of the negative charge by the silyl group is possible (Scheme 2).

NMR Spectra

The ^{1}H and ^{13}C NMR spectra of the isolated crystals were recorded in C_6D_6 and indicate three different $-CH_2-$ groups of the benzyl ligands and two different silyl groups. This is in accordance with the ^{29}Si and ^{7}Li NMR spectrum of the isolated crystal fraction. Two weak peaks (δ = 4.49 and 4.98) and two strong peaks (δ = −10.36 and 4.00) are present in the ^{29}Si NMR spectrum. Similar ^{29}Si NMR spectroscopic data were reported for other dimeric lithium silylhydrazides.[7,8] The ^{7}Li NMR spectrum exhibits two resonances at δ = −1.83 (major signal) and δ = −2.27. There is no change in the ^{29}Si and ^{1}H NMR spectra up to 60 °C. This indicates the presence of stable species in solution. According to the crystal symmetry of compound $(\mathbf{3})_2$, there are two different benzyl groups in the hydrazide unit, whereas the spectrum of compound $(\mathbf{2a})_2$ should exhibit only one set of signals for the benzylic groups in the case of free rotation of the substituents. The ^{1}H NMR spectroscopic data can be interpreted as a mixture of the dimer isomers $(\mathbf{2a})_2$ and $(\mathbf{3})_2$ in solution, since there are three signals for the N−CH$_2$−Ph groups, a resonance at δ = 3.74 (25%, isomer **2a**) and two peaks at δ = 3.78 and 4.07 (75%, isomer **3**).

The formation of the isomers **2a** and **3** can be explained by Scheme 3, which shows that during the lithiation of **2** the reaction proceeds in two different ways. In the first step, the monomer hydrazide **2a** is formed. In this monomer species, a rearrangement according to Scheme 2 is possible, leading to **3**.

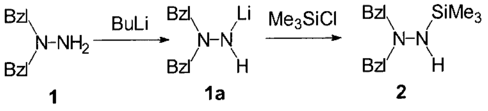


Scheme 3

The dimeric species $(\mathbf{2a})_2$ and $(\mathbf{3})_2$, once formed, are stable in solution and do not show any monomer−dimer equilibria or rearrangement equilibria, as indicated by measurement of high-temperature ^{29}Si NMR spectra in benzene up to 60 °C. The stability of the dimeric clusters is in agreement with rearrangement reactions observed in lithium silylhydrazides, which also show a high stability of the Li−N cluster once it is formed.[7,8]

Since the ^{7}Li and ^{29}Si NMR spectra of the solution and the crystals are similar, this indicates that the obtained crystal fraction is a mixture of the isomers $(\mathbf{2a})_2$ and $(\mathbf{3})_2$. It was not possible to isolate a suitable crystal of **2a** for a structure determination.[12] The rearrangement was not observed in hydrazines **1** and **2**, due to a weaker nucleophilic character of the deprotonated nitrogen atom.

An interesting feature of the synthesis of compound **2** from lithiated *N*,*N*-dibenzylhydrazine (**1a**) and chlorotrimethylsilane, is that the rearrangement was not observed during this reaction, although a hydrazide anion is formed as an intermediate according to Scheme 4.



Scheme 4

The different reactivity of the hydrazides **2a** and **1a** can be attributed to their coordination chemistry. The retention of the *N*,*N*-dibenzyl isomer in the reaction involving **1a**, may be due to the different degree of aggregation of the lithiated intermediate **1a**, which is insoluble in donor-free solvents, in contrast to the silylated species **2a** and **3**. The aggregation might involve only the deprotonated nitrogen atom of the hydrazide ligand leading to highly aggregated oligomers of the type $(\mathbf{1a})_n$, which prevent the rearrangement under normal reaction conditions. Such a kind of aggregation was observed in other magnesium and zinc hydrazides.[15] If the deprotonated nitrogen atom is shielded by intermolecular coordination, the S$_N$2-type benzylic rearrangement becomes less likely.

Reaction of *N*,*N*-Dibenzyl-*N*′-(trimethylsilyl)hydrazine with Dibutylmagnesium

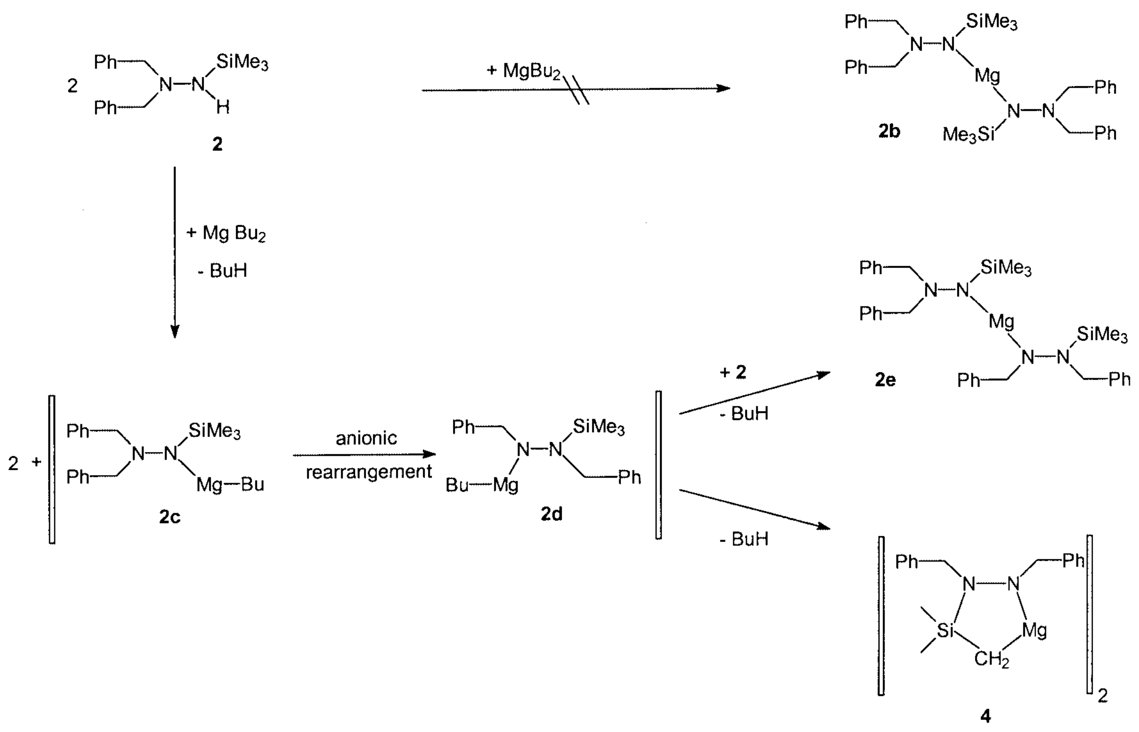
It was expected that the reaction of 2 equiv. of **2** with dibutylmagnesium would lead to the formation of a magnesium bis(hydrazide) **2b** according to Scheme 1. However, crystals of compound **4** were recovered in a 40% yield with respect to the magnesium content.

The solid-state structure of the isolated crystals of compound **4** reveals a magnesium hydrazide, where an additional deprotonation of a methyl group has taken place, leading to an −N$^-$(Bzl)−SiMe$_2$−CH$_2$$^-$ dianionic fragment. A mechanism explaining the formation of **4** is depicted in Scheme 5.

The first step of the reaction is the formation of organylmagnesium hydrazide **2c**. From this intermediate, migration of a benzyl group similar to that in lithium hydrazide **3** takes place, leading to the *N*,*N*′-dibenzyl isomer **2d**. From this intermediate **2d**, the reaction can proceed in two different directions. The butyl group acts as a base towards the proton of an Me$_3$Si− group in an intramolecular deprotonation reaction, leading to compound **4**, which was isolated and characterised by NMR spectroscopy and single-crystal diffractometry. The second reaction pathway leads to the formation of a magnesium bis(hydrazide) with unsymmetrically substituted ligands **2e**, by reaction of **2d** with the starting material **2**. Other types of deprotonation reactions involving N−SiMe$_3$− groups were reported for solutions of heterobimetallic lithium and magnesium amides by elimination of an amine,[16] and by deprotonation of transition metal compounds with strong bases like butyllithium or lithium and sodium silylamides.[17] The formation of the five-membered N−SiMe$_2$−CH$_2$−Mg ring structure in **4** may be attributed to the Lewis acidity of magnesium and the coordinating effects of the Mg−N−N− unit, although a kinetic effect caused by the presence of *n*- and *sec*-butyl groups in commercially available dibutylmagnesium might be possible. However, the latter influence was not observed in the synthesis of other magnesium amides[16,18] and hydrazides[15] with sterically demanding silyl substituents, nor in the synthesis of organylmagnesium amides and hydrazides.[15]

The ^{29}Si NMR spectrum of the solution shows the starting material **2** (δ = 1.73, highest intensity) to be present, as well as an additional signal at δ = 4.97, of equal intensity, which is attributed to compound **4**. The resonance for the isolated compound **4** in C$_6$D$_6$ is at δ = 3.82

Furthermore, weak resonances are present in the low-field region (δ = 3.65, 4.27, 4.92, 5.62, 11.24, 14.38) and in the high-field region (δ = −8.76, −8.06, −7.33, −6.67). The two resonances at lower field can be assigned to the



Scheme 5. Mechanism for the formation of the magnesium hydrazide **4**

rearranged dimeric organylmagnesium hydrazide **2d** (δ = 11.24, 14.38). The two sets of signals with four peaks each at δ = 3.65, 4.27, 4.92, 5.62 and δ = −8.76, −8.06, −7.33, −6.67 can be assigned to the dimeric magnesium hydrazide **2e**. At higher temperatures, no change in the intensity or peak shift was observed in the spectrum up to 60 °C.

An interesting feature to note is that there is no reaction when **4** is heated with the remaining starting material **2** up to 60 °C, although the basicity of the carbanion **4** should enable deprotonation of the hydrazide. This can be attributed to the high stability of the ionic core fragment and the steric shielding of **4**.

Conclusion

A new type of anionic rearrangement was observed in metalated benzylhydrazines, leading to the formation of *N,N′*-dibenzylhydrazides by migration of a benzyl group. With respect to the reaction of dibutylmagnesium with **2**, the rearrangement is the dominant reaction, instead of the formation of the corresponding magnesium hydrazide. The migration of the benzyl group is less dominant in the lithiation of the hydrazide **2**, which can be attributed to the different coordination and ionic nature of the metal−nitrogen bond. Furthermore, the influence of donor solvents on the coordination of the metal centres and the migration of the benzyl group has to be studied in more detail.

Experimental Section

General: All experiments were performed by using modified Schlenk techniques and anhydrous conditions under argon. Solvents were freshly distilled from Na/K alloy. Butyllithium (1.6 M in hexane), dibutylmagnesium (1 M in heptane, 1:1 isomer mixture of *n*- and *sec*-butyl groups), and *N,N*-dibenzylhydrazine were obtained commercially (Aldrich) and used as received. NMR spectra were recorded in C_6D_6 or $CDCl_3$ with a Bruker ACP 200 spectrometer (TMS as external standard; ^{1}H: 200 MHz, ^{13}C: 55.0 MHz, ^{29}Si: 39.7, ^{7}Li: 77.7 MHz). Attempts to prepare compound **3** and **4** in donor solvents like THF or ether failed and led to ether cleavage reactions, and deprotonation reactions of toluene were observed with compound **4** at higher temperatures. Compounds **3** and **4** may ignite if exposed to air. For the X-ray structure determination of the single crystals, a STOE IPDS diffractometer was used (Mo-K_α, λ= 0.71073 Å, graphite monochromator). The structures of the compounds **1** and **4** were solved by direct methods and for **2** the Patterson method was applied and refined by full-matrix least-squares methods (data are listed in Table 1). Anisotropic thermal parameters for all non-hydrogen atoms in the final cycles, isotropic refinement for hydrogen atoms positioned by geometry. SHELXS 97 and SHELXL 97 computer programs were used.[19] CCDC-168709 to -168711 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Preparative Details

***N,N*-Dibenzylhydrazine (1):** Benzyl chloride (36 mL, 312 mmol) was added to a stirred solution of hydrazine (5.0 g, 156 mmol) and trie-

Table 1. Crystallographic data of compounds **1**, (**3**)$_2$ and (**4**)$_2$

	1	(**3**)$_2$	(**4**)$_2$
Empirical formula	$C_{14}H_{16}N2$	$C_{17}H_{23}LiN_2Si$	$C_{34}H_{44}Mg_2N_4Si_2$
Formula mass [gmol^{-1}]	212.29	290.40	613.54
Colour, habit	colourless plates	light yellow rhombs	colourless rhombs
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	9.565(2)	10.723(2)	9.882(2)
b [Å]	5.6360(10)	10.878(2)	10.092(2)
c [Å]	22.886(5)	16.503(3)	10.394(2)
α [°]	90	83.38(3)	97.61(3)
β [°]	100.97(3)	78.02(3)	108.25(3)
γ [°]	90	69.89(3)	114.82(3)
V [Å^3]	1211.2(4)	1766.2(6)	850.6(3)
Z	4	4	1
d [g cm^{-3}]	1.164	1.092	1.154
crystal dimensions [mm]	0.3 × 0.3 × 0.5	0.5 × 0.5 × 0.5	0.5 × 0.5 × 0.5
μ, [mm^{-1}]	0.069	0.127	0.151
T [K]	293	293	293
2θ [°]	48.24	48.12	48.12
Index range	$-10 \leq h \leq 10$	$-12 \leq h \leq 11$	$-10 \leq h \leq 10$
	$-5 \leq k \leq 5$	$-12 \leq k \leq 12$	$-11 \leq k \leq 11$
	$-25 \leq l \leq 25$	$-18 \leq l \leq 18$	$-11 \leq l \leq 11$
R(int)	0.0619	0.0815	0.0791
No. of unique data	7070	11243	5378
No. of data [$I > 2\sigma(I)$]	1780	5228	2492
No. of parameters	153	385	200
$R1$ [$I > 2\sigma(I)$]	0.0365	0.0565	0.0691
$wR2$ (all data)	0.1030	0.1541	0.2132
max./min. e$^-$ density [eÅ^{-3}]	0.196/−0.114	0.518/−0.152	0.792/−0.387

thylamine (55 mL, 0.395 mmol) in 1 L of benzene, within 1 h. During the addition a white precipitate of the ammonium salt was formed. The mixture was heated for 2 h under reflux and the solid residue was then filtered off. The solvent was removed in vacuo and the remaining liquid was fractionally distilled. Bp. 110−112 °C/10^{-2} mbar. Yield: 13.2 g (40%). $C_{14}H_{16}N_2$ (212.29): calcd. C 79.21, H 7.59, N 13.20; found C 78.03, H 7.32, N 12.87. NMR ($CDCl_3$): $\delta^1H = 2.98$ (br, 2 H, $-NH_2$), 3.73 (s, 4 H, $-CH_2-$), 7.18−7.36 (m, 10 H, Ph); $\delta^{13}C = 64.63$ (Ph−CH_2−), 127.20 (*p*-Ph), 128.35 (*o*-Ph), 128.94 (*m*-Ph), 137.66 (*i*-Ph).

***N,N*-Dibenzyl-*N′*-(trimethylsilyl)hydrazine (2):** Butyllithium (12.7 mL of a 1.6 M solution) was added slowly to a solution of **1** (4.3 g, 20.2 mmol) in 250 mL of benzene, at room temperature. During the addition a white precipitate of the hydrazide was formed. The mixture was stirred for 1 h, after which chlorotrimethylsilane (2.6 mL, 20.2 mmol), dissolved in 10 mL of benzene, was added slowly over 1 h. The mixture was heated under reflux for 1 h, and after cooling, the solid residue was filtered off. The solvent was removed in vacuo and the remaining liquid was fractionally distilled. Bp. 104−106 °C/10^{-2} mbar. Yield: 4.20 g (73%). $C_{17}H_{24}N_2Si$ (284.48): calcd. C 71.78, H 8.50, N 9.85; found C 70.61, H 8.64, N 9.38. NMR ($CDCl_3$) $\delta^1H = -0.00$ (s, 9 H, $SiMe_3$), 2.22 (s, N−H, 1 H), 3.75 [s, 4 H, $(PhCH_2-)_2$], 7.38−7.50 [m, 10 H, $(PhCH_2-)_2$]; $\delta^{13}C = -0.67$ ($SiMe_3$), 65.10 [$(PhCH_2-)_2$], 126.96 (*p*-Ph), 127.93 (*o*-Ph), 129.85 (*m*-Ph), 138.10 (*i*-Ph); $\delta^{29}Si = 2.22$ ($SiMe_3$).

Lithium *N,N′*-Dibenzyl-*N′*-(trimethylsilyl)hydrazide (3): Butyllithium (2.9 mL of a 1.6 M solution) was added slowly to a solution of **2** (1.3 g, 4.6 mmol) in 25 mL of hexane, at room temperature. During the addition the solution became orange. After the evolution of butane was complete, the solution was stored at 4 °C. After one week, light yellow crystals were isolated. M.p. 131 °C (dec.). Yield: 0.20 g (15%). $C_{17}H_{24}LiN_2Si$ (290.41): calcd. C 70.31, H 7.98, N 9.65; found C 68.73, H 8.38, N 9.23. NMR (C_6D_6): $\delta^1H = -0.05-0.42$ ($SiMe_3$, 9 H), 3.74 (25%) + 3.78/4.07 (75%) [s, 4 H, $(PhCH_2-)_2$]; 6.93−7.35 (m, 10 H, Ph); $\delta^{13}C = -0.14$, 0.70, 1.46, 4.80, 5.79 ($SiMe_3$); 49.95, 53.21, 65.60, 66.28, 57.91, 60.18, ($PhCH_2-$); 125.96, 126.17, 126.43, 127.30, 128.29, 128.80, 129.08, 129.32, 129.56, 129.72, 130.22, 138.63, 139.17, 140.06, 140.63 (Ph); $\delta^{29}Si = 4.49$, 4.98 (weak); −10.36, 4.00 (strong); $\delta^7Li = -1.83$ (br), −2.27.

Formation of 1,2-Dibenzyl-3,3-dimethyl-1,2-diaza-3-sila-5-magnesacyclopentane (4) from the Reaction of 2 with Dibutylmagnesium: Dibutylmagnesium (1.3 mmol, 1.3 mL of a 1 M solution) in heptane was added to **2** (0.73 g, 2.55 mmol), dissolved in 25 mL of hexane. The solution became light yellow and after the solution was stored for one week at room temperature, colourless crystals were isolated. M.p. 167 °C (dec.). Yield: 0.31 g (40%). $C_{34}H_{44}Mg_2N_4Si_2$ (613.54): calcd. C 66.56, H 7.23, N 9.13; found C 67.68, H 7.65, N 8.75. NMR (C_6D_6): $\delta^1H = -0.02$, 0.25 [d, 2 H, $Si(CH_3)_2CH_2-$], 0.27 [s, 6 H, $Si(CH_3)_2CH_2-$], 3.78, 3.81 (d, 2 H, $PhCH_2-N-Mg$), 4.14 (s, 2 H, $PhCH_2-N-SiMe_2$), 7.14−7.31 [m, 10 H, $(PhCH_2-N-)_2$]; $\delta^{13}C = -0.50$ [$Si(CH_3)_2CH_2-$], −0.18 [$Si(CH_3)_2CH_2-$], 49.88 ($PhCH_2-N-Mg$), 53.17 ($PhCH_2-N-SiMe_2$), 127.24−129.32 (6 resonances), 139.14, 140.04 (*i*-Ph); $\delta^{29}Si = 3.82$ ($SiMe_3$); $^1J(^{29}Si^{13}C) = 57.6$ Hz.

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