New Aspects in the Coordination Chemistry of Magnesium Hydrazides

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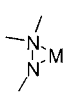
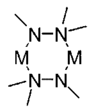
The coordination chemistry of alkaline earth metal hydrazides has been investigated, and the synthesis and crystal structures of monomeric magnesium bis[*N*-phenyl-*N*′,*N*′-bis(trimethylsilyl)hydrazide] (**1**) and dimeric magnesium bis[*N*,*N*-dimethyl-*N*′-(trimethylsilyl)hydrazide] (**2**) are presented. An unusual coordination sphere of the magnesium atom was observed in the first structurally characterized monomer magnesium hydrazide **1**, a highly reactive compound with side-on coordinated hydrazide ligands forming a bent butterfly-type structure. The Mg–N distances range from 1.92 to 2.45 Å and intramolecular C–H···Mg interactions in the range 2.42 to 2.63 Å are observed. This structural motif is unprecedented in the coordination chemistry of magnesium hydrazides.

Low-coordinated compounds of main-group metals are highly desired to study their structural chemistry and reactivity. They are considered to be potential candidates for the synthesis of ceramic composite materials by CVD techniques. Different ligand systems have been investigated to achieve low-coordinated, volatile compounds.[1,2] Hydrazines are interesting ligands due to an additional donor atom in the α-position, and metalated hydrazines exhibit a different coordination chemistry than the corresponding amides. Due to a second nitrogen atom in the adjacent α-position, intramolecular (**A**), as well as intermolecular (**B**) coordination of the metal centers is possible by the ligands.



A



B

The structural chemistry of the amides of group-1, -2 and -13 metals has already been widely characterized and indicates the formation of oligomeric or polymeric ring and cage structures.[3−5] Some recent aspects of the coordination chemistry of alkali metal hydrazides have been reported,[6−8] and the syntheses of aluminium and gallium hydraziedes were studied as possible precursors for AlN[3] and GaN.[10,11] These metal hydrazides share some common features with the corresponding amides, but also show significant differences in their coordination chemistry. Monomeric magnesium complexes containing monoanionic bidentate ligands are rare and the coordination chemistry of alkaline earth metal hydrazides is quite unexplored. The alkaline earth metal hydrazides were studied in order to compare the structures with the corresponding alkali metal hydrazides.

In this report, the structures of two magnesium hydrazides are presented. The aim was to investigate the coordination chemistry of alkaline earth metal hydrazides without the influence of donor solvents on the coordination sites at the metal atoms, hence a straightforward synthesis of the corresponding compounds was carried out. The deprotonation of the hydrazines was achieved by a solution of dibutylmagnesium in hexane according to Equations (1) and (2). This gave magnesium bis[*N*-phenyl-*N*′,*N*′-bis(trimethylsilyl)hydrazide] (**1**) and magnesium bis[*N*,*N*-dimethyl-*N*′-(trimethylsilyl)hydrazide] (**2**).

$$2\,(Me_3Si)_2N-N(H)Ph + MgBu_2 \rightarrow [(Me_3Si)_2N-N-Ph]_2Mg\ (\mathbf{1}) + 2\ Bu\text{-}H \tag{1}$$

$$2\ Me_2N-N(H)SiMe_3 + MgBu_2 \rightarrow [Me_2N-N-SiMe_3]_2Mg\ (\mathbf{2}) + 2\ Bu\text{-}H \tag{2}$$

In the case of hydrazide **1**, two isomers (**C**, **D**) are likely since migration of the silyl groups is a common feature of silylated hydrazines.[12] Silyl group migration also occurs during metalation and the resulting isomers are sometimes difficult to predict, as indicated by the formation of mixed isomers in lithiated silylhydrazines.[7,8] Structural characterizations of metalated phenylhydrazines have shown that a phenyl group is able to stabilize the negative charge of a hydrazide nitrogen atom better than a silyl group leading to an η^n coordination of the metal center ($n = 2-6$) by the π-electron system, hence the formation of isomer **C** is expected.[7b−7d]

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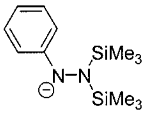
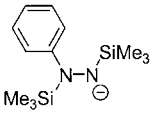


C



D

Compound **1** was obtained from the reaction of *N*-phenyl-*N′*,*N′*-bis(trimethylsilyl)hydrazine and dibutylmagnesium in hexane in a 73% yield in the form of colorless platelets according to Equation (1). It was characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and X-ray crystallography.

The ^{29}Si NMR spectrum in hexane solution, as well as the spectrum of the isolated crystals of **1** in C_6D_6, exhibits only one resonance at $\delta = 8.70$ ppm. The ^{1}H and ^{13}C NMR data reveal a single resonance for the silyl groups, and four signals in the ^{13}C NMR for the phenyl group, which indicates the free rotation of the aryl unit. The data reveal a high symmetry for compound **1**.

The magnesium hydrazide **1** could be isolated from a hexane solution and it crystallizes in the monoclinic system (space group $P2_1/n$) containing four molecules per unit cell. The most remarkable feature of compound **1** is that it is monomeric in the solid state and no intermolecular interactions could be observed. The molecular structure of **1** is depicted in Figure 1.

In spite of the tetrahedral coordination geometry of the magnesium atom, which is common in e.g. donor-coordinated magnesium amides, an unprecedented type of coordination is adopted by the magnesium atom of compound **1** which displays an unusual arrangement of the hydrazide ligands. The magnesium atom Mg(1) exhibits four bonds with the nitrogen atoms of two side-on-coordinated hydrazide ligands giving a butterfly-shaped conformation. The individual molecule reveals a symmetry close to C_2. There are two types of Mg−N distances, short ones to the atoms N(1) and N(3) [Mg(1)−N(1) 1.918(2) Å, Mg(1)−N(3) 1.917(2) Å], both linked to the phenyl groups of the hydrazide ligands and which can be considered equal, and longer distances to the nitrogen atoms N(2) and N(4) of the NSi_2 groups [Mg(1)−N(4) 2.399(2) Å, Mg(1)−N(2) 2.448(2) Å]. The structural features of **1** resemble an sp^{2}-type hybridization for all nitrogen atoms in each hydrazide unit [sum of the bond angles at N(1) 360.0°, N(2) 359.9°, N(3) 359.8°, N(4) 359.4°], indicating that the basicity of the atoms N(2) and N(4) is low and an sp^{3}-type hybridization does not occur from the coordinative interaction of the $-NSi_2-$ nitrogen atoms with the magnesium atom. The nearest C−H···Mg interactions occur with the trimethylsilyl groups of the atoms Si(2) and Si(4), involving the carbon atoms C(6) and C(12), and are in the range of 2.417 to 2.625 Å. The shortest Mg−C distances [Mg(1)···C(6) 2.688 Å, Mg(1)···C(12) 2.696 Å] are longer than those reported for a monomeric dialkylmagnesium compound $Mg[CH(SiMe_3)_2]_2$ [Mg···C 2.535(4) Å],[13] but are of comparable magnitude as those found in a monomeric magnesium diamide $Mg[N(SiPh_2Me)_2]_2$,[14] and can be considered as quite weak. The Si−N distances involving the silyl groups Si(2) and Si(4) [1.760(2), 1.771(2) Å, respectively] are significantly longer than the distances involving the silyl groups Si(1) and Si(3) without C−H···Mg contacts [1.745(2), 1.749(2) Å], and are in general longer than the Si−N distances of tetrameric $[Ph(Li)N-N(SiMe_3)_2]_4$ and of the ether adducts of $Ph(Na)N-N(SiMe_3)_2$, which all exhibit coordinative metal−aryl interactions.[7b−7d] According to the solid-state structure of **1**, the silyl groups of the $-NSi_2$ unit are different, but the ^{29}Si NMR spectrum displays only one signal indicating a more symmetric species in solution.

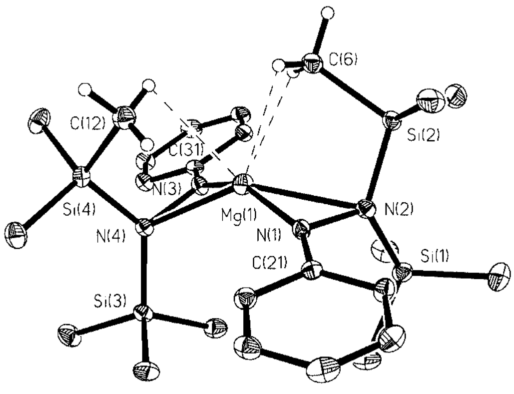


Figure 1. Molecular structure of monomeric magnesium bis[*N*-phenyl-*N′*,*N′*-bis(trimethylsilyl)hydrazide] (**1**); thermal ellipsoids are shown at a 25% probability level and only hydrogen atoms at C(6) and C(12) are shown; selected atom distances [Å] and angles [°]: N(1)−N(2) 1.497(2), N(3)−N(4) 1.493(2), Mg(1)−N(3) 1.917(2), Mg(1)−N(1) 1.918(2), Mg(1)−N(4) 2.399(2), Mg(1)−N(2) 2.448(2), Si(1)−N(2) 1.760(2), Si(2)−N(2) 1.745(2), Si(3)−N(4) 1.771(2), Si(4)−N(4) 1.749(2), N(1)−C(21) 1.372(2), N(3)−C(31) 1.372(2); N(3)−Mg(1)−N(1) 151.17(8), N(3)−Mg(1)−N(4) 38.47(6), N(1)−Mg(1)−N(4) 128.78(6), N(3)−Mg(1)−N(2) 130.34(6), N(1)−Mg(1)−N(2) 37.70(6), N(4)−Mg(1)−N(2) 144.85(6), C(21)−N(1)−N(2) 117.77(13), C(21)−N(1)−Mg(1) 151.48(12), N(2)−N(1)−Mg(1) 90.75(10), N(1)−N(2)−Si(2) 111.03(11), N(1)−N(2)−Si(1) 118.25(11), Si(2)−N(2)−Si(1) 130.61(9), N(1)−N(2)−Mg(1) 51.56(7), C(31)−N(3)−N(4) 117.72(13), C(31)−N(3)−Mg(1) 153.56(12), N(4)−N(3)−Mg(1) 88.51(9), N(3)−N(4)−Si(4) 110.82(11), N(3)−N(4)−Si(3) 118.64(11), Si(4)−N(4)−Si(3) 129.96(9), N(3)−N(4)−Mg(1) 53.02(7)

The Si−N−Si and C−N−Mg planes are almost orthogonal to each other [C(21)N(1)Mg(1)/Si(1)N(2)Si(2) 81.1°, C(31)N(3)Mg(1)/Si(3)N(4)Si(4) 98.8°], but the tilt is greater than in the corresponding lithium hydrazide (cf. 87.6°/92.3°).

The interplanar angle of the phenyl group and the N−N−Mg plane is quite small (4.2°), indicating a π interaction between the aromatic ring system and the lone pair of electrons at the nitrogen atom.

The N−Mg−N angles resulting from the side-on-coordinated hydrazide ligands are small [N(1)Mg(1)N(2) 37.70(6)°, N(3)Mg(1)N(4) 38.47(6)°], whereas the N(1)−Mg(1)−N(3) angle of 151.17(8)°, involving the deprotonated nitrogen atoms N(1) and N(3) of the hydrazide ligands, is in a similar range as reported for the monomeric magnesium bis(amide) $Mg[N(SiPh_2Me)_2]_2$ [N−Mg−N 162.8(3)°],[14] or the monomeric dialkylmagnesium compound $Mg[CH(SiMe_3)_2]_2$ [C−Mg−C 140.0(2)°].[13] The angle N(2)−Mg(1)−N(4), involving both NSi_2 groups is 144.85(6)°, and the N−Mg−N angles involving different hydrazide nitrogen atoms are in the range of ca. 130° [N(1)Mg(1)N(4) 128.78(6)°, N(2)Mg(1)N(3) 130.34(6)°]. There are two types of N−N−Mg angles of comparable magnitude, those centered at the deprotonated nitrogen atoms N(1) [90.75(10)°] and N(3) [88.51(10)°], and those involving the sp^2-type $-NSi_2$ groups at N(2) [51.56(7)°] and N(4) [53.02(7)°].

A significant difference in the coordination chemistry of comparable alkali metal phenylhydrazides, where the aromatic ring system may act as an η^n ligand ($n = 2-6$) to the metal atom, is the fact that the phenyl groups do not participate in the coordinative saturation of the magnesium atom. This difference is also the reason for the larger C−N distances between the nitrogen atom of the hydrazide unit and the *i*-C of the phenyl group [1.372(2) Å] than the corresponding C−N distances of the tetrameric lithium hydrazide $[Ph-N(Li)-N(SiMe_3)_2]_4$ [1.346(5), 1.349(5) Å] or of the ether adducts of the corresponding sodium hydrazides (1.34−1.36 Å).[7c][7d]

Table 1 depicts an overview of the bond lengths involving the $Ph-N^{-}-N(SiMe_3)_2$ hydrazide ligand and different metal atoms. Although the N−N distances of the *N*-phenyl-*N′*,*N′*-bis(trimethylsilyl)hydrazides of lithium, sodium, cesium[7b−7d] and magnesium are of comparable magnitude, a significant difference is seen in the C−N and Si−N bond lengths.

Compound **2** was obtained from the reaction of *N*,*N*-dimethyl-*N′*-(trimethylsilyl)hydrazine and dibutylmagnesium in hexane in a 86% yield, in the form of colorless crystals according to Equation (2). It was characterized by ^1H, ^{13}C and ^{29}Si NMR spectroscopy and X-ray crystallography.

The ^{29}Si NMR spectrum of the hexane solution indicates two peaks at $\delta = -2.62$ and -9.43 ppm, which is identical to the spectrum of the isolated crystals in C_6D_6. The ^1H and ^{13}C NMR spectra reveal two resonances each for the silyl groups and methyl groups, and indicate two different hydrazide ligands. No change was observed up to a temperature of 60 °C in the high-temperature ^{29}Si NMR spectra. The resonances observed in the ^{29}Si NMR spectrum can be interpreted as silyl groups located at three- and four-coordinated deprotonated nitrogen atoms.

Single crystals of the magnesium hydrazide **2** could be obtained from a hexane solution and they crystallize in the monoclinic system and space group $P2_1/n$ with four formula units per unit cell.

The crystal structure of the hydrazide **2** is shown in Figure 2. It is aggregated in the form of centrosymmetric dimers in the solid state with terminal and bridging hydrazide units. The magnesium atoms are coordinated by five nitrogen atoms with Mg−N distances ranging from 1.971(2) to 2.232(2) Å.

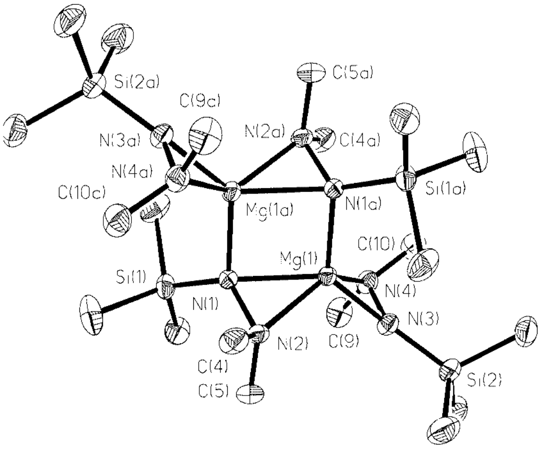


Figure 2. Molecular structure of dimeric magnesium bis[*N*,*N*-dimethyl-*N′*-(trimethylsilyl)hydrazide] (**2**); thermal ellipsoids are shown at a 25% probability level and hydrogen atoms are omitted for clarity; selected atom distances [Å] and angles [°]: Mg(1)−N(3) 1.971(2), Mg(1)−N(1a) 2.107(2), Mg(1)−N(2) 2.125(2), Mg(1)−N(1) 2.139(2), Mg(1)−N(4) 2.232(3), Mg(1)−Mg(1a) 2.9659(18), Si(1)−N(1) 1.726(2), N(1)−N(2) 1.501(3), N(1)−Mg(1a) 2.107(2), N(2)−C(4) 1.463(4), N(2)−C(5) 1.473(4), Si(2)−N(3) 1.696(2), N(3)−N(4) 1.474(3), N(4)−C(10) 1.451(5), N(4)−C(9) 1.469(5), Mg(1)−Mg(1a) 2.966(2); N(3)−Mg(1)−N(1a) 132.28(10), N(3)−Mg(1)−N(1) 136.19(10), N(2)−Mg(1)−N(4) 132.05(10), N(1a)−Mg(1)−N(1) 91.40(9), Mg(1a)−N(1)−Mg(1) 88.60(9), N(1)−Mg(1)−N(4) 121.53(10), N(3)−Mg(1)−Mg(1a) 176.87(9), N(2)−N(1)−Si(1) 124.59(16), N(2)−N(1)−Mg(1a) 111.70(15), N(2)−N(1)−Mg(1) 68.88(12), N(1)−N(2)−Mg(1) 69.91(12), N(4)−N(3)−Si(2) 126.58(18), N(4)−N(3)−Mg(1) 79.34(14), Si(2)−N(3)−Mg(1) 151.56(15), C(4)−N(2)−C(5) 109.6(3), C(10)−N(4)−C(9) 109.3(3)

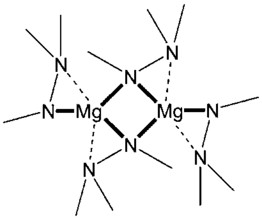
If the coordination sphere of the magnesium atoms is considered with respect to the deprotonated hydrazine nitrogen atoms only, they exhibit a trigonal-planar coordination sphere [sum of the bond angles at Mg(1) involving N(1), N(1a) and N(3): 359.9°], indicating that the coordination of the NMe_2 groups to the magnesium atoms does not cause a tetrahedron-type coordination. The coordination sphere of the nitrogen atoms N(3) and N(3a) of the ter-

Table 1. Bond lengths of *N*-phenyl-*N′*,*N′*-bis(trimethylsilyl)hydrazides

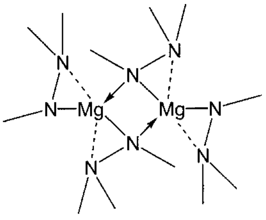
Compound	$Mg[N(Ph)-N(SiMe_3)_2]_2$	$LiN(Ph)-N(SiMe_3)_2$ [7c]	$NaN(Ph)-N(SiMe_3)_2 \cdot nOR_2$ [7d]	$Cs(Ph)-N(SiMe_3)_2$ [7c]
Aggregation	monomeric	tetrameric	monomeric to polymeric	polymeric
N−N [Å]	1.497(2), 1.493(2)	1.486(5), 1.493(5)	1.47−1.51	1.501(8)
N−Si [Å]	1.760(2), 1.745(2), 1.771(2), 1.749(2)	1.733(4), 1.736(4)	1.71−1.74	1.724(6), 1.735(6)
M−N [Å]	1.917(2), 1.918(2)	1.881(9), 1.883(9)	2.30−2.33	2.991(6)
C−N [Å]	1.372(2)	1.346(5), 1.349(5)	1.34−1.36	1.351(9)

minal hydrazide units are almost trigonal-planar (sum of the bond angles: 357.5°), whereas the remaining nitrogen atoms are four-coordinate. The N−N bond length of the terminal hydrazide ligand [N(3)−N(4) 1.474(3) Å] is slightly shorter than the bond length of the hydrazide ligand bridging the magnesium atoms [N(1)−N(2) 1.501(3) Å], due to the different coordination geometries of the nitrogen atoms involved. The N−Mg−N angles of the terminal and bridging hydrazide ligands are of comparable magnitude [N(1)Mg(1)N(2) 41.21(8)°, N(3)Mg(1)N(4) 40.47(9)°], and are only slightly larger as the corresponding N−Mg−N angles of **1**. The N−N−Mg angles range from 60.2 to 79.34°, and the angles of the central Mg_2N_2 unit are close to 90° [N(1)Mg(1)N(1a) 91.40(9)°, Mg(1a)N(1)Mg(1) 88.60(9)°]. The NMR spectra of the solution are in accordance with the dimeric structure of **2**.

The dimeric structure of **2** can be explained either as an association of two molecules with both side-on- and end-on-coordinated hydrazide units each (**E**), or as an arrangement of two monomeric hydrazide units with bent, side-on-coordinated ligands (**F**). The latter explanation arises since the structural unit of the bent coordination sphere in the monomer magnesium hydrazide **1** is also detected in the structure of the dimeric molecule **2**.



E



F

The structural arrangement of the nitrogen atoms in dimeric **2** ($\mathbf{2}_2$) reveals some strong similarities with the corresponding dimeric magnesium amides.[15] When only the deprotonated hydrazide nitrogen atoms N(1), N(3), N(1a) and N(3a) are considered, the remaining core structure of $\mathbf{2}_2$ is almost planar, with the exocyclic nitrogen atoms inclined by 3.1° from the central Mg_2N_2 plane. This structural motif is related to the structure of the dimeric magnesium amide $Mg[N(SiMe_3)_2]_2$, and the Mg−N and Si−N distances, as well as the N−Mg−N angles of the core structure of **2** and the latter magnesium amide are similar.

In spite of an expected tetrahedral coordination geometry, the magnesium atom in compound **1** displays a side-on coordination of the hydrazine ligands, whereas magnesium bis[*N*,*N*-dimethyl-*N*′-(trimethylsilyl)hydrazide] (**2**) reveals a dimeric structure in the solid state. The unusual coordination sphere of **1** explains its high reactivity, e.g. towards ethers or toluene. In the case where these solvents are used, a reaction of **1** with the solvents occurs with the formation of phenylbis(trimethylsilyl)hydrazine, which is identified using NMR spectroscopy,[7c] and other reaction products. It has been reported that magnesium amides are able to generate arene anions, which might also be likely to react with these low-coordinated magnesium hydrazides.[16]

Since the substituents of the hydrazine unit are not extremely bulky, the bent coordination sphere at the magnesium center can result from a weak Mg···H−C interaction involving the methyl groups of the silyl substituents. Regarding heavier alkaline earth metals, a bent coordination sphere of the two-coordinate species is due to core polarization effects, as indicated by theoretical investigations.[17] The aryl ligand does not coordinate to the metal center in the magnesium hydrazide **1**, which is in contrast to the corresponding alkali metal hydrazides. Further investigations with other ligands leading to low-coordinate magnesium compounds need to be carried out in order to explain the different coordinative behavior and the bent N−Mg−N moiety.

Experimental Section

General: All reactions were performed by using modified Schlenk techniques under argon. Solvents were freshly distilled from an Na/K alloy. Dibutylmagnesium (1 M in heptane) was obtained from commercial suppliers and used as received, and starting materials were prepared according to literature methods. NMR spectra were recorded in C_6D_6 solution by using a Bruker ACP 200 spectrometer (TMS as external standards; ^1H: 200 MHz; ^{13}C: 55.0 MHz; ^{29}Si: 39.7 MHz). Compounds **1** and **2** react with ethers and toluene and can ignite when exposed to air. Deviations in elemental analyses are attributed to the formation of silicon carbide during combustion. The data for the crystal structure of compound **1** were collected with a Siemens P4 automated four-circle diffractometer with CCD detector and LT2 cooling device (Mo-K_α, λ= 0.71073 Å, graphite monochromator). For the X-ray structure determination of **2**, a STOE IPDS diffractometer was used (Mo-K_α, λ= 0.71073 Å, graphite monochromator). The programs XS, SHELXTL Plus and SHELX97 were used for data collection, structure solution and refinement.[18] The structures of the compounds were solved by direct methods and refined by full-matrix least-square methods. Anisotropic thermal parameters for all non-hydrogen atoms in the final cycles, isotropic refinement for hydrogen atoms positioned by geometry. CCDC-168700 and -168701 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].

Magnesium Bis[*N*-phenyl-*N*′,*N*′-bis(trimethylsilyl)hydrazide] (1): A solution of freshly distilled *N*-phenyl-*N*′,*N*′-bis(trimethylsilyl)hydrazine (0.84 g, 3.3 mmol) in 15 mL of hexane was allowed to react at room temperature with dibutylmagnesium (1.7 mL of a 1 M solution; 1.7 mmol) in heptane. The mixture became light yellow and colorless crystals were formed at −18 °C within several days. Yield: 0.65 g (73%); m.p. 93−95 °C (dec.). ^1H NMR (C_6D_6): δ = 0.10 (s, Me_3Si, 18 H), 6.63−7.17 (m, Ph-N, 5 H) ppm. ^{13}C NMR: δ = 1.00 (Me_3Si), 112.58, 129.27 (*o*, *m*-C), 118.60 (*p*-C), 151.9 (*i*-C1) ppm. ^{29}Si NMR: δ = 8.70 ppm. $C_{24}H_{46}MgN_4Si_4$ (527.32): calcd. C 54.67, H 8.79, Mg 4.61, N 10.63; found C 52.64, H 8.29, Mg 4.36, N 10.99.

Magnesium Bis[*N*,*N*-dimethyl-*N*′-(trimethylsilyl)hydrazide] (2): Dibutylmagnesium (3.0 mL of a 1 M solution; 3.0 mmol) in heptane was added dropwise to a stirred solution of *N*,*N*-dimethyl-*N*′-(trimethylsilyl)hydrazine (0.79 g, 6.0 mmol) in 15 mL of hexane at ambient temperature. The evolution of butane occurred immediately. Colorless crystals separated from the solution within several days at room temperature. Yield 0.74 g (86%), m.p. 107−109 °C (dec.). ^{1}H NMR (C_6D_6): $\delta = 0.30$ (s, Me_3Si, 9 H), 0.36 (s, Me_3Si, 9 H), 2.58 (s, Me_2N-, 6 H), 2.61 (s, Me_2N-, 6 H) ppm. ^{13}C NMR: $\delta =$ 4.77 (Me_3Si), 5.65 (Me_3Si), 52.17 (Me_2N-), 53.39 (Me_2N-) ppm. ^{29}Si NMR: $\delta = -2.62$ [$^{1}J(^{13}C^{29}Si) = 54.0$ Hz], -9.43 [$^{1}J(^{13}C^{29}Si) =$ 52.4 Hz] ppm. $C_{10}H_{30}MgN_4Si_2$ (286.87): calcd. C 41.87, H 10.54, Mg 8.47, N 19.53; found C 41.24, H 10.22, Mg 8.33, N 19.38.

Crystal Data and Data Collection Parameters: 1: $C_{24}H_{46}MgN_4Si_4$, $M_r = 527.32$, crystal size 0.22 × 0.36 × 0.48 mm, monoclinic, $P2_1/n$, $a = 11.0017(2)$, $b = 12.4958(2)$, $c = 22.5633(4)$ Å, $\beta =$ 96.119(1)°, $V = 3084.22(9)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.136$ Mg/m^3, $\mu =$ 0.232 mm^{-1}, $F(000) = 1144$, index range: $-14 \leq h \leq 10$, $-16 \leq k \leq 16$, $-27 \leq l \leq 28$, $2\theta = 57.96°$, $T = 193$ K, refl. collected 17422, refl. unique 5969, refl. observed (4σ) 5324, R(int.) = 0.0352, no. of variables 367, weighting scheme $x/y = 0.0272/2.5741$, GOOF = 1.226, final $R(4\sigma) = 0.0476$, final $wR2 = 0.1039$, largest residual peak 0.281 e/Å^3, with: $w^{-1} = \sigma^2F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$. **2:** $C_{10}H_{30}MgN_4Si_2$, $M_r = 286.87$, $T = 293(2)$ K; monoclinic, $P2_1/n$, $a = 10.320(2)$, $b = 12.755(3)$, $c = 14.102(3)$ Å, $\beta = 98.19(3)°$, $V = 1837.3(7)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.037$ Mg/m^3, $\mu = 0.217$ mm^{-1}, $F(000) = 632$, crystal size: 0.35 × 0.5 × 0.5 mm, θ range for data collection: 2.16−22.51°, index ranges: $0 \leq h \leq 11$, $-13 \leq k \leq 0$, $-15 \leq l \leq 15$; reflections collected: 2400, independent reflections: 2400; refinement method: full-matrix least squares on F^2; data/restraints/parameters: 2400/0/274; GOOF on F^2: 1.193; final R indices [$I > 2\sigma(I)$]: $R1 = 0.0410$, $wR2 = 0.0946$; R indices (all data): $R1 = 0.0627$, $wR2 = 0.1095$; largest difference peak and hole: 0.166 and −0.179 e/Å^3.

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