ChemComm

Synthesis and structural characterization of a volatile, intramolecularly coordinated monomeric homoleptic magnesium alkylamide

William S. Rees Jr.,* Henry A. Luten and Oliver Just

School of Chemistry and Biochemistry and School of Materials Science and Engineering and Molecular Design Institute, Georgia Institute of Technology, Atlanta, GA 30332-0400, USA. E-mail: will.rees@chemistry.gatech.edu

Received (in Columbia, MO, USA) 2nd December 1999, Accepted 16th December 1999

The design, synthesis and X-ray crystal structure of the first intramolecularly coordinated homoleptic, monomeric and highly volatile magnesium alkylamide example, $Mg\{\overline{N[Si(CH_3)_3](CH_2)_3N}(CH_3)_2\}_2$, are described.

The majority of structurally characterized magnesium–amide complexes, monomeric[1] or dimeric,[2] contain three- or four-coordinate metal centers, with a few compounds reported containing two-[3] or six-coordinate[4] magnesium. Numerous examples exist with intermolecular Lewis-base complexation, however, an intramolecular coordination motif for the central atom is uncommon for magnesium amides. Monomeric magnesium complexes possessing bidentate monoanionic ligands also are rather rare. In an ongoing effort to design and synthesize precursors for electronic materials, we have focused on developing highly volatile, thermally robust, ambient atmosphere stable, coordinatively saturated, oxygen-free magnesium alkylamide compounds as potential dopant sources for the CVD of GaN : Mg.[5] The synthesis and structural examination of the first intramolecularly coordinated monomeric magnesium alkylamide, which concomitantly possesses both substantial volatility and vapor phase integrity, are described herein.[6]

Magnesium bis[(γ-dimethylaminopropyl)trimethylsilylamide] **1**,[†] was prepared by reaction of the new secondary amine, γ-dimethylaminopropyl(trimethylsilyl)amine **2**[‡] with dibutyl magnesium in hexane. This white solid has a high vapor pressure (intact sublimation at 80 °C and 10^{-2} Torr),[7] substantial vapor phase stability, and has been demonstrated, by TGA to have exceptionally clean transport characteristics (Fig. 1). The rather unusual combination of heightened vapor phase robustness and mild vaporization conditions are, to our knowledge, unique among magnesium compounds.

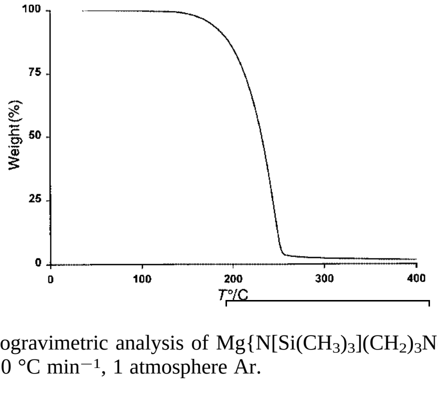

Fig. 1 Thermogravimetric analysis of $Mg\{\overline{N[Si(CH_3)_3](CH_2)_3N}(CH_3)_2\}_2$, heating rate 10 °C min^{-1}, 1 atmosphere Ar.

A single crystal of suitable quality, obtained from a hexane solution at −80 °C, was mounted on a diffractometer under a cooled argon stream. The solid state structure of **1**, determined by X-ray diffraction,[§] contains two crystallographically independent molecules in the asymmetric unit. Compound **1** is monomeric, has a four-coordinate distorted tetrahedral magnesium center, composed of four nitrogen atoms, two of which form covalent metal–amide interactions (ORTEP plot: Fig. 2). Nitrogen atoms bearing three fully saturated aliphatic groups and available lone pairs intramolecularly coordinate with the magnesium center, occupying the remaining two coordination sites.[8] The N1–Mg1–N3 (N5–Mg2–N7) interatomic angles of 137.57° (136.01°) are considerably wider than analogous angles present in di-solvated, four-coordinate, monomeric magnesium bis(amide) species $Mg\{N[Si(CH_3)_3]_2\}_2(THF)_2$[1a] (127.9°), $Mg\{N[Si(CH_3)_3]_2\}_2$((2,3,5-collidine)$_2$[1c] (120.9) and $Mg\{N[Si(CH_3)_3]_2\}_2$(4-picoline)$_2$[1c] (125.5). A similar trend is observed for the N2–Mg1–N4 and N6–Mg2–N8 angles (109.71 and 109.07°), which are substantially larger than the corresponding angles for the O(N)–Mg–O(N) donor interactions present in the compounds mentioned above: 89.9,[1a] 87.9[1c] and 86.8°.[1c] This may be explained by the diminished steric constraints imposed on the overall geometry of the complex by the newly designed, flexible, intramolecularly coordinated γ-dimethylaminopropyl(trimethylsilyl)amine ligand. A comparably disordered tetrahedral environment around the central metal atom (covalent N–Mg–N angles of 135.1 and 138.7°; dative N→Mg←N angles of 116.8 and 117.8°) also is encountered for the intramolecularly coordinated complex Mg[N(8-quinolyl)-(SiMe$_3$)]$_2$,[1d] which contains the rigid aromatic quinolyl ligand.

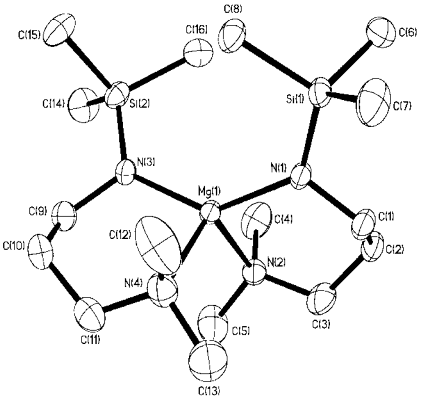

Fig. 2 ORTEP Representation of $Mg\{\overline{N[Si(CH_3)_3](CH_2)_3N}(CH_3)_2\}_2$ with 30% probability thermal ellipsoids, and all hydrogen atoms omitted for clarity in viewing. Selected interatomic distances (Å) and angles (°) for compound **1**: Mg1–N1 1.988(2), Mg1–N2 2.190(2), Mg1–N3 1.982(2), Mg1–N4 2.185(2); N1–Mg1–N2 97.20(8), N1–Mg1–N3 137.57(9), N2–Mg1–N4 109.71(10), N3–Mg1–N4 98.19(9), Mg1–N1–Cl 116.64(15), Mg1–N2–C3 114.31(17), Mg1–N3–C9 117.52(16), Mg1–N4–C11 113.23(18).

The interatomic angles present within the rings formed as a consequence of N:→Mg intramolecular coordination for **1** (114.3–115.4°), well within standard data,[9] are evidence of lack of significant molecular strain, imposed as a consequence of ring formation. The N3–Mg–N4 plane forms an angle of 80.08(8)° with the Ni–Mg–N2 plane (80.71° for N5–Mg2–N6 and N7–Mg2–N8), thereby lending **1** a pseudo spiro geometry.

The magnesium–nitrogen interatomic distances found for **1** can be placed into two categories. Dative bond distances, resulting from interactions between tertiary nitrogen atoms and Lewis-acid sites on Mg^{2+}, Mg1–N2 and Mg1–N4 (Mg2–N6 and

DOI: 10.1039/a909746e

Mg2–N8) 2.190(2) and 2.185(2) Å [2.188(2) and 2.198(2) Å] agree well with previously reported values ranging between 2.096 and 2.259 Å.[1,2] The metal–amide distances Mg1–N1 and Mg1–N3 (Mg2–N5 and Mg2–N7) of 1.988(2) and 1.982(2) Å [1.977(2) and 1.983(2) Å] represent relatively short interactions, compared with corresponding data for other magnesium–amide compositions, which fall into the range of 1.959–2.188 Å.[1,2] In the present structure, no significant perturbation is evidenced in either type of Mg–N interaction for **1**, as compared with earlier work involving non-intramolecularly coordinating ligands, be they anionic or neutral in character. It is suggested that, to a great degree, the observed combination of high vapor pressure and high vapor phase molecular integrity for **1** has its origin in these structural details. The design of an appropriate (*i.e.* flexible arm on a saturated alkyl tether) pendant amine to intramolecularly coordinate the metal center fulfills its requirements as manifested by the 'normalcy' of the metrical and geometrical data measured for **2**. As clearly demonstrated in the TGA (Fig. 1), **2** is quite volatile, even at 1 atm. Unlike simple organic compounds, where vapor pressure, to a first order, inversely follows molecular weight, organometallic compounds show not only simple van der Waals interactions in the condensed state. The dominant intermolecular forces for organometallic compounds in the condensed state are dipole–dipole interactions. Thus, the unusually high vapor pressure exhibited by **2** would seem to indicate that it might have a relatively small dipole moment. In related work, we have shown recently that such trends serve some predictive role for zinc bis(amide) compounds.

One interesting feature of **1** emerges upon examination of the ^{1}H and ^{13}C solution state NMR data. The methyl groups represented by C4, C5, C12 and C13 are magnetically inequivalent in this environment. This is understood best by examination of the plane represented by N3–Mg–N4 (or N1–Mg–N2), and noting that C12 resides on the side of the plane containing N2, while C13 resides on the N1-containing side. This is evidenced by a ^{1}H NMR chemical shift difference of 0.44 ppm for the methyl groups, and a 2.0 ppm ^{13}C NMR chemical shift difference. As expected, the ambient temperature solution dynamic structure portrays a single environment for the TMS methyl groups; however, ^{1}H inequivalence also is exhibited at C3 and C11 (difference of 0.38 ppm) and C1 and C9 (difference of 0.29 ppm), while C2 and C10 experience equivalence under these conditions. Apparently, ring flip motion equilibrates the later, while the methylene positions α to each nitrogen, both amide and amine, bear the influence of asymmetry. This may be compared with an extremely recent example of a Mg bis(1-azaalkyl) compound, which has a rigid chair skeletal conformation in the solid state, yet has solution NMR data reported which indicate dynamic behavior at ambient spectrometer conditions on the observational time scale.[10]

In summary, the first example of intramolecular coordination for a monomeric magnesium alkylamide has been designed, prepared and structurally characterized.[12] The two nearly perpendicular rings, exhibiting negligible strain, as evidenced by typical interatomic angles, are formed by the simultaneous occurrence of both tertiary amine donation at the end of a flexible alkyl tether and ionic amide attachment to the metal center. Compound **1**, highly stable in the vapor phase and portraying substantial vapor pressure, differs from earlier intermolecular adducts,[2d] which can irreversibly dissociate free Lewis base, penultimately producing lower coordinate transients that subsequently oligomerize into low vapor pressure species.[12]

We gratefully acknowledge the ONR for financial support. W. S. R. was awarded an Alexander von Humboldt Fellowship with Prof. H. Schumann at the TU Berlin in 1998–1999.

Notes and references

† *Selected data* for **1**: sublimation conditions: 80 °C/10^{-2} Torr, mp = 106 °C; ^{1}H NMR [400 MHz, $\mathrm{C_6D_6}$, 25 °C] δ 3.41 (m, 2 H, $\mathrm{C}H_{2(\mathrm{a})}\mathrm{N(CH_3)_2}$), 3.03 (m, 2 H, $\mathrm{C}H_{2(\mathrm{b})}\mathrm{N(CH_3)_2}$), 2.15 (s, 6 H, $\mathrm{N(C}H_{3(\mathrm{a})}\mathrm{)_2}$), 2.05 (m, 4 H, $\mathrm{NCH_2C}H_2\mathrm{CH_2}$), 1.71 (m, 6 H, $\mathrm{N(C}H_{3(\mathrm{b})}\mathrm{)_2}$), 1.57 (m, 2 H, $\mathrm{NC}H_{2(\mathrm{a})}$), 1.28 (m, 2 H, $\mathrm{NC}H_{2(\mathrm{b})}$), 0.49 (s, 9 H, $\mathrm{Si(C}H_3\mathrm{)_3}$); ^{13}C NMR [75.43 MHz, $\mathrm{C_6D_6}$, 25 °C] δ 62.91 (s, $C\mathrm{H_2NMe_2}$), 49.11 (s, $\mathrm{N}C\mathrm{H_2}$), 47.78 (s, $\mathrm{N(}C\mathrm{H_{3(a)})_2}$), 45.82 (s, $\mathrm{N(}C\mathrm{H_{3(b)})_2}$), 32.70 (s, $\mathrm{N}C\mathrm{H_2CH_2}$), 2.37 (s, $\mathrm{Si(C}H_3\mathrm{)}$; ^{29}Si NMR [59.59 MHz, $\mathrm{C_6D_6}$, 25 °C] δ −5.87 (s, $Si\mathrm{(CH_3)_3}$). Anal calc. for **1**: C, 51.79; H, 11.41; N, 15.10. Found: C, 51.74; H, 11.14; N, 15.89. MS [EI, 70 eV, 188 °C] 370 [$\mathrm{M^+}$], 355 [$\mathrm{M^+ - CH_3}$], 197 [$\mathrm{M^+ - Me_2N(CH_2)_3NSi(CH_3)_3}$].

‡ *Selected data* for **2**: bp = 177 °C (determined by DSC); ^{1}H NMR [400 MHz, $\mathrm{C_6D_6}$, 25 °C] δ 2.72 (d/tr, 2H, $\mathrm{HNC}H_2\mathrm{CH_2}$), 2.24 (tr, 2H, $\mathrm{CH_2C}H_2\mathrm{N(CH_3)_2}$), 2.20 (s, 6H, $\mathrm{N(C}H_3\mathrm{)_2}$), 1.54 (m, 4H, $\mathrm{HNCH_2C}H_2\mathrm{CH_2}$), 0.34 (br s, $H\mathrm{N}$), 0.02 (s, 9H, $\mathrm{Si(C}H_3\mathrm{)_3}$); ^{13}C NMR [75.43 MHz, $\mathrm{C_6D_6}$, 25 °C] δ 57.45 (s, $C\mathrm{H_2N(CH_3)_2}$), 45.40 (s, $\mathrm{N(}C\mathrm{H_3)_2}$), 40.00 (s, $\mathrm{N}C\mathrm{H_2}$), 32.66 (s, $\mathrm{N}C\mathrm{H_2CH_2}$), 0.20 (s, $\mathrm{Si(}C\mathrm{H_3)_3}$); ^{29}Si NMR [59.59 MHz, $\mathrm{C_6D_6}$, 25 °C] δ 2.10 (s, $Si\mathrm{(CH_3)_3}$); ^{14}N NMR [21.61 MHz, $\mathrm{C_6D_6}$, 25 °C] δ − 316 (s, $N\mathrm{(CH_3)_2}$), −353 (s, $N\mathrm{Si(CH_3)_3}$). Anal. calc. for **1**: C, 55.10; H, 12.72. Found: C, 55.16; H, 12.63. MS [EI, 70 eV] 174 [$\mathrm{M^+}$], 159 [$\mathrm{M^+ - CH_3}$], 85, 73, 58.

§ *Crystal data* for **1**: $\mathrm{Mg_1N_4C_{16}H_{42}}$, M_r = 371.03, crystal dimensions 0.850 × 0.238 × 0.102 mm, triclinic, space group $P\bar{1}$, a = 10.327(2), b = 15.066(3), c = 16.698(4) Å, α = 110.738(4), β = 92.948(4), γ = 92.182(4)°; V = 2422.1(9) Å^3, Z = 4, D_c = 1.017 g cm^{-3}, Siemens SMART CCD diffractometer, 1.31 < θ < 25.00°, MoKα radiation (λ = 0.71073 Å), ω scans, $F(000)$ = 824, μ = 0.177 mm^{-1}, T = 173(2) K; of 18267 measured reflections, 8489 were independent and 5688 observed with $I > 2\sigma(I)$, $-12 < h < 12$, $-17 < k < 17$, $-19 < l < 19$; R = 0.0443, wR = 0.1111, GOF = 1.021 for 467 parameters, $\Delta\rho_\mathrm{max}$ = 0.492 e Å^{-3}. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97). The hydrogen atoms coordinates were calculated in SHELXL using an appropriate riding model with varied thermal parameters. CCDC 182/1577. See http://www.rsc.org/suppdata/cc/a9/a909746e/ for crystallographic files in .cif format.

1 (*a*) D. C. Bradley, M. B. Hursthouse, A. A. Ibrahim, K. M. Abdul Malik, M. Motevalli, R. Möseler, H. Powell, J. D. Runnacles and A. C. Sullivan, *Polyhedron*, 1990, **9**, 2959; (*b*) W. S. Rees, Jr., J. S. Matthews and O. Just, unpublished results; (*c*) J. L. Sebestl, T. T. Nadasdi, M. J. Heeg and C. H. Winter, *Inorg. Chem.*, 1998, **37**, 1289; (*d*) L. M. Engelhardt, P. C. Junk, W. C. Patalinghug, R. E. Sue, C. L. Raston, B. W. Skelton and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1991, 930.

2 (*a*) B. Goldfuss, P. v. R. Schleyer, S. Handschuh, F. Hampel and W. Bauer, *Organometallics*, 1997, **16**, 5999; (*b*) V. R. Magnusson and G. D. Stucky, *Inorg. Chem.*, 1969, **8**, 1427; (*c*) M. Westerhausen and W. Schwarz, *Z. Anorg. Allg. Chem.*, 1992, **609**, 39; (*d*) D. Pfeiffer, M. J. Heeg and C. Winter, *Angew. Chem., Int. Ed.*, 1998, **37**, 2517; (*e*) A. W. Duff, P. B. Hitchock, M. F. Lappert, R. G. Taylor and J. A. Segal, *J. Organomet. Chem.*, 1985, **293**, 271; (*f*) M. Veith, W. Frank, F. Töllner and H. Lange, *J. Organomet. Chem.*, 1987, **326**, 315; (*g*) K. W. Henderson, R. E. Mulvey, W. Clegg and P. A. O'Neill, *J. Organomet. Chem.*, 1992, **439**, 237; (*h*) K. W. Henderson, R. E. Mulvey, W. Clegg and P. A. O'Neill, *Polyhedron*, 1993, **12**, 2535.

3 R. A. Bartlett, M. M. Olmstead and P. P. Power, *Inorg. Chem.*, 1994, **33**, 4800.

4 (*a*) T. E. Glassman, A. H. Liu and R. R. Schrock, *Inorg. Chem.*, 1991, **30**, 4723; (*b*) W. S. Rees, Jr., J. S. Matthews and O. Just, *Chem. Vap. Deposition*, in press.

5 (*a*) W. S. Rees, Jr. and A. Barron, *Adv. Mater. Opt. Electron.*, 1993, **2**, 271; (*b*) W. S. Rees, in *CVD of Nonmetals*, VCH New York, 1996.

6 The use of the nomenclature magnesium(alkylamide) is standard to differentiate the organic substituent present on the amide. For an example of a magnesium(arylamide) see ref. 1(*d*).

7 Compounds with intermolecular coordination have been reported recently; however, little data related to vapor phase stability was provided.

8 To our knowledge, the only other reported example of a structurally characterized intramolecular coordination in a magnesium amide involved the aromatic amine quinoline.

9 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, 5th edn., 1988, p. 144.

10 C. F. Caro, P. B. Hitchcock and M. F. Lappert, *Chem. Commun.*, 1999, 1433.

11 It is noted that an intramolecular agostic Si-H interaction recently has been observed for a dimeric species [see ref. 2(*a*)].

12 W. S. Rees, Jr., M. W. Carris and W. Hesse, *Inorg. Chem.*, 1991, **30**, 4479.