4800 *Inorg. Chem.* **1994,** *33,* 4800−4803

Structural Characterization of the "Magnesylamine" $[(Et_2O)Mg(Cl)\{N(SiMe_3)_2\}]_2$ and the Two-Coordinate Magnesium Amide $Mg\{N(SiMePh_2)_2\}_2$

Ruth A. Bartlett, Marilyn M. Olmstead, and Philip P. Power*

Department of Chemistry, University of California, Davis, California 95616

Received March 25, 1994⊗

The structural characterization of the "magnesylamine" compound $[(Et_2O)Mg(Cl)\{N(SiMe_3)_2\}]_2$, **1**, and the novel species $Mg\{N(SiMePh_2)_2\}_2$, **2**, by X-ray crystallography is described. The structure of **1** features dimeric molecules with two four-coordinate magnesium centers. Each magnesium is coordinated in a distorted tetrahedral fashion by terminally bound $-N(SiMe_3)_2$ and Et_2O ligands and by two symmetrically bridging chlorides. It represents the first such data for a magnesylamine species of the general formula $R_2NMgX{\cdot}n$ ether (R = alkyl, aryl, or related group; X = halide). The structure of **2** is composed of monomeric molecules with the magnesium bonded to two terminal amide groups with an average Mg−N bond length of 1.966(6) Å. The 2-fold coordination at the magnesium is distorted from linearity, and an N−Mg−N angle of 162.8(3)° is observed. This structure is the first for a magnesium bis(amide) of formula $Mg(NR_2)_2$ (R = alkyl, aryl, or related group) in the solid state. The deviation from linear geometry is attributed to weak Mg--aromatic ring interactions. Crystal data for **1** (Mo Kα, $\lambda = 0.710\,69$ Å) or **2** (Cu Kα, $\lambda = 1.541\,78$ Å) at 130 K: **1**, $a = 10.483(2)$ Å, $b = 13.558(3)$ Å, $c = 13.133(4)$ Å, $\beta = 104.04(2)°$, $V = 1810.8(8)$ Å^3, space group $P2_1/c$, $Z = 2$, 2753 ($I > 3\sigma(I)$) data, $R = 0.052$; **2**, $a = 10.951(2)$ Å, $b = 15.350(2)$ Å, $c = 26.890(5)$ Å, $\beta = 91.92(2)°$, $V = 4517.2(15)$ Å^3, space group $P2_1/c$, $Z = 4$, 3611 ($I > 2\sigma(I)$) data, $R = 0.069$.

Introduction

Structural reports for neutral magnesium amide compounds in the solid state were relatively few until recently.[1] At present, the range of structures is not excessive and is limited[2,3] to the following species: $[MeMgN(Me)CH_2CH_2NMe_2]_2$,[4] $[(THF)Mg\{N(t\text{-}Bu)\}_2SiMe_2]_2$,[3] $[(Et_2O)Mg\{N(SiMe_3)_2\}_2C_6H_4]_2$,[5] $[(THF)_2Mg\{N(t\text{-}Bu)\}_2(SiMe)_2\{N(t\text{-}Bu)\}_3]$,[6] $[NMg_6\{NH(t\text{-}Bu)\}_9]$,[7] $[(THF)Mg(NH)_2C_6H_4\text{-}o]_6$,[8] $\{(THF)Mg\{N(Ph)(2\text{-}py)\}_2$,[9] $[Mg(n\text{-}Bu)N(CH_2Ph)CH_2CH_2NMe_2)]_2$,[9a] $[Mg(NPh_2\{NPh(2\text{-}py)\}]_2$,[9b] bis{8-((trimethylsilyl)amino)quinolato-*N*,*N′*}magnesium,[10] $(THF)_2Mg\{N(SiMe_3)_2\}_2$,[11] $[s\text{-}BuMg\{N(SiMe_3)_2\}]_2$,[12] and $[Mg\{N(SiMe_3)_2\}_2]_2$.[13] With the exception of the latter two compounds, which have dimeric structures with three-coordinate magnesiums, the other structures involve four-coordinate magnesium centers. Moreover, chelating, rather than simple unidentate, amido ligands were used in almost all these complexes. It is also notable that no simple magnesium amide structures of the general formula $R_2NMgX{\cdot}n$ ether (R = alkyl, aryl, or related group; X = halide) have been reported. Such an amido/halide compound (also called (halomagnesyl)amine or magnesylamine)[14] is derived from the reaction of a secondary amine with a Grignard reagent. The formula corresponds closely to those of ether-solvated Grignard reagents themselves, in which the organic ligand is replaced by an amide. In addition, bis(amido)magnesium species may be derived from the reaction of 2 equiv of a secondary amine with a magnesium dialkyl. Except for the determination of the structure of the monomer $Mg\{N(SiMe_3)_2\}_2$, in the gas phase,[15] there are no structures of unassociated, base-free, magnesium amides. In this paper, the characterization of a simple halomagnesium amide (a magnesylamine), $[(Et_2O)Mg(Cl)\{N(SiMe_3)_2\}]_2$,[16] **1**, and a monomeric magnesium amide, $Mg\{N(SiMePh_2)_2\}_2$, **2**, are now described.

Experimental Section

General Procedures. All work was performed under anaerobic and anhydrous conditions by using Schlenk techniques on a Vacuum Atmospheres HE-43-2 drybox. Solvents were distilled from sodium/potassium alloy and degassed twice prior to use.

Physical Measurements. ^1H and ^{13}C spectra were obtained on a General Electric QE-300 spectrometer using C_6D_6 as a solvent.

Starting Materials. $MgBu_2$ (1 M in heptane, Aldrich) was used as recieved; **1**[16] and $HN(SiMePh_2)_2$[17] and were synthesized by literature procedures. Characterization of **2** was made by ^1H and ^{13}C NMR and C, H, and N elemental analyses.

⊗ Abstract published in *Advance ACS Abstracts,* September 1, 1994.

(1) (a) Holloway, C. E.; Melnik, M. *J. Organomet. Chem.* **1994**, *465*, 1. (b) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood: Chichester, U.K., 1979.

(2) Mixed-metal magnesium amides are also known but are not included in this list, *e.g.*: Her, T.-Y.; Chang, C.-C.; Liu, L. K. *Inorg. Chem.* **1992**, *31*, 2291.

(3) Veith, M.; Frank, W.; Tollner, F.; Lange, H. *J. Organomet. Chem.* **1987**, *326*, 315.

(4) Magnuson, V. R.; Stucky, G. D. *Inorg. Chem.* **1969**, *8*, 1427.

(5) Duff, A. W.; Hitchcock, P. B.; Lappert, M. F.; Taylor, R. G.; Segal, J. A. *J. Organomet. Chem.* **1985**, *293*, 271.

(6) Veith, M.; Goffing, F.; Huch, V. *Z. Naturforsch.* **1988**, *43B*, 846.

(7) Dozzi, G.; Del Piero, G.; Cesari, M.; Cucinella, S. *J. Organomet. Chem.* **1980**, *190*, 229.

(8) Clegg, W.; Frank, M.; Mulvey, R. E.; O'Neil, P. A. *J. Chem. Soc., Chem. Commun.* **1994**, 97.

(9) (a) Henderson, K. W.; Mulvey, R. E.; Clegg, W.; O'Neil, P. A. *J. Organomet. Chem.* **1992**, *439*, 237. (b) Henderson, K. W.; Mulvey, R. W.; Clegg, W.; O'Neil, P. A. *Polyhedron* **1993**, *12*, 2535.

(10) Engelhardt, L. M.; Lunk, P. C.; Patalinghug, W. C.; Sue, R. E.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1991**, 930.

(11) Bradley, D. C.; Hursthouse, M. B.; Ibrahim, A. A.; Abdul, A. M.; Motevalli, R.; Moseler, R.; Powell, H.; Runnacles, J. D.; Sullivan, A. C. *Polyhedron*, **1990**, *9*, 2459.

(12) Engelhardt, L. M.; Jolly, B. S.; Junk, P. C.; Raston, C. L.; Skelton, B. L.; White, A. L. *Aust. J. Chem.* **1988**, *39*, 1337.

(13) Westerhausen, M.; Schwartz, W. *Z. Anorg. Allg. Chem.* **1992**, *609*, 39.

(14) Meunier, L. *Comp. Rend.* **1903**, *136*, 758. Petyunin, P. A. *Russ. Chem. Rev.* **1962**, *31*, 100.

(15) Fjelberg, T.; Andersen, R. A. *J. Mol. Struct.* **1984**, *125*, 287.

(16) Wannagat, U.; Autzen, H.; Kuckertz, H.; Wismar, H.-J. *Z. Anorg. Allg. Chem.* **1972**, *394*, 254.

(17) Shostakovskii, M. F.; Kontrdrat'ev, K. I. *Izvest. Akad. Nauk. SSSR, Otdel. Khim. Nauk.* **1956**, 811; *Chem. Abstr.* **1957**, *31*, 3486.

0020-1669/94/1333-4800$04.50/0

Table 1. Summary of Data Collection and Structure Solution and Refinement Parameters for Compounds **1** and **2**

	1	**2**
formula	$C_{20}H_{56}Cl_2Mg_2N_2O_2Si_4$	$C_{52}H_{52}MgN_2Si_4$
fw	588.5	841.6
cryst description	colorless parallelepipeds	colorless needles
cryst size, mm	0.45 × 0.47 × 0.80	0.10 × 0.10 × 0.40
a, Å	10.483(2)	10.951(2)
b, Å	13.558(3)	15.350(2)
c, Å	13.133(4)	26.890(5)
β, deg	104.04(2)	91.92(2)
V, Å^3	1810.8(8)	4517.2(15)
Z	2	4
space group	$P2_1/c$	$P2_1/c$
d(calc), g cm^3	1.079	1.238
lin abs coeff, mm^{-1}	0.360	1.642
2θ range, deg	0−55	0−115
no. of rflns	2753 ($I > 3\sigma(I)$)	3611 ($I > 2\sigma(I)$)
no. of variables	145	544
R, R_w	0.052, 0.059	0.069, 0.064

$Mg\{N(SiMePh_2)_2\}_2$ (2). $HN(SiMePh_2)_2$ (1.64 g, 4 mmol) in PhMe (5 mL) and hexane (10 mL) was treated dropwise with 2 mL of a 1 M heptane solution of dibutylmagnesium and stirred for 48 h. The solution was refluxed for 2 h and filtered through a Celite-padded frit. The solvents were then removed under reduced pressure, and the residue was heated to 90 °C for 1 h. The remaining colorless oil was then treated with (warm 40−50 °C) hexane (30 mL). This dissolved the oily residue which quickly precipitated as colorless crystals (suitable for X-ray crystallography) upon standing at room temperature for 1 h. Yield: 1.45 g (86%). Mp: 154−156 °C. ^1H NMR (C_6D_6): δ 0.48 (s, 12H, Me), 7.18 (m, 12H, *o*- and *p*-H), 7.33 (m, 8H, *m*-H). ^{13}C NMR (C_6D_6): δ 1.806 (s, CH_3), 128.86 (s, *m*-C), 129.54 (s, *p*-C), 134.56 (s, *o*-C), 142.42 (s, *i*-C).

X-ray Crystallographic Studies. The crystals were removed from the Schlenk tube under a stream of N_2 and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream as described in ref 18.

Data for compound **1** were collected at 130 K with use of a Syntex P2$_1$ diffractometer equipped with a locally modified LT-1 device and using graphite-monochromated Mo Kα radiation. Crystallographic programs used for the structure solutions and refinements were those of SHELXTL-Plus (1989)[19] installed on a MicroVax work station 3200. Scattering factors were from ref 20. An absorption correction was applied using the method described in ref 21. Data for **2** were also collected at 130 K but with use of Cu Kα radiation. Crystallographic programs used were those of SHELXTL-Plus (version 4.2, 1990).[22] Scattering factors were from ref 23, and an absorption correction was applied.[21] Some details of data collection and refinement are given in Table 1; coordinates for selected atoms are given in Table 2. Important bond distances and angles are provided in Table 3. Further details are provided in the supplementary material.

Table 2. Selected Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for Compounds **1** and **2**

atom	x	y	z	U_{eq}[a]
		$[(Et_2O)Mg(Cl)\{N(SiMe_3)_2\}]_2$ (**1**)		
Mg	461(1)	4226(1)	6056(1)	27(1)
Cl	124(1)	5971(1)	5819(1)	34(1)
Si(1)	2494(1)	2542(1)	6776(1)	51(1)
Si(2)	3099(3)	4532(1)	7800(1)	56(1)
N	2101(3)	3729(2)	6986(2)	37(1)
O	1115(2)	3790(2)	6544(2)	35(1)
		$Mg\{N(SiMePh_2)_2\}_2$ (**2**)		
Mg	2409(3)	6891(2)	1422(1)	29(1)
N(1)	3001(5)	7239(4)	770(2)	18(2)
N(2)	1740(5)	6921(3)	2093(2)	17(2)
Si(1)	2368(2)	6654(1)	292(1)	19(1)
Si(2)	4008(2)	8088(1)	722(1)	19(1)
Si(3)	754(2)	7697(1)	2290(1)	18(1)
Si(4)	2411(2)	6067(1)	2405(1)	18(1)
C(7)	1156(7)	5968(5)	585(2)	20(2)
C(12)	286(7)	6358(5)	886(3)	23(3)
C(20)	4552(7)	8396(5)	1370(2)	19(2)
C(46)	3515(7)	5631(5)	1939(2)	18(2)
C(47)	3120(7)	5066(5)	1547(3)	28(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **1** and **2**

1		**2**	
Mg−N	1.970(3)	Mg−N(1)	1.963(6)
Mg−Cl	2.401(1)	Mg−N(2)	1.969(6)
Mg−Cl′	2.405(1)		
Mg−O	2.000(3)		
N−Si(1)	1.701(3)	N(1)−Si(1)	1.699(6)
N−Si(2)	1.697(3)	N(1)−Si(2)	1.716(6)
Si−C(av)	1.860(8)	N(2)−Si(3)	1.706(6)
Mg- -Mg′	3.425(3)	N(2)−Si(4)	1.708(6)
Cl−Mg−Cl′	89.1(1)	N(1)−Mg−N(2)	162.8(3)
Mg−Cl−Mg′	90.9(1)	Si(1)−N(1)−Si(2)	126.3(3)
Cl−Mg−N	119.8(1)	Si(2)−N(2)−Si(4)	130.5(3)
Cl−Mg−O	103.1(1)	Si(1)−N(1)−Mg	113.3(3)
N−Mg−O	111.4(1)	Si(2)−N(1)−Mg	120.4(3)
N−Mg−Cl′	124.3(1)	Si(3)−N(2)−Mg	124.1(3)
Mg−N−Si(1)	115.7(1)	Si(4)−N(2)−Mg	105.4(3)
Mg−N−Si(2)	118.9(2)		
Si(1)−N−Si(2)	124.9(2)		

The crystal structures of **1** and **2** were solved by direct methods and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement at calculated positions using a riding model with C−H = 0.96 Å and fixed U_H.

Structural Descriptions

$[(Et_2O)Mg(Cl)\{N(SiMe_3)_2\}]_2$, 1, crystallizes in the space group $P2_1/c$ as well-separated noninteracting dimers which have a crystallographically imposed center of symmetry (Figure 1). The magnesium centers are bridged by halide ions, and the Mg_2Cl_2 core forms an almost perfect square with Mg−Cl distances of 2.401(1) and 2.405(1) Å and internal angles of 90.9(1)° at Mg and 89.1(1)° at Cl. Each magnesium is further coordinated by an ether (Mg−O = 2.000(3) Å) and an $-N(SiMe_3)_2$ group (Mg−N = 1.970(3) Å) with an N−Mg−O angle of 111.4(1)°. Within the $-N(SiMe_3)_2$ group the N−Si distances are 1.701(3) and 1.697(3) Å and the Si−N−Si angle is 124.9(2)°. The planes formed at NMgO and Mg_2Cl_2 are perpendicular, and there is a 44.3° torsion angle between the perpendicular to the coordination plane at nitrogen and the Mg−O vector. The Mg- -Mg separation is 3.425(3) Å.

$Mg\{N(SiMePh_2)_2\}_2$, 2. The structure of **2** consists of well-separated noninteracting monomers. The magnesium is bound to two nitrogens, each from an $-N(SiMePh_2)_2$ group. The

---

(18) Hope, H. *In Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; Chapter 10.

(19) Sheldrick, G. M. SHELXTL Plus. *A Program for Crystal Structure Determination*, Version 4.0; Siemens Analytical X-ray Instruments: Madison, WI, 1989.

(20) International Tables for X-ray Crystallography; Kynoch Press: Birmingham, England, 1974.

(21) The absorption correction was made using the program XABS by H. Hope and B. Moezzi. The program obtains an absorption tensor from F_o-F_c differences (Moezzi, B. Ph.D. Dissertation, University of California, Davis, 1987).

(22) Sheldrick, G. M. SHELXTL-Plus *A Program for Crystal Structure Determination*, Version 4.2; Siemens Analytical X-ray Instruments: Madison, WI.

(23) *International Tables for Crystallography*; Reidel Publishing Co.: Boston, MA, 1992; Vol. C.

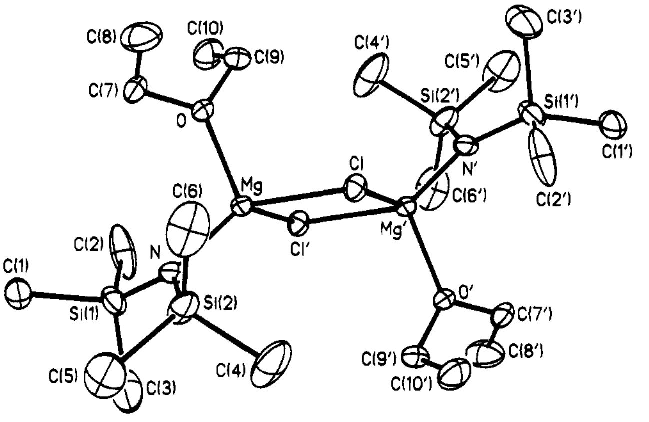

Figure 1. Computer-generated thermal ellipsoid plot of **1**. Selected bond distances (Å) and angles (deg) are given in Table 3.

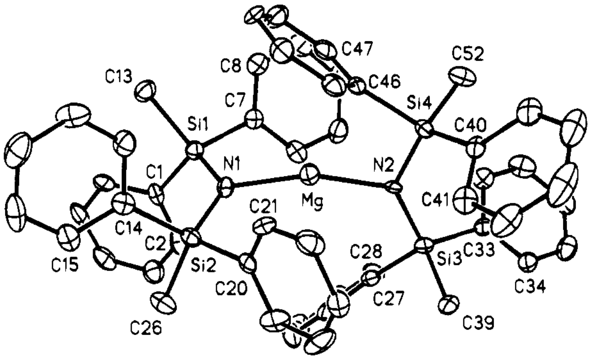

Figure 2. Computer-generated thermal ellipsoid plot of **2**. Selected bond distances (Å) and angles (deg) are given in Table 3.

average Mg—N distance is 1.966(6) Å, and the N—Mg—N angle is 162.8(3)°. Four phenyl groups surround the metal center as illustrated in Figure 2. The Mg–centroid distances for the two phenyl groups on the more exposed side of the metal are 3.29 Å (C(46) ring) and 3.55 Å (C(7) ring), whereas the corresponding distances for the C(20) and C(27) rings are 4.03 and 4.23 Å. The Mg—N(1)—Si(1) and Mg—N(2)—Si(4) angles, 113.3(3) and 105.4(3)°, respectively, are considerably narrower than those on the more crowded side (Mg—N(1)—Si(2) = 120.4(3)°, Mg—N(2)—Si(3) = 124.1(3)°). The closest Mg- -C interactions involve carbon atoms C(46), 2.65 Å, C(47), 2.92 Å, C(12), 2.82 Å, and C(7), 2.96 Å. The Si—N bond lengths are in the range 1.699(6)–1.716(6) Å, and the Si—N—Si angles at N(1) and N(2) are 126.3(3) and 130.5(3)°.

Discussion

The compounds **1** and **2** were synthesized by straightforward synthetic methods. The synthesis of **1**, involving the reaction between the Grignard reagent propylmagnesium chloride and hexamethyldisilazane in ether solution, has been described in the literature.[16] Reactions between primary and secondary amines and Grignard reagents have been known since the early 1900's,[14] and either one or two amine hydrogens may be replaced by a magnesium halide group with concomitant elimination of alkane to give the so-called magnesylamines as shown in eqs 1 and 2.

$$\mathrm{RNH_2 + R'MgX \rightarrow \text{“RN(H)MgX” (a monomagnesylamine)} + R'H} \quad (1)$$

$$\mathrm{RNH_2 + 2R'MgX \rightarrow \text{“RN(MgX)}'_2\text{” (a dimagnesylamine)} + 2R'H} \quad (2)$$

In comparison to the extensive interest in the structures and the degree of association of Grignards in the solid state and solution, relatively little is known about the corresponding amido derivatives of formula R_2NMgX (X = halide). A recent report from this group disclosed the first structure of a species crystallized from a dimagnesylamine ("$RN(MgX)_2$") ether solution.[24] It was shown that the phenyl derivative disproportionates to eliminate MgX_2 and forms the cage species $\{(EtO)Mg\}_6(NPh)_4X_4$, which has an adamantanyl Mg_6N_4 core with the nitrogens in the bridgehead positions.

Compound **1** (i.e. a monomagnesylamine) has a dimeric structure with bridging chloride and terminal amides, each magnesium also being solvated by an ether molecule. It thus has similarities to the proposed structures of some Grignard reagents which are thought to possess a halide-bridged dimeric structure in solution. Oddly, this structural type has not been structurally characterized in the solid state for ether-solvated Grignards.[1a,25] Dimeric structures such as $\{Mg(Br)(Et)NEt_3\}_2$[26a] or $\{Mg(Cl)(CH_2CHCH_2(TMEDA))\}_2$[26b] with halide-bridged magnesium are known, however. The metric features of **1** may be compared to the structures of $(THF)_2Mg\{N(SiMe_3)_2\}_2$,[11] [*s*-BuMgN(SiMe$_3$)$_2$]$_2$,[12] and $[Mg\{N(SiMe_3)_2\}]_2$.[13] The latter species has a symmetrically bridged dimeric structure with terminal Mg—N bond lengths of 1.970(7) Å. This distance is approximately the same as the Mg—N bond length observed in **1** in spite of the fact that the magnesium is three-coordinate in $[Mg\{N(SiMe_3)_2\}]_2$. It may be that the presence of more electronegative chloride and oxygen substituents in **1** may contract the effective radius of the magnesium ion so that similar Mg—N bond distances are observed. Support for this view comes from the longer Mg—N bond length (2.021(5) Å) observed in $(THF)_2Mg\{N(SiMe_3)_2\}_2$.[11] The structure of [*s*-BuMg{N(SiMe$_3$)$_2$}]$_2$[12] is significantly different from the structure of **1**. In this compound the amide ligands are in the bridging rather than in the terminal sites owing to the lower bridging tendency of the alkyl groups in comparison to amide ligands. The structure of **1** also demonstrates that the chloride ion has superior bridging ability over $-N(SiMe_3)_2$ at least toward the Mg^{2+} ion. The bridging Mg—N distances (2.118(4) Å) in [*s*-BuMg{N(SiMe$_3$)$_2$}]$_2$ are, however, shorter than those observed in $[Mg\{N(SiMe_3)_2\}_2]_2$ (*ca.* 2.15 Å), and this may be a consequence of the more crowded nature of the latter molecule.

The structure of **2** reveals a very rare example of two-coordination for magnesium. Prior reports for this geometry have concerned the species Mg{CH$_2$(*t*-Bu)}$_2$[27] and $Mg\{N(SiMe_3)_2\}_2$[15] (both structures determined by vapor phase electron diffraction) and the X-ray crystal structure of the compound $Mg\{C(SiMe_3)_3\}_2$.[28] In the alkyl compounds the interligand angle at magnesium is 180° and the Mg—C bond lengths are very similar (2.126(6) and 2.116(2) Å). An interligand angle of 180° was also observed for the gas phase structure of $Mg\{N(SiMe_3)_2\}_2$, and the Mg—N bond length was reported to be 1.91(3) Å.[13] The structure of **2** is thus notable in that it is only the second example of two-coordination for magnesium in the solid state.[29] In addition, significant deviation from the 180° interligand angle was observed. Such deviation is a common feature of the structure of the divalent metal amide

---

(24) Hascall, T.; Olmstead, M. M.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 356.

(25) Markie, P. R.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Adv. Organomet. Chem.* **1991**, *37*, 47.

(26) (a) Toney, J.; Stucky, G. O. *J. Chem. Soc., Chem. Commun.* **1967**, 1168. (b) Marsch, M.; Harms, K.; Massa, W.; Boche, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 696.

(27) Ashby, E. C.; Fernholt, L.; Haaland, A.; Seip, R.; Smith, R. S. *Acta Chem. Scand., Ser. A* **1980**, *34*, 213.

(28) Al-Juaid, S. S.; Eaborn, C.; Hitchcock, P. B.; McGeary, C. A.; Smith, J. D. *J. Chem. Soc., Chem. Commun.* **1989**, 273.

derivatives $M\{N(SiMePh_2)_2\}_2$ (M = Mn,[30] Co,[30] Fe,[30] Cu(I)[31] (anion), and Zn[31]). The deviation from linearity is least for the copper and zinc derivatives (N—M—N = 179.2(2) and 177.5(2)°) and greatest for the cobalt species (N—Co—N = 147.0(1)°). The structure of **2** resembles that of $Mn\{N(SiMePh_2)_2\}_2$ (Mn—N = 1.989(3) Å, N—Mn—N = 170.7(1))° quite closely, and the crystals are isomorphous. The bending observed in the above compounds and in **2** probably has its origins in dipolar interaction between the relatively positive metal center and the electron density in the aromatic rings. It is also notable that the open shell transition metals and magnesium possess empty low-lying orbitals that may be capable of enhancing such interactions. Nonetheless, the shortest Mg- -C contacts in **2** are all greater than or equal to 2.65 Å in length and thus quite weak.

The average Mg—N bond length in **2**, 1.966(6) Å, is rather longer than the corresponding distance, 1.91(3) Å, reported for $Mg\{N(SiMe_3)_2\}_2$ in the gas phase. Although the difference is not significant in view of the high uncertainty of the gas phase value, it is notable that discrepancies between crystallographic and gas phase data in other M—N species such as $Fe\{N(SiMe_3)_2\}_2$[32] have been observed previously. Some of the difference between the gas phase and solid state structures may be due to the greater size of the $-N(SiMePh_2)_2$ group in comparison to $-N(SiMe_3)_2$.[30] This may cause the M—N distances to increase for steric reasons. A possible alternative explanation arises from the fact that the Si—C distances, *ca.* 1.89 Å, are only marginally shorter than the distances estimated for M—N (*e.g.* 1.91 Å for Mg—N). Thus, the experimental radial distribution curves for the electron diffraction study of $Mg\{N(SiMe_3)_2\}_2$ show a composite peak for the Mg—N, Si—C, and Si—N vectors. It is, therefore, possible that there is some correlation betweeen the Mg—N bonds and similar Si—C distances which would give rise to the observed variance and increased uncertainty in the Mg—N distance in the vapor phase.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for financial support.

Supplementary Material Available: Full tables of data collection parameters, atom coordinates, bond distances, bond angles, hydrogen coordinates, and thermal parameters (16 pages). Ordering information is given on any current masthead page. Listings of structure factors (37 pages) are available from the author.

---

(29) It could be argued that the species $[Mg\{CH(SiMe_3)_2\}\{CH(SiMe_3)SiMe_2\text{-}\mu\text{-}Me\}]_\infty$ is two-coordinate. It is, however, associated with fairly strong intermolecular agostic interactions (*e.g.* Mg- -H = 2.333(4) Å and Mg—C = 2.535(4) Å). Moreover, the C—Mg—C angle is 140.0(2)°. Hitchcock, P. B.; Howard, J. A. K.; Lappert, M. F.; Leung, W.-P.; Mason, S. A. *J. Chem. Soc., Chem. Commun.* **1990**, 847.

(30) Chen, H.; Bartlett, R. A.; Dias, H. V. R.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 4338.

(31) Power, P. P.; Ruhlandt-Senge, K.; Shoner, S. C. *Inorg. Chem.* **1991**, *30*, 5013.

(32) (a) Andersen, R. A.; Faegri, K.; Green, J. C.; Haaland, A.; Lappert, M. F.; Leung, W.-P. *Inorg. Chem.* **1988**, *27*, 1782. (b) Olmstead, M. M.; Power, P. P.; Shoner, S. C. *Inorg. Chem.* **1991**, *30*, 2547.