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Ligand and Coligand Effects on Ion Association in Magnesium Amides

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We report here the examination of the effect of ligand bulk and coligand influence on ion association in a family of magnesium amides. Use of the sparsely employed, sterically demanding coligand HMPA (hexamethylphosphoramide, $O{=}P(N(Me)_2)_3$, in conjunction with four different silylamides $[N(SiMe_3)(R)]^-$ (R = $SiMe_3$, C_6H_5 (Ph), 2,4,6-MesC_6H_2 (Mes), 2,6-*i*-$Pr_2C_6H_3$ (Dipp)) provides unique insight into factors governing ion association. To this effect, we report three contact molecules, along with one example of a rare ion-association state with one amido group metal-bound, whereas the other is unassociated.

Introduction

Since the discovery of Grignard reagents in 1900,[1,2] the organometallic chemistry of magnesium has progressed in leaps and bounds.[3] Impressively, new applications for these reagents are being discovered continuously, making this family of compounds one of the most versatile in the Periodic Table. Organomagnesium species have been the most intensively studied;[3] less work has been devoted to the amido derivatives,[4] although the compounds have been established as important, versatile reagents. As an example, recent, remarkable reports on heterobimetallic alkali-metal/magnesium amido species illustrate their unique reactivity, which is markedly different from that of the homometallic counterparts.[5−8]

As new applications for organomagnesium reagents continue to be discovered, the need to tailor ligand systems to specific applications and to understand structure and function relationships remain a crucial part of the further development of magnesium chemistry. Several factors influence the properties of the reagents, including the type and size of the ligand, the size, hapticity, and donor strength of the coligands, and second-order bonding (including Mg−π and agostics), as well as ion association. Among those factors, ligand characteristics have been the most extensively examined, but significantly less is known about the other variables.

Structural elucidations of magnesium $[N(SiMe_3)_2]^-$ based amido compounds date back to the early 1990s, with reports on the synthesis and characterization of monomeric $Mg(N(SiMe_3)_2)(donor)_x$ and coligand-free dimeric $[Mg(N(SiMe_3)_2)_2]_2$ species. These compounds have developed into versatile starting materials and continue to serve as a springboard for more complex systems. The steric demand of the $[N(SiMe_3)_2]^-$ ligand effectively suppresses aggregation, while the presence of $-SiMe_3$ substituents ensures favorable solubility in a range of solvents. Extensive studies of these compounds have examined their utility as reagents, polymerization initiators, MOCVD precursors, and more.[4,9−13] Limited studies have examined the role of ligand size and electronics by replacing $-SiMe_3$ substituents by variously sized aryl groups; a selection of these ligands is shown in Figure 1.

Analogous to the $[N(SiMe_3)_2]^-$ ligand, $[N(SiMe_3)(Mes)]^-$, ligand **c**, led to a four-coordinate monomeric compound, $Mg[N(SiMe_3)(Mes)]_2(thf)_2$, with features very similar to those of $Mg[N(SiMe_3)]_2(thf)_2$.[14,15] However, use of the slightly bulkier ligand **d**, $[N(SiMe_3)(Dipp)]^-$, resulted in formation of a rare two-coordinate species, $Mg[N(SiMe_3)(Dipp)]_2$, available by crystallization from a nonpolar solvent.[16] In the case of ligand **d**, we see that steric bulk has a significant impact on kinetic metal stabilization, effectively suppressing aggregation.

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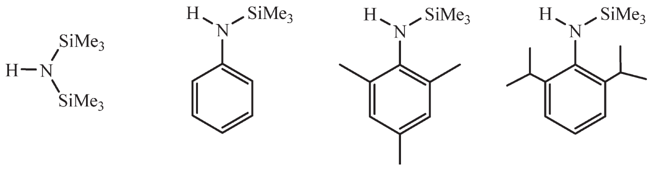
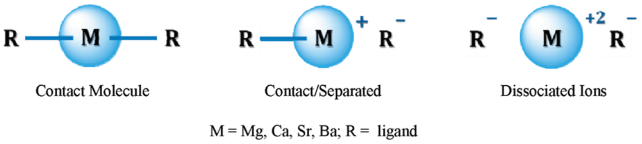


$HN(SiMe_3)_2$ (a) $HN(SiMe_3)(Ph)$ (b) $HN(SiMe_3)(Mes)$ (c) $HN(SiMe_3)(Dipp)$ (d)

Figure 1. Illustration of various silyl and aryl silylamine ligands.

Scheme 1. Ion-Association Modes for Alkaline-Earth Metals



A critical but not well-understood factor governing the reactivity of organomagnesium species is ion association. For alkaline-earth-metal species, three ion-association modes may be observed (Scheme 1), contact molecules, separated ions, and an intermediate state, with one ligand unassociated and the other bound to a metal.

An important factor in determining ion association is the metal−ligand bond character, with more covalently bound ligands less likely to dissociate. As a result, the formation of separated ions is more pronounced for the heavier s-block metals. Furthermore, the capacity of ligand charge delocalization plays a major role, as does the ability for the metal's steric saturation as achieved through a combination of factors. With a relatively high charge density for magnesium, only a few examples for separated magnesium ions have been reported, including $[Mg(15\text{-crown-}5)(pyr)_2][C_5H_5]_2$, $[Mg(15\text{-crown-}5)(thf)_2][C_5H_5]_2$, $[Mg(C_5H_5)(pmdta)][C_5H_5]$, and $[Mg(15\text{-crown-}5)(thf)_2][SMes^*]_2$ (Mes* = 2,4,6-tri-*tert*-butylphenyl).[17,18] Markedly absent from this list, however, are separated amido species.

We report here on studies utilizing HMPA, a strong Lewis donor with significant steric bulk. Notably, amido compounds containing HMPA are much less common, limited to a handful of magnesium compounds and one heavier calcium silylamido compound.[19−23] The lack of known HMPA early-s-block derivatives is attributed to the donor's capacity for inducing ion dissociation in solution and its dependency on donor concentration.[24−26] For example, addition of HMPA to organolithium reagents has been shown to typically increase their reactivity when used in organic reactions.[27,28] This dynamic behavior in solution allows for difficulty in isolating stable species in the solid state.

We report here on a family of magnesium amides based on the $[N(SiMe_3)(R)]^-$ ligand system (R = $SiMe_3$, C_6H_5 (Ph), 2,4,6-$MesC_6H_2$ (Mes), 2,6-i-$Pr_2C_6H_3$ (Dipp)) in conjunction with HMPA, allowing the investigation of ion association in the context of steric saturation. Contact molecules are observed for $Mg[N(SiMe_3)_2]_2(hmpa)_2$ (**1**), $Mg[N(SiMe_3)(Ph)]_2(hmpa)_2$ (**2**), and $Mg[N(SiMe_3)(Mes)]_2(hmpa)_2$ (**3**), in addition to the unique, partially separated $[Mg\{N(SiMe_3)(Dipp)\}(hmpa)_3][N(SiMe_3)(Dipp)]$ (**4**).

Experimental Details

General Procedures. All reactions were carried out under strict inert gas conditions using a Braun Labmaster 100 drybox and/or modified Schlenk techniques. The solvents, including hexanes, toluene, benzene, and tetrahydrofuran (THF), were dried on a Vacuum Atmospheres Co. Dri-Solv solvent purifier system and degassed just prior to use. Dibutylmagnesium (statistical mix of *n*- and *sec*-butyl, 1 M solution in heptanes) was obtained from a commercial source and used as received. $HN(SiMe_3)_2$, $HN(SiMe_3)(Ph)$, and HMPA (hexamethylphosphoramide) were purchased from Aldrich, while $HN(SiMe_3)(Mes)$, $HN(SiMe_3)(Dipp)$ were synthesized according to literature procedures.[29] All ligands and donors were dried and distilled over CaH_2 prior to use. IR spectra were obtained as Nujol mulls on a Nicolet IR200 spectrometer. ^1H NMR and ^{13}C NMR were recorded on a Bruker DPX-300 spectrometer at 25 °C in C_6D_6 and referenced to residual solvent peaks. Melting points were collected in sealed capillary tubes and are uncorrected. Due to the pyrophoric nature of these compounds, satisfactory elemental analysis could not be obtained. This is a well-established problem with alkali-metal and alkaline-earth-metal organometallics.[30,31]

Single-Crystal X-ray Diffraction Studies. X-ray-quality crystals for compounds **1**−**4** were grown as described below. The crystals were removed from the Schlenk tube under a stream of N_2 and immediately covered with a layer of viscous hydrocarbon oil (Infineum). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer.[32] The intensity data sets for all compounds were collected using a Bruker SMART system, complete with a three-circle goniometer and an APEX-CCD detector. Data for compounds **1**−**4** were collected at 97, 99, 97, and 96 K, respectively, using a custom-built low-temperature device from Professor H. Hope (UC Davis). Further data collection, structure solution, and refinement details have been reported previously.[33,34] Crystallographic data (excluding structure factors) for the structures reported herein (Table 1) have been deposited in the Cambridge Crystallographic Data Center (CCDC deposition numbers 794115−794117 for compounds **2**−**4**). CIF files can be obtained from the CCDC free of charge via http://www.ccdc.cam.ac.uk/data_request/cif. Disorder was typically handled by including split positions for the

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Table 1. Crystallographic Data[a] for Compounds 2−4

	2	**3**	**4**
formula	$MgN_8Si_2O_2P_2C_{30}H_{64}$	$MgN_8Si_2O_2P_2C_{36}H_{76}$	$MgN_{11}Si_2O_3P_3C_{48}H_{106}$
fw	711.32	795.48	1058.84
a (Å)	13.85(8)	11.69(8)	11.41(2)
b (Å)	16.67(9)	11.69(8)	21.72(4)
c (Å)	18.84(9)	34.79(3)	12.80(3)
α (deg)	90	90	90
β (deg)	109.20(10)	90	100.03(3)
γ (deg)	90	90	90
V (deg)	4111.1(4)	4748(6)	3127.3(6)
Z	4	4	2
space group	$P2_1/n$	$P4_122$	$P2_1$
d_{calcd} (Mg/m^3)	1.149	1.113	1.124
μ (mm^{-1})	0.215	0.193	0.188
T (K)	99(2)	97(2)	96(2)
2*θ* range (deg)	1.67−25.00	1.74−25.00	2.61−28.07
no. of indep rflns	7242	4152	10 956
no. of params	412	240	631
R1, wR2 (all data)[b]	0.0516, 0.1375	0.0893, 0.1303	0.0653, 0.1354
R1, wR2 (> 2σ)[b]	0.0434, 0.1308	0.0577, 0.1159	0.0570, 0.1311

[a] Mo Kα radiation (λ = 0.710 73 Å). [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

affected groups and included the refinement of the respective occupancies. Compound **1** was found to contain a high degree of positional disorder and refined using split positions for both ligands (60/40) and HMPA molecules (70/30); however, important structural features were able to be elucidated.

Typical Experiment. nBu$_2$Mg (1 mL, 1 mmol) was added slowly via syringe to a solution of the secondary amine (2 mmol) in 40 mL hexanes. This was refluxed overnight to afford a clear solution. The solution was then reduced in volume. A slight excess of HMPA (2.5 mmol, 0.44 mL) was added via syringe to create a cloudy suspension. Suitable crystals (colorless blocks) deposited at room temperature.

Mg[N(SiMe$_3$)$_2$]$_2$(hmpa)$_2$ (1). (2 mmol, 0.32 g, 0.42 mL) Yield: 0.99 g, 73%. Mp: 131−135 °C. ^{1}H NMR (300 MHz, 25 °C, C$_6$D$_6$): δ_H 0.549 (s, 36H, −SiC*H*$_3$), 2.32 (d, 36H, HMPA). ^{13}C NMR (300 MHz, 25 °C, C$_6$D$_6$): δ_C 7.743 (−Si*C*H$_3$), 37.21 (*C*H$_3$ HMPA). IR (cm^{-1}): ν 2916 s, 2882 m, 2723 m, 1450 s, 1377 s, 1298 m, 1210 w, 1182 w, 988 w, 902 s, 823 w, 360 w.

Mg[N(SiMe$_3$)(Ph)]$_2$(hmpa)$_2$ (2). (2 mmol, 0.33 g, 0.35 mL) Yield: 0.96 g, 63%. Mp: 160−169 °C. ^{1}H NMR (300 MHz, 25 °C, C$_6$D$_6$): δ_H 0.618 (s, 18H, −SiC*H*$_3$), 2.21 (d, 36H, HMPA), 6.03 (m, 4H, *o*-C*H*), 6.76 (m, 4H, *p*-C*H*), 7.28 (m, 8H, *m*-C*H*). ^{13}C NMR (300 MHz, 25 °C, C$_6$D$_6$): δ_C 4.10 (−Si*C*H$_3$), 36.71 (*C*H$_3$ HMPA), 118.3 (*m*-*C*H), 126.0 (*p*-*C*H), 129.9 (*o*-*C*H), 162.1 (*i*-*C*). IR (cm^{-1}): ν 2953 s, 2723 m, 1574 m, 1458 s, 1372 s, 1303 s, 1258 m, 1210 w, 1172 w, 919 w, 823 w, 718 w, 489 w.

Mg[N(SiMe$_3$)(Mes)]$_2$(hmpa)$_2$ (3). A white precipitate was isolated and redissolved in toluene. The solution was filtered, and crystals (colorless blocks) deposited at room temperature. (2 mmol, 0.49 g, 0.45 mL) Yield: 0.94 g, 59%. Mp: 167−174 °C. ^{1}H NMR (300 MHz, 25 °C, C$_6$D$_6$): δ_H 0.42 (s, 18H, −SiC*H*$_3$), 2.12 (d, 6H, *p*-C*H*$_3$), 2.17 (s, 12H, *o*-C*H*$_3$), 2.44 (d, 36H, HMPA), 6.84 (s, 4H, *m*-C*H*). ^{13}C NMR (300 MHz, 25 °C, C$_6$D$_6$): δ_C 4.5 (−Si*C*H$_3$), 36.71 (*C*H$_3$ HMPA), 20.9 (*p*-*C*H$_3$), 21.7 (*o*-*C*H$_3$), 125.0 (*p*-*C*H), 129.1 (*m*-*C*H), 135.0 (*o*-*C*H), 153.6 (*i*-*C*). IR (cm^{-1}): ν 2957 s, 2723 m, 2552 s, 1569 m, 1446 s, 1372 s, 1303 s, 1268 m, 1210 w, 1172 w, 919 w, 823 w, 718 w, 489 w, 365 w.

[Mg{N(SiMe$_3$)(Dipp)}(hmpa)$_3$][N(SiMe$_3$)(Dipp)] (4). (2 mmol, 0.49 g, 0.55 mL) Yield: 1.37 g, 65%. Mp: 180−185 °C. ^{1}H NMR (300 MHz, 25 °C, C$_6$D$_6$): δ_H 0.19 (s, 9H, −SiC*H*$_3$*), 0.51 (s, 9H, −SiC*H*$_3$), 1.08 (d, 12H, −CH(C*H*$_3$)$_2$*), 1.39 (d, 12H, −CH(C*H*$_3$)$_2$), 2.20 (d, 54H, HMPA), 3.99 (m, 2H, −C*H*(CH$_3$)$_2$), 4.7 (m, 2H, −C*H*(CH$_3$)$_2$*), 6.77 (m, 4H, *p*-C*H**), 6.99 (m, 4H, *p*-C*H*), 7.09 (m, 8H, *m*-C*H**), 7.12 (m, 8H, *m*-C*H*). ^{13}C NMR (300 MHz, 25 °C, C$_6$D$_6$): δ_C 4.3 (−Si*C*H$_3$), 4.85 (−Si*C*H$_3$*), 36.71 (*C*H$_3$ HMPA), 25.52 (*p*-*C*H(CH$_3$)$_2$*), 26.48 (*p*-CH(*C*H$_3$)$_2$*), 27.57 (*p*-*C*H(CH$_3$)$_2$), 29.46 (*p*-CH(*C*H$_3$)$_2$), 106.4 (*p*-*C*H*), 111.4 (*o*-*C*H*) 114.7 (*m*-*C*H*), 122.4 (*p*-*C*H), 123.7 (*o*-*C*H), 144.4 (*m*-*C*H), 145.6 (*i*-*C*), 146.67 (*i*-*C**). IR (cm^{-1}): ν 2965 s, 2732 m, 2542 s, 1569 m, 1446 s, 1364 s, 1323 s, 1248 m, 1210 w, 1173 w, 922w, 832 w, 738 w, 479 w, 345 w.

Results

Synthetic Aspects. All compounds were synthesized using alkane elimination, a reaction route utilized to synthesize a variety of magnesium compounds in both high yield and purity.[14,16,35−38] This route is attractive due to the commercial availability of dibutylmagnesium (*n*-/*sec*-Bu$_2$Mg), straightforward reaction conditions, and ease of workup (eq 1). These reactions have been shown to be solvent dependent; performing these reactions in the presence of polar solvents frequently led to incomplete reactions.[14,16] To avoid these issues, all reactions were conducted in hexane. Donor adducts were easily obtained by the addition of a donor to the hexane solutions after the reaction took place.[14,16]

$$n\text{-}/sec\text{-}Bu_2Mg + 2HN(SiMe_3)(R) \xrightarrow[\text{hexane, 65 °C}]{\text{HMPA}} \underset{\mathbf{1-3}}{Mg[N(SiMe_3)(R)]_2(hmpa)_2} + 2BuH \qquad (1)$$

$$R = SiMe_3\ (\mathbf{1}),\ Ph\ (\mathbf{2}),\ Mes\ (\mathbf{3})$$

Compounds **1−3** have been isolated using the above reaction route (eq 1). For the bulkier HN(SiMe$_3$)(Dipp), ligand **d**, addition of HMPA yielded a rare separated amido species **4** (eq 2).

$$n\text{-}/sec\text{-}Bu_2Mg + 2HN(SiMe_3)(Dipp) \xrightarrow[\text{hexane, 65 °C}]{\text{HMPA}} \underset{\mathbf{4}}{[Mg\{N(SiMe_3)(Dipp)\}(hmpa)_3][N(SiMe_3)(Dipp)]} + 2BuH \qquad (2)$$

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Table 2. Selected Bond Lengths and Secondary Interactions for Magnesium Amides

	ligand	CN	av Mg−N (Å)	av Mg−D (Å)	av N−Si (Å)	av N−Mg−D (deg)	av N−Mg−N (deg)	av D−Mg−D (deg)	ref
$Mg[N(SiMe_3)_2]_2(thf)_2$	**a**	4	2.021(5)	2.094(5)	1.706(5)	108.55(5)	127.9(2)	89.8(2)	15
$Mg[N(SiMe_3)_2]_2(hmpa)_2$ (**1**)	**a**	4	2.066(5)	1.994(4)	1.701(7)	109.24(18)	120.07(16)	98.1(17)	*b*
$Mg[N(SiMe_3)(Ph)]_2(hmpa)_2$ (**2**)	**b**	4	2.049(2)	1.965(1)	1.708(3)	107.68(7)	120.89(8)	103.89(7)	*b*
$Mg[N(SiMe_3)(Mes)]_2(thf)_2$	**c**	4	2.023(1)	2.055(1)	1.711(1)	105.06(6)	134.35(6)	103.25(5)	14
$Mg[N(SiMe_3)(Mes)]_2(hmpa)_2$ (**3**)	**c**	4	2.085(3)	1.989(3)	1.714(4)	108.33(13)	122.20(2)	98.93(2)	*b*
$Mg[N(SiMe_3)(Dipp)]_2$	**d**	2	1.919(2)		1.707(2)		180.00		16
$[Mg\{N(SiMe_3)(Dipp)\}(hmpa)_3][N(SiMe_3)(Dipp)]$ (**4**)	**d**	4	2.006(3)	1.949(3)	1.708(3), 1.647(4)[a]	114.39(13)		104.10(12)	*b*

[a] Values for uncoordinated anion. [b] This work.

Combination of the strong Lewis base HMPA with the bulkier $HN(SiMe_3)(Dipp)$ amine seems to provide the metal center with enough coordinative saturation for this to occur.

Structural Aspects. Compounds **1**−**3** crystallize at room temperature as discrete monomers with distorted-tetrahedral geometries around the metal center. Since they are closely related to the previously synthesized THF-containing compounds, we chose these for comparison. Compound **4** crystallizes as a rare example of a compound with one ligand bound to the metal while the other one remains unassociated. With only a very small number of early-main-group separated amido species known,[39−42] compound **4** represents the first example of such an alkaline-earth-metal derivative. Pertinent bond lengths and angles for both families of compounds are given in Table 2. Throughout compounds **1**−**4**, we consistently see the Mg−O bonds for HMPA to be shorter than for those of the THF adducts, attributed to the stronger basicity of HMPA and the lower coordination number of the donor. Compounds **1**−**4** exhibit a formal metal coordination number of 4, which is quite prevalent in magnesium chemistry.

$Mg[N(SiMe_3)_2]_2(hmpa)_2$ (**1**) crystallizes in a distorted-tetrahedral geometry, similar to the case for the THF adduct $M[N(SiMe_3)_2]_2(thf)_2$ reported in 1990 by Bradley et al. via redox transmetalation using a mercuric silylamide.[15] As expected, the stronger Lewis base HMPA allows for a shorter M−donor bond with a difference of 0.09 Å. The bulkier nature of HMPA is expressed by a D−Mg−D angle of 98.1(17)°, wider than that for the THF adduct compound, 89.8(2)°. The wide angle and the shortening of the Mg−D bond cause slightly longer Mg−N bonds in **1**, 2.066(5) Å as compared to 2.021(5) Å in the THF counterpart, and a narrower N−Mg−N angle of 120.07(16)°, as compared to 127.9(2)° in the THF species.

In $Mg[N(SiMe_3)(Ph)]_2(hmpa)_2$ (**2**), one of the trimethylsilyl groups is replaced by a phenyl group (Figure 2). Possibly due to the two-dimensional nature of the phenyl substituents as compared to $-SiMe_3$, and the resulting decrease in steric bulk, the Mg−D bond for **2** is slightly shorter (1.965(1) Å) than for **1** (1.994(4) Å); consequently the D−Mg−D angle widens to 103.89(7)°. Despite the smaller ligand size in **2** the N−M−N angle, 120.89(8)°, is similar to that of **1**, 120.07(16)°.

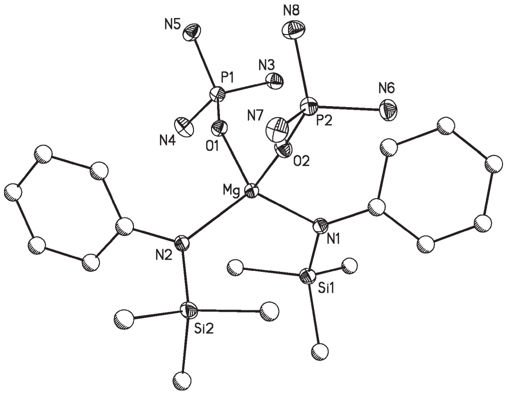

Figure 2. Structure of $Mg[N(SiMe_3)(Ph)]_2(hmpa)_2$ (**2**). Hydrogen atoms and methyl groups from HMPA are removed for clarity.

The structural effect of ligand/coligand bulk, as well as coligand basicity, is nicely demonstrated when comparing the THF adduct $Mg[N(SiMe_3)(Mes)]_2(thf)_2$[14] with the HMPA analogue $Mg[N(SiMe_3)(Mes)]_2(hmpa)_2$ (**3**) (Figure 3). Shorter Mg−D bonds are observed for **3** (1.989(3) Å) than for the THF adduct (2.055(1) Å), consistent with the trends discussed above. The comparison of D−Mg−D angles in $Mg[N(SiMe_3)(Ph)]_2(hmpa)_2$ (**2**) (103.89(7)°) and $Mg[N(SiMe_3)(Mes)]_2(hmpa)_2$ (**3**) (98.3(2)°) showcases the increased ligand bulk. This value closely resembles the D−Mg−D angle for compound **1** (98.1(17)°). Similarly, the M−N bonds in $Mg[N(SiMe_3)(Mes)]_2(hmpa)_2$ lengthen to 2.085(3) Å, as compared to 2.049(2) Å for $Mg[N(SiMe_3)(Ph)]_2(hmpa)_2$, again, an effect attributed to ligand bulk.

Replacement of the methyl substituents by isopropyl groups results in a further increase in ligand size, as also demonstrated by the previous isolation of the two-coordinate $Mg[N(SiMe_3)(Dipp)]_2$.[16] In the presence of 2.5 equiv of HMPA, a rare contact/separated amido species was obtained, $[Mg\{N(SiMe_3)(Dipp)\}(hmpa)_3][N(SiMe_3)(Dipp)]$ (**4**) (Figure 4). Clearly, the combination of $[N(SiMe_3)(Dipp)]^-$ along with three HMPA coligands provides favorable steric saturation to allow for the formation of this rare structural motif. Examples of separated amides in early-main-group chemistry are limited to alkali-metal species, including $[Li(12\text{-crown-}4)_2][N(SiPh_3)_2]\cdot THF$,[39,40] $[K(18\text{-crown-}6)N(Ph)_2]$,[41] and $\{[K(18\text{-crown-}6)N(SiMePh_2)_2]\}_\infty$.[42] No examples of separated alkaline-earth-metal amido complexes have been reported. Furthermore, separated ions involving alkaline-earth metals are almost exclusively limited to the heavier metals, where a lower metal charge density and thus weaker metal−ligand bonding is observed.

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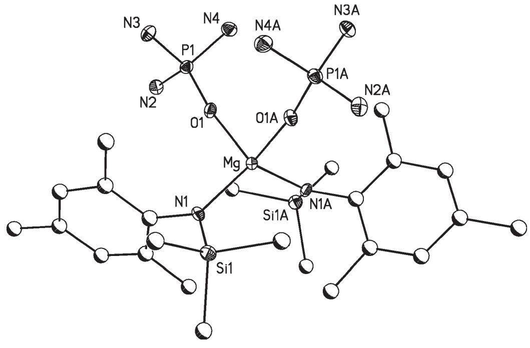

Figure 3. Structure of Mg[N(SiMe$_3$)(Mes)]$_2$(hmpa)$_2$ (**3**). Hydrogen atoms and methyl groups from HMPA are removed for clarity.

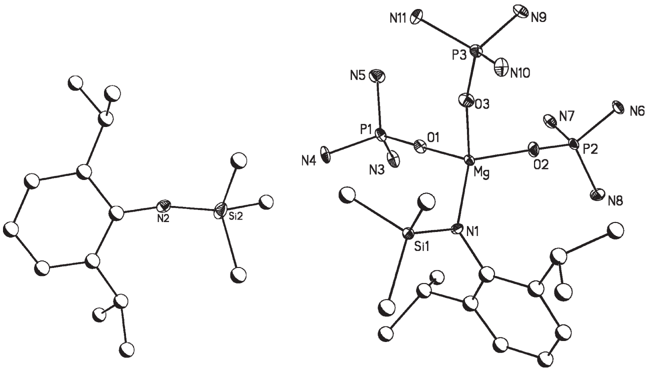

Figure 4. Structure of [Mg{N(SiMe$_3$)(Dipp)}(hmpa)$_3$][N(SiMe$_3$)(Dipp)] (**4**). Hydrogen atoms and methyl groups from HMPA are removed for clarity.

Consistent with the free amido anions for group I metals, the N−Si distance in **4** for the unassociated anion (1.647(4) Å) is shorter than for the metal-bound amido (1.708(3) Å) ligand. Further, widening of the N−Si−C angle for the separated ligand (137.41(3)°) as compared to metal-bound ligand (119.81°) also occurs, indicative of part of the negative charge being distributed into the ligand system. These values are summarized in Table 3.

Even though it is common for the heavier group II metals in the presence of HMPA,[43−45] a fully dissociated motif is not observed for magnesium, likely a consequence of the increased charge density for the lighter metal. This leads to increased polarization and capacity for covalent interactions. In contrast, an increase in metal size and reduction of electronegativity for the heavier alkali and alkaline-earth metals results in decreased covalency and thus facilitates ion separation.

The combination of 18-crown-6 and HMPA has been sufficient to create separated ion species for Ca−Ba for a plethora of ligands, including methanides, silanides, selenolates, thiolates, and stannates.[43−51] For magnesium, the list of separated species is small, but similar strategies have also proven successful for cyclopentadienides with the isolation of [Mg(15-crown-5)(pyr)$_2$][(C$_5$H$_5$)]$_2$ and [Mg(15-crown-5)(thf)$_2$][(C$_5$H$_5$)]$_2$, where the equatorial sphere of the metal center is occupied by the crown, whereas monodentate Lewis bases are located in the axial positions.[17] In the presence of the tridentate pentamethyldiethylenetriamine (PMDTA), the contact/separated compound [Mg(C$_5$H$_5$)(pmdta)][C$_5$H$_5$] was obtained.[17] A rare separated magnesium thiolate was obtained using a combination of crown ether and THF, affording [Mg(15-crown-5)(thf)$_2$][SMes*]$_2$.[18]

Ultimately, the rarity of separated amido complexes has to be attributed to the ligand itself: namely, the strength and nature of the metal−ligand bond and whether the deprotonated ligand can sustain the negative charge through delocalization or resonance stabilization. Therefore, a closer inspection of the substitution patterns on the amide ligand and its effect on the metal−ligand bond is warranted. HN(SiMe$_3$)$_2$ is sterically demanding enough to allow for the isolation of an array of compounds with low coordination numbers, but the limited capacity for charge delocalization results in contact molecules, a statement also supported by K(18-crown-6)[N(SiMe$_3$)$_2$][52] and Li(12-crown-4)[N(SiMe$_3$)$_2$],[53] which exhibit M−N bonding despite the presence of crown ether. The substitution of either one or both −SiMe$_3$ groups by phenyl groups increases the capacity for charge delocalization and, as such, the likelihood for ion dissociation. Demonstrating the added component of ligand bulk, only the most sterically demanding ligand [N(SiMe$_3$)(Dipp)]$^-$ (**d**) did initiate ion separation.

Upon inspection of the ligands used for the isolation of group I separated amido species, replacement of both −SiMe$_3$ with phenyl groups, as seen in [K(18-crown-6)N(Ph)$_2$], results in the cleavage of the K−N bond, although not separated ions.[41] Rather, the equatorial positions of the potassium cation are being filled by crown ether coordination, while the two axial positions are being occupied by K−η^6-Ph interactions. This coordinative preference may be understood on the basis of not a single K−π interaction but the sum of six, as made possible by the large size of the potassium. In contrast, the smaller magnesium is unable to engage in such a large number of π nteractions; as such, a similar coordination mode is not favored. This argument is further supported by the combination of the HN(Ph)$_2$ ligand with the smaller Li (CN = 6, Li = 0.76, K = 1.38 Å), affording a contact molecule [Li(12-crown-4)(N(Ph)$_2$] despite the presence of crown ether.[54] Furthermore, the increased capacity for M−π interactions, as a result of larger radii, provides an attractive avenue for achieving coordinative saturation.

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Table 3. Selected Bond Lengths and Angles for Separated Amide Species

	av N−Si (Å)	av N−C*i* (Å)	av C−N−C (deg)	av Si−N−Si (deg)	av Si−N−C*i* (deg)	ref
[K(18-crown-6)N(Ph)$_2$]		1.366(5)	120.3(3)			41
{[K(18-crown-6)N(SiMePh$_2$)$_2$]}$_\infty$	1.649(2)			135.56(9)		42
[Li(12-crown-4)$_2$][N(SiPh$_3$)$_2$]·THF	1.633(4)			154.9(3)		39, 40
[Mg{N(SiMe$_3$)(Dipp)}(hmpa)$_3$] [N(SiMe$_3$)(Dipp)] (**4**)	1.708(3), 1.647(4)[a]	1.410(5), 1.354(5)[a]			119.81(2), 137.41(3)[a]	*b*

[a] Values for uncoordinated anion. [b] This work.

Along the same line, replacement of one or two methyl groups in each of the −SiMe$_3$ substituents in [N(SiMe$_3$)$_2$]$^-$ demonstrates the effect of charge delocalization and steric bulk on ion association. If only one of the CH$_3$ groups is replaced by phenyl, the HN(SiMe$_2$Ph)$_2$ amine ligand in conjunction with 18-crown-6 affords the contact molecule K(18-crown-6)[N(SiMe$_2$Ph)$_2$].[52] Replacement of a second −CH$_3$ group by phenyl further increases the capacity for charge delocalization, affording the unique {[K(18-crown-6)N(SiMePh$_2$)$_2$]}$_\infty$.[42] In this species no K−N bond is present, but the trans positions are filled by K−η^1-Ph interactions. Interestingly, this strategy did not afford a separated ion for the lithium analogue, again likely a consequence of not only increased charge density but also a reduced capacity for M−π interactions due to reduced ionic radius. Only the replacement of all methyl groups in −SiMe$_3$ by phenyl afforded separated ions, as seen in [Li(12-crown-4)$_2$][N(SiPh$_3$)$_2$]·THF.[39,40]

Conclusion

Our results shed light on the delicate balance of metal−ligand bond strength attributed to charge/size ratios, ligand bulk, charge delocalization through the ligand system, and availability of coordinative saturation through either Lewis base or secondary interactions on ion association.

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Supporting Information Available: CIF files giving crystal data for compounds **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.