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β-Diketiminato Calcium and Magnesium Amides; Model Complexes for Hydroamination Catalysis

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In a study relevant to group 2-mediated hydroamination catalysis, the reaction of the β-diketiminato magnesium alkyl complex [{ArNC(Me)CHC(Me)NAr}Mg($^{n/s}$Bu)] (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) with benzylamine, 2-methoxyethylamine, pyrrolidine, and 2-methyl-4,4-diphenylpyrrolidine has been shown to yield the corresponding magnesium amide complexes [{ArNC(Me)CHC(Me)NAr}Mg(NR^{1}R^2)] (R^1 = H, R^2 = CH$_2$Ph, CH$_2$CH$_2$OMe; R^1 = R^2 = -(CH$_2$)$_4$-, -CH(Me)-CH$_2$CPh$_2$CH$_2$-) within the first point of analysis (30 min) at room temperature in near quantitative yield as monitored by ^{1}H NMR spectroscopy. Reactions proceeded non-reversibly, and the products have been characterized in both solution and the solid state. While single crystal X-ray diffraction analysis demonstrated that the magnesium amides are dimeric in the solid state, with aggregation occurring via μ^2-coordinated amide ligands, NMR studies suggest that for more sterically crowded amide ligands discreet monomeric species exist in solution. In contrast, the calcium complex [{ArNC(Me)CHC(Me)NAr}Ca{N(SiMe$_3$)$_2$}(THF)] reacted reversibly with benzylamine at room temperature to form an equilibrium mixture of a calcium benzylamide and bis(trimethylsilyl)amide. A series of Pulsed-Gradient Spin−Echo NMR studies upon β-diketiminato calcium amides were consistent with the formation of a dimer in solution. A van't Hoff analysis performed on this mixture allowed $\Delta H^\circ = -51.3$ kJ mol^{-1} and $\Delta S^\circ = -134$ J mol^{-1} of the protonolysis/dimerization reaction to be derived and the Gibbs' free energy to be calculated as ΔG° (298 K) = −11.4 kJ mol^{-1}.

Introduction

Hydroamination, the formal addition of a nitrogen−hydrogen bond across an unsaturated carbon−carbon or carbon−heteroatom bond is an atom-efficient method for the construction of new carbon−nitrogen bonds. The search for homogeneous reagents capable of catalyzing these processes has given rise to a burgeoning and mechanistically diverse area of research that spans the periodic table from group 1 to group 12.[1−5]

Studies within our group, and elsewhere, have demonstrated that heavier alkaline earth amides, including the homoleptic series [M{N(SiMe$_3$)$_2$}$_2$]$_2$ (M = Ca, Sr, Ba) and the heteroleptic complex [{ArNC(Me)CHC(Me)NAr}Ca{N-

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$(SiMe_3)_2\}(THF)]$ (**1**, Ar = 2,6-di-iso-propylphenyl), are capable of catalyzing the hydroamination of alkenes,[6] carbodiimides,[7] and isocyanates.[8] More recently we described a magnesium analogue of **1**, [{ArNC(Me)CHC(Me)NAr}-$Mg\{N(SiMe_3)_2\}(THF)]$ (**2**, Ar = 2,6-di-iso-propylphenyl) as a competent pre-catalyst for the intramolecular hydroamination of aminoalkenes, albeit at turnover frequencies inferior to those recorded for **1**.[6] While the initial model for this reactivity has been constructed by analogy to that proposed for trivalent lanthanide-mediated hydroamination catalysis,[9−25] vital to the understanding of the group 2 reaction chemistry have been parallel synthetic investigations into the discreet reaction steps proposed to make up the catalytic cycle (Figure 1). Current data suggest that hydroamination catalysis proceeds via (i) initiation of the pre-catalyst by reaction with a primary or secondary amine to form an intermediate heavier alkaline earth amide, (ii) insertion of the unsaturated substrate into the metal−nitrogen bond, and (iii) subsequent turnover by reaction of the insertion product with a further equivalent of amine.

With regard to the pre-catalyst initiation step, we have previously reported that **1**, originally described by Chisholm and co-workers in the context of lactide polymerization,[26] reacts stoichiometrically with primary amines and primary aromatic and secondary aromatic amines, via σ-bond metathesis (or protonolysis), to yield the corresponding calcium amido and anilido complexes, respectively.[27] These studies have allowed a greater understanding of pre-catalyst initiation in the intra- and intermolecular hydroamination of unsaturated substrates including alkenes, alkynes, carbodiimides, and isocyanates. In the latter two cases further stoichiometric

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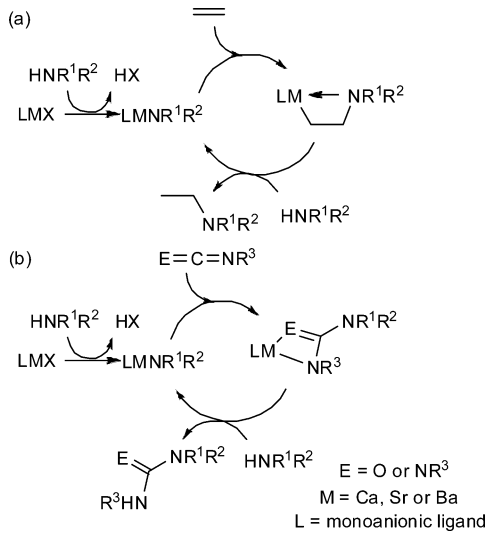


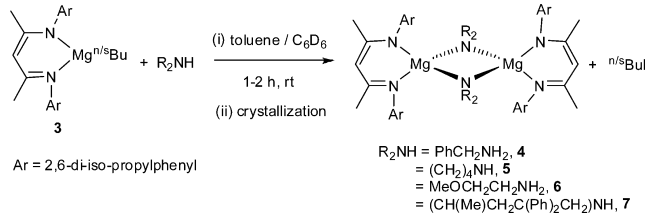
Figure 1. Simplified reaction mechanism for the group 2-mediated hydroamination of (a) alkenes and (b) carbodiimides and isocyanates.

reaction studies have also experimentally verified the insertion steps.[7,8] A number of well-defined primary amido and primary anilido complexes have also been characterized.[28,29] Most notably in this latter regard, Harder and co-workers have described the reaction of **1** with excess ammonia to yield the solvated metal amide [{ArNC(Me)CHC(Me)NAr}-$Ca(NH_2)(NH_3)_2]_2$.[28]

For magnesium a number of primary amide species have been known for some time.[30] Furthermore, similar σ-bond metathesis (or protonolysis) reactions have been reported in the literature, albeit with secondary amines, for derivatives of the magnesium-based pre-catalyst **2**. The complex [{ArNC-(Me)CHC(Me)NAr}$Mg(^{n/s}Bu)]_2$ (**3**, Ar = 2,6-di-iso-propylphenyl) has been shown to react with di-iso-propylamine and hexamethyldisilazane to give the corresponding magnesium amides.[31a]

In a study pertinent to hydroamination catalysis, we now report the non-reversible reactions of **3** with benzylamine, 2-methoxyethylamine, pyrrolidine, and the isolated hydroamination product 2-methyl-4,4-diphenylpyrrolidine, along with the reversible reaction of **1** with benzylamine. In the majority of cases, the reaction products have been characterized in solution and in the solid state, with dimerization occurring upon crystallization. Both the solution-state aggregation and reversibility of the protonolysis reaction are discussed with reference to catalytic systems.

Scheme 1. Non-Reversible Reaction of **3** with Primary and Secondary Amines



Results and Discussion

Magnesium. In contrast with the expectation provided by the work of Gibson and co-workers,[31a] the reactions of **3** with benzylamine, 2-methoxyethylamine, pyrrolidine, and 2-methyl-4,4-diphenylpyrrolidine all proceeded rapidly at room temperature to give the corresponding magnesium amide products [{ArNC(Me)CHC(Me)NAr}$Mg(NR^1R^2)$] (R^1 = H, $R^2 = CH_2Ph$, **4**; $R^1 = R^2 = -(CH_2)_4-$, **5**; R^1 = H, $R^2 = (CH)_2OMe$, **6**; $R^1 = R^2 = -CH(Me)CH_2CPh_2CH_2-$, **7**) in high yield at the first point of analysis (<30 min) as evidenced by ^{1}H NMR spectroscopy (Scheme 1). In all cases, non-reversible protonolysis was observed and, once formed, the alkane byproducts are effectively inert under the reaction conditions.

Repetition of these experiments on a preparative scale and crystallization of the reaction products from toluene solutions, provided compounds **4**−**7** as dimeric species, as evidenced by both solid-state and solution spectroscopic data. Single crystal X-ray diffraction studies were undertaken upon samples of **4**−**6**. In these cases recrystallization of samples by slow cooling of hot toluene solutions led to the isolation of samples suitable for X-ray diffraction. The results of these analyses are illustrated in Figures 2−4, and selected bond length and angle data and details of the X-ray determinations are provided in Tables 1 and 2, respectively.

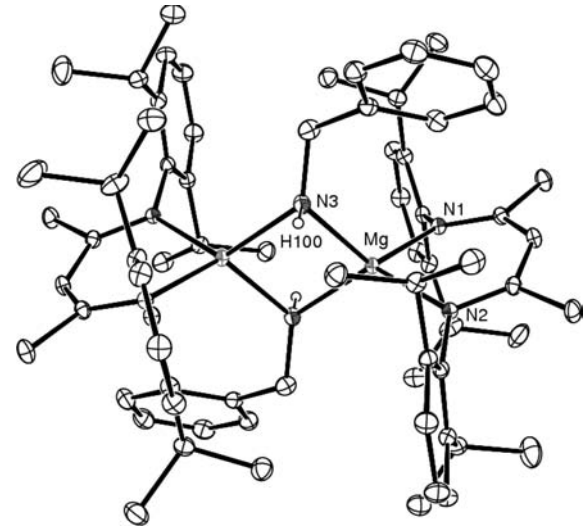


Figure 2. Oak Ridge Thermal Ellipsoid Plot (ORTEP) representation of **4** with thermal ellipsoids at 20% probability. H-atoms with the exception of N−H omitted for clarity. Equivalent atoms generated by $-x$, $-y + 1$, $-z + 1$ symmetry transformation.

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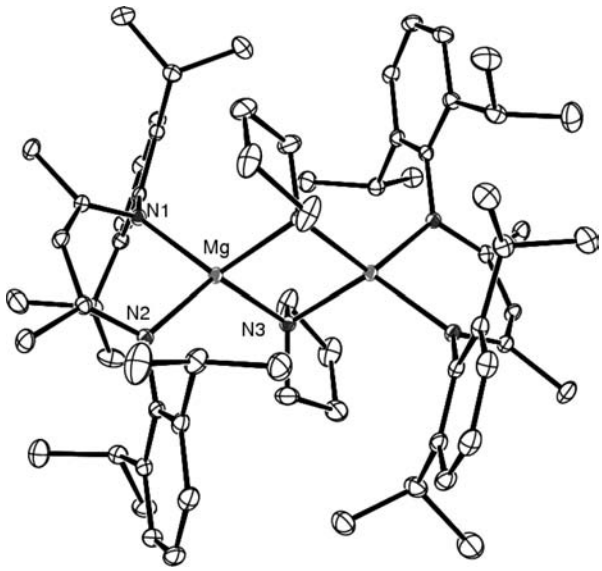

Figure 3. ORTEP representation of **5** with thermal ellipsoids at 20% probability. H-atoms omitted for clarity. Equivalent atoms generated with $-x + 2, y, -z + 1/2$ and $-x + 1, y, -z + 1/2$ symmetry transformations.

In the solid state compounds **4** and **5** exist as centrosymmetric dimers, in which the magnesium centers are bridged by unsymmetrical Mg−N−Mg′ interactions (Figures 2 and 3). As expected, the metal−nitrogen bond lengths to the β-diketiminate ligands [Mg−N: **4** 2.0918(14) and 2.1071(14) Å; **5**, 2.114(2) and 2.126(2) Å] are shorter than in the heavier group 2 analogue [{ArNC(Me)CHC(Me)NAr}Ca(NHCH$_2$Ph)]$_2$ (**8**) [Ca−N, 2.3464(15) and 2.3514(15) Å],[27c] but are in close correspondence with the similarly four-coordinate but monomeric complex [{ArNC(Me)CHC(Me)NAr}]Mg(N^{i}Pr$_2$)(THF)] [Mg−N, 2.071(2) and 2.091(2) Å, N(1)−Mg−N(2), 92.79(7)°].[31b] The magnesium-amide bond lengths in **4** and **5** [Mg−N(3): **4**, 2.1251(16) Å; **5**, 2.117(2)] are, however, longer than those reported for the four-coordinate species and those found in the monomeric three-coordinate magnesium amide complexes [{ArNC(Me)CHC(Me)NAr}]Mg(N^{i}Pr$_2$)] [Mg−N$_{amide}$, 1.938(2) Å] and [{ArNC(Me)CHC(Me)NAr}]Mg{N(SiMe$_3$)$_2$}] [Mg−N$_{amide}$, 1.961(2) Å].[31a] This observation is undoubtedly due to the higher coordination number at nitrogen in both **4** and **5**, a consequence of the amide acting as a bridging ligand.

Although not previously observed in β-diketiminate complexes, amide bridging interactions have extensive precedent in cyclopentadienyl magnesium complexes[30a] and in homoleptic complexes of the generalized formula [Mg(NR$_2$)$_2$(S)$_n$]$_m$ (S = coordinated Lewis-basic solvent) where the formation of higher aggregates is common.[30b,c] It is noteworthy, however, that bond angles within the asymmetric Mg$_2$N$_2$ core of the dimeric structures observed for **4** and **5** [Mg−N(3)-Mg′: **4**, 90.73(6)°; **5**, 91.58(9)° and N(3)−Mg−N(3)′: **4**, 89.27(6)°; **5**, 88.33(9)°] differ from those reported by Bailey and co-workers for the topologically related complex [{ArNC(Me)CHC(Me)NAr}Mg(μ-OCH$_2$Ph)]$_2$ [Mg−O−Mg′ 97.6(3)°, O−Mg−O′ 82.4(3)°].[32]

Compound **6** crystallized in the triclinic space group $P\bar{1}$ with two distinct molecules (**6A** and **6B**) in the asymmetric unit. Both are illustrated in Figure 4, and important bond lengths and bond angles are listed in Table 1. Conformer **6B** demonstrates a centro-symmetric dimeric structure in which the methoxyethylamide moieties asymmetrically bridge the two metal centers. While magnesium amide bond lengths [Mg−N: 2.090(4) and 2.104(2) Å] and the β-diketiminate bite angle [N(5)−Mg(2)−N(6) 91.86(8)°] are unremarkable in comparison to those observed in **4** and **5**, it is notable that the magnesium centers are four-coordinate and that the pendent ether group of the amide moiety does not coordinate to the metal [Mg(2)−O(2) > 2.8 Å].

In contrast, conformer **6A** is five-coordinate with additional ligation provided by chelation through the OMe group. While the resultant S$_2$-symmetric tricyclic ladder structure is analogous to that observed in the calcium analogue [{ArNC(Me)CHC(Me)NAr}Ca(NH(CH$_2$)OMe)]$_2$ (**9**),[27a,b] the metal−oxygen bond lengths [M−O: **9**, 2.438(2) Å, **6A**, 2.336(2) Å] of both complexes differ only slightly despite the large difference expected because of the difference in ionic radii of the group 2 dications (for 6-coordinate M^{2+}: Mg = 0.72 Å and Ca = 1.00 Å).[33] For comparison, metal−oxygen bond lengths in the similarly five-coordinate but monomeric complex [η^4-{(2-MeOC$_6$H$_4$)NC(Me)CHC(Me)N(2-MeOC$_6$H$_4$)}Mg{N(SiMe$_3$)$_2$}] [Mg−O, 2.129(1) and 2.144(1) Å],[34] where ligation at magnesium is augmented by coordination of both pendent ether groups, are considerably shorter. These data, in addition to the observation of conformer **A** within the unit cell of **6**, are consistent with a particularly weak metal−oxygen interaction in the solid state and a tightening of the coordination environment because of the shorter metal−ligand bond lengths to the smaller Mg^{2+} cation.

The compression of the coordination environments about the dimeric core of these magnesium compounds relative to that found for the previously reported calcium analogues **8** and **9** is also manifested in solution. Isolated samples of **4** and **7** demonstrated a series of ^{1}H and ^{13}C resonances characteristic of the retention of the dimeric constitution observed in the solid state with pairs of magnetically nonequivalent β-diketiminate and amide ligand sets. Thus, for **4** in d$_8$-toluene solution the benzylamide protons were observed as two distinct resonances at −0.52 (dd, 1H, J = 14.2, 2.7 Hz) and −0.49 (dd, 1H, J = 14.6, 3.0 Hz) ppm in the ^{1}H NMR spectrum. Similarly for **7** in C$_6$D$_6$ solution, characteristic pairs of ^{1}H resonances were observed for not only the β-diketiminate methine protons at 4.81 (s, 1H) and 4.82 (s, 1H) ppm but also the AB system of the metallated pyrrolidine rings at 1.40 (d, 1H, J = 15.5 Hz), 1.99 (d, 1H, J = 15.5 Hz), 3.70 (d, 1H, J = 12.0 Hz), and 4.09 (d, 1H, J = 12.0 Hz) ppm in C$_6$D$_6$ solution (Figure 5a). The low solubility of the methoxyethylamide analogue **5** prevented the acquisition of meaningful NMR data.

(32) Bailey, P. J.; Coxall, R. A.; Dick, C. M.; Fabre, S.; Henderson, L. C.; Herber, C.; Liddle, S. T.; Lorono-González, Parkin, A.; Parsons, S. *Chem.—Eur. J.* **2003**, *9*, 4820.
(33) Values quoted for 6 coordinate M^{2+}, Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.
(34) Chisholm, M. H.; Gallucci, J. C.; Phomphrai, K. *Inorg. Chem.* **2005**, *44*, 8004.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes **4**−**6** and **8**−**9**

	4	**5**	**6A**[a]	**6B**[a,b]	**8**[22]	**9**[22]
M−N(1)	2.1071(14)	2.114(2)	2.142(2)	2.110(2)	2.3514(15)	2.413(2)
M−N(2)	2.0918(14)	2.126(2)	2.155(2)	2.104(2)	2.3464(15)	2.398(2)
M−N(3)	2.1251(16)	2.117(2)	2.147(4)	2.113(4)	2.3802(17)	2.434(2)
M−N(3)`	2.1216(16)	2.088(2)	2.130(4)	2.100(4)	2.4069(19)	2.370(2)
M−O			2.336(2)			2.438(2)
N1−M−N2	92.65(6)	95.12(8)	88.75(8)	91.86(8)	82.20(5)	79.18(6)
N2−M−N3	114.66(6)	119.58(9)	153.59(13)	116.62(14)	134.84(6)	117.31(8)
N1−M−N3	122.65(6)	116.30(9)	113.08(12)	138.85(14)	109.32(6)	159.05(8)
M−N3−M	90.73(6)	91.58(9)	98.44(16)	95.19(16)	93.68(7)	97.85(8)
N3−M−N3`	89.27(6)	88.33(9)	81.56(16)	84.81(16)	86.32(7)	82.15(8)

[a] N3 atoms actually disordered over two sites, data presented for only one. [b] Because of the presence of two molecules within the asymmetric cell, for the purpose of this table atoms are labeled thus, N4 = N3, N5 = N2, N6 = N1.

Table 2. Crystallographic Data for Compounds **4**−**6** and **8**

	4	**5**	**6A-B**	**8**
molecular formula	$C_{36}H_{49}MgN_3$	$C_{32}H_{49}MgN_3 \cdot (C_7H_8)_{0.5}$	$C_{32}H_{49}MgN_3O \cdot (C_7H_8)_{0.5}$	$C_{72}H_{98}Ca_2N_6$
formula weight (g mol^{-1})	548.09	546.12	562.12	1127.72
crystal system	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P2_1/n$
a (Å)	11.6669(2)	19.1971(3)	13.6587(1)	11.5238(2)
b (Å)	12.9052(2)	21.1259(4)	13.6723(2)	20.5104(3)
c (Å)	13.0838(2)	17.7461(3)	21.4226(4)	14.4226(3)
α (deg)	99.145(1)	90	104.638(1)	90
β (deg)	110.902(1)	114.064(1)	92.948(1)	94.666(1)
γ (deg)	111.107(1)	90	117.902(1)	90
V (Å^3)	1620.79(4)	6571.5(2)	3352.72(8)	3397.6(1)
Z	2	8	4	2
μ (mm^{-1})	0.082	0.081	0.083	0.211
ρ (g cm^{-3})	1.123	1.104	1.114	1.102
θ range (deg)	4.09 to 27.53	3.02 to 27.51	3.77 to 27.48	3.99 to 27.49
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0532, 0.1373	0.074, 0.1984	0.0671, 0.1603	0.0510, 0.1184
$R1$, $wR2$ (all data)	0.0718, 0.1510	0.1147, 0.2312	0.1222, 0.1912	0.0787, 0.1354
measured/independent reflections/R_{int}	33768/7400/0.0424	72227/7534/0.0859	61034/15275/0.0731	44109/7741/0.048

The observed solution data acquired upon these isolated samples differed somewhat from that of the NMR scale reactions. Although the addition of 1 equiv of benzylamine or pyrrolidine to **3** in C_6D_6 reproduced the ^{1}H NMR spectra acquired for isolated and crystallographically characterized samples of **4** and **6**, a similar result was not observed for the NMR scale synthesis of **7**. After addition of 1 equiv of 2-methyl-4,4-diphenylpyrrolidine to **3** in C_6D_6 solution, both the β-diketiminate and amide ligands existed in a single environment as evidenced by ^{1}H NMR spectroscopy. This observation contrasted with the pairs of magnetically non-equivalent resonances that were observed upon re-dissolving recrystallized samples of **7** (Figure 5). The solution data is thus reminiscent of that reported for the monomeric species [{ArNC(Me)CHC(Me)NAr}Mg(N^{i}Pr$_2$)] and [{ArNC(Me)-CHC(Me)NAr}Mg{N(SiMe$_3$)$_2$}] (Ar = 2,6-di-iso-propyl-phenyl).[31a] Furthermore, heating a C_6D_6 solution of **7**, prepared by direct addition of 2-methyl-4,4-diphenylpyrro-lidine to **3**, to 75 °C overnight resulted in the formation of the apparently dimeric product. Although yet to be crystal-lographically characterized, upon recrystallization from a hexane/toluene solvent mixture, the latter sample provided satisfactory elemental analysis.

These observations may be explained by considering that the magnesium amide complexes reported herein undergo dimerization in solution with an ease reflected by unfavorable non-bonding interactions in the approach of two sterically congested monomeric units. While in the case of the benzylamide analogue **4** this solution dimerization is readily observed in solution at room temperature, for more congested molecules such as **7**, thermal activation is required to achieve dimerization.

It is noteworthy that, in contrast to the solution behavior of similar calcium amide complexes (vide infra), compounds **4**−**7** demonstrated no tendency to undergo Schlenk-like redistribution reactions in solution despite that fact that the homoleptic complex [(ArNC(Me)CHC(Me)NAr}$_2$Mg] is a known compound.[35]

Calcium. In a preliminary communication of this work,[27c] we have previously reported the result of an NMR scale reaction between **1** and benzylamine conducted in C_6D_6 solution. After 30 min at room temperature a mixture of the starting material **1** along with the benzylamide **8** was observed by ^{1}H NMR spectroscopy. Although heating the sample to 80 °C for 12 h followed by cooling back to room temperature had no effect on the position of the silylamide/benzylamide equilibrium, this experiment did reveal a propensity of the product **8** (or intermediate species) to undergo a Schlenk-like redistribution reaction with the formation of the known homoleptic species [{ArNC(Me)-CHC(Me)NAr}$_2$Ca].[35]

Variable temperature ^{1}H NMR studies upon a d_8-toluene solution of the reaction mixture formed from the addition of benzylamine to **1** were consistent with the formation of a dynamic equilibrium (Scheme 2). At high temperature the equilibrium favored the starting materials, and the resonances

(35) Harder, S. *Organometallics* **2002**, *21*, 3782.

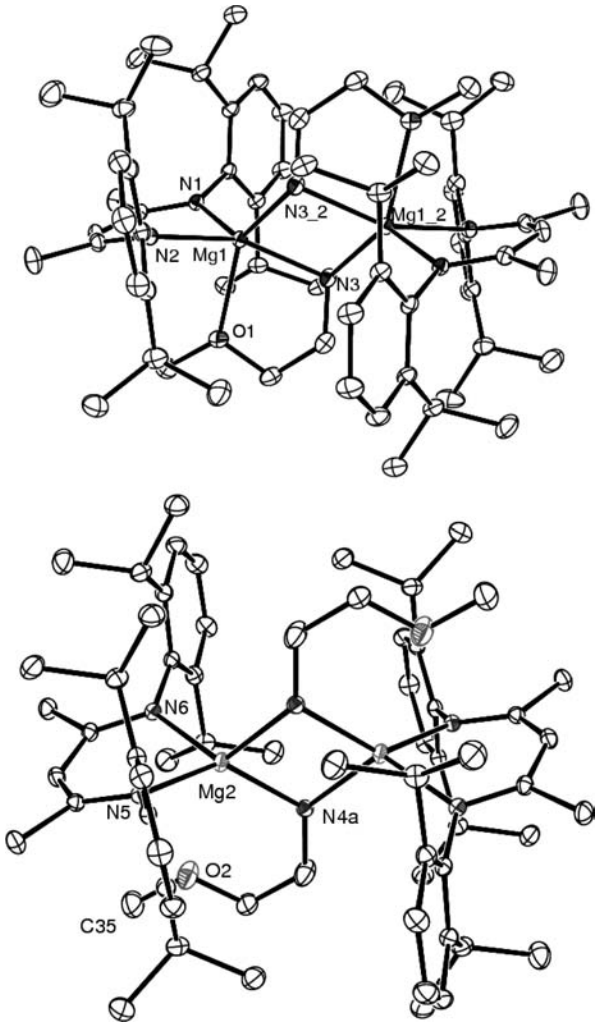

Figure 4. ORTEP representation of conformers **6A** and **6B** with thermal ellipsoids at 20% probability. H-atoms omitted for clarity. Equivalent atoms generated by $-x+1, -y+1, -z$ and $-x+2, -y+1, -z+1$ symmetry transformations.

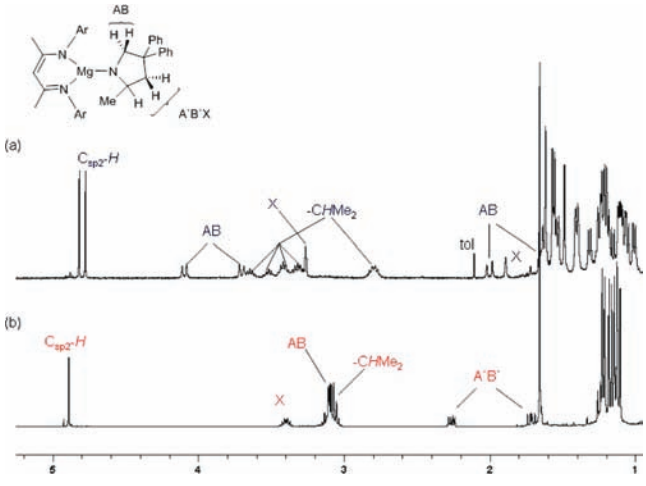

Figure 5. Selected ^{1}H NMR data (C_6D_6, 298 K, 400 MHz) for **7** (a) an isolated and crystallized sample following a preparative scale reaction and (b) NMR scale reaction. Values quoted in ppm. Ar = 2,6-di-iso-propylphenyl.

of both the protons of the β-diketiminate ligand of **1a** and the methylene group of benzylamine were observed. Although the latter signal appeared as a broad singlet at 3.50 ppm at 353 K, subsequent cooling resulted in an upfield shift and broadening of this resonance. This observation is consistent with (i) fast amide-amine exchange on the NMR time scale averaging the methylene resonances of the benzyl moieties in **8** and benzylamine and (ii) an increase in the concentration of the benzylamide **8** with decreasing temperature. More strikingly, the shift in the position of the equilibrium toward the reaction products (Scheme 2) at lower temperatures was characterized by an increase in intensity of the resonances of the protons of the β-diketiminate ligand of **8**. While further fluxional processes prevented the characterization of this equilibrium at temperatures below 273 K, these experiments did reveal the decoalescence of a broad high field resonance (−0.90 ppm at 213 K in d_8-toluene), whose coupling was not resolved, tentatively attributed to the benzylamide NH proton of **8**. This latter value is comparable to not only those observed for the analogous magnesium complex **4** (−0.52 and −0.49 ppm at 298 K in C_6D_6) but also that recorded for **9** (−1.63 ppm at 298 K in C_6D_6).

This result contrasts with the reactions of **1a** with 2,6-di-iso-propylaniline, diphenylamine, and 2-methoxyethylamine in C_6D_6 which all yield the corresponding amide species [{ArNC(Me)CHC(Me)NAr}Ca(NR^{1}R^2)(THF)$_n$] (R^1 = H, R^2 = CH_2CH_2OMe, n = 1; R^1 = H, R^2 = NAr, n = 1; R^1 = R^2 = Ph, n = 1) quantitatively within the first point of analysis (<30 min) as monitored by ^{1}H NMR spectroscopy.[7a,27a−c] In these cases, it is proposed that the improved thermodynamic stability of the calcium species, be it through ancillary ligation at the metal or charge stabilization across the amide ligand, effectively drives the reaction to completion.

Following a preparative scale experiment, fractional crystallization of **8** from hexane solution allowed the isolation and characterization of the β-diketiminate stabilized benzylamide, **8**. Although this structure has been reported previously, for comparison, selected data is presented in Tables 1 and 2.

The quantitative characterization of the equilibrium process illustrated in Scheme 2 requires a knowledge of the aggregation state of compound **8** in solution. In contrast to the solution data acquired for the magnesium complex **4**, multinuclear NMR data acquired for samples of **8** demonstrated a single β-diketiminate ligand environment. For the larger cation, it is unclear whether this is a consequence of the formation of a discreet monomeric species or a more coordinatively "open" dimer with ligands coordinated to calcium undergoing fast site-exchange and/or rotation.

Pulsed-gradient spin echo (PGSE) NMR has recently emerged as a useful technique to probe the nuclearity of organometallic species in solution,[36] These experiments allow the diffusion coefficient of the molecule to be measured and, via the Stokes−Einstein equation, the solution hydrodynamic radius to be calculated. A PGSE NMR experiment upon the equilibrium mixture formed from the addition of benzylamine to **1** at 298 K demonstrated the presence of two distinct species containing the β-diketiminate ligand, each with a

Scheme 2. Reversible Reaction of **1** with Benzylamine

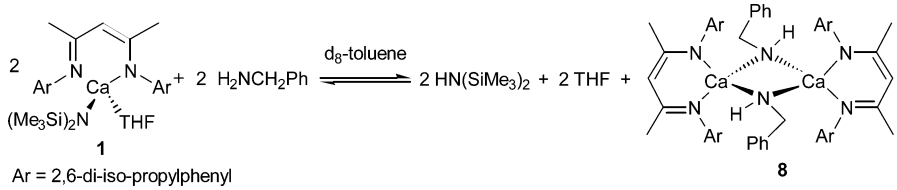

Table 3. Solution Nuclearity of Group 2 Complexes, LH = ArNC(Me)CHC(Me)NHAr

compound	**LH**	**1**	**8**	**9**	$(Me_3Si)_4Si$
diffusion coefficient ($\times 10^{-10}$ m^2 s^{-1})[a]	7.59	6.61		5.21	9.00
solution hydrodynamic radius (Å)[b]	4.8	5.5	6.5	7.0	3.6
crystallographic radius (Å)[c]		5.5	6.35	7.1	3.5[36]
solution nuclearity	mono	mono	dimer	dimer	

[a] Measured by PGSE NMR experiments in C_6D_6 at 298 K based on 20−50 mM concentrations, values normalized against $(Me_3Si)_4Si$. [b] Measured in d_8-toluene at 298 K. [c] Calculated using Gaussian03, from crystallographic coordinates.

unique diffusion coefficient. Use of the Stokes−Einstein equation gave a solution hydrodynamic radius for compound **8** of 6.5 Å.

For comparison, a series of similar experiments upon a number of group 2 compounds were conducted (Table 3). It has previously been shown that the primary amide **9** demonstrates a concentration-independent fluxional process which may only be explained by invoking dimer formation in solution. This compound, therefore, may be used as benchmark against which the relative nuclearity of the remaining compounds can be measured. In all cases, diffusion coefficients were normalized against a tetrakis(trimethylsilyl)silane internal standard.

The results of the PGSE experiments are presented in Table 3. Solution NMR experiments were conducted at 20−50 mM concentrations similar to those employed under the catalytic hydroamination conditions. In addition to solution data the solvation radius of the compounds under study was calculated (where available) from crystallographic coordinates using Gaussian03.[37] While the absolute values acquired from these analyses should be treated with caution, because of likely errors in measurement, it is apparent that the trends within a given series of compounds are statistically relevant. These experiments demonstrated that the calcium amide **1** is monomeric in C_6D_6 solutions at 298 K with a hydrodynamic radius of 5.5 Å. In contrast, the calcium primary amide, **9**, gave a much smaller diffusion coefficient corresponding to a larger hydrodynamic radius of 7.0 Å, a value that compares well to that calculated from the solid-state dimeric structure of 7.1 Å and consistent with previous deductions that **9** retains its dimeric constitution in solution.

To establish that aggregation does not occur at higher concentrations, the diffusion coefficient of the heteroleptic calcium amide **1** was measured at a series of concentrations up to, and far beyond, those employed under the catalytic and stoichiometric reaction conditions. Thus, PGSE NMR experiments on three separate C_6D_6 solutions of **1** at 30, 120, and 240 mM concentrations gave diffusion coefficients ranging from 6.46 to 6.61 $\times$ 10^{-10} m^2 s^{-1} corresponding to a hydrodynamic radius range of 5.5−5.6 Å.

Despite the observation that the organometallic species in solution for the equilibrium mixture formed upon addition of benzylamine to **1** are undergoing dynamic exchange, comparison of the experimental hydrodynamic radius of 6.5 Å against the data presented in Table 3 and the value calculated from the solid-state X-ray structure [**8**; $r_{crystal}$ = 6.35 Å] revealed a good correlation with the dimeric species. Having elucidated the nuclearity of the benzylamide **8** species in solution, a van't Hoff analysis was conducted upon the equilibrium mixture. The concentrations of **1**, **8**, and benzylamine were measured by ^{1}H NMR using a known quantity of tetrakis(trimethylsilyl)silane as an internal standard, and the equilibrium constant (K_c) determined according to the stoichiometry illustrated in Scheme 2. These data gave ΔH° = −51.3 kJ mol^{-1} and ΔS° = −134 J mol^{-1} for the forward process depicted in Scheme 2 allowing ΔG°(298 K) to be calculated as −11.4 kJ mol^{-1}. Although interpretation of this latter value remains difficult as it requires deconvolution of the protonolysis and dimerization reactions, the negative Gibbs' free energy is consistent with the facile reaction of **1** with amines at room temperature and fast, but reversible, pre-catalyst intiation observed in intramolecular hydroamination catalysis.

Conclusions

This series of experiments demonstrated several important features of catalyst initiation for group 2-mediated hydroamination catalysis: (i) σ-Bond metathesis reactions of amines with **1** or **3** are facile, with the reaction of **1** with benzylamine occurring with a negative Gibbs' free energy of −11.4 kJ mol^{-1} at room temperature; (ii) This reaction may be

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(37) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez C.; Pople, J. A. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

reversible and the potential exists to form equilibrium mixtures of the form $LMX^1 + HX^2/LMX^2 + HX^1$ when the species HX^1 has a pK_a value similar to that of HX^2 (Scheme 2); (iii) In the case of **8** this compound was shown to undergo fast amide/amine exchange in the presence of an excess of benzylamine. Similar site-exchange has been observed by Harder and co-workers in [{ArNC(Me)CHC(Me)NAr}Ca$(NH_2)(NH_3)_2]_2$ (Ar = 2,6-di-iso-propylphenyl);[28] (iv) While the β-diketiminate calcium and magnesium amide reaction products derived from reaction of **1** or **3** with simple linear amines are dimeric in both solution and the solid state, the magnesium analogue **7** only dimerizes upon heating and is monomeric in solution prior to this event; (v) At elevated temperatures and/or over long reaction times the heteroleptic calcium primary amide compounds show a propensity to undergo Schlenk-like equilibria. No such equilibria are observed for magnesium species.

We have recently reported a detailed synthetic study of the catalytic intramolecular hydroamination of aminoalkenes to yield 5-, 6-, and 7-membered heterocyclic products mediated by **1**−**3**.[6f] The model complexes and model reactivity presented herein, provide an important background for, not only observations made during in pre-catalyst initiation, but also discussion of the nuclearity of catalytic species and resting states in solution.

Experimental Section

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of either nitrogen or argon. NMR experiments were conducted in Youngs tap NMR tubes made up and sealed in a Glovebox, NMR spectra were recorded either on a Bruker AV-400 spectrometer at 100.6 MHz (^{13}C), Bruker AV-300 at 75.5 MHz (^{13}C) spectrometer, or a Bruker AV-250 spectrometer at 62.9 MHz (^{13}C). The spectra were referenced relative to residual solvent resonances. Data quoted was recorded at 298 K. Elemental analyses were performed by Stephen Boyer at SACS, London Metropolitan University. Solvents (Toluene, Benzene, THF, Hexane) were dried by distillation from sodium-benzophenone ketyl, under nitrogen and stored in ampoules over molecular sieves. C_6D_6 and d_8-toluene were purchased from Goss Scientific Instruments Ltd. and dried over molten potassium before distilling under nitrogen and storing over molecular sieves. Amines were distilled from CaH_2 and stored in a glovebox. The β-diketiminate ligand precursor [ArNC(Me)CHC(Me)NHAr] and β-diketiminato calcium amide [{ArNC(Me)CHC(Me)NAr}Ca{$N(SiMe_3)_2$}] were synthesized according to the literature procedures.[26,38]

Synthesis of [{ArNC(Me)CHC(Me)NAr}Mg{$NHCH_2Ph$}]$_2$ (4). To a solution of [ArNC(Me)CHC(Me)NHAr] (Ar = 2,6-di-iso-propylphenyl, 1.3 g, 3.11 mmol) in toluene (20 mL) was added $^{n/s}Bu_2Mg$ (1.0 M in heptane, 3.2 mL, 3.2 mmol). The reaction mixture was heated to 50 °C for 1 h, cooled to room temperature and benzylamine (0.3 mL, 3.1 mmol) added neat. After 2 h the product crystallized directly from the reaction mixture, isolation by filtration, and recrystallization from hot toluene solution to give [{ArNC(Me)CHC(Me)NAr}Mg{$NHCH_2Ph$}]$_2$ as a colorless crystalline solid (0.79 g, 0.77 mmol, 47%). ^{1}H NMR (d_8-toluene, 298 K, 400 MHz) −0.52 (dd, 1H, J = 14.2, 2.7 Hz), −0.49 (dd, 1H, J = 14.6, 3.0 Hz), −0.06 (d, 3H, J = 6.9 Hz), 0.00 (d, 3H, J = 6.9 Hz), 0.17 (d, 3H, J = 6.9 Hz), 0.17 (d, 3H, J = 6.9 Hz), 0.25 (d, 3H, J = 6.9 Hz), 0.70 (d, 3H, J = 6.6 Hz), 0.79 (d, 3H, J = 6.6 Hz), 0.83 (d, 3H, J = 6.7 Hz), 0.92 (d, 3H, J = 6.7 Hz), 1.14 (d, 6H, J = 6.8 Hz), 1.17 (d, 3H, J = 6.7 Hz), 1.17 (d, 3H, J = 7.0 Hz), 1.18 (d, 3H, J = 1.18 Hz), 1.19 (d, 3H, J = 6.6 Hz), 1.21 (d, 6H, J = 6.7 Hz), 1.42 (s, 3H), 1.44 (s, 3H), 1.45 (s, 3H), 1.49 (s, 3H), 2.29 (qq, 1H, J = 6.9, 6.6 Hz), 2.47 (qq, 1H, J = 6.9, 6.6 Hz), 2.86 (qq, 1H, J = 6.9, 6.7 Hz), 2.98 (qq, 1H, J = 6.9, 6.7 Hz), 3.27 (qq, 1H, J = 6.8, 6.7 Hz), 3.46−3.68 (m, 3H), 3.87 (ddd, 2H, J = 15.0, 14.6, 3.0 Hz), 4.15 (ddd, 2H, J = 15.0, 14.2, 2.7 Hz), 4.97 (s, 1H), 4.98 (s, 1H), 6.75 (dd, 1H, J = 6.9, 2.3 Hz), 6.83−6.88 (m, 2H), 6.94−7.13 (m, 11H), 7.23−7.28 (m, 4H), 7.48−7.52 (m, 4H); ^{13}C NMR (d_8-toluene, 298 K, 100 MHz) 23.4, 23.9, 24.0, 24.1, 24.2, 24.5, 24.6, 24.7, 24.8, 24.8, 25.2, 25.4 (2 peaks), 25.4, 25.5, 25.5 (2 peaks), 25.6, 25.7, 26.5, 26.7, 27.4, 27.5, 28.6, 29.0, 29.2, 29.5, 29.7, 50.9, 51.2, 96.0 (2 peaks), 124.4, 124.5, 124.6, 124.7, 125.2, 125.3, 125.5, 126.5, 126.6, 126.7, 126.8, 128.1, 128.4, 128.7, 129.2, 129.7, 143.0, 143.1, 143.2, 143.6, 144.5, 144.7, 145.0, 145.1, 147.5, 147.7, 147.8, 148.2, 148.3, 148.0, 169.1, 169.2, 169.3, 169.4; Anal. Calcd for $C_{72}H_{100}Mg_2N_6$: C, 78.74; H, 9.18; N, 7.65; Found: C, 78.68; H, 9.08; N, 7.62.

Synthesis of [{ArNC(Me)CHC(Me)NAr}Mg{$N(CH_2)_4$}]$_2$ (5). To a solution of [ArNC(Me)CHC(Me)NHAr] (Ar = 2,6-di-iso-propylphenyl, 1.3 g, 3.11 mmol) in toluene (20 mL) was added $^{n/s}Bu_2Mg$ (1.0 M in heptane, 3.2 mL, 3.2 mmol). The reaction mixture was heated to 50 °C for 1 h, cooled to room temperature, and pyrrolidine (0.25 g, 3.1 mmol) added neat. After 1 h, upon cooling to room temperature and storage at 5 °C the product crystallized directly from the reaction mixture, isolation by filtration, and recrystallization from hot toluene solution to give [{ArNC(Me)CHC(Me)NAr}Mg{$N(CH_2)_4$}]$_2$ as a colorless crystalline solid (0.50 g, 0.46 mmol, 30%). ^{1}H NMR (d_8-toluene, 298 K, 400 MHz) 0.47 (d, 6H, J = 6.8 Hz), 1.01 (d, 6H, J = 6.4 Hz), 1.17 (d, 6H, J = 6.8 Hz), 1.41 (d, 6H, J = 6.4 Hz), 1.52 (s, 6H), 2.44 (broad m, 2H), 2.94 (hept, 2H, J = 6.8 Hz), 3.00 (broad m, 2H), 3.35 (hept, 2H, J = 6.4 Hz), 4.56 (s, 1H), 6.97−7.11 (m, 6H); ^{13}C NMR (d_8-toluene, 298 K, 100 MHz) 24.4, 25.9, 26.2, 26.7, 26.8, 27.6, 27.6, 30.0, 51.9, 94.5, 123.8, 125.7, 126.1, 129.1, 129.8, 143.5, 144.3, 148.2, 169.4; Anal. Calcd for $C_{72}H_{100}Mg_2N_6$: C, 77.25; H, 9.82; N, 8.19; Found: C, 77.23; H, 9.77; N, 8.25.

Synthesis of [{ArNC(Me)CHC(Me)NAr}Mg{$NH(CH_2)_2OMe$}]$_2$ (6). To a solution of [ArNC(Me)CHC(Me)NHAr] (Ar = 2,6-di-iso-propylphenyl, 1.3 g, 3.11 mmol) in toluene (20 mL) was added $^{n/s}Bu_2Mg$ (1.0 M in heptane, 3.2 mL, 3.2 mmol). The reaction mixture was heated to 50 °C for 1 h, cooled to room temperature and pyrrolidine (0.226 g, 3.18 mmol) added neat. After 2 h the product crystallized directly from the reaction mixture, isolation by filtration, and recrystallization from hot toluene solution to give [{ArNC(Me)CHC(Me)NAr}Mg{$N(CH_2)_2OMe$}]$_2$ as a colorless crystalline solid (0.50 g, 0.75 mmol, 48%). Because of the extremely low solubility of this compound in toluene, benzene, and DMSO multinuclear NMR data has not been acquired. Anal. Calcd for $C_{72}H_{100}Mg_2N_6$: C, 77.25; H, 9.82; N, 8.19; Found: C, 77.23; H, 9.77; N, 8.25.

Synthesis of [{ArNC(Me)CHC(Me)NAr}Mg{NC_4H_4(2-Me)(4,4′-Ph_2)}] (7). Method A. To a solution of [ArNC(Me)CHC(Me)NHAr] (Ar = 2,6-di-iso-propylphenyl, 1.3 g, 3.11 mmol) in toluene (20 mL) was added $^{n/s}Bu_2Mg$ (1.0 M in heptane, 3.2 mL, 3.2 mmol). The reaction mixture was heated to 50 °C for 1 h, cooled to room temperature, and 2-methyl-4,4-diphenylpyrrolidine (0.5 g, 3.1 mmol) added as a solution in toluene (10 mL). The reaction mixture was heated to 80 °C overnight. Following cooling to room temperature the solvent volume was reduced to 5 mL in vacuo;

(38) Stender, M.; Wright, R. J.; Eichler, B. E.; Prust, J.; Olmstead, M. M.; Roesky, H. W.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **2001**, 3465.

this solution was layered with hexane (20 mL) and left overnight, giving the product **7** as a colorless crystalline solid (1.05 g, 0.80 mmol, 52%). ^{1}H NMR (C_6D_6, 298 K, 400 MHz) −0.26 (d, 3H, J = 6.7 Hz), 0.76 (d, 3H, J = 6.7 Hz), 1.00 (d, 3H, J = 6.7 Hz), 1.05−1.28 (m, 12H), 1.15 (d, 3H, J = 6.9 Hz), 1.16−1.26 (m, 18H), 1.31 (d, 3H, J = 6.8 Hz), 1.39−1.41 (m, 6H), 1.40 (d, 1H, J = 15.5 Hz), 1.48 (s, 3H), 1.50−1.54 (m, 2H), 1.53 (s, 3H), 1.55 (s, 3H), 1.57 (s, 3H), 1.60−1.63 (m, 2H), 1.62 (s, 3H), 1.89 (broad m, 1H), 1.99 (d, 1H, J = 15.5 Hz), 2.76−2.84 (m, 2H), 3.26 (broad m, 1H), 3.26−3.44 (m, 4H), 3.52 (qq, 1H, J = 6.6 Hz), 3.64 (qq, 1H, J = 6.7 Hz), 3.70 (d, 1H, J = 12.0 Hz), 4.09 (d, 1H, J = 12.0 Hz), 4.77 (s, 1H), 4.82 (s, 1H), 6.45−6.47 (m, 2H), 6.72−6.74 (m, 1H), 6.84−6.92 (m, 4H), 7.00−7.24 (m, 15H); ^{13}C NMR (C_6D_6, 298 K, 100 MHz) 22.0, 23.0, 23.4 (2 signals), 23.6, 24.1, 24.2, 24.4, 24.5, 24.7 (2 signals) 24.8, 25.1 (2 signals) 25.3, 25.5, 26.9, 27.2, 27.6 (2 signals), 27.7, 28.5, 28.6, 28.7, 29.2, 29.6, 29.8, 31.9, 37.5, 50.4, 54.9, 68.7, 95.5, 96.1, 123.4, 123.5, 123.6, 124.0, 124.5, 124.8, 124.9, 125.2, 125.4, 125.5, 125.6 (2 signals), 126.4, 126.6, 127.8, 128.0, 128.2, 128.6, 128.8, 129.3, 141.9, 142.3, 142.5, 142.7, 143.2, 143.5, 143.6, 144.1, 145.7, 146.3, 146.7, 146.9, 147.0, 150.3, 168.0, 168.5, 168.6, 169.4, 189.9. Anal. Calcd for $C_{46}H_{59Mg}N_3$: C, 81.45; H, 8.77; N, 6.20; Found: C, 81.37; H, 8.62; N, 6.13.

Method B. In a glovebox, a solution of 2-methyl-4,4-diphenylpyrrolidine (50 mg, 0.31 mmol) in C_6D_6 was added to a solution of [{ArNC(Me)CHC(Me)NAr}Mg($^{n/s}$Bu)] (154 mg, 0.31 mmol). The reaction mixture was transferred to an NMR tube, removed from the glovebox, loaded into an NMR spectrometer, and monitored by ^{1}H NMR spectroscopy. In situ data from NMR scale reaction: ^{1}H NMR (C_6D_6, 298 K, 400 MHz) 0.48 (d, 3H, J = 6.0 Hz), 1.17 (d, 6H, J = 6.9 Hz), 1.20 (d, 6H, J = 6.9 Hz), 1.23 (d, 6H, J = 6.9 Hz), 1.28 (d, 6H, J = 6.9 Hz), 1.72 (s, 6H), 1.78 (dd, 1H, J = 11.8, 8.6 Hz), 2.32 (dd, 1H, J = 11.8, 6.0 Hz), 3.09−3.21 (m, 6H), 3.46 (dq, 1H, J = 8.6, 6.0 Hz), 4.95 (s, 1H), 7.04−7.27 (m, 16H); ^{13}C NMR (C_6D_6, 298 K, 100 MHz) 23.0, 23.3, 23.5, 23.6, 23.6, 24.0, 24.5, 24.6, 24.9, 25.1, 28.7, 28.8, 49.8, 57.6, 58.1, 65.1, 94.9, 124.3, 124.4, 125.1, 125.2, 126.0, 127.6, 127.7, 128.1, 128.3, 141.8, 141.9, 144.0, 151.0, 151.4, 169.8.

Synthesis of [{ArNC(Me)CHC(Me)NAr}Ca{NHCH$_2$Ph}]$_2$ (8). To a solution of **1** (0.5 g, 0.74 mmol) in hexane (15 mL) was added a solution of benzylamine (79 μL, 0.74 mmol) in hexane (10 mL). The resulting reaction mixture immediately turned red and demonstrated an, as yet, unexplained, thermochromism. After 15 min, concentration of the solution to about 20 mL at room temperature yielded colorless crystals of the title compound (99 mg, 0.088 mmol, 24%). ^{1}H NMR (C_6D_6, 298 K, 400 MHz) −0.45 (broad s, 1H), 1.00 (d, 12H, J = 6.8 Hz), 1.15 (d, 12H, J = 6.4 Hz), 1.68 (s, 6H), 3.11 (hept, 4H, J = 6.8 Hz), 3.88 (broad s, 2H), 4.89 (s, 1H), 7.10−7.35 (m, 11 H); ^{13}C NMR (C_6D_6, 298 K) 24.4, 24.6, 25.2, 28.4, 51.6, 94.1, 124.0, 124.5, 126.1, 126.8, 129.3, 141.8, 146.4, 166.2; Anal. Calcd for $C_{72}H_{98}Ca_2N_6$: C, 76.61; H, 8.69; N, 7.45; Found: C, 76.00; H, 8.85; N, 7.33.

Molecular Volume Calculations. Solid state molecular volumes of compounds **1**, **8**, and **9** (Table 3) were estimated by single point calculations employing the solid-state crystallographic coordinates through use of the "volume" keyword in the Gaussian03 suite of programs at the default Hartree−Fock (3-21G) level.[37] A hydrodynamic radius was determined through an assumption that the tumbling molecules are "spherical" (i.e., volume = $4/3\pi r^3$) with regard to their apparent radii in solution.

Crystallographic Data. Data for **4**, **5**, **6**, and **8** were collected at 150 K on a Nonius KappaCCD diffractometer, [λ($Mo_{k\alpha}$) = 0.71073 Å], solved by direct methods and refined against all F^2 using SHELXL-97 with non-hydrogen atoms anisotropic and hydrogen atoms in riding mode.[39] For all four structures a semiempirical absorption correction was applied.

For **4** the asymmetric unit consisted of half of a dimeric molecule, proximate to a crystallographic inversion center. The hydrogen atom attached to N3 was located and refined at 0.90 Å from the parent atom.

The asymmetric unit in **5** also consisted of one half of a dimer, which straddled a crystallographic 2-fold rotation axis, plus one half of a toluene molecule. In the fragment of lattice solvent, two phenyl ring carbons and the methyl group lie on a 2-fold rotation axis. Hydrogens included for this methyl carbon are at calculated positions and 1/2 site-occupancy, which necessarily means that this group is disordered throughout the crystal.

In **6** the asymmetric unit comprises two crystallographically independent dimer halves, each proximate to an inversion center, plus one molecule of toluene. N3/N3A and N4/N4A represent 55:45 disorder over two sites for the NH groups. The associated partial hydrogens could not be reliably located and hence were omitted from the refinement. Mg−N and N−C distances were restrained to being similar within each dimer half. These similarity restraints were not used universally for both dimers because of the evident differences in the Mg−O(ligand) distances. The solvent molecule was also disordered over two sites, again in a 55:45 ratio. Rings therein were treated as regular hexagons, and some distance restraints were employed in relation to the C(methyl)−C(ring) distances.

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Supporting Information Available: Crystallographic information files (CIF) for **4**, **5**, **6**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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