Synthesis and M−C_γ Hemilability of Group 2 Bis(phosphinimino)methanides

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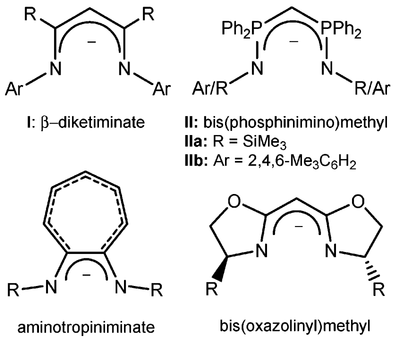
Received September 19, 2005

The sterically demanding bis(phosphinimino)methanide $[CH(Ph_2PNC_6H_2\text{-}2,4,6\text{-}Me_3)_2]^-$, formed by deprotonation of the bis(phosphinimino)methane $[CH_2(Ph_2PNC_6H_2\text{-}2,4,6\text{-}Me_3)_2]$, has been employed in the synthesis of a variety of homo- and heteroleptic complexes of the group 2 metals Mg, Ca, Sr, and Ba. The crystallographically characterized magnesium complexes, the dimer $[\{CH(Ph_2PNC_6H_2\text{-}2,4,6\text{-}Me_3)_2\}MgCl]_2$ and the monomer $[\{CH(Ph_2PNC_6H_2\text{-}2,4,6\text{-}Me_3)_2\}MgCl(THF)]$, were synthesized in a similar manner by deprotonation of the ligand precursor with MeMgCl but crystallized either without or in the presence of THF. The synthetically useful $[\{CH(Ph_2PNC_6H_2\text{-}2,4,6\text{-}Me_3)_2\}K]$, formed from $[CH_2(Ph_2PNC_6H_2\text{-}2,4,6\text{-}Me_3)_2]$ and $[KN(SiMe_3)_2]$ in toluene, was shown in the solid state to consist of dimeric species formed by K-mesityl multihapto interactions. Homoleptic $[\{CH(Ph_2PNC_6H_2\text{-}2,4,6\text{-}Me_3)_2\}_2Ae]$ (Ae = Ca and Ba) and heteroleptic $[\{CH(Ph_2PNC_6H_2\text{-}2,4,6\text{-}Me_3)_2\}AeN(SiMe_3)_2(THF)]$ (Ae = Ca, Sr) complexes of the heavier alkaline earth metals Ca, Sr, and Ba were most readily provided by a "one-pot" procedure utilizing the appropriate AeI_2 reagent and variation of $[CH_2(Ph_2PNC_6H_2\text{-}2,4,6\text{-}Me_3)_2]$ and $[KN(SiMe_3)_2]$ stoichiometry in THF. The complexes were shown by $^{31}P\{^1H\}$ NMR to adopt variable and hemilabile ($\Delta G^\ddagger$ = ca. 50 kJ mol^{-1}) coordination geometries involving, most likely, M−C_γ coordination and re-coordination. The ionic nature of the bonding was also implicated in our lack of success in the application of these complexes in reactivity studies with a variety of bulky protic reagents. This behavior was investigated by DFT (B3LYP/LANL2DZ) methods to highlight the differences in NBO charge distribution between model ionic bis(phosphinimino)methanide and β-diketiminato complexes.

Introduction

Numerous recent advances in coordination chemistry and catalysis have been dependent upon the application of stable N,N-bidentate monoanions (Chart 1). Especially prominent among these ligands have been variations upon the β-diketiminato framework, **I**, which has proved to be extraordinarily amenable to precise adjustment of steric demands and charge donation.[1] Indeed our own research has employed a variety of β-diketiminates to explore unusual catalytic reactivity and bonding patterns within the heavier s- and p-block metals.[2−6] A topological relationship to the β-diketiminates has led a number of groups to explore ligands derived from the bis(phosphinimino)methanide framework, **II**, which offer apparently similar potential for kinetic and electronic tuning about a chelated metal center.[7−9] Despite similarities in charge, potential denticity, donor identity, and steric demands, the data available for this class of ligand have highlighted some notable contrasts in the provision of the coordination environment. Most evident is the frequent adoption of a twist boat conformation and a pronounced interaction between the metal center and the methanide (C_γ) carbon (Figure 1). A range of derivatives of the silyl-substituted monoanion, **IIa**, have been reported, while

Chart 1



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(1) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031.

(2) (a) Avent, A. G.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B. *Dalton Trans.* **2004**, 3166. (b) Avent, A. G.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B. *Dalton Trans.* **2005**, 278.

(3) Avent, A. G.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B. *Organometallics* **2005**, *24*, 1184.

(4) Crimmin, M. R.; Casely, I. J.; Hill, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 2042.

(5) (a) Hill, M. S.; Hitchcock, P. B. *Chem. Commun.* **2004**, 1818. (b) Hill, M. S.; Hitchcock, P. B.; Pongtavornpinyo, R. *Dalton Trans.* **2005**, 273.

(6) Hill, M. S.; Hitchcock, P. B.; Pongtavornpinyo, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 4231.

(7) Examples of s-block bis(phosphinimino)methanide complexes: (a) Gamer, M. T.; Roesky, P. W. *Z. Anorg. Allg. Chem.* **2001**, *627*, 877. (b) Babu, R. P. K.; Kasani, A.; McDonald, R.; Cavell, R. G. *Inorg. Chem.* **2000**, *39*, 4981. (c) Babu, R. P. K.; Kasani, A.; McDonald, R.; Cavell, R. G. *Organometallics* **2001**, *20*, 1451. (d) Wei, P.; Stephan, D. *Organometallics* **2003**, *22*, 601. (e) Hill, M. S.; Hitchcock, P. B. *Chem. Commun.* **2003**, 1758. (f) Panda, T. K.; Zulys, A.; Gamer, M. T.; Roesky, P. W. *J. Organomet. Chem.* **2005**, *690*, 5078.

(8) Examples of p-block bis(phosphinimino)methanide complexes: (a) Aparna, K.; McDonald, R.; Ferguson, M.; Cavell, R. G. *Organometallics* **1999**, *18*, 4241. (b) Hill, M. S.; Hitchcock, P. B.; Karagouni, S. M. A. *J. Organomet. Chem.* **2004**, *689*, 722.

10.1021/om050811h CCC: $33.50

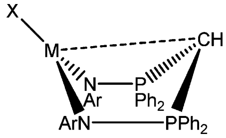

Figure 1.

Cavell has exploited the possibility of further deprotonation of this species in the isolation of a variety of methanediide complexes.[10] Our own work has concentrated upon N-aryl-substituted variants, such as the mesityl derivative **IIb**.[9h,i] We have noted that occurrence of either η^2- or η^3-coordination is subtly dependent upon both the identity of the metal center and the nature and disposition of the co-ligands. Caulton has made a similar observation with regard to Ru(II) chemistry and has indicated that the existence of a pronounced transannular $M\cdots C_\gamma$ interaction designates compounds containing this class of ligand as true organometallic derivatives and places these ligands within a similar category as other heteroatom (e.g., Si, S)-substituted methanides.[9k] This pronounced carbanionic character clearly discriminates the bis(phosphinimino)methanides from the β-diketiminates, where distortion of chelate ring planarity most commonly occurs by an out-of plane folding of the ligated metal from the coordination plane while the planarity of the (exclusively sp^2 hybridized) NCCCN chelate is maintained.[11] Although the seemingly facile annihilation of the $M-C_\gamma$ interaction hints at an intriguing possibility for a "methyl hemilability", we have found that a consequent increase in the basicity and nucleophilicity of C_γ also mitigates against more extensive application of bis(phospinimino)methanide ligands as supporting environments in a catalytic and synthetic context. This submission presents a complete account of our studies of these ligands for the preparation of derivatives of the group 2 metals.[7e] Related compounds supported by stable β-diketiminato ligation have provided a starting point for many of our recent explorations of novel heteroleptic group 2 species and our demonstration of calcium-mediated hydroamination catalysis.[2−4] Others have reported the properties of homoleptic β-diketiminato species as promisingly robust and volatile precursors for the chemical vapor deposition of alkaline earth materials.[12,13] We also therefore present a critique of the potential of bis(phosphinimino)methanides to provide comparable supporting ligation in the exploration of novel group 2 reaction chemistry.

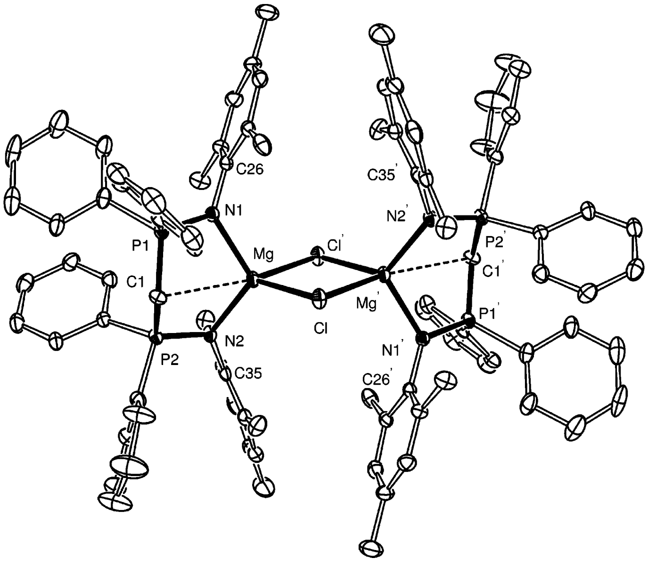

Figure 2. ORTEP drawing (30% ellipsoids) of the dimeric structure of compound **2a**. Hydrogen atoms are omitted for clarity.

Results and Discussion

The synthesis of the homoleptic compounds **3**, **4**, and **5** and the heteroleptic compounds **2**, **6**, and **7** was straightforward and involved either the metalation of the *N*-mesityl bis(phosphinimino)methane, **1**, with a single equivalent of MeMgCl (**2a**,**b**) or in situ metalation of **1** by potassium bis(trimethylsilyl)amide (to form the potassium derivative **3**) and metathesis with the appropriate alkaline earth iodide (Scheme 1) in THF. For the heteroleptic bis(trimethylsilyl)amides, **6** and **7**, the synthesis was carried out in a 1:1 stoichiometry and in the presence of a further reacting equivalent of potassium bis(trimethylsilyl)amide. All compounds with the exception of **2b** (vide infra) were crystallized from toluene solution and isolated as colorless or pale yellow crystalline materials.

The constitution of the magnesium chloride complex, **2**, was found to be dependent upon the conditions employed during the synthesis and the solvent system selected for crystallization. The reaction of **1** and a 1.0 M solution of MeMgCl performed entirely in toluene resulted in the production of methane and isolation of the solvent-free dimer **2a**. Addition of THF and crystallization from a toluene/THF mixture provided X-ray quality crystals of the THF-coordinated monomer **2b**. This latter complex, once crystallized, is only sparingly soluble in aromatic hydrocarbons. For this reason the NMR spectroscopic data listed in the Experimental Section refer exclusively to **2a**. We interpret this observation to reflect the maintenance of the more lipophilic dimeric structure in noncoordinating solvents. Similar variability in the constitution of magnesium halide derivatives of **IIb** was noted in the only previous report of magnesium bis(phosphinimino)methanides.[7d] The NMR spectroscopic data for **1a** at 298 K are comparable to those of the similarly dimeric [**IIa**Mg(μ-Cl)]$_2$ and are consistent with retention of the C_2-symmetric dimer on the NMR time scale. The results of an X-ray diffraction analysis performed on **2a** are illustrated in Figure 2, while details of the analysis and selected bond length and angle data are presented in Tables 1, 2, and 3, respectively.

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(9) Examples of d-block bis(phosphinimino)methanide complexes: (a) Katti, K. V.; Seseke, U.; Roesky, H. W. *Inorg. Chem.* **1987**, *26*, 814. (b) Imhoff, P.; Elsevier, C. J. *J. Organomet. Chem.* **1989**, *361*, C61. (c) Imhoff, P.; Guelpen, G. H.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L.; Elsevier, C. J. *Inorg. Chim. Acta* **1995**, *235*, 77. (d) Imhoff, P.; Van Asselt, R.; Elsevier, C. J.; Zoutberg, M. C.; Stam, C. H. *Inorg. Chim. Acta* **1991**, *184*, 73. (e) Avis, M. W.; Elsevier, C. J.; Veldman, N.; Koojiman, H.; Spek, A. L. *Inorg. Chem.* **1996**, *35*, 1518. (f) Kasani, A.; Babu, R. P. K.; McDonald, R.; Cavell, R. G. *Organometallics* **1999**, *18*, 3775. (g) Al-Benna, S.; Sarsfield, M. J.; Thornton-Pett, M.; Ormsby, D. L.; Maddox, P. J.; Brès, P.; Bochmann, M. *Chem. Soc., Dalton Trans.* **2000**, 4247. (h) Hill, M. S.; Hitchcock, P. B. *J. Chem. Soc., Dalton Trans.* **2002**, 4694. (i) Evans, D. J.; Hill, M. S.; Hitchcock, P. B. *Dalton Trans.* **2003**, 570. (j) Wei, P.; Stephan, D. *Organometallics* **2002**, *21*, 1308. (k) Bibal, C.; Pink, M.; Smurnyy, Y. D.; Tomaszewski, J.; Caulton, K. G. *J. Am. Chem. Soc.* **2004**, *126*, 2312.

(10) Review: Cavell, R. G.; Babu, R. P. K.; Aparna, K. *J. Organomet. Chem.* **2001**, *617*, 158.

(11) Although related distortions from planarity have been observed in a number of β-diketiminato complexes (see ref 1 for a general discussion and ref 12 for examples from heavier alkaline earth chemistry), this behavior is considerably more pronounced in the bis(phopsphinimino)methanides. For example, the compounds reported in ref 12 are described as η^5- with short contacts to all three carbon centers in the ligand "backbone". This is ostensibly not the case in the bis(phopsphinimino)methanides, where the distortion at the P(V) centers is markedly more pronounced (angles between the PCP and NPPN planes ca. 72° versus ca. 25° for the CCC and NCCN planes).

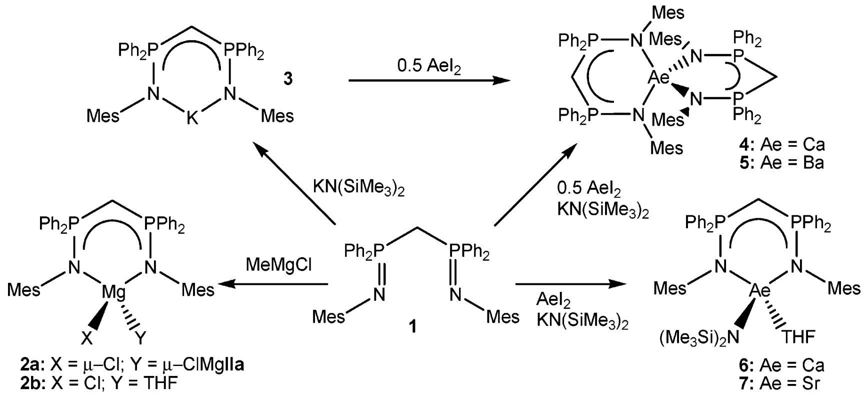
(12) El-Kaderi, H. M.; Heeg, M. J.; Winter, C. H. *Organometallics* **2004**, *23*, 4995.

(13) (a) Chisholm, M. H.; Gallucci J.; Phomphrai, K. *Chem., Commun.* **2003**, 48. (b) Chisholm, M. H.; Gallucci J.; Phomphrai, K. *Inorg. Chem.* **2004**, *43*, 6717. (c) Harder, S. *Organometallics* **2002**, *21*, 3782.

Table 1. Selected Crystallographic and Data Collection Parameters for Compounds 2a, 2b, 4, 6, and 7

	2a	**2b**	**5**	**6**	**7**
chemical formula	$C_{86}H_{86}Cl_2Mg_2N_4P_4{\cdot}2(C_7H_8)$	$C_{47}H_{51}ClMgN_2OP_2{\cdot}(C_7H_8)$	$C_{86}H_{86}BaN_4P_4{\cdot}0.5(C_7H_8)$	$C_{53}H_{69}CaN_3OP_2Si_2$	$C_{53}H_{69}N_3OP_2Si_2Sr$
fw	1603.26	873.73	1482.88	922.31	969.85
T (K)	173(2)	173(2)	173(2)	173(2)	173(2)
cryst size (mm^3)	0.2 × 0.1 × 0.1	0.30 × 0.15 × 0.15	0.1 × 0.1 × 0.1	0.30 × 0.05 × 0.05	0.2 × 0.1 × 0.1
cryst syst	monoclinic	tetragonal	triclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$I\bar{4}$ (No.82)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	12.0127(3)	30.8401(2)	13.0294(2)	12.6861(6)	12.7105(1)
b (Å)	11.8443(3)	30.8401(2)	13.3312(2)	22.9406(11)	23.1523(2)
c (Å)	30.8127(8)	10.2288(1)	25.5773(4)	18.2982(10)	18.4217(1)
α (deg)	90	90	100.566(1)	90	90
β (deg)	96.916(1)	90	92.303(1)	104.334(2)	104.566(3)
γ (deg)	90	90	118.149(1)	90	90
Z	2	8	2	4	4
V (Å^3)	4352.2(2)	9728.73(13)	3809.47(10)	5159.5(4)	5246.85(7))
d_c (Mg m^{-3})	1.22	1.19	1.29	1.19	1.23
μ (mm^{-1})	0.21	0.20	0.65	0.27	1.17
θ range (deg)	3.75 to 23.02	3.74 to 27.51	3.72 to 27.53	3.73 to 23.03	3.75 to 27.48
R1; wR2 [$I > 2\sigma(I)$]	0.051, 0.105	0.038, 0.083	0.047, 0.088	0.089, 0.142	0.039, 0.082
R1; wR2 all data	0.076, 0.115	0.047, 0.087	0.080, 0.098	0.174, 0.172	0.056, 0.089
no. of measd/indep rflns/R(int)	17 213/5578/0.062	61 840/11 117/0.064	45 010/17 111/0.063	28 754/7073/0.226	66 071/11 945/0.057
no. of rflns with $I > 2\sigma(I)$	4307	9918	12 563	4054	9793

Scheme 1



Compound **2a** crystallized as a bis-toluene-solvated centrosymmetric dimer from toluene solution containing a small quantity of residual diethyl ether that was introduced during the synthesis. The most notable contrast within the structure of **2a** to that of the previously reported [**IIa**Mg(μ-Cl)]$_2$ is provided by the Mg−C(1) distance of 2.787(3) Å, which represents a lengthening of some 13% in comparison to that observed in the N-silylated analogue [2.460(8) Å]. We interpret this variability as a reflection of the hemilability of the highly polarized covalent C_γ−Mg interaction and to indicate that relatively subtle factors, such as crystal-packing effects and the relative delocalization of anionic charge into the respective mesityl versus trimethylsilyl nitrogen substituents, are responsible for the ligand binding mode observed in the solid-state structures of these group 2 derivatives (vide infra). As a result of this weakened interaction, the Mg−N [2.067(3), 2.070(3) Å] and Mg−Cl [2.415(2), 2.438(2) Å] bond lengths in **2a** are significantly shorter than the respective distances in its N-trimethylsilyl-substituted analogue [Mg−N 2.104(7), 2.163(7) Å; Mg−Cl 2.427(3) Å; Mg−Cl′ 2.440(3) Å].

Table 2. Selected Bond Lengths (Å) for Compounds 2a, 2b, 5, 6, and 7

	2a[a]	**2b**	**5**[c]	**6**[d]	**7**[e]
M−N(1)	2.067(3)	2.045(2)	2.768(2)	2.411(6)	2.5557(17)
M−N(2)	2.070(3)	2.040(2)	2.736(2)	2.467(6)	2.5951(17)
M−Cl/N(3)	2.415(1)[b]	2.315(1)		2.331(6)	2.4740(18)
M−O		2.028(2)		2.433(5)	
M−C(1)	2.787(3)	3.059		2.713(7)	2.861(2)
P(1)−N(1)	1.617(3)	1.618(2)	1.612(2)	1.609(5)	1.6042(17)
P(1)−C(1)	1.706(3)	1.715(2)	1.713(3)	1.733(6)	1.740(2)
P(1)−C(8)	1.821(3)	1.833(2)	1.823(3)	1.807(7)	1.823(2)
P(1)−C(2)	1.824(3)	1.831(2)	1.822(3)	1.830(7)	1.828(2)
P(2)−N(2)	1.624(3)	1.625(2)	1.609(2)	1.601(5)	1.6048(17)
P(2)−C(1)	1.714(3)	1.715(2)	1.708(3)	1.702(7)	1.725(2)
P(2)−C(14)	1.810(4)	1.831(2)	1.838(3)	1.821(6)	1.823(2)
P(2)−C(20)	1.825(3)	1.831(2)	1.841(3)	1.818(6)	1.831(2)
N(1)−C(26)	1.436(4)	1.439(2)	1.410(4)	1.444(8)	1.422(3)
N(2)−C(35)	1.447(4)	1.438(2)	1.431(4)	1.415(8)	1.413(3)

[a] Symmetry transformations used to generate equivalent atoms: $-x+1$, $-y+1$, $-z+1$. [b] Mg−Cl′ 2.4375(13). [c] Ba−N(3) 2.756(2), Ba−N(4) 2.754(2), P(3)−N(3) 1.604(3), P(3)−C(44) 1.722(3), P(3)−C(51) 1.818(3), P(3)−C(45) 1.825(3), N(3)−C(69) 1.417(4), P(4)−N(4) 1.602(2), P(4)−C(44) 1.702(3), P(4)−C(57) 1.817(3), P(4)−C(63) 1.835(3), N(4)−C(78) 1.424(4). [d] Si(1)−N(3) 1.693(6), Si(2)−N(3) 1.691(6). [e] Si(1)−N(3) 1.6866(19), Si(2)−N(3) 1.6868(19).

A view of the structure of the THF-solvated monomer **2b** is illustrated in Figure 3. It is clearly apparent that the bis(phosphinimino)methanide adopts a much less pronounced boat configuration than was the case in the previously described chloro-bridged dimers. The Mg−Cγ distance [3.059 Å] is considerably elongated in comparison with that of **2b**, such that the ligand is best described as providing (NN) η^2-coordination. Stephan has previously attributed the (NCN) η^3-coordination mode observed in both mono- and dinuclear magnesium complexes of **IIa** to the Lewis acidity of the metal center.[7d] Although the pseudo-boat conformation of the ligand is retained in all of the current complexes, it is again apparent that relatively

Table 3. Selected Bond Angles (deg) for Compounds 2a, 2b, 5, 6, and 7

	2a[a]	**2b**[b]	**5**[c]	**6**[d]	**7**[e]
N(1)−M−N(2)	113.44(11)	110.07(7)	89.30(7)	103.31(18)	98.97(5)
P(1)−C(1)−P(2)	130.9(2)	138.09(12)	131.40(17)	133.2(4)	132.11(12)
N(1)−P(1)−C(1)	107.60(15)	110.09(8)	119.55(13)	107.4(3)	108.94(9)
N(1)−P(1)−C(8)	112.25(15)	114.56(8)	107.41(13)	114.3(3)	113.57(9)
C(1)−P(1)−C(8)	114.66(17)	102.89(9)	108.14(14)	107.5(3)	106.28(9)
N(1)−P(1)−C(2)	118.55(14)	111.57(8)	110.12(13)	111.9(3)	111.90(9)
C(1)−P(1)−C(2)	101.84(16)	114.89(9)	108.46(13)	111.8(3)	112.36(10)
C(8)−P(1)−C(2)	101.76(16)	102.48(8)	101.66(12)	104.0(3)	103.64(10)
N(2)−P(2)−C(1)	108.27(15)	111.27(8)	112.68(13)	106.6(3)	108.21(9)
N(2)−P(2)−C(14)	114.36(15)	116.08(8)	111.15(12)	114.7(3)	114.50(9)
C(1)−P(2)−C(14)	107.10(16)	100.40(9)	113.95(14)	112.4(3)	112.56(10)
N(2)−P(2)−C(20)	113.21(14)	107.97(8)	116.10(13)	116.5(3)	115.65(9)
C(1)−P(2)−C(20)	110.59(16)	118.07(9)	101.50(13)	103.8(3)	102.42(9)
C(14)−P(2)−C(20)	103.11(16)	102.98(9)	100.67(13)	102.4(3)	102.92(9)

[a] N(1)−Mg−Cl 111.97(9), N(2)−Mg−Cl 122.86(9), N(1)−Mg−Cl′ 107.88(8), N(2)−Mg−Cl′ 107.55(9), Cl−Mg−Cl′ 89.25(4), Mg−Cl−Mg′ 90.75(4). [b] O−Mg−N(2) 105.97(8), O−Mg−N(1) 102.95(7), O−Mg−Cl 102.38, N(2)−Mg−Cl 115.87(6), N(1)−Mg−Cl 117.67(6). [c] N(2)−Ba−N(4) 126.95(7), N(2)−Ba−N(3) 110.86(7), N(4)−Ba−N(3) 96.10(7), N(4)−Ba−N(1) 114.74(7), N(3)−Ba−N(1) 121.45(7). [d] N(3)−Ca−N(1) 133.1(2), N(3)−Ca−O 94.80(19), N(1)−Ca−O 84.86(18), N(3)−Ca−N(2) 109.68(19). [e] N(3)−Sr−N(1) 132.85(6), N(3)−Sr−O 96.72(6), N(1)−Sr−O 85.99(6), N(3)−Sr−N(2) 109.74(6).

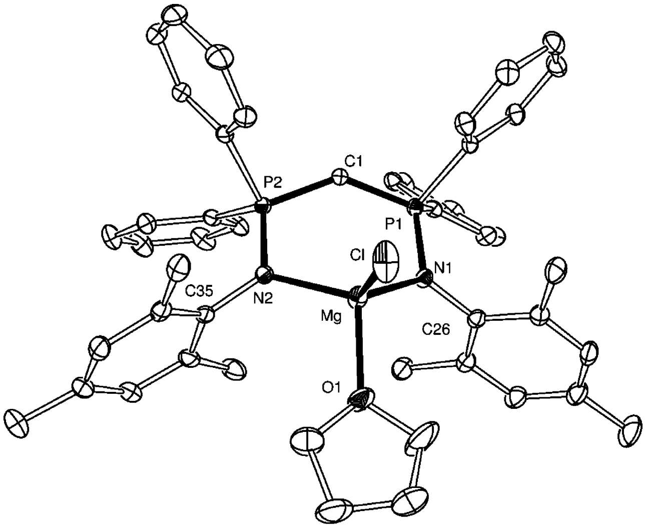


Figure 3. ORTEP drawing (30% ellipsoids) of compound **2b**. Hydrogen atoms are omitted for clarity.

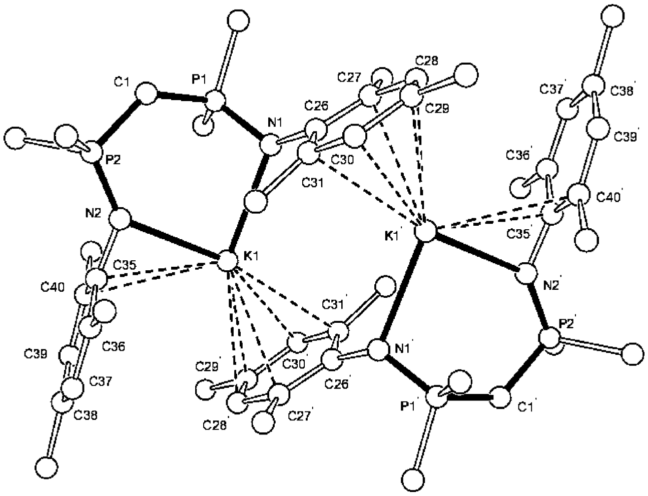


Figure 4. Ball-and-stick drawing of one of the dimeric molecules within the structure of compound **3**. All P-phenyl carbons (except *ipso*-C) and hydrogen atoms are omitted for clarity.

minor perturbation to the coordination environment is responsible for significant reorganization of the ligand conformation in the crystalline state.

Successful synthetic approaches to organometallic derivatives of the heavier alkaline earth metals are commonly dependent upon clean KI elimination from a group 2 iodide and a potassium derivative of an organometallic anion.[4] Addition of a single equivalent of potassium bis(trimethylsilyl)amide in toluene to **1** resulted in the formation of the potassium bis(phosphinimino)methanide, compound **3**. Slow cooling of a concentrated toluene solution of **3** provided large, colorless, and analytically pure crystals suitable for an X-ray diffraction analysis. Although the crystals appeared to be well formed, they diffracted only weakly and refinement was hampered by the presence of three poorly defined and disordered molecules of toluene. The results, however, were unambiguous and revealed that **3**, in contrast to the only previously reported potassium bis(phophinimino)methanides, the “loose” dimer [K{CH(PPh$_2$-NSiMe$_3$)$_2$}] formed via long [>3 Å] K−N contacts and the monomeric THF-solvate [(THF)$_2$K{CH(PPh$_2$NSiMe$_3$)$_2$}],[7c,f] dimerizes via η^6-K−aryl interactions between the N1N2-chelated potassium center and the N1-bound mesityl group ring of an adjacent chelate ligand (Figure 4).[15]

Variable-temperature NMR studies in d_8-toluene provided evidence for likely dynamic behavior in solution. At 298 K the observed ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR spectra of **3** were entirely consistent with a C_2-symmetric formulation. The ^{1}H NMR assignments of the P-phenyl and N-mesityl methine protons listed in the Experimental Section were confirmed by irradiation of the various aromatic signals and NOE difference spectra. At 298 K the ^{31}P{^{1}H} NMR spectrum consisted of a single resonance at 16.2 ppm. As the temperature was reduced below ca. 230 K, however, this signal first broadened and then spilt into an AX pattern of two resonances in a 1:1 ratio of intensity centered at 16.5 and 15.1 ppm. At 203 K these resonances were sufficiently well resolved to observe a homonuclear $^2J_{PP}$ coupling of 20.0 Hz. At this limiting temperature the ^{1}H NMR spectrum was considerably more complex. The *ortho* mesityl methyl signals split into at least four broadened signals, which were shown to be interconverting on the NMR time scale by spin saturation transfer experiments. We tentatively interpret these data as evidence that a dimeric structure similar to that observed in the X-ray crystallographic analysis is maintained to some degree in aromatic solvent. The largely ionic and, hence, electrostatic (vide infra) nature of the ligand−potassium interaction renders, most likely intermolecular, structural reorganization

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(14) Hanusa, T. P. *Coord. Chem. Rev.* **2000**, *210*, 329.

(15) For examples of other K-arene interactions see: Smith, J. D. *Adv. Organomet. Chem.* **1998**, *43*, 267.

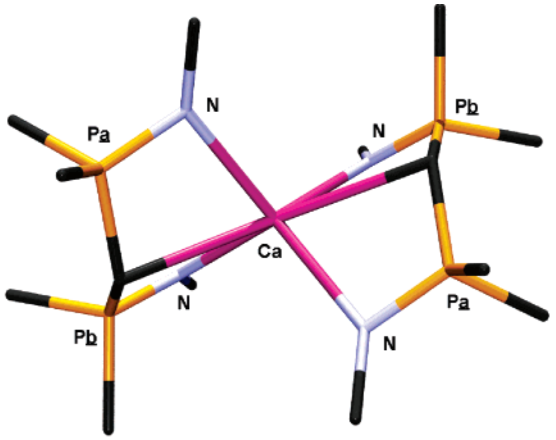

Figure 5. POVRAY representation of the calcium coordination geometry within compound **4** emphasizing the approximate C_2 symmetry.

facile, as evidenced by the activation energy for this process, 52.5 kJ mol^{-1}, calculated from the estimated coalescence temperature (228 K) of the ^{31}P{^{1}H} NMR signals.

Overnight reaction of 2 molar equiv of **3** and CaI_2 or BaI_2 in THF solution at room temperature followed by crystallization from toluene yielded well-formed crystals of the respective homoleptic complexes, **4** and **5**. Although crystallization from this solvent produced large clear crystals, repeated attempts to obtain a high-quality single-crystal X-ray structure of the calcium complex **4** were unsuccessful. Disorder within the chelated structure and three molecules of toluene solvent resulted in unacceptably high thermal parameters and residuals (ca. 17%), while attempts to obtain suitable single crystals from other solvents or combinations of solvents were unsuccessful. Although discussion of bond length and angle data is therefore precluded, the binding mode of the two chelated bis(phosphinimino)methanide ligands within **4** may be described as η^3 whereby the third contact is provided by the methanide carbon center at a distance of ca. 2.8 Å. A representation of the approximately C_2-symmetric core geometry about Ca within **4** is shown in Figure 5. The view presented is down the approximate C_2 axis and allows for straightforward visualization of the two different phosphorus environments (designated Pa and Pb) arising from each of the two magnetically equivalent tridentate ligands.

The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **3** in d_8-toluene at 298 K indicated complete equivalence of both ligands on the NMR time scale. The ^{31}P{^{1}H} NMR spectrum at this temperature displayed a single sharp peak centered at 18.6 ppm, indicating that the C_2 symmetry observed in the solid state is not retained at this temperature. Upon cooling below 260 K, however, this signal again broadened and split into an AX pattern with resonances centered at 19.1 and 18.0 ppm. At 213 K both these peaks displayed a homonuclear $^2J_{PP}$ coupling of 20.1 Hz, similar to that observed in the low-temperature spectrum of compound **3** and confirmed that the two phosphorus centers describe different magnetic environments within two magnetically equivalent ligands. We tentatively interpret these data as evidence for the maintenance of the crystallographically determined coordination geometry and hence of the methanide carbon−calcium contacts at low temperature. Above this temperature an intramolecular dynamic process involving continual Ca−C$_\gamma$ de-coordination and re-coordination may be defined with a $\Delta G^\ddagger$ of 50.3 kJ mol^{-1}. The low-temperature ^{1}H NMR data corroborated this view of the hemilabile nature of the methanide carbon−calcium interaction. At 218 K the resonance of the room-temperature ^{1}H NMR spectrum at 2.31 ppm, ascribed to the *para*-mesityl methyl groups, split into at least four broadened signals. These resonances were shown to be undergoing chemical interconversion by spin saturation transfer experiments, and their appearance was accompanied by a dramatic increase in the overall complexity of the spectrum.

Attempts to isolate the corresponding homoleptic strontium derivative have, thus far, been unsuccessful. We have noted that the repeated success of some of the heavier alkaline earth preparations detailed in this study was, somewhat unpredictably, dependent upon the nature and source of the starting reagents. For example, SrI_2 in bead form from commercial suppliers did not react with **3**, while use of an “in-house” strontium reagent prepared from strontium metal and di-iodoethane provided either a similar outcome or the heteroleptic complex **7**. In contrast, the barium analogue of **4**, compound **5**, was easily prepared by reaction of commercially available BaI_2 and **3** in THF solution or a “one-pot” procedure involving addition of THF to a solid mixture of BaI_2, **1**, and $KN(SiMe_3)_2$. It was discovered that the formation of **5** was independent of the ratio of BaI_2 to **3**, **1**, or $KN(SiMe_3)_2$ employed in the synthesis, and all variations upon this procedure intended to facilitate the synthesis of heteroleptic derivatives resulted in the isolation of **5**.

Analysis by multinuclear NMR spectroscopy indicated that **5** was free of THF, while an X-ray structural analysis confirmed that **5** was the homoleptic barium derivative illustrated in Figure 6. Although **5** does not crystallize with crystallographic C_2 symmetry, the C(1)- and C(44)-containing ligands differ only slightly in conformation. In contrast to **4**, the Ba−C(1) [3.949 Å] and Ba−C(44) [3.580 Å] distances are too long to indicate the formation of a direct Ba−methyl carbon interaction. Prior to our isolation of **4**, we ascribed this observation to the prevention of formation of a homoleptic six-coordinate complex by intraligand steric interactions. This now seems unlikely, however, when consideration is given to the relative sizes of the Ca^{2+} and Ba^{2+} cations. We instead prefer to ascribe the observed solid-state coordination geometry of **5** to the hemilability of the Ba−C$_\gamma$ binding and the relative influence of crystal-packing forces. Although the bis(phosphinimino)methanide ligands are effectively bidentate, the Ba−N distances of **5** are longer than those observed in both the homoleptic β-diketiminato barium complex [(CH{(Me)$_2$CN-2,6-^{i}Pr$_2$C$_6$H$_3$}$_2$)$_2$Ba] [range: 2.695(2)−2.742(2) Å][12c] and the terminal β-diketiminato ligand of a related heteroleptic cluster complex formed from reaction of [Ba{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] and the N-cyclohexyl-substituted analogue of the β-iminoamine precursor to **I** [2.689(4), 2.635(4) Å].[16]

Cooling a sample of **5** in d_8-toluene and monitoring of the ^{31}P{^{1}H} NMR signal did not reveal any splitting of the peaks observed for **4**. Rather, the single resonance observed at 298 K at 8.5 ppm merely broadened down to the low-temperature limit of the deuterated solvent. This contrasting behavior is, most likely, a reflection of the increased hemilability of the barium−ligand combination and a consequence of decreased charge density versus that of Ca^{2+}.

Although the larger size of the barium cation would also appear to predicate more open access to the metal center, attempts to synthesize heteroleptic species [{CH(Ph$_2$PN-2,4,6-Me$_3$C$_6$H$_2$)$_2$}AeI] (Ae = Ca or Ba), via redistribution of **4** and **5** with the respective alkaline earth di-iodides, were unsuccessful. Stoichiometric reactions of **4** or **5** with CaI_2 or BaI_2 respectively, even when conducted in refluxing THF, gave no

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(16) Clegg, W.; Coles, S. J.; Cope, E. K.; Mair, F. S. *Angew. Chem., Int. Ed.* **1998**, *37*, 796.

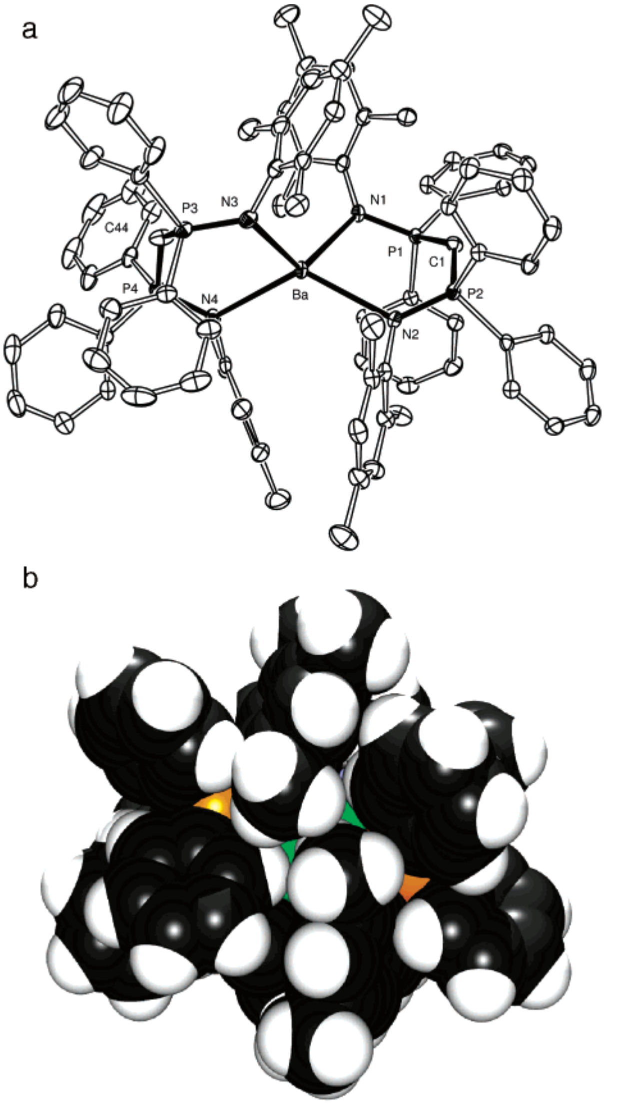

Figure 6. (a) ORTEP drawing (30% ellipsoids) of compound **5**. Hydrogen atoms are omitted for clarity. (b) POVRAY-generated space-filling representation of compound **5**.

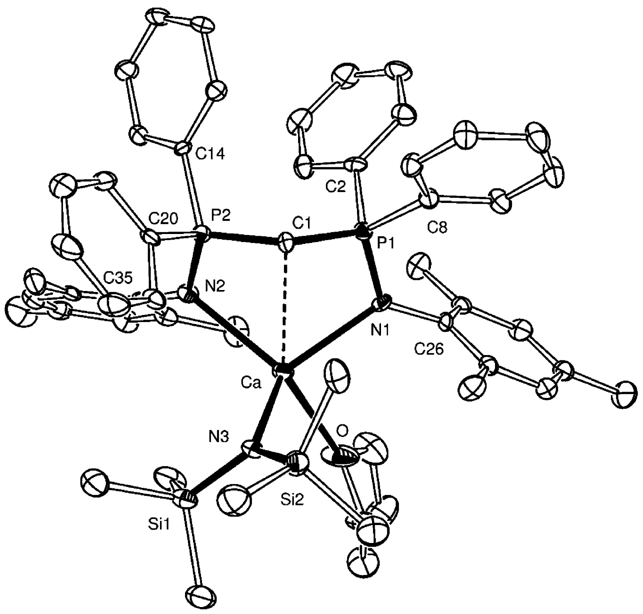

Figure 7. ORTEP drawing (30% ellipsoids) of compound **7**. Hydrogen atoms are omitted for clarity.

reaction, most likely due to the steric protection afforded the metal centers by the sterically demanding bis(phosphinimino)-methanide ligands. This is graphically illustrated by the space-filling diagram of **5** (Figure 6b) pictured in the same orientation as that depicted in Figure 6a.

Heteroleptic derivatives of both Ca and Sr were accessible through use of the sterically demanding hexamethyldisilazide co-ligand. This was most straightforwardly achieved by room-temperature addition of THF to a solid mixture of 2 molar equiv of [$KN(SiMe_3)_2$] together with a single equivalent of both CaI_2 or SrI_2 and the ligand precursor **1**. This procedure resulted in the formation of the heteroleptic bis(phosphinimino)methanide complexes [$\{CH(Ph_2PN\text{-}2,4,6\text{-}Me_3C_6H_2)_2\}Ca\{N(SiMe_3)_2\}\cdot THF$] and [$\{CH(Ph_2PN\text{-}2,4,6\text{-}Me_3C_6H_2)_2\}Sr\{N(SiMe_3)_2\}\cdot THF$], compounds **6** and **7**, respectively, in good yields. Alternatively the syntheses can be performed equally successfully by addition of the preformed potassium derivative **3** to a slurry containing the appropriate alkaline earth iodide and a single equivalent of [$KN(SiMe_3)_2$]. Multinuclear NMR spectra of both **6** and **7** at 298 K were consistent with time-averaged C_{2v}-symmetric structures in solution. This observation may be explained by rapid dissociation and re-coordination of the THF molecule and a reorganization of the bis(phosphinimino)methyl ligand by an undefined mechanism. The nature of these dynamic processes could not be further elucidated because solid compounds precipitated upon lowering the temperature of NMR samples in d_8-toluene. Crystals of both **6** and **7** suitable for single-crystal X-ray diffraction analyses were grown by slow cooling of toluene solutions, and details of the crystallographic analyses and selected bond length and angle data are provided in Tables 1, 2, and 3, respectively. Although **6** provided only very weak diffraction with limited higher angle data, it was clear that **6** and **7** were isostructural and, for brevity, only the structure of **6** is illustrated in Figure 7. Both structures contain five-coordinate alkaline earth metal centers, which form part of a boat-shaped six-membered MNPCPN metallacycle. In both cases the bis(phosphinimino)methanide ligand acts as a tridentate donor through both the phosphinimino nitrogen centers and the C(1) methyl carbon atom. The respective M−C(1) distances of 2.713(7) and 2.861(2) Å for **6** and **7** are longer than those of other structurally authenticated compounds containing Ae−sp^{3}C σ bonds, for example the Ca−C bond of the two-coordinate [$Ca\{C(SiMe_3)_2\}_2$] [2.459(9) Å][17] and the Sr−C bonds of the homoleptic strontium benzyl complex [$\{(2\text{-}Me_2N(\alpha\text{-}Me_3SiCH)\text{-}C_6H_4)_2Sr(THF)_2\}$] [2.798(2), 2.770(2) Å].[18] They are however comparable to those observed in the “ate” complexes [$Ca\{Al(CH_2(SiMe_3)_4\}_2\{N(SiMe_3)_2\}_2$] [2.678(3), 2.638(3) Å][19] and [$Sr(THF)_2\{Zn(CH_2SiMe_3)_3\}_2$] [2.857(7), 2.806(8) Å], in which the methyl carbon atom bridges between the two dissimilar metal centers.[20] We have noted previously that the M−N bond lengths observed when the anion formed by deprotonation of **1** acts as a strictly bidentate chelate to either three- or four-coordinate metal centers are almost identical to those of analogous complexes supported by β-diketiminato ligands. In **6** and **7** the corresponding bond lengths are significantly longer than those reported in both the heteroleptic calcium derivative [$CH\{(Me)_2CN\text{-}2,6\text{-}{}^iPr_2C_6H_3\}_2Ca\{N(SiMe_3)_2\cdot THF$] [2.352(1), 2.370-

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[17] Eaborn, C.; Hawkes, S. A.; Hitchcock, P. B.; Smith, J. D. *Chem. Commun.* **1997**, 1961.

[18] Feil, F.; Harder, S. *Organometallics* **2001**, *20*, 4616.

[19] Westerhausen, M.; Birg, C.; Nöth, H.; Knizek, J.; Seifert, T. *Eur. J. Inorg. Chem.* **1999**, 2209.

[20] Westerhausen, M.; Gückel, C.; Habereder, T.; Vogt, M.; Warchold, M.; Nöth, H. *Organometallics* **2001**, *20*, 893.

(1) Å][12a,b] and the homoleptic derivatives [$\{CH\{(Me)_2CN\text{-}2,6\text{-}{}^iPr_2C_6H_3\}_2\}_2M$] [M = Ca, 2.374(1), 2.384(1) Å; M = Sr, 2.506(2), 2.513(2) Å],[12c] signifying diminished charge donation as a result of the additional M−C(1) interactions.

As mentioned above, all attempts to synthesize the corresponding barium amide were unsuccessful and resulted in isolation of the homoleptic complex **5** regardless of order of reagent addition or temperature of reaction. This is most likely a reflection of the increased size of the Ba^{2+} cation and increased propensity of the heteroleptic silazide, if formed at all, to undergo solution redistribution to the more kinetically stable homoleptic complex. We have recently made similar observations with respect to β-diketiminato derivatives of heavier alkaline earth amides and anilides.[2b]

Roesky and co-workers have very recently reported the successful syntheses of a series of heteroleptic bis(phospinimino)methanide complexes utilizing the N-trimethylsilylated anion **IIa** with the composition [**IIa**AeI(THF)$_x$]$_y$ (Ae = Ca, $x = 2$, $y = 1$; Ae = Sr, $x = 1$, $y = 2$; Ae = Ba, $x = 2$, $y = 2$).[7f] While these compounds were synthesized by straightforward reaction of AeI_2 with a single equivalent of **IIa**K in THF, analogous reactions of **3** and AeI_2 did not produce any evidence for the formation of the desired heteroleptic iodides. A number of variations upon this basic procedure were attempted for the smallest member of the series, calcium. However the only isolable calcium derivative was the homoleptic species, **4**, independent of the precise reactions conditions. Evidently, replacement of the trimethylsilyl substituents of **IIa** with the bulky but planar mesityl results in less efficient protection of the group 2 metal center. Presumably the formation of **4** in these reactions occurs through the intermediacy of the target iodide, which is insufficiently stabilized to prevent further reaction, and is reminiscent of our previously reported synthesis of the analogous Sm(II) derivative, **IIb**$_2$Sm.[21] In the latter case all attempts to synthesize heteroleptic derivatives, even with a sterically demanding hexamethyl disilazido co-ligand, were unsuccessful and were reasoned to result from the large (seven-coordinate) ionic radius of the Sm^{2+} cation [1.36 Å].[22] For comparison, the respective (seven-coordinate) ionic radii of Ca^{2+}, Sr^{2+}, and Ba^{2+} are 1.20, 1.35, and 1.52 Å.

Reactivity of Compound 5. We have recently demonstrated that the homoleptic calcium β-diketiminate [$Ca\{(NDipp\text{-}CMe)_2CH\}\{N(SiMe_3)_2\}(THF)$] [(Dipp = $C_6H_3{}^iPr_2$-2,6)] can function as a useful and readily accessible starting material for explorations of calcium-centered stoichiometric and catalytic reactivity.[2−4] Our initial motivation for the current work was to utilize the similar topology and comparable steric profile of the bis(phosphinimino)methanide anion **IIb** in the synthesis of further well-defined organocalcium and calcium coordination compounds. We had previously applied a protolytic strategy to the synthesis of a range of alkoxy and aryloxy zinc derivatives **IIb**ZnOR/Ar, which were of interest as catalysts for the ring-opening polymerization of *rac*-lactide.[9h] NMR-scale reactivity studies of **6** with stoichiometric quantities of a variety of bulky or potentially bidentate protic (hydroxy and amino) reagents (see Experimental Section) however resulted in indiscriminate protonation of the bis(phosphinimino)methanide or hexmethyldisilazide ligand, irrespective of temperature or order of addition. This was readily apparent from the appearance of the resonances ascribed to the bis(phosphinimino)methane, **1**, at −16.1 and 3.90 ppm in the respective $^{31}P\{^1H\}$ and ^1H NMR spectra and dictated the abandonment of this strategy.

The success or failure of this protolytic approach is apparently dependent upon the steric demands and consequent protection of the metal center as well as the electronic nature of the N-chelated anionic ligand. The spectacular growth in popularity of the β-diketiminate class of ligands for the support of unusual modes of bonding and the observation of previously unknown reactivity is based upon ease of synthesis as well their ability to provide a robust and coordinatively stable supporting environment under oxidative, reductive, and even mildly acidic conditions. In simple valence bond terms, delocalization about a β-diketiminate ligand occurs via an effectively planar and exclusively sp^2-hybridized NCCCN chelate, whereas the methanide charge resulting from the formal deprotonation of a bis(phosphinimino)methane occurs by (negative) hyperconjugative interaction between the methanide center and, most likely, P(V) σ^* orbitals of appropriate π-symmetry.[23] These differing modes of charge distribution are likely therefore to have profound consequences for the relative basicity and nucleophilicity of the two classes of monoanion.

In an attempt to shed light upon the effects of these constitutional differences, we have carried out DFT calculations upon the model complexes [$HC\{(Me)C(Me)N\}_2K$], **8**, and [$HC\{(Me)_2P(Me)N\}_2K$], **9**, using the B3LYP density functional theory and LANL2DZ pseudopotentials (and basis set) implemented in Gaussian 03.[24] Examination of the charge distribution within **8** and **9** by a natural bond orbital (NBO) analysis provided qualitative insight into the effects of these differences (Figure 8). The data illustrate a similarly ionic nature for the metallacyclic structures. Although the potassium ion bears a similar charge in both cases (**8**, +0.952; **9**, +0.942), the nature of the delocalization of anionic charge about the chelate ligands contrasts greatly. In the case of **9**, there is a dramatic increase in the negative charge borne by the C_γ carbon center, emphasizing the methanide character of the bis(phosphinimino)methanide ligand. The effect of this charge accumulation will be to greatly enhance the potential reactivity (in terms of both nucleophilicity and basicity) at this carbon center and to impede the successful application of this class of anion as a readily "tunable" spectator ligand. Whereas reaction at the γ-position of β-diketiminato anions is a rarity and restricted to $-GeCl_3$ and $-PPh_2$ derivatives,[25,26] the significantly more limited data relating to bis(phosphinimino)methanides suggest that insertion into the latent M···C_γ interaction and/or protonation of C_γ is likely to be a predominant reaction pathway in reaction with a much wider

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(21) Hill, M. S.; Hitchcock, P. B. *Dalton Trans.* **2003**, 4570.

(22) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

(23) (a) Schleyer, P. von R.; Clark, T.; Kos, A. J.; Spitznagel, W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467. (b) Brinkmann, E. A.; Berger, S.; Braumann, J. I. *J. Am. Chem. Soc.* **1994**, *116*, 8304.

(24) 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.; Bakken, V.; 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. The validity of the optimized structures as true energy minima was confirmed by the absence of any imaginary frequencies within the computed vibrational spectra.

(25) Ragogna, P. J.; Burford, N.; D'eon, M.; McDonald, R. *Chem. Commun.* **2003**, 1052.

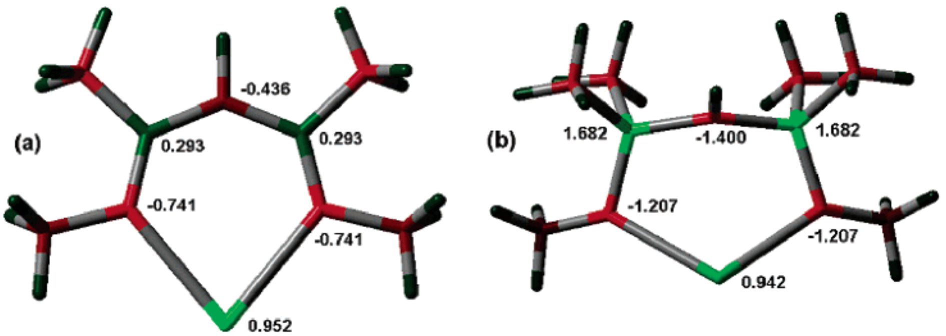

Figure 8. Gaussview representation of NBO charges within (a) **8** and (b) **9**.

range of electrophilic or protic substrates. The observation by Cavell and co-workers of insertion of heterocumulenes such as adamantyl isocyanate between Zn and C_γ of [**IIa**ZnMe] with retention of the Zn−CH_3 bond is a notable example of this expected reactivity in the presence of a less electropositive metal center.[9f,27,28] Our own work has sought to apply alkoxy- and aryloxy-zinc complexes, **IIb**ZnOR/Ar, as catalysts for the ring-opening polymerization of *rac*-lactide.[9h] In contrast to the striking molecular weight and tacticity control provided by similar β-diketiminato derivatives,[29] these compounds were shown to be of only limited utility, most likely because of the noninnocent nature of the chelate ligand. This carbanionic character, in conjunction with the hemilability of the M−C_γ interaction when M is a large and electropositive mono- or dication, is likely to be the key-determining feature of the structural and reaction chemistry of the compounds reported in this study.[30]

Experimental Section

General Procedures. All manipulations involving alkaline earth metals were carried out using standard Schlenk and glovebox techniques under an inert atmosphere of dinitrogen. All solvents were distilled under dinitrogen and dried from conventional drying agents. 2,4,6-Trimethylaniline, bis(diphenylphosphino)methane, and alkaline earth reagents were purchased from Sigma-Aldrich and used as received. NMR spectra were recorded at 270 or 500 (^{1}H), 125.8 (^{13}C), and 99.9 (^{29}Si) MHz from samples in either C_6D_6 or d_8-toluene; chemical shifts are given relative to $SiMe_4$. ^{31}P NMR (109.4 MHz) were referenced externally to H_3PO_4 (85% aqueous solution). Repeated attempts to accumulate mass spectral data on isolated compounds were unsuccessful due to their air and moisture sensitivity. Elemental analyses were performed by Mr. Stephen Boyer of London Metropolitan University. Samples were thoroughly ground and subjected to a dynamic vacuum prior to submission. Mesityl azide and the ligand precursor **1** were synthesized by literature procedures.[9g]

[{CH(Ph$_2$PNC$_6$H$_2$Me$_3$-2,4,6)$_2$}MgCl]$_2$, 2a; [{CH(Ph$_2$PNC$_6$H$_2$Me$_3$-2,4,6)$_2$}MgCl(THF)] 2b. A solution of methylmagnesium chloride (1.7 mL, 1.0 M in Et_2O) was added at room temperature to a solution of **1** (1.10 g, 1.69 mmol) in toluene (25 mL). The pale yellow, but slightly turbid solution was stirred for 2 h before filtration. The resultant solution was concentrated to incipient crystallization, warmed to dissolve precipitated solids, and allowed to cool to provide pale yellow crystals of **2a** as a bis-toluene solvate (0.85 g, 63%). Crystals of the monomeric THF coordination complex **2b** were obtained by crystallization from a toluene/THF mixture. Anal. Calcd for $C_{86}H_{86}Cl_2Mg_2N_4P_4$: C, 72.78; H, 6.12; N, 3.95. Found: C, 73.33; H, 6.09; N, 3.78. ^{1}H NMR (C_6D_6, 25 °C): δ 2.10 (s, 1H, PCHP) 2.13 (s, 6H, 4-Me), 2.20 (s, 12H, 2,6-Me), 6.90 (s, 4H, 3,5-H,mes), 6.60 (m, 8H, 3,5-H, PhP), 7.19 (m, 4H, 4-H,PhP), 7.41 (m, 8H, 2,6-H,PhP). ^{13}C NMR (C_6D_6, 25 °C): δ 20.7 (4-Me,mes), 21.1 (t, PCHP) 22.0 (2,6-Me,mes), 127.5 (Ar), 129.6 (Ar), 129.9 (Ar), 131.9 (Ar), 132.4 (Ar), 137.0 (Ar), 146.8.0 (Ar). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ 18.1.

[{CH(Ph$_2$PNC$_6$H$_2$Me$_3$-2,4,6)$_2$}K], 3. Toluene (20 mL) was added at room temperature to a solid mixture of **1** (1.0 g, 1.54 mmol) and [KN(SiMe$_3$)$_2$] (0.31 g, 1.54 mmol) to give an exothermic reaction and the formation of a colorless suspension in a pale yellow solution. This was stirred overnight before complete removal of all volatiles. The cream-colored solution was redissolved in hot toluene and concentrated to incipient crystallization. Slow cooling of a hot concentrated solution produced large colorless crystals of **3** (0.85 g, 80%). Anal. Calcd for $C_{43}H_{43}KN_2P_2$: C, 74.96; H, 6.30; N, 4.07. Found: C, 75.03; H, 6.36; N, 3.96. ^{1}H NMR (C_6D_6, 25 °C): δ 2.00 (s, 12H, 2,6-Me), 2.24 (s, 1H, PCH, $^2J_{PH} = 3.3$ Hz), 2.31 (s, 6H, 4-Me), 6.62 (m, 8H, 3,5-H,mes), 6.75 (s, 4H, 3,5-H, PhP), 6.78 (m, 8H, 2,6-H, PhP), 7.22 (m, 4H, 4-H, PhP). ^{13}C NMR (C_6D_6, 25 °C): δ, 20.1 (4-Me,mes), 21.2 (t, PCHP) 22.6 (2,6-Me,-mes), 127.3 (ArH), 129.4 (ArH), 129.9 (ArH), 132.2 (ArH), 134.3 (Ar), 137.3 (*i*-C$_6$H$_5$,PPh), 145.9 (*i*-mes,N). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ 16.3.

[{CH(Ph$_2$PNC$_6$H$_2$Me$_3$-2,4,6)$_2$}$_2$Ca], 4. THF (30 mL) was added at room temperature to a solid mixture of CaI_2 (0.45 g, 0.77 mmol), **1** (1.00 g, 1.54 mmol), and [KN(SiMe$_3$)$_2$] (0.31 g, 1.54 mmol). The resultant slurry was stirred overnight, before in vacuo removal of solvent. Extraction into toluene (20 mL), filtration, and concentration to incipient crystallization produced large colorless crystals of **4** (0.73 g, 71%). Anal. Calcd for $C_{86}H_{86}CaN_4P_4$: C, 82.64; H, 6.95; N, 2.24. Found: C, 82.43; H, 7.17; N, 2.35. ^{1}H NMR (C_6D_6, 25 °C): δ 2.09 (s, 12H, 2,6-Me), 2.32 (s, 6H, 4-Me), 2.42 (s, 1H, PCH, $^2J_{PH} = 2.8$ Hz), 6.59 (m, 8H, 3,5-H,mes), 6.73 (s, 4H, 3,5-H, PhP), 6.75 (m, 8H, 2,6-H, PhP), 7.20 (m, 4H, 4-H, PhP). ^{13}C NMR (C_6D_6, 25 °C): δ, 19.9 (4-Me,mes), 21.1 (t, PCHP) 23.0 (2,6-Me,mes), 125.2 (ArH), 127.1 (ArH), 128.3 (ArH), 132.7 (ArH), 135.1 (Ar), 137.3 (*i*-C$_6$H$_5$,PPh), 145.9 (*i*-mes,N). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ 18.6.

[{CH(Ph$_2$PNC$_6$H$_2$Me$_3$-2,4,6)$_2$}$_2$Ba], 5. This compound was made by the same general method as that described for **4** and isolated as colorless crystals from toluene in typically 70% yield. Mp: 210−212 °C. Anal. Calcd for $C_{86}H_{86}BaN_4P_4 \cdot 0.5(C_7H_8)$: C, 72.49; H, 6.13; N, 3.78. Found: C, 72.61; H, 6.18; N, 3.61. ^{1}H

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(26) Rake, B.; Zulch, F.; Ding, Y.; Prust, J.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Z. Anorg. Allg. Chem.* **2001**, *627*, 836.

(27) Cavell has also observed cummulene insertion into the Al−C_γ bonds of bimetallic aluminium diides: Aparna, K.; McDonald, R.; Ferguson, M.; Cavell, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 9314.

(28) Jordan has reported reversible [2+2] cycloaddition/insertion into Al−C_γ of ethylene with cationic β-diketiminato aluminum alkyls: Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 9384.

(29) Cheng, M.; Attygalle, A. B.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 11583.

(30) Although previous studies of ligand structures have reached similar conclusions regarding charge distribution within phosphinimine and imine donor centers, this is the first work that has dealt with the potential outcome of these differences so explicitly. See: Spencer, L. P.; Altwer, R.; Wei, P.; Gelmini, L.; Gauld, J.; Stephan, D. W. *Organometallics* **2003**, *22*, 3841.

NMR (C_6D_6, 25 °C): δ 2.03 (s, 12H, 4-Me), 2.10 (s, 2H, PCHP), 2.30 (s, 24H, 2,6-Me), 6.82 (m, 16H, 3,5-H, PhP), 6.88 (s, 16H, 3,5-H,mes), 6.90 (m, 8H, 4-H,PhP), 7.50 (m, 16H, 2,6-H,PhP). ^{13}C NMR (C_6D_6, 25 °C): δ 16.2 (t, PCHP, $^1J_{PC}$ = 146 Hz), 20.9 (4-Me,mes), 22.3 (2,6-Me,mes), 127.6 (Ar), 129.1 (Ar), 129.8 (Ar, J_{PC} = 33 Hz), 132.3 (Ar), 134.1 (Ar), 138.8 (Ar, J_{PC} = 94 Hz), 145.8 (Ar). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 8.44.

[{$CH(Ph_2PNC_6H_2Me_3$-2,4,6$)_2$}$CaN(SiMe_3)_2$(THF)], 6. A solution of [$KN(SiMe_3)_2$] (1.35 g, 6.80 mmol) in THF (10 mL) was added at room temperature to a slurry of CaI_2 (1.00 g, 3.40 mmol) in a THF (30 mL) solution of **1** (2.21 g, 3.40 mmol). The resulting slurry was stirred at room temperature for 14 h before in vacuo removal of volatiles and extraction into toluene. Filtration and concentration followed by slow cooling of a concentrated toluene solution produced **6** as large colorless crystals suitable for X-ray diffraction analysis (1.76 g, 56%). Mp: 189−191 °C (dec). Anal. Calcd for $C_{53}H_{69}CaN_3OP_2Si$: C, 69.01; H, 7.56; N, 4.56. Found: C, 68.86; H, 7.68; N, 4.59. ^1H NMR (C_6D_6, 25 °C): δ 0.39 (s, 18H, $SiMe_3$), 1.04 (m, 4H, THF), 2.11 (s, 1H, PCHP) 2.16 (s, 6H, 4-Me), 2.24 (s, 12H, 2,6-Me), 3.36 (m, 4H, THF), 6.78 (s, 4H, 3,5-H,mes), 6.84 (m, 8H, 3,5-H, PhP), 6.92 (m, 4H, 4-H,PhP), 7.61 (m, 8H, 2,6-H,PhP). ^{13}C NMR (C_6D_6, 25 °C): δ 6.1 (SiMe), 16.0 (t, PCHP, $^1J_{PC}$ = 137 Hz), 20.7 (4-Me,mes), 22.6 (2,6-Me,mes), 24.8 (THF), 68.6 (THF), 127.7 (Ar), 129.3 (Ar), 129.9 (Ar, J_{PC} = 20 Hz), 132.1 (Ar), 132.7 (Ar), 137.4 (Ar, J_{PC} = 89 Hz), 146.0 (Ar). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 8.03. ^{29}Si NMR (C_6D_6, 25 °C): δ −16.3.

[{$CH(Ph_2PNC_6H_2Me_3$-2,4,6$)_2$}$SrN(SiMe_3)_2$(THF)], 7. This compound was synthesized by the same general method as that outlined above for **6** and isolated as colorless crystals after crystallization from toluene solution (68%). Mp: 195−198 °C (dec). Anal. Calcd for $C_{53}H_{69}CaN_3OP_2SiSr$: C, 65.63; H, 7.19; N, 4.33. Found: C, 65.63; H, 7.23; N, 4.17. ^1H NMR (C_6D_6, 25 °C): δ 0.44 (s, 18H, $SiMe_3$), 1.05 (m, 4H, THF), 2.15 (s, 6H, 4-Me), 2.21 (s, 1H, PCHP), 2.27 (s, 12H, 2,6-Me), 3.48 (m, 4H, THF), 6.79 (s, 4H, 3,5-H,-mes), 6.84 (m, 8H, 3,5-H, PhP), 6.92 (m, 4H, 4-H,PhP), 7.59 (m, 8H, 2,6-H,PhP). ^{13}C NMR (C_6D_6, 25 °C): δ 6.3 (SiMe, $^1J_{SiC}$ = 52 Hz), 15.9 (t, PCHP, $^1J_{PC}$ = 132 Hz), 20.6 (4-Me,mes), 23.0 (2,6-Me,mes), 24.7 (THF), 68.7 (THF), 127.7 (Ar), 129.9 (Ar), 130.2 (Ar), 132.4 (Ar), 133.3 (Ar), 137.0 (Ar, J_{PC} = 89 Hz), 145.7 (Ar). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 10.79. ^{29}Si NMR (C_6D_6, 25 °C): δ −14.0.

General Procedure for NMR-Scale Reactions of 6. To a solution of **6** (30−40 mg) in C_6D_6 (ca. 0.5 mL) prepared in the drybox was added a stoichiometric quantity of the appropriate alcohol (C_2H_5OH, Ph_3COH), phenol (2,4,6-$Me_3C_6H_2OH$, 2,4-$^tBu_2C_6H_3OH$, 2,6-$^tBuC_6H_3OH$), aniline (2,6-$^iPr_2C_6H_3NH_2$), or amine ($^tBuNH_2$, $CH_3O(CH_2)_2NH_2$). Liquid reagents were added via a calibrated micropipet. The resulting solution was shaken before being transferred to an NMR tube fitted with a Youngs' tap. Spectra were recorded immediately afterward.

Crystal Structure Determinations. Data for **2a**, **2b**, **4**, **6**, and **7** were collected at 173 K on a Nonius KappaCCD diffractomer, λ(Mo Kα) = 0.71073 Å. An absorption correction (MULTISCAN) was applied to **5**, **6**, and **7**. The structures were solved by direct methods (SHELXS-97)[31] and refined by full matrix least squares (SHELXL-97)[32] with non-H atoms anisotropic and H atoms included in riding mode.

Acknowledgment. We thank the Royal Society for a University Research Fellowship (M.S.H.) and the EPSRC for provision of a DTA studentship (S.A.A.). We would also like to thank the referees for their valuable comments.

Supporting Information Available: X-ray crystallographic data, including **3**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) Sheldrick, G. M. *SHELXS-97*, Program for the Solution of Crystal Structures; Göttingen, 1997.

(32) Sheldrick, G. M. *SHELXL-97*, Program for the Refinement of Crystal Structures; Göttingen, 1997.