

# Sandwich Complexes of the Heavier Alkaline Earth Metals Containing $\eta^5$ - $\beta$ -Diketiminato Ligand Sets

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Treatment of *N*-*tert*-butyl-4-(*tert*-butylimino)-2-penten-2-amine ( $L^{\text{tBu}}\text{H}$ ) with 0.5 equiv of  $M(\text{N}(\text{SiMe}_3)_2)_2(\text{THF})_2$  ( $M = \text{Ca}, \text{Sr}, \text{Ba}$ ) in toluene at ambient temperature afforded  $\text{Ca}(\eta^5\text{-}L^{\text{tBu}})_2$  (98%),  $\text{Sr}(\eta^5\text{-}L^{\text{tBu}})_2$  (93%), and  $\text{Ba}(\eta^5\text{-}L^{\text{tBu}})_2$  (93%). Crystal structure determinations of these complexes revealed bent sandwich structures in which the  $\beta$ -diketiminato ligands are coordinated in a  $\eta^5$ -fashion to the metal centers. Similar treatment of *N*-isopropyl-4-(isopropylimino)-2-penten-2-amine ( $L^{\text{Pr}}\text{H}$ ) with 0.5 equiv of  $M(\text{N}(\text{SiMe}_3)_2)_2(\text{THF})_2$  led to the isolation of  $\text{Ca}(\eta^5\text{-}L^{\text{Pr}})_2$  (72%),  $\text{Sr}(\eta^5\text{-}L^{\text{Pr}})_2$  (80%), and a novel dinuclear barium complex  $[(\eta^5\text{-}L^{\text{Pr}})\text{Ba}(\mu\text{-}\eta^5\text{-}\eta^5\text{-}L^{\text{Pr}})(\mu\text{-}\eta^1\text{-}\eta^1\text{-}L^{\text{Pr}})\text{Ba}(\eta^5\text{-}L^{\text{Pr}})]$  (39%). Structural assignments for these complexes were based on spectral and analytical data as well as X-ray crystallography.  $[(\eta^5\text{-}L^{\text{Pr}})\text{Ba}(\mu\text{-}\eta^5\text{-}\eta^5\text{-}L^{\text{Pr}})(\mu\text{-}\eta^1\text{-}\eta^1\text{-}L^{\text{Pr}})\text{Ba}(\eta^5\text{-}L^{\text{Pr}})]$  exhibits three different bonding modes for the  $\beta$ -diketiminato ligands, including  $\eta^5$ ,  $\mu\text{-}\eta^1\text{-}\eta^1$ , and  $\mu\text{-}\eta^5\text{-}\eta^5$ . Variable-temperature NMR studies suggest that the dinuclear structure of  $[(\eta^5\text{-}L^{\text{Pr}})\text{Ba}(\mu\text{-}\eta^5\text{-}\eta^5\text{-}L^{\text{Pr}})(\mu\text{-}\eta^1\text{-}\eta^1\text{-}L^{\text{Pr}})\text{Ba}(\eta^5\text{-}L^{\text{Pr}})]$  persists in solution.

## Introduction

There is great interest in the coordination chemistry of  $\beta$ -diketiminato ligands with metals across the periodic table.<sup>1</sup> The steric and electronic nature of these ligands are easily adjusted by changing the nitrogen atom substituents, and the ligands themselves are available in large amounts through simple synthetic procedures. Complexes containing  $\beta$ -diketiminato ligands are well known to stabilize metal centers in both low oxidation states and low coordination environments.<sup>2</sup>  $\beta$ -Diketiminato complexes are also being increasingly employed in single-site polymerization catalysis.<sup>3</sup> Despite their growing importance, complexes containing  $\beta$ -diketiminato ligands have received little study as film growth precursors in chemical vapor deposition (CVD).<sup>4</sup> Recently, several reports have described the synthesis of heavier alkaline earth metal complexes containing  $\beta$ -diketiminato ligands and their bis(phosphinimino)-methyl analogues.<sup>5–7</sup> Exploration of this field is driven by the potential use of these complexes in catalysis,

organic synthesis, and CVD film growth. All of the heavier group 2 complexes described thus far feature sterically demanding  $\beta$ -diketiminato ligands bearing either 2,6-diisopropylphenyl<sup>5</sup> or cyclohexyl<sup>6</sup> moieties as the nitrogen substituents. Calcium, strontium, and barium complexes containing the 2,6-diisopropylphenyl-substituted ligand  $[\text{CH}(\text{C}(\text{CH}_3)\text{N}(2,6\text{-Pr}_2\text{C}_6\text{H}_3))_2]^-$  ( $L^{\text{Ar}}$ ) exhibit the  $\eta^2$ -coordination mode, through the nitrogen atoms of  $L^{\text{Ar}}$ . These complexes have not been reported to be volatile, probably as a result of the high molecular weights imparted by  $L^{\text{Ar}}$  and intermolecular  $\pi$ -stacking associated with the aryl groups. Use of the *N*-cyclohexyl-substituted diketiminato ligand  $[\text{CH}(\text{C}(\text{CH}_3)\text{N}(\text{C}_6\text{H}_{11}))_2]^-$  ( $L^{\text{Cy}}$ ) afforded the dimeric barium cluster  $\text{Ba}_2(\text{L}^{\text{Cy}})_3\text{-}(\text{N}(\text{SiMe}_3)_2)$ , which contains  $\eta^5$ -,  $\mu\text{-}\eta^2\text{-}\eta^2\text{-}\eta^5$ -, and  $\mu\text{-}\eta^2\text{-}\eta^3$ - $\beta$ -diketiminato ligands.<sup>6</sup>

Sandwich complexes of the heavier group 2 metals are dominated by cyclopentadienyl ligands and their substituted derivatives.<sup>8,9</sup> The use of these complexes in CVD applications was reviewed recently.<sup>8a,10</sup> Since the  $\eta^5$ - $\beta$ -diketiminato coordination mode has been documented in  $\text{Ba}_2(\text{L}^{\text{Cy}})_3(\text{N}(\text{SiMe}_3)_2)$ ,<sup>6</sup> in some lanthanide  $\beta$ -diketiminato complexes,<sup>11</sup> as well as in several other metal complexes,<sup>1a</sup> and given the chemical similarities

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between the lanthanide and heavier group 2 metals, it seemed very likely that this bonding mode would be observed in heavier group 2 metal complexes. Thus, it might be possible to obtain sandwich complexes of calcium, strontium, and barium with  $\beta$ -diketiminato ligands, and these complexes might be volatile and of potential utility in CVD film growth. Within this context, we describe the synthesis, structure, and properties of a series of calcium, strontium, and barium complexes containing  $\beta$ -diketiminato ligands derived from *N*-*tert*-butyl-4-(*tert*-butylimino)-2-penten-2-amine ( $L^{tBuH}$ ) and *N*-isopropyl-4-(isopropylimino)-2-penten-2-amine ( $L^{iPrH}$ ). For  $M(L^{tBu})_2$  and  $Sr(L^{iPr})_2$ , sandwich complexes with  $\eta^5$ - $\beta$ -diketiminato ligands are obtained.  $Ca(L^{iPr})_2$  contains  $\eta^2$ - $\beta$ -diketiminato ligands, while  $Ba_2(L^{iPr})_4$  adopts a dinuclear structure with  $\eta^5$ -,  $\mu$ - $\eta^5$ -,  $\eta^5$ -, and  $\mu$ - $\eta^1$ : $\eta^1$ - $\beta$ -diketiminato ligands. All of the new complexes are thermally stable and volatile, and offer new insight into ligand design for CVD precursors. The generality of the  $\eta^5$ - $\beta$ -diketiminato ligand coordination mode, as documented herein, is surprising and provides new directions for the development of group 2 chemistry.

## Results

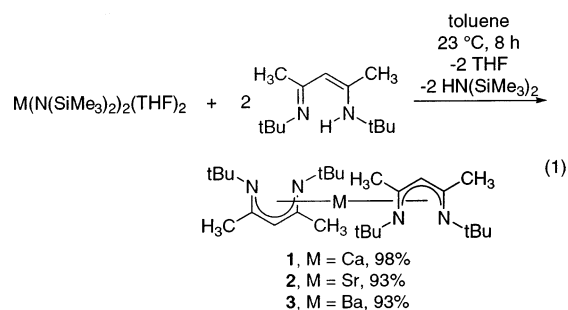
**Synthetic Aspects.** The diketimines  $L^{tBuH}$  and  $L^{iPrH}$  were prepared according to literature procedures.<sup>12</sup> Salt metathesis reactions of  $KL^{tBu}$  or  $KL^{iPr}$  and the metal iodides provided complex mixtures of products and were not pursued further. However, protonolysis reactions involving  $M(N(SiMe_3)_2)_2(THF)_2$  ( $M = Ca, Sr, Ba$ ) proved to be successful.<sup>13</sup> Treatment of  $M(N(SiMe_3)_2)_2(THF)_2$  with  $L^{tBuH}$  (2 equiv) in toluene afforded the  $\beta$ -diketiminato complexes **1–3** after workup as described in the Experimental Section (eq 1). Complexes **1–3** were extremely soluble in hexane and toluene and could not be crystallized well from these media. However, they sublimed readily, and this was the method of choice for purification and for growth of crystals suitable for X-ray diffraction experiments. The structural assignments for **1–3** were based upon spectral and analytical data as well as X-ray structure determinations. In the solid state, **1–3** exist as base-free, bent sandwich molecules in which the  $\beta$ -diketiminato ligands are coordinated to the metal centers in an  $\eta^5$ -fashion. Further details of the ligand bonding modes are described below.

The  $^1H$  NMR spectra of **1–3** consist of sharp singlets in a ratio of 36:12:2 for the *tert*-butyl, methyl, and  $\beta$ -CH protons, respectively, and are in agreement with one set of magnetically equivalent ligands. The hydrogen atoms on the  $\beta$ -CH fragments of the  $\beta$ -diketiminato ligands in **1–3** resonate at  $\delta$  4.25, 4.26, and 4.37, respectively, which are upfield compared to  $L^{tBuH}$  ( $\beta$ -CH =  $\delta$  4.47). In the  $^{13}C\{^1H\}$  NMR spectra, the  $\beta$ -CH fragments in **1–3** resonate at 91.90, 90.39, and 89.50 ppm and are upfield compared to  $L^{tBuH}$  ( $\beta$ -CH = 97.69 ppm).

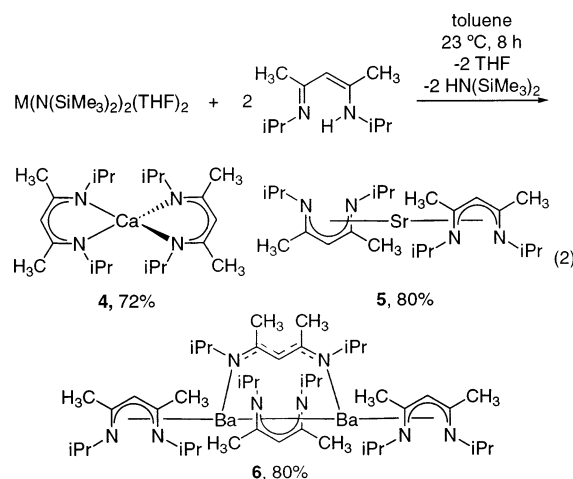
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Similar treatment of  $M(N(SiMe_3)_2)_2(THF)_2$  with  $L^{iPrH}$  (2 equiv) in toluene at ambient temperature afforded  $Ca(\eta^2-L^{iPr})_2$  (**4**, 72%),  $Sr(\eta^5-L^{iPr})_2$  (**5**, 80%), and  $[(\eta^5-L^{iPr})-Ba(\mu-\eta^5:\eta^5-L^{iPr})(\mu-\eta^1:\eta^1-L^{iPr})Ba(\eta^5-L^{iPr})]$  (**6**, 39%), as outlined in eq 2. The structural assignments for **4–6** were based upon spectral and analytical data as well as X-ray structure determinations. In the solid state, **4** is monomeric with two  $\eta^2$ - $\beta$ -diketiminato ligands. Complex **5** crystallizes as a sandwich complex with a structure similar to those of **1–3**. Unlike **1–3** and **5**, **6** crystallizes from hexane as a dinuclear complex. The barium atoms are bridged by  $\mu$ - $\eta^5$ : $\eta^5$ - and  $\mu$ - $\eta^1$ : $\eta^1$ - $\beta$ -diketiminato ligands, and each barium atom is also capped with a terminal  $\eta^5$ - $\beta$ -diketiminato ligand.



The  $^1H$  NMR spectra of **4** and **5** consist of sharp signals with a well-resolved doublet ( $CH(CH_3)_2$ ), a septet ( $CH(CH_3)_2$ ), and a singlet ( $\beta$ -CH). The hydrogen atoms of the  $\beta$ -CH fragments appear at  $\delta$  4.36 and 4.21 and are shifted upfield compared to  $L^{iPrH}$  ( $\beta$ -CH =  $\delta$  4.46). In the  $^{13}C\{^1H\}$  spectra of **4** and **5**, the corresponding  $\beta$ -CH carbon atoms resonate at 92.43 and 87.33 ppm. These values are upfield with respect to  $L^{iPrH}$  ( $\beta$ -CH = 94.53 ppm). There are no diagnostic chemical shifts that allow differentiation between  $\eta^5$ - and  $\eta^2$ -coordination of the  $\beta$ -diketiminato ligands.

In contrast to **1–5**, compound **6** exhibits temperature-dependent  $^1H$  NMR and  $^{13}C\{^1H\}$  spectra. To gain insight into the solution behavior of **6**, variable-temperature  $^1H$  NMR spectra were recorded in toluene- $d_8$  between  $-80$  and  $80$  °C. At  $80$  °C, the  $^1H$  NMR spectrum of **6** was very similar to that of **5**, which suggested either rapid exchange of the  $\beta$ -diketiminato ligand sites within a dimeric molecule or formation of a monomeric structure at this temperature. The  $^{13}C\{^1H\}$  NMR spectrum at  $80$  °C exhibited extremely broad resonances, which may

**Table 1. Crystal Data and Data Collection Parameters for 1–6**

	1	2	3	4	5	6
formula	C <sub>26</sub> H <sub>50</sub> CaN <sub>4</sub>	C <sub>26</sub> H <sub>50</sub> SrN <sub>4</sub>	C <sub>26</sub> H <sub>50</sub> BaN <sub>4</sub>	C <sub>22</sub> H <sub>42</sub> CaN <sub>4</sub>	C <sub>22</sub> H <sub>42</sub> SrN <sub>4</sub>	C <sub>44</sub> H <sub>84</sub> Ba <sub>2</sub> N <sub>8</sub>
fw	458.78	506.32	556.04	402.68	450.22	999.87
space group	<i>Pbca</i>	<i>P2(1)/c</i>	<i>P2(1)/c</i>	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> (Å)	16.5507(16)	10.4966(13)	10.4513(13)	49.240(5)	13.195(2)	20.420(4)
<i>b</i> (Å)	18.1645(15)	11.7125(14)	11.8734(14)	9.1254(10)	14.604(2)	11.201(2)
<i>c</i> (Å)	20.1236(18)	24.465(3)	24.455(3)	16.8294(16)	13.680(2)	23.645(5)
$\beta$ (deg)	90	93.621(2)	92.010(3)	95.801(3)	90.237(3)	107.347(4)
<i>V</i> (Å <sup>3</sup> )	6049.9(9)	3001.7(6)	3032.9(6)	7523.3(13)	2636(8)	5162.3(17)
<i>Z</i>	8	4	4	12	4	4
<i>T</i> (K)	295(2)	295(2)	295(2)	295(2)	295(2)	295(2)
$\lambda$ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
$\rho_{\text{calcd}}$ (g, cm <sup>-3</sup> )	1.007	1.120	1.218	1.067	1.134	1.287
$\mu$ (mm <sup>-1</sup> )	0.225	1.813	1.327	0.263	2.057	1.551
<i>R</i> ( <i>F</i> ) (%) <sup>a</sup>	5.74	3.13	2.86	5.27	4.03	2.05
<i>R</i> <sub>w</sub> ( <i>F</i> ) (%) <sup>b</sup>	17.34	6.43	5.19	12.41	8.94	5.47

$$^a R(F) = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad ^b R_w(F) = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}$$

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

Ca–N(1)	2.358(2)	Ca–C(17)	2.901(3)
Ca–N(2)	2.3418(19)	N(1)–C(1)	1.320(4)
Ca–N(3)	2.349(2)	C(1)–C(3)	1.422(4)
Ca–N(4)	2.358(2)	C(3)–C(4)	1.427(4)
Ca–C(1)	2.840(3)	N(2)–C(4)	1.301(3)
Ca–C(3)	2.817(3)	N(3)–C(14)	1.352(3)
Ca–C(4)	2.846(3)	C(14)–C(16)	1.426(4)
Ca–C(14)	2.857(3)	C(16)–C(17)	1.425(3)
Ca–C(16)	2.865(3)	N(4)–C(17)	1.334(3)
Ca–C <sub>cent2</sub>	2.214(3)	Ca–C <sub>cent1</sub>	2.215(3)
N(1)–Ca–N(2)	78.49(7)		
N(3)–Ca–N(4)	78.69(7)		
C <sub>cent1</sub> –Ca–C <sub>cent2</sub>	138.0(1)		

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

Sr–N(4)	2.4727(16)	N(1)–C(1)	1.307(3)
Sr–N(2)	2.4913(16)	N(2)–C(4)	1.304(2)
Sr–N(1)	2.4974(15)	C(1)–C(3)	1.428(3)
Sr–N(3)	2.5171(15)	C(3)–C(4)	1.427(3)
Sr–C(1)	3.017(2)	N(3)–C(14)	1.311(2)
Sr–C(3)	2.991(2)	N(4)–C(17)	1.311(2)
Sr–C(4)	2.9954(19)	C(14)–C(16)	1.423(3)
Sr–C(14)	3.004(2)	C(16)–C(17)	1.425(3)
Sr–C(16)	2.928(2)	Sr–C <sub>cent1</sub>	2.399(2)
Sr–C(17)	2.9621(19)	Sr–C <sub>cent2</sub>	2.375(3)
N(2)–Sr–N(1)	73.82(5)		
N(4)–Sr–N(3)	73.41(5)		
C <sub>cent1</sub> –Sr–C <sub>cent2</sub>	148.4(0.1)		

**Table 4. Selected Bond Lengths (Å) and Angles (deg) for 3**

Ba–N(1)	2.6169(2)	Ba–C(8)	3.157(3)
Ba–N(2)	2.6802(19)	N(1)–C(5)	1.304(3)
Ba–N(3)	2.649(2)	N(2)–C(8)	1.307(3)
Ba–N(4)	2.656(2)	C(5)–C(7)	1.424(4)
Ba–C(7)	3.055(3)	C(7)–C(8)	1.425(4)
Ba–C(5)	3.084(3)	N(3)–C(18)	1.307(3)
Ba–C(20)	3.117(3)	N(4)–C(21)	1.304(3)
Ba–C(21)	3.147(3)	C(18)–C(20)	1.417(4)
Ba–C(18)	3.155(3)	C(20)–C(21)	1.429(4)
Ba–C <sub>cent1</sub>	2.541(3)	Ba–C <sub>cent2</sub>	2.565(3)
N(1)–Ba–N(2)	68.29(6)		
N(3)–Ba–N(4)	69.64(6)		
C <sub>cent1</sub> –Ba–C <sub>cent2</sub>	147.6(1)		

support the former interpretation. Between 20 and 40 °C, the isopropyl group resonances were broad and several new broad resonances appeared in the ligand backbone  $\beta$ -CH region. At or below 10 °C, the resonances were consistent with a dimeric structure similar to that observed in the solid state. At –40 °C, the  $\beta$ -CH resonances were observed at  $\delta$  4.80, 4.08, and 4.06 in a ratio of 1:2:1. According to the X-ray crystal structure of **6**, the  $\beta$ -CH hydrogen atom of the W-shaped  $\beta$ -diketiminato ligand is pointed directly toward the open mouth of the  $\mu$ - $\eta^5$ : $\eta^5$ - $\beta$ -diketiminato ligand. This hydrogen atom is in the deshielding region of the ligand aromatic  $\pi$ -system, and it is possible that the downfield resonance at  $\delta$  4.80 corresponds to the  $\beta$ -CH atom of the W-shaped  $\beta$ -diketiminato ligand. If so, this is evidence for retention of the solid state structure in solution. The isopropyl group methine resonances were observed as multiplets at  $\delta$  3.78 and 3.60, in a ratio of 1:3. The  $\beta$ -diketiminato ligand backbone methyl groups appeared as singlets at  $\delta$  2.03, 1.93, and 1.84, in a 1:2:1 ratio. Finally, the isopropyl methyl groups were observed as doublets at  $\delta$  1.45, 1.32, and 1.22, in a ratio of 1:1:2. The <sup>1</sup>H NMR spectrum did not change further upon cooling to –80 °C, except for small changes in chemical shifts with temperature.

**Volatility Study.** The volatilities of **1–6** were evaluated by preparative sublimation experiments. The crude solids of **1–3** (~4 g each) were loaded into a horizontal sublimation apparatus and were sublimed at 110 (**1**), 125 (**2**), and 135 (**3**) °C at 0.05 Torr to afford colorless crystalline solids in >80% yields for **1** and **2** and ~40% for **3**. Complexes **4** and **5** have lower sublimation rates in a horizontal sublimation apparatus and melt prior to sublimation at 100–110 °C/0.05 Torr (mp **4** = 92–94

°C, mp **5** = 87–89 °C). It was found that **4** and **5** sublime best in a vertical sublimation apparatus onto a coldfinger that is cooled with tap water. Unlike **4** and **5**, **6** has a higher melting point (176–178 °C) and it sublimates in a coldfinger apparatus at 125 °C/0.05 Torr without melting. Sublimation of **6** using the horizontal oven required higher temperatures (~170 °C/0.05 Torr). Complexes **4–6** were recovered in ~60% yields using the coldfinger apparatus.

**Structural Aspects.** The X-ray crystal structures of **1–6** were determined to establish the geometry about the metal centers and the bonding modes of the  $\beta$ -diketiminato ligands. Experimental crystallographic data are summarized in Table 1, selected bond lengths and angles are given in Tables 2–7, and perspective views are presented in Figures 1–6. A summary of the bonding parameters of the  $\beta$ -diketiminato ligands in **1–6** is given in Table 8.

The molecular structures of **1–3** are very similar overall and are shown in Figures 1–3. They exist as

**Table 5. Selected Bond Lengths (Å) and Angles (deg) for 4**

Ca–N(1)	2.357(2)	C(4)–C(5)	1.401(4)
Ca–N(2)	2.351(2)	C(5)–C(6)	1.408(4)
Ca–N(3)	2.354(2)	N(3)–C(15)	1.319(4)
Ca–N(4)	2.358(2)	N(4)–C(17)	1.323(4)
N(1)–C(4)	1.331(3)	C(15)–C(16)	1.419(4)
N(2)–C(6)	1.308(3)	C(16)–C(17)	1.406(5)
N(2)–Ca–N(1)	83.68(8)		
N(4)–Ca–N(3)	83.43(9)		

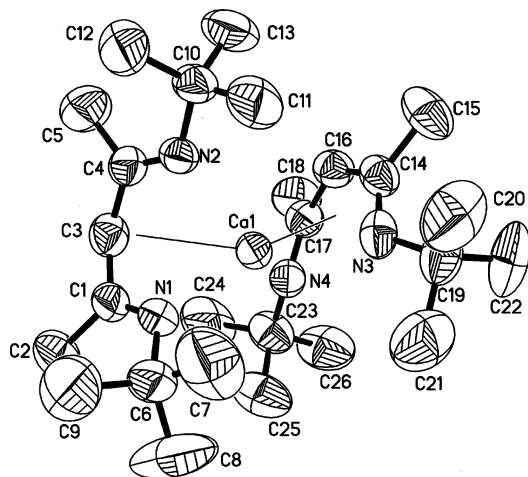
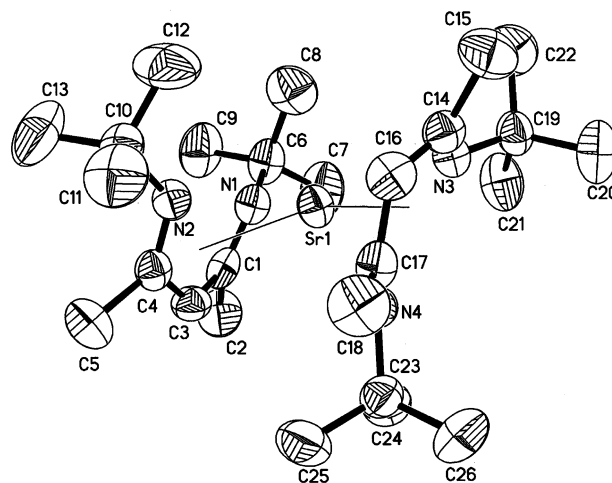
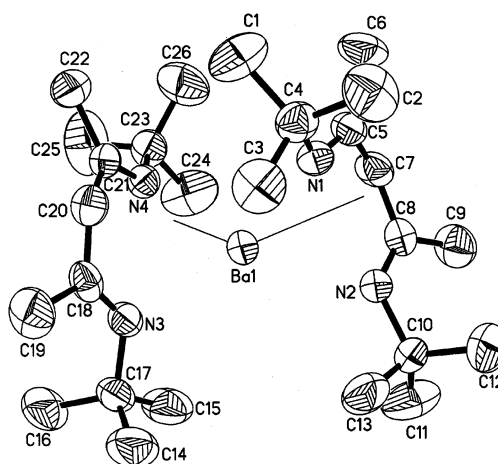
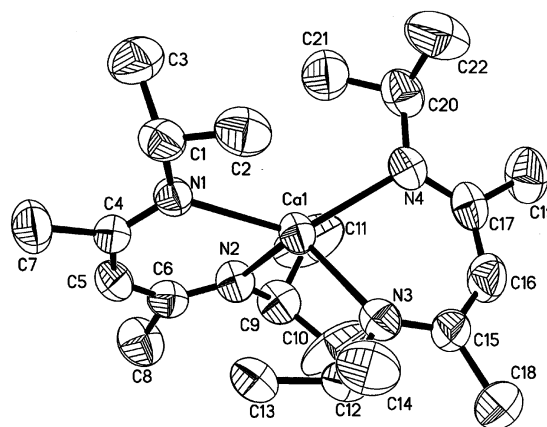
**Table 6. Selected Bond Lengths (Å) and Angles (deg) for 5**

Sr–N(1)	2.486(2)	N(1)–C(1)	1.304(4)
Sr–N(2)	2.487(2)	N(2)–C(4)	1.309(4)
Sr–C(1)	2.970(3)	C(1)–C(3)	1.416(4)
Sr–C(3)	3.003(3)	C(3)–C(4)	1.428(5)
Sr–C(4)	3.016(3)	C <sub>cent1</sub> –Sr	2.386(3)
N(1)–Sr–N(2)	75.83(8)		
C <sub>cent1</sub> –Sr–C <sub>cent2</sub>	143.6(1)		

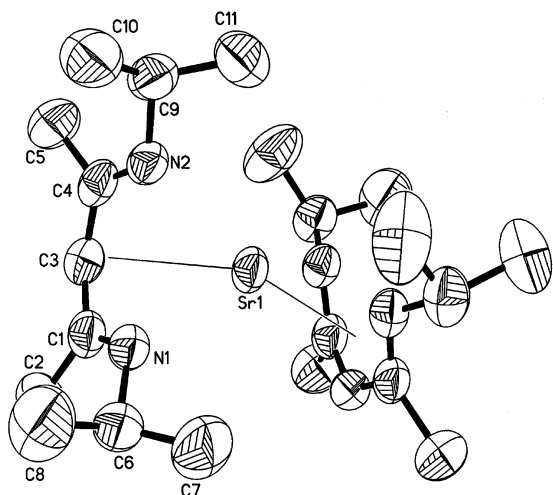
**Table 7. Selected Bond Lengths (Å) and Angles (deg) for 6**

Ba–N(1)	2.7220(17)	Ba–N(3)#1	2.8140(15)
Ba–N(2)	2.6853(16)	Ba–N(3)	2.9268(15)
Ba–C(1)	3.180(2)	Ba–N(4)	2.7896(17)
Ba–C(3)	3.144(2)	Ba–C(18)	3.561(2)
Ba–C(4)	3.168(2)	Ba–C(20)	3.585(2)
Ba–C(12)	3.3549(18)	N(4)–C(18)	1.322(3)
Ba–C(12)#1	3.2180(19)	C(18)–C(20)	1.406(2)
Ba–C(14)	3.3861(19)	Ba–Ba	4.5492(7)
Ba–C <sub>cent1</sub>	2.594(2)	Ba–C <sub>cent2</sub>	2.763(2)
N(1)–Ba–N(2)	70.38(5)		
N(3)#1–Ba(1)–N(3)	68.16(4)		
N(4)–C(18)–C(20)	119.12(18)		
C(18)–C(20)–C(18)#1	133.6(2)		
C <sub>cent1</sub> –Ba–C <sub>cent2</sub>	107.5(1)		

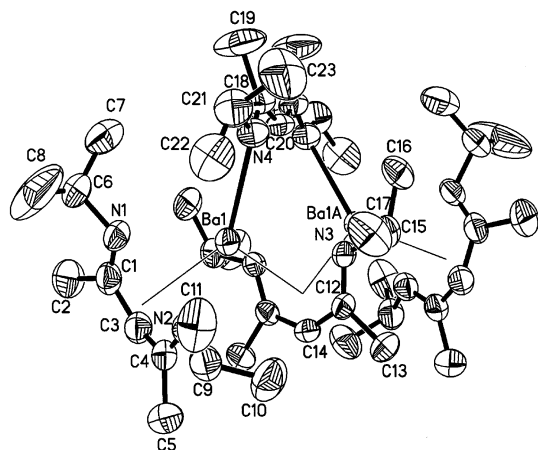
sandwich structures in which a *tert*-butyl group of one ligand is situated over the mouth of the other  $\beta$ -diketiminate ligand and between the two *tert*-butyl groups. The calcium–nitrogen bond distances in **1** range from 2.342(2) to 2.358(2) Å, with an average of 2.352(2) Å. The calcium–carbon distances are much longer and range from 2.817(3) to 2.846(3) Å for the ligand containing N(1) and N(2) and 2.857(3)–2.901(3) Å for the ligand containing N(3) and N(4). The strontium–nitrogen bond distances in **2** range from 2.4727(16) to 2.5171(15) Å, with an average of 2.4946(16) Å. The strontium–carbon

**Figure 1.** Perspective view of **1** with thermal ellipsoids at the 50% probability level.**Figure 2.** Perspective view of **2** with thermal ellipsoids at the 50% probability level.**Figure 3.** Perspective view of **3** with thermal ellipsoids at the 50% probability level.**Figure 4.** Perspective view of **4** with thermal ellipsoids at the 50% probability level.

distances range from 2.991(2) to 3.107(2) Å for the ligand containing N(1) and N(2) and 2.928(2)–3.004(2) Å for the ligand containing N(3) and N(4). The barium–nitrogen bond distances in **3** range from 2.616(2) to 2.680(2) Å, with an average of 2.650(2) Å. The barium–carbon distances are in the range 3.055(3)–3.157(3) Å for the ligand containing N(1) and N(2) and 3.117(3)–3.155(3) Å for the ligand containing N(3) and N(4). The angle formed by C<sub>cent1</sub>–M–C<sub>cent2</sub> is 138.0(1)° for **1**,



**Figure 5.** Perspective view of **5** with thermal ellipsoids at the 50% probability level.



**Figure 6.** Perspective view of **6** with thermal ellipsoids at the 50% probability level.

148.4(1)° for **2**, and 147.6(1)° for **3**. The dihedral angle between the best planes of the  $\beta$ -diketiminato ligand cores is 15.90(1)° for **1**, 3.4(1)° for **2**, and 8.1(2)° for **3**. The nitrogen–carbon and carbon–carbon bond lengths within the  $\beta$ -diketiminato ligand core are consistent with delocalized bonding. Further analysis of the bonding between the metal ions and the  $\beta$ -diketiminato ligands in **1–3** is given below.

A perspective view of **4** is depicted in Figure 4. Complex **4** crystallizes with 1.5 independent molecules, with the molecule containing Ca(2) lying on a 2-fold axis. The structures of the independent molecules are identical within experimental error, so only the data from the molecule containing Ca(1) are described herein. In contrast to **1–3**, the  $\beta$ -diketiminato ligands in **4** are bonded to the calcium ion with the  $\eta^2$ -bonding mode. The calcium–nitrogen bond lengths range from 2.351(2) to 2.358(2) Å ( $av = 2.355(2)$  Å). These values are similar to those of **1** and are slightly shorter than those of Ca(L<sup>Ar</sup>)<sub>2</sub> ( $av = 2.379(1)$  Å).<sup>5c</sup> The nitrogen–carbon and carbon–carbon bond lengths within the  $\beta$ -diketiminato ligand core are in the range 1.308(4)–1.331(4) and 1.401(4)–1.419(4) Å, respectively, and are consistent with delocalized bonding. These values are identical to those observed in **1–3** within experimental error and suggest that the presence or absence of  $\pi$ -orbital contact

**Table 8.** Summary of Metrical Data for the  $\beta$ -Diketiminato Ligands in **1–6**

complex	$a$ – $b$ angle (deg) <sup>a</sup>	$b$ – $c$ angle (deg) <sup>a</sup>	M···C <sub><math>\alpha</math></sub> (Å)	M···C <sub><math>\beta</math></sub> (Å)
<b>1</b>	72.21(10)	25.7(2)	2.840(3)	2.817(3)
	71.17(10)	25.7(2)	2.846(3)	2.865(3)
			2.901(3)	
<b>2</b>	70.25(6)	25.2(3)	3.017(2)	2.991(2)
	72.17(7)	29.1(3)	2.995(2)	2.928(2)
			3.004(2)	2.962(2)
<b>3</b>	73.13(8)	28.9(4)	3.084(3)	3.055(3)
	70.67(8)	25.1(4)	3.157(3)	3.117(3)
			3.155(3)	3.147(3)
<b>4</b>	20.19(13)	3.8(4)	3.265(3)	3.536(3)
	29.4(2)	6.1(6)	3.262(3)	3.472(3)
	23.6(2)	5.8(6)	3.235(3)	3.472(3)
			3.219(3)	
			3.244(3)	3.502(3)
<b>5</b>	69.11(11)	22.1(3)	3.260(3)	3.003(3)
			2.970(3)	3.016(5)
<b>6</b>	70.67(7)	25.0(3)	3.180(2)	3.144(2)
	73.06(3)	1.06(19)	3.168(2)	3.3861(2)
			3.3549(18)	3.2181(19)

<sup>a</sup>  $a$  = plane defined by MN<sub>2</sub>,  $b$  = plane defined by N<sub>2</sub>(C <sub>$\omega$</sub> )<sub>2</sub>,  $c$  = plane defined by (C <sub>$\omega$</sub> )<sub>2</sub>C <sub>$\beta$</sub> .

with a metal ion has little structural impact upon the ligand  $\pi$ -system. The calcium–nitrogen–calcium bite angles are 83.68(8)° and 83.43(9)°. These values compare well with the corresponding angles in Ca(L<sup>Ar</sup>)<sub>2</sub> (83.09(4)°),<sup>5c</sup> but are greater than those of **1**, most likely due to accommodation of the bulky isopropyl groups about the calcium ion. The dihedral angle formed by the best planes of the  $\beta$ -diketiminato ligand core atoms is 103.1(3)°.

Unlike **4**, **5** crystallizes as a sandwich complex analogous to **1–3** (Figure 5). The molecule is located on a 2-fold rotation axis that relates the two halves of the molecule. The strontium–nitrogen bond distances are 2.486(2) and 2.487(2) Å, while the strontium–carbon distances range from 2.970(3) to 3.016(3). The angle formed by C<sub>cent1</sub>–Sr–C<sub>cent2</sub> is 143.6(1)°. The dihedral angle between the best planes of the  $\beta$ -diketiminato ligands is 28.6(2)°. The nitrogen–carbon and carbon–carbon bond lengths within the  $\beta$ -diketiminato ligand core are identical to those observed in **1–4**, within experimental error. Further analysis of the bonding between the strontium ion and the  $\beta$ -diketiminato ligands in **5** is given below.

Complex **6** crystallizes as a dinuclear complex with a very different structure from those observed for **1–5** (Figure 6). The molecule of **6** is highly symmetric and is located on a 2-fold rotation axis that bisects the two bridging ligands and passes through C(14) and C(20). The barium–barium distance is 4.549(1) Å. The two barium ions are held together by one W-shaped  $\mu$ - $\eta^1$ : $\eta^1$ - $\beta$ -diketiminato ligand and one U-shaped  $\mu$ - $\eta^5$ : $\eta^5$ - $\beta$ -diketiminato ligand. The coordination sphere of each barium ion is completed with one  $\eta^5$ - $\beta$ -diketiminato ligand. The barium–nitrogen bond distances are 2.6853(16) and 2.7220(17) Å (terminal  $\eta^5$ - $\beta$ -diketiminato ligand), 2.7896(17) Å ( $\mu$ - $\eta^1$ : $\eta^1$ - $\beta$ -diketiminato ligand), and 2.8140(15) and 2.9268(15) Å ( $\mu$ - $\eta^5$ : $\eta^5$ - $\beta$ -diketiminato ligand). The barium–carbon bond distances are in the

range 3.144(2)–3.180(2) Å for the terminal  $\eta^5$ - $\beta$ -diketiminato ligand, 3.2180(19)–3.3549(18) Å for the  $\mu$ - $\eta^5$ : $\eta^5$ - $\beta$ -diketiminato ligand, and 3.561(2)–3.585(2) Å for the  $\mu$ - $\eta^1$ : $\eta^1$ - $\beta$ -diketiminato ligand. The barium–centroid distances are 2.594(2) Å (terminal  $\eta^5$ - $\beta$ -diketiminato ligand) and 2.763(2) Å ( $\mu$ - $\eta^5$ : $\eta^5$ - $\beta$ -diketiminato ligand). The angles formed by  $C_{\text{cent}1}$ –Ba(1)– $C_{\text{cent}2}$  and Ba(1)– $C_{\text{cent}2}$ –Ba(1)#1 are 107.5(1)° and 110.8(1)° (cent1 is the centroid of the ligand core containing N(1) and N(2); cent2 is the centroid of the ligand core containing N(3)). These values demonstrate that the barium ion lies predominantly over the nitrogen atoms of the  $\beta$ -diketiminato ligands. The nitrogen–barium–nitrogen bite angles for the  $\beta$ -diketiminato ligands are 70.38(4)° (terminal  $\eta^5$ - $\beta$ -diketiminato ligand) and 68.16(4)° ( $\mu$ - $\eta^5$ : $\eta^5$ - $\beta$ -diketiminato ligand).

### Discussion

Table 8 summarizes key metrical parameters associated with the  $\eta^5$ - $\beta$ -diketiminato ligands in **1**–**6**. To assess the bonding, the angles between the planes incorporating the atoms  $MN_2$  (*a*),  $N_2(C_{\alpha})_2$  (*b*), and  $(C_{\alpha})_2C_{\beta}$  (*c*) were calculated. The *a/b* angle assesses the position of the metal ions over the  $\pi$ -face of the  $\beta$ -diketiminato ligand, while the *b/c* angle measures the distortion of  $C_{\beta}$  toward the metal atom due to possible bonding interactions. Also listed are  $M$ – $C_{\alpha}$  and  $M$ – $C_{\beta}$  distances, which allow assessment of the degree of  $\pi$ -orbital contact with the metal ions. On the basis of the bonding analysis in Table 8, we propose that **1**–**3**, **5**, and **6** contain  $\eta^5$ - $\beta$ -diketiminato ligands. This proposal is supported by the large *a/b* angles for **1**–**3**, **5**, and **6** (69–73°), the much smaller *a/b* values for **4** (20–29°), and the relatively short metal–carbon distances to the  $\beta$ -diketiminato ligand core carbon atoms. We have recently reported the synthesis and structure of  $Mg(C_5H_5)(L^{\text{tBu}})$  and suggested that this complex possesses a  $\pi$ -coordinated  $\beta$ -diketiminato ligand on the basis of an *a/b* value of 55.5(1)°.<sup>14</sup> We specifically avoided describing the bonding in  $Mg(C_5H_5)(L^{\text{tBu}})$  as  $\eta^5$ , since the magnesium–carbon bond lengths in the  $\beta$ -diketiminato ligand (2.69–2.83 Å) were 11–15% longer than those for the cyclopentadienyl ligand. In **1**–**3**, **5**, and **6**, the metal–carbon bond lengths are within 10% of metal–carbon bond lengths in a variety of organometallic complexes of calcium, strontium, and barium. For example, **1** has calcium–carbon distances that are between 2.84 and 2.90 Å, **2** and **5** have strontium–carbon distances that are between 2.93 and 3.02 Å, and **3** and **6** have barium–carbon distances that span 3.06–3.18 Å. Comparison structures for calcium include  $Ca(C_5Me_5)_2$  (Ca–C 2.64(2) Å),<sup>15</sup>  $Ca(2,5\text{-di-}t\text{-butylpyrrolyl})_2$  (Ca–C 2.617(4)–2.735(4) Å),<sup>16</sup>  $Ca(2,4\text{-di-}t\text{-butylpentadienyl})_2$  (Ca–C 2.74(1)–2.81(2), av 2.76(2) Å),<sup>17</sup>  $Ca(C_5Me_5)_2(Me_3SiC\equiv C\equiv CSiMe_3)$  (Ca– $C_{Cp^*}$  2.64 Å, Ca– $C_{\pi}$  2.991(5), 3.024(5) Å),<sup>18</sup>  $Ca(CH(Ph)_2P=N(2,4,6\text{-Me}_3C_6H_2))_2$  (Ca–C 2.713(7) Å),<sup>7</sup> and

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**Table 9.** Summary of Metrical Data for Selected  $\pi$ -Coordinated  $\beta$ -Diketiminato Ligands in Complexes from the Literature

complex <sup>a</sup>	M–N (Å)	M···C <sub>α</sub> (Å)	M···C <sub>β</sub> (Å)
Ba <sub>2</sub> L <sup>Cy</sup> <sub>3</sub> (N(SiMe <sub>3</sub> ) <sub>2</sub> ) <sub>6</sub>	2.635(4)	3.161(5)	3.202(5)
	2.689(4)	3.244(5)	
ZrCl <sub>3</sub> (L) <sup>29a</sup>	2.138(5)	2.61(1)	2.54(1)
	2.187(5)	2.60(1)	
Zr(L)(indenyl)Cl <sub>2</sub> <sup>29b</sup>	2.201(2)	2.748(2)	2.703(2)
	2.192(1)	2.713(2)	
Ti(L)Cl <sub>3</sub> <sup>29c</sup>	1.995(4)	2.559(5)	2.535(4)
		2.535(5)	
[CpZr(L)Cl] <sub>2</sub> [B(ArF) <sub>4</sub> ] <sub>2</sub> <sup>29d</sup>	2.110(3)	2.651(3)	2.657(3)
	2.141(2)	2.706(3)	
Nd(L) <sub>2</sub> Cl <sup>11b</sup>	2.397(6)	2.972	3.051
	2.442(6)	3.021	

<sup>a</sup> L = substituted  $\beta$ -diketiminato ligand; see references for substituents on N and C<sub>α</sub>.

$Ca(C(SiMe_3)_2(\eta^2\text{-Ph}))_2$  (Ca–C<sub>σ</sub> 2.649(2) Å, Ca–C<sub>π</sub> 2.893(2), 2.959(2) Å).<sup>19</sup> The calcium–carbon distances in **1** are clearly longer than those observed in calcoenes, open calcoenes, pyrrolyl, and bis(phosphinimino)methyl complexes (2.61–2.76 Å), but are equal to or shorter than calcium–carbon distances to neutral  $\pi$ -donor ligands (2.89–3.02 Å). Reference structures for strontium are less numerous, but include  $Sr(C_5Me_5)_2(C_3N_2(CH_3)_4)$  (Sr– $C_{Cp^*}$  2.850(4) Å, Sr– $C_{\text{carbene}}$  2.854(5), 2.868(5) Å),<sup>20</sup>  $Sr(C_5Me_5)_2(C_3N_2(\text{Pr})_2(CH_3)_2)$  (Sr– $C_{\text{carbene}}$  2.768(5) Å),<sup>21</sup> and  $Sr(C_5(t\text{Bu})_3H_2)_2(\text{THF})$  (Sr– $C_{Cp^*}$  2.87 Å av).<sup>9b</sup> Relevant structures for barium include  $Ba(C_5Me_5)_2$  (Ba–C 2.98(1), 2.99(2) Å),<sup>15</sup>  $Ba(\text{fluorenyl})_2(\text{NH}_3)_4$  (Ba–C 3.15–3.24 Å),<sup>22</sup>  $Ba(C(SiMe_3)_2(SiMe_2\text{OME}))_2(\text{MeOCH}_2\text{CH}_2\text{OME})$  (Ba–C 3.049(2), 3.0363(18) Å),<sup>23</sup>  $Ba(C_5Me_4SiMe_2Ph)$  (Ba– $C_{Cp^*}$  2.96–3.10 Å, Ba– $C_{\pi}$  3.24–4.39 Å),<sup>24</sup> and  $Ba((3,5\text{-Me}_2\text{pz})_3\text{Ge})_2$  (Ba–C 3.27–3.40 Å).<sup>25</sup> Accordingly, the barium–carbon bond lengths in **3** and **6** are similar to or slightly longer than those observed in barocenes and a complex with a barium–carbon  $\sigma$ -bond, but are shorter than the distances observed in barium complexes containing neutral  $\pi$ -donor ligands. An additional comparison can be made with  $Ba_2(L^{\text{Cy}})_3(N(SiMe_3)_2)$ .<sup>6</sup> The terminal  $\eta^5$ - $\beta$ -diketiminato ligand in this complex has barium–carbon distances of 3.16–3.24 Å, which are similar to or slightly longer than those observed in **6**. The  $\mu$ - $\eta^2$ : $\eta^2$ : $\eta^5$ - $\beta$ -diketiminato ligand has barium–carbon distances of 3.21–3.41 Å, the longer of which are similar to those in **6**.

Table 9 lists bond length parameters from selected previously reported complexes that possess  $\pi$ -bonded  $\beta$ -diketiminato ligands. These data allow some comparison to the  $\beta$ -diketiminato ligand bonding modes described herein. Inspection of the bond length trends in Table 9 reveals that the shortest bond lengths in  $\pi$ - $\beta$ -diketiminato ligands are to the nitrogen atoms. The

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bond lengths from the metal atoms to  $C_\alpha$  and  $C_\beta$  are about 0.47–0.60 and 0.35–0.56 Å longer than the metal–nitrogen bond lengths. For **1–3** and **5**, bond lengths from the metal atoms to  $C_\alpha$  and  $C_\beta$  are about 0.43–0.55 and 0.40–0.52 Å longer than the metal–nitrogen bond lengths. Thus, the overall bonding modes in the sandwich complexes **1–3** and **5** are similar to previously reported  $\pi$ -bonded  $\beta$ -diketiminato ligands. The complexes listed in Table 9 consist of large metal ions with predominantly ionic bonding (Ba, Nd) or metal ions that are capable of  $d\pi$ – $p\pi$  bonding to the carbon-based out of plane  $\pi$ -orbitals of the  $\beta$ -diketiminato ligand (Ti, Zr). The bonding in these complexes has been described either as  $\eta^5$  or as  $\pi$ . The bonding in **1–6** should be predominantly ionic. The bending of  $C_\beta$  toward the metal center probably reflects a localization of electron density on this carbon atom and resultant attractive electrostatic interactions with the metal ion.

There has been considerable interest in the fact that the centroid–metal–centroid angles in the heavier group 2 metallocenes deviate substantially from the 180° angle expected from valence shell electron repulsion ideas. In a recent review, these angles were tabulated for a broad range of calcocenes, strontocenes, and barocenes.<sup>8b</sup> These angles range between 147° and 154° for the monomeric, base-free metallocenes  $M(C_5Me_5)_2$ , which are similar to the values observed in **1–3** and **5** (138–148°). The bent centroid–metal–centroid moieties in **1–3** and **5** are not directly comparable to those of the metallocenes, however, since the metal atoms in **1–3** and **5** reside almost directly above the nitrogen atoms. Such dispositions necessarily lead to centroid–metal–centroid angles of <180°. Nevertheless, there are significant analogies between the structures of **1–3** and **5** and those of the calcocenes, strontocenes, and barocenes.

Complexes **4** and **6** adopt very different structures from the closely related analogues **1** and **3**. If **1** were to possess  $\eta^2$ - $\beta$ -diketiminato ligands, then the four *tert*-butyl groups would be placed about a crowded inner coordination sphere. This situation must be less favorable sterically than adoption of the observed  $\eta^5$ - $\beta$ -diketiminato ligands. Since **1** and **4** differ only by four methyl groups, it is likely that  $\eta^2$ - and  $\eta^5$ - $\beta$ -diketiminato ligands are close in energy on calcium centers. The fact that **2** and **5** both adopt sandwich structures is surprising in comparison with **1** and **4**. We suggest that the formation of  $\eta^5$ - $\beta$ -diketiminato ligands in **5** is driven by the larger size of the strontium ion and its increased coordinative unsaturation, relative to **4**. Thus,  $L^{Pr}$  adopts  $\eta^5$ -coordination in **5** to satisfy the coordination requirements of the strontium ion. In a fashion similar to **1** and **4**, **3** adopts a sandwich structure with  $\eta^5$ - $\beta$ -diketiminato ligands to saturate the coordination sphere of the barium ion.

One of the central discoveries described herein is that the  $\eta^5$ - $\beta$ -diketiminato ligand is a surprisingly good ligand for large metal ions such as strontium and barium. Complex **6** contains additional surprises. It exists as a dinuclear complex, like  $Ba_2(L^{Cy})_3(N(SiMe_3)_2)$ .<sup>6</sup> While  $Ba_2(L^{Cy})_3(N(SiMe_3)_2)$  contains  $\eta^5$ -,  $\mu$ - $\eta^2$ - $\eta^2$ - $\eta^5$ -, and  $\mu$ - $\eta^2$ - $\eta^3$ - $\beta$ -diketiminato ligands, the coordination modes in **6** are  $\eta^5$ -,  $\mu$ - $\eta^5$ - $\eta^5$  and  $\mu$ - $\eta^1$ - $\eta^1$ . It is clear that the steric bulk of the nitrogen atom substituents and other ligands in the coordination sphere significantly impact the exact

coordination modes of the bridging  $\beta$ -diketiminato ligands. On the basis of the present work, further reduction in the steric bulk of the nitrogen atom substituents in  $\beta$ -diketiminato ligands may lead to many new and unexpected bridging coordination modes on large metal centers. Triple-decker complexes of the group 2 metals remain rare.<sup>7,26</sup>

## Conclusions

A series of calcium, strontium, and barium complexes containing  $L^{Bu}$  and  $L^{Pr}$  have been synthesized and characterized.  $M(L^{Bu})_2$  and  $Sr(L^{Pr})_2$  possess sandwich structures with  $\eta^5$ - $\beta$ -diketiminato ligands, while  $Ca(L^{Pr})_2$  contains  $\eta^2$ - $\beta$ -diketiminato ligands and  $Ba_2(L^{Pr})_4$  exhibits a dinuclear structure with  $\eta^5$ -,  $\mu$ - $\eta^5$ - $\eta^5$ -, and  $\mu$ - $\eta^1$ - $\eta^1$ - $\beta$ -diketiminato ligands. The  $\eta^5$ - $\beta$ -diketiminato ligand bonds surprisingly well to large metal ions. Furthermore, use of  $L^{Pr}$  in a barium complex led to a dinuclear complex with bridging  $\beta$ -diketiminato ligands, suggesting that  $\beta$ -diketiminato ligands can act as bridging ligands in complexes with large metal ions. All of the complexes are volatile and may serve as chemical vapor deposition precursors for the growth of group 2-containing thin films.

## Experimental Section

**General Considerations.** All reactions were performed under argon using either glovebox or Schlenk line techniques. Tetrahydrofuran and toluene were distilled from sodium. Hexane was distilled from  $P_2O_5$ . *N-tert*-Butyl-4-(*tert*-butylimino)-2-penten-2-amine,<sup>12</sup> *N*-isopropyl-4-(isopropylimino)-2-penten-2-amine,<sup>12</sup> and  $M(N(SiMe_3)_2(THF)_2)$ <sup>13</sup> were prepared according to literature methods.

<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were obtained at 500, 300, 125, or 75 MHz in toluene-*d*<sub>6</sub> or benzene-*d*<sub>6</sub>. Infrared spectra were obtained using Nujol as the medium. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. The low carbon values are a common problem for the heavy alkaline earth complexes.<sup>5c,27</sup> Melting points were obtained on a Haake-Buchler HBI digital melting point apparatus and are uncorrected.

**Preparation of  $Ca(L^{Bu})_2$  (**1**).** A 100 mL Schlenk flask was charged with  $Ca(N(SiMe_3)_2)_2(THF)_2$  (0.48 g, 0.95 mmol), a stir bar, and toluene (30 mL). To this stirred solution at ambient temperature was slowly added  $L^{Bu}H$  (0.40 g, 1.90 mmol) dissolved in 20 mL of toluene. The resultant mixture was stirred for 8 h at ambient temperature, and then the volatile components were removed under reduced pressure to afford **1** as a pale yellow solid (0.43 g, 98%). The analytical sample and single crystals for the X-ray crystallographic analysis were obtained by sublimation at 110 °C/0.05 Torr: mp 168–170 °C; IR (Nujol,  $cm^{-1}$ ) 1628 (w), 1546 (m), 1407 (s), 1358 (s), 1253 (m), 1212 (m), 1181 (s), 1026 (m), 1006 (m), 973 (w), 760 (m); <sup>1</sup>H NMR ( $C_6D_6$ , 23 °C,  $\delta$ ) 4.25 (s, 2H,  $\beta$ -CH), 1.99 (s, 12H, C-CH<sub>3</sub>), 1.35 (s, 36H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_6$ , 23 °C, ppm) 160.93 (s, C-CH<sub>3</sub>), 91.90 (s,  $\beta$ -CH), 53.99 (s, C(CH<sub>3</sub>)<sub>3</sub>), 32.58 (s, C(CH<sub>3</sub>)<sub>3</sub>), 24.73 (s, C-CH<sub>3</sub>). Anal. Calcd for  $C_{26}H_{50}$ ·CaN<sub>4</sub>: C, 68.07; H, 10.99; N, 12.21. Found: C, 68.37; H, 10.90; N, 12.04.

**Preparation of  $Sr(L^{Bu})_2$  (**2**).** In a fashion similar to the preparation of **1**, treatment of  $Sr(N(SiMe_3)_2)_2(THF)_2$  (0.45 g, 0.83 mmol) with  $L^{Bu}H$  (0.35 g, 1.66 mmol) afforded **2** as a pale

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yellow solid (0.39 g, 93%). The analytical sample and single crystals for the X-ray crystallographic analysis were obtained by sublimation at 125 °C/0.05 Torr: mp 127–129 °C; IR (Nujol,  $\text{cm}^{-1}$ ) 1631 (m), 1548 (m), 1411 (s), 1260 (s), 1209 (w), 1187 (s), 1091 (m), 1023 (m), 798 (s), 754 (w);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C,  $\delta$ ) 4.26 (s, 2H,  $\beta\text{-CH}$ ), 2.01 (s, 12H,  $\text{C-CH}_3$ ), 1.33 (s, 36H,  $\text{C}(\text{CH}_3)_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C, ppm) 160.39 (s,  $\text{C-CH}_3$ ), 90.39 (s,  $\beta\text{-CH}$ ), 53.95 (s,  $\text{C}(\text{CH}_3)_3$ ), 32.65 (s,  $\text{C}(\text{CH}_3)_3$ ), 24.83 (s,  $\text{C-CH}_3$ ). Anal. Calcd for  $\text{C}_{26}\text{H}_{50}\text{N}_4\text{Sr}$ : C, 61.68; H, 9.95; N, 11.07. Found: C, 60.39; H, 9.65; N, 11.06.

**Preparation of  $\text{Ba}(\text{L}^{\text{Bu}})_2$  (3).** In a fashion similar to the preparation of **1**, treatment of  $\text{Ba}(\text{N}(\text{SiMe}_3)_2)_2(\text{THF})_2$  (0.72 g, 1.19 mmol) with  $\text{L}^{\text{Bu}}\text{H}$  (0.50 g, 2.38 mmol) afforded **3** as a pale yellow solid (0.60 g, 90%). The analytical sample and single crystals for the X-ray crystallographic analysis were obtained by sublimation at 135 °C/0.05 Torr: mp 184–186 °C; IR (Nujol,  $\text{cm}^{-1}$ ) 1627 (w), 1547 (m), 1406 (s), 1355 (s), 1259 (m), 1248 (m), 1204 (m), 1182 (s), 1093 (w), 1019 (m), 1000 (w), 968 (w), 798 (m), 747 (m);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C,  $\delta$ ) 4.37 (s, 2H,  $\beta\text{-CH}$ ), 2.03 (s, 12H,  $\text{C-CH}_3$ ), 1.32 (s, 36H,  $\text{C}(\text{CH}_3)_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C, ppm) 158.37 (s,  $\text{C-CH}_3$ ), 89.50 (s,  $\beta\text{-CH}$ ), 54.18 (s,  $\text{C}(\text{CH}_3)_3$ ), 32.72 (s,  $\text{C}(\text{CH}_3)_3$ ), 24.81 (s,  $\text{C-CH}_3$ ). Anal. Calcd for  $\text{C}_{26}\text{H}_{50}\text{BaN}_4$ : C, 56.16; H, 9.06; N, 10.08. Found: C, 55.31; H, 8.94; N, 10.07.

**Preparation of  $\text{Ca}(\text{L}^{\text{Pr}})_2$  (4).** In a fashion similar to the preparation of **1–3**, treatment of  $\text{Ca}(\text{N}(\text{SiMe}_3)_2)_2(\text{THF})_2$  (1.38 g, 2.75 mmol) with  $\text{L}^{\text{Pr}}\text{H}$  (1.00 g, 5.49 mmol) afforded **1** as a light yellow solid (0.80 g, 72%). The analytical sample was obtained by sublimation at 100 °C/0.05 Torr onto a cold-finger: mp 92–94 °C; IR (Nujol,  $\text{cm}^{-1}$ ) 1629 (w), 1536 (s), 1516 (m), 1411 (s), 1334 (s), 1307 (s), 1261 (m), 1156 (m), 1140 (m), 1116 (m), 1019 (s), 975 (w), 806 (s);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C,  $\delta$ ) 4.36 (s, 2H,  $\beta\text{-CH}$ ), 3.59 (septet,  $J = 6.0$  Hz, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 1.89 (s, 12H,  $\text{C-CH}_3$ ), 1.26 (d,  $J = 6.0$  Hz, 24H,  $\text{CH}(\text{CH}_3)_2$ );  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ , 23 °C, ppm) 163.42 (s,  $\text{C-CH}_3$ ), 92.43 (s,  $\beta\text{-CH}$ ), 49.96 (s,  $\text{CH}(\text{CH}_3)_2$ ), 25.85 (s,  $\text{CH}(\text{CH}_3)_2$ ), 22.42 (s,  $\text{C-CH}_3$ ). Anal. Calcd for  $\text{C}_{22}\text{H}_{42}\text{CaN}_4$ : C, 65.62; H, 10.51; N, 13.91. Found: C, 65.27; H, 10.57; N, 13.95.

**Preparation of  $\text{Sr}(\text{L}^{\text{Pr}})_2$  (5).** In a fashion similar to the preparation of **1**, treatment of  $\text{Sr}(\text{N}(\text{SiMe}_3)_2)_2(\text{THF})_2$  (1.00 g, 1.81 mmol) with  $\text{L}^{\text{Pr}}\text{H}$  (0.66 g, 3.62 mmol) afforded **2** as a yellow powder (0.65 g, 80%). The analytical sample was obtained by sublimation at 110 °C/0.05 Torr onto a cold-finger: mp 87–89 °C; IR (Nujol,  $\text{cm}^{-1}$ ) 1629 (w), 1597 (w), 1542 (s), 1416 (s), 1329 (s), 1306 (m), 1261 (s), 1242 (w), 1159 (m), 1139 (m), 1115 (s), 1010 (s), 964 (w), 868 (w), 748 (s);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C,  $\delta$ ) 4.21 (s, 2H,  $\beta\text{-CH}$ ), 3.63 (septet,  $J = 6.0$  Hz, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 1.87 (s, 12H,  $\text{C-CH}_3$ ), 1.19 (d,  $J = 6.0$  Hz, 24H,  $\text{CH}(\text{CH}_3)_2$ );  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ , 23 °C, ppm) 161.24 (s,  $\text{C-CH}_3$ ), 87.33 (s,  $\beta\text{-CH}$ ), 49.89 (s,  $\text{CH}(\text{CH}_3)_2$ ), 26.11 (s,  $\text{CH}(\text{CH}_3)_2$ ), 22.08 (s,  $\text{C-CH}_3$ ). Anal. Calcd for  $\text{C}_{22}\text{H}_{42}\text{N}_4\text{Sr}$ : C, 58.69; H, 9.40; N, 12.44. Found: C, 56.17; H, 9.15; N, 12.52.

**Preparation of  $\text{Ba}_2(\text{L}^{\text{Pr}})_4$  (6).** In a fashion similar to the preparation of **1**, treatment of  $\text{Ba}(\text{N}(\text{SiMe}_3)_2)_2(\text{THF})_2$  (1.65 g, 2.74 mmol) with 2 equiv of  $\text{L}^{\text{Pr}}\text{H}$  (1.00 g, 5.49 mmol) afforded **6** as yellow crystals from hexane at –30 °C (0.54 g, 39%): mp 176–178 °C; IR (Nujol,  $\text{cm}^{-1}$ ) 1628 (w), 1543 (m), 1330 (w), 1299 (w), 1280 (w), 1261 (m), 1159 (m), 1114 (m), 1012 (m), 802 (m);  $^1\text{H}$  NMR (toluene- $d_6$ , 80 °C,  $\delta$ ) 4.17 (s, 4H,  $\beta\text{-CH}$ ), 3.66 (m, 8H,  $\text{CH}(\text{CH}_3)_2$ ), 1.88 (s, 24H,  $\text{C-CH}_3$ ), 1.18 (d,  $J = 6.3$  Hz, 48H,  $\text{CH}(\text{CH}_3)_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (toluene- $d_6$ , 80 °C, ppm) 162.0, (br s,  $\text{C-CH}_3$ ), 87.85 (m,  $\beta\text{-CH}$ ), 50.35 (s,  $\text{CH}(\text{CH}_3)_2$ ), 26.00 (s,  $\text{CH}(\text{CH}_3)_2$ ), 21.22 (s,  $\text{C-CH}_3$ ). Anal. Calcd for  $\text{C}_{44}\text{H}_{84}\text{Ba}_2\text{N}_8$ : C, 52.86; H, 8.47; N, 11.21. Found: C, 49.38; H, 8.19; N, 10.55.

**X-ray Crystallographic Structure Determinations for 1–6.** Diffraction data were collected on a Bruker P4/CCD diffractometer equipped with Mo  $K\alpha$  radiation and a graphite monochromator. All samples were mounted in sealed thin-walled glass capillaries under an inert atmosphere for data collection. A complete sphere of data was collected at 10 s/frame and 0.2° width at room temperature. The manufacturer's SMART and SAINT software were used for processing. Absorption corrections were made with Sheldrick's SADABS program distributed by Bruker. The structures were solved and refined with Sheldrick's SHELX-97.<sup>28,29</sup> Complexes **1–6** crystallized as neutral complexes without solvent.

Complex **1** crystallizes as colorless multifaceted crystals. A sample of dimensions 0.5 × 0.4 × 0.4 mm<sup>3</sup> was used for the data collection. 2450 CCD frames were collected, yielding 42 764 reflections, of which 7219 were independent. Hydrogen atom positions were calculated or observed.

Complex **2** crystallizes as colorless multifaceted crystals. A single crystal of dimensions 0.4 × 0.3 × 0.3 mm<sup>3</sup> was used for the data collection. 1650 CCD frames were collected, yielding 21 455 reflections, of which 7045 were independent. Hydrogen atom positions were calculated or observed.

Complex **3** crystallizes as colorless mounds. A cut fragment of dimensions 0.30 × 0.30 × 0.25 mm<sup>3</sup> was used for the data collection. 2450 CCD frames were collected, yielding 21 557 reflections, of which 7165 were independent. Hydrogen atom positions were calculated or observed.

Complex **4** crystallizes as yellow cubes. A cut fragment measuring 0.30 × 0.25 × 0.25 mm<sup>3</sup> was used for the data collection. 2450 CCD frames were collected, yielding 27214 reflections, of which 8846 were independent. Hydrogen atom positions were calculated. The asymmetric unit contains 1.5 independent molecules; one molecule occupies a 2-fold axis.

Complex **5** crystallizes as colorless rods. A crystal of dimensions 0.40 × 0.15 × 0.15 mm<sup>3</sup> was used for the data collection. 1850 CCD frames were collected, yielding 9307 reflections, of which 3072 were independent. Hydrogen atom positions were calculated. The strontium atom occupies a crystallographic 2-fold axis.

Complex **6** crystallizes as yellow rhomboids. A crystal of dimensions 0.40 × 0.32 × 0.25 mm<sup>3</sup> was used for the data collection. 2450 CCD frames were collected, yielding 18 164 reflections, of which 6052 were independent. Hydrogen atom positions were calculated. The molecule occupies a 2-fold axis. Large thermal parameters are displayed by the pendant isopropyl groups, indicating disorder.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for the structure determinations of **1–6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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