complexes. These results suggest that the oxidized $Ru^{IV}O^{2+}$ complexes based on these Ru(II) precursors may show striking chiral selectivities not only in their known DNA cleavage reactions[7,12] but also in oxidations of numerous small molecules.[16]

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Registry No. $Ru(tpy)(bpy)OH_2^{2+}$, 20154-63-6; $Ru(tpy)(phen)OH_2^{2+}$, 101241-02-5; $Ru(tpy)(tmen)OH_2^{2+}$, 127714-17-4; $Ru(bpy)_2(OH_2)_2^{2+}$, 72174-09-5; $Ru(bpy)_2(py)OH_2^{2+}$, 67202-42-0; $Ru(phen)_2(OH_2)_2^{2+}$, 47668-18-8; $Ru(phen)_2(py)OH_2^{2+}$, 47768-50-3.

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Formation and Reactions of Mono- and Bis(peralkylcyclopentadienyl) Complexes of Calcium and Barium. The X-ray Crystal Structure of $[(Me_4EtC_5)Ca(\mu\text{-}\overline{NSiMe_2CH_2CH_2Si}Me_2)]_2$

S. Craig Sockwell,[†] Timothy P. Hanusa,[*,†] and John C. Huffman[‡]

Contribution from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, and Molecular Structure Center, Department of Chemistry, Indiana University, Bloomington, Indiana 47405. *Received June 3, 1991*

Abstract: The reaction of $K(Me_4EtC_5)$ and CaI_2 in THF forms the colorless metallocene $(Me_4EtC_5)_2Ca(THF)$ in high yield. Both it and $Cp^*{}_2Ca(THF)_2$ ($Cp^* = Me_5C_5$) can be used in a variety of reactions to form mono(peralkylcyclopentadienyl) complexes of calcium, in which disproportionation via Schlenk equilibrium plays a smaller than expected role. Thus, $(Me_4EtC_5)CaI(THF)_2$ reacts with $K[OC_6H_2\text{-}t\text{-}Bu_2\text{-}2,6\text{-}Me\text{-}4]$, K[Otamp] (Otamp = 2,4,6-tris[(dimethylamino)methyl]phenoxide) or $K\overline{NSiMe_2CH_2CH_2Si}Me_2$ to produce $(Me_4EtC_5)Ca(OC_6H_2\text{-}t\text{-}Bu_2\text{-}2,6\text{-}Me\text{-}4)$, $(Me_4EtC_5)Ca(Otamp)$, and $[(Me_4EtC_5)Ca(\mu\text{-}\overline{NSiMe_2CH_2CH_2Si}Me_2)]_2$. These compounds represent the first mixed cyclopentadienyl amide or aryl oxide complexes of the heavy alkaline-earth metals to be described. Crystals of $[(Me_4EtC_5)Ca(\mu\text{-}\overline{NSiMe_2CH_2CH_2Si}Me_2)]_2$ grown from toluene are monoclinic, space group $P2_1/a$, with $a = 17.846$ (4) Å, $b = 12.405$ (2) Å, $c = 18.140$ (3) Å, $\beta = 97.32$ (1)° and D(calcd) = 1.160 g cm^{-3} for $Z = 4$. Least-squares refinement on the basis of 2200 observed reflections measured at −172 °C led to a final R value of 0.057. The compound crystallizes in the form of a dimer containing a planar $[Ca\text{–}N\text{–}]_2$ ring. The two shorter Ca–N distances average 2.41 (1) Å, and the two longer Ca–N′ distances average 2.48 (1) Å. The average Ca–C(ring) distance is 2.70 (3) Å. $Cp^*{}_2Ca(THF)_2$ ($Cp^* = Me_5C_5$) reacts with $LiN(SiMe_3)_2$ and $LiCH(SiMe_3)_2$ in THF to form a precipitate of $LiCp^*$ and generate the hydrocarbon-soluble mono(pentamethylcyclopentadienyl) complexes $Cp^*CaE(THF)_3$ ($E = N(SiMe_3)_2$, $CH(SiMe_3)_2$). Mixing THF solutions of $Cp^*{}_2Ba(THF)_2$ with $LiN(SiMe_3)_2$ or $LiCH(SiMe_3)_2$ does not form $LiCp^*$, and the hydrocarbon-insoluble organobarates $Li[Cp^*{}_2BaE](THF)_2$ ($E = N(SiMe_3)_2$, $CH(SiMe_3)_2$) can be isolated from the reaction mixtures in near quantitative yield.

Introduction

Increasing interest in the organometallic chemistry of the calcium subgroup metals (Ca, Sr, and Ba) has strikingly revealed how comparatively little is known about the stoichiometry, structure, and reactivity of these compounds.[1] The large metal radii, polar metal–ligand bonding, and high kinetic lability associated with the alkaline earths (Ae) should create opportunities for developing unusual stoichiometric and catalytic chemistry. These same attributes, however, can lead to insoluble, nonvolatile compounds with high air and moisture sensitivity and a propensity for ligand loss and decomposition.

Monocyclopentadienyl complexes (Cp′AeX) offer attractive possibilities for exploiting the potential chemistry offered by the Ae elements while avoiding some of the difficulties.[2] The use of a variety of Cp rings and the addition or removal of neutral donor ligands provide considerable flexibility in adjusting the metal coordination environments. In addition, the relatively exposed metal center in a monocyclopentadienyl complex should simplify the construction of poly- and heterometallic complexes.

Two general methods have been described in the literature for preparing monoring compounds of the calcium subgroup metals, lanthanides, and actinides. The first of these involves the addition of a ring to a metal, metal halide, or metal aryl oxide; this can be achieved by oxidizing a metal with a cyclopentadienyl iodide,[3] but is usually done by reacting an alkali metal or thallium cyclopentadienide with a metal halide or aryl oxide.[4-8] The second general method selectively removes a cyclopentadienyl ring from

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[†] Vanderbilt University.

[‡] Indiana University.

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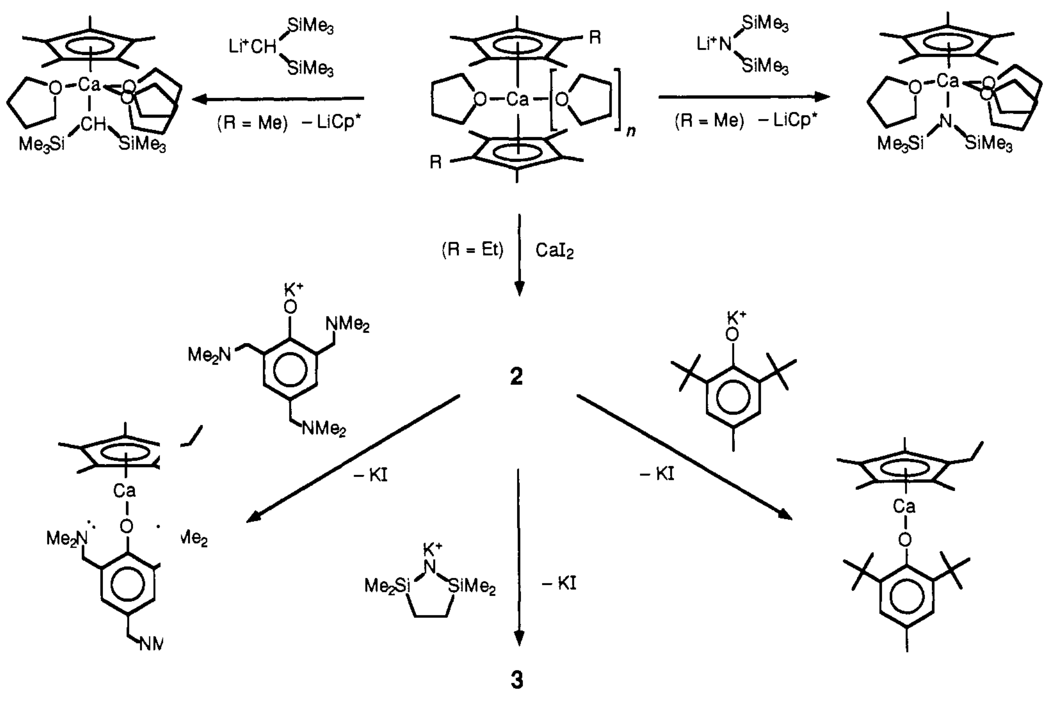

Figure 1. Formation of monocyclopentadienyl complexes of calcium. When R = Me in $(C_5Me_4R)_2Ca(THF)_n$, $n = 1$; when R = Et, $n = 0$.

a dicyclopentadienyl complex. This has been achieved in several ways, including (a) the substitution of a ring with a halide, as in the formation of $[Cp^*Ca(\mu\text{-}I)(THF)]_2$ (**1**) from $Cp^*_2Ca(THF)_2$ and CaI_2 ($Cp^* = C_5Me_5$)[2] or the preparation of $Cp^*YbCl(OEt_2)$ from $Cp^*_2Yb(OEt_2)$ and *t*-BuCl;[9] (b) the protonation of a ring with an organic acid, as in the formation of $[Cp^*Eu(\mu\text{-}C{\equiv}CPh)(THF)_2]_2$ from $Cp^*_2Eu(THF)_2$ and $HC{\equiv}CPh$;[10] or (c) the precipitation of a ring as an insoluble salt, as was used to prepare $Cp^*Yb(CH_3)_2Li$ from Cp^*_2Yb and CH_3Li.[11] No systematic comparisons have been made of the relative efficiency of these methods, and few examples exist of successful derivatization of a previously existing monoring complex; the formation of $Cp^*La[CH(SiMe_3)_2]_2$ from $\{Cp^*LaI_2\}_n$ and $KCH(SiMe_3)_2$,[12] and $Cp^*Ce[CH(SiMe_3)_2]_2$ from $Cp^*Ce(2,6\text{-di-}tert\text{-butylphenoxide})_2$ and $LiCH(SiMe_3)_2$[7] are notable exceptions.

Although it does not seem to be a significant problem with tri- and tetravalent organolanthanides and -actinides, derivatization of monoring species of the divalent alkaline earths is potentially complicated by the existence of the Schlenk equilibrium (eq 1).

$$2Cp^*AeX \rightleftharpoons Cp^*_2Ae + AeX_2 \qquad (1)$$

In a THF solution of **1**, for example, extensive dissociation occurs, so that only half the calcium in a solution of "$Cp^*CaI(THF)_2$" exists as the monoring species ($K_d = 0.25$).[2] Hence, derivatization of the monoring complex is not necessarily a simple matter of adding a reagent that will replace the halide, as the same reagent also may react with the inevitably present metallocene and metal dihalide.

The position of the Schlenk equilibrium, however, is strongly affected by the nature of the solvent (e.g., K_d for **1** in benzene $= 1.7 \times 10^{-3}$) and by the ligands on the metal. We describe here combinations of ligands and solvents that can be used to synthesize a variety of mono(peralkylcyclopentadienyl) derivatives of calcium, including derivatized species, the substantially different chemistry observed with barium, and a description of the factors that may play a role in differentiating their chemistry.

Results

A schematic of the reactions of the calcium-based metallocenes and monocyclopentadienyl complexes is provided in Figure 1. These are discussed in detail below, along with the reactions of organobarium complexes.

Synthesis of Metallocenes and Monocyclopentadienyl Iodides. When 2 equiv of $K(Me_4EtC_5)$ is allowed to react with CaI_2 in THF, a cloudy solution forms that on workup yields the colorless metallocene $(Me_4EtC_5)_2Ca(THF)$ in a quantitative yield. The compound is comparable to $Cp^*_2Ca(THF)_2$ in its solubility in aromatic hydrocarbons and slight solubility in alkanes.[13] $(Me_4EtC_5)_2Ca(THF)$ reacts with CaI_2 in THF to form the monoring species $(Me_4EtC_5)CaI(THF)_2$, **2**. The crude material is 85% **2**, the remainder being $(Me_4EtC_5)_2Ca(THF)$ and $CaI_2(THF)_2$. When the crude product is washed with toluene, 94% of the remaining material appears as **2** (^1H NMR in C_6D_6).

The monoring product also can be formed from the metathetical reaction of CaI_2 and $K(Me_4EtC_5)$. This behavior is similar to that previously observed for the pentamethylcyclopentadienyl analogue.[2] Generally, although not always, reactions using either $Cp^*_2Ca(THF)_2$ or $(Me_4EtC_5)_2Ca(THF)$ to produce monoring species give roughly comparable results; the (Me_4EtC_5) complexes usually have somewhat better solubility and crystallinity, however. It should also be noted that the extent of reaction of CaI_2 with $(Me_4EtC_5)_2Ca(THF)$ is greater (or equivalently, that the extent of disproportionation of **2** via Schlenk equilibrium is less) than that observed with $Cp^*_2Ca(THF)_2$.[2] In conformity with the elemental analysis, which indicates that **2** is free from both $(Me_4EtC_5)_2Ca(THF)$ and $CaI_2(THF)_2$, in subsequent reactions **2** is assumed to be pure, and the ~6% $(Me_4EtC_5)_2Ca(THF)$ observed in NMR spectra is believed to arise primarily from Schlenk equilibria.

Derivatization of Monocyclopentadienyl Complexes. When **2** is allowed to react with K[BHT] (BHT = $OC_6H_2\text{-}t\text{-}Bu_2\text{-}2,6\text{-}Me\text{-}4$) in toluene, the solution immediately becomes turbid. Removal of the white precipitate leaves a colorless solution that contains an approximately 3:1 mixture of the monoring species $(Me_4EtC_5)Ca(BHT)$ and the previously described bis(aryl oxide) $Ca(BHT)_2(THF)_3$.[14,15] A single hexane wash preferentially

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Table I. Crystal Data and Summary of Data Collection for $[(Me_4EtC_5)Ca(\mu\text{-}NSiMe_2CH_2CH_2SiMe_2)]_2$

formula	$C_{34}H_{66}Ca_2N_2Si_4$
fw	695.41
color of crystal	colorless
cryst dimens, mm	0.25 × 0.25 × 0.25
space group	$P2_1/a$
cell dimens (at −172 °C, 64 reflctns)	
a, Å	17.846 (4)
b, Å	12.405 (2)
c, Å	18.140 (3)
β, deg	97.32 (1)
V, Å^3	3983 (2)
Z	4
D(calcd), g/cm^3	1.160
wavelength, Å	0.71069
abs coeff, cm^{-1}	4.206
type of scan	continuous θ–2θ
scan speed, deg/min	6.0
scan width	2.0 + dispersn
bkgd counting	4 s at extremes of scan
limits of data collectn	$6° \leq 2\theta \leq 45°$
total no. of reflections collected	9952
no. of unique intensities	5195
no. with $F > 0.0$	4418
no. with $F > 2.33s(F)$	2200
R for averaging	0.091
$R(F)$	0.0573
$R_w(F)$	0.0605
goodness of fit	1.241
max Δ/σ in final cycle	0.34

removes the bis(aryl oxide), leaving a spectroscopically pure monoring product. Interestingly, the material is isolated on recrystallization from toluene without coordinated THF.

The substituted phenol 2,4,6-tris[(dimethylamino)methyl]phenol (HOtamp) is readily deprotonated with potassium hydride in THF to produce the salt K[Otamp]·THF as a white friable solid. It reacts on mixing with **2** to yield the aryl oxide complex $(Me_4EtC_5)Ca(Otamp)$. As with the BHT derivative, the material is isolated without coordinated solvent.

The cyclic amine 2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentane, $HNSiMe_2CH_2CH_2SiMe_2$, is converted into its potassium salt on reaction with KH in THF. The mixture of **2** and $K\text{-}NSiMe_2CH_2CH_2SiMe_2$ produces a cloudy solution, from which a white precipitate can be removed by filtration. Evaporation of the filtrate and extraction of the residue with hexane leave the off-white solid $(Me_4EtC_5)Ca(NSiMe_2CH_2CH_2SiMe_2)$, **3**. Consistent with the difficulty found in hydrogenolysis of Mg–N bonds in organomagnesium amides,[16] **3** is not hydrogenolyzed in toluene by H_2 (1 atm, 22 °C, overnight).

Structure of $[(Me_4EtC_5)Ca(\mu\text{-}NSiMe_2CH_2CH_2SiMe_2)]_2$. Despite repeated attempts with all the monoring complexes to grow crystals, only those of **3** proved suitable for an X-ray structure determination. A summary of data collection parameters is presented in Table I. The compound crystallizes from toluene as an amide-bridged dimer, in which each calcium atom is coordinated by a single tetramethylethylcyclopentadienyl ring and two bridging $(NSiMe_2CH_2CH_2SiMe_2)$ groups. An ORTEP view of the molecule providing the numbering scheme used in the tables is displayed in Figure 2, and average structural parameters are summarized in Table II.

The dimer is approximately centrosymmetric, although it does not contain a crystallographically imposed center of inversion. The central $[Ca\text{–}N\text{–}]_2$ core is planar to within 0.0001 Å, and the least-squares plane through the four-atom core and the two ring centroids is planar to within 0.094 Å. There are two shorter Ca–N distances with an average length of 2.41 (1) Å, and two longer contacts at 2.48 (1) Å; although the difference is statistically significant, the asymmetry parameter ϕ for the $[Ca\text{–}N\text{–}]_2$ core is 4.8%, near the average for structurally characterized homometallic bridged dimers.[2] The ring carbons bearing the ethyl groups are rotated 162° from each other, and the planes of the rings form an angle of 5.0° to each other.

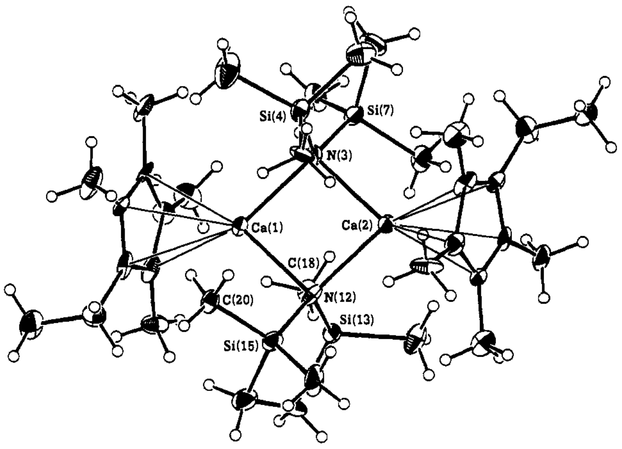

Figure 2. ORTEP view of **3**, with thermal ellipsoids drawn at the 50% probability level.

Table II. Selected Bond Lengths (Å) and Angles (deg) in $[(Me_4EtC_5)Ca(\mu\text{-}NSiMe_2CH_2CH_2SiMe_2)]_2$

atoms	distance	atoms	angle
Ca(1)···Ca(2)	3.645 (3)	N(3)–Ca(1)–N(12)	83.9 (3)
Ca(1)–N(3)	2.406 (9)	N(3)–Ca(2)–N(12)	83.4 (3)
Ca(1)–N(12)	2.474 (9)	N(12)–Si(13)–C(18)	109.7 (4)
Ca(2)–N(3)	2.489 (8)	Ca(1)–N(3)–Ca(2)	96.2 (3)
Ca(2)–N(12)	2.412 (10)	Ca(1)–N(3)–Si(4)	116.4 (4)
Ca(1)–C(18)	2.932 (12)	Ca(1)–N(3)–Si(7)	125.3 (5)
Si(4)–N(3)	1.730 (9)	Ca(2)–N(3)–Si(4)	101.7 (4)
Si(7)–N(3)	1.739 (8)	Ca(2)–N(3)–Si(7)	104.7 (4)
Si(13)–N(12)	1.730 (9)	Si(4)–N(3)–Si(7)	107.9 (5)
Si(16)–N(12)	1.710 (10)	Ca(1)–N(12)–Ca(2)	96.5 (3)
		Ca(1)–N(12)–Si(13)	100.1 (4)
		Ca(1)–N(12)–Si(16)	106.0 (4)
		Ca(2)–N(12)–Si(13)	109.3 (5)
		Ca(2)–N(12)–Si(16)	130.4 (5)
		Si(13)–N(12)–Si(16)	109.4 (6)

Ca–C(ring) (av)	2.70 (3)
Ca–ring centroid	2.418, 2.413
C–C(ring) (av)	1.42 (5)
C(ring)–C(methyl) (av)	1.50 (4)
planarity of rings	within 0.007 Å
av displacement of Me groups from ring plane	0.153 Å
displacement angle (α)	5.8°

Several structural parameters give evidence of appreciable steric crowding in the dimer. For example, the average Ca–ring centroid distance is 2.42 Å, which is substantially longer than the 2.26-Å value expected from the sum of the radius of 5-coordinate Ca^{2+} (0.93 Å)[17] and the cyclopentadienyl ring thickness (1.33 Å).[18] This is particularly notable as it has recently been found that the metal radius alone is usually a reliable predictor (within 0.03 Å) of metal–Cp distances in *divalent* organolanthanide and organo-alkaline-earth complexes.[18] Thus, in Cp^*_2Ca and $[Cp^*Ca(\mu\text{-}I)(THF)_2]_2$, for example, the observed Ca–centroid distances differ from those expected from the sum of metal radii and the cyclopentadienyl ring thickness by only 0.02 and 0.01 Å, respectively.[18] Curiously, the lengthening of the Ca–ring distances does not appear to be associated with any anomalous Ca–N contacts. For example, the average length of all the Ca–N bonds, 2.45 (2) Å, is approximately the same as the 2.49 (2) Å distance observed in $[((THF)_3Ca)(HAlN\text{-}t\text{-}Bu)_3]\cdot THF$, when the 0.07-Å

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distance between 6- and 5-coordinate Ca^{2+} is taken into account.[19]

Crowding is also apparent in several close intramolecular contacts, the shortest of which at 2.93 (1) Å is between the trimethylsilyl carbon C(18) and Ca(1). The shortest calculated Ca···H separation involves H(64) on C(18) and Ca(1) at 2.40 Å. This distance is short enough that the possibility of agostic M···H···C bonding should be considered.[20] Since the hydrogen atoms were not directly located in the crystal structure, no great weight can be assigned to the Ca···H distance itself. The $Ca\cdots CH_3$ distance, however, can be compared with the closest intermolecular $Ca\cdots CH_3'$ contact in $Cp^*{}_2Ca$ at 2.98 Å. If the 0.07-Å difference between 5- and 6-coordinate Ca^{2+} is considered, the $Ca\cdots CH_3$ distance in **3** is no shorter than that in $Cp^*{}_2Ca$. Subtracting the Ca^{2+} radius from the calcium–methyl distance provides a relative distance of 2.00 Å, which is at the average for analogous distances found in alkaline-earth and lanthanide decamethylmetallocenes (1.99 Å).[21] Consistent with the lack of structural evidence for an agostic interaction, no especially low C–H stretching frequencies are evident in the IR spectrum of the solid.

A consequence of the relatively low coordination number of calcium is that the Ca(1)···Ca(2) separation in **3** appears at 3.654 (3) Å, a full 1.0 Å shorter than the Ca···Ca′ distance in **1**,[2] and 0.3 Å less than the distance in elemental α-Ca.[22] The compound visibly fluoresces under 254-nm UV radiation, although neither $(Me_4EtC_5)_2Ca(THF)$ nor $K\overline{NSiMe_2CH_2CH_2Si}Me_2$ does so. Studies to determine whether such fluorescence stems from an interaction between the closed-shell Ca^{2+} centers[23] are in progress.[24]

Monocyclopentadienyl Complexes from Metallocenes. $Cp^*{}_2Ca(THF)_2$ reacts with $LiN(SiMe_3)_2$ in THF or toluene to produce a precipitate of $LiCp^*$ and generate the monoring complex $Cp^*CaN(SiMe_3)_2(THF)_3$ (eq 2). The use of 2 equiv of the dialkylamide with the metallocene still yields the monoring complex, and not the bis(dialkylamide) that might be expected (eq 3). The colorless monoring complex dissociates in solution via Schlenk equilibrium to generate $Ca[N(SiMe_3)_2]_2(THF)_2$[25] and regenerate $Cp^*{}_2Ca(THF)_2$ (eq 4). K_d for the process in a saturated C_6D_6 solution is 9.8×10^{-3}, somewhat larger than the value for the iodide complex $Cp^*CaI(THF)_2$ (1.7×10^{-3}).[2] As is the case with **3**, the monoring calcium amide is not hydrogenolyzed in toluene by H_2 (1 atm, 22 °C, 3 days).

$$Cp^*{}_2Ca(THF)_2 + LiN(SiMe_3)_2 \xrightarrow{THF} Cp^*CaN(SiMe_3)_2(THF)_3 + LiCp^*\downarrow \quad (2)$$

$$\begin{tikzcd} Cp^*{}_2Ca(THF)_2 + 2LiN(SiMe_3)_2 \arrow[r, "THF", "/\!/"'] \arrow[d, "THF"'] & Ca[N(SiMe_3)_2]_2(THF)_2 + 2LiCp^*\downarrow \\ Cp^*CaN(SiMe_3)_2(THF)_3 + LiN(SiMe_3)_2 + LiCp^*\downarrow & \end{tikzcd} \quad (3)$$

$$2Cp^*CaN(SiMe_3)_2(THF)_3 \overset{K}{\rightleftharpoons} Cp^*{}_2Ca(THF) + Ca[N(SiMe_3)_2]_2(THF)_2 \quad (4)$$

The reaction of $Cp^*{}_2Ca(THF)_2$ with the bulky lithium alkyl $LiCH(SiMe_3)_2$ produces a precipitate of $LiCp^*$ and a solution of $Cp^*CaCH(SiMe_3)_2(THF)_3$. The compound is only slightly dissociated in C_6D_6 solution ($K_d = 4.2 \times 10^{-4}$), but it is not indefinitely stable at room temperature either in the solid state or in solution. The THF ligands appear to be important for stability, as even washing the solid with hexane can induce some disproportionation. In C_6D_6 solution, $CH_2(SiMe_3)_2$ appears over time as a decomposition product; the source of the hydrogen in the silylated methane is not certain, but it may arise from the THF ligand or the Cp* ring;[26-28] deuterium incorporation from the solvent is not observed. The instability of bis(trimethylsilyl)methyl complexes of trivalent uranium,[29] lanthanum,[12] and cerium[7] has been previously reported.

Attempts to form monoring amide or alkyl complexes from $(Me_4EtC_5)_2Ca(THF)$ and the appropriate lithium reagent were not as successful, and complex mixtures of products were formed. $Cp^*{}_2Ca(THF)_2$ does react with other lithium reagents including $LiC{\equiv}CSiMe_3$, $LiC(SiMe_3)_3$, $LiP(Ph)_2$, $LiC{\equiv}CPh$, $LiSiPh_3$, and $LiN[CH(CH_3)_2]_2$ to produce precipitates analogous to those from $LiE(SiMe_3)_2$. No monoring species were isolated from these reaction mixtures, however.

When $Cp^*CaCH(SiMe_3)_2(THF)_3$ is put under an atmosphere of hydrogen in toluene, a light grey precipitate forms overnight. Evaporation of the solution yields the metallocene $Cp^*{}_2Ca(THF)_2$ as the only identifiable organometallic product. No direct evidence for a "$Cp^*CaH(THF)_x$" species is observed.

Reactions with Barium Metallocenes. Unlike the reaction of $Cp^*{}_2Ca(THF)_2$ with $LiN(SiMe_3)_2$, no precipitate of $LiCp^*$ is formed when $Cp^*{}_2Ba(THF)_2$ reacts with either 1 or 2 equiv of $LiN(SiMe_3)_2$ in THF. After the solution is evaporated, the dried reaction mixture is not soluble in toluene, and therefore it does not contain unreacted $Cp^*{}_2Ba(THF)_2$ or $LiN(SiMe_3)_2$. The ^1H NMR spectrum in THF-d_8 reveals the presence of both $Cp^*{}_2Ba(THF)_2$ and resonances characteristic of $N(SiMe_3)_2^-$. If the same reaction is conducted in toluene, a precipitate does form that exhibits the same NMR resonances as the dried filtrate from the THF reaction. A reasonable explanation of this data is that the reaction of $Cp^*{}_2Ba(THF)_2$ with $LiN(SiMe_3)_2$ forms a hydrocarbon-insoluble complex that dissociates when placed in THF (eq 5). We formulate the complex as a lithium barate, in analogy to the organolanthanide complexes $Li[Cp^*YbCl_3](THF)$ and $Li[Cp^*LuCl_3](ether)_2$ isolated by Watson.[3,11] A similar reaction is observed with $Cp^*{}_2Ba(THF)_2$ and $LiCH(SiMe_3)_2$ in THF, in that an organometallic compound of the composition $Li[Cp^*{}_2BaCH(SiMe_3)_2](THF)_2$ forms that is not soluble in toluene but dissociates to regenerate the metallocene and alkyl anion in THF.

$$Cp^*{}_2Ba(THF)_2 + LiN(SiMe_3)_2 \underset{toluene}{\overset{THF}{\rightleftharpoons}} \begin{matrix} [LiN(SiMe_3)_2][Cp^*{}_2Ba(THF)_2] \\ \text{or} \\ Li[Cp^*{}_2BaE](THF)_2 \end{matrix} \quad (5)$$

Discussion

The formation of the complexes described here underscores the sensitivity of the composition of organo-alkaline-earth complexes to the ligand environment of the metal centers. For instance, replacement of one methyl group on each ring in $Cp^*{}_2Ca(THF)_2$ with the only slightly larger ethyl group prevents the isolation of a disolvated metallocene, and bis(tetramethylethylcyclopentadienyl)calcium is isolated from THF solution with only one coordinated THF per metal center. This observation may be related to our previous finding that one THF is readily removed from $Cp^*{}_2Ca(THF)_2$ in toluene solution, i.e., that the metal center is nearly oversaturated,[30] and will readily extrude a ligand from the metal coordination sphere. A combination of steric demands, lattice packing, and entropic forces may serve to prevent the

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formation of "$(Me_4EtC_5)_2Ca(THF)_2$" as a stable solid.

Formation of Monoring Complexes by Derivatization Reactions. The operation of Schlenk equilibrium in the reactions of organo-alkaline-earth complexes (eq 1) has been considered a major obstacle to derivatizing monoring halide complexes. This problem cannot be entirely avoided, but its consequences can be minimized by the proper combinations of ligands and solvents. Sterically bulky ligands, for example, promote solubility in nonpolar solvents, which in turn discourage dissociation of monoring species.

Thus, the reaction of **2** and K[BHT] in toluene produces a mixture of $(Me_4EtC_5)Ca(BHT)$ and $Ca(BHT)_2(THF)_2$, from which the bis(aryl oxide) complex can be removed because of its greater solubility in hexane. Similarly, **2** and K[Otamp] or $K\overline{NSiMe_2CH_2CH_2Si}Me_2$ react on mixing to yield the complex $(Me_4EtC_5)Ca(Otamp)$ or **3**, respectively. These compounds represent the first mixed cyclopentadienyl amide or aryl oxide complexes of the heavy alkaline-earth metals to be described. It is notable that the monoring products are isolated in high yield (ca. 80% or greater) from these reactions. The steric bulk of the *t*-Bu, dimethylamino, or dimethylsilyl groups in positions close to the metal center evidently supplies the steric bulk that allows these complexes to be isolated free from coordinated THF. The Otamp ligand has recently been used to synthesize an oxoaryl oxide of barium in THF that crystallizes without coordinated solvent. An X-ray crystal structure of the compound indicates that the dimethylamino methyl groups coordinate to the barium centers, apparently occupying sites that otherwise would have been filled by THF.[31]

Attempts to isolate organometallic hydrides from these monoring species by hydrogenolysis were not successful. Treatment of $Cp^*CaCH(SiMe_3)_2(THF)_3$ with H_2 in toluene yields $Cp^*_2Ca(THF)_2$ as the only observable organometallic product. Conceivably the $Cp^*_2Ca(THF)_2$ could arise from the decomposition of a transiently formed "Cp^*CaH" species (i.e., 2"$Cp^*CaH(THF)_x$" $\rightarrow Cp^*_2Ca(THF)_2 + CaH_2\downarrow$). Calcium hydride was not unambiguously identified in the decomposition product mixture, however. A different, perhaps more bulky, set of supporting ligands will probably be required to isolate a stable organocalcium hydride.[32]

Formation of Monoring Complexes by Displacement Reactions. The almost complete insolubility of $LiCp^*$ in hydrocarbons and ethers provides a driving force for the selective precipitation of a ring from metallocenes to generate monocyclopentadienyl species. The reaction of $Cp^*_2Ca(THF)_2$ with $LiN(SiMe_3)_2$ and $LiCH(SiMe_3)_2$ in THF produces the corresponding monoring complexes $Cp^*CaE(THF)_3$ along with precipitated $LiCp^*$. The formation of $Cp^*CaN(SiMe_3)_2(THF)_n$ in toluene proceeds with similar yields,[33] so that solvent effects are not important with this combination of reagents. It is notable that the addition of a second equivalent of $LiN(SiMe_3)_2$ does not remove the other Cp* ring from $Cp^*CaN(SiMe_3)_2$. This is an indication of the stability of the Cp′–Ae–E combination of liquids, further supported by the low value of the dissociation constant in benzene.

The general utility of the precipitation route to the monoring complexes may be somewhat limited, as the outcome appears to be highly dependent on the steric and electronic properties of the reagents. Simply replacing Cp* with the Me_4EtC_5 group, for example, yields complicated reaction mixtures from which the isolation of monoring species is difficult. The greater solubility of $Li(Me_4EtC_5)$ in organic solvents may be partially responsible, since it would allow ligand redistribution to occur to a larger extent. This is particularly noticeable in a reaction such as $(Me_4EtC_5)_2Ca(THF)$ with $Li\overline{NSiMe_2CH_2CH_2Si}Me_2$, which does not reproducibly yield the expected compound **3**, although as noted above, the same complex is readily prepared by a derivatization reaction. Even with the Cp* ligand, precipitation reactions do not yield isolable complexes with many types of lithium reagents, including those that could supply such bulky groups as $C(SiMe_3)_3^-$, $SiPh_3^-$, or $N[CH(CH_3)_2]_2^-$.

Reaction of Barium Metallocenes with Lithium Reagents. Another variable that can profoundly affect the outcome of reactions with monoring species is the identity of the metal ion. Unexpectedly, the reaction of $Cp^*_2Ba(THF)_2$ with $LiN(SiMe_3)_2$ or $LiCH(SiMe_3)_2$ in THF results in the formation of hydrocarbon-insoluble organobarium species that can be formulated as barates, i.e., $Li[Cp^*_2BaE](THF)_2$. The fact that precipitation of $LiCp^*$ does *not* occur, as happens with calcium complexes, suggests that the stability of the barium/lithium aggregate is high.

The differences between the reactions with Ca and Ba are not easily rationalized. Although a precipitate does form when $Cp^*_2Ba(THF)_2$ and $LiN(SiMe_3)_2$ are allowed to react in toluene, it behaves the same as that isolated from the THF reactions; solvent effects, therefore, are apparently not a controlling factor. What role, if any, is played by the $[Li(solv)]^+$ ion in the reaction sequence is not known. If analogies with related organolanthanide systems are valid, there seems to be no obvious steric constraint that would prevent the calcium metallocene from forming a calcate comparable to that of barium (i.e., $Cp^*_2Ca[N(SiMe_3)_2]^-$). For example, $Cp^*_2Nd[N(SiMe_3)_2]$ is an isolable compound,[4] even though the radius of 7-coordinate Nd^{3+} is slightly smaller (by 0.03 Å) than that of 7-coordinate Ca^{2+}.[17] In addition, the loss by $Cp^*_2Ba(THF)_2$ of a Cp* ring and its replacement by the sterically more compact $N(SiMe_3)_2$ unit[34] should not prevent a monoring barium complex such as "$Cp^*Ba[N(SiMe_3)_2](THF)_n$" from forming.

Such considerations only address the likely stability of the products, however, and do not directly apply to the mechanism of formation of an organocalcate. Regardless of whether the addition of the silylamide ion and displacement of THF occur in a stepwise or concerted fashion, the net change in the coordination sphere of calcium would be the exchange of two *neutral* oxygen donors for one *anionic* nitrogen donor. The energetics of such a process are a matter of some conjecture. In the solid state, loss of THF is a relatively facile process for $Cp^*_2Ba(THF)_2$, but removal of both THF ligands from $Cp^*_2Ca(THF)_2$ is sufficiently difficult that base-free Cp^*_2Ca must be produced by heating the diethyl etherate, rather than the THF solvate.[21] Applying such solid-state data to the solution phase may not be meaningful, especially when solvation effects might substantially alter the relative stabilities of species.

It is tempting to try to apply recently obtained solution thermodynamic data on the relative strengths of M–O and M–N bonds for compounds of the f- and early d-block elements to the present organo-alkaline-earth systems.[35,36] Unfortunately, the bond disruption energies found in these studies refer to formally *charged* ligands (e.g., OR^-, NR_2^-), and it is by no means certain that the data can be extrapolated reliably to cases in which neutral and anionic ligands are being compared. Acquisition of information on the energetics of addition and removal of neutral donors in solution may help to clarify the relative importance of kinetic and

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[34] Evaluating the relative steric bulk of ligands as dissimilar as Cp* and $N(SiMe_3)_2$ is not trival. If only the *primary* atoms that bind to the metal are considered, the C_5 ring of Cp* obviously exerts greater steric demands than does the single N atom of $N(SiMe_3)_2$. When the ligands are considered to be freely rotating on the metal center, however, and the volume swept out by each ligand is compared, $N(SiMe_3)_2$ is found to be somewhat bulkier than Cp* (Sockwell, S. C.; Hanusa, T. P. Unpublished results). On the other hand, the bulk of $N(SiMe_3)_2$ is not as uniformly distributed as that of Cp*, and larger numbers of the amido group can pack around a metal center than can Cp* (e.g., $Sc[N(SiMe_3)_2]_3$ and $Al[N(SiMe_3)_2]_3$ are known, but not their Cp^*_3M counterparts (Tesh, K. F.; Hanusa, T. P.; Huffman, J. C. *Inorg. Chem.* **1990**, *29*, 1584–1586). But see: Evans, W. J.; Gonzales, S. L.; Ziller, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 7423–7424.

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electronic influences on reactivity in highly electropositive systems.

Conclusions

The chemistry described here provides a dramatic illustration of the flexibility available in organo-alkaline-earth chemistry, and of the many variables that can be controlled in the formation of mono- and dicyclopentadienyl systems. Not only can monocyclopentadienyl complexes be formed with relative ease, but these also can be further derivatized without great difficulty. The extensive ligand exchange that might have been thought to render such complexes inaccessible is not as serious a problem as it once appeared to be.

Of greater surprise is the dramatic difference in chemistry exhibited between calcium and barium in attempts to form monoring complexes. Differences in the accessibility of the metal center and metal–ligand bond strength may be important, but it is equally clear that these differences are such that the heavy alkaline-earth metals, at least in their monoring complexes, can now be seen to possess distinctive traits that are not readily extrapolated from one metal to another. Such variety suggests the possibility of incorporating even greater selectivity into the reactions of organo-alkaline-earth chemistry.

Experimental Section

All manipulations were performed with the rigid exclusion of air and moisture. Chemicals were handled with standard high-vacuum, Schlenk, or drybox techniques. Proton NMR spectra were obtained at 300 MHz with a Bruker NR-300 spectrometer and were referenced to the residual proton resonances of THF-d_8 (δ 3.58) or C_6D_6 (δ 7.15); carbon (^{13}C) NMR spectra were recorded at 50.3 MHz on a Bruker NR-200 spectrometer and were referenced to the residual ^{13}C resonances of THF-d_8 (δ 67.4, 25.3) or C_6D_6 (δ 128.0). Infrared data were obtained on a Perkin-Elmer 710 B or a Perkin-Elmer 1600 Series FT-IR spectrometer; the KBr pellets were prepared as previously described.[37] Elemental analyses were performed by Analytische Laboratorien, Engelskirchen, Germany, but did not always correspond to the compositions determined by NMR analysis of freshly prepared samples. Such discrepancies may reflect the extremely air- and moisture-sensitive nature of the compounds, or the loss of solvent (whether coordinated to the metal or simply present in the lattice). Problems with analysis have been observed before in other organo-alkaline-earth systems[2,38] and similarly ionic organolanthanide systems,[39] and are most often marked by anomalously low C and H values. Cases of large discrepancies are noted individually below.

Materials. $Cp^*_2Ca(THF)_2$ and $Cp^*_2Ba(THF)_2$ were prepared as previously described.[13] $LiCH(SiMe_3)_2$ was made by the method of Lappert.[40] $LiN(SiMe_3)_2$, tetramethylethylcyclopentadiene, 2,6-di-*tert*-butyl-4-methylphenol, and 2,4,6-tris[(dimethylamino)methyl]phenol were purchased commercially (Aldrich); 2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentane was obtained from Hüls America. The tetramethylethylcyclopentadiene and azacyclopentane were dried over molecular sieves and CaH_2, respectively, before use; the phenols were used without further purification. All were converted into their potassium salts by reaction with KH in THF; details for the reaction with 2,4,6-tris[(dimethylamino)methyl]phenol are given below. Solvents for reactions were distilled under nitrogen from sodium or potassium benzophenone ketyl. NMR solvents were stirred over sodium or potassium and vacuum transferred before use.

Synthesis of $(Me_4EtC_5)_2Ca(THF)$. Anhydrous CaI_2 (1.251 g, 4.26 mmol) and $K(Me_4EtC_5)$ (1.604 g, 8.52 mmol) were added to a 250-mL Erlenmeyer flask containing 125 mL of THF. The cloudy reaction mixture was stirred overnight. The turbid solution was then filtered through a fine glass frit, which retained a white precipitate. The solvent was evaporated from the filtrate, leaving $(Me_4EtC_5)_2Ca(THF)$ as a white solid (1.76 g, quantitative). Anal. Calcd for $C_{26}H_{42}CaO$: Ca, 9.76. Found: Ca, 9.42. ^1H NMR (C_6D_6, 20 °C): δ 3.29 (m, 4 H, α-C_4H_8O); 2.45 (q, 4 H, J = 7.4 Hz, CH_2); 2.07 (s, 12 H, *Me*); 2.06 (s, 12 H, *Me*); 1.28 (m, 4 H, β-C_4H_8O); 1.06 (t, 6 H, J = 7.5 Hz, ethyl *Me*). ^{13}C NMR (C_6D_6, 20 °C, proton decoupled): δ 119.5 (Me_4EtC_5), 112.5 (Me_4EtC_5), 111.9 (Me_4EtC_5), 68.5 (α-C_4H_8O), 25.4 (β-C_4H_8O), 19.4 (Me_4EtC_5), 17.1 (Me_4EtC_5), 11.1 (Me_4EtC_5), 10.9 (Me_4EtC_5). Major IR bands (KBr pellet, cm^{-1}): 2915 (s, br), 2860 (s, br), 2730 (m, sh), 1460 (s, sh), 1445 (m, br), 1025 (s, br), 875 (m), 850 (w), 675 (w), 425 (w).

2 from $(Me_4EtC_5)_2Ca(THF)$ and CaI_2. $(Me_4EtC_5)_2Ca(THF)$ (0.300 g, 0.731 mmol) was added to anhydrous CaI_2 (0.215 g, 0.732 mmol) in 75 mL of THF and the mixture stirred for 4 h. The reaction mixture was evaporated to dryness, and a ^1H NMR spectrum of the residue in C_6D_6 indicated a **2**:$(Me_4EtC_5)_2Ca(THF)$ ratio of 85:15. The crude material was then washed with hexane (2 × 30 mL). The retained solid provided 0.311 g (46% yield) of a white solid that proved to have a **2**:$(Me_4EtC_5)_2Ca(THF)$ ratio of 94:6 (^1H NMR, C_6D_6). Anal. Calcd for $C_{19}H_{33}CaIO_2$: Ca, 8.71; I, 27.56. Found: Ca, 8.65; I, 28.22. The I:Ca ratio is 1.03, suggesting that there is little, if any, free CaI_2 or $(Me_4EtC_5)_2Ca(THF)$ in the product. The small amount of $(Me_4EtC_5)_2Ca(THF)$ observed in ^1H NMR spectra presumably arises from Schlenk equilibria. In the calculation of the stoichiometry of subsequent reactions, **2** is assumed to be pure. The NMR resonances assignable to **2** are as follows. ^1H NMR (C_6D_6, 20 °C): δ 3.57 (m, 8 H, α-C_4H_8O); 2.73 (q, 2 H, J = 7.4 Hz, CH_2); 2.32 (s, 6 H, *Me*); 2.30 (s, 6 H, *Me*); 1.34 (m, 8 H, β-C_4H_8O); 1.28 (t, 3 H, J = 7.4 Hz, ethyl *Me*). ^{13}C NMR (C_6D_6, 20 °C, proton decoupled): δ 68.8 (α-C_4H_8O), 25.4 (β-C_4H_8O), 20.3 ($MeEtC_5$), 17.0 (Me_4EtC_5), 11.7 (Me_4EtC_5), 11.5 (Me_4EtC_5). Owing partially to limited solubility, the quaternary carbons were not observed. Major IR bands (KBr pellet, cm^{-1}): 2980 (s, br), 2850 (s, br), 2725 (w), 1447 (s, br), 1340 (w), 1310 (w), 1295 (w), 1260 (w), 1175 (w, br), 1065 (s), 955 (w), 925 (m), 880 (s), 675 (m), 330 (m).

2 from $K(Me_4EtC_5)$ and CaI_2. Using a procedure similar to that given above, anhydrous CaI_2 (2.00 g, 6.81 mmol) and $K(Me_4EtC_5)$ (1.28 g, 6.81 mmol) were stirred in 150 mL of THF overnight. After being filtered through a fine glass frit, the filtrate from the reaction mixture was evaporated to dryness. Examination of the residue indicated a **2**:$(Me_4EtC_5)_2Ca(THF)$ ratio of 81:19. The residue was then washed with hexane (2 × 30 mL) and filtered again through a fine frit. The retained solid provided 2.11 g (67% yield) of **2**, identified by its ^1H NMR spectrum. The proton NMR spectrum of this material in C_6D_6 indicated a **2**:$(Me_4EtC_5)_2Ca(THF)$ ratio of 94:6. The hexane wash was evaporated to dryness, and a ^1H NMR spectrum of that residue showed a **2**:$(Me_4EtC_5)_2Ca(THF)$ ratio of 31:69. The unavoidable loss of product through washing is a major source of reduced yields.

$(Me_4EtC_5)Ca(BHT)$ from 2 and K[BHT]. K[BHT] (0.084 g, 0.325 mmol) was added to **2** (0.150 g, 0.326 mmol) in 50 mL of toluene. The solution immediately turned cloudy and was stirred overnight. The resulting mixture was gravity filtered through a medium glass frit and the filtrate evaporated to dryness. A separate earlier study of ours indicated that the dried filtrate could contain the bis(aryl oxide) $Ca(BHT)_2(THF)_2$.[14] Thus, in this case the residue was washed with hexane (30 mL) to remove any possible aryl oxide, leaving 0.139 g of $(Me_4EtC_5)Ca(BHT)$ (quantitative). Anal. Calcd for $C_{26}H_{40}CaO$: C, 76.41; H, 9.87; Ca, 9.81. Found: C, 69.36; H, 9.22; Ca, 8.32. ^1H NMR (C_6D_6, 20 °C): δ 7.19 (s, 2 H, C_6H_2); 2.32 (s, 3 H, *Me*); 2.23 (q, 2 H, J = 7.4 Hz, CH_2); 1.83 (s, 6 H, *Me*); 1.76 (s, 6 H, *Me*); 1.41 (s, 18 H, C_4H_9); 0.97 (t, 3 H, J = 7.5 Hz, ethyl *Me*). Low solubility in C_6D_6 and instability in THF-d_8 precluded obtaining ^{13}C NMR data. Major IR bands (KBr pellet, cm^{-1}): 2970 (s, br), 2930 (s, br), 2865 (s, br), 1447 (w, br), 1415 (m, sh), 1385 (m), 1360 (w), 1345 (w), 1265 (m), 1255 (w), 1230 (m, sh), 1215 (m, sh), 895 (w), 867 (w), 820 (w), 797 (m, sh), 785 (m).

Synthesis of K[Otamp]·THF. Potassium hydride (0.11 g, 2.7 mmol) was added to a solution of 2,4,6-tris[(dimethylamino)methyl]phenol (0.55 g, 2.1 mmol) in 20 mL of THF. Hydrogen evolution was observed during the next 5 min as most of the KH went into solution. The excess KH was removed with a medium porosity glass frit, and the filtrate was evaporated to dryness, yielding K[Otamp]·THF as a white solid (0.53 g, 68%). ^1H NMR (C_6D_6, 20 °C): δ 7.29 (s, 2 H, C_6H_2); 3.51 (m, 4 H, o-CH_2NMe_2); 3.57 (m, 4 H, α-C_4H_8O); 3.37 (s, 2 H, p-CH_2NMe_2); 2.19 (s, 6 H, p-CH_2NMe_2); 2.07 (s, 12 H, o-CH_2NMe_2); 1.39 (m, 4 H, β-C_4H_8O). ^1H NMR (THF-d_8, 20 °C): δ 6.72 (s, 2 H, C_6H_2); 3.24 (m, 4 H, o-CH_2NMe_2); 3.11 (s, 2 H, p-CH_2NMe_2); 2.08 (s, 6 H, p-CH_2NMe_2); 2.13 (s, 12 H, o-CH_2NMe_2).

$(Me_4EtC_5)Ca(Otamp)$ from 2 and K[Otamp]·THF. K[Otamp]·THF (0.394 g, 1.05 mmol) was added to **2** (0.483 g, 1.05 mmol) in 100 mL of toluene. The solution immediately turned cloudy and was stirred overnight. The resulting mixture was gravity filtered through a medium glass frit and the filtrate evaporated to produce a yellow oil. The oil was triturated with 25 mL of hexane. The hexane was removed by rotary evaporation, leaving an off-white friable solid (0.49 g, quantitative). Anal. Calcd for $C_{26}H_{43}CaN_3O$: Ca, 8.83; N, 9.26. Found: Ca, 7.52; N, 10.28. ^1H NMR (C_6D_6, 20 °C): δ 7.35 (s, 2 H, C_6H_2); 3.43 (s, 2 H, p-CH_2NMe_2); 3.38 (m, 6 H, o-CH_2NMe_2 and $C_5Me_4CH_2CH_3$); 2.24 (s, 6 H, p-CH_2NMe_2); 2.18 (s, 12 H, o-CH_2NMe_2); 1.88 (s, 6 H, C_5Me_4Et); 1.84 (s, 6 H, C_5Me_4Et); 0.99 (t, 3 H, J = 7.4 Hz, ethyl *Me*).

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^{13}C NMR ($\mathrm{C_6D_6}$, 20 °C, saturated solution, proton decoupled): δ 159.3 ($\mathrm{CaO}C$); 132.2 (m-$C_6\mathrm{H_2}$); 125.8 (o-$C_6\mathrm{H_2}$); 120.2 ($\mathrm{C_4Me_4}C\mathrm{Et}$); 112.9 ($C_4\mathrm{Me_4CEt}$); 64.4 ($p$-$C\mathrm{H_2NMe_2}$); 62.4 ($o$-$C\mathrm{H_2NMe_2}$); 46.4 ($o$-$\mathrm{CH_2N}Me_2$); 45.2 ($p$-$\mathrm{CH_2N}Me_2$); 19.9 (ethyl $C\mathrm{H_2}$); 16.8 (ethyl Me); 11.2 ($\mathrm{C_5}Me_4\mathrm{Et}$); 11.0 ($\mathrm{C_5}Me_4\mathrm{Et}$). Major IR bands (KBr pellet, cm^{-1}): 2925 (s, br), 2860 (s, br), 2815 (s, br), 2770 (s, br), 2730 (m), 1615 (m, sh), 1465 (s, br), 1360 (s), 1320 (m), 1285 (m), 1260 (m), 1177 (m, sh), 1145 (m, sh), 1100 (m, sh), 1045 (m), 1035 (m), 987 (m), 897 (m), 840 (m), 815 (m), 770 (w), 740 (w), 625 (w), 555 (w), 460 (w), 417 (w), 340 (w, br).

3 from 2 and K($\overline{\mathbf{NSiMe_2CH_2CH_2SiMe_2}}$). **2** (0.300 g, 0.652 mmol) was added to $\mathrm{K}\overline{\mathrm{NSiMe_2CH_2CH_2SiMe_2}}$ (0.129 g, 0.653 mmol) in 50 mL of toluene. The solution immediately turned cloudy and was stirred for 48 h. The resulting mixture was gravity filtered through a medium glass frit, and the filtrate was removed by rotary evaporation. The resulting solid was triturated with 20 mL of hexane. Removal of the hexane left 0.20 g (79% yield) of off-white, solid **3**. Anal. Calcd for $\mathrm{C_{17}H_{33}CaNSi_2}$: Ca, 11.53; N, 4.03. Found: Ca, 9.56; N, 3.35. Although both the Ca and N analysis were low, the Ca:N molar ratio is still the expected 1.0. ^{1}H NMR ($\mathrm{C_6D_6}$, 20 °C): δ 2.57 (q, 2 H, J = 7.3 Hz, $\mathrm{C}H_2$); 2.12 (s, 6 H, $Me_4\mathrm{EtC_5}$); 2.06 (s, 6 H, $Me_4\mathrm{EtC_5}$); 1.07 (t, 3 H, J = 7.3 Hz, $\mathrm{CH_2C}H_3$); 0.80 (s, 4 H, $\overline{\mathrm{NSiMe_2C}H_2\mathrm{CH_2SiMe_2}}$); 0.15 (s, 12 H, $\overline{\mathrm{NSi}Me_2\mathrm{CH_2CH_2SiMe_2}}$). ^{13}C NMR ($\mathrm{C_6D_6}$, 20 °C, saturated solution, proton decoupled): δ 122.2 ($C_5\mathrm{Me_4Et}$), 115.4 ($C_5\mathrm{Me_4Et}$), 114.7 ($C_5\mathrm{Me_4Et}$), 20.8 ($\mathrm{C_5Me_4}C\mathrm{H_2CH_3}$), 16.1 ($\mathrm{C_5Me_4CH_2}C\mathrm{H_3}$), 12.4 ($\mathrm{C_5}Me_4\mathrm{Et}$), 12.1 ($\mathrm{C_5}Me_4\mathrm{Et}$), 10.7 ($\overline{\mathrm{NSiMe_2}CH_2\mathrm{CH_2SiMe_2}}$), 3.85 ($\overline{\mathrm{NSi}Me_2\mathrm{CH_2CH_2SiMe_2}}$). Major IR bands (KBr pellet, cm^{-1}): 2921 (br), 2730 (w), 1449 (br), 1415 (s), 1368 (m), 1254 (s), 1019 (br), 910 (br), 854 (br), 778 (br), 667 (s), 579 (m), 416 (br), 331 (br).

Cp*CaN(SiMe$_3$)$_2$(THF)$_3$ from Cp*$_2$Ca(THF)$_2$ and LiN(SiMe$_3$)$_2$. $\mathrm{LiN(SiMe_3)_2}$ (0.188 g, 1.12 mmol) was added to $\mathrm{Cp^*_2Ca(THF)_2}$ (0.465 g, 1.02 mmol) in THF (75 mL). The mixture immediately turned cloudy from the precipitation of LiCp*. After stirring for 2 days, the mixture was filtered through a medium glass frit, and the filtrate evaporated to dryness, giving 0.317 g of the title compound (56% yield). Anal. Calcd for $\mathrm{C_{28}H_{57}CaNO_3Si_2}$: C, 60.92; H, 10.41; Ca, 7.26; N, 2.54. Found: C, 53.59; H, 8.39; Ca, 8.35; N, 2.80. Although the combustion was evidently not complete, the observed Ca:N ratio of 1.0 establishes that the solid is free from both $\mathrm{Cp^*_2Ca(THF)_2}$ and $\mathrm{Ca[N(SiMe_3)_2]_2}$. In addition, if one molecule of THF was lost between the time of sample preparation and analysis, the calculated values for Ca and N in $\mathrm{Cp^*N(SiMe_3)_2(THF)_2}$ would be 8.35% and 2.92%, respectively, close to what was found.

In $\mathrm{C_6D_6}$ solution, $\mathrm{Cp^*CaN(SiMe_3)_2(THF)_3}$, $\mathrm{Cp^*_2Ca(THF)_2}$, and $\mathrm{Ca[N(SiMe_3)_2]_2(THF)_2}$ can be identified in NMR spectra, the latter two by their proton chemical shifts at δ 2.05 (lit.[13] for $\mathrm{Cp^*_2Ca(THF)_2}$ δ 2.06) and δ 0.36 (lit.[25] for $\mathrm{Ca[N(SiMe_3)_2]_2(THF)_2}$ δ 0.33). The resonances assignable to $\mathrm{Cp^*CaN(SiMe_3)_2(THF)_3}$ (91% of total) are as follows. ^{1}H NMR ($\mathrm{C_6D_6}$, 20 °C): δ 3.48 (m, 12 H, α-$\mathrm{C_4H_8O}$); 2.23 (s, 15 H, Cp*); 1.33 (m, 12 H, β-$\mathrm{C_4H_8O}$); 0.23 (s, 18 H, $\mathrm{N(Si}Me_3)_2$). ^{13}C NMR (THF-d_8, 20 °C, saturated solution, proton decoupled): δ 112.7 ($C_5\mathrm{Me_5}$), 11.9 ($\mathrm{C_5}Me_5$), 6.07 ($\mathrm{Si}Me_3$). Major IR bands (KBr pellet, cm^{-1}): 3700 (m), 3450 (br), 2975 (vs), 2600 (w), 2560 (w), 1640 (w), 1460 (w), 1240 (s), 1040 (m), 945 (w), 825 (m).

Cp*CaCH(SiMe$_3$)$_2$(THF)$_3$ from Cp*$_2$Ca(THF)$_2$ and LiCH(SiMe$_3$)$_2$. $\mathrm{LiCH(SiMe_3)_2}$ (0.040 g, 0.24 mmol) was added with stirring to $\mathrm{Cp^*_2Ca(THF)_2}$ (0.100 g, 0.220 mmol) in THF (30 mL). The solutioin immediately turned cloudy from precipitation of LiCp*. After stirring for 10 min, the solution was filtered through a medium glass frit and evaporated to dryness, giving 0.134 g of $\mathrm{Cp^*CaCH(SiMe_3)_2(THF)_3}$ in quantitative yield. Anal. Calcd for $\mathrm{C_{29}H_{58}CaO_3Si_2}$: C, 63.21; H, 10.61; Ca, 7.27; Si, 10.19. Found: C, 63.23; H, 9.65; Ca, 9.90; Si, 10.45. In $\mathrm{C_6D_6}$ solution, $\mathrm{Cp^*CaCH(SiMe_3)_2(THF)_3}$, $\mathrm{Cp^*_2Ca(THF)_2}$, and $\mathrm{CH_2(SiMe_3)_2}$ can be identified in NMR spectra, the latter two by their proton chemical shifts at δ 2.05[13] and δ 0.05 and –0.37.[41] On the basis of integration of the Cp* peaks in the ^{1}H NMR spectrum, 98% of the calcium in solution occurs as $\mathrm{Cp^*CaCH(SiMe_3)_2(THF)_3}$. Likewise, integration reveals that 4% of the total trimethylsilyl resonances are present as $\mathrm{CH_2(SiMe_3)_2}$. The resonances assignable to $\mathrm{Cp^*CaCH(SiMe_3)_2(THF)_3}$ are as follows. ^{1}H NMR ($\mathrm{C_6D_6}$, 20 °C): δ 3.48 (m, 12 H, α-$\mathrm{C_4H_8O}$); 2.22 (s, 15 H, Cp*); 1.33 (m, 12 H, β-$\mathrm{C_4H_8O}$); 0.32 (s, 18 H, $\mathrm{Si}Me_3$), –1.65 (s, 1 H, $\mathrm{C}H\mathrm{(SiMe_3)_2}$). ^{13}C NMR ($\mathrm{C_6D_6}$, 20 °C, saturated solution, proton decoupled): δ 112.8 ($C_5\mathrm{Me_5}$), 68.7 (α-$\mathrm{C_4H_8O}$), 25.3 (β-$\mathrm{C_4H_8O}$), 11.9 ($\mathrm{C_5}Me_5$), 6.27 ($\mathrm{Si}Me_3$). Major IR bands (KBr pellet, cm^{-1}) 2956 (s), 1608 (w), 1447 (w), 1253 (m), 1045 (m), 840 (m).

Li[Cp*$_2$BaN(SiMe$_3$)$_2$](THF)$_2$ from Cp*$_2$Ba(THF)$_2$ and LiN(SiMe$_3$)$_2$. $\mathrm{LiN(SiMe_3)_2}$ (0.061 g, 0.364 mmol) was added to $\mathrm{Cp^*_2Ba(THF)_2}$ (0.200 g, 0.362 mmol) in 30 mL of THF and stirred for 30 min. The resulting clear solution was evaporated to dryness, giving 0.258 g of $\mathrm{Li[Cp^*_2BaN(SiMe_3)_2](THF)_2}$ in near quantitative yield. Anal. Calcd for $\mathrm{C_{34}H_{64}BaNLiO_2Si_2}$: C, 56.77; H, 8.97; Ba, 19.09; N, 1.95; Li, 0.96. Found: C, 62.99; H, 8.51; Ba, 19.30; N, 1.84; Li, 0.99. ^{1}H NMR (THF-d_8, 20 °C): δ 1.86 (s, 30 H, Cp*); –0.16 (s, 15 H, $\mathrm{Si}Me_3$). A variable amount of a substance having a single resonance at δ 0.04 was observed in solutions of the barate; it may represent a decomposition product. ^{13}C NMR (THF-d_8, 20 °C, saturated solution, proton decoupled): δ 112.7 ($C_5\mathrm{Me_5}$), 11.1 ($\mathrm{C_5}Me_5$), 6.06 ($\mathrm{Si}Me_3$). Major IR bands (KBr pellet, cm^{-1}): 3450 (br), 2975 (vs), 2555 (w), 1590 (m), 1445 (m), 1395 (m), 1345 (w), 1255 (s), 1185 (m), 1045 (s), 930 (m), 840 (s), 750 (m).

Li[Cp*$_2$BaCH(SiMe$_3$)$_2$](THF)$_2$ from Cp*$_2$Ba(THF)$_2$ and LiCH(SiMe$_3$)$_2$. $\mathrm{LiCH(SiMe_3)_2}$ (0.033 g, 0.20 mmol) was added to $\mathrm{Cp^*_2Ba(THF)_2}$ (0.100 g, 0.181 mmol) in 30 mL of THF and stirred for 15 min. The resulting clear solution was evaporated to dryness, giving 0.128 g (98% yield) of $\mathrm{Li[Cp^*_2BaCH(SiMe_3)_2](THF)_2}$. Anal. Calcd for $\mathrm{C_{35}H_{65}BaLiO_2Si_2}$: Ba, 19.12; Li, 0.97; Si, 7.82. Found: Ba, 23.45; Li, 1.64; Si, 4.83. The otherwise unacceptable analysis can be partially explained by assuming that extensive desolvation/decomposition of the complex occurred. If all the THF were lost, for example, the calculated elemental values would be Ba, 23.92; Li, 1.21; Si, 9.78. The formulation of the complex as a THF disolvate is primarily based on analogy with the amide complex and on spectroscopic data. ^{1}H NMR (THF-d_8, 20 °C): δ 1.86 (s, 30 H, Cp*); 0.03 (s, $\mathrm{Si}Me_3$); –0.23 (s, 1 H, $\mathrm{C}H\mathrm{(SiMe_3)_2}$). ^{13}C NMR (THF-$d_8$, 20 °C, saturated solution, proton decoupled): δ 112.2 ($C_5\mathrm{Me_5}$), 11.2 ($\mathrm{C_5}Me_5$), 6.5 ($\mathrm{Si}Me_3$), 1.45 ($C\mathrm{H(SiMe_3)_2}$). Major IR bands (KBr pellet, cm^{-1}) 2950 (br), 2555 (w), 1580 (w), 1445 (m), 1400 (m), 1240 (m), 1040 (s), 870 (m), 810 (m).

X-ray Crystallography of 3. General procedures for data collection and reduction have been described previously.[42] Clear, colorless crystals were grown from toluene. A suitable colorless crystal measuring 0.25 × 0.25 × 0.25 mm was transferred using standard inert atmosphere techniques to a Picker four-circle goniostat equipped with a Furnas monochromator (HOG crystal) and Picker X-ray generator. The crystal was cooled to –172 °C for characterization and data collection. Relevant crystal and data collection parameters for the present study are given in Table I.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/a$ (alternative setting of $P2_1/c$, no. 14). Subsequent solution and refinement of the structure confirmed this choice.

Data collection was performed using standard moving-crystal/moving-detector techniques with fixed backgrounds. No correction for absorption or decay was made. Data were reduced to a unique set of intensities and associated σ's in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques, using locally modified versions of the Los Alamos Crystallographic Program Library. A difference Fourier synthesis revealed the location of some, but not all, hydrogen atoms. All hydrogen atom positions were therefore calculated using idealized geometries and d(C–H) = 0.95 Å. These calculated positions were fixed for the final cycles of refinement. Selected bond distances and angles are listed in Table II.

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Supplementary Material Available: Tables of fractional coordinates, bond distances and angles, and anisotropic thermal parameters and a fully numbered diagram of **3** (8 pages); table of calculated and observed structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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