Synthesis and Crystallographic Study of Indenyl and Isopropylated Indenyl Complexes of Calcium, Strontium, and Barium

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Reaction of 2 equiv of potassium indenide (KInd) with AeI_2 (Ae = Ca, Sr, Ba) in THF produces the bis(indenyl) complexes $(Ind)_2Ae(thf)_n$ ($n = 1$ for Sr, Ba; $n = 2$ for Ca) in high yields. The use of potassium 1,3-diisopropylindenide ($KInd^{2i}$) with the same diiodides produces the analogous complexes $(Ind^{2i})_2Ae(thf)_n$ ($n = 1$ for Ca; $n = 2$ for Sr and Ba). All the complexes are air-sensitive solids. Single-crystal X-ray diffraction studies were completed for $(Ind)_2Ca(thf)_2$, $(Ind^{2i})_2Ca(thf)$, $(Ind^{2i})_2Ba(thf)_2$, and $(Ind)_2Sr(thf)$; these represent the first structurally characterized indenyl complexes of the heavier alkaline-earth metals. The calcium and barium compounds are monomeric, with bent metallocene geometries and average Ae−C distances of 2.73(3), 2.69(2), and 3.03(4) Å for $(Ind)_2Ca(thf)_2$, $(Ind^{2i})_2Ca(thf)$, and $(Ind^{2i})_2Ba(thf)_2$, respectively. The strontium complex is an infinite coordination polymer, $[(Ind)_2Sr(thf)]_\infty$, with both terminal (Sr−C = 2.94 Å (av)) and bridging (Sr−C = 3.07 Å (av)) indenyl ligands. Although the individual Sr−C bond distances differ as much as 0.25 Å, there is no clear indication of slippage toward an η^3-configuration. The presence of the two isopropyl substituents on the indenyl ligands makes them effectively as bulky as triisopropylcyclopentadienyl rings.

Introduction

In recent years, the organometallic chemistry of the heavy alkaline-earth metals (Ca, Sr, Ba) has expanded considerably, largely through a focus on complexes containing bulky cyclopentadienyl rings with alkyl or phenyl substituents.[1,2] Although there are a few exceptions,[3] such compounds generally display good solubility in organic solvents, are reasonably volatile, and possess high thermal stability. Comparable properties, although with perhaps some distinctive differences, should be displayed by alkaline-earth compounds containing the indenyl ligand and its various substituted derivatives. Much less work has been done with indenyl complexes, however, despite the first report of their synthesis more than 20 years ago.[4]

A variety of synthetic approaches have been used to prepare alkaline-earth indenyl species. The reaction of Ph_2Ca or $(Ph_3C)CaI$ with indene in THF leads to the complex $(Ind)_2Ca(thf)_2$ (Ind = C_9H_7), which has been characterized by NMR and IR spectroscopy.[4] This compound has also been synthesized by metalating indene with either calcium or calcium amide in liquid ammonia to produce the ammonia-solvated $(Ind)_2Ca(NH_3)_2$;[5] the ammonia can easily be displaced by THF to produce $(Ind)_2Ca(thf)_2$. Barium granules have been allowed to react with indene in THF/NH_3(l) or HMPA/NH_3(l) to yield either $(Ind)_2Ba(thf)_2$ or $(Ind)_2Ba(hmpa)_2$, respectively.[6,7] The unsolvated bis(indenyl) complexes, $[(Ind)_2Ae]_x$ (Ae = Ca, Sr, Ba), have been prepared from bis(indenyl)mercury and the bulk metals[8] or by the cocondensation of excess indene with the metal vapor at −196 to −78 °C.[9] The unsolvated complexes have been characterized with NMR spectroscopy.

Our initial goals in working with heavy group 2 indenyl complexes were threefold: (1) to develop a unified synthetic approach that would be applicable to the synthesis of indenyl complexes of all three metals and that would obviate the need for metal vapor apparatus or the use of poorly characterized species such as $(Ph_3C)CaI$; (2) to prepare indenyl complexes containing substituted indenyl ligands, which should improve the solubility of the compounds in nonpolar solvents; (3) to obtain structural data on the complexes, which would allow us to determine whether the indenyl ligands remain symmetrically (i.e., η^5) bound to the metal centers or whether they display evidence for slippage ($\eta^5 \rightarrow \eta^3$). Such data would also add to the limited structural information that is available for main-group indenyl complexes.[10−13] We report here our progress toward meeting these goals.

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(6) Drake has reported the barium compound as a di-thf solvate, $Ba(C_9H_7)_2(thf)_2\cdot C_6H_{14}$ (ref 7). The analytical data fit a monosolvated compound more closely, however (Anal. Found: C, 63.9; H, 7.0. Calc for $C_{28}H_{36}BaO$: C, 63.95; H, 6.90). In the absence of other supporting data (e.g., integrated NMR intensities) and in view of our own results, we believe the barium indenyl complex that was isolated was the monosolvated species.

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Experimental Section

General Experimental Considerations. All manipulations were performed with the rigid exclusion of air and moisture using high vacuum, Schlenk, or drybox techniques. Proton and carbon (^{13}C) NMR spectra were obtained on a Bruker NR-300 spectrometer at 300 and 75.5 MHz, respectively, and were referenced to the residual proton and ^{13}C resonances of C_6D_6 (δ 7.15 and 128.0) or THF-d_8 (δ 3.58 and 67.4). Infrared data were obtained on a Perkin-Elmer 1600 Series FT-IR spectrometer. KBr pellets for IR spectroscopy were prepared as previously described.[14] Elemental analyses were performed by the University of Illinois Microanalytical Laboratory.

Materials. Anhydrous calcium, strontium, and barium iodide were commercial samples (Strem Chemicals or Cerac, 95%); they were heated under vacuum (150 °C, 10^{-6} Torr) to remove residual amounts of free iodine. Indene was purchased from Aldrich and distilled before use. Potassium indenide was prepared by reaction of $K[N(SiMe_3)_2]$ and indene in toluene. 1,3-Diisopropylindene ($HInd^{2i}$) and potassium (diisopropylindenide) ($KInd^{2i}$) were prepared by standard procedures.[15] Other solvents for reactions were distilled under nitrogen from sodium or potassium benzophenone ketyl. NMR solvents were vacuum distilled from Na/K (22/78) alloy and stored over 4A molecular sieves.

Synthesis of Bis(indenyl)calcium Bis(tetrahydrofuranate), $(Ind)_2Ca(thf)_2$. Potassium indenide (0.50 g, 3.24 mmol) was added to CaI_2 (0.476 g, 1.62 mmol) in 30 mL of THF and the mixture stirred overnight. The mixture was then filtered through a medium glass frit. The yellow filtrate was evaporated to dryness to yield a beige crystalline solid identified as $(Ind)_2Ca(thf)_2$ (0.589 g, 88%) by its ^{1}H NMR spectrum in C_6D_6.[4] X-ray-quality crystals of $(C_9H_7)_2Ca(thf)_2$ were grown by slow evaporation from a THF solution.

Synthesis of Bis(indenyl)strontium Tetrahydrofuranate, $(Ind)_2Sr(thf)$. In a procedure analogous to that used for $(Ind)_2Ca(thf)_2$, potassium indenide (0.50 g, 3.24 mmol) and SrI_2 (0.553 g, 1.62 mmol) were magnetically stirred overnight in 30 mL of THF. The resulting cloudy solution was filtered through a medium glass frit and the light brown filtrate evaporated to dryness, washed with a small portion of hexane (10 mL), and dried in vacuo, leaving $(Ind)_2Sr(thf)$ (0.40 g, 63%) as a beige powder, mp 220−224 °C. ^{1}H NMR (THF-d_8, δ): 7.30 (m, 4 H, C_6 ring *H*); 6.57 (m, 4 H, C_6 ring *H*); 6.37 (t, 2 H, J = 3.3 Hz, C_5 ring *H*); 5.85 (d, 4 H, J = 3.3 Hz, C_5 ring *H*). ^{13}C NMR (THF-d_8, δ): 129.2 (bridge *C*); 121.0 (C_6-ring *C*H); 118.8 (C_6-ring *C*H); 116.6 (C_5-ring *C*H); 95.8 (C_5-ring *C*H); 68.2 (α-C_4H_8O); 26.4 (β-C_4H_8O). Principal IR bands (KBr, cm^{-1}): 3059 (m), 2968 (s), 2878 (s), 1594 (m), 1456 (m), 1322 (s), 1255 (m), 1174 (w), 1079 (sh), 1031 (vs), 873 (m), 761 (vs), 435 (w). X-ray-quality crystals of $(C_9H_7)_2Sr(thf)$ were grown by slow evaporation from a THF solution.

Synthesis of Bis(indenyl)barium Tetrahydrofuranate, $(Ind)_2Ba(thf)$. In a manner similar to that used for $(Ind)_2Ca(thf)_2$, BaI_2 (0.634 g, 1.62 mmol) and potassium indenide (0.50 g, 3.24 mmol) were stirred overnight in 30 mL of THF. The solution was filtered through a medium glass frit to remove precipitated KI, and the filtrate was evaporated to yield a light gray solid identified as $(Ind)_2Ba(thf)$ (0.247 g, 35%) from its ^{1}H NMR spectrum in THF-d_8.[7]

Synthesis of Bis(diisopropylindenyl)calcium Tetrahydrofuranate, $(Ind^{2i})_2Ca(thf)$. $KInd^{2i}$ (0.30 g, 1.26 mmol) and CaI_2 (0.184 g, 0.63 mmol) were placed in a 125-mL flask. To this was added 30 mL of THF, at which time the mixture became bright yellow. The mixture was magnetically stirred overnight and then filtered through a medium glass frit to remove precipitated KI. The yellow THF filtrate was evaporated to dryness, and the resulting solid was washed with two small portions of hexane. After drying in vacuo, $(Ind^{2i})_2Ca(thf)$ (0.22 g, 69%) was isolated as a yellow powder, mp 113−116 °C. ^{1}H NMR (C_6D_6, δ): 7.33 (broad m, 8 H, C_6 ring *H*); 6.69 (broad m, 8 H, C_6 ring *H*); 6.60 (s, 2 H, C_5 ring *H*); 3.31 (septet, 4 H, J = 6.8 Hz, C*H*Me$_2$); 2.57 (m, 4 H, α-C_4H_8O); 1.53 (d, 12 H, J = 6.9 Hz, C*H*$_3$); 1.32 (d, 12 H, J = 6.8 Hz, C*H*$_3$); 1.09 (m, 4 H, β-C_4H_8O). ^{13}C NMR (C_6D_6, δ): 126.1 (C_5-ring *C*CHMe$_2$); 119.9 (bridge *C*); 117.2 (C_6-ring *C*H); 115.4 (C_6-ring *C*H); 114.0 (C_5-ring *C*H); 68.3 (α-C_4H_8O); 27.7 (*C*HMe$_2$); 25.3 (β-C_4H_8O); 25.0 (*C*H$_3$); 24.0 (*C*H$_3$). Principal IR bands (KBr, cm^{-1}): 3059 (m), 2972 (m), 2879 (m), 1590 (m), 1459 (m), 1394 (w), 1325 (s), 1255 (m), 1176 (w), 1111(w), 1033 (s), 999 (w), 873 (m), 791 (s), 434 (m). X-ray-quality crystals of $(Ind^{2i})Ca(thf)$ were grown by slow evaporation of a THF/hexane solution.

Synthesis of Bis(diisopropylindenyl)strontium Bis(tetrahydrofuranate), $(Ind^{2i})_2Sr(thf)_2$. This compound was prepared similarly to $(Ind^{2i})_2Ca(thf)$. SrI_2 (0.215 g, 0.629 mmol) and $K(Ind^{2i})$ (0.30 g, 1.26 mmol) were stirred together in 30 mL of THF overnight. The resulting yellow solution was filtered through a medium glass frit and the THF filtrate evaporated to dryness leaving a yellow oil. Upon addition of hexane, the oil became a yellow wax. This material was washed with two small portions (10 mL each) of hexane and dried in vacuo to yield $(Ind^{2i})_2Sr(thf)_2$ (0.20 g, 51%) as a yellow powder, mp 75−78 °C. On long standing (>1 week), the compound partially desolvates, as indicated by analysis. Anal. Calcd for $C_{34}H_{46}SrO$: Sr, 15.69. Found: Sr, 15.17. ^{1}H NMR (C_6D_6, δ): 7.34 (m, 4 H, C_6 ring *H*); 6.74 (m, 4 H, C_6 ring *H*); 6.62 (s, 2H, C_5 ring *H*); 3.29 (septet, 4 H, J = 6.8 Hz, C*H*Me$_2$); 3.11 (m, 8 H, α-C_4H_8O); 1.44 (d, 12 H, J = 6.8 Hz, C*H*$_3$); 1.38 (d, 12 H, J = 6.9 Hz, C*H*$_3$); 1.23 (m, 8 H, β-C_4H_8O). ^{13}C NMR (C_6D_6, δ): 126.8 (C_5-ring *C*CHMe$_2$); 119.9 (bridge *C*); 117.6 (C_6-ring *C*H); 114.8 (C_6-ring *C*H); 113.8 (C_5-ring *C*H); 68.1 (α-C_4H_8O); 28.0 (*C*HMe$_2$); 26.3 (β-C_4H_8O); 24.8 (*C*H$_3$); 23.9 (*C*H$_3$). Principal IR bands (KBr, cm^{-1}): 3061 (m), 2957 (vs), 2866 (vs), 1460 (s), 1384 (m), 1323 (s), 1260 (m), 1183 (m), 1103 (m), 1030 (s), 1001 (m), 872 (m), 736 (s), 439 (m).

Synthesis of Bis(diisopropylindenyl)barium Bis(tetrahydrofuranate), $(Ind^{2i})_2Ba(thf)_2$. This compound was prepared similarly to $(Ind^{2i})Ba(thf)$. BaI_2 (0.246 g, 0.69 mmol) and $K(Ind^{2i})$ (0.30 g, 1.26 mmol) were stirred together in 30 mL of THF overnight. The resulting yellow solution was filtered through a medium glass frit and the THF filtrate evaporated to a yellow oil. The addition of hexane caused the precipitation of a yellow wax. This material was washed with two small portions of hexane (10 mL each) and dried in vacuo to yield yellow $(Ind^{2i})_2Ba(thf)_2$ (0.246 g, 54%), mp 130−133 °C. Anal. Calcd for $C_{38}H_{54}BaO_2$: Ba, 20.19. Found: Ba, 20.61. ^{1}H NMR (C_6D_6, δ): 7.24 (m, 4 H, C_6 ring *H*); 6.51 (m, 4 H, C_6 ring *H*); 6.29 (s, 2H, C_5 ring *H*); 3.57 (br s, 8 H, α-C_4H_8O); 3.24 (septet, 4 H, J = 6.8 Hz, C*H*Me$_2$); 1.71 (m, 8 H, β-C_4H_8O); 1.27 (d, 24 H, J = 6.5 Hz, C*H*$_3$). ^{13}C NMR (C_6D_6, δ): 126.9 (C_5-ring *C*CHMe$_2$); 118.6 (bridge *C*); 118.2 (C_6-ring *C*H); 114.2 (C_6-ring *C*H); 112.8 (C_5-ring *C*H); 68.0 (α-C_4H_8O); 27.8 (*C*HMe$_2$); 25.5 (β-C_4H_8O); 25.1 (*C*H$_3$); 23.4 (*C*H$_3$). Principal IR bands (KBr, cm^{-1}): 3062 (m), 2959 (vs), 2869 (vs), 1596 (w), 1460 (s), 1381 (m), 1323 (m), 1261 (m), 1070 (m), 1014 (m), 972 (m), 800 (m), 756 (s). X-ray-quality crystals were grown by slow evaporation of a THF/hexane solution.

General Procedures for X-ray Crystallography. Suitable crystals of the compounds were located and sealed in glass capillary tubes. All measurements were performed on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα (λ = 0.710 69 Å) radiation. Relevant crystal and data collection parameters for the present study are given in Table 1.

Cell constants and orientation matrices for data collection were obtained from systematic searches of limited hemispheres of reciprocal space; sets of diffraction maxima were found whose setting angles were refined by least squares. The space groups were determined from consideration of unit cell pa-

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Table 1. Crystal Data and Summary of X-ray Data Collection

	compound			
	$(Ind)_2Ca(thf)_2$	$(Ind^{2i})_2Ca(thf)$	$(Ind^{2i})_2Ba(thf)_2$	$[(Ind)_2Sr(thf)]_\infty$
formula	$C_{26}H_{30}CaO_2$	$C_{34}H_{46}CaO$	$C_{38}H_{54}BaO_2$	$C_{22}H_{22}OSr$
fw	414.60	510.82	680.17	390.04
color of cryst	colorless	pale yellow	yellow	beige
cryst dimens, mm	0.44 × 0.44 × 0.57	0.90 × 0.42 × 0.12	0.50 × 0.45 × 0.33	0.52 × 0.32 × 0.27
space group	$C2/c$	$P2_1/n$	$P2_1/n$	$P2_1$
temp, °C	20	20	20	20
a, Å	13.492(8)	13.566(5)	13.423(6)	9.237(4)
b, Å	11.060(5)	13.514(6)	17.276(14)	9.077(4)
c, Å	15.530(3)	17.444(7)	15.518(6)	10.912(4)
β, deg	93.07(3)	103.79(3)	92.00(4)	103.70(3)
V, Å^3	2314(1)	3106(4)	3596(4)	889(1)
Z	4	4	4	2
D(calcd), g/cm^3	1.190	1.092	1.256	1.457
abs coeff, cm^{-1}	2.80	2.17	11.30	29.44
transm factors	no corr	no corr	0.86−1.00	0.73−1.00
scan speed, deg/min	8.0	4.0	8.0	8.0
scan width	$1.47 + 0.30 \tan\theta$	$1.05 + 0.30 \tan\theta$	$1.00 + 0.30 \tan\theta$	$1.52 + 0.30 \tan\theta$
limits of data collcn	$6° \le 2\theta \le 50°$	$6° \le 2\theta \le 45°$	$6° \le 2\theta \le 50°$	$6° \le 2\theta \le 50°$
tot. reflcns	2298	4511	6868	1780
unique reflcns	2174	4302	6575	1675
no. with $I > n\sigma(I)$	1166 ($n = 3.0$)	1816 ($n = 3.0$)	3005 ($n = 3.0$)	1019 ($n = 2.0$)
$R(F)$	0.045	0.058	0.053	0.045
$R_w(F)$	0.055	0.065	0.060	0.045
goodness of fit	1.82	1.97	1.75	1.25
max Δ/σ in final cycle	0.15	0.02	0.12	0.07
max/min peak (final diff map), (e/Å^3)	0.23/−0.20	0.27/−0.22	0.86/−0.41	0.47/−0.58

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(Ind)_2Ca(thf)_2$[a]

Ca(1)−O(1)	2.360(3)	C(1)−C(2)	1.366(7)
Ca(1)−C(1)	2.694(4)	C(1)−C(9)	1.403(6)
Ca(1)−C(2)	2.702(4)	C(2)−C(3)	1.389(6)
Ca(1)−C(3)	2.725(4)	C(3)−C(4)	1.401(6)
Ca(1)−C(4)	2.771(4)	C(4)−C(9)	1.431(6)
Ca(1)−C(9)	2.738(4)		
O(1)−Ca(1)−O(1)′	82.6(1)	C(1)−C(2)−C(3)	109.4(4)
Ca(1)−O(1)−C(10)	125.6(2)	C(2)−C(3)−C(4)	107.7(4)
Ca(1)−O(1)−C(13)	127.1(3)	C(3)−C(4)−C(9)	107.5(4)
C(10)−O(1)−C(13)	107.2(3)	C(1)−C(9)−C(4)	106.3(4)
C(2)−C(1)−C(9)	109.1(4)		
Ca(1)−C_5 ring centroid	2.45 Å		
planarity of rings	within 0.013 Å		
C_5 ring centroid−Ca(1)−C_5 ring centroid	128.3°		
C_5 ring normal−Ca(1)−C_5 ring normal	126.4°		

[a] The coordinates of the primed atoms are related to those of the unprimed atoms by the expression $1 - x, +y, {}^1/_2 - z$.

rameters, statistical analysis of intensity distribution, and, where appropriate, systematic absences. Subsequent solution and refinement of the structures confirmed the choice in each case.

Data collections were performed using continuous $\omega-2\theta$ scans with stationary backgrounds (peak/bkgd counting time = 2:1). Data were reduced to a unique set of intensities and associated σ values in the usual manner. The structures were solved by direct methods (SHELXS-86, DIRDIF) and Fourier techniques. All non-hydrogen atoms were refined anisotropically. Except as noted below, hydrogen atoms were inserted in calculated positions on the basis of packing considerations and d(C−H) = 0.95 Å. The positions were fixed for the final cycles of refinement. Final difference maps were featureless.

X-ray Crystallography of $(Ind)_2Ca(thf)_2$. Systematic absences and a statistical analysis of intensity distribution suggested that the proper space group was $C2/c$ (No. 15), which required the calcium atom to lie on a 2-fold rotation axis. No correction for decay or absorption was necessary. All hydrogen atoms of the indenyl ligand and two hydrogens of the THF were located in difference maps and successfully refined; the remaining hydrogen atoms on the THF were inserted in calculated positions on the basis of packing considerations, and d(C−H) = 0.95 Å; they were not refined. Selected bond distances and angles are listed in Table 2.

X-ray Crystallography of $(Ind^{2i})_2Ca(thf)$. The space group $P2_1/n$ (No. 14) was chosen from systematic absences. The intensities of three representative reflections measured after every 150 reflections declined by 12%; a linear correction factor was applied to the data to account for the decay. Azimuthal scans of several reflections indicated that no absorption correction was needed. The hydrogen atoms were inserted in calculated positions on the basis of packing considerations, and d(C−H) = 0.95 Å; they were not refined. Selected bond distances and angles are listed in Table 3.

X-ray Crystallography of $(Ind^{2i})_2Ba(thf)_2$. The space group $P2_1/n$ (No. 14) was identified from systematic absences. No correction for decay was necessary, but an empirical absorption correction, based on azimuthal scans of several reflections, was applied that resulted in transmission factors ranging from 0.86 to 1.00. Disorder is associated with the THF groups that makes them appear planar; there was no indication for alternate locations of the disordered atoms that would allow them to be experimentally resolved. The hydrogen atoms were inserted in calculated positions on the basis of packing considerations, and d(C−H) = 0.95 Å; they were not refined. Selected bond distances and angles are listed in Table 4.

X-ray Crystallography of $[(Ind)_2Sr(thf)]_\infty$. Systematic absences and a statistical analysis of intensity distribution suggested that the proper space group was $P2_1$ (No. 4). No correction for decay was necessary, but an empirical absorption correction, based on azimuthal scans of several reflections, was applied that resulted in transmission factors ranging from 0.73 to 1.00. The hydrogen atoms were inserted in calculated positions on the basis of packing considerations, and d(C−H) = 0.95 Å; they were not refined. An attempt was made to establish the absolute configuration of the molecule by refining the model to convergence, including anomalous dispersion terms and using all reflections (including Friedel pairs) for which $F > 0.0$. The signs of the coordinates were then inverted, and the model was again refined to convergence. R_w(F) for both refinements was identical (0.105); the absolute configuration is therefore indeterminate. Selected bond distances and angles are listed in Table 5.

Table 3. Selected Bond Lengths (Å) and Angles (deg) $(Ind^{2i})_2Ca(thf)$

Ca(1)−O(2)	2.323(5)	C(1)−C(2)	1.414(9)
Ca(1)−C(1)	2.673(7)	C(1)−C(9)	1.407(9)
Ca(1)−C(2)	2.684(7)	C(2)−C(3)	1.393(9)
Ca(1)−C(3)	2.706(7)	C(3)−C(4)	1.403(9)
Ca(1)−C(4)	2.729(7)	C(4)−C(5)	1.403(9)
Ca(1)−C(9)	2.692(7)	C(4)−C(9)	1.431(9)
Ca(1)−C(16)	2.695(7)	C(8)−C(9)	1.416(9)
Ca(1)−C(17)	2.665(7)	C(16)−C(17)	1.39(1)
Ca(1)−C(18)	2.647(8)	C(17)−C(18)	1.37(1)
Ca(1)−C(19)	2.702(8)	C(18)−C(19)	1.43(1)
Ca(1)−C(24)	2.706(7)	C(19)−C(24)	1.422(9)

Ca(1)−O(2)−C(31)	128.9(5)	C(1)−C(9)−C(4)	107.4(6)
Ca(1)−O(2)−C(34)	122.9(5)	C(17)−C(16)−C(24)	105.8(7)
C(2)−C(1)−C(9)	106.6(6)	C(16)−C(17)−C(18)	112.2(8)
C(1)−C(2)−C(3)	110.6(6)	C(17)−C(18)−C(19)	106.0(8)
C(2)−C(3)−C(4)	106.5(6)	C(18)−C(19)−C(24)	107.4(8)
C(3)−C(4)−C(9)	108.9(6)	C(16)−C(24)−C(19)	108.4(8)

Ca(1)−C_5 ring centroid (av)	2.410 Å
planarity of C_5 rings	within 0.023 Å
C_5 ring centroid−Ca(1)−C_5 ring centroid	142.5°
C_5 ring normal−Ca(1)−C_5 ring normal	141.9°
av displacement of methine C's from C_5 ring plane	0.12 Å
CH_3−CH−CH_3(av)	113(5)°
C(ring)−CH(av)	1.49(1) Å
CH−CH_3(av)	1.48(5) Å

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $(Ind^{2i})_2Ba(thf)_2$

Ba(1)−O(1)	2.757(9)	Ba(1)−C(24)	3.01(1)
Ba(1)−O(2)	2.805(9)	C(1)−C(2)	1.40(1)
Ba(1)−C(1)	3.033(9)	C(1)−C(9)	1.40(1)
Ba(1)−C(2)	3.06(1)	C(2)−C(3)	1.40(1)
Ba(1)−C(3)	3.05(1)	C(3)−C(4)	1.40(1)
Ba(1)−C(4)	2.99(1)	C(4)−C(9)	1.44(1)
Ba(1)−C(9)	3.002(9)	C(16)−C(17)	1.36(1)
Ba(1)−C(16)	3.06(1)	C(16)−C(24)	1.40(1)
Ba(1)−C(17)	3.10(1)	C(17)−C(18)	1.41(1)
Ba(1)−C(18)	3.03(1)	C(18)−C(19)	1.39(1)
Ba(1)−C(19)	2.96(1)	C(19)-C(24)	1.47(1)

Ba(1)−O(1)−C(35)	127(1)	C(2)−C(3)−C(4)	108(1)
Ba(1)−O(1)−C(38)	129(1)	C(3)−C(4)−C(9)	108(1)
Ba(1)−O(2)−C(31)	131(1)	C(1)−C(9)−C(4)	107(1)
Ba(1)−O(2)−C(34)	119(1)	C(17)−C(16)−C(24)	109(1)
C(35)−O(1)−C(38)	103(1)	C(16)−C(17)−C(18)	110(1)
C(31)−O(2)−C(34)	110(1)	C(17)−C(18)−C(19)	107.7(9)
O(1)−Ba(1)−O(2)	83.4(4)	C(18)−C(19)−C(24)	107(1)
C(2)−C(1)−C(9)	108(1)	C(16)−C(24)−C(19)	107(1)
C(1)−C(2)−C(3)	109(1)		

Ba(1)-C_5 ring centroid(av)	2.784 Å
C(ring)−CH(av)	1.51(1) Å
CH−CH_3 (av)	1.49(1) Å
planarity of C_5 rings	within 0.017 Å
C_5 ring centroid−Ba(1)−C_5 ring centroid	140.2°
C_5 ring normal−Ba(1)−C_5 ring normal	136.0°
av displacement of methine C's from C_5 ring plane	0.089 Å

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[(Ind)_2Sr(thf)]_\infty$[a]

Sr(1)−O(1)	2.560(9)	Sr(1)−C(13)′	3.02(1)
Sr(1)−C(1)	2.93(3)	Sr(1)−C(18)	3.05(2)
Sr(1)−C(2)	2.81(2)	Sr(1)−C(18)′	3.01(2)
Sr(1)−C(3)	2.90(2)	C(1)−C(2)	1.36(4)
Sr(1)−C(4)	3.06(2)	C(1)−C(9)	1.37(3)
Sr(1)−C(9)	3.00(2)	C(2)−C(3)	1.40(4)
Sr(1)−C(10)	2.92(2)	C(3)−C(4)	1.40(4)
Sr(1)−C(10)′	2.91(2)	C(4)−C(9)	1.43(3)
Sr(1)−C(11)	3.04(2)	C(10)−C(11)	1.35(3)
Sr(1)−C(11)′	2.78(2)	C(10)−C(18)	1.43(3)
Sr(1)−C(12)	3.15(2)	C(11)−C(12)	1.36(3)
Sr(1)−C(12)′	2.90(2)	C(12)−C(13)	1.44(2)
Sr(1)−C(13)	3.21(1)	C(13)−C(18)	1.39(2)

Sr(1)−O(1)−C(19)	126(1)	C(1)−C(9)−C(4)	106(3)
Sr(1)−O(1)−C(22)	116.5(3)	C(11)−C(10)−C(18)	107(2)
C(19)−O(1)−C(22)	108(1)	C(10)−C(11)−C(12)	111(2)
C(2)−C(1)−C(9)	117.3(5)	C(11)−C(12)−C(13)	108(2)
C(1)−C(2)−C(3)	108(3)	C(12)−C(13)−C(18)	105(1)
C(2)−C(3)−C(4)	107(2)	C(10)−C(18)−C(13)	109(2)
C(3)−C(4)−C(9)	108(2)		

Sr(1)−C_5 ring centroid (av)	2.693 Å (terminal), 2.840 Å (bridging)
planarity of C_5 rings	within 0.049 Å
C_5 ring centroid−Sr(1)−C_5 ring centroid	120.3°
C_5 ring normal−Sr(1)−C_5 ring normal	119.9°

[a] The coordinates of the primed atoms are related to those of the unprimed atoms by the expression $1 - x, y - {}^1/_2, 1 - z$.

Results and Discussion

Synthesis of Alkaline-Earth Indenides. The synthesis of the bis(indenyl) and bis(1,3-diisopropylindenyl) alkaline-earth complexes was undertaken as an extension of our previous work with tri- and tetraisopropylcyclopentadienyl complexes of the alkaline-earth metals.[14,16,17] The 2:1 metathetical reaction of potassium indenide with the diiodides of calcium, strontium, or barium in THF produces the corresponding bis(indenyl) alkaline-earth complexes in high yield (eq 1). The bis-

$$2K(Ind) + AeI_2 \xrightarrow{THF} (Ind)_2Ae(thf)_n + 2KI\downarrow \quad (1)$$

$$Ae = Ca, Sr, Ba$$

(indenyl)calcium and -barium complexes were identified by their previously reported NMR spectra;[4,7] the THF-solvated $(Ind)_2Sr(thf)$ complex is new, but its spectroscopic properties are similar to those of the Ca and Ba compounds. The degree of THF solvation observed in the NMR spectra of the calcium ($n = 2$) and strontium ($n = 1$) complexes was subsequently confirmed by X-ray crystallography (see below). The solvated calcium indenyl complex displays moderate solubility in toluene, but the analogous strontium and barium compounds are soluble only in THF, although they contain coordinated THF. Such limited solubility parallels that observed for unsubstituted heavy alkaline-earth metallocenes, even those with coordinated Lewis bases.[18]

The thermally stable bis(1,3-diisopropylindenyl) alkaline-earth complexes $(Ind^{2i})_2Ae(thf)_n$ are formed in good yields in reactions similar to those used for the unsubstituted complexes (eq 2). The diisopropylindenyl

$$2K(Ind^{2i}) + AeI_2 \xrightarrow{THF} (Ind^{2i})_2Ae(thf)_n + 2KI\downarrow \quad (2)$$

$$Ae = Ca, Sr, Ba$$

compounds are initially isolated as oils when synthesized in THF solutions. They can be induced to solidify into waxes upon the addition of hexane; upon its removal, they remain as powders.

Although the unsubstituted calcium indenyl complex accommodates two THF ligands, the substituted complex $(Ind^{2i})_2Ca(thf)$ contains only one coordinated THF molecule, presumably a consequence of the steric hin-

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(16) Burkey, D. J.; Williams, R. A.; Hanusa, T. P. *Organometallics* **1993**, *12*, 1331−1337.

(17) Burkey, D. J.; Hanusa, T. P.; Huffman, J. C. *Adv. Mater. Opt. Electron.* **1994**, *4*, 1−8.

(18) McCormick, M. J.; Williams, R. A.; Levine, L. J.; Hanusa, T. P. *Polyhedron* **1988**, *7*, 725−730.

drance provided by the four isopropyl groups on the two indenyl ligands. Interestingly, the strontium and barium metal complexes with substituted ligands can accommodate two THF molecules on their metal centers, unlike the unsubstituted analogues, which are found with only one THF. This reversal in the solvation pattern between calcium and strontium/barium presumably occurs because both calcium complexes are monomeric, and the extent of their solvation is controlled by the size of the indenyl ligands. In contrast, the unsubstituted strontium complex (and probably the barium species as well) is polymeric (see below), and adjacent molecules occupy portions of the coordination sphere of the metals. Isopropylation of the indenyl ligands forces the barium complex (and the strontium analogue[19]) to be monomeric, and the longer Sr−C and Ba−C bonds increase the room available for THF coordination.

Such solvation behavior is similar to that of the corresponding triisopropylcyclopentadienyl alkaline-earth compounds, $(Cp^{3i})_2Ae(thf)_n$.[16] Although the unsubstituted $Cp_2(Sr, Ba)$ complexes are isolated with only one THF (for Ae = Sr) or ~0.25 THF (for Ae = Ba) per metal center,[18] the strontium and barium $(Cp^{3i})_2Ae$ complexes are isolated as disolvates despite the presence of three isopropyl groups per ring. The isopropylated versions of the cyclopentadienyl and indenyl complexes display roughly the same high level of air sensitivity as the parent compounds, indicating the small effect the steric bulk of the ligands has on this physical property.

Few indenyl complexes of the main-group metals have been structurally characterized, and among the group 2 elements, only the polymeric $(Ind)_2Mg$ has been previously examined.[20] In order to augment the meager data that exists for this class of compounds, we undertook X-ray structural studies of several of the compounds.

Solid-State Structures

$(Ind)_2Ca(thf)_2$. The compound crystallizes from THF as large colorless blocks. It possesses a bent geometry similar to that observed with solvated alkaline-earth metallocenes,[16,21,22] with the two indenyls and the two THF ligands arranged around the metal center in a distorted tetrahedral geometry. A crystallographically imposed C_2 axis through the calcium atom renders only half the molecule unique. This structure, along with the other calcium and barium compounds described below, represents the first crystallographically characterized monomeric indenyl complex of the main-group elements. An ORTEP view of the complete molecule displaying the numbering scheme used in the tables is provided in Figure 1.

The average calcium−carbon distance of 2.73(3) Å is the same as the 2.733 Å Ca−C length in $[(t\text{-Bu})C_5H_4]_2Ca(thf)_2$, which also contains an 8-coordinate calcium center.[21] Both these distances are marginally longer than the 2.676(9) Å Ca−C bond in 8-coordinate $(MeCp)_2Ca(dme)$,[23] but the difference is not significant at the 3σ level. The small spread in the Ca−C distances (2.694(4)−2.771(4); $\Delta = 0.077$ Å) is almost half that in $[(t\text{-Bu})C_5H_4]_2Ca(thf)_2$ ($\Delta = 0.13$ Å) and indicates that there is no slippage of the indenyl ligand. This conclusion is further supported by the small calculated value for the slip parameter (see below).

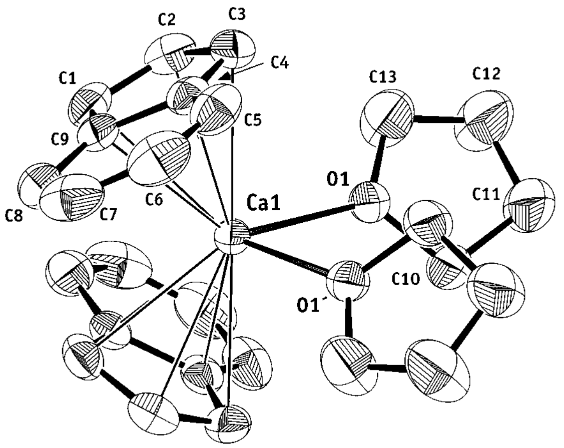

Figure 1. ORTEP diagram of the non-hydrogen atoms of $(Ind)_2Ca(thf)_2$, giving the numbering scheme used in the text. Thermal ellipsoids are shown at the 30% level.

The indenyl ligands have an almost completely staggered arrangement; the angle between the lines connecting the centers of the five- and six-membered rings on each ligand is 171.4° (Figure 2). Without the steric interference of the *t*-Bu groups present on the rings in $[(t\text{-Bu})C_5H_4]_2Ca(thf)_2$, but with larger coordinated bases than the dme in $(MeCp)_2Ca(dme)$, the indenyl ligands in $(Ind)_2Ca(thf)_2$ can bend back to create a ring centroid−Ca−ring centroid angle of only 128.3°. This is appreciably smaller than the analogous angles of 133.3 and 134.8° in $[(t\text{-Bu})C_5H_4]_2Ca(thf)_2$ and $(MeCp)_2Ca(dme)$ and is the smallest angle yet observed in a monomeric calcocene with independent rings.[24,25]

The Ca−O(thf) distance of 2.360(3) Å is slightly shorter than the same distance observed in $[(t\text{-Bu})C_5H_4]_2Ca(thf)_2$ (2.402 Å) but is comparable to the 2.310(9) Å distance observed in $\{C_5H_3\text{-}1,3\text{-}(SiMe_3)_2\}_2Ca(thf)$ when the 0.06 Å difference between 7- and 8-coordinate Ca^{2+} is taken into account.[26] The O−Ca−O′ angle of 82.6(1)° is comparable to the angle between the thf ligands in $[(t\text{-Bu})C_5H_4]_2Ca(thf)_2$ (83.2°) and $[(t\text{-Bu})C_5H_4]_2Sr(thf)_2$ (83.1°), although it is much larger than the 68.7° O(1)−Ca−O(2) angle in $(MeCp)_2Ca(dme)$, which is limited by the bite of the chelating DME.

$(Ind^{2i})_2Ca(thf)$. The compound crystallizes from a THF/hexane mixture as pale yellow prisms. It possesses a bent geometry like that of the parent calcium indenyl species but has only a single coordinated THF. The two indenyl ligands and the THF form a distorted trigonal arrangement around the metal center. The molecule possesses approximate C_2 symmetry, although it is not crystallographically imposed. An ORTEP view

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(19) A preliminary X-ray study of $(Ind^{2i})_2Sr(thf)_2$ has found it isomorphic with the barium complex (Overby, J. S.; Hanusa, T. P. Unpublished results).

(20) Atwood, J. L.; Smith, K. D. *J. Am. Chem. Soc.* **1974**, *96*, 994−998.

(21) Gardiner, M. G.; Raston, C. L.; Kennard, C. H. L. *Organometallics* **1991**, *10*, 3680−3686.

(22) Jutzi, P.; Dickbreder, R. *J. Organomet. Chem.* **1989**, *373*, 301−306.

(23) Hammel, A.; Schwarz, W.; Weidlein, J. *J. Organomet. Chem.* **1989**, *378*, 347−361.

(24) In the *ansa*-metallocene complex $[\{Me_2Et_2C_2(C_5H_4)_2\}Ca(^tBuN{=}CHCH{=}N^tBu)]$ (ref 25) the angle between the calcium and the center of the rings is 119.0°, but the rings are not independent.

(25) Rieckhoff, M.; Pieper, U.; Stalke, D.; Edelmann, F. T. *Angew. Chem.* **1993**, *105*, 1102−1104.

(26) Shannon, R. D. *Acta Crystallogr., Sect A.* **1976**, *32*, 751−767.

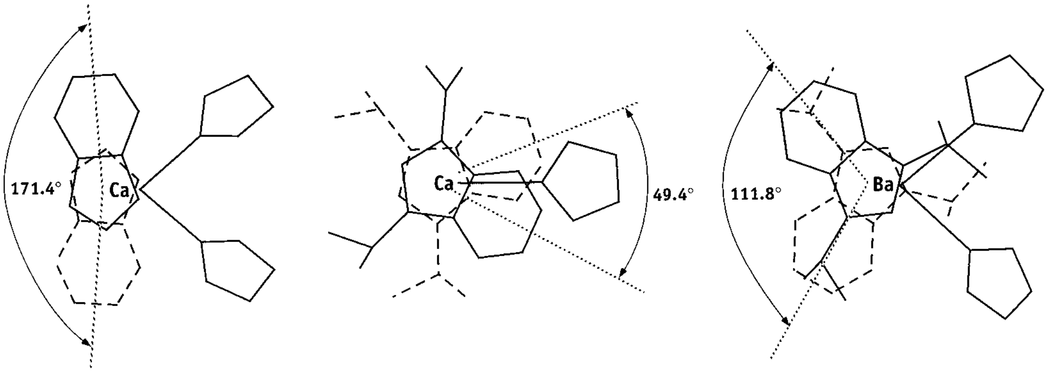

Figure 2. Orientation of the indenyl ligands in the crystallographically characterized alkaline-earth complexes. From left to right are the structures of $(Ind)_2Ca(thf)_2$, $(Ind^{2i})_2Ca(thf)$, and $(Ind^{2i})_2Ba(thf)_2$.

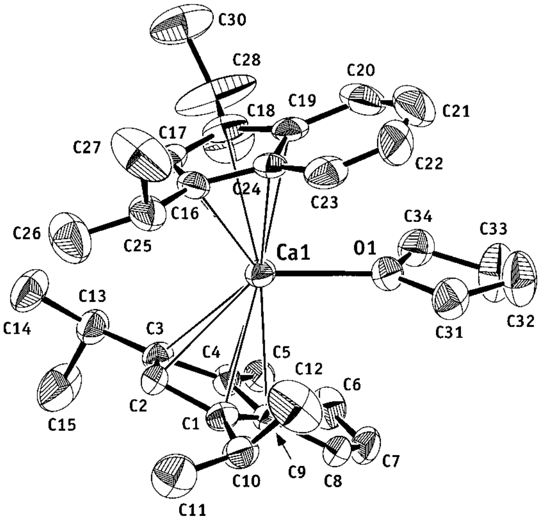

Figure 3. ORTEP diagram of the non-hydrogen atoms of $(Ind^{2i})_2Ca(thf)$ giving the numbering scheme used in the text. Thermal ellipsoids are shown at the 30% level.

of the complete molecule displaying the numbering scheme used in the tables is provided in Figure 3.

The average Ca−C distance of 2.69(2) Å is as expected for a 7-coordinate calcium center (cf. 2.678(8) Å for the Ca−C distance in $\{C_5H_3\text{-}1,3\text{-}(SiMe_3)_2\}_2Ca(thf)$[27] and 2.67(1) Å in $[(Me_5C_5)CaI(thf)_2]_2$[28]). The Ca−O(thf) distance of 2.323(5) Å is comparable to the 2.329(3) Å distance observed in $\{C_5H_3\text{-}1,3\text{-}(SiMe_3)_2\}_2Ca(thf)$, but is somewhat shorter than the average Ca−O(thf) distance observed in $[(Me_5C_5)CaI(thf)_2]_2$ (2.40(2) Å), which may reflect greater steric crowding in the latter.

Although the *i*-Pr substituents do not affect the Ca−C distance, they markedly change the inter-indenyl group orientations. The ring centroid−Ca−ring centroid angle has opened to 142.5°, and the arene portions of the indenyl ligands have moved together near the "open" side of the complex (Figure 2). The combination of the widened angle between the indenyl ligands and their twist angle places the closest inter-ring contact between *i*-Pr methyl groups (C(14)−C(26)) at 4.16 Å, outside van der Waals's contact. The closest contact between the THF ligand and a carbon atom of a six-member ring (O···C(21)), however, is much closer at 3.30 Å. The more crowded environment on this side of the molecule is evidently the reason that only one THF molecule binds to the calcium, even when the compound is recrystallized from THF.

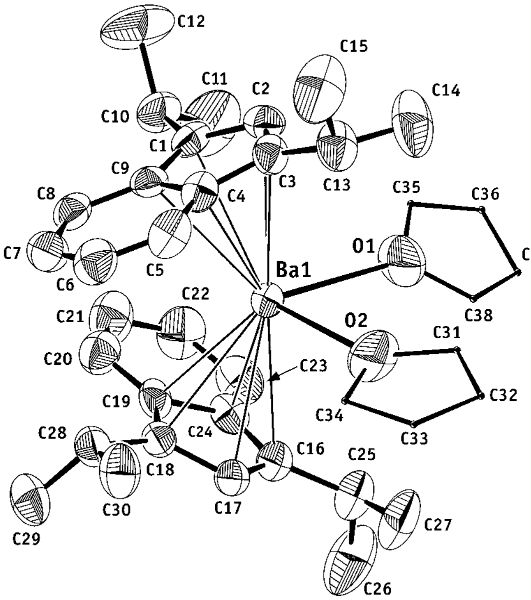

Figure 4. ORTEP diagram of the non-hydrogen atoms of $(Ind^{2i})_2Ba(thf)_2$, giving the numbering scheme used in the text. Thermal ellipsoids are shown at the 30% level, and the carbon atoms of the thf ligand are represented as dots.

$(Ind^{2i})_2Ba(thf)_2$. The compound crystallizes from a THF/hexane mixture as yellow blocks. Like $(Ind)_2Ca(thf)_2$, it is bent, with the two indenyl ligands and the two THF ligands bound to the metal in a distorted tetrahedral geometry. The molecule possesses approximate C_2 symmetry, although it is not crystallographically imposed. An ORTEP view of the complete molecule displaying the numbering scheme used in the tables is provided in Figure 4.

The average Ba−C distance of 3.03(4) Å is identical to that in the only structurally characterized disolvated barocene, $[(C_3H_7)_3C_5H_2]_2Ba(thf)_2$ (3.03(2) Å).[16] The spread in the Ba−C distances (2.97(1)−3.10(1); $\Delta = 0.13$ Å) is also about the same as that in $[(C_3H_7)_3C_5H_2]_2Ba(thf)_2$ ($\Delta = 0.11$ Å); the variation in bond lengths does not occur in a way that suggests there is any slippage of the indenyl ligand.

The presence of the isopropyl substituents on the indenyl rings and the two THF ligands adds appreciable bulk to the coordination sphere of the barium atom, but the long Ba−C bonds partially offset their effect. As a result, the ring centroid−Ba−ring centroid angle of

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(27) Jutzi, P.; Leffers, W.; Müller, G.; Huber, B. *Chem. Ber.* **1989**, *122*, 879−884.

(28) McCormick, M. J.; Sockwell, S. C.; Davies, C. E. H.; Hanusa, T. P.; Huffman, J. C. *Organometallics* **1989**, *8*, 2044−2049.

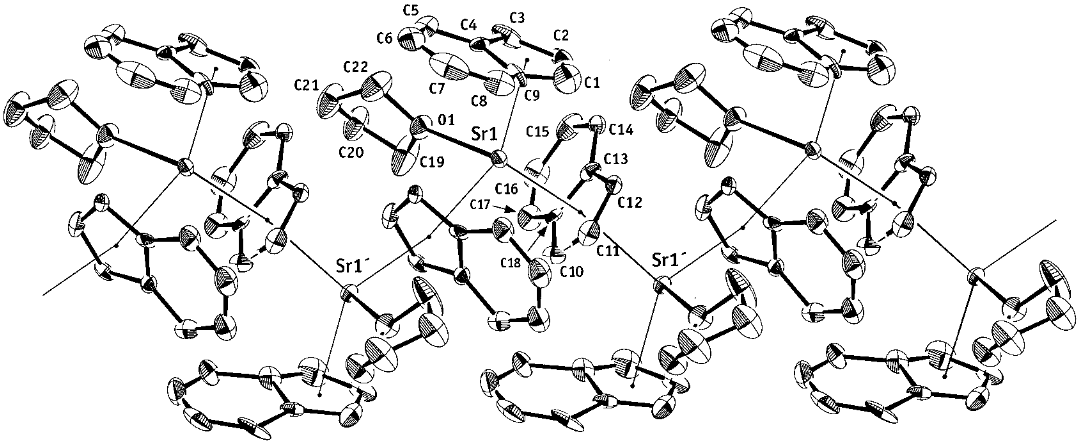

Figure 5. Packing diagram of the non-hydrogen atoms of $[(\mathrm{Ind})_2\mathrm{Sr(thf)}]_\infty$, giving the numbering scheme used in the text. Thermal ellipsoids are shown at the 30% level.

140.2° is nearly the same as in $(\mathrm{Ind}^{2i})_2\mathrm{Ca(thf)}$, and notably larger than in $[(C_3H_7)_3C_5H_2]_2\mathrm{Ba(thf)}_2$ (131.7°). The angle between the line connecting the five- and six-membered rings on each ligand is 111.8°, which has closed appreciably from the value in the $(\mathrm{Ind})_2\mathrm{Ca(thf)}_2$ complex (171.4°) (Figure 2). There is disorder associated with the THF groups that makes them appear almost planar, but this does not affect the Ba−O bond metrics. For example, the Ba−O(thf) distances of 2.757(9) and 2.805(9) Å bracket the value found in $[(C_3H_7)_3C_5H_2]_2\mathrm{Ba(thf)}_2$ (2.77(1) Å), and the O(1)−Ba−O(2) angle of 83.4(4)° is indistinguishable from that in the barocene complex.

$[(\mathrm{Ind})_2\mathrm{Sr(thf)}]_\infty$. The compound crystallizes from THF as beige prisms. Unlike the calcium and barium indenyl complexes, $(\mathrm{Ind})_2\mathrm{Sr(thf)}$ forms an infinite coordination polymer in the solid state. Each Sr atom is coordinated by a terminal indenyl and THF ligand and is associated with two bridging indenyls, so that a roughly tetrahedral geometry around the metal center is generated. A packing diagram of the molecule displaying the numbering scheme used in the tables is provided in Figure 5.

To a first approximation, the average Sr−C distance to the terminal indenyl ligand of 2.94 Å is close to that expected from a C_5 ring on a formally 10-coordinate Sr^{2+} center, given the Sr−C distance of 2.864 Å in $[(t\text{-Bu})C_5H_4]_2\mathrm{Sr(thf)}_2$[21] and the estimated 0.08 Å difference between 8- and 10-coordinate Sr^{2+}.[26,29] Unlike the situation with the monomeric complexes, the spread in the metal−carbon distances is large enough (2.81(2)−3.06(2); $\Delta = 0.25$ Å) that its significance must be given closer examination. The Sr−C(2) distance is the shortest (2.81(2) Å), flanked by the Sr−C(1,3) lengths at 2.93(2) and 2.90(2) Å; the Sr−C(4,9) distances are the two longest, at 3.06(2) and 3.00(2) Å. This amount of variation is roughly the same as that observed in the crystal structure of $(\mathrm{Ind})_2\mathrm{Mg}$ (Mg−C lengths range 2.31(1)−2.54(1) and 2.34(1)−2.60(1) Å for the two magnesium centers[20]), and it is also consistent with the greater steric congestion around C(4) and C(9). Although the C−C bond lengths were not determined with high precision, they are not consistent with an allylic type location of the indenyl ligand. For example, the C(4)−C(9) length at 1.43(3) Å is marginally longer than C(1)−C(9) (1.37(3) Å); for an allylic bonding arrangement, these distances should represent formal double and single bonds, respectively. The small value for the slip parameter (below) confirms the absence of any significant distortions in this ligand.

The average Sr−C distances to the bridging indenyl ligands differ considerably; those to the C(10−13,18) ring center around 3.07 Å, a predictably longer value than the terminal Sr−indenyl lengths, whereas those to the symmetry-related ring (C(10′−13′,18′)) average to a value no different from the terminal bond lengths (2.92 Å). In both cases, however, there is a substantial spread in the values ($\Delta = 0.29$ Å for Sr−C(10−13,18); $\Delta = 0.24$ Å for Sr−C(10′−13′,18′)). The variation in bond lengths involving the C(10−13,18) ring arises from a sideways slippage; i.e., the closest distance (2.92(2) Å) involves C(10), and not C(11) (at 3.04(2) Å), as would occur if allylic-type bonding were involved. The spread in Sr−C(10′−13′,18′) lengths are more in line with an expected η^3-bonding pattern, however; i.e., the Sr−C(11)′ distance is the shortest (2.78(2) Å), bordered by the Sr−C(10′,12′) lengths at 2.91(2) and 2.90(2) Å; the Sr−C(13′,18′) distances are the longest, at 3.02(1) and 3.01(2) Å. Unlike the case with the terminal indenyl ligand, the pattern of C−C distances does fit an η^3-bonding scheme; i.e., the "single" C(12)−C(13) and C(10)−C(18) bonds of 1.44(3) and 1.43(3) Å length are sandwiched between the shorter C(13)−C(18) (1.39(2) Å) and C(10)−C(11) and C(11)−C(12) separations (1.35(3), 1.36(3) Å). The comparatively small spread in C−C lengths ($\Delta = 0.09$ Å) and their large errors weaken the significance that can be placed on these distances, however. They are in any case much less pronounced than in slipped transition metal indenyl complexes such as $(\eta^5\text{-Ind})(\eta^3\text{-Ind})\mathrm{V(CO)}_2$[30] and $(\eta^5\text{-Ind})(\eta^3\text{-Ind})\mathrm{W(CO)}_2$.[31]

In view of the sometimes close analogy between the structures of organolanthanide and organoalkaline-earth complexes,[2] it is interesting to note that an analogous samarium complex has been prepared and crystallizes as a monomeric trisolvate, $(\mathrm{Ind})_2\mathrm{Sm(thf)}_3$.[32] Since the ionic radii of Sr^{2+} and Sm^{2+} are essentially

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(29) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; pp 537, 538.

(30) Kowaleski, R. M.; Rheingold, A. L.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1986**, *108*, 2460−2461.

(31) Nesmeyanov, A. W.; Ustynyuk, N. A.; Makarova, L. G.; Andrianov, V. G.; Struckov, Y. T.; Andrae, S.; Ustynyuk, Y. A.; Malyugina, S. G. *J. Organomet. Chem.* **1978**, *159*, 189−199.

(32) Evans, W. J.; Gummersheimer, T. S.; Boyle, T. J.; Ziller, J. W. *Organometallics* **1994**, *13*, 1281−1284.

the same,[26] this highlights the subtle balance of forces that can influence structure in conformationally flexible systems. Although the strontium center evidently could coordinate a total of three THF molecules, it oligomerizes and keeps only one THF to fill its coordination sphere. The apparently more oxophilic samarium center retains three THF molecules and remains monomeric.

Slip Parameter Assessments. Previous work on transition metal indenyl complexes has lead to the development of several parameters that quantify the distortions within the ligand and in the metal−indenyl binding.[33−35] Among these, the slip parameter Δ_{M-C} can be employed to quantify $\eta^5-\eta^3$ slippage within the complex. This parameter is calculated from the difference in the averages of the metal−carbon distances to the two bridgehead atoms and the distances to the other three atoms of the C_5 ring.

A series of tris(indenyl)lanthanide tetrahydrofuran-solvated complexes $[(Ind)_3Ln(thf)]$ (Ln = Pr,[36] Nd, Gd[37]) have Δ_{M-C} values ranging from 0.101 for Ln = Pr to 0.359 for Ln = Gd.[38] Even the largest of these is much less than the value of 0.72 found in $(\eta^5$-Ind$)(\eta^3$-Ind)W-$(CO)_2)$,[31] which has a true η^3-bound ring. In view of these numbers, the values of the slip parameter for $(Ind)_2Ca(thf)_2$ (0.047), $(Ind^{2i})_2Ca(thf)$ (0.022, 0.035), $(Ind^{2i})_2Ba(thf)_2$ (0.052, 0.078), and $[(Ind)_2Sr(thf)]_\infty$ (0.048, terminal ring only) suggest how distortion-free the group 2 complexes are, which is consistent with a fundamentally ionic interaction between the metals and the rings.

Conclusions

Bis(indenyl) and bis(diisopropylindenyl) complexes of calcium, strontium, and barium can be prepared by straightforward salt elimination reactions from the metal diiodides. They possess physical properties comparable to analogous unsubstituted and triisopropyl-substituted cyclopentadienyl compounds, and some of their structural parameters are also similar. They illustrate the balance of steric and electronic forces that influence the composition of heavy alkaline-earth compounds. The $(Ind)_2Ca(thf)_2$ complex, with its unsubstituted indenyl ligand and more Lewis acidic metal center, crystallizes from THF in the disolvated form, whereas the strontium and barium compounds with their larger and less acidic metals remain monosolvated species. The latter two complexes apparently prefer to oligomerize rather than retain a coordinated THF. However, this solvation trend is reversed with the more sterically encumbered diisopropylindenyl ligand, as the barium compound forms a disolvate but the calcium analogue can only accommodate one THF molecule. Thus by adjustment of the steric bulk of the ligand, solvation preferences based on the inherent Lewis acidities of the metal centers can either be reinforced or reversed.

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Supporting Information Available: Listings of complete atom fractional coordinates and *B* values, bond distances and angles, and anisotropic thermal parameters (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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