Formation and crystal structures of a monomer–dimer pair of mono(cyclopentadienyl)calcium complexes, $[C_5(t\text{-}Bu)_3H_2]_2CaI(THF)_2$ and $\{[C_5(t\text{-}Bu)_3H_2]_2CaI(THF)\}_2$

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Abstract

The mono(cyclopentadienyl)calcium iodide complex $[\{(Cp^{3T})CaI(THF)_x\}_n]$ $(Cp^{3T} = [C_5(t\text{-}Bu)_3H_2]^-)$ is generated from the 1:1 reaction of $K[Cp^{3T}]$ and CaI_2 in THF. No redistribution into $[(Cp^{3T})_2Ca]$ and $CaI_2(THF)_n$ is observed in THF solution. The mono(ring) compound crystallizes from THF as a monomer with a distorted piano stool geometry; the coordination environment around the calcium consists of a pentahapto $[Cp^{3T}]^-$ ligand, an iodide, and two THF molecules. It is the first structurally authenticated monomeric mono(ring) halide complex of a heavy alkaline-earth metal. From a toluene–THF mixture, the mono(ring) complex crystallizes as an iodide-bridged dimer, with a pentahapto $[Cp^{3T}]^-$ ligand and one terminal THF on each metal atom. The Ca–I and Ca–I′ distances are nearly equal at 3.087(2) and 3.101(2) Å. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Calcium; Cyclopentadienyl; Crystal Structures; Group 2; Iodide
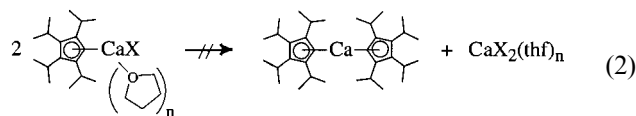
1. Introduction

Owing to their highly electropositive nature, the heavy alkaline-earth (Ae) metals, calcium, strontium and barium form polar metal–ligand bonds that are kinetically labile [1]. Consequently, a general difficulty with the manipulation of the heteroleptic compounds RAeX of these elements is the occurrence of Schlenk equilibria, in which the complexes undergo a ligand redistribution to form a mixture of heteroleptic and homoleptic species Eq. (1).

$$2RAeX \rightleftharpoons R_2Ae + AeX_2 \qquad (1)$$

(R, X = two different mono(anionic) ligands, e.g. alkyl, halide)

We have previously found that mono(cyclopentadienyl) complexes of calcium (Cp′CaX) can be stabilized against ligand rearrangement reactions in solution if Cp′ is a sterically bulky, 'encapsulating' ring, such as

1,2,3,4-tetraisopropylcyclopentadiene (Cp^{4i}) [2]. When two such rings are bound to calcium, the substituents sterically restrict access to the metal, and the metallocene $(Cp^{4i})_2Ca$ cannot form adducts with Lewis bases such as ethers and amines. In solution, coordinated THF must dissociate from a $(Cp^{4i})CaX(THF)_n$ complex before the metallocene forms (e.g. Eq. (2)), and as loss of THF is disfavored by the strong $Ca \leftarrow :OC_4H_8$ interaction, ligand redistribution is blocked.

$$2 \quad \text{[structure]} \text{—CaX} \quad \xrightarrow{\quad//\quad} \quad \text{[structure]}\text{—Ca—}\text{[structure]} \quad + \quad CaX_2(thf)_n \qquad (2)$$

Using this strategy, the kinetic stabilization of mono(ring) complexes of the heavy alkaline-earth metals was successfully extended to the larger metals strontium and barium using the bulkier 1,2,4-tris(trimethylsilyl)cyclopentadienyl ligand (Cp^{3Si}) [3].

Even with Schlenk exchange inhibited, however, derivatization of the X ligand is not always straightforward. Although a trimethylsilylamido derivative of
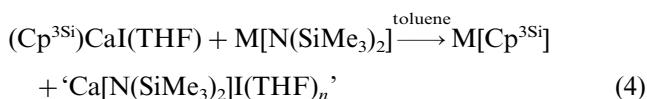
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$(Cp^{4i})CaI(THF)$ can be prepared in high yield with the use of the potassium amido reagent in toluene (Eq. (3)) [2],

$$(Cp^{4i})CaI(THF) + K[N(SiMe_3)_2] \xrightarrow{\text{toluene}}$$

$$(Cp^{4i})Ca[N(SiMe_3)_2](THF) + KI\downarrow \quad (3)$$
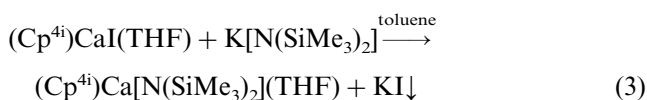
reactions of $(Cp^{3Si})CaI(THF)$ with various bis(trimethylsilylamido) sources take a different course in that the alkali metal cyclopentadienide is either the major or exclusive product (Eq. (4)) [3].

$$(Cp^{3Si})CaI(THF) + M[N(SiMe_3)_2] \xrightarrow{\text{toluene}} M[Cp^{3Si}]$$

$$+ \text{'Ca}[N(SiMe_3)_2]I(THF)_n\text{'} \quad (4)$$

M = Li, Na, K

The 1,2,4-tris(trimethylsilyl)cyclopentadienyl ligand is distinctive because it is bulky enough to stabilize mono(ring) complexes of strontium and barium [3], but it is substituted by silyl groups rather than electron-donating alkyl groups. The electronic effects of silyl substituents on cyclopentadienyl rings are not well understood, although they are acknowledged to be different from alkyl groups [4]. In order to elucidate the origins of the unusual reactivity of $(Cp^{3Si})CaI(THF)$ in exchange reactions, we investigated mono(ring) complexes of the 1,2,4-tri(*tert*-butyl)cyclopentadienyl ligand $[Cp^{3T}]^-$. The substituents in $[Cp^{3T}]^-$ should impose steric restrictions comparable to that of the trimethylsilyl analog, but they are electronically similar to the alkylated rings we have previously examined.

During the course of our work with this ligand, we obtained structures of both the dimeric and monomeric forms of the mono(ring) calcium iodide complex, $[\{(Cp^{3T})CaI(THF)_x\}_n]$. Although $[(Cp^{4i})CaI(THF)_2]$ was thought to be monomeric [2], the present paper includes the first structural characterization of a monomeric mono(ring) halide complex of a heavy alkaline-earth metal.

2. Experimental

2.1. General considerations

All manipulations were performed with the rigorous exclusion of air and moisture using high vacuum, Schlenk, or drybox techniques. Proton (^{1}H) 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 resonances of THF-d_8 (δ 3.58 and 67.4). The infrared data were measured with KBr pellets as previously described [5]. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

2.2. Materials

Anhydrous calcium iodide (Cerac, 95%) was heated under vacuum (150°C, 10^{-6} torr) to remove residual amounts of free iodine. Potassium hydride was purchased from Aldrich, and was washed with hexanes and dried under vacuum prior to use. HCp^{3T} (1,2,4-tri(*tert*-butyl)cyclopentadiene) was prepared with literature procedures [6]. Solvents for reactions were distilled under nitrogen from potassium benzophenone ketyl. The NMR solvent was vacuum distilled from Na/K (22/78) alloy and stored over 4Å molecular sieves.

2.3. Synthesis of potassium 1,2,4-tri(tert-butyl)cyclopentadienide, K[Cp^{3T}]

HCp^{3T} (2.65 g, 11.3 mmol) and KH (0.450 g, 11.2 mmol) were added to a mixture of 10 ml of THF and 25 ml of hexanes in a 125 ml flask. The reaction was stirred overnight, during which time a precipitate formed. The precipitate was collected by filtration of the reaction mixture through a glass frit, washed with hexanes, and dried under vacuum to give 2.60 g of $K[Cp^{3T}]$ (85% yield) as a beige powder that is only slightly soluble in THF. It can be identified from its ^{1}H-NMR spectrum (THF-d_8, 20°C): $\delta = 5.44$ (s, 2H, ring-CH), 1.32 (s, 18H, C(CH_3)$_3$), 1.16 (s, 9H, C(CH_3)$_3$).

2.4. Synthesis of [(Cp^{3T})CaI(THF)$_n$] (1 and 2)

CaI_2 (0.224 g, 0.76 mmol) and $K[Cp^{3T}]$ (0.204 g, 0.75 mmol) were added to a flask at room temperature (r.t.). THF (50 ml) was added to the flask, and the reaction mixture was stirred overnight, stripped to dryness, and the residue extracted with toluene. The extract was filtered, and the filtrate evaporated to dryness. Recrystallization from THF yielded 0.250 g (61%) of colorless crystals of the disolvated complex $[(Cp^{3T})CaI(THF)_2]$ (**1**), m.p. 202–204°C. ^{1}H-NMR (THF-d_8, 20°C): $\delta = 6.00$ (s, 2H, ring-CH), 1.46 (s, 18H, C(CH_3)$_3$), 1.25 (s, 9H, C(CH_3)$_3$). ^{13}C-NMR (THF-d_8, 20°C): $\delta = 131.6$, 130.0, 107.2 (ring-C); 35.0, 32.8 (C(CH_3)$_3$); 34.0, 32.4 (C(CH$_3$)$_3$). Acceptable elemental analysis on crystalline samples could not be obtained, perhaps because of the compound's high air-sensitivity. Principal IR bands (KBr, cm^{-1}): 2970 (vs, br), 2924 (vs), 1568 (br, m), 1460 (m), 1417 (m), 1387 (m), 1364 (s), 1239 (m), 1199 (w), 1068 (m), 1030 (s), 917 (w), 867 (w), 803 (w), 578 (w), 547 (w). Crystals for X-ray structural analysis of **1** were grown by slow evaporation of a saturated THF solution at r.t. X-ray quality crystals of the dimer $[(Cp^{3T})CaI(THF)]_2$ (**2**) formed from slow evaporation of a saturated THF–toluene solution at r.t.

2.5. X-ray crystallography

A suitable crystal of each sample was located, attached to a glass fiber, and mounted on a Siemens SMART system for data collection at 173(2) K. Data collection (SAINT: Siemens Industrial Automation Inc, Madison, WI) and structure solution were conducted at the X-Ray Crystallography Laboratory at the University of Minnesota. All calculations were performed using SGI INDY R4400-SC or Pentium computers using the SHELXTL V5.10 suite of programs (SHELXTL-Plus V5.1, Siemens Industrial Automation Inc, Madison, WI. Final cell constants were calculated from a set of strong reflections measured during the actual data collection. Relevant crystal and data collection parameters for each of the compounds are given in Table 1.

The space groups were determined based on a consideration of reflection conditions and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Several full-matrix least squares difference Fourier cycles were performed that located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The crystal of **2** was found to be cracked.

Table 1
Crystal data and summary of X–ray data collection for **1** and **2**

Empirical formula	$C_{25}H_{45}CaIO_2$ (**1**)	$C_{21}H_{37}CaIO$ (**2**)
Formula weight	544.59	472.49
Color of crystal	Colorless	Colorless
Crystal dimensions (mm)	$0.25 \times 0.22 \times 0.18$	$0.22 \times 0.20 \times 0.16$
Space group	$P\bar{1}$	$P\bar{1}$
Temperature (K)	173(2)	173(2)
a (Å)	8.8249(9)	9.054(2)
b (Å)	9.798(1)	10.105(2)
c (Å)	17.553(2)	13.808(3)
α (°)	76.080(2)	103.954(4)
β (°)	80.753(2)	105.293(4)
γ (°)	67.590(2)	98.750(4)
V (Å^3)	1358.0(2)	1150.8(5)
Z	2 (dimers)	2
D_{calc} (g cm^{-3})	1.332	1.364
Radiation type	Mo–K$_\alpha$	Mo–K$_\alpha$
Absorption coefficient (cm^{-1})	13.85	16.19
$F(000)$	568	488
Limits of data collection (°)	$1.20 \leq \theta \leq 27.50$	$1.60 \leq \theta \leq 25.11$
Total reflections, (unique)	15880, (6128)	6787, (4068)
Number with $I > 2\sigma(I)$	5444	2611
$R(F^2)$, $wR(F^2)$	0.0312, 0.0845	0.0797, 0.1919
Goodness-of-fit	1.062	1.001
Max/min peak (final difference map) (e Å^{-3})	1.163/−0.837	1.107/−2.494

Treating the data with UNTWIN [7] improved the refinement from 0.09 to 0.08. Additionally, the bridging THF was disordered in a 0.57:0.43 ratio; 46 restraints were added to aid in its refinement. Absorption corrections were performed with the program SADABS (SADABS: Area-Detector Absorption Correction; Siemens Industrial Automation Inc., Madison, WI, 1996).

3. Results and discussion

3.1. Synthesis of [(Cp^{3T})CaI(THF)$_n$]

The mono[1,2,4-tri(*t*-butyl)cyclopentadienyl]calcium iodide compound [(Cp^{3T})CaI(THF)$_n$] can be isolated from the 1:1 reaction of K[Cp^{3T}] and CaI$_2$ in THF Eq. (5).

$$K[Cp^{3T}] + CaI_2 \rightarrow [(Cp^{3T})CaI(THF)_n] + KI\downarrow \qquad (5)$$
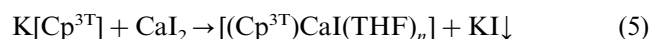
The product was characterized by spectroscopic methods and X-ray crystallography, which were consistent with the proposed formulation. Both monomeric and dimeric mono(ring) complexes display considerable kinetic stability in solution; there is no evidence for any other Cp^T-containing species in the ^{1}H-NMR spectra, as would be expected if ligand rearrangement were occurring in solution. Like [Cp^{4i}]$^-$ [2] and [Cp^{3Si}]$^-$ [3], the [Cp^{3T}]$^-$ ring is able to suppress ligand redistribution reactions in mono(cyclopentadienyl) calcium complexes, presumably by a similar 'encapsulation' effect.

The complex can be isolated from THF solution as a monomer with two THFs, or from THF–toluene as a dimer with only one THF per calcium atom; the calcium in a monomeric '(Cp^{3T})CaI(THF)' structure is evidently coordinately unsaturated enough that dimerization of the compound occurs upon the loss of one THF. Dimerization upon the loss of one THF has also been observed in the related [(Cp^{4i})CaI(THF)$_n$] ($n = 1$ or 2) complexes; the monomeric species displays a different ^{1}H-NMR spectra in C$_6$D$_6$ from that of the structurally characterized dimeric complex, [{(Cp^{4i})(μ-I)(THF)}$_2$] [2]. X-ray quality crystals of the presumably monomeric [(Cp^{4i})CaI(THF)$_2$] could not be obtained; consequently, [(Cp^{3T})CaI(THF)$_2$] is the first structurally characterized example of a monomeric mono(ring)-calcium halide complex.

3.2. Solid state structure of [(Cp^{3T})CaI(THF)$_2$] (1)

Compound **1** crystallizes from THF as a monomer with a distorted piano stool geometry, in which the calcium atom is coordinated by a single tri(*tert*-butyl)cyclopentadienyl ring, two THF molecules, and one terminal iodide. A summary of bond distances and angles for **1** is given in Table 2; an ORTEP view of the complex is displayed in Fig. 1.

Table 2
Selected bond distances (Å) and angles (°) for **1**

Bond distances	
I(1)–Ca(1)	3.0157(5)
Ca(1)–O(1)	2.334(2)
Ca(1)–O(2)	2.367(2)
Ca(1)–C(1)	2.688(2)
Ca(1)–C(2)	2.668(2)
Ca(1)–C(3)	2.658(2)
Ca(1)–C(4)	2.692(2)
Ca(1)–C(5)	2.678(2)
Ca–ring centroid	2.39
Bond angles	
O(1)–Ca(1)–I(1)	94.72(4)
O(2)–Ca(1)–I(1)	88.78(4)
ring centroid–Ca–O(1)	122.2
ring centroid–Ca–O(2)	117.0
O(1)–Ca(1)–O(2)	92.61(6)
I–Ca–ring centroid	131.3
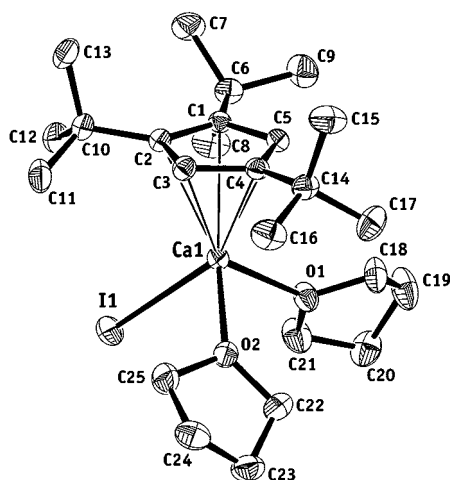
Fig. 1. ORTEP diagram of the non-hydrogen atoms of $[C_5(t\text{-}Bu)_3H_2]CaI(THF)_2$ (**1**), giving the numbering scheme used in the text. Thermal ellipsoids are shown at the 50% level.

The average Ca–C(ring) and Ca–centroid distances of 2.677(4) and 2.39 Å in **1** are slightly longer than those in **2** (2.63(2) and 2.34 Å, respectively); this is also true of the Ca–O2 bond length in **1** (2.367(2) Å), although the Ca–O1 distances in both **1** and **2** are identical (2.334(2) and 2.33(2) Å, respectively). The Ca–ring centroid separation in **1** is longer than the analogous distance in all other six-coordinate mono(ring)calcium iodide complexes (Table 3); the lengthened metal–ligand bond distances may be attributed to increased steric crowding in the complex.

In contrast, the Ca–I distance of 3.0157(5) Å in **1** is short when compared to other six-coordinate calcium complexes with terminal iodides (e.g. [{4-Cl-$C_6H_4CH_2(C_6H_5)_2O$}CaI(THF)$_4$], 3.108(3) Å [8]; [{2,6-i-Pr-C_6H_2O}CaI(THF)$_4$], 3.1478(8) Å [9]; and [CaI$_2$(THF)$_4$], 3.106(2) Å [8]), and represents the short-

est reported calcium–iodide bond distance. The average Ca–O bond lengths in **1** and [CaI$_2$(THF)$_4$] (2.351(3) and 2.34(1) Å, respectively[8]) are indistinguishable, but they are substantially shorter than the analogous distances in [{4-Cl-$C_6H_4CH_2(C_6H_5)_2O$}CaI(THF)$_4$] and [{2,6-i-Pr-C_6H_2O}CaI(THF)$_4$] (2.43(2) and 2.391 Å, respectively). The longer Ca–I and Ca–O(THF) bonds in the latter two compounds possibly reflect the strong donating ability of the alkoxide and aryloxide ligands; the other ligands may respond by lengthening their separation from the metal.

3.3. Solid state structure of $[(Cp^{3T})CaI(THF)]_2$ (**2**)

A crystal of **2** grown from THF–toluene was used to determine its structure with X-ray crystallography. The compound exists in the solid state as an iodide-bridged dimer with a pentahapto $[Cp^{3T}]^-$ ligand and a terminal THF molecule on each calcium atom. A crystallographically imposed inversion center relates the two halves of the molecule. A summary of bond distances and angles for **2** is given in Table 3. An ORTEP diagram with the numbering scheme used in the table is provided in Fig. 2.

The average Ca–C(ring) and the Ca–centroid bond lengths of 2.63(2) and 2.34 Å in **2** are comparable to those in [{(Cp^{4i})Ca(μ-I)(THF)}$_2$] (2.67(2) and 2.376 Å) [2], [{(Cp^{3Si})Ca(μ-I)(THF)}$_2$] (2.65(4) and 2.36(2)) [3], and [$C_5Me_4(SiMe_2t\text{-}Bu)Ca(\mu\text{-}I)(THF)]_2$ (2.61(3) Å, 2.313(13) Å).[10] The [Ca–I]$_2$ core in [(Cp^{3T})CaI(THF)]$_2$ is nearly square, with Ca–I and Ca–I' distances of 3.101(2) and 3.087(2) Å, and Ca–I–Ca' and I–Ca–I' angles of 93.36(5) and 86.64(5)°, respectively. The symmetry exhibited by the bridging Ca–I bonds in **2** is also observed in [Cp'Ca(μ-I)(THF)]$_2$ (Cp' = Cp^{4i}, Cp^{3Si}, and

Table 3
Selected bond distances (Å) and angles (°) for **2**

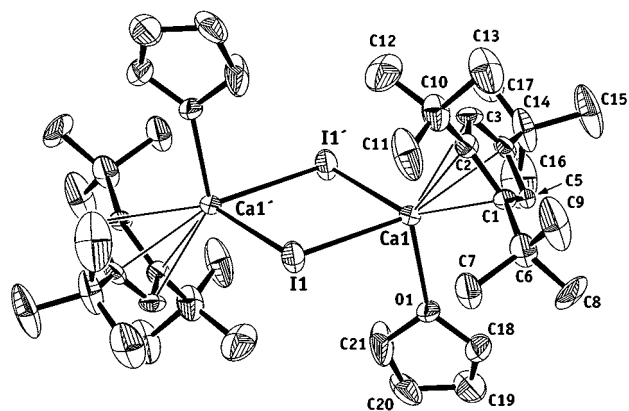| *Bond distances*	
I(1)–Ca(1)	3.101(2)
I(1)–Ca(1)′	3.087(2)
Ca(1)–O(1)	2.33(2)
Ca(1)–C(1)	2.645(9)
Ca(1)–C(2)	2.622(9)
Ca(1)–C(3)	2.609(8)
Ca(1)–C(4)	2.631(8)
Ca(1)–C(5)	2.627(8)
Ca(1)–Ca(1)′	4.50
I(1)–I′(1)	4.25
Ca–ring centroid	2.34
Bond angles	
Ca(1)′–I(1)–Ca(1)	93.36(5)
I(1)′–Ca(1)–I(1)	86.64(5)
O(1)–Ca(1)–I(1)	101.0(6)
O(1)–Ca(1)–I(1)′	92.6(6)
I–Ca–ring centroid	121.3
I′–Ca–ring centroid	131.4

Fig. 2. ORTEP diagram of the non-hydrogen atoms of {[C$_5$(*t*-Bu)$_3$H$_2$]Ca(μ-I)(THF)}$_2$ (**2**), giving the numbering scheme used in the text. Thermal ellipsoids are shown at the 40% level.

C$_5$Me$_4$(SiMe$_2$*t*-Bu)) (Table 4), but contrasts with the Ca–I′ bonds in the two conformers of [{Cp*Ca(μ-I)(THF)$_2$}$_2$], which are markedly asymmetric (differences in bond lengths of 0.0624 and 0.146 Å, respectively). This has been attributed to greater intramolecular crowding and lattice packing in [Cp*Ca(μ-I)(THF)$_2$]$_2$ [11].

3.4. Comparative features of mono(cyclopentadienyl) iodide complexes of calcium, strontium, and barium

Cp′AeI(THF)$_n$ species now represent one of the largest structurally characterized classes of organometallic compounds of the heavy Group 2 elements (Table 4). With the exception of monomeric **1** and the oligomeric [{(Cp^{3Si})BaI(THF)$_2$}$_\infty$],[3] all of them are bridged dimers, with either one or two coordinated THF molecules per metal. As a group, they illustrate the strong interconnection that exists between

metal radius, coordination number and ring size. Thus calcium (six-coordinate radius = 1.00 Å[12]) can fit two THF molecules in a dimeric framework only with the smallest of the cyclopentadienyl rings, Cp*. Addition of a second THF to the metal when the bulkier rings are present is evidently only possible if the dimeric structure breaks up into a monomer, as in **1**. With the larger metals, these restrictions are relaxed, and if calcium is replaced with strontium (six-coordinate radius = 1.18 Å), for example, two THF ligands can be accommodated in a dimer, as in [(Cp^{3Si})Sr(μ-I)(THF)$_2$]$_2$.

A large amount of bond length variation has been observed with the highly polarizable iodide ligand [3,8], and there is not always a characteristic difference between terminal and bridging bond lengths. Nevertheless, it is interesting that the two non-dimeric complexes, **1** and [{(Cp^{3Si})BaI(THF)$_2$}$_\infty$], have effective iodide radii that are shorter (by at least 0.04 Å) than any of the dimeric compounds. The effective iodide radius, calculated by subtracting the coordination number-adjusted radius of the metal [12] from the metal–iodide distance, gives a measure of the relative length of the M–I bond. Compared to monomers or oligomeric chains, dimeric organoalkaline-earth compounds may represent a crowded structural type and require an effective iodide radius of greater than ~2.05 Å.

4. Conclusions

The sterically demanding 1,2,4-tri(*tert*-butyl)-cyclopentadienyl ring has now been identified as another 'encapsulating' ligand that can be used to inhibit unwanted redistribution reactions in organocalcium chemistry. The monomeric compound derived from it, **1**, is an attractive base from which to explore other transformations of the alkaline-earth halide bond.

Table 4
Selected structural data for Cp′AeI(THF)$_n$ complexes (distances in (Å), angles in (°))

Compound	CN	Ae–I, I′	Ae–ring centroid	Ae–I–Ae′	Effective I⁻ radius	Ae–O(THF)	Reference
[C$_5$(*t*-Bu)$_3$H$_2$]CaI(THF)$_2$ (**1**)	6	3.0157(5)	2.39		2.02	2.351(3) [a]	this work
{[C$_5$(*t*-Bu)$_3$H$_2$]Ca(μ-I)(THF)}$_2$ (**2**)	6	3.101 (2), 3.087(2)	2.34	93.36(5)	2.10, 2.09	2.33(2)	this work
[Cp*Ca(μ-I)(THF)$_2$]$_2$	7	3.1356(15), 3.1980(16)	2.380	94.59(4)	2.08, 2.14	2.422(6) [a]	[11]
	7	3.1283(15), 3.2743(16)	2.390	97.73(4)	2.07, 2.21	2.387(7) [a]	
[(Cp^{4i})Ca(μ-I)(THF)]$_2$	6	3.101(4), 3.110(4)	2.376	93.9(1)	2.10, 2.11	2.34(1)	[2]
[(Cp^{3Si})Ca(μ-I)(THF)]$_2$	6	3.066(4), 3.102(4)	2.36(2)	92.27(9)	2.07, 2.10	2.31(2)	[3]
[C$_5$Me$_4$(SiMe$_2$*t*-Bu)Ca(μ-I)-(THF)]$_2$	6	3.068(3), 3.056(3)	2.313(13)	86.7(8)	2.07, 2.06	2.322(10)	[10]
[(Cp^{3Si})Sr(μ-I)(THF)$_2$]$_2$	7	3.278 (3), 3.355(3)	2.604(7)	103.17(7)	2.10, 2.18	2.548(7) [a]	[3]
[{(Cp^{3Si})BaI(THF)$_2$}$_\infty$]	7	3.390(1), 3.475(2)	2.76(1)	180, 177.78(9)	2.01, 2.10	2.74(1) [a]	[3]

[a] The average value is listed.

5. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 148 394 for compound **1** and 148 395 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223-336033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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