

Encapsulated Alkaline-Earth Metallocenes. 5.¹ Kinetic Stabilization of Mono[tetraisopropylcyclopentadienyl]calcium Complexes

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In the solid state, 1,2,3,4-tetraisopropylcyclopentadiene (HCp⁴ⁱ) forms stacked parallel rings in which the isopropyl groups display the same semigeared orientation as is found for the [Cp⁴ⁱ]⁻ anion in its metal complexes. The [tetraisopropylcyclopentadienyl]calcium halide (Cp⁴ⁱ)CaI(THF)₂ (1) is isolated in high yield (>90%) from the 1:1 reaction of KCp⁴ⁱ and CaI₂ in THF or by the conproportionation of (Cp⁴ⁱ)₂Ca and CaI₂ in THF. One THF ligand in (Cp⁴ⁱ)CaI(THF)₂ is easily removed by recrystallization from toluene to generate the monosolvated derivative (Cp⁴ⁱ)CaI(THF) (2); allowing KCp⁴ⁱ and CaI₂ (1:1) to react in a toluene/THF solvent mixture produces (Cp⁴ⁱ)CaI(THF) directly. (Cp⁴ⁱ)CaI(THF) crystallizes from toluene as an iodide-bridged dimer, [(Cp⁴ⁱ)Ca(μ-I)(THF)]₂·C₇H₈, with a pentahapto [Cp⁴ⁱ]⁻ ligand and a terminal THF on each calcium atom. The Ca-I and Ca-I' distances are nearly equal at 3.101(4) Å and 3.110(4) Å. No disproportionation of (Cp⁴ⁱ)CaI(THF)_(1,2) into (Cp⁴ⁱ)₂Ca and CaI₂(THF)_n is observed in either THF or aromatic solvents at room temperature. This stability arises from the inability of THF to dissociate completely from the oxophilic calcium center in the mono-(cyclopentadienyl) complexes, which consequently blocks the formation of the necessarily base-free (Cp⁴ⁱ)₂Ca. Refluxing a toluene solution of (Cp⁴ⁱ)CaI(THF)_(1,2) for 4 h, however, does lead to its near quantitative (93%) conversion into (Cp⁴ⁱ)₂Ca and CaI₂(THF)_n. Disproportionation is also observed after adding 1,4-dioxane to a THF solution of (Cp⁴ⁱ)CaI(THF)_(1,2). Heating (Cp⁴ⁱ)CaI(THF)_(1,2) at 110 °C and 10⁻⁶ Torr for 4 h removes all coordinated THF without causing disproportionation, leaving unsolvated [(Cp⁴ⁱ)CaI]_n (3). In aromatic solution, [(Cp⁴ⁱ)CaI]_n slowly disproportionates into (Cp⁴ⁱ)₂Ca and CaI₂; this underscores the importance of coordinated THF to the stability of (Cp⁴ⁱ)CaI(THF)_(1,2). Heating solid [(Cp⁴ⁱ)CaI]_n at 215–220 °C and 10⁻⁶ Torr produces (Cp⁴ⁱ)₂Ca as a white sublimate in good yield (ca. 65%). Attempts to synthesize complexes analogous to (Cp⁴ⁱ)CaI(THF)_(1,2) using pyridine, diethyl ether, or 1,2-dimethoxyethane were not as successful; only (Cp⁴ⁱ)CaI(DME) (4) could be obtained in a mixture with CaI₂(DME)_n. (Cp⁴ⁱ)CaI(THF)_(1,2) can be derivatized by metathetical reactions with K[N(SiMe₃)₂] and K[BHT] (HBHT = HOC₆H₂-*t*-Bu₂-2,6-Me-4) to yield (Cp⁴ⁱ)Ca[N(SiMe₃)₂](THF) (5) and (Cp⁴ⁱ)Ca[BHT](THF) (6), respectively, in high yield. (Cp⁴ⁱ)Ca[BHT](THF) also can be cleanly prepared by the reaction of (Cp⁴ⁱ)Ca[N(SiMe₃)₂](THF) with HBHT in toluene. Unlike the reaction that occurs between (Cp⁴ⁱ)₂Ca and CaI₂, (Cp⁴ⁱ)₂Ca and Ca[N(SiMe₃)₂]₂ do not conproportionate in THF to form a mono(ring) complex. (Cp⁴ⁱ)Ca[N(SiMe₃)₂](THF) sublimes readily at 120 °C and 10⁻⁶ Torr in ca. 50–60% yield to give a waxy material containing (Cp⁴ⁱ)Ca[N(SiMe₃)₂](THF), (Cp⁴ⁱ)₂Ca, and Ca[N(SiMe₃)₂]₂(THF)_n. In the solid state, (Cp⁴ⁱ)Ca[N(SiMe₃)₂](THF) is monomeric with a pseudotrigonal planar arrangement of the ligands around the calcium. Two crystallographically independent enantiomers are present in the asymmetric unit, with Ca-N bond distances of 2.29(1) and 2.30(1) Å. Both molecules of (Cp⁴ⁱ)Ca[N(SiMe₃)₂](THF) possess structural features that suggest an agostic interaction exists between the calcium and one of the trimethylsilyl groups of the amido ligand, with Ca...C(Me) contacts at 2.99(2) and 2.95(2) Å. These results illustrate the high level of kinetic control possible over the reactions of organocalcium species containing encapsulating ligands.

Introduction

In the absence of metal valence electrons, the bonding between alkaline-earth metals and their ligands must rely primarily on electrostatic or Lewis acid/base interactions.² Exertion of kinetic control over complexes of these elements is consequently difficult, and the tendency for ligand rearrangement and decomposition is high.² The ability to establish such control, however, is crucial to the rational design of synthetic reagents that incorporate these metals.

The kinetic lability associated with Group 2 organometallic complexes is exemplified in the dynamic solution behavior of Grignard reagents. Their conventional formulation as "RMgX" obscures the fact that in solution they exist as mixtures of heteroleptic and homoleptic species, neutral, charged, and radical, that are related by complex equilibria.^{3,4} The simplest representation of the dynamic nature of Grignard reagents in solution is the Schlenk equilibrium (eq 1), which corresponds to the disproportionation of a heteroleptic "RMgX" species into its homoleptic counterparts.^{5,6}

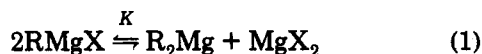
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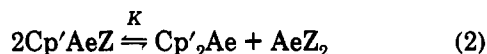
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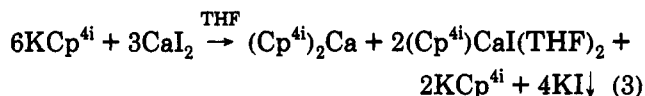


In synthetic organic chemistry, the operation of Schlenk equilibria in Grignard reagents is rarely of any consequence. In our studies of the related mono(cyclopentadienyl) complexes of the heavy alkaline-earth metals ($\text{Cp}'\text{AeZ}$; Ae = Ca, Sr, Ba; Z = R, NR_2 , OR), however, disproportionation equilibria have presented a challenge to both synthesis and subsequent studies of reactivity (eq 2).^{7,8} The position of the equilibrium in these complexes



is highly solvent dependent, and even a small value for the equilibrium constant does not insure that a compound can be easily manipulated.⁹

We have recently used sterically bulky ligands such as $[\text{Cp}^{\text{di}}]^-$, $[\text{Cp}^{\text{tri}}]^-$ ($\text{Cp}^{\text{ni}} = (i\text{-Pr})_n\text{C}_5\text{H}_{5-n}$), and $[\text{Ph}_4\text{C}_5\text{H}]^-$ to form "encapsulated" Group 2 metallocenes with enhanced volatility and oxidative stability.^{1,10-12} In an initial attempt to synthesize the calcium metallocene $(\text{Cp}^{\text{di}})_2\text{Ca}$, we allowed KCp^{di} and CaI_2 to react (2:1) in THF. Unexpectedly, we isolated from this reaction a 1:2 mixture of the desired metallocene and another complex, tentatively identified as the mono(ring) calcium iodide complex, $(\text{Cp}^{\text{di}})\text{CaI}(\text{THF})_2$. (A similar mixture was observed in the reaction of KCp^{tri} and CaI_2 .¹¹) The equation for this reaction appears to be the following (eq 3):



The persistence of the mono(ring) species in solution, even in the presence of unreacted KCp^{di} , suggested that $(\text{Cp}^{\text{di}})\text{CaI}(\text{THF})_2$ must enjoy a reasonable amount of kinetic stability. We therefore attempted to synthesize the $(\text{Cp}^{\text{di}})\text{CaI}(\text{THF})_2$ complex and its derivatives directly, with the goal of generating a class of mono(cyclopentadienyl) complexes that would help elucidate the factors that lead to kinetic stability in organoalkaline-earth compounds.

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 (¹³C) 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 ¹³C resonances of C_6D_6 (δ 7.15 and 128.0) or THF-*d*₈ (δ 3.58 and 67.4). Assignments in the ¹³C NMR spectra were made with the help of DEPT pulse experiments. Infrared data were obtained on a Perkin-Elmer 1600 Series FT-

IR spectrometer. KBr pellets for IR spectroscopy were prepared as previously described.¹⁰ Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Materials. Anhydrous calcium iodide (Strem Chemicals or Cerac, 95%) was heated under vacuum (150 °C, 10⁻⁶ Torr) to remove residual amounts of free iodine. Potassium hydride was obtained from Aldrich as a dispersion in oil and was washed with hexane and dried before use. $\text{K}[\text{N}(\text{SiMe}_3)_2]$ was purchased from Aldrich and used as received. HCp^{di} (1,2,3,4-tetraisopropylcyclopentadiene),¹⁰ $(\text{Cp}^{\text{di}})_2\text{Ca}$,¹⁰ $\text{Cp}^*\text{CaI}(\text{THF})_2$,⁷ $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$,²¹ and KBHT^{13} (HBHT = 2,6-di-*tert*-butyl-4-methylphenol) were prepared using literature procedures. Anhydrous pyridine, 1,2-dimethoxyethane (DME), 1,4-dioxane, and diethyl ether (Et_2O) were purchased from Aldrich and were dried over 4A molecular sieves prior to use. 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 KCp^{di} from HCp^{di} and $\text{K}[\text{N}(\text{SiMe}_3)_2]$. In a typical preparation, HCp^{di} (1.337 g, 5.70 mmol) and $\text{K}[\text{N}(\text{SiMe}_3)_2]$ (1.141 g, 5.72 mmol) were added to 25 mL of toluene in a 125-mL flask. The reaction was stirred overnight, during which time a white precipitate formed. The precipitate was collected by filtration of the reaction mixture through a glass frit and dried under vacuum to give 1.49 g of KCp^{di} (96% yield) as a snow white powder, identified from its ¹H NMR spectrum (THF-*d*₆).¹⁰

Reaction of KCp^{di} and CaI_2 (2:1) in THF. KCp^{di} (4.00 g, 14.68 mmol) and CaI_2 (2.16 g, 7.35 mmol) were suspended in 75 mL of THF in an Erlenmeyer flask. The mixture was stirred for 72 h and then filtered through a glass frit to remove precipitated KI. The pale yellow THF filtrate was evaporated to dryness to give 4.51 g of an off-white powder. An ¹H NMR (C_6D_6) spectrum of the product indicated the presence of $(\text{Cp}^{\text{di}})_2\text{Ca}$ ¹⁰ and $(\text{Cp}^{\text{di}})\text{CaI}(\text{THF})_2$ (see below) in a ratio of 1:2. The yield for the reaction (based on the mixture consisting of a 1:2:2 ratio of $(\text{Cp}^{\text{di}})_2\text{Ca}$, $(\text{Cp}^{\text{di}})\text{CaI}(\text{THF})_2$ and unreacted KCp^{di}) was 86%.

Synthesis of $(\text{Cp}^{\text{di}})\text{CaI}(\text{THF})_2$ (1). Method a. KCp^{di} (0.84 g, 3.08 mmol) and CaI_2 (0.90 g, 3.06 mmol) were added to 20 mL of THF in an Erlenmeyer flask. The resulting gray slurry was stirred overnight. The reaction mixture was filtered through a glass frit to remove precipitated KI. The solvent was then removed from the filtrate under vacuum, leaving 1.53 g of a cream-colored powder, identified spectroscopically as 1 (92% yield). Anal. Calcd for $\text{C}_{25}\text{H}_{45}\text{CaI}_2\text{O}_2$: C, 55.14; H, 8.33; I, 23.30. Found: C, 55.16; H, 8.35; I, 23.38. ¹H NMR (C_6D_6): δ 5.93 (s, 1 H, ring-CH); 3.61 (t, $J = 6.5$ Hz, 8 H, $\alpha\text{-C}_4\text{H}_5\text{O}$); 3.39 (septet, $J = 7.2$ Hz, 2 H, CHMe_2); 3.28 (septet, $J = 6.8$ Hz, 2 H, CHMe_2); 1.60 (d, $J = 7.2$ Hz, 6 H, CH_3); 1.54 (d, $J = 7.2$ Hz, 6 H, CH_3); 1.45 (d, $J = 6.8$ Hz, 6 H, CH_3); 1.35 (t, $J = 6.5$ Hz, 8 H, $\beta\text{-C}_4\text{H}_5\text{O}$); 1.32 (d, $J = 6.7$ Hz, 6 H, CH_3). ¹H NMR (THF-*d*₈): δ 5.67 (s, 1 H, ring-CH); 3.61 (m, 8 H, $\alpha\text{-C}_4\text{H}_5\text{O}$); 3.21 (septet, $J = 7.2$ Hz, 2 H, CHMe_2); 3.12 (septet, $J = 6.8$ Hz, 2 H, CHMe_2); 1.77 (m, 8 H, $\beta\text{-C}_4\text{H}_5\text{O}$); 1.39 (d, $J = 7.2$ Hz, 6 H, CH_3); 1.34 (d, $J = 7.0$ Hz, 12 H, CH_3); 1.07 (d, $J = 6.7$ Hz, 6 H, CH_3). Colorless crystals of 1 can be grown by slow evaporation of a saturated THF solution; the crystals quickly turn opaque and disintegrate upon removal from a THF-saturated atmosphere, frustrating efforts to obtain an X-ray crystal structure.

Method b. An Erlenmeyer flask was charged with CaI_2 (0.80 g, 2.71 mmol) and freshly sublimed $(\text{Cp}^{\text{di}})_2\text{Ca}$ (1.38 g, 2.71 mmol). THF (30 mL) was added to the flask, and the resulting clear solution was stirred overnight. Removal of the THF under vacuum gave 2.56 g of 1 (quantitative) as a white microcrystalline solid.

Synthesis of $(\text{Cp}^{\text{di}})\text{CaI}(\text{THF})_2$ (2). Method a. $(\text{Cp}^{\text{di}})\text{CaI}(\text{THF})_2$ (1.58 g, 2.90 mmol) was dissolved in 40 mL of toluene, and the resulting clear solution was stirred for 2 h. Subsequent removal of the toluene under vacuum gave 1.35 g (quantitative) of 2 as a cream-colored powder (mp 175–180 °C). Anal. Calcd for $\text{C}_{21}\text{H}_{37}\text{CaI}_2\text{O}_2$: C, 53.38; H, 7.89; Ca, 8.48. Found: C, 53.45; H,

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(9) $\text{Cp}^*\text{CaCH}(\text{SiMe}_3)_2(\text{THF})_3$ only slightly dissociates in C_6D_6 solution ($K = 4.2 \times 10^{-4}$), for example, but washing the solid with hexane induces significant disproportionation (see ref 8).

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7.80; Ca, 8.57. ^1H NMR (C_6D_6): δ 5.98 (s, 1 H, ring-CH); 3.72 (t, $J = 6.5$ Hz, 4 H, $\alpha\text{-C}_4\text{H}_8\text{O}$); 3.39 (septet, $J = 7.2$ Hz, 2 H, CHMe_2); 3.29 (septet, $J = 6.8$ Hz, 2 H, CHMe_2); 1.59 (d, $J = 7.2$ Hz, 6 H, CH_3); 1.53 (d, $J = 7.1$ Hz, 6 H, CH_3); 1.47 (d, $J = 6.8$ Hz, 6 H, CH_3); 1.32 (d, $J = 6.6$ Hz, 6 H, CH_3); 1.29 (t, $J = 6.5$ Hz, 4 H, $\beta\text{-C}_4\text{H}_8\text{O}$). ^1H NMR (THF- d_6): δ 5.67 (s, 1 H, ring-CH); 3.61 (m, 4 H, $\alpha\text{-C}_4\text{H}_8\text{O}$); 3.21 (septet, $J = 7.2$ Hz, 2 H, CHMe_2); 3.12 (septet, $J = 6.8$ Hz, 2 H, CHMe_2); 1.77 (m, 4 H, $\beta\text{-C}_4\text{H}_8\text{O}$); 1.40 (d, $J = 7.2$ Hz, 6 H, CH_3); 1.34 (d, $J = 7.0$ Hz, 12 H, CH_3); 1.07 (d, $J = 6.6$ Hz, 6 H, CH_3). ^{13}C NMR (C_6D_6) δ 128.9 (ring-CCHMe₂); 125.5 (ring-CCHMe₂); 100.1 (ring-CH); 69.0 ($\alpha\text{-C}_4\text{H}_8\text{O}$); 27.5 (CHMe_2); 27.2 (CHMe_2); 26.9 (CH_3); 25.6 (CH_3); 25.4 ($\beta\text{-C}_4\text{H}_8\text{O}$ and CH_3); 25.2 (CH_3). Principal IR bands (KBr, cm^{-1}): 2923 (s, vbr), 1460 (s), 1377 (s), 1363 (s), 1330 (w), 1310 (m), 1278 (w), 1248 (w), 1178 (m), 1146 (m), 1107 (m), 1022 (s), 988 (m), 956 (w), 920 (m), 873 (s), 762 (m), 690 (m), 508 (s). X-ray quality crystals of $2\text{-C}_7\text{H}_8$ were grown by cooling a saturated toluene solution of 1 to -40°C .

Method b. An Erlenmeyer flask was charged with KCp^{d} (0.73 g, 2.68 mmol) and CaI_2 (0.77 g, 2.62 mmol); to this were added 30 mL of toluene and 15 mL of THF, and the resulting gray slurry was stirred overnight. The precipitated KI was removed by filtration through a glass frit; the solvent mixture was removed under reduced pressure to leave 1.070 g of a cream-colored powder, identified as 2 by ^1H NMR (C_6D_6) (86% yield).

Preparation of $[(\text{Cp}^{\text{d}})\text{CaI}]_n$ (3). A sample of 1 (0.50 g, 0.916 mmol) was placed in a sublimation apparatus, which was then evacuated to 1×10^{-6} Torr. The solid was heated at 110°C for 3 h, leaving 0.30 g of 3 as a grayish-white solid (82% yield). Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{CaI}$: C, 51.00; H, 7.30; Ca, 10.01; I, 31.69. Found: C, 47.37; H, 6.85; Ca, 9.97; I, 31.70. There have been several examples of organoalkaline-earth complexes that have reproducibly low C, H analyses.^{8,14} ^1H NMR (C_6D_6): δ 6.11 (s, 1 H, ring-CH); 3.30 (septet, $J = 7.2$ Hz, 2 H, CHMe_2); 3.19 (septet, $J = 6.8$ Hz, 2 H, CHMe_2); 1.55 (d, $J = 6.8$ Hz, 6 H, CH_3); 1.51 (d, $J = 7.2$ Hz, 6 H, CH_3); 1.47 (d, $J = 7.2$ Hz, 6 H, CH_3); 1.23 (d, $J = 6.6$ Hz, 6 H, CH_3). ^1H NMR (THF- d_6): δ 5.67 (s, 1 H, ring-CH); 3.21 (septet, $J = 7.2$ Hz, 2 H, CHMe_2); 3.12 (septet, $J = 6.8$ Hz, 2 H, CHMe_2); 1.40 (d, $J = 7.2$ Hz, 6 H, CH_3); 1.34 (d, $J = 7.0$ Hz, 12 H, CH_3); 1.08 (d, $J = 6.6$ Hz, 6 H, CH_3). Principal IR bands (KBr, cm^{-1}): 2922 (s, vbr), 1459 (s), 1377 (s), 1362 (s), 1310 (m), 1277 (w), 1178 (s), 1105 (s), 1061 (w), 1038 (w), 986 (m), 777 (s), 690 (m), 512 (s), 500 (s). $[(\text{Cp}^{\text{d}})\text{CaI}]_n$ partially melts at 215°C ; the remaining solid does not melt below 300°C . Solid samples of 3 reproducibly turn blue-green on long standing (ca. 2 weeks). A toluene solution of the blue-green solid is colorless, however, and there is no change in the NMR spectrum of the compound.

Preparation of $[\text{Cp}^*\text{CaI}]_n$. A sample of $\text{Cp}^*\text{CaI}(\text{THF})_2$ (0.96 g, 2.2 mmol) was placed in a sublimation apparatus, which was then evacuated to 1×10^{-6} Torr. The solid was heated at 125°C for 3 h, leaving 0.52 g of $[\text{Cp}^*\text{CaI}]_n$ (80% yield) as a nonvolatile white powder. Anal. Calcd for $\text{C}_{10}\text{H}_{15}\text{CaI}$: C, 39.67; H, 4.99; Ca, 13.08; I, 42.37. Found: C, 39.74; H, 5.00; Ca, 13.26; I, 41.99. ^1H NMR (THF- d_6): δ 2.00 (s, CH_3 of $\text{Cp}^*\text{CaI}(\text{C}_4\text{D}_8\text{O})_2$); 1.87 (s, CH_3 of $\text{Cp}^*\text{Ca}(\text{C}_4\text{D}_8\text{O})_2$); the two peaks have approximately the same intensity. Principal IR bands (KBr, cm^{-1}): 2855 (s, vb), 1437 (s), 1389 (m), 1340 (w), 1262 (w), 1095 (m), 1020 (m), 800 (w), 670 (w), 592 (w), 458 (w). Attempts to obtain a ^1H NMR spectrum of $[\text{Cp}^*\text{CaI}]_n$ in C_6D_6 were not successful, owing to its lack of solubility in aromatic solvents. No sublimate was produced on heating $[\text{Cp}^*\text{CaI}]_n$ at temperatures up to 240°C at 10^{-6} Torr.

Synthesis of $(\text{Cp}^{\text{d}})_2\text{Ca}$ from $(\text{Cp}^{\text{d}})\text{CaI}(\text{THF})_n$. **Method a.** 1,4-Dioxane (25 mL) was added to a stirring solution of 1 (2.28 g, 4.19 mmol) in 20 mL of THF. Over the course of 10 h, a white precipitate separated from solution. The reaction mixture was then filtered to remove precipitated $\text{CaI}_2(\text{dioxane})_n$ (identified by the presence of only free 1,4-dioxane in its ^1H NMR spectrum (THF- d_6)). The solvents were removed by rotary evaporation under vacuum to leave 1.00 g of $(\text{Cp}^{\text{d}})_2\text{Ca}$ (94% yield). The

identity of the product was confirmed by ^1H NMR (C_6D_6) spectroscopy. 1 also could be dissolved in 1,4-dioxane alone to give $(\text{Cp}^{\text{d}})_2\text{Ca}$ and $\text{CaI}_2(\text{dioxane})_n$.

Method b. A sublimation vessel was charged with 1 (0.50 g, 0.92 mmol) and evacuated to 1×10^{-6} Torr. A white solid began subliming on the cold finger as the temperature was raised to 210°C . The flask was heated at $215\text{--}20^\circ\text{C}$ for 4 h, which resulted in the production of 0.15 g of a sublimate. Subsequent spectroscopic investigation (^1H NMR, C_6D_6) determined that the sublimed solid was $(\text{Cp}^{\text{d}})_2\text{Ca}$ (65% yield).

Method c. A solution of 1 (0.39 g, 0.72 mmol) in 30 mL of toluene was heated to reflux for 4 h, during which time a gray solid slowly precipitated. The solution was allowed to cool, and the precipitate was removed by centrifugation. Removal of the toluene from the filtrate under vacuum left 0.18 g of a cream-colored powder; this was identified by ^1H NMR as $(\text{Cp}^{\text{d}})_2\text{Ca}$ (93% yield).

Synthesis of $(\text{Cp}^{\text{d}})\text{CaI}(\text{DME})$ (4). **Method a.** KCp^{d} (0.62 g, 2.28 mmol) and CaI_2 (0.69 g, 2.35 mmol) were combined in an Erlenmeyer flask; DME (30 mL) was added and the resulting cloudy, yellowish suspension was stirred for 24 h. The reaction mixture was then filtered through a glass frit. The solvent was removed by rotary evaporation to leave 0.80 g of a cream-colored solid. Subsequent analysis of this solid (^1H NMR, C_6D_6) revealed the presence of two components: $(\text{Cp}^{\text{d}})_2\text{Ca}$ and a new compound identified as 4 on the basis of the similarity of its proton NMR resonances to that of 1. 4 and $(\text{Cp}^{\text{d}})_2\text{Ca}$ were present in an approximate ratio of 4:1. The $(\text{Cp}^{\text{d}})_2\text{Ca}$ could be removed from the mixture by toluene extraction with only a slight loss of 4, since the latter is only sparingly soluble in aromatics. However, it was not possible to remove the corresponding $\text{CaI}_2(\text{DME})_x$ impurity that was also present, so elemental analysis on 4 was not obtained. Spectroscopic data for 4. ^1H NMR (C_6D_6): δ 5.94 (s, 1 H, ring-CH); 3.46 (septet, $J = 7.2$ Hz, 2 H, CHMe_2); 3.31 (septet, $J = 6.8$ Hz, 2 H, CHMe_2); 3.11 (br s, 6 H, CH_3 of DME); 2.95 (s, 4 H, $-\text{CH}_2-$ of DME); 1.65 (d, $J = 7.2$ Hz, 6 H, CH_3); 1.57 (d, $J = 7.1$ Hz, 6 H, CH_3); 1.48 (d, $J = 6.8$ Hz, 6 H, CH_3); 1.37 (d, $J = 6.7$ Hz, 6 H, CH_3). Principal IR bands (KBr, cm^{-1}): 2952 (s, vbr), 1458 (s), 1372 (m), 1359 (m), 1282 (w), 1247 (m), 1174 (m), 1048 (s), 990 (m), 866 (s), 834 (w), 757 (m), 683 (w), 566 (w), 530 (w), 500 (w). When 4 is dissolved in THF, it quantitatively converts to 1 and free DME.

Method b. To a flask charged with $(\text{Cp}^{\text{d}})_2\text{Ca}$ (0.50 g, 0.99 mmol) and CaI_2 (0.29 g, 0.99 mmol) was added 25 mL of DME. The clear solution was stirred for 12 h, and then the DME was removed under vacuum. The ratio of 4 and $(\text{Cp}^{\text{d}})_2\text{Ca}$ in the off-white solid that remained (0.95 g) was ca. 4:1, as determined by ^1H NMR (C_6D_6).

Method c. A 0.22-g sample of 3 was dissolved in 15 mL of DME. The clear solution that formed was stirred for 30 min; then the DME was removed by rotary evaporation under vacuum to leave a cream-colored solid. The ratio of 4 and $(\text{Cp}^{\text{d}})_2\text{Ca}$ in the solid was ca. 4:1, as determined by ^1H NMR (C_6D_6).

Reaction of KCp^{d} and CaI_2 (1:1) in Et_2O . An Erlenmeyer flask was charged with KCp^{d} (0.45 g, 1.65 mmol) and CaI_2 (0.49 g, 1.67 mmol). Diethyl ether (20 mL) was added to the flask, and the resulting yellow slurry was stirred overnight. The precipitated KI was removed from the flask by filtration through a glass frit. Removal of the Et_2O under vacuum left 0.342 g of a yellowish solid that contained an approximately 3:2 mixture of 3 and $(\text{Cp}^{\text{d}})_2\text{Ca}$, as determined by ^1H NMR (C_6D_6).

Synthesis of $(\text{Cp}^{\text{d}})\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})$ (5). An Erlenmeyer flask was charged with 2 (0.94 g, 1.99 mmol) and $\text{K}[\text{N}(\text{SiMe}_3)_2]$ (0.40 g, 2.00 mmol); 25 mL of toluene was added, and the resulting slurry was stirred overnight. After the reaction mixture was filtered to remove precipitated KI, toluene was removed under vacuum to leave a waxy white solid. Recrystallization of this material from small amounts of hexane afforded 0.67 g of 5 (67% yield) as a spectroscopically pure, white crystalline solid. The compound also could be synthesized from 1 (1.04 g, 1.91 mmol) and $\text{K}[\text{N}(\text{SiMe}_3)_2]$ (0.39 g, 1.96 mmol) using the above procedure; 5 was isolated from this reaction in 76% yield (0.73 g) (mp $160\text{--}165^\circ\text{C}$). Anal. Calcd for $\text{C}_{27}\text{H}_{55}\text{CaNOSi}_2$: C, 64.09;

H, 10.96; Ca, 7.92; N, 2.77; Si, 11.10. Found: C, 64.93; H, 11.32; Ca, 8.00; N, 2.49; Si, 11.29. ^1H NMR (C_6D_6): δ 5.78 (s, 1 H, ring-CH); 3.53 (t, $J = 6.5$ Hz, 4 H, $\alpha\text{-C}_4\text{H}_8\text{O}$); 3.32 (septet, $J = 7.2$ Hz, 2 H, CHMe_2); 3.11 (septet, $J = 6.8$ Hz, 2 H, CHMe_2); 1.52 (d, $J = 7.2$ Hz, 12 H, CH_3); 1.29 (d, $J = 7.2$ Hz, 6 H, CH_3); 1.27 (d, $J = 7.0$ Hz, 6 H, CH_3); 1.14 (t, $J = 6.5$ Hz, 4 H, $\beta\text{-C}_4\text{H}_8\text{O}$); 0.20 (s, 18 H, $\text{Si}(\text{CH}_3)_3$). ^1H NMR ($\text{THF-}d_6$): δ 5.73 (s, 1 H, ring-CH); 3.61 (m, 4 H, $\alpha\text{-C}_4\text{H}_8\text{O}$); 3.22 (septet, $J = 7.2$ Hz, 2 H, CHMe_2); 3.09 (septet, $J = 6.7$ Hz, 2 H, CHMe_2); 1.77 (m, 4 H, $\beta\text{-C}_4\text{H}_8\text{O}$); 1.41 (d, $J = 7.2$ Hz, 6 H, CH_3); 1.33 (d, $J = 6.8$ Hz, 6 H, CH_3); 1.325 (d, $J = 7.2$ Hz, 6 H, CH_3); 1.06 (d, $J = 6.6$ Hz, 6 H, CH_3); -0.085 (s, 18 H, $\text{Si}(\text{CH}_3)_3$). ^{13}C NMR (C_6D_6): δ 124.9 (ring-C CHMe_2); 100.2 (ring-CH); 70.6 ($\alpha\text{-C}_4\text{H}_8\text{O}$); 27.3 (CHMe_2 and CH_3); 27.1 (CHMe_2); 25.5 (CH_3); 25.0 (two CH_3 peaks); 24.8 ($\beta\text{-C}_4\text{H}_8\text{O}$); 5.5 ($\text{Si}(\text{CH}_3)_3$). Principal IR bands (KBr, cm^{-1}): 2948 (s, vbr), 1460 (m), 1377 (m), 1362 (m), 1325 (w), 1308 (w), 1237 (s, br), 1186 (m), 1176 (m), 1143 (w), 1105 (m), 1031 (s, br), 988 (m), 918 (w), 879 (s, br), 823 (s, br), 763 (s), 690 (m), 663 (m), 593 (s), 505 (m). Crystals for X-ray structural analysis were grown by slow evaporation of a saturated hexane solution of **5** at room temperature. $(\text{Cp}^{41})\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})$ can be sublimed at 120 °C and 10^{-6} Torr to give a glassy or waxy white sublimate in ca. 50–60% yield. ^1H NMR analysis (C_6D_6 and $\text{THF-}d_6$) revealed that the sublimed material is a mixture of $(\text{Cp}^{41})\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})$, $(\text{Cp}^{41})_2\text{Ca}$, and $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})_n$, in an approximate 3:3:1 ratio.

Reaction of $(\text{Cp}^{41})_2\text{Ca}$ and $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$ in THF. $(\text{Cp}^{41})_2\text{Ca}$ (0.50 g, 1.38 mmol) and $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$ (0.50 g, 1.39 mmol) were dissolved into 30 mL of THF in an Erlenmeyer flask. After the clear solution was stirred for 24 h, the THF was removed under vacuum. ^1H NMR analysis (C_6D_6) of the resulting solid revealed that it contained ca. 10% of **5**; the remaining solid was a mixture of $(\text{Cp}^{41})_2\text{Ca}$ and $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})_2$.¹⁵ There was no observable reaction on stirring equimolar amounts of $(\text{Cp}^{41})_2\text{Ca}$ and $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$ in hexane; the starting materials were isolated unchanged upon removal of the solvent.

Synthesis of $(\text{Cp}^{41})\text{Ca}[\text{BHT}](\text{THF})$ (6**).** **Method a.** HBHT (0.124 g, 0.56 mmol) and **5** (0.294 g, 0.58 mmol) were added to 20 mL of toluene in an Erlenmeyer flask; the resulting clear solution was stirred overnight. The toluene was then removed by rotary evaporation at reduced pressure to give a white powder. Subsequent recrystallization of the crude product from hexane at room temperature gave 0.26 g of **6** (82% yield) as a white, microcrystalline solid. Anal. Calcd for $\text{C}_{36}\text{H}_{60}\text{CaO}_2$: C, 76.54; H, 10.70. Found: C, 76.71; H, 10.36. ^1H NMR (C_6D_6): δ 7.16 (s, 2 H, Ar-CH); 5.94 (s, 1 H, ring-CH); 3.33 (septet, $J = 7.2$ Hz, 2 H, CHMe_2); 3.27 (t, $J = 6.5$ Hz, 4 H, $\alpha\text{-C}_4\text{H}_8\text{O}$); 3.19 (septet, $J = 6.8$ Hz, 2 H, CHMe_2); 2.39 (s, 3 H, Ar- CH_3); 1.52 (s, 18 H, Ar-C(CH_3)₃); 1.49 (d, $J = 7.0$ Hz, 12 H, CH_3); 1.34 (d, $J = 6.9$ Hz, 6 H, CH_3); 1.30 (d, $J = 6.8$ Hz, 6 H, CH_3); 0.97 (m, 4 H, $\beta\text{-C}_4\text{H}_8\text{O}$). ^1H NMR ($\text{THF-}d_6$): δ 6.68 (s, 2 H, Ar-CH); 5.79 (s, 1 H, ring-CH); 3.61 (t, $J = 6.5$ Hz, 4 H, $\alpha\text{-C}_4\text{H}_8\text{O}$); 3.19 (septet, $J = 7.0$ Hz, 2 H, CHMe_2); 3.12 (septet, $J = 6.5$ Hz, 2 H, CHMe_2); 2.07 (s, 3 H, Ar- CH_3); 1.77 (t, $J = 6.5$ Hz, 4 H, $\beta\text{-C}_4\text{H}_8\text{O}$); 1.39 (d, $J = 7.1$ Hz, 6 H, CH_3); 1.35 (s, 18 H, Ar-C(CH_3)₃); 1.30 (d, $J = 6.9$ Hz, 6 H, CH_3); 1.22 (d, $J = 7.0$ Hz, 6 H, CH_3); 1.05 (d, $J = 6.6$ Hz, 6 H, CH_3). ^{13}C NMR (C_6D_6): δ 162.2 (Ar-CO); 136.2 (Ar-C(CH_3)); 125.6 (Ar-CH); 124.6 (ring-C CHMe_2); 120.7 (Ar- CH_3); 100.8 (ring-CH); 70.0 ($\alpha\text{-C}_4\text{H}_8\text{O}$); 35.0 (Ar-C(CH_3)₃); 31.4 (Ar-C(CH_3)₃); 27.3 (CHMe_2); 27.1 (CHMe_2); 26.6 (CH_3); 25.2 (CH_3); 25.1 (CH_3); 24.9 ($\beta\text{-C}_4\text{H}_8\text{O}$ and CH_3); 21.6 (Ar- CH_3). Principal IR bands (KBr, cm^{-1}): 2940 (s, vbr), 1458 (s), 1420 (m), 1383 (m), 1374 (s), 1357 (s), 1324 (w), 1307 (w), 1266 (s, br), 1250 (w), 1178 (w), 1101 (m), 1032 (s, br), 991 (m), 956 (w), 920 (m), 885 (s, br), 807 (m), 800 (w), 761 (m), 690 (w), 508 (s).

Method b. Following the same procedure used for synthesizing **5**, **2** (0.34 g, 0.72 mmol) and $\text{K}[\text{BHT}]$ (0.19 g, 0.73 mmol) were allowed to react to give 0.25 g of **6** as a cream-colored powder (61% yield). The identity of the product as **6** was confirmed by ^1H NMR (C_6D_6).

Details of Decomposition Study of **3.** A solution of **3** was made by suspending 10 mg of **3** in approximately 1 mL of C_6D_6 .

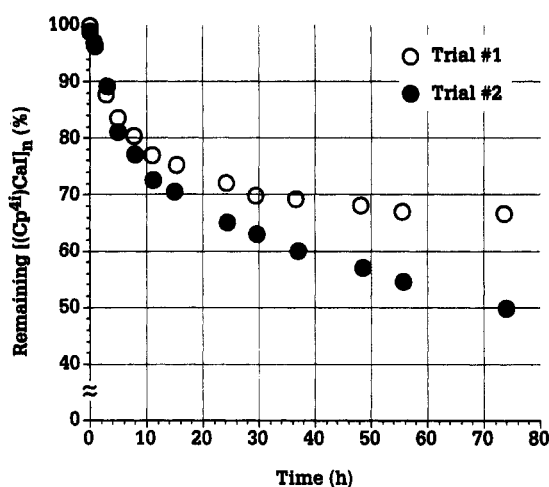


Figure 1. Disproportionation of **3** in toluene into $(\text{Cp}^{41})_2\text{Ca}$ and CaI_2 ; the sample in trial no. 1 is approximately twice as concentrated as in trial no. 2.

The supernatant liquid was then decanted from the undissolved solid. Approximately 0.5 mL of the solution (<25 mM) was used directly as trial no. 1; the remaining 0.5 mL was diluted with an additional 0.5 mL of C_6D_6 for trial no. 2. For both trials, the time of the initial addition of C_6D_6 to solid **3** was taken as $t = 0$.

Proton NMR spectra were used to measure the relative concentration of $[(\text{Cp}^{41})\text{Ca}]_n$ and $(\text{Cp}^{41})_2\text{Ca}$ in the two solutions. Dividing the integrated intensity of the peak at 6.11 ppm by $1/2$ the integrated intensity of the peak at 5.83 ppm gave the number of molecules of $[(\text{Cp}^{41})\text{Ca}]_n$ per molecule of $(\text{Cp}^{41})_2\text{Ca}$ in solution (x). Since 2 equiv of $(\text{Cp}^{41})\text{CaI}$ must decompose to produce 1 equiv of $(\text{Cp}^{41})_2\text{Ca}$, the percentage of the initial amount of $[(\text{Cp}^{41})\text{Ca}]_n$ remaining in solution is given by the expression $x/(x + 2) \times 100$; a plot of this amount vs time is given in Figure 1. Decomposition of $[(\text{Cp}^{41})\text{Ca}]_n$ by routes other than disproportionation into $(\text{Cp}^{41})_2\text{Ca}$ and CaI_2 were not considered. Monitoring of the solutions was stopped after 74 h, at which point the amount of cyclopentadiene (HCp^{41}) impurity in the spectra (approximately 5% of the total amount of Cp^{41} resonances) became too large to ignore in calculating the amount of $[(\text{Cp}^{41})\text{Ca}]_n$ left in solution.

General Procedures for X-ray Crystallography. A suitable crystal of each compound was located and sealed in a quartz capillary tube. All measurements were performed on a Rigaku AFC6S diffractometer at Vanderbilt University with either graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71069$ Å) or $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178$ Å). 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 a systematic search of a limited hemisphere of reciprocal space; sets of diffraction maxima were located whose setting angles were refined by least squares. The space groups were determined from consideration of unit cell parameters, statistical analyses of intensity distribution, and, where appropriate, systematic absences. Subsequent solution and refinement of the structures confirmed the choice in each case.

Data collection was performed using continuous ω -2 θ scans (ω scans for **5**) 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. Except as noted below, all non-hydrogen atoms were refined anisotropically. To improve the refinement of the non-hydrogen atoms, hydrogen atoms were inserted in calculated positions based on packing considerations and $d(\text{C-H}) = 0.95$ Å. The positions were fixed for the final cycles of refinement. Final difference maps were featureless. Fractional coordinates and isotropic thermal parameters for the non-hydrogen atoms are listed in Tables 2–4; selected bond distances and angles are listed in Tables 5–7. Special considerations given to the structure determinations of **2** and **5** are noted below.

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

compound	(C ₃ H ₇) ₄ C ₃ H ₂	2	5
formula	C ₁₇ H ₃₀	C ₂₁ H ₃₇ CaIO ^{1/2} (C ₇ H ₈)	C ₂₇ H ₃₅ CaNOSi ₂
fw	234.43	518.58	505.99
color of crystal	colorless	colorless	colorless
cryst dimens, mm	0.15 × 0.20 × 0.40	0.25 × 0.25 × 0.30	0.25 × 0.45 × 0.47
space group	P $\bar{1}$	P2 ₁ /c	Pbcn
temp (°C)	20	20	20
a, Å	9.330(10)	8.569(5)	18.401(6)
b, Å	11.874(12)	17.564(6)	19.384(9)
c, Å	8.406(4)	18.561(5)	36.725(12)
α, deg	109.57(5)		
β, deg	90.66(7)	102.67(3)	
γ, deg	110.89(7)		
V, Å ³	811(3)	2725(2)	13 099(15)
Z	2	2 (dimers)	16
D(calcd), g/cm ³	0.960	1.264	1.026
radiation type	Mo Kα	Cu Kα	Mo Kα
abs coeff, cm ⁻¹	0.49	110.4	2.7
transmission factors	no correction	0.53–1.60	no correction
scan speed, deg/min	4.0	2.0	4.0
scan width, deg	1.73 + 0.30 tan θ	1.00 + 0.30 tan θ	0.80 + 0.30 tan θ
limits of data collection	6° ≤ 2θ ≤ 45°	6° ≤ 2θ ≤ 120°	6° ≤ 2θ ≤ 45°
total reflections	2274	4514	8273
unique reflections	2143	4198	8273
no. with F > 3.0σ(F)	893	1666	1863
R(F)	0.063	0.063	0.058
R _w (F)	0.075	0.078	0.061
goodness of fit	2.30	2.31	1.56
max Δ/σ in final cycle	0.01	0.14	0.04
max/min peak (final diff map) (e ⁻ /Å ³)	0.22/-0.19	0.76/-0.54	0.28/-0.26

Table 2. Atomic Fractional Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms in (C₃H₇)₄C₃H₂

atom	x/a	y/b	z/c	B _{iso} (Å ²)
C(1)	0.9434(7)	0.7262(6)	0.3069(8)	4.1(3)
C(2)	0.8375(7)	0.6563(6)	0.4047(8)	3.7(3)
C(3)	0.9141(7)	0.6900(6)	0.5607(8)	3.5(3)
C(4)	1.0757(7)	0.7852(6)	0.5745(8)	3.4(2)
C(5)	1.0915(7)	0.8062(6)	0.4255(8)	3.6(3)
C(6)	0.6710(8)	0.5678(7)	0.332(1)	4.9(3)
C(7)	0.6541(9)	0.4732(7)	0.152(1)	6.9(4)
C(8)	0.5720(8)	0.6452(8)	0.331(1)	8.3(4)
C(9)	0.8479(8)	0.6407(7)	0.6961(8)	4.4(3)
C(10)	0.9216(8)	0.5582(7)	0.740(1)	5.8(3)
C(11)	0.8310(9)	0.7437(8)	0.848(1)	6.2(3)
C(12)	1.1986(8)	0.8443(7)	0.7305(9)	5.0(3)
C(13)	1.3373(8)	0.8077(8)	0.699(1)	6.9(4)
C(14)	1.244(1)	0.9885(8)	0.818(1)	7.3(4)
C(15)	1.2287(7)	0.8910(6)	0.3719(8)	4.2(3)
C(16)	1.2874(8)	0.8135(8)	0.225(1)	7.1(4)
C(17)	1.1929(9)	0.9910(8)	0.324(1)	7.2(4)

X-ray Crystallography of [(Cp^{4t})Ca(μ-I)(THF)]₂C₇H₈ (2). Crystals of 2 grown from toluene were so weakly diffracting that data were collected using a copper X-ray tube to take advantage of its higher radiation flux. Even so, data had to be collected at a slow scan speed of 2.0°/min; the resulting long exposure time (203 h) produced a linear 13% decline in the intensities of three representative reflections measured after every 150 reflections. A correction was applied to the data to account for the decay. The use of Cu Kα radiation also complicated the absorption problem; a semiempirical absorption correction was applied using the program DIFABS. The asymmetric unit was found to contain half a dimeric complex; the other half was related through an inversion center. A molecule of toluene was found associated with each dimer; it was disordered across an inversion center, and the methyl group was not identified. The atoms of the C₆ ring were refined isotropically.

X-ray Crystallography of (Cp^{4t})Ca[N(SiMe₃)₂](THF) (5). A total of 7 crystals of 5 were examined on the diffractometer; all were weakly diffracting. Data sets were collected on two of them using ω scans because of the long c axis; both data sets suffered from a lack of strong high-angle reflections. The results reported here are based on the crystal with the better quality (ω_{1/2} = 0.35°; discrepancy between equivalent reflections = 2.3%; 96% of observed reflections were below 2θ = 38°). A slight (3%)

Table 3. Atomic Fractional Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms in [(Cp^{4t})Ca(μ-I)(THF)]₂ (2)

atom	x/a	y/b	z/c	B _{iso} (Å ²)
I(1)	0.2241(2)	0.05057(9)	0.04655(7)	5.57(6)
Ca(1)	0.0270(4)	0.0338(2)	-0.1146(2)	4.0(2)
O(1)	0.162(2)	-0.0765(7)	-0.1380(7)	5.9(7)
C(1)	-0.160(2)	0.144(1)	-0.1773(9)	4.1(9)
C(2)	-0.019(2)	0.180(1)	-0.140(1)	3.8(8)
C(3)	0.102(2)	0.164(1)	-0.176(1)	4.0(9)
C(4)	0.039(2)	0.114(1)	-0.2382(9)	4.0(9)
C(5)	-0.125(2)	0.104(1)	-0.239(1)	3.7(9)
C(6)	-0.012(2)	0.234(1)	-0.074(1)	4.1(9)
C(7)	-0.140(3)	0.218(1)	-0.031(1)	8(1)
C(9)	0.270(2)	0.193(1)	-0.151(1)	5(1)
C(10)	0.398(2)	0.133(1)	-0.126(1)	7(1)
C(11)	0.320(3)	0.249(1)	-0.208(1)	7(1)
C(12)	0.133(2)	0.094(1)	-0.296(1)	5(1)
C(13)	0.133(3)	0.007(1)	-0.314(1)	7(1)
C(14)	0.074(3)	0.140(1)	-0.368(1)	8(1)
C(15)	-0.245(2)	0.062(1)	-0.2948(9)	4.5(9)
C(16)	-0.287(3)	-0.018(1)	-0.264(1)	9(1)
C(17)	-0.397(3)	0.106(1)	-0.320(1)	8(1)
C(18)	0.080(3)	-0.145(1)	-0.173(1)	7(1)
C(19)	0.211(3)	-0.197(2)	-0.176(2)	10(2)
C(20)	0.357(4)	-0.162(2)	-0.154(2)	15(3)
C(21)	0.329(3)	-0.089(2)	-0.114(2)	9(2)
C(22)	0.653(3)	-0.010(2)	0.505(2)	9.8(7)
C(23)	0.401(4)	-0.070(2)	0.518(2)	14(1)
C(24)	0.577(5)	-0.090(2)	0.523(2)	17(1)

linear decline was observed in the intensities of three representative reflections measured after every 150 reflections; a correction was applied to the data to account for the decay. Two independent molecules were found in the unit cell. The large number of atoms combined with the lack of reflections meant that not all atoms could be refined anisotropically; the carbon atoms of both Cp^{4t} rings were left with isotropic thermal parameters in the least-squares refinement.

Results

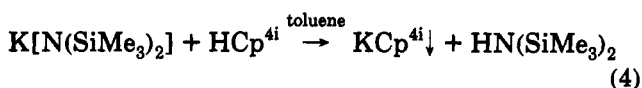
Alternate Synthesis of KCp^{4t}. The reaction of K[N(SiMe₃)₂] and HCp^{4t} in toluene produces the potassium salt KCp^{4t} in near quantitative (>95%) yields;

Table 4. Atomic Fractional Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms in (Cp⁴ⁱ)Ca[N(SiMe₃)₂](THF) (5)^a

atom	x/a	y/b	z/c	B _{iso} (Å ²)
Ca(1)	0.2319(2)	0.5592(1)	0.37549(8)	3.9(2)
Ca(2)	-0.2447(2)	0.7242(1)	0.36957(8)	4.2(2)
Si(1)	0.3189(3)	0.5134(3)	0.4575(1)	5.6(3)
Si(2)	0.1723(3)	0.4570(3)	0.4385(1)	6.3(3)
Si(3)	-0.4162(3)	0.7564(3)	0.4135(1)	5.4(3)
Si(4)	-0.3801(3)	0.8111(3)	0.3397(1)	5.4(3)
O(1)	0.1625(6)	0.6528(5)	0.3966(3)	6.1(7)
O(2)	-0.2767(6)	0.6298(5)	0.3328(3)	6.5(7)
N(1)	0.2459(7)	0.5053(6)	0.4305(3)	4.1(6)
N(2)	-0.3607(6)	0.7656(6)	0.3776(3)	4.2(7)
C(1)	0.2178(8)	0.5984(7)	0.3069(4)	3.7(4)
C(2)	0.1980(8)	0.5289(7)	0.3067(4)	3.6(4)
C(3)	0.2618(8)	0.4889(7)	0.3137(3)	3.3(3)
C(4)	0.3186(7)	0.5356(7)	0.3175(3)	2.9(3)
C(5)	0.2942(8)	0.6030(8)	0.3135(4)	4.0(4)
C(6)	0.1245(8)	0.5001(8)	0.2983(4)	4.8(4)
C(7)	0.119(1)	0.4756(8)	0.2579(5)	7.6(5)
C(8)	0.063(1)	0.5531(9)	0.3041(5)	7.7(5)
C(9)	0.2636(8)	0.4105(8)	0.3149(4)	5.1(4)
C(10)	0.303(1)	0.381(1)	0.2816(5)	8.0(5)
C(11)	0.2947(9)	0.3815(8)	0.3498(4)	6.9(5)
C(12)	0.3991(8)	0.5131(7)	0.3217(4)	4.9(4)
C(13)	0.441(1)	0.5321(9)	0.2869(5)	7.7(5)
C(14)	0.438(1)	0.5418(8)	0.3551(4)	7.2(5)
C(15)	0.3350(8)	0.6708(8)	0.3146(4)	5.2(4)
C(16)	0.327(1)	0.711(1)	0.2791(5)	9.2(6)
C(17)	0.316(1)	0.7167(9)	0.3457(5)	7.0(5)
C(18)	0.297(1)	0.517(1)	0.5071(5)	11(2)
C(19)	0.367(1)	0.597(1)	0.4480(5)	10(1)
C(20)	0.387(1)	0.443(1)	0.4530(5)	9(1)
C(21)	0.192(1)	0.363(1)	0.4456(5)	10(1)
C(22)	0.113(1)	0.4617(9)	0.3964(4)	7(1)
C(23)	0.113(1)	0.487(1)	0.4771(4)	11(1)
C(24)	0.175(1)	0.678(1)	0.4323(6)	10.3(7)
C(25)	0.116(1)	0.723(1)	0.4415(5)	8.5(5)
C(26)	0.087(1)	0.748(1)	0.4065(5)	7.1(5)
C(27)	0.108(1)	0.694(1)	0.3790(5)	6.4(5)
C(28)	-0.1051(8)	0.6906(7)	0.3631(4)	3.8(4)
C(29)	-0.1073(7)	0.7586(7)	0.3523(4)	3.4(3)
C(30)	-0.1257(8)	0.7983(7)	0.3832(4)	3.6(4)
C(31)	-0.1328(7)	0.7525(7)	0.4131(4)	2.5(3)
C(32)	-0.1204(7)	0.6850(8)	0.4004(3)	3.2(3)
C(33)	-0.0882(8)	0.7886(7)	0.3136(4)	4.8(4)
C(34)	-0.008(1)	0.8130(8)	0.3139(5)	7.4(5)
C(35)	-0.099(1)	0.7359(9)	0.2839(4)	7.2(5)
C(36)	-0.1305(9)	0.8773(8)	0.3840(4)	5.2(4)
C(37)	-0.068(1)	0.9106(9)	0.4044(4)	7.0(5)
C(38)	-0.2025(9)	0.9057(8)	0.3956(4)	6.1(5)
C(39)	-0.1422(9)	0.7759(8)	0.4528(4)	5.3(4)
C(40)	-0.0787(9)	0.7575(8)	0.4768(4)	6.5(4)
C(41)	-0.2130(9)	0.7477(9)	0.4687(4)	7.2(5)
C(42)	-0.1232(8)	0.6188(8)	0.4219(4)	4.5(4)
C(43)	-0.054(1)	0.5753(9)	0.4167(4)	7.2(5)
C(44)	-0.187(1)	0.573(1)	0.4115(4)	7.3(5)
C(45)	-0.5144(9)	0.751(1)	0.4019(5)	8(1)
C(46)	-0.409(1)	0.830(1)	0.4473(5)	9(1)
C(47)	-0.396(1)	0.673(1)	0.4390(5)	9(1)
C(48)	-0.2966(9)	0.8129(8)	0.3097(4)	7(1)
C(49)	-0.454(1)	0.774(1)	0.3102(5)	9(1)
C(50)	-0.404(1)	0.904(1)	0.3479(5)	9(1)
C(51)	-0.239(1)	0.592(1)	0.3055(5)	7.0(5)
C(52)	-0.283(1)	0.531(1)	0.2961(5)	9.6(6)
C(53)	-0.354(1)	0.546(1)	0.3114(6)	11.4(7)
C(54)	-0.346(1)	0.597(1)	0.3386(6)	10.8(7)

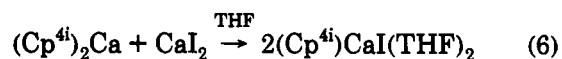
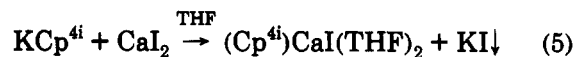
$$^a B_{eq} = (8\pi^2/3) \sum_i U_{ij} a_i^* a_j^* \rho_i \rho_j$$

precipitation of KCp⁴ⁱ helps drive the reaction to completion (eq 4). The reaction is much more rapid (8–12 h) than



our previously reported synthesis using KH (3 days),¹⁰ although both methods produce comparable yields.

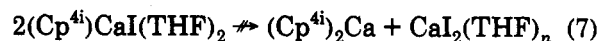
Synthesis of (Cp⁴ⁱ)CaI(THF)₂ and [(Cp⁴ⁱ)CaI(THF)₂]. [Tetraisopropylcyclopentadienyl]calcium iodide compound (Cp⁴ⁱ)CaI(THF)₂ (1) is isolated from the 1:1 reaction of KCp⁴ⁱ and CaI₂ in THF (eq 5). The same complex is also produced from the conproportionation of (Cp⁴ⁱ)₂Ca and CaI₂ in THF (eq 6):



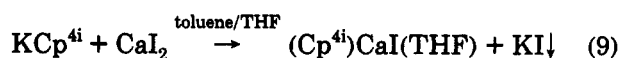
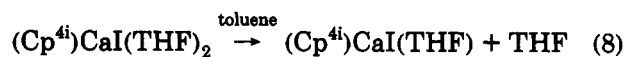
The yield of 1 from KCp⁴ⁱ and CaI₂ is routinely greater than 90%; the yield from (Cp⁴ⁱ)₂Ca and CaI₂ is quantitative. Both reactions are remarkably clean; (Cp⁴ⁱ)₂Ca is not present as an observable impurity, as would be expected if disproportionation of 1 were occurring in solution. The product was characterized by ¹H NMR (C₆D₆ and THF-*d*₈) and displays a characteristic peak at 5.93 ppm for the [Cp⁴ⁱ]-ring hydrogen in its C₆D₆ spectrum; this is shifted downfield compared to the analogous peak at 5.83 ppm for (Cp⁴ⁱ)₂Ca.¹⁶ Confirmation of the identity of 1 as (Cp⁴ⁱ)CaI(THF)₂ was obtained by elemental analysis and IR spectroscopy, both of which were consistent with the proposed formulation.

The freedom of 1 from disproportionation in either THF or aromatics is striking; a C₆D₆ solution of 1 remained free from decomposition products for up to 12 days. After 2 weeks, however, decomposition of 1 by protonation of the cyclopentadienyl ligand became significant (as evidenced by the gradual appearance of resonances corresponding to HCp⁴ⁱ¹⁰); only after this did peaks corresponding to (Cp⁴ⁱ)₂Ca begin to appear in the spectrum.

The unprecedented stability of 1 evidently stems from the impossibility of forming a THF-solvate of the corresponding metallocene, (Cp⁴ⁱ)₂Ca.¹⁰ Because of this, the THF must be completely removed from the oxophilic calcium in order for another [Cp⁴ⁱ]-ring to bind to the metal center; this process is unfavorable enough in aromatic and/or THF solutions at room temperature that disproportionation is prevented (eq 7).



One THF ligand in 1 is highly labile and can be removed in a variety of ways to give (Cp⁴ⁱ)CaI(THF) (2): (a) recrystallizing of 1 from toluene either at -40 °C or room temperature (eq 8); (b) washing solid 1 with hexane; (c) allowing solid 1 to stand in an inert atmosphere for long periods of time (≥2 mo); or (d) heating solid 1 to 50 °C under vacuum (10⁻² Torr) for 3 h. Allowing KCp⁴ⁱ and CaI₂ (1:1) to react in a toluene/THF solvent mixture produces 2 directly (eq 9).



(Cp⁴ⁱ)CaI(THF) was characterized by NMR (¹H, ¹³C), IR

(16) Although the ring proton resonance for 1 fortuitously coincides with the analogous peak for (Cp⁴ⁱ)₂Ca in THF-*d*₈, the remaining resonances for 1 are shifted significantly downfield from those in (Cp⁴ⁱ)₂Ca. The previously unreported THF-*d*₈ proton NMR spectrum for (Cp⁴ⁱ)₂Ca is as follows: δ 5.67 (s, 2 H, ring-CH); 3.09 (septet, *J* = 7.2 Hz, 4 H, CHMe₂); 2.98 (septet, *J* = 6.8 Hz, 4 H, CHMe₂); 1.37 (d, *J* = 6.8 Hz, 12 H, CH₃); 1.29 (d, *J* = 7.2 Hz, 12 H, CH₃); 1.26 (d, *J* = 7.2 Hz, 12 H, CH₃); 0.97 (d, *J* = 6.8 Hz, 12 H, CH₃).

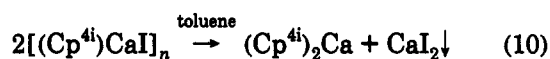
spectroscopy, elemental analysis, and a single-crystal X-ray structural study (see below). It is easily distinguished from 1 by the downfield shift observed in ^1H NMR (C_6D_6) spectra for the $[\text{Cp}^{41}]^-$ ring proton resonance, which now occurs at 5.98 ppm. Like 1, 2 is stable with respect to disproportionation in aromatics and THF solution at room temperature.

Preparation of $[(\text{Cp}^{41})\text{CaI}]_n$ (3). Heating 1 or 2 at 110 °C and 10^{-6} Torr for up to 4 h leaves a residue with an ^1H NMR (C_6D_6) spectrum that displays resonances for the $[\text{Cp}^{41}]^-$ ion that do not match either $(\text{Cp}^{41})_2\text{Ca}$, 1 or 2. The greatest change occurs for the $[\text{Cp}^{41}]^-$ ring proton resonance, which now appears at 6.11 ppm. There are no resonances corresponding to THF in the spectrum. The compound is modestly soluble in toluene, but on isolation from toluene solution, the compound was found to have been partially converted into $(\text{Cp}^{41})_2\text{Ca}$ (see below). On the basis of these results, the new compound was identified as the unsolvated mono(ring) species $[(\text{Cp}^{41})\text{CaI}]_n$ (3). The proton NMR spectrum of 3 in THF- d_8 is identical with those of 1 and 2, supporting its identification as $[(\text{Cp}^{41})\text{CaI}]_n$. The IR spectrum of 3 is nearly identical with the spectrum of 2, except for the absence of peaks assignable to coordinated THF at 1022, 988, and 872 cm^{-1} .

The extent of oligomerization in 3 is not known, although its toluene solubility argues against a highly polymeric structure. An attempt to determine the degree of oligomerization of 3 by MS-FAB was not successful.

In a parallel experiment, heating $\text{Cp}^*\text{CaI}(\text{THF})_2$ to 125 °C at a pressure of 10^{-6} Torr led to complete desolvation to form the corresponding unsolvated mono(ring) complex $[\text{Cp}^*\text{CaI}]_n$ (see Experimental Section). In contrast to 3, $[\text{Cp}^*\text{CaI}]_n$ is completely insoluble in toluene (even at reflux) and is most likely extensively polymerized.

Although 3 will dissolve in aromatics, the solutions are unstable, and the complex slowly disproportionates into $(\text{Cp}^{41})_2\text{Ca}$ and CaI_2 (eq 10). The decomposition is irreversible, as CaI_2 precipitates from solution.

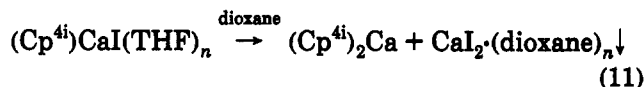


The slow disproportionation of 3 was monitored in C_6D_6 solution over the course of several days (see Figure 1). Two different concentrations of 3 were used in the study; the sample in trial no. 1 was roughly twice as concentrated as in trial no. 2. The two samples decomposed at nearly the same rate for the first 8 h, but the rates diverged substantially after this; in trial no. 1, about 67% of the mono(ring) was still present in solution after 74 h, whereas only 50% of the initial mono(ring) remained after 74 h in trial no. 2. An accelerated rate of disproportionation in aromatics accompanying high dilution was previously observed for $\text{Cp}^*\text{CaI}(\text{THF})_2$.⁷ Unfortunately, owing to the low initial concentration of 3 in the samples, the relative concentration of other decomposition products (mostly HCp^{41}) increased to the point that the disproportionation could not be accurately followed by NMR after 3 days.

Conversion of $(\text{Cp}^{41})\text{CaI}(\text{THF})_n$ into $(\text{Cp}^{41})_2\text{Ca}$. Although dissociation of THF from the calcium in 1 or 2 in aromatic solution does not occur enough to allow disproportionation at room temperature, heating the solution provides the energy required for dissociation of THF and faster subsequent disproportionation. Thus, refluxing a toluene solution of 1 or 2 leads to its near quantitative (93%) conversion into $(\text{Cp}^{41})_2\text{Ca}$ and $\text{CaI}_2(\text{THF})_n$ in only

4 h, in contrast to the slow (>3 d) decomposition of 3 at room temperature.

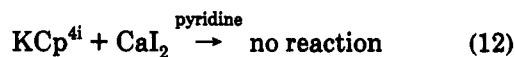
Addition of 1,4-dioxane to a THF solution of 1 or 2 generates a precipitate over several hours. Subsequent workup of the reaction reveals that the starting complex has completely decomposed, as only $(\text{Cp}^{41})_2\text{Ca}$ is isolated (in up to 94% yield) from solution. The precipitate was identified as the THF-insoluble $\text{CaI}_2(\text{dioxane})_n$ adduct (eq 11). Addition of dioxane to solutions of Grignard



reagents also leads to their complete disproportionation to homoleptic materials and was used as an early test for the existence of Schlenk equilibria.¹⁷ Therefore, although no spectroscopically observable formation of $(\text{Cp}^{41})_2\text{Ca}$ or $\text{CaI}_2(\text{THF})_n$ occurs in THF solutions of 1 and 2, some CaI_2 must be present from disproportionation to allow precipitation of $\text{CaI}_2(\text{dioxane})_n$, with a consequently irreversible shift of the equilibrium to the bis(ligand) products.¹⁸

Heating 1 or 2 at 215–220 °C and 10^{-6} Torr leads to the slow production of a white sublimate; the reaction proceeds at a rate of about 30–40 mg of solid sublimed per hour. Subsequent analysis (C_6D_6 , ^1H NMR) of the sublimed solid revealed that it was not 3 but the corresponding metallocene $(\text{Cp}^{41})_2\text{Ca}$ (conversion yield is 65%). Apparently, solid 3 is thermally unstable with respect to disproportionation at this temperature and pressure and is converted into $(\text{Cp}^{41})_2\text{Ca}$ and CaI_2 ; the metallocene subsequently sublimes onto the cold finger.¹⁹ Interestingly, 3 partially melts at 215 °C at atmospheric pressure; it is possible that thermally induced disproportionation into $(\text{Cp}^{41})_2\text{Ca}$ and CaI_2 is occurring here as well, the metallocene (mp 196–200 °C) subsequently melting. In contrast, $[\text{Cp}^*\text{CaI}]_n$ displays no evidence of volatility or decomposition at temperatures up to 240 °C under high vacuum.

Reactions Involving Bases Other Than THF. Attempts to synthesize [tetraisopropylcyclopentadienyl]-calcium iodide in donor solvents other than THF were not as successful. No reaction occurred between KCp^{41} and CaI_2 when pyridine was used as the solvent; only unreacted KCp^{41} could be identified in the solid isolated from solution (^1H NMR, THF- d_8) (eq 12). Remarkably, the same result



was obtained when the reaction was conducted in pyridine/THF solvent mixtures with THF:pyridine ratios as high as 5:1. Insolubility of CaI_2 in pyridine was not responsible for the lack of reactivity; separate control experiments found that more than 100 mg of CaI_2 would dissolve in the amounts of pyridine or pyridine/THF used in these reactions (25–30 mL).

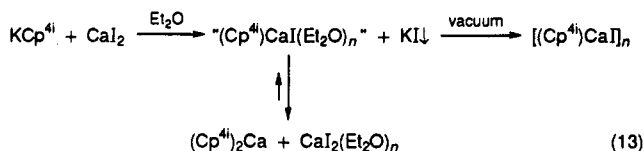
Reaction of KCp^{41} and CaI_2 (1:1) in diethyl ether did not lead to the formation of $(\text{Cp}^{41})\text{CaI}(\text{Et}_2\text{O})_n$ but instead produced a mixture of $[(\text{Cp}^{41})\text{CaI}]_n$ and $(\text{Cp}^{41})_2\text{Ca}$ in a

(17) Schlenk, W.; Schlenk, W. *Chem. Ber.* 1929, 62, 920–924.

(18) Based on a detection limit of 0.5% for the metallocene in the NMR spectra of 2 in THF, the equilibrium constant K for 2 calculated according to eq 14 must be at least 4.0×10^4 .

(19) It is possible that 3 is volatilizing at 215–220 °C and 10^{-6} Torr and then disproportionating completely in the gas phase. However, this process would require 3 to have a sublimation temperature only 25–30 °C higher than $(\text{Cp}^{41})_2\text{Ca}$ (190 °C, 10^{-6} Torr), which given the two times higher mass of 3 is not likely.

roughly 3:2 ratio (eq 13); spectroscopically undetectable $\text{CaI}_2(\text{Et}_2\text{O})_n$ was presumably also present.



Apparently, $(\text{Cp}^{4i})\text{CaI}(\text{Et}_2\text{O})_n$ is not stable with respect to disproportionation into $(\text{Cp}^{4i})_2$ and CaI_2 , unlike the THF-solvated complexes 1 and 2. Although no direct evidence exists for the formation of $(\text{Cp}^{4i})\text{CaI}(\text{Et}_2\text{O})_n$, its presence is indicated by the isolation of 3 from the reaction. The ease with which the Et_2O is displaced from $(\text{Cp}^{4i})\text{CaI}(\text{Et}_2\text{O})_n$ upon removal of solvent indicates that the $\text{Ca}-\text{OEt}_2$ bond is highly labile.

If the amount of isolated 3 is equal to the amount of $(\text{Cp}^{4i})\text{CaI}(\text{Et}_2\text{O})_n$ present in solution at equilibrium, K for the disproportionation of $(\text{Cp}^{4i})\text{CaI}(\text{Et}_2\text{O})_n$ in ether as calculated according to eq 14 is ~ 2 . The fact that this

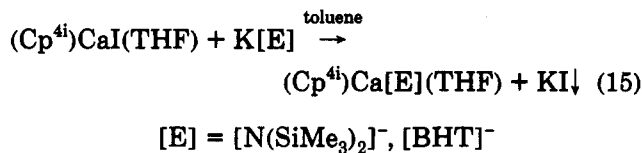
$$K = \frac{[(\text{Cp}^{4i})\text{CaI}(\text{L})_n]^2}{[(\text{Cp}^{4i})_2\text{Ca}][\text{CaI}_2(\text{L})_n]} \quad (14)$$

value is less than that for complete ligand scrambling in solution ($K = 4$)⁷ indicates that the equilibrium in ether is shifted slightly in favor of the metallocene and calcium iodide, and not the mono(ring) complex.

Three separate reactions were employed in an attempt to synthesize $(\text{Cp}^{4i})\text{CaI}(\text{DME})$ (4): (a) a metathetical reaction between KCp^{4i} and CaI_2 using DME as the solvent; (b) a conproportionation reaction of $(\text{Cp}^{4i})_2\text{Ca}$ and CaI_2 in DME; and (c) the dissolution of 3 in DME. Analysis of the resulting products (^1H NMR, C_6D_6) revealed the presence of $(\text{Cp}^{4i})_2\text{Ca}$ and a new mono(ring) complex that was identified as the desired 4, on the basis of the similarity of its proton NMR spectrum to that of 1 (the ring- CH proton resonances for 4 and 1 differ by only 0.01 ppm). The ratio of 4 to $(\text{Cp}^{4i})_2\text{Ca}$ in the product isolated from all three reactions was approximately 4:1. Thus, like $(\text{Cp}^{4i})\text{CaI}(\text{Et}_2\text{O})_n$ in Et_2O , 4 is not stable with respect to disproportionation in DME, and an equilibrium mixture of 4, $(\text{Cp}^{4i})_2\text{Ca}$, and $\text{CaI}_2(\text{DME})_n$ is obtained. The equilibrium constant K for the disproportionation of 4 in DME as calculated from eq 14 is 16.²⁰

Unlike $(\text{Cp}^{4i})\text{CaI}(\text{THF})_n$, 4 is only slightly soluble in aromatic solutions, and hence $(\text{Cp}^{4i})_2\text{Ca}$ can be separated from the product mixture described above by a simple toluene extraction with only minimal loss of 4. However, because of its low solubility in aromatics, it was not possible to separate 4 from the $\text{CaI}_2(\text{DME})_n$ also present. Proton NMR spectra of the toluene-washed 4/ $\text{CaI}_2(\text{DME})_n$ mixtures did not contain resonances for $(\text{Cp}^{4i})_2\text{Ca}$ and provided no evidence for subsequent disproportionation on standing for short periods of time. Thus 4, like 1 and 2, is stable toward disproportionation into $(\text{Cp}^{4i})_2\text{Ca}$ and CaI_2 in aromatic solvents.

Derivatization of $(\text{Cp}^{4i})\text{CaI}(\text{THF})_{(1,2)}$. $(\text{Cp}^{4i})\text{CaI}(\text{THF})_{(1,2)}$ can be derivatized by metathetical reactions with potassium complexes in toluene (eq 15):

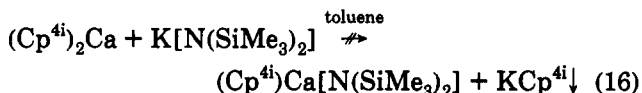


Two such derivatives have been synthesized: $(\text{Cp}^{4i})\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})$ (5) and $(\text{Cp}^{4i})\text{Ca}[\text{BHT}](\text{THF})$ (6); the products are obtained in 75 and 60% yield, respectively. Like 1 or 2, both are stable with respect to disproportionation in aromatic and THF solution. Both 5 and 6 have been completely characterized by NMR (^1H , ^{13}C) and IR spectroscopy and elemental analysis, and all data are consistent with the proposed formulation of the compounds. Especially diagnostic are the proton NMR spectra, which contain only a single set of $[\text{Cp}^{4i}]^-$ and $[\text{E}]^-$ ligand resonances that are shifted from the corresponding peaks for the bis(ligand) compounds. For example, the ring- CH peak, for 5 and 6 in C_6D_6 appear at 5.77 and 5.94 ppm, respectively, whereas for $(\text{Cp}^{4i})_2\text{Ca}$ this peak occurs at 5.83 ppm.

Interestingly, when the reaction of 2 and $\text{K}[\text{N}(\text{SiMe}_3)_2]$ was attempted in THF instead of toluene, it did not proceed cleanly, and a mixture of 5, $(\text{Cp}^{4i})_2\text{Ca}$, and $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})_2$ was obtained in a ratio of ca. 4:1:1. It is not known why the reaction does not work in THF as well as it does in toluene, as both the starting material and the desired product are stable in either solvent.

Several other methods used to synthesize 5 or its base-free analogue were not successful. No reaction was observed on mixing equimolar amounts of $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$ and HCp^{4i} in THF, toluene, or hexane. As $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$ will deprotonate both HCp^* and $\text{HC}_5\text{Me}_4\text{Et}$,²¹ a likely reason for its inability to deprotonate HCp^{4i} is that the latter's steric bulk prohibits the reaction from occurring. In addition, products of the reaction of $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$ with HCp^{4i} would be soluble, removing precipitation of the product as a potential driving force, as occurs in the reaction of $\text{K}[\text{N}(\text{SiMe}_3)_2]$ and HCp^{4i} (eq 4).

In contrast to the facile synthesis of 1 by conproportionation, the attempted synthesis of 5 by the reaction of $(\text{Cp}^{4i})_2\text{Ca}$ and $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$ in THF yielded only ca. 10% of the heteroleptic compound. Thus replacement of iodide with the larger, more basic $[\text{N}(\text{SiMe}_3)_2]^-$ anion significantly retards the conproportionation reaction with $(\text{Cp}^{4i})_2\text{Ca}$. In addition, $(\text{Cp}^{4i})_2\text{Ca}$ and $\text{K}[\text{N}(\text{SiMe}_3)_2]$ did not react in toluene to form base-free $(\text{Cp}^{4i})\text{Ca}[\text{N}(\text{SiMe}_3)_2]$ and a precipitate of KCp^{4i} , as had been anticipated (eq 16).²² Apparently, the bis(trimethylsilylamido) salts are especially inefficient in reacting with the highly encapsulated calcium in $(\text{Cp}^{4i})_2\text{Ca}$.



$(\text{Cp}^{4i})\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})$ can be sublimed readily at 120 °C and 10^{-6} Torr in ca. 60% yield to give a glassy or waxy material. This result was unexpected, as the corresponding bis(ligand) calcium complexes $(\text{Cp}^{4i})_2\text{Ca}$ and $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$ are not as volatile: $(\text{Cp}^{4i})_2\text{Ca}$ sublimates at

(21) Tanner, P. S.; Burkey, D. J.; Hanusa, T. P., submitted for publication.

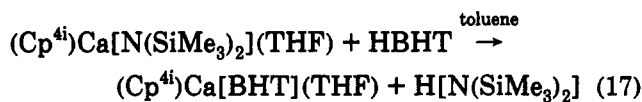
(22) We have previously used a similar reaction between $\text{Cp}^*\text{Ca}(\text{THF})_n$ and various lithium salts in THF to prepare mono(ring) calcium complexes of the type $\text{Cp}^*\text{Ca}(\text{E})(\text{THF})_n$; the precipitation of the LiCp^* drives the reactions to completion (see ref 8).

(20) Since it was determined that 4 does not undergo Schlenk equilibrium in aromatic solution (see below), the product mixtures seen in the C_6D_6 NMR spectra should represent the equilibrium amounts of the compounds present in DME.

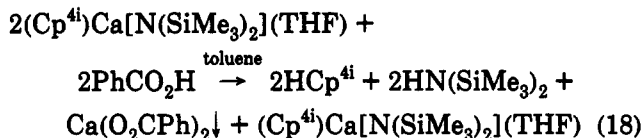
190 °C and 10⁻⁶ Torr,¹⁰ and Ca[N(SiMe₃)₂]₂(DME)₂ has been reported to sublime with much decomposition at 150 °C under high vacuum.¹⁵

However, the stability of **5** with respect to disproportionation is lost in the gas phase. Although a portion of the sublimed material is unchanged, significant amounts of (Cp⁴ⁱ)₂Ca and Ca[N(SiMe₃)₂]₂(THF)_n are also present. The ratio of **5**, (Cp⁴ⁱ)₂Ca, and Ca[N(SiMe₃)₂]₂(THF)_n in the sublimed material is consistently near 3:3:1 (by ¹H NMR in both C₆D₆ and THF-*d*₈). The small proportion of the calcium amide likely reflects its known thermal instability.¹⁵ It is noteworthy that **5** sublimes with desolvation, in contrast to **1** or **2**, which are completely desolvated to form **3** at nearly the same temperature and pressure. That **5** does not readily desolvate may be a consequence of its inability to form a corresponding oligomerized structure (see below).

Preliminary studies on the reactivity of **5** indicate that it is possible to protonate the [N(SiMe₃)₂]⁻ ligand selectively with acidic reagents. For example, **6** can be cleanly prepared by the reaction of **5** with HBHT in toluene (eq 17). The yield from this protonolysis reaction (quantitative



by NMR, 82% isolated) is higher than that seen for the metathesis route to the same complex. No protonation of the [Cp⁴ⁱ]⁻ ligand was observed in the 1:1 reaction, but excess HBHT will protonate it. Not all acidic reagents selectively protonate the [N(SiMe₃)₂]⁻ ligand in **5**; indiscriminate protonation occurs with benzoic acid (pK_a = 4.2), for example, even when the ratio of PhCO₂H to **5** is 1:1 (eq 18).



Solid State Structures

(1,2,3,4-C₃H₇)₄C₅H₂. During this work, the single-crystal X-ray structure of 1,2,3,4-tetraisopropylcyclopentadiene (HCp⁴ⁱ) was obtained; it is to our knowledge the first solid-state structure of an alkylated cyclopentadiene.²³ Crystals used for the study were grown from hexane by slow evaporation. A summary of bond distances and angles for HCp⁴ⁱ is given in Table 5.

As expected, the diene has a rigorously planar five-membered ring; the largest deviation from the plane is 0.003 Å (Figure 2). Interestingly, the C–C bonds to the sp³-hybridized carbon (C(1)–C(2,5), 1.494(8), 1.484(8) Å) are the same, within error, as the vinylic C(3)–C(4) distance (1.502(8) Å). In cyclopentadiene itself²⁴ and in its tetra- and pentaphenylated derivatives,^{25,26} the bond between the two sp² carbons (C(3)–C(4)) is the shortest in the ring,

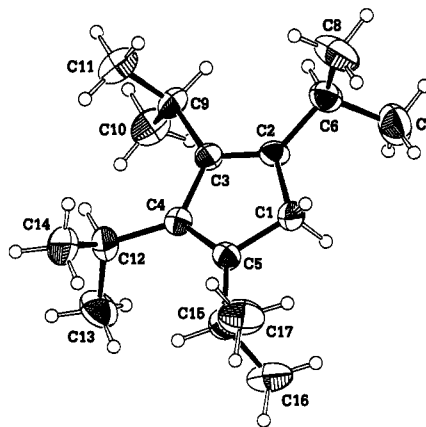


Figure 2. ORTEP diagram of (C₃H₇)₄C₅H₂, giving the numbering scheme used in the text. Thermal ellipsoids are shown at the 35% level; the hydrogen atoms are represented by spheres of arbitrary size.

Table 5. Selected Bond Distances (Å) and Angles (deg) for (C₃H₇)₄C₅H₂

atoms	distance	atoms	angle
C(1)–C(2)	1.494(8)	C(2)–C(1)–C(5)	105.1(5)
C(1)–C(5)	1.484(8)	C(1)–C(2)–C(3)	109.0(5)
C(2)–C(3)	1.347(8)	C(2)–C(3)–C(4)	108.5(5)
C(3)–C(4)	1.502(8)	C(3)–C(4)–C(5)	108.6(5)
C(4)–C(5)	1.357(8)	C(4)–C(5)–C(1)	108.8(5)
C(ring)–CH (av)	1.505(8)	CH ₃ –CH–CH ₃ (av)	111(1)
CH–CH ₃ (av)	1.511(9)		
planarity of ring	within 0.003		
av displacement of methine carbon from ring plane	0.023		

although the difference is usually only slightly above detectability. Only minor deviations from the C₅ plane (0.026–0.057 Å) were found for the methine carbons of the four isopropyl groups.

All the isopropyl groups are rotated so that they are nearly perpendicular to the plane of the ring, with twist angles²⁷ of 77.6–89.9° (average 86.0°); three of them are geared in the same direction and one points in the opposite direction toward the unsubstituted carbon atom in the ring. This semigeared orientation is the same orientation found for the [Cp⁴ⁱ]⁻ ligand in (Cp⁴ⁱ)₂Ca, (Cp⁴ⁱ)₂Ba¹⁰, **2**, and **5** (see below) and has previously been shown to be the most stable configuration of the anion.¹⁰

The diene molecules stack in the lattice along the crystallographic *b* axis, with an interplanar separation of 5.11 Å (Figure 3). The stacking direction forms an angle of 31° with the crystallographic axis. It is notable that a qualitatively similar packing arrangement was recently discovered for the C₅(*i*-Pr)₅[•] radical, although the interplanar distance was substantially larger (5.82 Å) and the stacking angle was narrower (23°).²⁸ Since in both structures the rings stack in a nearly parallel fashion, there should be no significant additional steric encumbrance between individual rings due to the extra isopropyl group in C₅(*i*-Pr)₅[•]. Thus, factors other than steric interactions must be responsible for the greater interplanar spacing in the radical.

[(Cp⁴ⁱ)CaI(THF)₂·C₇H₈]. A crystal of **2** grown from toluene was used to determine its structure by X-ray

(23) The structure of pentakis(methoxycarbonyl)cyclopentadiene is known; however, the compound is a zwitterion in the solid state (i.e., H⁺[C₅(CO₂Me)₅]⁻ with the proton coordinated by two of the carbonyl oxygens. See: Bruce, M. I.; White, A. H. *Aust. J. Chem.* 1990, 43, 949–995.

(24) Liebling, G.; Marsh, R. E. *Acta Crystallogr.* 1965, 19, 202–205.

(25) Evrard, P. G.; Piret, P.; Germain, G.; Van Meerssche, M. *Acta Crystallogr., Sect. B: Struct. Sci.* 1971, 27, 661–667.

(26) Field, L. D.; Hambley, T. W.; Lindall, C. M.; Masters, A. F. *Inorg. Chem.* 1992, 21, 2366–2370.

(27) The twist angle of an *i*-Pr group is found by calculating the angle between the ring plane and the plane formed by the two methyl carbons of an *i*-Pr group and its adjacent ring carbon.

(28) Sitzmann, H.; Bock, H.; Boese, R.; Dezember, T.; Havlas, Z.; Kaim, W.; Moscherosch, M.; Zanathy, L. *J. Am. Chem. Soc.* 1993, 115, 12003–12009.

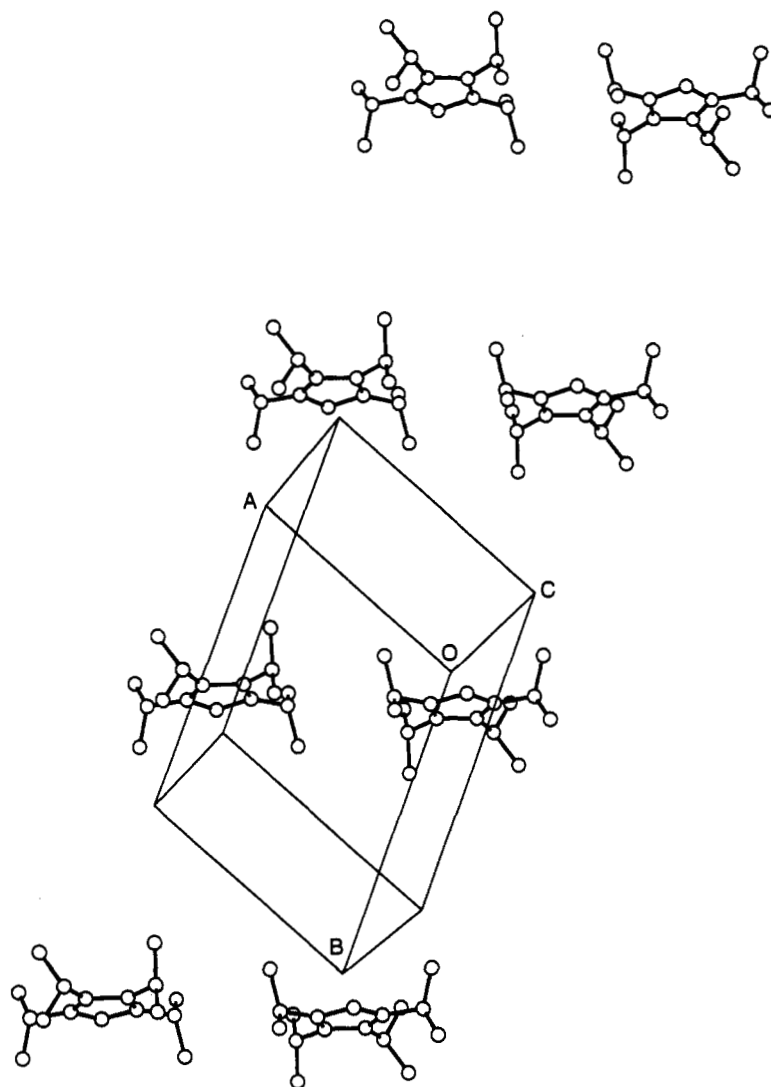


Figure 3. Stacking of HCp^{4i} rings along the crystallographic b axis. The interplanar ring space is 5.11 Å; the angle of stacking is inclined by 31° relative to the cell axis.

Table 6. Selected Bond Distances (Å) and Angles (deg) for $[(\text{Cp}^{4i})\text{Ca}(\mu\text{-I})(\text{THF})_2]$ (2)

atoms	distance	atoms	angle
Ca-I	3.101(4)	Ca-I-Ca'	93.9(1)
Ca-I'	3.110(4)	I-Ca-I'	86.1(1)
Ca-O	2.34(1)	I-Ca-O	94.1(3)
Ca-C(1)	2.62(2)	I'-Ca-O	96.1(4)
Ca-C(2)	2.62(2)	I-Ca-ring centroid	123.9
Ca-C(3)	2.69(2)	I'-Ca-ring centroid	121.2
Ca-C(4)	2.72(2)		
Ca-C(5)	2.69(2)		
Ca...Ca'	4.538(7)		
I...I'	4.241(3)		
C-C(ring) (av)	1.42(2)	CH ₃ -CH-CH ₃ (av)	109(2)
C(ring)-CH (av)	1.51(2)		
CH-CH ₃ (av)	1.54(3)		
planarity of the ring	within 0.009 Å		
Ca-ring centroid	2.376 Å		

crystallography. A disordered molecule of toluene was located in the asymmetric unit; its closest approach to the dimer (3.72 Å) is at the isopropyl carbon C(17), and it does not display any interaction with the complex. A summary of bond distances and angles for 2 is given in Table 6.

The compound exists in the solid state as an iodide-bridged dimer, $[(\text{Cp}^{4i})\text{Ca}(\mu\text{-I})(\text{THF})_2]$, with a pentahapto $[\text{Cp}^{4i}]^-$ ligand and a terminal THF on each calcium atom (Figure 4). Apparently, the calcium in a monomeric $(\text{Cp}^{4i})\text{CaI}(\text{THF})$ structure is coordinately unsaturated enough that dimerization of the compound occurs. In-

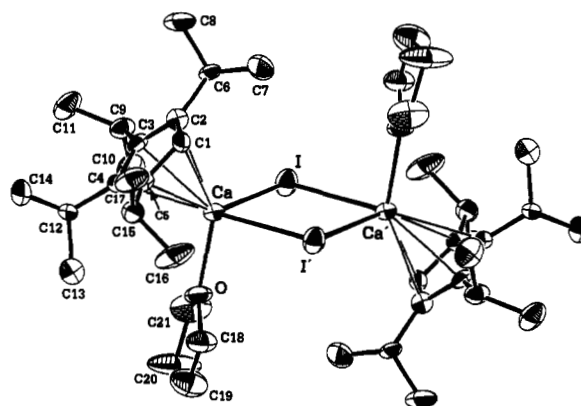


Figure 4. ORTEP diagram of the non-hydrogen atoms of 2, illustrating the numbering scheme used in the text. Thermal ellipsoids are shown at the 30% level, and the lattice solvent has been omitted for clarity.

terestingly, a space-filling model of 2 reveals that both calcium centers are almost completely encapsulated as a result of the dimerization (Figure 5). This suggests that 1, with another THF bound to calcium, could not exist as an iodide-bridged dimer in the solid state and is almost certainly monomeric.

The average Ca-C(ring) and the Ca-centroid bond lengths of 2.67(2) and 2.376 Å in 2 are nearly the same as

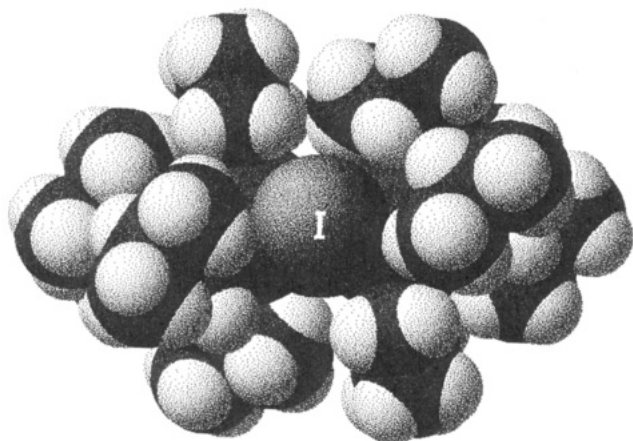


Figure 5. Space filling drawing of **2**, illustrating the sterically encumbered coordination environment of the calcium atoms. The addition of a second THF ligand to each calcium, as exists in **1**, would require the molecule to be monomeric.

those in $[\text{Cp}^*\text{CaI}(\text{THF})_2]_2$ (2.67(1), 2.385 Å), despite the higher coordination number of calcium in the latter. The $[\text{Ca}-\text{I}]_2$ core in the dimer is almost perfectly symmetric, with Ca-I and Ca-I' distances of 3.101(4) and 3.110(4) Å, and Ca-I-Ca' and I-Ca-I' angles of 93.9(1)° and 86.1(1)°, respectively. The symmetry exhibited by the bridging Ca-I bonds in **2** is in sharp contrast to the corresponding bonds in the two conformers of $[\text{Cp}^*\text{Ca}(\mu\text{-I})(\text{THF})_2]_2$, which are markedly asymmetric (differences of 0.0624 and 0.146 Å, respectively). The wide variation seen in Ca-I distances in the two conformers of $[\text{Cp}^*\text{CaI}(\text{THF})_2]_2$ indicates that little energy is required to change these distances significantly; hence the symmetry in the Ca-I bridging bonds in **2** must also be of little energetic importance.

Remarkably, the bridging Ca-I lengths in **2** (coordination number of 6 for Ca^{2+}) are indistinguishable from the three crystallographically established terminal Ca-I distances, i.e., those in $\text{CaI}_2(\text{THF})_4$,²⁹ $\text{CaI}_2(\text{H}_2\text{O})_4$,³⁰ and $\text{ICa}(\text{OC}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{C}_6\text{H}_4\text{Cl-4})(\text{THF})_4$ ²⁹ (3.106(2), 3.127(7), and 3.108(3) Å, respectively). Bridging ligand bonds are usually longer than analogous terminal ligand bonds in metal complexes.³¹ That no lengthening of the Ca-I bridging bond is seen in **2** relative to Ca-I terminal bonds underscores the large amount of bond length variation that is possible with the highly polarizable iodide ligand.²⁹

$(\text{Cp}^{41})\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})$. The complex is monomeric in the solid state, with a pseudotrigonal planar coordination geometry of the ligands around the calcium. Two crystallographically independent monomeric units of **5** are present in the asymmetric unit; the bond parameters of each conformer are very similar. The two molecules present in the asymmetric unit are enantiomers; in each molecule the calcium is bound to opposite faces of the prochiral $[\text{Cp}^{41}]$ -ligand, which destroys the mirror plane in the ring. Selected bond distances and angles for **5** are given in Table 7. A view of one conformer ("B") is presented in Figure 6.

(29) Tesh, K. F.; Burkey, D. J.; Hanusa, T. P. *J. Am. Chem. Soc.* **1994**, *116*, 2409-2417.

(30) Thiele, G.; Putzas, D. *Z. Anorg. Allg. Chem.* **1984**.

(31) A recent example involving iodides is the complex $[\text{ZnI}_2(\text{PEt}_3)]_2$, in which the terminal Zn-I distance of 2.532(3) Å is substantially shorter than the bridging distances of 2.687(3) and 2.690(3) Å (Bricklebank, N.; Godfrey, S. M.; McAuliffe, C. A.; Mackie, A. G.; Pritchard, R. G. *J. Chem. Soc., Chem. Commun.* **1992**, 944-945). Similarly, the calcium bis(alkoxide) $[\text{Ca}(\text{OC}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{C}_6\text{H}_4\text{Cl-4})_2(\text{THF})]_2$ has a terminal Ca-O distance of 2.105(2) Å, significantly shorter than the two bridging Ca-O distances of 2.268(2) to 2.299(2) Å (ref 33).

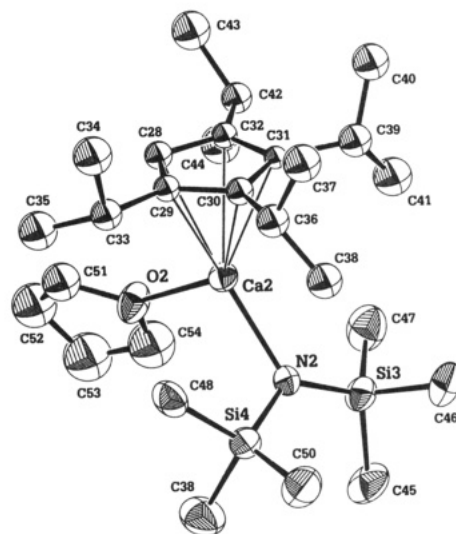


Figure 6. ORTEP diagram of the non-hydrogen atoms of one molecule of **5**, illustrating the numbering scheme used in the text. Thermal ellipsoids are given at the 30% level.

Table 7. Selected Bond Distances (Å) and Angles (deg) for $(\text{Cp}^{41})\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})$ (**5**)

atoms	distance	atoms	angle
Ca(1)-N(1)	2.29(1)	centroid(1)-Ca(1)-O(1)	118.9
Ca(2)-N(2)	2.30(1)	centroid(1)-Ca(1)-N(1)	144.1
Ca(1)-O(1)	2.35(1)	N(1)-Ca(1)-O(1)	97.0(4)
Ca(2)-O(2)	2.35(1)	centroid(2)-Ca(2)-O(2)	116.0
Ca(1)-C(1)	2.64(1)	centroid(2)-Ca(2)-N(2)	147.5
Ca(1)-C(2)	2.67(1)	N(2)-Ca(2)-O(2)	96.5(4)
Ca(1)-C(3)	2.70(1)	Ca(1)-N(1)-Si(1)	124.7(7)
Ca(1)-C(4)	2.70(1)	Ca(1)-N(1)-Si(2)	108.5(6)
Ca(1)-C(5)	2.69(1)	Si(1)-N(1)-Si(2)	126.8(6)
Ca(1)-centroid(1)	2.397	Ca(2)-N(2)-Si(3)	128.9(6)
Ca(2)-C(28)	2.66(1)	Ca(2)-N(2)-Si(4)	105.9(6)
Ca(2)-C(29)	2.69(1)	Si(3)-N(2)-Si(4)	125.1(7)
Ca(2)-C(30)	2.67(1)	N(1)-Si(1)-C(18)	114.0(7)
Ca(2)-C(31)	2.66(1)	N(1)-Si(1)-C(19)	110.6(8)
Ca(2)-C(32)	2.66(1)	N(1)-Si(1)-C(20)	114.7(7)
Ca(2)-centroid(2)	2.387	N(1)-Si(2)-C(21)	114.3(8)
Ca(1)...C(22)	2.99(2)	N(1)-Si(2)-C(22)	107.3(6)
Ca(1)...Si(2)	3.236(6)	N(1)-Si(2)-C(23)	115.5(8)
Ca(1)...C(48)	2.95(2)	N(2)-Si(3)-C(45)	114.6(7)
Ca(1)...Si(4)	3.203(6)	N(2)-Si(3)-C(46)	113.1(7)
Si(1)-N(1)	1.68(1)	N(2)-Si(3)-C(47)	110.8(7)
Si(2)-N(1)	1.67(1)	N(2)-Si(4)-C(48)	108.6(7)
Si(3)-N(2)	1.68(1)	N(2)-Si(4)-C(49)	115.3(8)
Si(4)-N(2)	1.69(1)	N(2)-Si(4)-C(50)	114.7(7)
C-C(ring) (av)	1.41(2)		
Si-C(methyl) (av)	1.88(2)		
planarity of rings	within 0.008		
Ca(1)-N(1)-Si(2)-C(22) (torsion angle)			5.1(8)
Ca(2)-N(2)-Si(4)-C(48) (torsion angle)			-4.1(8)

The Ca-C(ring) distances in **5** span narrow ranges (2.64(1)-2.70(1) and 2.66(1)-2.69(1) Å). The average Ca-C(ring) distances of 2.68(1) and 2.67(1) Å are slightly longer than that found in $(\text{Cp}^{41})_2\text{Ca}$ (2.64(1) Å), despite the higher formal coordination number in the metallocene.¹⁰

The Ca-N bond distances of 2.29(1) and 2.30(1) Å in **5** are similar to the analogous distances found in $[\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2]_2$ (2.282(6) and 2.267(7) Å), $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$ -(DME) (2.271(3) Å),³² and $(\text{OC}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{C}_6\text{H}_4\text{Cl-4})\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})_3$ (2.353(5) Å).²⁹ The two Ca-O(THF) distances of 2.35(1) Å are near the short end of the range of 2.33-2.46 Å found in previously characterized THF-

(32) Westerhausen, M.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1991**, *604*, 127-140.

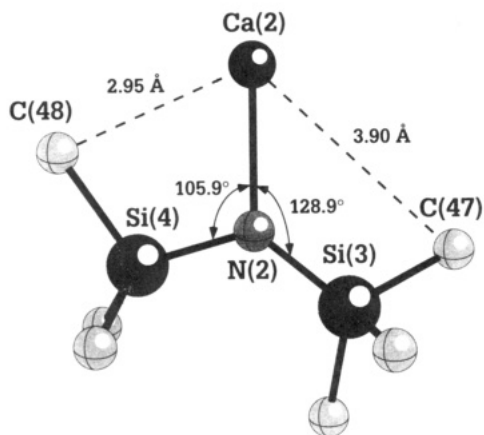


Figure 7. Ball-and-stick diagram of the $[\text{N}(\text{SiMe}_3)_2]^-$ ligand in **5**, illustrating the structural distortions stemming from the $\text{Ca}\cdots\text{SiMe}_3$ agostic interaction.

solvated calcium complexes.³³ The calcium center in both conformers lies directly in the plane defined by the oxygen, nitrogen, and ring centroid; the sum of the angles around the calcium is 360° . However, steric repulsion between the bulky $[\text{Cp}^{4i}]^-$ and $[\text{N}(\text{SiMe}_3)_2]^-$ ligands widens the ring-centroid-Ca-N angles considerably from 120° (144.1° for centroid(1)-Ca(1)-N(1) and 147.5° for centroid(2)-Ca(2)-N(2)). Consequently, the O-Ca-N angles are much narrower than 120° (97.0° for O(1)-Ca(1)-N(1) and 96.5° for O(2)-Ca(2)-N(2)).

Both molecules of **5** possess structural features indicative of an "agostic" interaction between the calcium and one of the trimethylsilyl groups of the amido ligand.³⁴ In conformer A, both the $\text{Ca}(1)\cdots\text{Si}(2)$ and $\text{Ca}(1)\cdots\text{C}(22)$ distances of 3.236(6) and 2.99(1) Å, respectively, are substantially shorter than those involving the other trimethylsilyl group (i.e., $\text{Ca}(1)\cdots\text{Si}(1)$ is 3.525(6) Å and $\text{Ca}(1)\cdots\text{C}(19)$ is 3.72(2) Å). The differences in contact distances for conformer B are even greater: the $\text{Ca}(2)\cdots\text{Si}(4)$ distance is 3.203(6) Å and the $\text{Ca}(2)\cdots\text{C}(48)$ distance is 2.95(2) Å, whereas $\text{Ca}(2)\cdots\text{Si}(3)$ is 3.600(6) Å and $\text{Ca}(2)\cdots\text{C}(47)$ is 3.90(2) Å (Figure 7). For comparison, the donor Ca-methyl contacts seen in $[\text{Cp}^*_2\text{Ca}(\mu\text{-Me}_3\text{Al-THF})_2]$ occur at distances of 2.948(7) and 2.999(7) Å.³⁵

The agostic interaction in **5** results in a significant narrowing of the Ca-N-Si angle for the trimethylsilyl group closer to the calcium: the $\text{Ca}(1)\text{-N}(1)\text{-Si}(2)$ and $\text{Ca}(2)\text{-N}(2)\text{-Si}(4)$ angles are $108.5(6)^\circ$ and $105.9(6)^\circ$, compared to the values of $124.7(7)^\circ$ and $128.9(6)^\circ$ for the $\text{Ca}(1)\text{-N}(1)\text{-Si}(1)$ and $\text{Ca}(2)\text{-N}(2)\text{-Si}(3)$ angles, respectively. The orientation of the amido ligands is such that the Ca-N-Si-C(Me) atoms that comprise the agostic interactions are nearly planar, with mean deviations of only 0.032 and 0.026 Å and torsion angles of only $5.1(8)^\circ$ and $-4.1(8)^\circ$ for $\text{Ca}(1)\text{-N}(1)\text{-Si}(2)\text{-C}(22)$ and $\text{Ca}(2)\text{-N}(2)\text{-Si}(4)\text{-C}(48)$, respectively. For comparison, torsion angles of 8.2° and -9.5° for two La-C-Si-C(Me) units of the $[\text{CH}(\text{SiMe}_3)_2]^-$ ligands of $\text{Cp}^*\text{La}[\text{CH}(\text{SiMe}_3)_2]_2$ were cited as evidence for the presence of a significant agostic interaction between two trimethylsilyl groups and the La atom.³⁶ Since the hydrogen atoms of $(\text{Cp}^{4i})\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})$ were not

located in the crystal structure, it is not possible to say definitively that the deformations of the $[\text{N}(\text{SiMe}_3)_2]^-$ ligand are the result of interactions of the Ca atom with the C-H bonds of the trimethylsilyl group. It is possible that the agostic interaction in **5** is that of a Si-C bond with the calcium; this kind of interaction has been proposed to occur in some lanthanide complexes containing the $[\text{CH}(\text{SiMe}_3)_2]^-$ ligand.³⁷ No lengthening of the Si-C bond closest to Ca occurs to support this possibility, however.³⁸

The ability of $[\text{N}(\text{SiMe}_3)_2]^-$ to participate in such agostic bonding interactions explains why it often stabilizes complexes of large, highly electropositive metals with low formal coordination numbers. Several reports of lanthanide and alkaline-earth complexes with the $[\text{N}(\text{SiMe}_3)_2]^-$ ligand have also described agostic interactions between the metal center and the ligand's trimethylsilyl groups. In these complexes, the metal center is always coordinately and electronically unsaturated, with structural distortions in the $[\text{N}(\text{SiMe}_3)_2]^-$ ligand(s) similar to those found in **5** (Table 8).

Discussion

Kinetic Stability of $(\text{Cp}^{4i})\text{Ca}[\text{E}](\text{THF})_n$. The clean, high-yield preparation of **1** and **2** and the lack of observable Schlenk equilibrium in their C_6D_6 or THF- d_8 solutions contrasts sharply with that of the previously characterized $[\text{Cp}^*\text{Ca}(\mu\text{-I})(\text{THF})_2]_2$.⁷ The latter is only moderately stable toward disproportionation in aromatics and is completely scrambled in THF, giving a 1:2:1 mixture of $\text{Cp}^*_2\text{Ca}(\text{THF})_2$, $\text{Cp}^*\text{CaI}(\text{THF})_2$, and CaI_2 . On the basis of the stability observed in **1** and **2**, the instability of $\text{Cp}^*\text{CaI}(\text{THF})_2$ can be traced to the ability of Cp^*_2Ca to form solvates with THF; thus $\text{Cp}^*\text{CaI}(\text{THF})_2$ need not lose all its coordinated THF for disproportionation to occur. The fact that unsolvated **3** is not stable toward decomposition via disproportionation confirms the importance of a bound THF molecule(s) in maintaining the solution integrity of **1** and **2**. In the absence of coordinated THF, rearrangement of the ligands in solution to give $(\text{Cp}^{4i})_2\text{Ca}$ is no longer prohibited.

Both **5** and **6** were isolated as mono-THF solvates; as with **1** and **2**, the presence of THF stabilizes the complexes against disproportionation in solution by preventing the formation of $(\text{Cp}^{4i})_2\text{Ca}$. It should be noted that the reaction of $(\text{C}_5\text{Me}_4\text{Et})\text{CaI}(\text{THF})$ with various potassium reagents (e.g., $\text{K}[\text{NSiMe}_2\text{CH}_2\text{CH}_2\text{SiMe}_2]$, $\text{K}[\text{BHT}]$, and $\text{K}[\text{OC}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_3\text{-2,4,6}]$) led to the unsolvated mono(ring) complexes $(\text{C}_5\text{Me}_4\text{Et})\text{Ca}[\text{E}]$.⁸ An X-ray structural determination of $\{(\text{C}_5\text{Me}_4\text{Et})\text{Ca}[\text{NSiMe}_2\text{CH}_2\text{CH}_2\text{SiMe}_2]\}_2$ revealed that this compound is a sterically crowded dimer with bridging amido groups; the short bridging Ca-N bonds (compared to the longer bridging Ca-I bonds in $\text{Cp}^*\text{CaI}(\text{THF})_2$ and **2**) force the calcium atoms to be close together ($3.645(3)$ Å). Such a congested dimer structure can form only on complete removal of the calcium-bound THF. For

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(38) Support for the involvement of the C-H bond in the agostic interaction was provided by ^{13}C NMR, i.e., a slight reduction (to 115.4 Hz) is seen for the $^1J_{\text{CH}}$ coupling constant in the trimethylsilyl groups as compared to that in the free amine $\text{HN}(\text{SiMe}_3)_2$ ($J = 118.0$ Hz). A similar reduction was observed in $\text{Cp}^*_2\text{YN}(\text{SiMe}_3)_2$ ($^1J_{\text{CH}} = 116.0$ Hz), which was used to support the identification of an agostic interaction between the yttrium and a C-H bond of the trimethylsilyl group. See ref 48.

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Table 8. Structural Parameters for "Agostic" $-\text{N}(\text{SiMe}_3)_2$ Ligands in Alkaline-Earth and f-Block Complexes

compound	CN ^a	metal radius (Å) ^b	M...C(Me) (Å)	M...Si (Å)	M-N-Si "bonding" angle (deg) ^c	M-N-Si "nonbonding" angle (deg) ^d	ref
[Ca[N(SiMe ₃) ₂] ₂] ₂	5	0.93	2.855(9)	3.200	95.7(3)	130.8(4)	32
			2.834(12)	3.176	105.3(3)	133.0(4)	
			2.827(10)	3.219	98.4(2)	128.9(4)	
			3.068(9)	3.266	110.1(4)	126.3(3)	
{Yb[N(SiMe ₃) ₂] ₂] ₂	5	0.97	2.785(4)	3.161	103.27(13)	133.45(16)	45
			2.820(4)	3.199	94.06(12)	132.60(14)	
			2.823(4)	3.236	98.57(12)	129.69(14)	
			2.888(4)	3.168	104.02(14)	128.31(16)	
NaYb[N(SiMe ₃) ₂] ₃	5	0.97	2.86(2)	3.218	100.4(6)	131.1(7)	46
			2.89(2)	3.248	101.3(6)	127.4(7)	
(Cp ^{4f})Ca[N(SiMe ₃) ₂](THF)	6	1.00	2.99(2)	3.236(6)	108.5(6)	124.7(7)	this work
			2.95(2)	3.203(6)	105.9(6)	128.9(6)	
Yb[N(SiMe ₃) ₂] ₂ (dmpe)	6	1.02	3.04	3.268	108.5(6)	121.0(7)	47
Cp ^{4f} ₂ Y[N(SiMe ₃) ₂]	8	1.02	2.970(6)	3.218	107.1(3)	129.7(3)	48
			3.181	3.331	114.0(3)	120.2(3)	
(C ₈ H ₈)Th[N(SiMe ₃) ₂] ₂	8	1.05	3.147(15)	3.355	110.8(5)	131.5(5)	49
			3.041(13)	3.287	106.6(5)	133.6(6)	
Cp ^{4f} Ce[N(SiMe ₃) ₂] ₂	7	1.07	2.972(9)	3.279	106.2(3)	131.4(4)	50
			2.952(9)	3.268	106.3(3)	130.0(4)	
NaEu[N(SiMe ₃) ₂] ₃	5	1.11	3.042(8)	3.400	104.5(2)	127.4(3)	46
			3.093(1)	3.426	106.2(2)	127.8(3)	
			2.971(7)	3.379	102.3(2)	130.4(3)	
			3.132(7)	3.445	107.8(2)	127.2(3)	
{Sr[N(SiMe ₃) ₂] ₂] ₂	5	1.12	3.00(2)	3.437	102.8(5)	111.8(6)	51
			3.09(2)	3.460	101.8(6)	111.0(6)	
			3.09(4)	3.552	108.4(6)	<i>e</i>	
			3.12(2)	3.471	104.6(6)	111.6(6)	
			3.18(2)	3.490	106.0(6)	106.7(5)	
			3.06(4)	3.450	103.9(6)	<i>e</i>	
Yb[N(SiMe ₃) ₂] ₂ [AlMe ₃] ₂	8	1.14	3.067(2)	3.402	104.5(1)	123.0(1)	52
			3.039(2)	3.401	102.0(1)	126.9(1)	
{Sr[N(SiMe ₃) ₂] ₂ (μ-dioxane) _n }	6	1.18	3.16(1)	<i>f</i>	<i>f</i>	<i>f</i>	53
{Ba[N(SiMe ₃) ₂] ₂] ₂	5	1.30	3.169	3.589	103.0	<i>e</i>	54
			3.335	3.684	107.3	<i>e</i>	

^a Coordination number for these complexes count all close M...CH₃ contacts as a full coordination site on the metal center. ^b Shannon radii.⁵⁵ Values for coordination numbers of five were extrapolated from the six-coordinate values using Pauling's formula.⁵⁶ ^c Refers to the angle involving the trimethylsilyl group that exhibits close contacts to the metal center. ^d Refers to the angle involving the trimethylsilyl group that is not in close contact to the metal center. ^e Both trimethylsilyl groups of the amido ligand exhibit close contacts to the metal center, so there is no "non-bonding" M-N-Si angle. ^f Not reported.

the bulkier [Cp^{4f}]⁻ mono(ring) complexes, the formation of analogous dimer structures (i.e., {(Cp^{4f})Ca[N(SiMe₃)₂]₂}₂ and {(Cp^{4f})Ca[BHT]₂}₂) is most likely not sterically feasible. Therefore, these compounds remain monomeric in the solid state and can retain a THF molecule.

It is important to note that the disproportionation of **3** in aromatics is not instantaneous (half-life of ca. 3 d), even though the formation of (Cp^{4f})₂Ca is no longer sterically prohibited. Furthermore, the rate of disproportionation decreases over time, substantially so for the more concentrated solution (e.g., for a saturated solution of **3**, only 72% remains after 24 h, but 67% is left after 74 h (see Figure 1). This behavior indicates that there is a nonnegligible energetic barrier to the disproportionation of the (Cp^{4f})CaI moiety, even in the absence of coordinated THF. It should be noted that at the same concentrations, Cp^{4f}CaI(THF)₂ exhibits decomposition behavior similar to that of **3**,³⁹ thus some inherent stability of the cyclopentadienyl-calcium-halide unit is evident here as well. The barrier to decomposition of **3** at room temperature can be readily surmounted at higher temperatures; it completely decomposes to (Cp^{4f})₂Ca and CaI₂(THF)_n in only a few hours when it is formed in refluxing toluene from **1** or **2**. The instability at higher temperatures is also observed in *solid* samples of **3**, which undergo complete disproportionation above 215 °C, and in the gas phase for

5, which partially disproportionates on sublimation at 120 °C (10⁻⁶ Torr).⁴⁰

Improvements in the thermal stability of mono(ring) calcium complexes will require a barrier to disproportionation that does not depend upon preserving the Ca-THF bond. Such a barrier could be provided by an anionic ligand bulky enough to sterically prohibit the formation of a bis(ligand) disproportionation product. An example of such a situation has been reported for magnesium pyrazoylborate complexes: the monosubstituted complexes {η³-HB(3-Bu^ppz)₃}MgX do not disproportionate, because the bulk of the pyrazoylborate anion prevents the formation of the bis(ligand) magnesium complex {η³-HB(3-Bu^pPz)₃}₂Mg.⁴¹ Unfortunately, there has been no report to date of a comparable ligand bulky enough to preclude the generation of bis(ligand) complexes of the larger alkaline-earth metals.

Differential Strengths of Donor Bonds. The combination of THF's compact size, strong donor bonds, and an almost invariable tendency to serve as a terminal ligand⁴² makes it a uniquely suitable neutral ligand for

(40) In a separate experiment, **5** was also found to undergo significant amounts of thermally induced disproportionation in solution, i.e., a C₆D₆ solution of **5** heated to 90 °C for 2 h gave an equal mixture of **5**, (Cp^{4f})₂Ca, and Ca[N(SiMe₃)₂]₂(THF)₂. Unlike **1** and **2**, the disproportionation of **5** is not complete, most likely due to the lack of precipitation of any of the products.

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(42) A few cases are known in which THF functions as a bridging ligand. See: Brooker, S.; Edelman, F. T.; Kottke, T.; Roesky, H. W.; Sheldrick, G. M.; Stalke, D.; Whitmire, K. H. *J. Chem. Soc., Chem. Commun.* 1991, 114-146, and references therein.

(39) Owing to the greater solubility of Cp^{4f}CaI(THF)₂ in aromatics, substantially higher concentrations are possible than for **3**. Consistent with this, the rate of decomposition of Cp^{4f}CaI(THF)₂ at these higher concentrations is much slower (>90% remaining after 2 weeks) than that seen for saturated solutions of **3**.

alkaline-earth complexes. This became evident in our inability to use donor ligands other than THF to prepare mono(ring) complexes whose stabilities approach those with THF. The lability of the Ca-OEt₂ donor bond prevents Et₂O from functioning as a stabilizing donor ligand for the (Cp⁴ⁱ)CaI fragment. Such lability is understandable, considering its lower basicity and larger size relative to THF.

The gradual loss of THF from solid 1 on long standing (≥2 mo) at room temperature initially suggested that it might be "sterically oversaturated"² and thus expels a ligand to relieve crowding at the metal center. However, assuming 1 is monomeric, the expelled THF is effectively replaced by a much larger "(Cp⁴ⁱ)CaI(THF)" ligand upon formation of 2, which argues against relief from steric strain as a driving force for the dimerization of 1. Therefore, the facile loss of one THF from 1 indicates that the second dative Ca-O(THF) bond is not robust enough to prevent slow oligomerization to the dimeric 2.

The inability to synthesize 4 free from disproportionation products also suggested that the formation of a second dative bond to (Cp⁴ⁱ)CaI(L) complexes is not as favorable as the formation of a dimeric structure. It was initially surprising to use that 4 was not entirely stable in DME solution, as we believed a chelating DME ligand could bind the Ca²⁺ center at least as well as THF and thus prevent the formation of (Cp⁴ⁱ)₂Ca. However, it may be that DME is actually not able to function as a bidentate ligand in this system. Given the presumably monomeric structure of 1, the binding of both oxygen atoms of DME to the same calcium center would require 4 also to be monomeric. If at any time in solution only one oxygen atom of the DME is bound to the calcium, oligomerization to a dimeric structure with monodentate DME ligands (i.e., [(Cp⁴ⁱ)Ca(μ-I)(η¹-DME)]₂) could occur. If the dimeric structure cannot be broken up by the binding of the second oxygen of the DME, any entropic benefits gained from chelation would then be eliminated, and the DME would be equivalent to a monodentate open-chain ether (such as diethyl ether). Thus, as observed for the attempted formation of (Cp⁴ⁱ)CaI(Et₂O), complete dissociation of the DME from [(Cp⁴ⁱ)CaI(η¹-DME)]₂ occurs enough to allow for its partial disproportionation into CaI₂ and (Cp⁴ⁱ)₂Ca.

A situation similar to this was recently reported for a series of base adducts of the neodymium alkoxide complex Nd(OCH(C₃H₇)₂)₃(L) (L = py, THF, or DME).⁴³ For each complex, a highly stable dimeric framework of the type [Nd(μ-OR)(OR)₂]₂ was found in the solid state, leaving only one coordination site open for the binding of the donor ligands on each Nd atom. Consequently, the DME ligands bind to the Nd atoms in an η¹ fashion and bridge the alkoxide dimers to form a linear, polymeric structure.

Enhanced Thermal Stability of the Heteroleptic Complex 5. The fact that the heteroleptic compound 5 can be sublimed at a somewhat lower temperature than (Cp⁴ⁱ)₂Ca, and that less decomposition is observed on sublimation than with {Ca[N(SiMe₃)₂]₂}, emphasizes that it is not always possible to predict the properties of a heteroleptic complex from those of the homoleptic counterparts. In this case, the larger [Cp⁴ⁱ]-ligand in 5 confers added stability compared to the bis(amido) complex, and the reduced mass of the [N(SiMe₃)₂]-ligand in 5 increases its volatility relative to the metallocene. The possible extent of such "ligand synergism" in heavy alkaline-earth

complexes has until now remained largely unexplored, owing to the paucity of well-characterized, stable heteroleptic complexes for these elements. This concept has important ramifications in the search for suitable heavy alkaline-earth precursors to ceramics and metal oxides by CVD fabrication methods, which to date have focused exclusively on compounds with identical anionic ligands. It is apparent from the properties of 5 (e.g., increased volatility and gas phase stability) that heteroleptic complexes provide an additional degree of freedom in designing complexes with such desirable physical characteristics.⁴⁴

Conclusions

A high degree of kinetic stability can be built into organoalkaline-earth compounds through careful ligand choice. Disproportionation of (Cp⁴ⁱ)Ca[E](THF)_n into the symmetrical (Cp⁴ⁱ)₂Ca and Ca[E]₂ species does not occur under ambient conditions because complete loss of THF from the calcium center is unfavorable enough to block formation of the necessarily base-free metallocene. If THF is removed under more forcing conditions, disproportionation then becomes possible. These kinetically stabilized (Cp⁴ⁱ)Ca[E](THF)_n complexes provide a well-defined platform for the rational expansion of mono-(cyclopentadienyl) alkaline-earth chemistry. In particular, the ability to protonate selectively the [N(SiMe₃)₂]-ligand in (Cp⁴ⁱ)Ca[N(SiMe₃)₂](THF) opens up a facile synthetic route to many new (Cp⁴ⁱ)Ca[E] complexes; these will be central to an investigation of the extent to which the chemical and thermal behavior of heavy alkaline-earth complexes can be influenced by "ligand synergism". We are actively exploring these possibilities.

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Supplementary Material Available: Tables of bond distances and angles and anisotropic thermal parameters (16 pages). Ordering information is given on any current masthead page.

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