choline. They agree moderately well with the results of Bohorquez and Patterson for diffusion in DOPC[17] and are somewhat larger than the values obtained earlier by Subramanian and Patterson.[16] Alsins and Almgren[22] have noted that, in measurements based on the pyrene excimer system, neglect of excimer dissociation leads to low D values. This could in part account for the lower results of Subramanian and Patterson. Almgren et al.[29] have also noted that use of the three-dimensional analysis in a two-dimensional situation likewise underestimates D. In their pyrene excimer based study, Bohorquez and Patterson made use of the "semiempirical" relation $D = k/4$, originally introduced by Galla and Sackmann,[5] where k is a quasi-second-order rate constant "forced" on the data. Our analysis of this procedure leads us to conclude that this approach is also likely to lead to a low value of D.

Conclusion

Derivation of lateral diffusion coefficients from bimolecular quenching data obtained for an air-water monolayer leads to values comparable to those obtained by the direct, FRAP method. Both the steady-state and time-resolved data show clear evidence for the features predicted for diffusion-controlled reaction in a two-dimensional environment.

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Encapsulated Alkaline-Earth Metallocenes. Synthesis, Solution Behavior, and Solid-State Structures of Bis(tetraisopropylcyclopentadienyl)calcium and -barium, $[(C_3H_7)_4C_5H]_2Ca$ and $[(C_3H_7)_4C_5H]_2Ba$

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Abstract: Reaction of 2 equiv of KCp^{4i} ($Cp^{4i} = (C_3H_7)_4C_5H$) with CaI_2 in diethyl ether or BaI_2 in THF produces the metallocenes $(Cp^{4i})_2Ca$ and $(Cp^{4i})_2Ba$ in 77 and 83% yields, respectively. The calcium metallocene $(Cp^{4i})_2Ca$ displays a remarkable degree of air stability and can be handled in dry air for several minutes without decomposition. It displays virtually no tendency to form adducts in solution with ethers or aromatic amines. The barium metallocene is the most volatile known organobarium compound, subliming at 90 °C and 0.01 Torr. These physical properties of the metallocenes are most likely related to the ability of the isopropyl groups of the Cp^{4i} rings to interlock, forming "cages" around the metal centers. DNMR experiments have provided evidence for hindered rotation in the complexes, either around the ring-C–$CHMe_2$ bonds or around the metal–ring centroid axis, with energies of activation of $\Delta G^{\ddagger} \leq 11.1$ kcal mol^{-1} in $(Cp^{4i})_2Ca$ and 11.1 (±0.5) kcal mol^{-1} in $(Cp^{4i})_2Ba$. Conformations of the Cp^{4i} anions were probed with semiempirical MO (AM1) calculations and found to be consistent with the solid-state structures. Crystals of $(Cp^{4i})_2Ca$ grown from hexane are monoclinic, space group $C2/c$, with $a = 34.033$ (6) Å, $b = 12.432$ (6) Å, $c = 16.495$ (5) Å, $\beta = 111.29$ (2)°, and $D_c = 1.036$ g cm^{-3} for $Z = 8$. Least-squares refinement on the basis of 2102 observed reflections measured at 23 °C led to a final R value of 0.044. The average Ca–C distance is 2.64 (1) Å, and the ring centroid–Ca–ring centroid angle is 162°. Crystals of $(Cp^{4i})_2Ba$ grown from hexane are triclinic, space group $P\bar{1}$, with $a = 16.682$ (4) Å, $b = 17.862$ (2) Å, $c = 12.396$ (4) Å, $\alpha = 108.02$ (3)°, $\beta = 90.56$ (3)°, $\gamma = 111.12$ (2)°, and $D_c = 1.236$ g cm^{-3} for $Z = 4$. Least-squares refinement on the basis of 6021 observed reflections measured at −120 °C led to a final R value of 0.039. Two crystallographically independent but nearly identical molecules occur in the unit cell. The average Ba–C distance is 2.94 (2) Å, and the ring centroid–Ba–ring centroid angle is 154°.

Introduction

The extent to which coordinated ligands can influence the chemistry of main-group organometallic compounds has traditionally been considered fairly limited.[1] Most main-group metals, for example, have only one or two accessible oxidation states, which restricts the stoichiometry of possible compounds. In addition, the highly ionic bonding associated with the electropositive early main-group elements (groups 1 and 2) frequently lowers the solubility and volatility of their complexes.

Recent developments in early-main-group chemistry have seen some of these limitations narrowed. In particular, the organometallic chemistry of calcium, strontium, and barium has undergone considerable expansion in the last several years as the special ligand requirements for stabilizing these large, electropositive metals have become recognized.[2] Many of the current developments have used the pentamethylcyclopentadienyl ligand (Cp^*) as a sterically bulky, stabilizing group, which has lead to complexes with greatly increased solubility in nonpolar media, lower metal coordination numbers, and improved volatility.[3-7] These complexes are perhaps even more sensitive to air and moisture than are their cyclopentadienyl counterparts, however, and they rapidly form adducts with a wide range of Lewis bases, including ethers, aromatic amines, phosphines, isonitriles,[3] and unsaturated hydrocarbons.[8]

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Some degree of control over the reactions of Cp*-stabilized organo-alkaline-earth complexes is provided by the decreasing Lewis acidity of the cations in the order $Ca^{2+} > Sr^{2+} > Ba^{2+}$, which explains why certain alkynes, for example, will form isolable adducts with $Cp^*{}_2Ca$ but not $Cp^*{}_2Ba$.[9] In an effort to introduce greater selectivity into the reactions of early-main-group organometallics, we have been seeking to develop "encapsulated" metallocenes in which direct access to the metal center is controlled by the presence of sterically bulky ligands. Such "encapsulation" has been demonstrated among compounds of the transition metals and f elements, and dramatic effects on the chemistry of the resulting complexes have been induced.[10,11] For instance, unlike uranocene itself, octaphenyluranocene is air-stable and can be refluxed in aqueous THF for hours without decomposition.[12] The stability has been attributed to the presence of the phenyl ring cage surrounding the uranium.[10] A similar explanation is invoked to explain why, unlike vanadocene itself, octaphenylvanadocene does not bind CO or 2,2′-bipyridine.[11]

In our search for encapsulated organo-alkaline-earth systems, our attention was drawn to the recent reports of the synthesis and use of the tetraisopropylcyclopentadienyl ligand (Cp^{4i}), which has been used to form ferrocene derivatives displaying hindered rotation around the metal–ring centroid axis.[13,14] Since rotation barriers in ferrocenes are generally low even with rings as sterically demanding as tetraphenylcyclopentadiene,[15] it was clear that Cp^{4i} was functioning as a uniquely bulky ligand, one that might be appropriate as an encapsulating group in organo-alkaline-earth chemistry.

Experimental Section

All manipulations of air-sensitive compounds were performed with standard high-vacuum, Schlenk, or drybox techniques. Elemental analyses were performed by Analytische Laboratorien, Engelskirchen, West Germany, by Galbraith Laboratories, Knoxville, TN, and at Vanderbilt University on a Carlo Erba EA-1106 Analyzer.

Materials. Anhydrous calcium iodide and barium iodide (Strem Chemicals or Cerac, 95%) were heated under vacuum to remove residual amounts of free iodine. Adogen 464 and isopropyl bromide were commercial samples (Aldrich); the latter was dried over molecular sieves and degassed by freeze–pump–thaw cycles before use. Solvents were dried and degassed by standard methods.[16] All other commercially available reagents were used without purification.

NMR Spectroscopy. Proton NMR spectra were obtained at either 300 or 400 MHz with a Bruker NR-300 (AM-400) spectrometer and were referenced to the residual methyl proton resonances of toluene-d_8 (δ 2.09); carbon (^{13}C) NMR spectra were recorded at 50.3 MHz on a Bruker NR-200 spectrometer and were referenced to the residual ^{13}C resonances of C_6D_6 (δ 128.0). NOE difference spectra were obtained at 300 MHz with the Bruker program NOEDIFF.AU. Temperatures in DNMR experiments were calibrated with use of CH_3OH.[17] Free energies of activation were derived from the spectra with the Eyring equation[17] as given in eq 1.

$$\Delta G^* = -RT[\ln (k/T) + \ln (h/\kappa)] \text{ (kcal mol}^{-1}\text{)} \qquad (1)$$

Infrared Spectroscopy. Infrared data were obtained on a Perkin-Elmer 1430 spectrometer. Although Nujol mulls are quickly prepared and easily spread between NaCl or KBr plates for protection from the atmosphere, the Nujol oil blocks several important regions of the spectrum. The use of KBr pellets avoids this problem, but insulating them from the air can be cumbersome.[18] We have developed a simple way to manipulate KBr pellets of highly air-sensitive samples using a KBr "sandwich" prepared in a drybox. A layer of ground optical-grade KBr (about 100 mg) is placed in a KBr die, then a layer of the sample (3–5 mg) ground with KBr (about 45 mg) is added, and finally another layer of KBr (100 mg) is placed on top. All three layers of powder are then compressed in the die, which produces a translucent sample pellet. Diffusion of air and moisture through the outer layers of KBr is slow, as IR spectra of samples held in air for several hours are virtually identical with those taken immediately after a sample is removed from the drybox. Samples can be held overnight in a desiccator with little or no degradation.

Synthesis of Tri- and Tetraisopropylcyclopentadienes (Mixture). Aqueous KOH (50%; 1.575 L, ca. 20 mol) and Adogen 464 (20 g) were placed in a 3-L three-neck Morton flask fitted with a condenser, mechanical stirrer, heating mantle, thermometer, and an inlet adapter. Freshly cracked cyclopentadiene (41 mL, 0.50 mol) and isopropyl bromide (235 mL, 2.5 mol) were added through the condenser, and stirring was begun. The mixture turned brown and became warm (50 °C). The vigorously stirred mixture was maintained at 55 °C overnight, after which the contents of the flask were decanted into a 2-L separatory funnel, and the flask and remaining solid were washed with hexane (3 × 75 mL). The washings were combined with the contents of the separatory funnel and the layers separated. The hexane layer was washed with water (2 × 100 mL) and dried over $MgSO_4$, and the solvent evaporated, leaving a yellow-brown oil.

The oil was transferred to a 25 × 7.5 cm silica gel chromatography column and eluted with hexane (approximate elution volume 2200 mL). A yellow band was collected, and the solvent was removed by rotary evaporation. The yellow oil remaining after evaporation was heated to 210–220 °C to drive off volatiles. The residue was purified by a trap-to-trap vacuum distillation, yielding 73.1 g of a yellow oil that was dried over 3-Å molecular sieves. The material was characterized as a mixture of tri- and tetraisopropylcyclopentadienes by ^1H NMR.[13]

Synthesis of Potassium Tri- and Tetraisopropylcyclopentadienides (Mixture). The diene mixture was added dropwise over a period of 1 h to a magnetically stirred suspension of KH (14.4 g, 0.36 mol) in THF (400 mL). Gas was evolved, the flask became warm, and the suspension became slightly yellow. One-half hour after the addition was complete, the flask was slowly heated until the THF began to reflux, which was allowed to continue for 0.5 h. The mixture was then allowed to stir at room temperature overnight, during which time colorless crystals appeared. The solid was collected by filtration, washed with THF (2 × 50 mL), and dried under vacuum, yielding 33.1 g of a white solid that was identified as KCp^{3i} by the characteristic ^1H NMR spectrum of the anion.[13] A second crop could be obtained by concentrating the filtrate and washings to 100 mL and allowing the solution to stand. Total yield: 55.7 g (48% based on cyclopentadiene). Evaporation of the final filtrate to dryness yielded 27.2 g of a tan solid that was found by NMR to consist of KCp^{4i} and KCp^{3i} in a molar ratio of 64/36. This material was saved for hydrolysis (see below).

Synthesis of 1,2,3,4-Tetraisopropylcyclopentadiene. KCp^{3i} (55.5 g, 0.24 mol) was suspended in THF (375 mL) in a 500-mL Schlenk tube fitted with a reflux condenser and a septum. After the magnetically stirred suspension was cooled to 0 °C, isopropyl bromide (25 mL, 0.29 mol) was added by syringe over a period of 5 min. The mixture was allowed to warm slowly to room temperature and stirred for 48 h. The suspension was filtered through a medium-porosity frit and the filtrate evaporated to a light yellow oil.

The oil was added to a magnetically stirred suspension of KH (10.0 g, 0.25 mol) in THF (320 mL) over a period of 5 min. Gas was slowly evolved, and the reaction was heated to reflux and allowed to stir overnight. The suspension was filtered through a medium-porosity glass frit and then washed with hexane (50 mL). The solid was then dried under vacuum for 6 h, yielding 42.3 g of a white solid. A second crop of material was obtained by evaporating the filtrate and washings, leaving a suspension of a white solid in a slightly yellow oil. The oil was extracted into hexane and the suspension filtered. The retained precipitate was allowed to dry in the glovebox, yielding an off-white solid. The combined solids (44.8 g) were identified as a mixture of KCp^{4i} and KCp^{3i} in a 75/25 molar ratio (^1H NMR).

The KCp^{4i}/KCp^{3i} mixture was suspended in about 350 mL of hexane in a 500-mL Schlenk tube fitted with a reflux condenser and a septum. Degassed water (40 mL) was slowly added to the magnetically stirred suspension. After all the solids had dissolved, the hexane layer was separated and washed with a 50-mL portion of water. The solvent was removed at 50 °C with use of a rotary evaporator, and the residual oil

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was allowed to cool, producing a copious precipitate of colorless crystals. These were collected by vacuum filtration through a glass frit and washed with methanol (50 mL). A second crop of crystals was obtained by cooling the filtrate and washings to −18 °C. Additional HCp^{4i} could be had by hydrolyzing the dried tan filtrate from the first reaction of the isopropylcyclopentadienes with KH, giving a combined total yield of 22.0 g (19% based on starting cyclopentadiene).[19] Anal. Calcd for $C_{17}H_{30}$: C, 87.10; H, 12.90. Found: C, 86.95; H, 13.34. Its ^{1}H NMR spectrum is identical with that of the previously described material.[13] The diene is mildly air-sensitive, and should be kept under an inert atmosphere if long-term storage (> 1 week) is anticipated.

Synthesis of Potassium 1,2,3,4-Tetraisopropylcyclopentadienide (KCp^{4i}). Potassium hydride (1.32 g, 33 mmol) was added with stirring to a solution of 1,2,3,4-tetraisopropylcyclopentadiene (8.12 g, 35 mmol) in THF (100 mL) over a period of 3 min. Hydrogen was gradually evolved as the reaction proceeded, which was allowed to continue for 3 days. The reaction mixture was then filtered through a medium glass frit and the retained solid dried under vacuum. A second crop of the compound could be obtained by evaporating the filtrate to dryness and washing the residue with 2 × 20 mL portions of hexane. The combined yield of off-white, air-sensitive KCp^{4i} was 8.59 g (96%). Anal. Calcd for $C_{17}H_{29}K$: C, 74.93; H, 10.73; K, 14.35. Found: C, 75.42; H, 10.34; K, 13.92. The tetraisopropylcyclopentadiene should be either freshly prepared or recrystallized from ethanol before use; partially oxidized material provides substantially poorer yields (ca. 50%).

Synthesis of (Cp^{4i})$_2$Ca. KCp^{4i} (5.11 g, 18.7 mmol) was added to anhydrous CaI_2 (2.75 g, 9.4 mmol) in 125 mL of ether and the reaction stirred overnight. The mixture was then filtered through a medium glass frit and the filtrate evaporated to dryness. Hexane (75 mL) was added to the dried solid and the mixture stirred for 20 min. After the mixture was filtered, the filtrate was evaporated to dryness, leaving 4.03 g of a yellow solid of composition (Cp^{4i})$_2$Ca·0.16OEt$_2$ (ether content determined by ^{1}H NMR). After sublimation at 190 °C and 10^{-6} Torr, ether-free (Cp^{4i})$_2$Ca (3.65 g, 77%) was recovered as a white crystalline solid. Mp: 196–200 °C. Anal. Calcd for $C_{34}H_{58}Ca$: C, 80.56; H, 11.53; Ca, 7.91. Found: C, 80.93; H, 10.94; Ca, 7.84. ^{1}H NMR (C_7D_8, 300 MHz, 20 °C): δ 5.80 (s, 2 H, ring-C*H*); 3.08 (septet, 4 H, *J* = 7.2 Hz, C*H*Me$_2$); 2.97 (septet, 4 H, *J* = 6.7 Hz, C*H*Me$_2$); 1.42 (d, 12 H, *J* = 6.9 Hz, C*H*$_3$); 1.31 (d, 12 H, *J* = 7.2 Hz, C*H*$_3$); 1.29 (d, 12 H, *J* = 7.2 Hz, C*H*$_3$); 1.10 (d, 12 H, *J* = 6.6 Hz, C*H*$_3$). ^{13}C NMR (C_6D_6, 20 °C, saturated solution, proton decoupled): δ 129.3 (ring-*C*(*i*-Pr)), 124.4 (ring-*C*(i-Pr)), 101.6 (ring-*C*H), 27.5, 27.4, 26.9, 24.9, 24.7, 24.6. IR bands (KBr pellet, cm^{-1}): 2960 s, br; 1454 m; 1373 m, sh; 1358 m, sh; 1325 w; 1305 w; 1272 w; 1256 w; 1183 m; 1174 m; 1140 w; 1101 m; 1085 w; 1057 w; 1045 w; 1033 w; 984 mw; 768 m, sh; 685 m; 496 m; 455 w, br; 397 w; 374 w; 297 w.

Synthesis of (Cp^{4i})$_2$Ba. Potassium tetraisopropylcyclopentadienide (5.45 g, 20.0 mmol) was added to anhydrous BaI_2 (3.910 g, 10.0 mmol) in 110 mL of THF and the reaction stirred overnight. The mixture was then filtered through a fine glass frit and the filtrate evaporated to dryness. The dried solid was extracted with 125 mL of toluene and the suspension filtered through a fine frit. The filtrate was evaporated to dryness, leaving a white solid that still contained traces of THF (^{1}H NMR). The material begins to sublime at 90 °C and 0.01 Torr, although sublimation is more rapid at 160 °C and 10^{-3} Torr. Off-white (Cp^{4i})$_2$Ba is produced in 83% yield (5.04 g). Mp: 149–150 °C. Anal. Calcd for $C_{34}H_{58}Ba$: C, 67.59; H, 9.68; Ba, 22.73. Found: C, 67.09; H, 9.56; Ba, 23.50. ^{1}H NMR (C_7D_8, 400 MHz, 20 °C): δ 5.64 (s, 2 H, ring-C*H*); 3.08 (septet, 4 H, *J* = 7.2 Hz, C*H*Me$_2$); 2.94 (septet, 4 H, *J* = 6.8 Hz, C*H*Me$_2$); 1.31 (d, 12 H, *J* = 6.8 Hz, C*H*$_3$); 1.26 (d, 12 H, *J* = 7.2 Hz, C*H*$_3$); 1.22 (d, 12 H, *J* = 7.3 Hz, C*H*$_3$); 1.20 (d, 12 H, *J* = 6.8 Hz, C*H*$_3$). ^{13}C NMR (C_6D_6, 20 °C, saturated solution, proton decoupled): δ 129.0 (ring-*C*(i-Pr)), 123.8 (ring-*C*(i-Pr)), 101.3 (ring-*C*H), 27.2, 27.0, 26.8, 25.0, 24.0, 23.7. IR bands (KBr pellet, cm^{-1}): 2950 vs, br; 1448 s; 1408 w, sh; 1368 s; 1351 s, sh; 1320 s; 1302 m; 1263 m, v sh; 1178 s, sh; 1172 s, sh; 1138 m, sh; 1098 s; 1081 m; 1055 m; 1044 m; 1030 m; 981 m, sh; 875 w; 760 vs, sh; 686 vs, sh; 616 w, sh; 538 w; 518 w; 485 vs; 385 w; 365 m.

Molecular Orbital Calculations. Calculations on the Cp^{4i} anions were performed by the AM1 semiempirical approach[20] contained in the AMPAC (Version 3.0) set of programs. Methyl groups were idealized, and appropriate symmetry constraints were applied during optimization. Optimization for each geometry required about 45 min of CPU time on a VAX 8800 computer. A trial optimization removing all except symmetry constraints on configuration f (Figure 4) increased the required CPU time to 80 min but lowered ΔH_f by only 2 kcal mol^{-1} and produced only negligible changes in the geometry.

Table I. Crystal Data and Summary of Data Collection for $[(C_3H_7)_4C_5H]_2Ca$ and $[(C_3H_7)_4C_5H]_2Ba$

formula	$C_{34}H_{58}Ca$	$C_{34}H_{58}Ba$
fw	506.91	604.17
color of crystal	colorless	pale yellow
cryst dimens, mm	0.40 × 0.40 × 0.30	0.60 × 0.50 × 0.40
space group	*C*2/*c*	$P\bar{1}$
cell dimens[a]		
a, Å	34.033 (6)	16.682 (4)
b, Å	12.432 (6)	17.862 (2)
c, Å	16.495 (5)	12.396 (4)
α, deg		108.02 (3)
β, deg	111.29 (2)	90.56 (3)
γ, deg		111.12 (2)
V, Å^3	6503 (4)	3246 (2)
Z	8	4
D(calcd), g/cm^3	1.036	1.236
wavelength, Å	0.71069	
abs coeff, cm^{-1}	2.05	12.40
type of scan	ω–2θ	
scan speed, deg/min	16.0 (in ω)	
scan width, deg	1.21 + 0.30 tan θ	0.73 + 0.30 tan θ
bkgd counting	stationary counts; peak/background counting time 2:1	
limits of data collectn	6° ≤ 2θ ≤ 45°	6° ≤ 2θ ≤ 50°
total no. of reflecns collected	4586	11 885
no. of unique intensities	4495	11 454
no. with $F > 3.0\sigma(F)$	2102	6021
R for averaging	0.048	0.049
R(*F*)	0.044	0.039
$R_w(F)$	0.044	0.042
goodness of fit	1.40	1.23
max Δ/s in final cycle	0.18	0.03
max/min peak (final diff map) (e$^-$/Å^3)	0.16/−0.19	0.16/−0.27

[a] At 23 °C, 25 reflections (Ca); −120 °C, 25 reflections (Ba).

X-ray Crystallography of (Cp^{4i})$_2$Ca. Crystals of (Cp^{4i})$_2$Ca were grown from hexane. A suitable prism measuring 0.40 × 0.40 × 0.30 mm was located, coated with mineral oil, and sealed in epoxy in a capillary tube. All measurements were performed at Molecular Structure Corp. (The Woodlands, TX) on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation and a 12-kW rotating anode generator. Data were collected at 23 ± 1 °C. Relevant crystal and data collection parameters for the present study are given in Table I.

Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections. Based on systematic absences, packing considerations, and a statistical analysis of intensity distribution, the space group was determined to be the monoclinic *C*2/*c* (No. 15). Subsequent solution and refinement of the structure confirmed this choice. Data collection was performed with use of continuous ω–2θ scans with stationary backgrounds. The intensities of three representative reflections measured after every 150 reflections declined by 15%. A polynomial correction factor was applied to the data to account for the decay. Azimuthal scans of several reflections indicated no need for an absorption correction. Data were reduced to a unique set of intensities and associated σ values in the usual manner. The structure was solved by a combination of direct methods (MITHRIL and DIRDIF) and Fourier techniques. All non-hydrogen atoms were refined anisotropically. As not all of the hydrogens were evident on a difference Fourier map, their positions were calculated with idealized geometries based on packing considerations and *d*(C–H) = 0.95 Å. The positions were fixed for the final cycles of refinement. A final difference map was featureless. Non-hydrogen bond distances and angles are summarized in Table II.

X-ray Crystallography of (Cp^{4i})$_2$Ba. With use of methods analogous to those above, a crystal measuring 0.60 × 0.50 × 0.40 mm was located, transferred to the goniostat of a Rigaku AFC6R diffractometer, and cooled to −120 ± 1 °C for characterization and data collection. Crystal and data collection parameters are in Table I. Data collection was performed at Molecular Structure Corp.; subsequent data reduction and solution of the structure were performed at Vanderbilt University.

The space group was identified as the triclinic $P\bar{1}$ (No. 2) by a consideration of unit cell parameters, a statistical analysis of intensity distribution, and probable crystal packing. The choice of the unit cell was

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(19) If the oil remaining after the HCp^{4i} has been removed (largely HCp^{3i}) is sequentially treated with KH, *i*-PrBr, and then water, an additional 4.7 g of HCp^{4i} can be obtained. This raises the total yield to 26.7 g (23%).

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Table II. Average Bond Lengths (Å) and Angles (deg) in $[(C_3H_7)_4C_5H]_2Ca$ and $[(C_3H_7)_4C_5H]_2Ba$

$[(C_3H_7)_4C_5H]_2Ca$	
Ca–C(ring)	2.64 (1)
Ca–ring centroid	2.349, 2.352
C–C(ring)	1.41 (2)
C–C(Me) (*i*-Pr group)	1.52 (3)
ring centroid–Ca–ring centroid	162.3
C(Me)–C–C(Me) (*i*-Pr group)	110.2 (1.1)
planarity of rings	within 0.005 Å
twist angle between rings	29.4

$[(C_3H_7)_4C_5H]_2Ba$	conformer A	conformer B
Ba–C(ring)	2.94 (2)	2.94 (2)
Ba–ring centroid	2.679, 2.676	2.681, 2.683
C–C(ring)	1.42 (3)	1.42 (3)
C–C(Me) (*i*-Pr group)	1.53 (4)	1.53 (4)
ring centroid–Ba–ring centroid	154.3	154.1
C(Me)–C–C(Me) (*i*-Pr group)	110.0 (1.8)	110.3 (1.8)
planarity of Cp rings	within 0.005 Å	within 0.011 Å
twist angle between rings	31.4	32.0

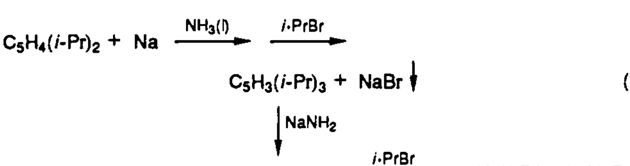
confirmed by subsequent solution and refinement of the structure. No decay was evident in the intensities of three representative reflections measured throughout the data collection. Azimuthal scans of several reflections indicated transmission factors ranging from 0.85 to 1.00; a correction for absorption was applied to the data. The structure was solved by a combination of Patterson techniques, direct methods (DIRDIF), and Fourier techniques. Two independent molecules were located in the asymmetric unit. All non-hydrogen atoms were refined anisotropically. As not all the hydrogen atoms were located in difference Fourier maps, their positions were calculated with use of idealized geometries based on packing considerations and d(C–H) = 0.95 Å. Their positions were fixed for the final cycles of refinement. A final difference Fourier map was featureless. Non-hydrogen bond distances and angles are summarized in Table II.

Results and Discussion

Synthesis of Tetraisopropylcyclopentadiene. Despite the dramatic advances in early-transition-metal and f-element chemistry that have been made possible by the development of facile syntheses for pentamethylcyclopentadiene[21,22] and a number of tetramethylalkyl ring systems,[23,24] routes to other highly alkylated cyclopentadienes have received substantially less attention.[25-27] The production of diisopropylcyclopentadiene can be accomplished in 85% yield by the stepwise addition of alkyl groups to cyclopentadiene in liquid ammonia (eq 2).[28]

$$C_5H_6 + Na \xrightarrow{NH_3(l)} \xrightarrow{i\text{-}PrBr} \xrightarrow{Na} \xrightarrow{i\text{-}PrBr} C_5H_4(i\text{-}Pr)_2 + 2NaBr\downarrow \quad (2)$$

Sitzmann has recently reported the conversion of this diene into tetraisopropyl- and pentaisopropylcyclopentadiene by an extension of the addition process (eq 3).[13,14] Although each step is relatively efficient, conversion of the intermediate dienes to their sodium salts, followed by reaction with isopropyl bromide, generates large quantities of alkali-metal halides that complicate manipulation. In addition, the many steps required make the preparation a relatively time-consuming one.



$$\begin{tikzcd} C_5H_4(i\text{-}Pr)_2 + Na \arrow[r, "NH_3(l)"] & \arrow[r, "i\text{-}PrBr"] & C_5H_3(i\text{-}Pr)_3 + NaBr\downarrow \arrow[d, "NaNH_2"] \\ & & NaC_5H_2(i\text{-}Pr)_3 \arrow[r, "i\text{-}PrBr"] & C_5H_2(i\text{-}Pr)_4 + NaBr\downarrow \end{tikzcd} \quad (3)$$

Recently, Venier and Casserly described the convenient phase-transfer-catalyzed productions of di- and tri-*tert*-butylcyclopentadienes using large excesses of KOH and *tert*-butyl bromide in the presence of a methyltrialkylammonium halide.[29] We have found that replacement of the alkyl bromide with isopropyl bromide generates in one step an oily mixture of tri- and tetraisopropylcyclopentadienes, which when treated with KH yields KCp^{3i} in 48% yield. Subsequent reaction with isopropyl bromide and a second treatment with KH yield a mixture of KCp^{4i} and KCp^{3i}, which on hydrolysis liberates free 1,2,3,4-tetraisopropylcyclopentadiene. After crystallization and recycling of small amounts of KCp^{4i} produced in earlier steps, the diene is produced in a net 23% yield. Undoubtedly part of the reason for the lower than desirable yield is the production of *gem*-dialkylated tetraisopropylcyclopentadienes during the alkylation of triisopropylcyclopentadiene; these resist conversion into the potassium salt (KCp^{4i}).[14] Although the synthesis at the current stage of optimization provides essentially the same yield as the reactions expressed in eqs 2 and 3 (21% total), it is somewhat more convenient and requires fewer steps. It is easily performed on a 0.5-mol scale.

Synthesis of $(Cp^{4i})_2Ae$. The reaction of KCp^{4i} with CaI_2 in diethyl ether or BaI_2 in THF yields the metallocenes $(Cp^{4i})_2Ca$ and $(Cp^{4i})_2Ba$ in good yield (eq 4). Unlike other soluble organo-alkaline-earth metallocenes,[8] $(Cp^{4i})_2Ca$ and $(Cp^{4i})_2Ba$ are obtained from ether solutions with only small amounts of associated solvent; the residue is easily removed by sublimation or extraction into aromatic hydrocarbons. Both metallocenes are thermally stable solids that readily crystallize from hexane. Several of their physical properties are notably different from that of the other alkaline-earth metallocenes, particularly the decamethyl derivatives. For example, unlike the nearly pyrophoric $Cp^*{}_2Ca$, crystals of $(Cp^{4i})_2Ca$ can be handled for several minutes in dry air without visible signs of decomposition. On occasion, a large crystal of $(Cp^{4i})_2Ca$ has displayed only moderate degradation after 0.5 h of exposure. Solid $(Cp^{4i})_2Ba$, although less sensitive than $Cp^*{}_2Ba$, will turn yellow after several seconds of exposure to air.

$$2KCp^{4i} + (Ca,Ba)I_2 \rightarrow (Cp^{4i})_2(Ca,Ba) + 2KI\downarrow \quad (4)$$

The volatility of $(Cp^{4i})_2Ba$ is enhanced over that of the decamethylmetallocene counterpart; it begins to sublime at 90 °C and 0.01 Torr, substantially less than the 190 °C and 10^{-6} Torr required for $Cp^*{}_2Ba$.[7] This change has occurred despite a 48% increase in molecular weight (from 408 to 604 g/mol). The volatility of $(Cp^{4i})_2Ba$ compares favorably with $Ba(FOD)_2$ (FOD = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate) and especially $Ba(TMHD)_2$ (TMHD = 2,2,6,6-tetramethyl-3,5-heptanedionate) (sublimes 230–240 °C, 10^{-5} Torr), compounds that have found use in chemical vapor deposition (MOCVD) applications, particularly in the fabrication of superconducting metal oxides.[30-33] Interestingly, $(Cp^{4i})_2Ca$ is considerably less volatile than $(Cp^{4i})_2Ba$; we have no completely satisfactory explanation for this, but packing arrangements in the solid undoubtedly play some role.

Mixtures of $(Cp^{4i})_2Ca$ and aromatic nitrogen heterocycles in toluene are virtually colorless, unlike the rapid reaction of $Cp^*{}_2Ca$ with bipyridine and pyrazines to form deep red and orange adducts.[3,34] $(Cp^{4i})_2Ba$ will form orange solutions with aromatic

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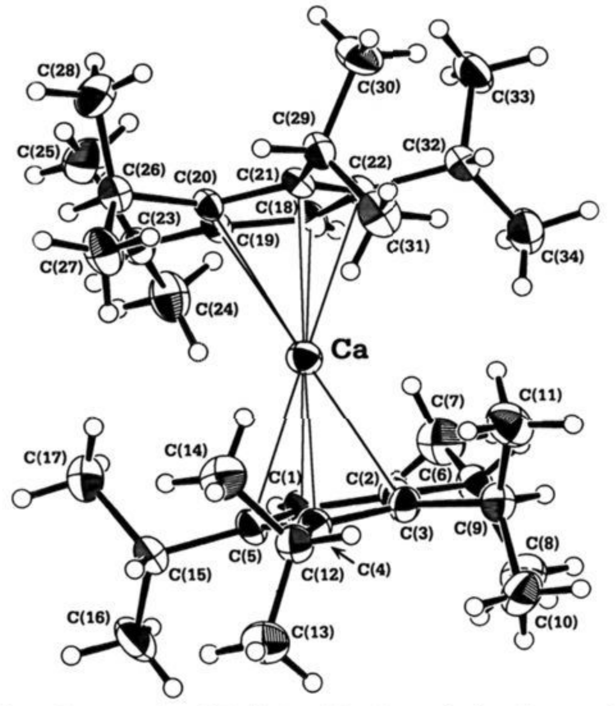

Figure 1. ORTEP view of $(Cp^{4i})_2Ca$, giving the numbering scheme used in the tables.

nitrogen heterocycles, presumably containing adducts like those generated from the decamethylmetallocenes.[3]

Solid-State Structure of $(Cp^{4i})_2Ca$. Bis(tetraisopropylcyclopentadienyl)calcium crystallizes with η^5 Cp^{4i} rings framing a Ca core in a "bent metallocene" geometry.[35] An ORTEP view of the molecule providing the numbering scheme used in the tables is displayed in Figure 1, and average structural parameters are summarized in Table II.

The average Ca–C distance of 2.64 (1) Å is identical with that in Cp^*_2Ca (solid state) (2.64 (2) Å)[7] and is comparable to that in $[Cp^*Ca(\mu\text{-}I)(THF)_2]_2$ (2.67 (1),[6] $(1,3\text{-}(SiMe_3)_2C_5H_3)_2Ca(THF)$ (2.68 (1)),[36,37] and $(MeCp)_2Ca(DME)$ (2.676 (9))[38] when the 0.06-Å difference between the radii of 7- and 6-coordinate Ca^{2+} is taken into account.[39]

The ring centroid–Ca–ring centroid angle of 162.3° in $(Cp^{4i})_2Ca$ is appreciably larger than the analogous angle found in Cp^*_2Ca, either in the solid state (147.0°)[7] or in the gas phase (154 (3)°).[40] A close examination of the Cp^{4i} rings reveals that they effectively enshroud the metal center. This is achieved not only through their intrinsic steric bulk but also through the orientation of the *i*-Pr groups relative to the ring. The dihedral angles between the three carbons of the *i*-Pr groups and the Cp ring vary from 69.9° to 89.6° (average 81.5°); i.e., the ring substituents are nearly perpendicular to the ring plane. Those methyl groups on the *i*-Pr groups adjacent to the unsubstituted ring carbon are oriented toward the cyclopentadienyl hydrogen, while the two other *i*-Pr groups are geared with each other (conformation f in Figure 4). Thus, only three of the four groups interlock in the completely geared arrangement found in, for example, hexaisopropylbenzene[41] and the pentaisopropylcobalticinium ion.[42]

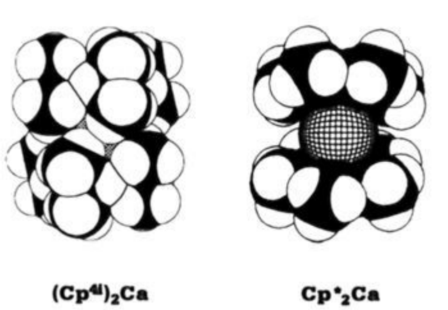

Figure 2. Space-filling viewes of $(Cp^{4i})_2Ca$ (on the left) and Cp^*_2Ca, indicating the near-total encapsulation of the metal center (crosshatched area) in the former.

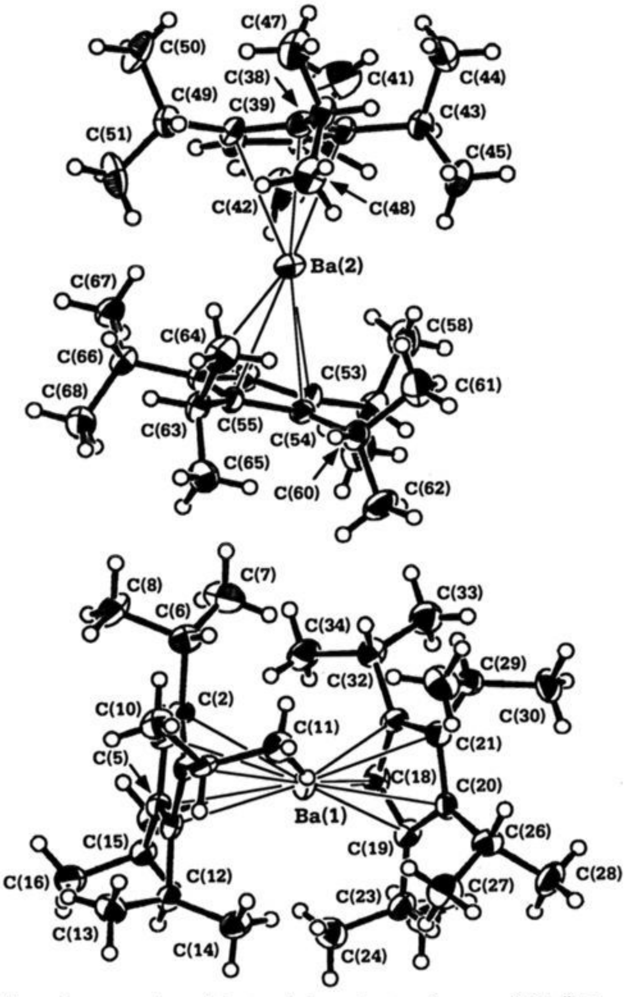

Figure 3. ORTEP view of the two independent conformers of $(Cp^{4i})_2Ba$, giving the numbering scheme used in the tables.

The orientation of the *i*-Pr groups is such that they mesh with the substituents of the other ring, forming a "cage" around the metal center. A guide to the nature of the *i*-Pr cage is provided by the space-filling drawing in Figure 2. The depiction of $(Cp^{4i})Ca$ is perhaps most meaningful when directly compared with an analogous drawing of the much more reactive Cp^*_2Ca. The combination of a nearly inaccessible metal center with the complex's improved air stability suggests that reaction of $(Cp^{4i})_2Ca$ with oxygen involves rate-determining attack on the metal center.

Solid-State Structure of $(Cp^{4i})_2Ba$. Bis(tetraisopropylcyclopentadienyl)barium crystallizes with a bent geometry analogous to that of the calcium derivative. Two crystallographically in-

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dependent, but otherwise nearly identical, molecules are present in the asymmetric unit. An ORTEP view of both molecules providing the numbering scheme used in the tables is displayed in Figure 3, and average structural parameters for the conformers are summarized in Table II. As the difference between the molecules is minimal, only one of them (A) will be discussed here.

The average Ba–C distance of 2.94 (1) Å is somewhat shorter than that in Cp$^*{}_2$Ba (solid state) (2.99 (2) Å)[7] but correlates well with the 2.96 (2) Å distance in [Cp$^*{}_2$Ba]$_2$(μ-C$_4$H$_4$N$_2$),[34] as the radii of 6- and 7-coordinate Ba^{2+} differ by 0.03 Å.[39]

As in the case of the calcium complex, the ring centroid–Ba–ring centroid angle of 154.3° in (Cp^{4i})$_2$Ba is substantially larger than the analogous angle found in the decamethylmetallocene counterpart in the solid state (131.0°);[7] the difference from the gas-phase value (148 (6)°) may be only marginally significant.[40] Again, the planes formed by the three carbons of the *i*-Pr groups are almost perpendicular to the ring planes (minimum 62.7°; maximum 88.6°; average 80.9°), and the *i*-Pr groups adopt the same semigeared arrangement observed in the calcium analogue (type f in Figure 4). The larger separation between the Cp^{4i} rings in the barium complex, a consequence of the metal's greater radius, may account for the greater air sensitivity of (Cp^{4i})$_2$Ba over (Cp^{4i})$_2$Ca.

Implications for Bending Forces in Ionic Metallocenes. A recent analysis of the structure of the decamethylmetallocenes of Ca, Ba, Sm, Eu, and Yb has determined that the unusual bent structures observed for these species are not a consequence of a readily identifiable pattern in lattice packing, but most likely reflect intramolecular electronic forces that are still imperfectly understood.[7] Electron diffraction studies of Cp$^*{}_2$Ca, Cp$^*{}_2$Sr, Cp$^*{}_2$Ba, and Cp$^*{}_2$Yb, which find them to be bent in the gas phase, support this conclusion.[40,43,44]

The results obtained with the decamethylmetallocenes are reinforced in the present study of (Cp^{4i})$_2$Ca and (Cp^{4i})$_2$Ba. Both complexes are bent and are separated in the solid state even more than the Cp* analogues. The closest intermolecular methyl-methyl contact in (Cp^{4i})$_2$Ca is at 3.77 Å, somewhat more than the 3.52-Å separation observed in Cp$^*{}_2$Ca; the analogous numbers for the barium systems are 3.67 and 3.49 Å.[7] In particular, (Cp^{4i})$_2$Ba displays none of the "chainlike" behavior observed in Cp$^*{}_2$Ba, which may contribute to distortions in the latter's structure and serve to lower its volatility.

The ring centroid–metal–ring centroid angles in the (Cp^{4i})$_2$Ae complexes are larger by 15° (Ca) and 23° (Ba) than in the crystalline Cp$^*{}_2$Ae analogues. The unsubstituted carbon positions on the rings, which offer the least resistance to bending, are brought most closely together in both (Cp^{4i})$_2$Ae metallocenes, but the bending cannot be solely the result of steric interactions between the rings. The closest intramolecular methyl-methyl contact in (Cp^{4i})$_2$Ba, for example, is between C(7) and C(34) at 3.94 (1) Å, approximately the sum of the van der Waals radii of the methyl groups (4.0 Å).[45] Conversely, because the intramolecular contacts are so long, it is probably incorrect to view the larger bending angles in (Cp^{4i})$_2$Ae simply as the result of the bulky Cp^{4i} rings "forcing" the rings closer to parallelism. The different angles observed between (Cp^{4i})$_2$Ae and Cp$^*{}_2$Ae thus most likely stem from electronic differences between the Cp^{4i-} and Cp^{*-} anions. Even though such differences may be small, changing the angle between Cp rings in ionic metallocenes is not expected to be energetically costly.[44]

Conformations of the Cp^{4i-} Anion. Although the steric inducements for perfect gearing are reduced in a cyclopentadienyl ring with less than complete substitution, the partially geared arrangement of *i*-Pr groups found in the solid state structure of (Cp^{4i})$_2$Ca and (Cp^{4i})$_2$Ba was initially unexpected. We were interested in determining whether this conformational preference could be modeled with MO calculations performed on the Cp^{4i-} ligand itself. Even though the MO results apply strictly to gas-phase Cp^{4i-} ions, the energies might parallel those of the Cp^{4i-} ligand in a highly ionic environment such as the alkaline-earth metallocenes. Furthermore, although the AM1 semiempirical approach has been parametrized for neutral molecules, it successfully reproduces the heats of formation of many organic anions,[20] and at least qualitative trends determined by it should be valid.

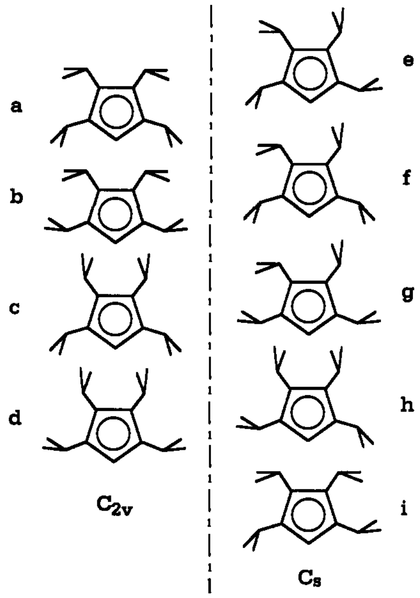

Figure 4. Possible conformers of the Cp^{4i} ligand. The short arms represent the orientation of the isopropyl methyl groups.

The Cp^{4i-} ligand offers a rich array of conformational possibilities, depending on the orientation of the *i*-Pr groups (Figure 4). Only three of these (a, e, and f) do not have potentially destabilizing close methyl-methyl contacts, and they were chosen for initial study. The configuration of the Cp^{4i-} anion found in the solid-state structure of (Cp^{4i})$_2$Ca (f) is calculated to have the lowest heat of formation (−45.1 kcal mol^{-1}), although the completely geared arrangement (e) is negligibly different (−44.0 kcal mol^{-1}). The heat of formation for the one other configuration that does not have direct methyl-methyl contacts (a) is −41.4 kcal mol^{-1}, still not significantly different from the solid-state arrangement. These results parallel those from molecular mechanics studies, which have found nongeared isopropyl groups to be energetically competitive with geared arrangements when neighboring groups are small.[46] It is noteworthy that nongeared isopropyl groups are found in [tris(4,5-diisopropylimidazol-2-yl)phosphine]dichlorozinc(II), which has only two adjacent *i*-Pr groups on a rigid five-membered ring system.[47]

The other Cp^{4i} configurations (b–d, g–i) all have unavoidably short (<3.3-Å) methyl-methyl contacts that significantly destabilize them. An attempt to optimize the AM1 geometry for configuration g failed, and the calculated heat of formation remained positive. These configurations would seem at best to represent transition geometries, rather than energy minima.[48]

Solution Behavior of (Cp^{4i})$_2$Ca and (Cp^{4i})$_2$Ba. Rotational barriers in metallocenes have been of considerable help in evaluating the importance of inter- and intramolecular interactions in cyclic polyenes.[49] Data have been obtained on the rates of

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(48) The X-ray crystal structure of a TCNQ adduct of (Cp^{4i})$_2$Fe has recently been determined, and the Cp^{4i} rings are found in configuration a of Figure 4. This supports our finding that it represents one of the three lowest energy configurations of the Cp^{4i} anion. Sitzmann, H. Personal communication.

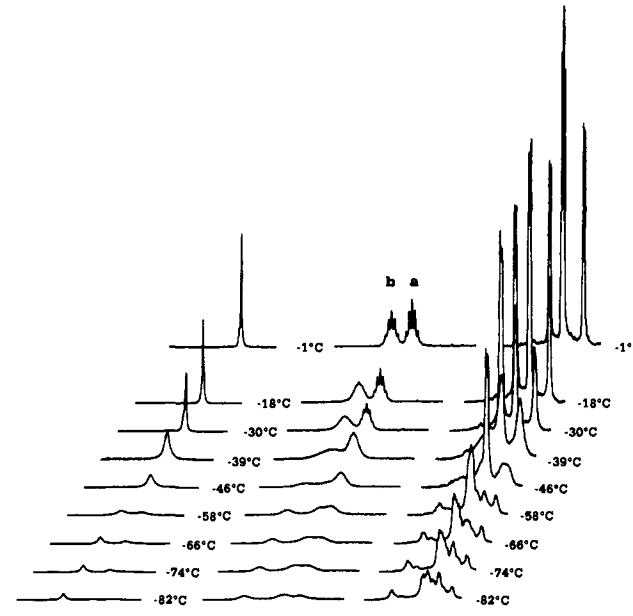

Figure 5. Variable-temperature ^{1}H NMR spectra of $(Cp^{4i})_2Ca$ in toluene-d_8 (400 MHz). The spectrum of −1 °C, which is essentially identical with that observed at ambient temperature (20 °C), has been offset for clarity.

phenyl group rotation in octaphenylferrocene[15] and 1,1′-diphenyluranocene[50] and for the rates of rotation around the metal ring–centroid axis in a number of transition-metal metallocenes.[51–53] Unless substituents of substantial bulk are present on the cyclopentadienyl ring, however, the energies of activation for ring rotation are low ($\Delta G^{\ddagger} < 3$ kcal mol^{-1}). Thus, the barriers in 1,1′,3,3′-tetra-*tert*-butylferrocene[54] and octaisopropylferrocene[13] are 13.1 and 13.6 kcal mol^{-1}, respectively, although no barrier is measurable for octaphenylferrocene.[15]

Evaluation of rotational barriers in isopropyl-substituted metallocenes is complicated because of the variable effective steric bulk of an *i*-Pr group. It can be nearly as bulky as a *t*-Bu group when viewed from the side of the two methyl groups, but as compact as a methyl group if viewed from the opposite face. This bifunctional behavior creates opportunities for anisotropic effects not possible from more symmetrical ligands.[55] The "cage-forming" ability of the *i*-Pr groups of the Cp^{4i} ligand in the $(Cp^{4i})_2Ae$ metallocenes was of considerable interest in this regard, and the *i*-Pr conformations proved amenable to experimental study of DNMR spectroscopy.

The room-temperature (20 °C) ^{1}H NMR spectra of $(Cp^{4i})_2Ca$ and $(Cp^{4i})Ba$ in toluene-d_8 are similar and consist of a singlet for the cyclopentadienyl hydrogen, two septets from the isopropyl methine hydrogens, and four doublets for the methyl protons, as expected for two sets of CH_3 groups endo and exo to the metal. Cooling the solutions causes dramatic changes in each part of the spectra, which differ somewhat for each compound. The spectra of $(Cp^{4i})_2Ca$ in toluene-d_8 are illustrated in Figure 5; those of $(Cp^{4i})_2Ba$ are similar except for the behavior of the cyclopentadienyl hydrogen, presented in Figure 6.

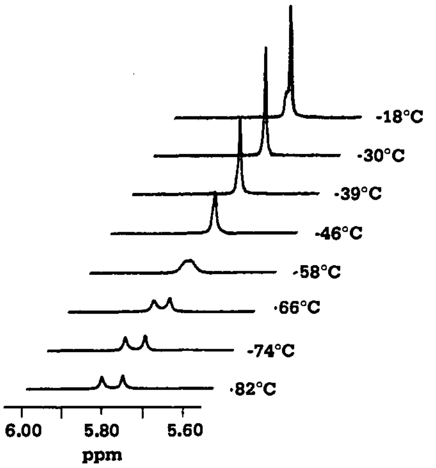

Figure 6. Variable-temperature ^{1}H NMR spectra of the cyclopentadienyl proton resonance in $(Cp^{4i})_2Ba$ in toluene-d_8 (400 MHz).

The methine resonances of $(Cp^{4i})_2Ca$ broaden as the temperature is lowered, with the downfield septet (b) losing resolution more rapidly than its upfield counterpart (a). Below −39 °C, peak b decoalesces into two resonances that gradually become sharper and show some evidence of coupling patterns. The peaks continue to move apart as the temperature is lowered, reaching a separation of 93.5 Hz at −89 °C, but a limiting spectrum is not obtained. Septet a broadens more slowly than does b, and coupling is not lost until −58 °C. Some spectra show evidence of a second peak (a shoulder) at −74 °C, but all definition is lost shortly below that. In $(Cp^{4i})_2Ba$, the downfield septet b again broadens more rapidly than does the upfield; below −39 °C, the peak decoalesces into two resonances that gradually become sharper and show coupling patterns. A limiting separation of 47.0 Hz is reached at −74 °C. As in $(Cp^{4i})_2Ca$, the upfield septet a in $(Cp^{4i})_2Ba$ broadens more slowly than does the downfield resonance, splitting below −58 °C into two peaks that reach a separation of 39.9 Hz at −82 °C, but a limiting spectrum is not obtained.

An attempt was made to identify the septets that arose from the methine protons adjacent to the cyclopentadienyl hydrogen with use of difference NOE spectroscopy. $^3J_{HH}$ coupling constants allowed for the ready assignment of methine and methyl groups on any isopropyl substituent for either the Ca or Ba analogue. NOE enhancement of the cyclopentadienyl hydrogen signal in $(Cp^{4i})_2Ca$ was observed when methyl peaks associated with septet a were selectively irradiated, suggesting that septet a arises from the methine hydrogens on the *i*-Pr groups closest to the cyclopentadienyl hydrogen. The NOE results at 20 °C were not conclusive with $(Cp^{4i})_2Ba$, but given the similarity between other features of the $Cp(^{4i})_2Ca$ and $(Cp^{4i})_2Ba$ spectra, the NOE results for $(Cp^{4i})_2Ca$ can probably be transferred to the barium compound as well.

The behavior of the methyl resonances in $(Cp^{4i})_2Ca$ is more complex, but a general broadening is observed as the temperature is lowered, with the coupling on the farthest downfield methyl peak (associated with septet a) being the last to disappear. As the sample is cooled below −30 °C, several new peaks become evident; at −82 °C, the tops of six broad peaks are present, but shoulders on them suggest the presence of eight or more resonances. An analogous array of at least six broad peaks are observed at −82 °C for $(Cp^{4i})_2Ba$.

The cyclopentadienyl hydrogen singlet in $(Cp^{4i})_2Ca$ shifts slowly downfield as the temperature is lowered (ca. 0.01 ppm/10 °C) until it broadens and splits below −46 °C into two peaks in an area ratio of 3 (downfield) to 2 (upfield). A separation of 42.2 Hz is reached at −82 °C, but a limiting spectrum is not obtained. The behavior of the singlet in $(Cp^{4i})_2Ba$ is similar (Figure 6), with the singlet splitting at −58 °C into a symmetrical doublet, reaching a limiting separation of 20.7 Hz at −82 °C.

The changes in the NMR spectra can be interpreted as a consequence of dynamic processes involving hindered rotation

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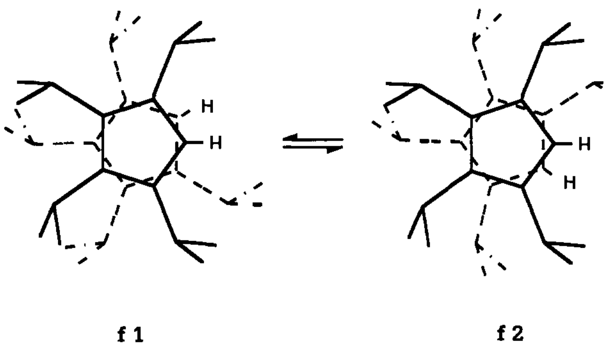

Figure 7. Equilibrium between two rotamers of $(Cp^{4i})_2Ae$. The hydrogen atoms are diastereomeric and give rise to separate resonances.

either around the metal–ring centroid axes or around the ring–C–$CHMe_2$ bonds. If the conformation of the Cp^{4i} rings at low temperature is essentially that observed in the solid state, slowing of ring rotation would eventually produce the two rotamers depicted in Figure 7. Four methine protons would be inequivalent in each rotamer, giving rise to a total of eight resonances, which are only imperfectly resolved at the lowest temperatures. The splitting of the cyclopentadienyl hydrogen singlet also follows from hindered ring rotation, as the ring protons in the two rotamers are diastereomeric, and sufficiently slow equilibration of structure f1 and f2 would produce the two NMR resonances observed at low temperature. The two conformers are detectably unequal in energy in $(Cp^{4i})_2Ca$, as evidenced by the 3/2 area ratio of the peaks; steric interactions may make the more crowded conformer f1 somewhat higher in energy. This is evidently not a problem with $(Cp^{4i})_2Ba$, since the peaks are of equal area. Application of the Eyring equation to the data from the spectra of $(Cp^{4i})_2Ca$ ($T_c = 227$ K, $\Delta\nu \geq 42.2$ Hz) leads to $\Delta G^{\ddagger} \leq 11.1$ kcal mol^{-1}; with $(Cp^{4i})_2Ba$ ($T_c = 198$ K, $\Delta\nu = 20.7$ Hz), $\Delta G^{\ddagger} = 10.8$ (± 0.4) kcal mol^{-1}.

Spectra of equivalent complexity would be observed if slowing of rotation around the ring–C–$CHMe_2$ bonds were the primary process observed at low temperatures. If the *i*-Pr orientations are limited to those identified as of lowest energy (a, e, and f in Figure 4), three metallocene conformers could be generated (Figure 8). Conformation f3 seems unlikely to be present in any appreciable concentration, as two of the three close interligand interactions would occur next to the ring proton, and thus on the most sterically crowded side of the metallocene (cf. the bending observed in the crystal structure). Conformations f4 and f5 are probably of comparable energy, since f4's single unfavorable *i*-Pr/*i*-Pr interaction is on the "open" side of the metallocene. Each conformation would give rise to four resonances from the methine protons and to a single resonance from the ring hydrogen, generating a maximum of eight methine resonances and two cyclopentadienyl resonances. As before, coincidental overlap or imperfect resolution prevents all the methyl resonances from being observed.

Without a limiting separation, activation parameters for septet b in $(Cp^{4i})_2Ca$ cannot be reliably calculated, but based on a coalescence temperature of −39 °C, and a maximum observed peak separation of 93.5 Hz, $\Delta G^{\ddagger}$ should not be greater than 11.1 kcal mol^{-1}. Use of the Eyring equation for the data on septet b in $(Cp^{4i})_2Ba$ ($T_c = 234$ K, $\Delta\nu = 47.0$ Hz) yields $\Delta G^{\ddagger} = 11.4$ (± 0.3) kcal mol^{-1}; for septet a ($T_c = 215$ K, $\Delta\nu \geq 39.9$ Hz), $\Delta G^{\ddagger} \leq 10.5$. The values for b are similar to those measured for the exchange of *i*-Pr groups between two geared conformations in 1,3-dibenzyl-4,5-diisopropylimidazoline-2-thione ($\Delta G^{\ddagger}_{229K} = 11.5 \pm 0.1$ kcal mol^{-1})[55] and 3,4-diisopropyl-5-methyl-Δ^4-thiazolin-2-one ($\Delta G^{\ddagger}_{227K} = 11.9$ kcal mol^{-1}),[56] which like the Cp^{4i} ligand have adjacent *i*-Pr groups on rigid five-membered rings. As with the thione and thiazolinone, the value of $\Delta G^{\ddagger}$ is appropriate for stepwise, rather than concerted, rotation of the *i*-Pr groups.[46,57]

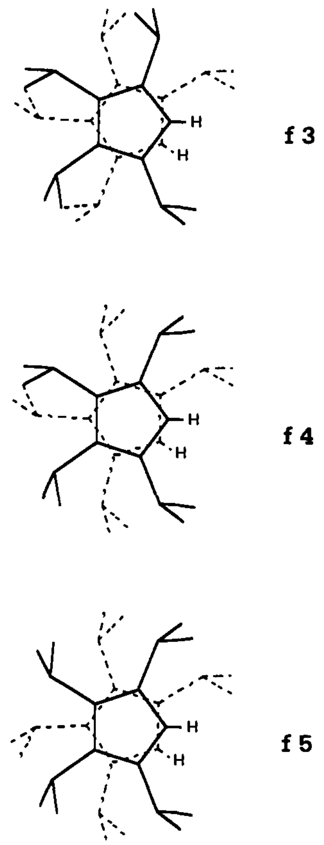

Figure 8. Equilibrium between the $(Cp^{4i})_2Ae$ rotamers that might arise from *i*-Pr group rotation.

If other ring or *i*-Pr orientations were present in enough concentration to be detectable by NMR spectroscopy, considerably more complicated spectra would arise. Which of the two rotation mechanisms is primary cannot be definitely established on the basis of the available metallocene data. Considering that the average $\Delta G^{\ddagger}$ values in $(Cp^{4i})_2Ca$ (≤ 11.1 kcal mol^{-1}) and $(Cp^{4i})_2Ba$ (11.1 (± 0.5) kcal mol^{-1}) are identical, however, we tentatively suggest that hindered *i*-Pr rotation, which should be more independent of the metal environment, may be of greater importance. Clarification of this point will require studies with other ring systems; these are in progress.[9]

Owing to their identical ligand sets, a direct comparison of the activation energies in $(Cp^{4i})_2Ae$ can be made with the value of $\Delta G^{\ddagger} = 13.6$ kcal mol^{-1} measured for hindered rotation in tetraisopropylferrocene in toluene-d_8. It is not surprising that the barrier is lower in the alkaline-earth species (whether for ring or *i*-Pr group rotation), given the greater separation of the rings in the latter (the metal radius of 6-coordinate Fe^{2+} is 0.61 Å; values for Ca^{2+} and Ba^{2+} are 1.00 and 1.35 Å, respectively[39]).

Conclusions

The use of cage-forming tetraisopropylcyclopentadienyl rings endows the metallocenes of calcium and barium with higher levels of air stability and volatility than previously observed in organo-alkaline-earth systems and has provided evidence for selective reactivity toward bases. Solution measurements have demonstrated that hindered rotation of the *i*-Pr groups within the Cp^{4i} rings or around the metal–ring centroid axis is observable at low temperatures. Such behavior might be considered somewhat at odds with the expectation that compounds of the heavy alkaline-earth metals should have high kinetic lability. It is becoming increasingly clear, however, that ligands and solvents can engender

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(57) The somewhat lower energy of activation for the *i*-Pr groups adjacent to the cyclopentadienyl hydrogen could be a result of reduced steric hindrance to rotation (i.e., its being bordered by a hydrogen and an *i*-Pr group, instead of two *i*-Pr groups). This difference is not observed in methylcyclohexane-d_{14} solution, however, and solvent interactions may play a significant role in the effect. Williams, R. A.; Hanusa, T. P. Unpublished results.

marked variations in this property. In compounds such as $(Cp^{4i})_2Ae$, which are readily soluble in aromatics and even alkanes, tight ion pairing between metal and ligand can endow the complexes with a type of "pseudo-covalency" that suppresses ligand exchange and rearrangement.

The effects of encapsulating ligands on the properties of alkaline-earth metallocenes demonstrate some of the control that is available over the reactions of highly ionic compounds. We expect elaboration of this principle to broaden even further the range of chemistry accessible to organometallics of the heavy s-block elements.

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Supplementary Material Available: Tables of atomic fractional coordinates, bond distances and angles involving non-hydrogen atoms, dihedral angles between Cp and *i*-Pr groups in $[(C_3H_7)_4C_5H]_2Ca$ and $[(C_3H_7)_4C_5H]_2Ba$, and anisotropic thermal parameters (25 pages); listings of observed and calculated structure factor amplitudes (71 pages). Ordering information is given on any current masthead page.

Interaction of Bis(platinum) Complexes with the Mononucleotide 5′-Guanosine Monophosphate. Effect of Diamine Linker and the Nature of the Bis(platinum) Complex on Product Formation

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Abstract: The reactions of bis(platinum) complexes containing bidentate or monodentate coordination spheres with the mononucleotide guanosine 5′-monophosphate (GMP) have been studied in solution by ^1H and ^{195}Pt NMR spectroscopy. The structures of the complexes are $[\{cis\text{-}PtCl_2(NH_3)\}_2(diamine)]$ (bidentate coordination spheres, 2,2/c,c) and $[\{trans\text{-}PtCl(NH_3)_2\}_2(diamine)]Cl_2$ (monodentate coordination spheres, 1,1/t,t) where diamine = 1,4-butanediamine $(NH_2(CH_2)_4NH_2$, BN) or 2,5-dimethyl-2,5-hexanediamine $(NH_2C(CH_3)_2(CH_2)_2C(CH_3)_2NH_2$, TMET). The 2,2/c,c complexes were studied as the aqua species $[\{cis\text{-}Pt(H_2O)_2(NH_3)\}_2(diamine)]^{4+}$ by reaction of the iodide with 4 equiv of $AgNO_3$ in water. In the case of the monodentate bis(platinum) complexes, the stepwise substitution of two GMP groups is easily seen, giving $[\{trans\text{-}Pt(GMP)(NH_3)_2\}_2(diamine)]$. The rate of reaction at 30 °C as measured by $t_{1/2}$ from the spectra was faster with TMET (3.5 h) than with BN (4.5 h). For bis(platinum) complexes with bidentate coordination spheres, the final product is $[\{cis\text{-}Pt(GMP)_2(NH_3)\}_2(diamine)]^{4-}$ but the mode of formation is dependent on the diamine. Whereas no intermediate species were observed with the linear $NH_2(CH_2)_4NH_2$, the sterically more demanding $NH_2C(CH_3)_2(CH_2)_2C(CH_3)_2NH_2$ gave in the initial stages of the reaction the species with only one GMP bound to each Pt $[\{Pt(GMP)(H_2O)(NH_3)\}_2(diamine)]$. All GMP ligands are N7 bound. The reactions are discussed in relation to the DNA binding and antitumor activity of the complexes.

The mechanism of action of the antitumor activity of bis(platinum) complexes containing two platinum–amine units linked by a variable-length diamine chain is of considerable interest. We have now reported the synthesis and properties of complexes containing bidentate coordination spheres $[\{cis\text{-}PtCl_2(NH_3)\}_2(diamine)]$ and monodentate coordination spheres $[\{trans\text{-}PtCl(NH_3)_2\}_2(diamine)]Cl_2$.[1,2] The antitumor activity of both sets of complexes is characterized by activity in both murine and human tumor cell lines with natural and acquired resistance to cisplatin.[2-4] It is particularly noteworthy that the presence of a cisplatin group is not necessary for antitumor activity, especially in cisplatin-resistant cells. DNA-binding studies have shown that an important interaction, inaccessible to cisplatin, is the formation of interstrand cross-links through binding of the two platinum centers to opposite DNA strands.[2,5] Our present studies include the description of this DNA-binding mode and its importance in the mechanism of cytotoxicity of these complexes.

The mechanism by which bis(platinum) complexes overcome cisplatin resistance is important, because it is possible that unique modes of the DNA binding of bis(platinum) complexes inaccessible to monomeric species are responsible for overcoming the resistance, either through enhanced cytotoxicity or because the bis(platinum)-induced DNA lesions are inherently more difficult to repair. Thus, there may exist a molecular basis to enhancement of non-cross-resistance, and the exploration of this aspect may eventually lead to discovery of platinum complexes with a spectrum of clinical anticancer activity different from cisplatin and its "second-generation" analogues.

The modes of DNA binding of bis(platinum) complexes with bidentate coordination spheres (2,2/c,c) are a complex array including interstrand cross-links (by each Pt binding to opposite strands) and intrastrand cross-links (by cisplatin-like binding to two adjacent bases on a single strand). Bis(platinum) complexes with monodentate coordination spheres, on the other hand, can

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