

# Structures of Ionic Decamethylmetallocenes: Crystallographic Characterization of $(\text{Me}_5\text{C}_5)_2\text{Ca}$ and $(\text{Me}_5\text{C}_5)_2\text{Ba}$ and a Comparison with Related Organolanthanide Species

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Distillation of a toluene solution of  $\text{Cp}^*_2\text{Ca}[\text{O}(\text{C}_2\text{H}_5)_2]$  ( $\text{Cp}^* = \text{Me}_5\text{C}_5$ ) or vacuum sublimation of  $\text{Cp}^*_2\text{Ba}(\text{THF})_2$  readily produces the solvent-free metallocenes.  $\text{Cp}^*_2\text{Ca}$  crystallizes from hexane in the monoclinic space group  $P2_1/n$ , with  $a = 9.721(2) \text{ \AA}$ ,  $b = 12.361(2) \text{ \AA}$ ,  $c = 30.849(10) \text{ \AA}$ ,  $\beta = 96.34(1)^\circ$ , and  $D_c = 1.12 \text{ g cm}^{-3}$  for  $Z = 8$ . Least-squares refinement on the basis of 3560 observed reflections measured at 116 K led to a final  $R$  value of 0.0594. Two independent bent metallocenes appear in the asymmetric cell, with average Ca-C distances of 2.64 (1)  $\text{ \AA}$  [2.64 (2)  $\text{ \AA}$ ] and ring centroid-Ca-ring centroid angles of  $147.7^\circ$  [ $146.3^\circ$ ]. The smallest intermolecular Ca $\cdots$ CH $_3$ ' contact is 2.98  $\text{ \AA}$ .  $\text{Cp}^*_2\text{Ba}$  crystallizes from toluene in the space groups  $P2_1/n$ , with  $a = 18.043(4) \text{ \AA}$ ,  $b = 11.830(2) \text{ \AA}$ ,  $c = 18.206(4) \text{ \AA}$ ,  $\beta = 105.67(1)^\circ$ , and  $D_c = 1.45 \text{ g cm}^{-3}$  for  $Z = 8$ . Least-squares refinement on the basis of 4482 reflections collected at 118 K produced a final  $R$  of 0.0295. Two independent metallocenes also appear in the asymmetric unit, with average Ba-C distances of 2.98 (1)  $\text{ \AA}$  [2.99 (1)  $\text{ \AA}$ ] and ring centroid-Ba-ring centroid angles of  $130.9^\circ$  [ $131.0^\circ$ ]. The shortest intermolecular Ba $\cdots$ CH $_3$ ' distance is 3.349 (5)  $\text{ \AA}$ . The metallocene units pack so that, in addition to the two  $\text{Cp}^*$  rings directly bonded to the barium center, the face of a third  $\text{Cp}^*$  ring is in close proximity to the metal. A comparison of the solid-state structures for the ionic metallocenes  $\text{Cp}^*_2\text{M}$  ( $\text{M} = \text{Ca}$ ,  $\text{Yb}$ ,  $\text{Sm}$ ,  $\text{Eu}$ ,  $\text{Ba}$ ) reveals a strong linear correlation between the metal ionic radius and the ring centroid-M-ring centroid angles; this correlation is analyzed in terms of intra- and intermolecular steric interactions. Intramolecular methyl-methyl repulsions may contribute to the regularity in the bending angles in all the decamethylmetallocenes.

## Introduction

Compounds constructed around highly electropositive metal centers (groups 1-3) are often structural chameleons, with geometries that are highly sensitive to the amount of ligand-ligand contact on the metal coordination sphere. Assignment of the degree of covalent bonding in such compounds by means of structural criteria is consequently fraught with ambiguities.<sup>1</sup> A particularly intriguing example of these difficulties is provided by the recent discoveries that various bis(pentamethylcyclopentadienyl)-alkaline-earth-metal and -lanthanide complexes are bent in the solid state ( $\text{M} = \text{Sm}$ ,  $\text{Eu}$ )<sup>2,3</sup> and in the gas phase ( $\text{M} = \text{Yb}$ ,  $\text{Ca}$ ,  $\text{Sr}$ ,  $\text{Ba}$ ).<sup>4-6</sup> Discussions of the relative importance of electrostatic and covalent bonding in these compounds<sup>7-9</sup> are clouded by the difficulties in assessing the importance of crystal packing forces in the solid state and thermal averaging effects in the gas phase. Because of the latter, parallel sandwich geometries cannot be rigorously excluded for the vapor-phase structures of  $\text{Cp}^*_2\text{Yb}$ ,  $\text{Cp}^*_2\text{Ca}$ ,  $\text{Cp}^*_2\text{Sr}$ , and  $\text{Cp}^*_2\text{Ba}$ .<sup>6</sup>

It was with the intent to examine more closely the structural relationships in ionic metallocenes that we sought to determine the solid-state geometries of  $\text{Cp}^*_2\text{Ca}$  and  $\text{Cp}^*_2\text{Ba}$ . The crystal structure of insoluble  $\text{Cp}_2\text{Ca}$  was determined several years ago but was found to possess a complex polymeric structure.<sup>10</sup> On the basis of the hydrocarbon solubility and relatively high volatility of  $\text{Cp}^*_2\text{Ca}$  and  $\text{Cp}^*_2\text{Ba}$ ,<sup>11</sup> we expected the decamethylmetallocenes of calcium and barium to be monomeric, or at least oligomeric ( $[\text{Cp}^*_2\text{M}]_n$ ,  $n = 2-5$ ), in the solid state. The noble-gas cores of  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  are both smaller and larger, respectively, than the metal centers of the crystallographically characterized divalent  $\text{Cp}^*_2\text{Ln}$  species,<sup>12</sup> and hence comparisons among the complexes might reveal size-related structural trends that would not otherwise be

evident. A portion of this work has already appeared in a preliminary account.<sup>13</sup>

## Experimental Section

All manipulations were performed with the rigid exclusion of air and moisture. Chemicals were handled with high-vacuum or Schlenk techniques, or in a Vacuum Atmospheres HE-143 drybox equipped with an MO40-1 recirculating purifier. NMR spectra were obtained at 300 MHz with a Bruker NMR spectrometer.

**Materials.**  $\text{Cp}^*_2\text{Ca}(\text{THF})_2$  and  $\text{Cp}^*_2\text{Ba}(\text{THF})_2$  were prepared from the reaction of  $\text{KCp}^*$  and  $\text{AeI}_2$  ( $\text{Ae} = \text{alkaline-earth metal}$ ) in THF.<sup>14</sup> Coordinated THF is difficult to remove from the calcium disolvate, and various attempts at desolvation, including sublimation, gave unsatisfactory results. To overcome this problem, the diethyl ether adduct of the complex was prepared,

- (1) Sockwell, S. C.; Hanusa, T. P. *Inorg. Chem.* **1990**, *29*, 76-80.
- (2) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270-4272.
- (3) Evans, W. J.; Hughes, L. A.; Hanusa, T. P.; Doedens, R. J. *Organometallics* **1986**, *5*, 1285-1291.
- (4) Andersen, R. A.; Boncella, J. M.; Burns, C. J.; Blom, R.; Haaland, A.; Volden, H. V. *J. Organomet. Chem.* **1986**, *312*, C49-C52.
- (5) Andersen, R. A.; Blom, R.; Boncella, J. M.; Burns, C. J.; Volden, H. V. *Acta Chem. Scand.* **1987**, *A41*, 24-35.
- (6) Andersen, R. A.; Blom, R.; Burns, C. J.; Volden, H. V. *J. Chem. Soc. Chem. Commun.* **1987**, 768-787.
- (7) Ortiz, J. V.; Hoffmann, R. *Inorg. Chem.* **1985**, *24*, 2095-2104. Actual calculations were performed on the parent  $\text{Cp}_2\text{Sm}$  complex. The addition of the methyl groups is not expected to change the conclusions regarding bonding.
- (8) Andersen, R. A.; Boncella, J. M.; Burns, C. J.; Green, J. C.; Hohl, D.; Rosch, N. *J. Chem. Soc., Chem. Commun.* **1986**, 405-406. As in ref 7, calculations were performed on the unmethylated complexes.
- (9) Green, J. C.; Hohl, D.; Rosch, N. *Organometallics* **1987**, *6*, 712-720.
- (10) Zenger, R.; Stucky, G. *J. Organomet. Chem.* **1974**, *80*, 7-17.
- (11) Burns, C. J.; Andersen, R. A. *J. Organomet. Chem.* **1987**, *325*, 31-37.
- (12) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751-767.
- (13) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1045-1046.
- (14) McCormick, M. J.; Williams, R. A.; Levine, L. J.; Hanusa, T. P. *Polyhedron* **1988**, *7*(9), 725-730.

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which desolvates much more readily.<sup>11</sup> The etherate was heated in three portions of toluene with use of a modification of the "toluene-reflux method"<sup>11</sup> designed to operate at atmospheric pressure. In a typical preparation, Cp\*<sub>2</sub>Ca(OEt<sub>2</sub>)<sub>0.82</sub> (2.49 g, ether content determined by <sup>1</sup>H NMR spectroscopy) was dissolved in 125 mL of toluene in a flask fitted with a distillation head and a 250-mL pressure-equalizing dropping funnel filled with toluene. While being magnetically stirred, the toluene was removed by distillation until about 30 mL remained. Approximately half of the toluene from the dropping funnel was added, and the volume was again reduced to the same amount. The remaining toluene was added to the flask, and the solution was distilled for a third time, leaving 30 mL of solution. After the distillation was complete, the solvent was removed from the remaining yellow liquid, and the pale yellow residue (2.05 g, 0.03 ether molecule per calcium, 98%) was sublimed at 90 °C and 10<sup>-6</sup> Torr. The resulting Cp\*<sub>2</sub>Ca was base-free by NMR spectroscopy.

Considerable difficulty was encountered in growing crystals of the calcium complex. Slow evaporation of toluene, hexane, or methylcyclohexane solutions produced colorless crystals that either were microcrystalline or rapidly became opaque on removal from the solvent. Slow cooling of alkane solutions of the complex to -18 °C produced analogous results. Solvent-free crystals were finally obtained by rapidly cooling a saturated hexane solution of the complex in liquid nitrogen and then slowly warming the partially frozen solution to -18 °C. Presumably solvent-free seed crystals formed during the freezing, which then continued to grow as the solvent melted.

The barium complex can be desolvated by using the distillation method, but it is also readily desolvated in small quantities (0.5 g) by a single slow sublimation at 190 °C under a dynamic vacuum of 10<sup>-6</sup> Torr. The white sublimate obtained in this way is highly soluble in aromatic hydrocarbons, and slow cooling of a hot toluene solution of the compound results in the formation of large, colorless prisms suitable for X-ray diffraction.

**X-ray Crystallography of Cp\*<sub>2</sub>Ca.** General procedures for data collection and reduction have been described previously.<sup>15</sup> A suitable crystal measuring 0.25 × 0.25 × 0.25 mm was located and transferred with use of standard inert-atmosphere techniques to a Picker four-circle goniostat equipped with a Furnas monochromator (HOG crystal) and Picker X-ray generator. The crystal was cooled to 116 K for characterization and data collection. Relevant crystal and data collection parameters for the present study are given in Table I.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group P<sub>2</sub><sub>1</sub>/n (alternate setting of P<sub>2</sub><sub>1</sub>/c, No. 14). Subsequent solution and refinement of the structure confirmed this choice. Data collection was performed by use of a continuous θ-2θ scan with fixed backgrounds. 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 (MULTAN78) and Fourier techniques. Two independent molecules were located in the asymmetric unit. All hydrogen atoms were clearly visible in a difference Fourier synthesis phased on the non-hydrogen parameters. All hydrogen atoms were refined isotropically and non-hydrogen atoms anisotropically in the final cycles. Positional parameters are supplied in Table II; non-hydrogen bond distances and angles are summarized in Table III.

**X-ray Crystallography of Cp\*<sub>2</sub>Ba.** With use of methods analogous to those above, a crystal measuring 0.25 × 0.25 × 0.25 mm was located, transferred to the goniostat, and cooled to 118 K for characterization and data collection. Crystal and data collection parameters are in Table I.

The space group was identified as the monoclinic P<sub>2</sub><sub>1</sub>/n (alternate setting of P<sub>2</sub><sub>1</sub>/c, No. 14) by systematic absences, a choice confirmed by subsequent solution and refinement of the structure. Data collection, reduction, and solution of the structure were as for the calcium analogue. Two independent molecules were again located in the asymmetric unit. All hydrogen atoms were located and refined as above. A final difference Fourier was featureless, with the largest peak being 0.45 e/Å<sup>3</sup>. Positional parameters are

**Table I. Crystal Data and Summary of Data Collection for Cp\*<sub>2</sub>Ca and Cp\*<sub>2</sub>Ba**

formula fw	C <sub>20</sub> H <sub>30</sub> Ca 310.54	C <sub>20</sub> H <sub>30</sub> Ba 407.79
color of cryst		colorless
cryst dimens, mm	0.25 × 0.25 × 0.25	
space group		P <sub>2</sub> <sub>1</sub> /n
cell dimens <sup>a</sup>		
a, Å	9.721 (2)	18.043 (4)
b, Å	12.361 (2)	11.830 (2)
c, Å	30.849 (10)	18.206 (4)
β, deg	96.34 (1)	105.67 (1)
V, Å <sup>3</sup>	4331.63	3741.79
Z		8
D(calcd), g/cm <sup>3</sup>	1.120	1.448
wavelength, Å		0.710 69
abs coeff, cm <sup>-1</sup>	3.250	21.156
type of scan		continuous θ-2θ
scan speed, deg/min	4.0	6.0
scan width	2.0 + dispersn	1.8 + dispersn
bkgd counting, s	4 (Ca), 6 (Ba), at extremes of scan	
limits of data collectn, deg		6 ≤ 2θ ≤ 45
total no. of rflns collected	5556	7027
no. of unique intens	4847	4883
no. with F > 0.0	4248	4728
no. with F > 2.33σ(F)	3560	4482
R for averaging	0.043	0.054
R(F)	0.0594	0.0295
R <sub>w</sub> (F)	0.0587	0.0323
goodness of fit	1.147	0.985
max Δ/σ in final cycle	0.15	0.05

<sup>a</sup> For Ca, 76 reflections were used at 116 K; for Ba, 40 reflections were used at 118 K.

listed in Table II; non-hydrogen bond distances and angles are summarized in Table III.

## Results and Discussion

Removal of THF from Cp\*<sub>2</sub>Ca(THF)<sub>2</sub> is difficult; distilling a toluene solution of the compound at atmospheric pressure will initially remove all but about one-third of a THF molecule per metal center, and the remaining THF is not completely removed either by repeating the procedure or by sublimation. Synthesis of the metallocene in the weaker base diethyl ether generates the monosolvated Cp\*<sub>2</sub>Ca(OEt<sub>2</sub>), from which the ether is readily liberated.<sup>11</sup>

Considering the difficulty encountered in dislodging THF from a Ca<sup>2+</sup> center, it was thought that its removal from the larger Ba<sup>2+</sup> in Cp\*<sub>2</sub>Ba(THF)<sub>2</sub> should be even more problematic. Barium prefers high coordination numbers in its inorganic compounds (up to 12),<sup>16</sup> and the resulting six-coordinate Cp\*<sub>2</sub>Ba would be extremely coordinatively unsaturated. Interestingly, however, Cp\*<sub>2</sub>Ba(THF)<sub>2</sub> is easily rendered solvent-free by a single sublimation at 190 °C. Evidently the lower charge density of barium causes it to be a weaker Lewis acid than calcium and, hence, less tenacious in its binding to a basic ether. The varying ease of desolvation provides an example of the importance of charge density on the relative stability of organoalkaline-earth-metal complexes.<sup>17</sup>

**Solid-State Structure of Cp\*<sub>2</sub>Ca.** Base-free bis(pentamethylcyclopentadienyl)calcium crystallizes with two crystallographically independent but essentially identical molecules in the unit cell. Like the gas-phase structure, but unlike the polymeric Cp<sub>2</sub>Ca parent metallocene,<sup>10</sup> Cp\*<sub>2</sub>Ca contains η<sup>5</sup>-Cp\* rings flanking a Ca core in a bent

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(17) Comparable differences in the ease of removal of THF from Cp\*<sub>2</sub>Sm and Cp\*<sub>2</sub>Eu have also been noted.<sup>3</sup> In this case, an explanation for the discrepancy is not as obvious, as the difference in radii between Sm<sup>2+</sup> and Eu<sup>2+</sup> is only ~0.01 Å.<sup>12</sup>

(15) Chisholm, M. H.; Folting, K.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 1021-1037.

**Table II. Fractional Coordinates ( $\times 10^4$ ) and Isotropic Thermal Parameters ( $\times 10^3 \text{ \AA}^2$ ) for the Non-Hydrogen Atoms in  $\text{Cp}^*_2\text{Ca}$  and  $\text{Cp}^*_2\text{Ba}$** 

atom	x	y	z	$B_{\text{iso}}^a$	atom	x	y	z	$B_{\text{iso}}^a$
<b><math>\text{Cp}^*_2\text{Ca}</math></b>									
Ca(1)	2407 (1)	991 (1)	1318.5 (3)	15	Ca(22)	7745 (1)	-5921 (1)	1216.1 (3)	15
C(2)	45 (4)	293 (4)	898 (2)	17	C(23)	6063 (5)	-5009 (4)	592 (2)	26
C(3)	1005 (5)	280 (4)	592 (2)	23	C(24)	5202 (4)	-5413 (4)	894 (2)	17
C(4)	1336 (5)	1397 (4)	507 (2)	23	C(25)	5276 (4)	-6566 (4)	871 (2)	18
C(5)	595 (5)	2045 (4)	772 (2)	23	C(26)	6161 (5)	-6849 (4)	559 (2)	24
C(6)	-200 (4)	1384 (4)	1016 (2)	18	C(27)	6648 (5)	-5868 (5)	390 (2)	32
C(7)	-740 (5)	-668 (4)	1042 (2)	24	C(28)	6205 (7)	-3820 (5)	468 (3)	52
C(8)	1500 (6)	-685 (5)	364 (2)	35	C(29)	4275 (5)	-4794 (5)	1162 (2)	34
C(9)	2203 (6)	1768 (5)	158 (2)	35	C(30)	4438 (6)	-7317 (5)	1123 (2)	30
C(10)	509 (6)	3278 (4)	750 (2)	31	C(31)	6388 (7)	-7985 (6)	395 (2)	50
C(11)	-1173 (5)	1750 (4)	1334 (2)	22	C(32)	7489 (6)	-5783 (9)	5 (2)	71
C(12)	2418 (4)	-374 (4)	1966 (1)	16	C(33)	8232 (5)	-4203 (4)	1702 (2)	19
C(13)	3384 (4)	-771 (4)	1694 (2)	16	C(34)	7751 (5)	-4976 (4)	1984 (2)	19
C(14)	4528 (4)	-54 (4)	1729 (1)	17	C(35)	8766 (5)	-5800 (4)	2058 (1)	18
C(15)	4250 (4)	792 (3)	2014 (1)	16	C(36)	9875 (5)	-5526 (4)	1817 (2)	18
C(16)	2939 (4)	601 (4)	2157 (2)	1.8	C(37)	9542 (4)	-4545 (4)	1594 (2)	17
C(17)	1106 (5)	-932 (4)	2068 (2)	25	C(38)	7579 (5)	-3118 (4)	1579 (2)	26
C(18)	3317 (5)	-1838 (4)	1457 (2)	24	C(39)	6982 (6)	-4885 (5)	2225 (2)	29
C(19)	5841 (5)	-214 (4)	1522 (2)	27	C(40)	8761 (5)	-6712 (9)	2381 (2)	26
C(20)	5251 (5)	1669 (4)	2188 (2)	24	C(41)	11249 (5)	-6099 (4)	1863 (2)	26
C(21)	2299 (6)	1244 (4)	2503 (2)	26	C(42)	10435 (5)	-3945 (4)	1303 (2)	25
<b><math>\text{Cp}^*_2\text{Ba}</math></b>									
Ba(1)	7606.8 (2)	1272.4 (2)	3139.2 (1)	17	Ba(22)	1891.6 (1)	2377.5 (2)	2415.9 (2)	17
C(2)	8087 (3)	2388 (4)	4684 (3)	19	C(23)	2586 (2)	4655 (4)	3023 (2)	18
C(3)	7319 (3)	2018 (4)	4612 (3)	21	C(24)	2673 (2)	4552 (4)	2269 (2)	17
C(4)	7326 (3)	817 (4)	4618 (2)	20	C(25)	3241 (2)	3724 (4)	2274 (2)	16
C(5)	8088 (3)	454 (4)	4697 (2)	19	C(26)	3512 (2)	3319 (4)	3039 (2)	16
C(6)	8552 (3)	1417 (4)	4733 (2)	17	C(27)	3102 (2)	3882 (4)	3489 (3)	18
C(7)	8376 (3)	3582 (4)	4810 (3)	27	C(28)	2115 (3)	5499 (4)	3313 (3)	22
C(8)	6647 (3)	2742 (5)	4652 (3)	29	C(29)	2232 (3)	5166 (4)	1556 (3)	23
C(9)	6630 (3)	72 (5)	4535 (3)	26	C(30)	3470 (3)	3329 (4)	1591 (3)	23
C(10)	8373 (3)	-751 (4)	4754 (3)	25	C(31)	4198 (3)	2584 (4)	3345 (3)	23
C(11)	9411 (3)	1409 (5)	4863 (3)	27	C(32)	3239 (3)	3774 (4)	4337 (3)	25
C(12)	7048 (3)	3542 (4)	2482 (3)	19	C(33)	434 (3)	2842 (4)	2759 (3)	20
C(13)	7766 (2)	3399 (4)	2303 (2)	17	C(34)	363 (2)	1706 (4)	2513 (3)	21
C(14)	7664 (3)	2564 (4)	1730 (2)	17	C(35)	269 (2)	1689 (4)	1717 (3)	20
C(15)	6891 (3)	2191 (4)	1553 (2)	17	C(36)	284 (3)	2817 (4)	1467 (3)	21
C(16)	6510 (2)	2780 (4)	2022 (2)	17	C(37)	378 (3)	3535 (4)	2116 (3)	21
C(17)	6862 (3)	4383 (4)	3025 (3)	24	C(38)	556 (3)	3223 (5)	3575 (3)	30
C(18)	8511 (3)	3991 (4)	2676 (3)	24	C(39)	335 (3)	692 (5)	2997 (3)	32
C(19)	8261 (3)	2196 (4)	1343 (3)	24	C(40)	140 (3)	662 (4)	1215 (3)	28
C(20)	6494 (3)	1448 (4)	900 (3)	24	C(41)	120 (3)	3220 (5)	659 (3)	30
C(21)	5680 (3)	2674 (4)	2004 (3)	27	C(42)	332 (3)	4792 (4)	2082 (3)	26

<sup>a</sup> Isotropic values for those atoms refined anisotropically are calculated by using the formula given in: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609-610.

**Table III. Average Bond Lengths ( $\text{\AA}$ ) and Angles ( $\text{deg}$ ) in  $\text{Cp}^*_2\text{Ca}$  and  $\text{Cp}^*_2\text{Ba}$** 

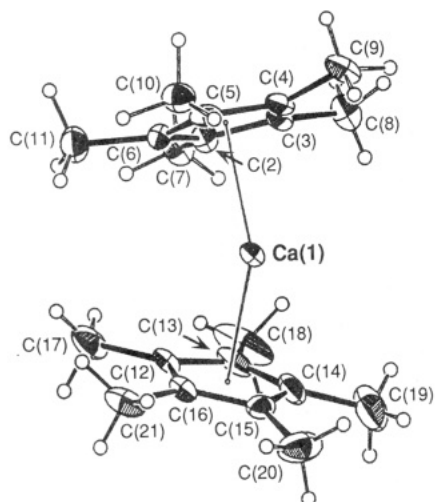
	conformer A	conformer B
<b><math>\text{Cp}^*_2\text{Ca}</math></b>		
Ca-C(ring)	2.64 (1)	2.64 (2)
C-C(ring)	1.41 (2)	1.41 (2)
C(ring)-C(methyl)	1.51 (2)	1.51 (2)
C-C-C(ring)	108.0 (1.3)	108.0 (1.3)
C-C-CH <sub>3</sub>	126.5 (1.9)	125.4 (1.9)
planarity of rings, $\text{\AA}$	within 0.01	within 0.005
displacement of CH <sub>3</sub> groups from ring plane, $\text{\AA}$	0.13	0.14
displacement angle ( $\alpha$ )	1.5	1.5
twist angle between rings	19.1	24.7
<b><math>\text{Cp}^*_2\text{Ba}</math></b>		
Ba-C(ring)	2.98 (1)	2.99 (1)
C-C(ring)	1.42 (2)	1.42 (2)
C(ring)-C(methyl)	1.50 (2)	1.50 (2)
C-C-C(ring)	108.0 (1.3)	108.0 (1.3)
C-C-CH <sub>3</sub>	125.9 (1.5)	125.9 (1.5)
planarity of rings, $\text{\AA}$	within 0.007	within 0.006
displacement of CH <sub>3</sub> groups from ring plane, $\text{\AA}$	0.102	0.108
displacement angle ( $\alpha$ )	3.9	4.1
twist angle between rings	32.1	28.1

metallocene geometry.<sup>18</sup> In view of the potential importance of crystal packing effects on the geometries of these structures, the structural parameters for both conformers will be described; those for the conformer based on Ca(1) (A) will be listed first, and those for the second conformer [B] will follow in brackets. An ORTEP view of conformer A providing the numbering scheme used in the tables is displayed in Figure 1.

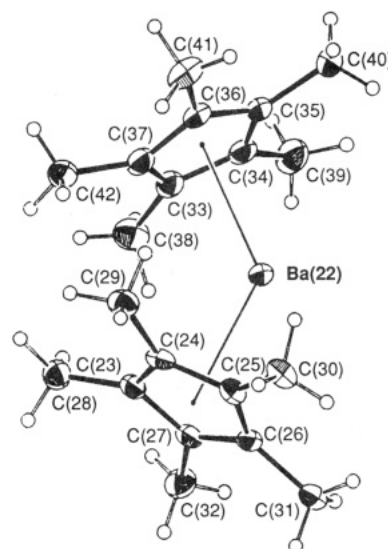
The average Ca-C distance of 2.64 (1)  $\text{\AA}$  [2.64 (2)  $\text{\AA}$ ] observed in the crystal is only slightly greater than that found in the GED-determined structure (GED = gas-phase electron diffraction) of the metallocene (2.609 (6)  $\text{\AA}$ ), and the ring centroid-Ca-ring centroid angle of 147.7° [146.3°] found in the solid is 6° [8°] more acute than that observed in the gas phase (154 (3)°).

The metal-Cp\* ring distances in  $\text{Cp}^*_2\text{Ca}$  are in line with the values observed in other crystallographically characterized organocalcium structures. In polymeric  $\text{Cp}_2\text{Ca}$ , each calcium ion is surrounded by two  $\eta^5$ -, one  $\eta^3$ -, and one  $\eta^1$ -Cp rings, with an average Ca-C( $\eta^5$ ) distance of 2.80  $\text{\AA}$ .<sup>10</sup> If Ca<sup>2+</sup> is taken as 9-coordinate with a radius of 1.18  $\text{\AA}$ ,<sup>12</sup>

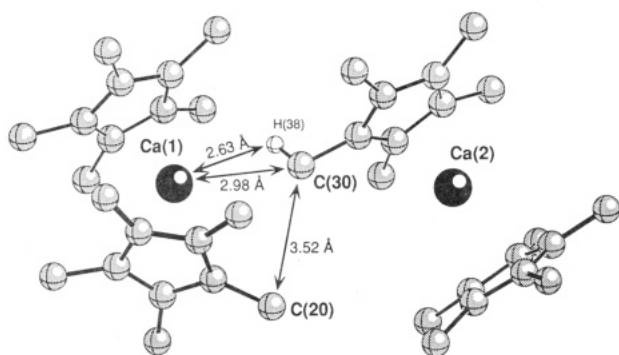
(18) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729-1742.



**Figure 1.** ORTEP view of  $\text{Cp}^*_2\text{Ca}$  (conformer A), giving the numbering scheme used in the tables. The same scheme is used for conformer A of  $\text{Cp}^*_2\text{Ba}$ .



**Figure 3.** ORTEP view of  $\text{Cp}^*_2\text{Ba}$  (conformer B), giving the numbering scheme used in the tables. The same scheme is used for conformer B of  $\text{Cp}^*_2\text{Ca}$ .



**Figure 2.** Illustration of the side-by-side approach of the two conformers of  $\text{Cp}^*_2\text{Ca}$ , indicating the closest intermolecular contacts.

the 0.18-Å difference between this value and the 6-coordinate radius of  $\text{Ca}^{2+}$  (1.00 Å) agrees well with the 0.16-Å shorter Ca-C distance of 2.64 Å in  $\text{Cp}^*_2\text{Ca}$ . Comparisons can also be made with the structures of  $[\text{Cp}^*\text{Ca}(\mu\text{-I})(\text{THF})_2]_2$ <sup>19</sup> and  $(1,3\text{-}(\text{SiMe}_3)_2\text{C}_5\text{H}_3)_2\text{Ca}(\text{THF})$ ,<sup>20,21</sup> which display average Ca-C distances of 2.67 (1) and 2.68 (1) Å, respectively. The difference of 0.06 Å between the radii of 7- and 6-coordinate  $\text{Ca}^{2+}$ <sup>12</sup> compares favorably with the 0.03- and 0.04-Å difference in Ca-C bond lengths observed between  $[\text{Cp}^*\text{Ca}(\mu\text{-I})(\text{THF})_2]_2/\text{Cp}^*_2\text{Ca}$  and  $(1,3\text{-}(\text{SiMe}_3)_2\text{C}_5\text{H}_3)_2\text{Ca}(\text{THF})/\text{Cp}^*_2\text{Ca}$ .

Useful structural comparisons are also possible with divalent ytterbium complexes. The average metal-C(Cp\*) distances in  $\text{Cp}^*_2\text{Yb}(\text{MeC}\equiv\text{CMe})$  (2.659 (9) Å),<sup>22</sup>  $\text{Cp}^*_2\text{Yb}(\text{THF})(\text{CH}_3\text{C}_6\text{H}_5)_{0.5}$  (2.66 (2) Å),<sup>23</sup> and  $\text{Cp}^*_2\text{Yb}$  (2.665 (3) Å)<sup>24</sup> differ from that found in  $\text{Cp}^*_2\text{Ca}$  (2.64 (1) Å) by 0.02 Å. For the first two Yb complexes, this amount is 0.06 Å less than the difference in the  $\text{Yb}^{2+}$  and  $\text{Ca}^{2+}$  radii,<sup>12</sup> but it matches the difference in radii for  $\text{Cp}^*_2\text{Yb}/\text{Cp}^*_2\text{Ca}$ .

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

(20) Engelhardt, L. M.; Junk, P. C.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1988**, 1500-1501.

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

(22) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 941-942.

(23) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Ruben, H.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1980**, *19*, 2999-3003.

(24) Burns, C. J. Ph.D. Thesis, University of California at Berkeley, Dec 1987, p 20.

The closest intermolecular  $\text{CH}_3\cdots\text{CH}_3'$  contact between two conformers of the same type occurs between C(17) and C(21)' of the A conformer at 3.99 Å, equal to the sum of the van der Waals radii.<sup>25</sup> A much closer  $\text{CH}_3\cdots\text{CH}_3'$  contact occurs between C(30) of conformer A and C(20) of conformer B at 3.52 Å (Figure 2). The closest intermolecular  $\text{Ca}\cdots\text{CH}_3'$  approach occurs between the different conformers, i.e., Ca(on A) $\cdots$ C(30)'(on B) at 2.98 Å, with the nearest  $\text{Ca}\cdots\text{H}'$ (on C30') contact at 2.63 Å. The significance of the intermolecular calcium-methyl distance will be discussed below in the context of other metallocenes, but it should be noted that it is similar to the  $\text{Yb}^{2+}\cdots\text{CH}_3'$  distances observed in  $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2[\text{dmpe}]$  (3.04 Å)<sup>26</sup> and  $\text{NaYb}[\text{N}(\text{SiMe}_3)_2]_3$  (2.86 (2) Å).<sup>27</sup> Since the difference in radii between 6-coordinate  $\text{Ca}^{2+}$  and 4- and 3-coordinate  $\text{Yb}^{2+}$  is 0.10 and 0.18 Å, respectively, the calcium-methyl distance is effectively 0.06-0.16 Å shorter than in these complexes. No structural consequences appear to stem from the  $\text{Ca}\cdots\text{CH}_3'$  contact, such as a distortion in angles or a reduction in the thermal parameters associated with C(30), as was observed with the  $\text{Yb}^{2+}\cdots\text{CH}_3'$  contacts in the [bis(trimethylsilyl)amido]ytterbium structures.<sup>26,27</sup>

Considering that 8-coordinate  $\text{Yb}^{2+}$  is ca. 0.14 Å larger than 6-coordinate  $\text{Ca}^{2+}$ , the  $\text{Ca}\cdots\text{H}'$  contact of 2.63 Å is effectively 0.14-0.24 Å longer than the shortest  $\text{Yb}^{2+}\cdots\text{H}'$  distances observed to date (2.53 and 2.63 Å in  $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2[\text{AlMe}_3]_2$ <sup>28</sup>). No structural distortion of the bond angles involving C(30) or H(38) is evident; the three C(25)-C(30)-H(37-39) angles are statistically indistinguishable.

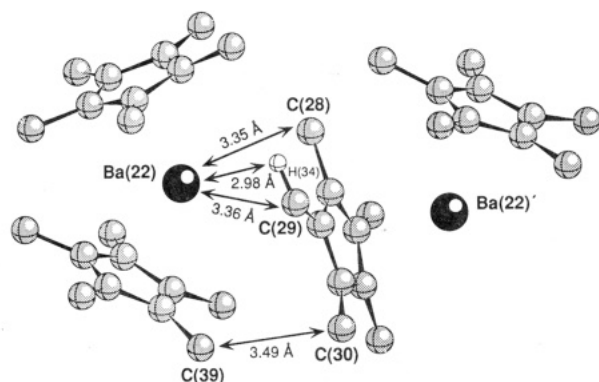
**Solid-State Structure of  $\text{Cp}^*_2\text{Ba}$ .** Like the calcium analogue, base-free bis(pentamethylcyclopentadienyl)-barium crystallizes with two crystallographically independent molecules in the unit cell and also displays a bent metallocene geometry. Again, the differences between the two molecules are relatively minor, but the parameters for both conformers will be listed here. An ORTEP view of

(25) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; p 261.

(26) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1982**, *104*, 3725-3727.

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(28) Boncella, J. M.; Andersen, R. A. *Organometallics* **1985**, *4*, 205-206.



**Figure 4.** Illustration of the closest approach of two  $\text{Cp}^*_2\text{Ba}$  units, indicating the intermolecular contacts.

conformer B providing the numbering scheme used in the tables is displayed in Figure 3.

Greater divergence is evident between the solid-state and gas-phase structures than occurs with  $\text{Cp}^*_2\text{Ca}$ . Notably, the average Ba–C distance of 2.98 (1) Å [2.99 (1) Å] observed in the crystal is 0.08 Å [0.09 Å] greater than that found in the GED-determined structure of the metallocene (2.898 (17) Å). In addition, the ring centroid–Ba–ring centroid angle of 130.9° [131.0°] found in the solid is 17° more acute than that observed in the gas phase (148°) and is the smallest such angle yet observed in a  $\text{Cp}^*_2\text{M}$  complex lacking coligands.

The metal– $\text{Cp}^*$  distances in  $\text{Cp}^*_2\text{Ba}$  are slightly longer than would be expected on the basis of comparisons with organobarium and -strontium complexes. The average Ba–C distance for both conformers of 2.99 (2) Å is slightly longer than the Ba–C distance of 2.96 (2) Å observed in  $[(\text{Cp}^*_2\text{Ba})_2(\mu\text{-C}_4\text{H}_4\text{N}_2)]$ .<sup>29</sup> Since the 7-coordinate radius of  $\text{Ba}^{2+}$  is estimated to be 0.03 Å larger than the 6-coordinate value,<sup>12</sup> however, one would expect the metal–ring distances in  $\text{Ca}^*_2\text{Ba}$  to be somewhat shorter than in  $[(\text{Cp}^*_2\text{Ba})_2(\mu\text{-C}_4\text{H}_4\text{N}_2)]$ . A similar but smaller effect is noticed in the Sr–C distance of 2.82 Å in  $(1,3\text{-SiMe}_3)_2\text{C}_5\text{H}_3)_2\text{Sr}(\text{THF})$ .<sup>20</sup> This distance is 0.17 Å smaller than the Ba–C distance, which in turn is marginally longer than the 0.14-Å difference in radii. The Ba–C lengthening is also observed by comparing the Ba–ring centroid distance of 1.38 Å to that of the average value found in ionic cyclopentadienyl complexes with divalent metal centers, 1.33 (3) Å.<sup>1</sup>

The shortest intermolecular  $\text{Ba}\cdots\text{CH}_3'$  distance in the unit cell is 3.349 (5) Å, between Ba(22) and C(28)'; the closest distance involving Ba(1) is at 3.395 (5) Å, between Ba(1) and C(17)'. Any intermolecular agostic Ba–H–C linkages appear to be absent. The closest intermolecular  $\text{Ba}\cdots\text{H}'$  distance is 2.98 Å and involves a hydrogen atom on the C(29) methyl group (Figure 4) and the barium of an adjacent complex. As in the case of the calcium complex, no structural distortions are evident involving the bond angles of the C(29) methyl group. In agreement with the structural evidence, no especially low C–H stretching frequencies are evident in the IR spectrum of the solid (Fluorolube mull),<sup>30</sup> which would indicate the presence of intermolecular agostic Ba–H–C bonding.<sup>31</sup>

(29) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. Manuscript in preparation.

(30) Williams, R. A.; Hanusa, T. P. Unpublished results.

(31) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395–408. The orientation of the methyl group is also not optimum for a Ba–H interaction; rotation by 54° would place the hydrogen within 2.54 Å of the Ba center, but this presumably low-energy motion has not occurred.

The organobarium structure is not as stereochemically "regular" as that of  $\text{Cp}^*_2\text{Ca}$ . The individual Ba–C distances within the complexes vary by as much as 0.16 Å, compared to a range of only 0.07 Å in the calcium analogue. Likewise, the Ba–ring centroid distances differ by 0.057 and 0.076 Å in the two conformers, although they differ by only 0.005 and 0.025 Å in  $\text{Cp}^*_2\text{Ca}$ . Both the slight Ba–C bond lengthening and the structural asymmetry may be associated with the relatively close packing of the complexes in the solid state. Those  $\text{Cp}^*$  rings involved in the shortest intermolecular Ba–C(methyl) contacts are also those that display the longest intramolecular Ba–C and Ba–ring centroid distances. The large ring centroid–metal–ring centroid angle allows the individual  $\text{Cp}^*_2\text{Ba}$  units to approach each other in a chainlike manner, with the face of a third  $\text{Cp}^*$  ring in close proximity to the metal center (Figure 4). The structure thus approaches that of truly polymeric species such as  $\text{Cp}^*_2\text{Tl}$ , in which unique metal–ring units cannot be identified.<sup>32</sup>

#### Comparisons with Other Decamethylmetallocenes.

Ever since the unexpected discovery that  $\text{Cp}^*_2\text{Sm}$  displays a bent geometry in the solid state,<sup>2,3</sup> much effort has been spent in determining the source of its bending and that of related organolanthanide species. Concerns that the bent structures at least partially represent artifacts of crystal packing forces or other intermolecular interactions are not entirely misplaced. Crystal packing is evidently responsible for the two conformers found in the unit cell of  $\text{Cp}^*_2\text{Si}$ , for example; in one conformer, the rings are parallel, and in the second, the rings form an interplanar angle of 25.3°.<sup>33</sup> In addition, no obvious energetic reason for the bending in these molecules has emerged from molecular orbital calculations on the structures of  $\text{Cp}_2\text{Sm}$ ,  $\text{Cp}_2\text{Eu}$ , and  $\text{Cp}_2\text{Yb}$  performed at the extended Hückel<sup>7</sup> and quasi-relativistic SW– $X\alpha$  levels.<sup>9</sup> The energy required to bend the molecule is calculated to be small, however, and packing forces might be able to supply it. Simple steric considerations would also suggest that structures with parallel rings should be favored, thus minimizing intramolecular repulsions.

The finding that  $\text{Cp}^*_2\text{Yb}$ ,  $\text{Cp}^*_2\text{Ca}$ ,  $\text{Cp}^*_2\text{Sr}$ , and  $\text{Cp}^*_2\text{Ba}$  are bent in the vapor phase would seem to lessen the possibility that the bent geometries are confined to the solid state,<sup>4,6</sup> yet the GED data do not present consistent structural trends. As previously noted,<sup>6</sup> the metal–ring distances increase in a linear fashion on moving from  $\text{Ca}^{2+}$  (radius 1.00 Å) to  $\text{Ba}^{2+}$  (1.35 Å), but the ring centroid–metal–ring centroid angles do not: the angles for  $\text{Cp}^*_2\text{Ba}$  (148 (6)°) and  $\text{Cp}^*_2\text{Sr}$  (149 (3)°), for example, differ by 1°, despite a difference in 0.17 Å in metal ionic radii; the angles of  $\text{Cp}^*_2\text{Ca}$  (154 (3)°) and  $\text{Cp}^*_2\text{Yb}$  (158 (4)°) differ by 4°, even though  $\text{Yb}^{2+}$  is slightly larger than  $\text{Ca}^{2+}$  (by ~0.02 Å).<sup>12</sup> Such discrepancies might arise from the fact that the reported geometries are thermal average structures and that temperatures ranging from 160 °C ( $\text{Cp}^*_2\text{Ca}$ ) to 270 °C ( $\text{Cp}^*_2\text{Ba}$ ) were used in obtaining the GED data. Given the relatively larger errors in the ring centroid–metal–ring centroid angles, the values cannot be distinguished from each other at the 2 $\sigma$  level.

Far greater regularity is observed in the crystalline forms of the decamethylmetallocenes. All crystallize in the monoclinic space group  $P2_1/n$  and contain either one or two independent molecules per asymmetric unit. The range of ring centroid–metal–ring centroid angles in the

(32) Werner, H.; Otto, H.; Kraus, H. *J. Organomet. Chem.* **1986**, *315*, C57–C60.

(33) Jutzki, P.; Kanne, D.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 164.

Table IV. Comparative Structural Parameters in Solid-State Decamethylmetallocenes

complex	ionic radius, Å	av M-C dist, Å	closest M...CH <sub>3</sub> ' , Å	rel dist, Å	diff between closest intermolecular contact and longest intramolecular M...CH <sub>3</sub> ' bond, Å	diff in M-Ω lengths, Å	diff between longest and shortest M-C dist, Å	ref
Cp* <sub>2</sub> Ca	1.00	2.64 (2)	2.98	1.98	0.30	0.015	0.07	this work
Cp* <sub>2</sub> Yb	1.02	2.665 (4)	2.94	1.92	0.26	0.017	0.05	26
Cp* <sub>2</sub> Sm	1.17	2.79 (1)	3.22	2.05	0.41	0.006	0.04	2, 3
Cp* <sub>2</sub> Eu	1.17	2.79 (1)	3.19	2.02	0.37	0.008	0.06	3
Cp* <sub>2</sub> Ba	1.35	2.99 (2)	3.35	2.00	0.28	0.067	0.16	this work

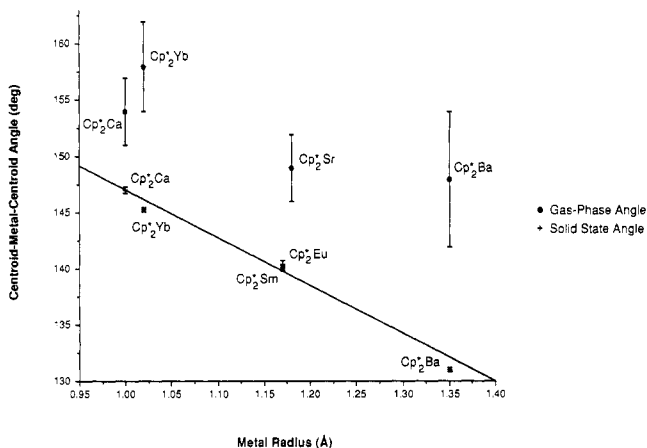


Figure 5. Plot of ring centroid-metal-ring centroid angles vs metal radii (with estimated standard deviations) for ionic decamethylmetallocenes in both the solid and gas phases.

solid-state structures varies from 130.9° (Cp\*<sub>2</sub>Ba) to 147.7° (Cp\*<sub>2</sub>Ca). A plot of the ring centroid-metal-ring centroid angles vs the metal ionic radii for the solid-state and gas-phase data is presented in Figure 5. Two differences between the data sets are immediately apparent: the solid-state bending angles are always smaller than the gas-phase angles for the same metal radii, and in the solid state a strong linear relationship is observed between the angles and ionic radii.<sup>34</sup>

There is no immediately obvious property of the metal ions that would cause the bending of the decamethylmetallocenes to vary linearly with it. It is possible that if electronic grounds exist for the bending, the regularity observed in the solid-state structures stems from solid-state interactions unrelated to the internal sources of bending. It must be borne in mind that any such "interactions" must be weak, as all the decamethylmetallocenes are soluble in alkanes. This is in accord with the findings on the gas-phase structures, which established that if the equilibrium structures truly possess parallel rings, less than 2 kJ/mol would be required to bend the complexes by 20°. A similar conclusion was reached in an MO study.<sup>7</sup>

**Intermolecular Contacts.** A logical place to begin searching for solid-state features that might be responsible for the strong metal radius/bending angle correlation would be with intermolecular interactions. If such contacts played an important role in the bending, one might expect the more severely bent complexes to have the closest contact distances, but no such general agreement is found.

(34) The structure of Cp\*<sub>2</sub>Mg has been determined in the gas phase, but the rings were constrained to be parallel.<sup>6</sup> It is interesting to note that the extrapolated value for the solid-state bending angle of Cp\*<sub>2</sub>Mg is 159°. Models suggest that, even with the small radius of Mg<sup>2+</sup> (0.72 Å), such an angle would not require intramolecular CH<sub>3</sub>...CH<sub>3</sub>' contacts of less than 3.8 Å, so that steric reasons alone do not force the structure to have parallel rings. The structure of the present metallocene Cp\*<sub>2</sub>Mg does have parallel rings in the solid state (Bünder, W.; Weiss, E. J. *Organomet. Chem.* 1975, 92, 1-6).

All the metallocenes have their closest intermolecular CH<sub>3</sub>...CH<sub>3</sub>' contacts in the range from 3.3 to 3.5 Å, with no obvious correlation to the bending angles; in Cp\*<sub>2</sub>Ba (131°), for example, the contact is 3.49 Å (C(30)...C(39)'), in Cp\*<sub>2</sub>Sm (140°) the distance is 3.34 Å (C(11)...C(11)'), and in Cp\*<sub>2</sub>Ca (146°) the contact is 3.52 Å (C(20)...C(30)'). The same conclusion can be reached by examining the closest intermolecular M...CH<sub>3</sub>' contacts; all the decamethylmetallocenes have similar contacts (~2.0 Å) when the differences in metal radii are taken into account (Table IV).

An alternate method of evaluating the importance of the intermolecular M...CH<sub>3</sub>' contacts is to compare their distances with the longest intramolecular M...C (Cp\*) distances. The differences between these two values are tabulated in Table IV. Although some small differences are evident, they do not vary systematically with the bending angle; in particular, Cp\*<sub>2</sub>Ba, with the most bending, has contacts essentially the same as those of Cp\*<sub>2</sub>Ca, with the least.

**Orientation of Complexes.** Simple comparisons of closest contacts are only meaningful if all the compounds share at least roughly the same packing arrangements. It is clear that such is not the case with the decamethylmetallocenes. For example, although the closest Ca...CH<sub>3</sub>' contact in Cp\*<sub>2</sub>Ca is at 2.98 Å, the next closest are at 4.43 and 5.21 Å; i.e., a ring from an adjacent complex approaches another nearly on edge. This "edge-on" approach is also observed in Cp\*<sub>2</sub>Yb, Cp\*<sub>2</sub>Sm, and Cp\*<sub>2</sub>Eu. In contrast, the closest intermolecular Ba...CH<sub>3</sub>' contact in Cp\*<sub>2</sub>Ba is at 3.35 Å, but the next two closest are at 3.36 and 3.45 Å, an indication of the more nearly face-on approach of the third Cp\* ring (Figure 4).

The combination of relative orientation of rings and closest contacts appears to be reflected in the symmetry of the complexes. As noted above, the metal-ring centroid distances and minimum/maximum Ba-C distances differ appreciably for Cp\*<sub>2</sub>Ba. Comparable values for the other metallocenes are listed in Table IV. These criteria suggest that the barium structure is markedly more asymmetric than the other structures, an asymmetry which might reasonably be attributed to packing effects and which might contribute to the complex's large bending angle. There is no clear pattern for the other metallocenes that suggests an explanation for the trend in the ring-metal-ring bending.

**Intramolecular Methyl-Methyl Contacts.** If in the absence of steric constraints the preferred bending angle would be greater than any actually observed in the complexes, an alternate source for the regular increase in bending with increasing radii might be found in intramolecular methyl-methyl contacts. The closest average intramolecular methyl-methyl contact in each complex is relatively constant, with a range of 3.55-3.59 Å. Since the complexes display metal-ring distances that vary inversely with the bending angle (Table IV), in those complexes with longer metal-ring distances, greater bending can be tolerated before methyl-methyl repulsions become too se-

vere.<sup>35</sup> There is evidently some flexibility in this distance; i.e., a conformer with a closer than normal methyl–methyl contact can cocrystallize with one longer than normal, so that the average is the same. The two independent conformers of Cp\*<sub>2</sub>Ba and Cp\*<sub>2</sub>Ca have closest CH<sub>3</sub>...CH<sub>3</sub>' distances of 3.49 and 3.65 Å and 3.48 and 3.64 Å, respectively, yet they average to 3.57 and 3.56 Å.<sup>36</sup>

**Bonding in Ionic Decamethylmetallocenes.** Because of the inability of molecular orbital calculations on the structures of Cp<sub>2</sub>Sm, Cp<sub>2</sub>Eu, and Cp<sub>2</sub>Yb to provide an energetic rationale for their bending, and the inability of photoelectron spectra to detect significant covalent contributions to the bonding in the Cp\* derivatives,<sup>8</sup> alternative explanations based on "reverse" polarization effects have been proposed; viz., that negatively charged Cp<sup>-</sup> rings will induce a dipole in a large, polarizable cation, thus favoring a bent geometry.<sup>3,9</sup> This is the same reasoning offered for the bending observed in the gas-phase Ae dihalides, and details are presented elsewhere.<sup>37</sup> Although there is nothing intrinsically wrong with the argument, it should not be used to imply that a fundamental dichotomy exists between an "ionic" and "covalent" approach to analyzing the bonding in the metallocenes. Polarization explanations simply use the language of electrostatics to describe a phenomenon that could also be couched in molecular orbital terms; i.e., an ion is "polarizable" to the extent that it has low-lying vacant orbitals (in the case of these complexes, (*n* - 1 d or *n* s orbitals). Interaction of the Cp<sup>-</sup> rings with a "polarizable" metal center is equivalent to interaction with these vacant orbitals. Hence, if

(35) The existence of a sterically imposed bending restraint in the lanthanide decamethylmetallocenes has been proposed before (pp 23, 23 of ref 24).

(36) The question might then arise as to why the molecules do not bend *more* than they do; for example, if all other distances remained the same, increasing the Cp\* ring twist angle in Cp\*<sub>2</sub>Sm from 19 to 31° would allow the Ω-Sm-Ω angle to close from 140 to 134.5° while holding the closest intramolecular CH<sub>3</sub>...CH<sub>3</sub>' distance at 3.55 Å. This question, however, is unanswerable without considering a variety of lattice energy terms, all of them small; presumably unfavorable intermolecular interactions would arise if the rings were to twist more.

(37) Guido, M.; Gigli, G. *J. Chem. Phys.* **1976**, *65*, 1397–1402.

the bending in these systems can be rationalized on electrostatic grounds, it follows that it should ultimately be possible to do the same with MO approaches. Considering the small energy differences that are being sought and the difficulty of performing accurate calculations with heavy-metal centers, it is not surprising that current MO techniques have failed to identify bent geometries as energy minima; progress in this direction is being made, however.<sup>38</sup>

## Conclusions

The decamethylmetallocenes of the alkaline-earth metals Ca and Ba display bent geometries in the solid state and form part of a series with the analogous organolanthanide compounds. A strongly linear relationship exists between the bending angle in the complexes and the ionic radius of the metal center. Comparisons between all these molecules suggest that the proximity of the molecules in the solid (i.e., crystal packing) does not provide an adequate explanation for the bent geometries and that the bending must ultimately stem from intramolecular electronic forces.

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**Supplementary Material Available:** Tables of selected bond lengths and angles of non-hydrogen atoms, hydrogen atom fractional coordinates, bond distances and angles involving hydrogen atoms, and anisotropic thermal parameters (22 pages); listings of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

(38) Recent Hartree-Fock-Slater calculations on CaH<sub>2</sub>, CaF<sub>2</sub>, CeO<sub>2</sub>, and YbCl<sub>2</sub> have successfully predicted bent geometries for these species. See: DeKock, R. L.; Timmer, L. K.; Baerends, E. J.; Vernooijs, P. *Abstracts of Papers*, 198th National Meeting of the American Chemical Society, Miami Beach, FL, Sept 1989; American Chemical Society: Washington, DC, 1989; INOR 234.