Why Are Bis(pentamethylcyclopentadienyl) Complexes, $[MCp^{*}_2]$, of Calcium, Strontium, Barium, Samarium, Europium, and Ytterbium Bent?

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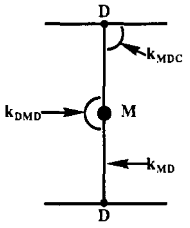
Summary: A molecular mechanics force field is applied to minimize the structures of $[MCp^{*}_2]$, M = Ca, Sr, Ba, Sm, Eu, and Yb, complexes. It is found that van der Waals attractive forces between Cp rings cause all of the molecules to be bent and the calculated and observed structures correspond to a remarkable degree. The differences in energy between the bent and linear geometries is small (<2.1 kcal mol^{-1}), and it is predicted that the bis(pentaisopropylcyclopentadienyl) complexes of these metals should be linear.*

Transition metal complexes of the type $[MCp_2]$, where Cp is the π-bonded cyclopentadienyl ligand or its derivatives, are said to be linear metallocenes when the Cp rings are parallel to each other. Bent metallocenes, where the rings are not parallel, are found for higher coordination complexes of the type $[MCp_2X_n]$, $n = 1$–3, and for $[MCp_2]$ complexes of Ge, Sn, and Pb for which it is assumed that stereochemically active lone pair electrons are present. Until recently, it was generally accepted that the disposition of the Cp rings in bis-Cp complexes could be predicted by the classification; $[MCp_2]$ complexes are linear, and $[MCp_2(\text{lone pair})]$ and $[MCp_2X_n]$ complexes are bent.[1] It is therefore surprising that the bis(pentamethylcyclopentadienyl) (Cp*) complexes $[MCp^{*}_2]$, M = Ca,[2] Sr,[3a] Ba,[2a,3] Sm,[4] Eu,[4b] and Yb,[2b,c] are bent in the solid state and, moreover, the Ca, Sr, Ba, and Yb complexes are also bent in the gas phase.[2b,c,3a] The $[MgCp_2]$[5] and $[MgCp^{*}_2]$[2b,c] complexes, however, are essentially linear. These unexpected observations have been considered theoretically by a variety of methods.[6] None of these has provided persuasive electronic reasons for the nonparallel dispositions of the rings. Theoretical calculations suggest, however, that electronic factors may give rise to the parallel rings in the Mg complexes.[5b,6b]

It occurred to us,[7] as it had to others,[2c] that the bent structures may be the result of interligand van der Waals (VDW) attractive forces. Whereas this may seem counterintuitive, it has been noted[2b,c] that the shortest interligand methyl group VDW contact distances for several of the $[MCp^{*}_2]$ complexes remain constant and, consequently, the degree of bending increases with an increase in the metal radius. It is now possible to test this hypothesis with our recently developed molecular mechanics force field for metallocenes.[8]

In order to find the minimum molecular mechanics force field energy, we require the calculation of the sum of the energy terms associated with bond stretching, angle bending, torsional deformations, and nonbonded interactions. Vibrational data are available for the skeletal modes of $[MgCp_2]$.[9] The three force constants, k_{MD}(metal–Cp stretch) = 120 kcal mol^{-1} (Å)$^{-2}$, k_{DMD}(Cp centroid–metal–Cp centroid bend) = 60 kcal mol^{-1} (rad)$^{-2}$, and k_{MDC}(metal–Cp centroid–Cp carbon tilt) = 50 kcal mol^{-1} (rad)$^{-2}$, **1**, were derived from these data and, except for k_{DMD}, were applied to all metals. The dihedral force constant for the relative rotation of the Cp rings with respect to one another, **3** (β), was set to zero. The VDW energy was calculated using the Leonard–Jones (6–12) potential[10] with a well depth of 0.001 kcal mol^{-1} and a metal VDW radius of 1.0 Å for all metals. The VDW parameters for the organic atoms were those found in CHARMM.[11] Electrostatic interactions were excluded. We found, however, that the inclusion of electrostatic interactions, by using charges calculated by the approx-



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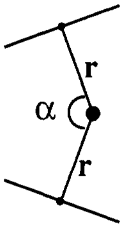

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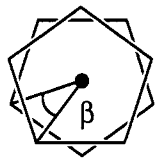

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[1] The $[(Ph_5C_5)_2Sn]$ molecule in the crystal is found to be linear (Heeg, M. J.; Janiak, C.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 4259) possibly because of repulsive steric interactions of the phenyl groups. The complex $[Cp^{*}_2Si]$ molecule exists in both linear and bent forms in the crystal (Jutzi, P.; Kanne, D.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 164).

[2] (a) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *Organometallics* **1990**, *9*, 1128. (b) Andersen, R. A.; Boncella, J. M.; Burns, C. J.; Blom, R.; Haaland, A.; Volden, H. V. *J. Organomet. Chem.* **1986**, *312*, C49. (c) Andersen, R. A.; Blom, R.; Boncella, J. M.; Burns, C. J.; Volden, H. V. *Acta Chem. Scand.* **1987**, *A41*, 24.

[3] (a) Andersen, R. A.; Blom, R.; Burns, C. J.; Volden, H. V. *J. Chem. Soc., Chem. Commun.* **1987**, 768. (b) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1045.

[4] (a) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270. (b) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1285.

[5] (a) Bünder, W.; Weiss, E. *J. Organomet. Chem.* **1975**, *92*, 1. (b) Haaland, A.; Lusztyk, J.; Brunvoll, J.; Starowieyski, K. B. *J. Organomet. Chem.* **1975**, *85*, 279.

[6] (a) Kaupp, M.; Schleyer, P. v. R.; Dolg, M.; Stoll, H. *J. Am. Chem. Soc.* **1992**, *114*, 8202. (b) Blom, R.; Faegri, K., Jr.; Volden, H. V. *Organometallics* **1990**, *9*, 372 and references cited therein. (c) Green, J. C.; Hohl, D.; Rösch, N. *Organometallics* **1987**, *6*, 712. (d) Andersen, R. A.; Boncella, J. M.; Burns, C. J.; Green, J. C.; Hohl, D.; Rösch, N. *J. Chem. Soc., Chem. Commun.* **1986**, 405. (e) Ortiz, J. V.; Hoffman, R. *Inorg. Chem.* **1985**, *24*, 2095.

[7] Burdett, J. K. In *Accurate Molecular Structures: Their Determination and Importance*; Domenicano, A., Hargittai, I., Eds.; Oxford University Press, New York, 1992; p 501.

[8] Doman, T. N.; Landis, C. R.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 7264.

[9] Lippincott, E. R.; Xavier, J.; Steele, D. *J. Am. Chem. Soc.* **1961**, *83*, 2262.

[10] The VDW equation in ref 8 is incorrect. The correct equation is $E_{VDW} = \sum \epsilon_{ij}[(r_0/r_{ij})^{12} - 2(r_0/r_{ij})^6]$ and $r_0 = {}^1/_2(r_{ii} + r_{jj})$ where the labels i and j refer to the ith and jth atoms.

[11] Brooks, R.; Bruccoleri, R. E.; Olafson, B. D.; States, D. J.; Swaminathan, S.; Karplus, M. *J. Comput. Chem.* **1983**, *4*, 187.

0276-7333/93/2312-3385$04.00/0

Table I. Calculated and Observed Bond Lengths and Bond Angles for the Bent Forms and Energy Differences between the Bent and Linear Forms of [MCp$^*_2$] Complexes

	bond length[a]				tilt angle[a]			stagger angle		energy diff[a]	
M	r_0[b]	r_{calc}[c]	r_x[d]	r_g[e]	α_{calc}[c]	α_x[d]	α_g[e]	β_{calc}[c]	β_x[d]	ΔE_T[f]	ΔE_{vdw}[g]
Mg	2.03	2.00		2.019(9)	172		180	20		−0.08	0.10
Yb	2.34	2.33		2.326(5)	153		158(4)	22		−1.21	−1.07
Ca	2.36	2.35	2.33–2.36[h]	2.313(6)	152	146, 148[h]	154(3)	19	19, 25[h]	−1.29	−1.15
Sr	2.49	2.48		2.469(3)	147		149(3)	18		−1.65	−1.58
Sm	2.53	2.52	2.53		145	140		18	19	−1.74	−1.68
Eu	2.53	2.52	2.53		145	140		18	19	−1.74	−1.68
Ba	2.74	2.73	2.70–2.78[h]	2.631(6)	138	131	148(6)	26	32, 28[h]	−2.03	−2.10

[a] Bond lengths in angstroms, tilt angles in degrees, energy differences in kilocalories per mole. [b] Equilibrium bond length, M–D. [c] Molecular mechanics calculated values. [d] X-ray diffraction values; see references. [e] Gas phase values; see references. [f] Difference in total energy of the bent minus the linear geometry. [g] Difference in VDW energy of the bent minus the linear geometry. [h] Values refer to different molecules in the unit cell; only cases where appreciable differences are found are included.

Table II. Calculated Geometry of [M((i-Pr)$_5$C$_5$)$_2$] Complexes with the Head–Tail Clockwise–Anticlockwise Isopropyl Conformation (See 5)

M	r_{calc}[a] (Å)	α_{calc}[a] (deg)	β_{calc}[a] (deg)	γ_{calc}[b] (deg)
Yb	2.41	180	21	8
Ca	2.43	180	21	8
Sr	2.55	180	23	6
Sm	2.58	180	23	6
Eu	2.58	180	23	6
Ba	2.77	180	26	3

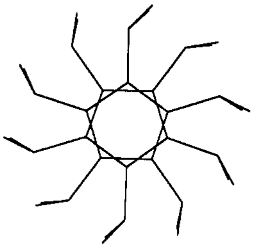
[a] See Figures 2 and 3 for definition of symbols. [b] Out of plane angle made by the isopropyl group and the Cp plane.

imate charge equilibration method,[12] did not alter the minimized geometries. On the assumption that electronic factors play no role in determining the bent structures, the bending constant, k_{DMD}, was set to zero so that the final tilt angle, α, would be controlled solely by nonbonded interactions.

The results are collected in Table I. The calculated bond lengths, r_{calc}, tilt angles, α_{calc}, and stagger angles, β_{calc}, are in remarkable agreement with experiment, particularly when potential crystal packing effects are considered, when the assumptions used in the analysis of gas phase electron diffraction data are recognized,[13] and if the possibility of an electronic component leading to linearity in the Mg species is accepted. It should be noted, however, that the tilt angle depends critically on the Mg–D distance. Thus we find that for a Mg–D distance of 1.97 Å, α = 178°, suggesting that for [MgCp$^*_2$] nonbonded interactions may be sufficient to produce the observed linearity. The ΔE_{VDW} values increase in magnitude with an increase in metal radius mainly because the VDW attractive energy decreases in the linear geometry as the M–D distance increases. The differences in total energy (ΔE_T) between bent and linear geometries is almost entirely accounted for by the differences in VDW energy (ΔE_{VDW}). The small energy differences between the bent and linear geometries indicate that, at 25 °C, these are "floppy" molecules where the tilt angle can vary widely. In all structures the M–D–C angle is calculated as close to 90° as is found experimentally. The shortest methyl group carbon–carbon distances of the two Cp* ligands fall in the range 3.5–3.7 Å. Experimentally, these values are found to be about 4.1 Å[2b,c] for these bent metallocenes.

Except perhaps for the Mg species, these results provide a persuasive case for VDW attractions being the dominant, if not the sole factor, in causing the bending. This conclusion is robust because the calculated geometries are essentially controlled by the M–D bond length and based on the assumption that the tilting energy term is small relative to the other terms.

On this basis we predict that all bis(pentaisopropyl)-metallocenes of the metals in Table I should be linear because of interligand methyl–methyl repulsions. Two minimized structures of the Ba complex with different orientations of the probably locked[14] isopropyl groups are shown in 4 and 5 (without hydrogens). These differ in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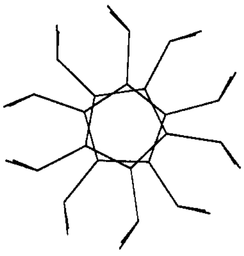
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energy by only 0.16 kcal mol^{-1} (4 > 5). The calculated M–D bond length is 2.77 Å, and the isopropyl groups bend out of the Cp plane away from the Ba by about 3°. The predicted bond lengths and bond angles for [M((i-Pr)$_5$C$_5$)$_2$] are collected in Table II. It should be noted that the Cp rings require full substitution with isopropyl groups in order to obtain the linear structures by our calculations. Thus the [Ba((i-Pr)$_4$C$_5$)$_2$] molecule is found to be bent (α = 154°)[15] and we calculate a bend angle of 151° with the same relative orientation of (i-Pr)$_4$C$_5$ ligands as found in the crystal.

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Supplementary Material Available: Textual details of the molecular mechanics calculations and tables of the results of calculations on the complex [MgCp$_2$] (4 pages). Ordering information is given on any current masthead page.

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(12) Rappé, A. K.; Goddard, W. A., III. *J. Phys. Chem.* **1991**, *95*, 3358.

(13) Hargittai, I., Hargittai, M., Eds.; *Stereochemical Applications of Gas Phase Electron Diffraction*; Verlag Chemie: Weinheim, 1988.

(14) Siegel, J.; Mislow, K. *J. Am. Chem. Soc.* **1983**, *105*, 7763. Siegel, J.; Gutiérrez, A.; Schweizer, W. B.; Ermer, O.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 1569.

(15) Williams, R. A.; Tesh, K. F.; Hanusa, T. P. *J. Am. Chem. Soc.* **1991**, *113*, 4843.