

The Ions MCp_2^+ ($M = Sc, La$): Significantly Bent Sandwich Species

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Summary: Ab initio calculations show that the hypothetical organometallic cations MCp_2^+ ($M = Sc, La$) have bent-metallocene structures. This is due to covalent σ -bonding contributions involving the totally symmetric metal d_σ orbitals, which favor bent geometries. While these orbitals contribute much less to covalent bonding in these systems than the d_π orbitals, their involvement is sufficient to result in bent structures.

Do heavy alkaline-earth-metal and lanthanide(II) metallocenes MCp_2 ($M = Ca, Sr, Ba, Sm, Eu, Yb$) prefer bent or linear sandwich structures?²⁻⁵ While experimental structure determinations indicate bent geometries^{2,3} (cf. Figure 1 for the definition of the bending angle), these refer either to gas-phase thermal average structures at elevated temperatures² or to solid-state structures where nonnegligible intermolecular interactions are present.³ Our recent ab initio pseudopotential calculations show that all of these species have very shallow bending potentials.⁵ While the calculated equilibrium structures for $M = Ba, Sm, Eu$ deviate slightly from linearity, $CaCp_2$ and $YbCp_2$ probably are linear.⁵ These results for the metallocenes contrast sharply with those for simpler MX_2 species (e.g., $X = \text{halogen, H, CH}_3, \text{NH}_2, \text{OH}$). The latter show significantly bent structures (except for the lighter metal Ca).^{6a-e} Covalent σ -MX-bonding contributions (involving

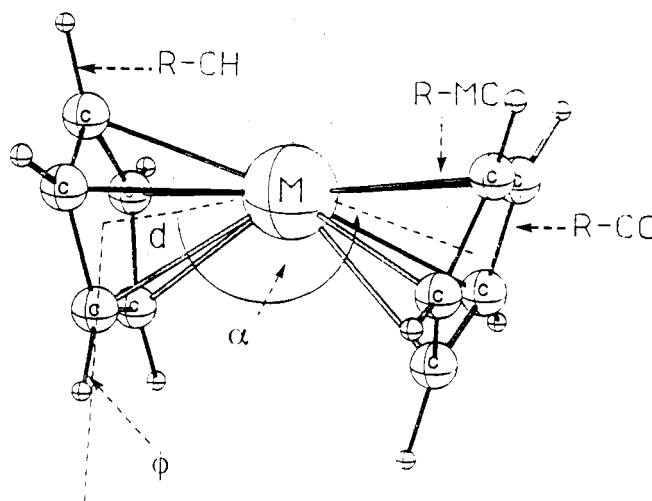


Figure 1. Definition of internal coordinates for MCp_2 and MCp_2^+ .

metal d orbitals) favor bent structures,⁶ but π -bonding contributions favor linear MX_2 geometries.^{6d} Since the Cp^- ligand functions mainly as a π donor, the reduced preference for bent structures in the MCp_2 compounds becomes clear.⁵

In addition to these covalent bonding contributions, the polarization of the cation by the anions favors bent structures, whereas the repulsion and polarization of the anions favors linear geometries.^{6a,c} Thus, two explanations for the at least slightly bent equilibrium geometries of the heavier MCp_2 species (e.g. $M = Ba, Sm$) may be envisaged: (a) the polarization of the metal cation by the ligands^{2d,5} or (b) the presence of small σ -bonding contributions

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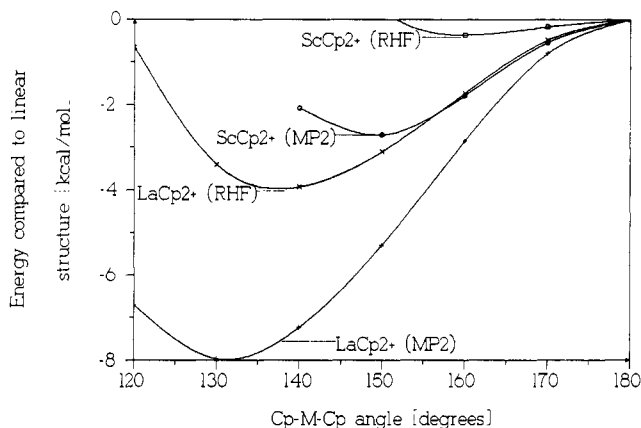
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Table I. M-X Distances R-MX (Å), Bond Length Expansions upon Linearization ΔR_1 (Å), XMX Angles (deg), and Linearization Energies ΔE_1 (kcal/mol) for MX_2^+ (M = Sc, La; X = H, F, Cp)⁷

	SCF				MP2			
	R-MX	ΔR_1	XMX	ΔE_1	R-MX	ΔR_1	XMX	ΔE_1
ScH ₂ ⁺	1.740	0.084	111.9	15.5	1.699	0.091	104.1	24.3
ScF ₂ ⁺	1.786	0.032	125.8	6.6	1.769	0.037	116.2	11.4
ScCp ₂ ⁺	2.163	0.003	162.5	0.4	2.104	0.008	149.0	2.8
LaH ₂ ⁺	2.066	0.154	108.7	28.4	2.020	0.160	106.4	34.7
LaF ₂ ⁺	2.108	0.055	113.6	13.4	2.090	0.062	108.8	16.6
LaCp ₂ ⁺	2.590	0.028	138.0	4.2	2.522	0.043	130.7	8.6

**Figure 2.** Bending potentials for MCp_2^+ (M = Sc, La) obtained by SCF and MP2 single-point calculations, respectively.⁷

(dwarfed by the π contributions but still sufficient to cause bending). The isoelectronic systems MCp_2^+ (e.g. M = Sc, La) are expected to be much more covalent than the neutral MCp_2 species, but the trications are less polarizable. Hence, these species are ideal model complexes to differentiate between the two possible explanations: If the complexes are linear, explanation (a) gains credibility for the rather polarizable dications Ba^{2+} and Sm^{2+} . If they are bent, this supports the σ -bonding hypothesis (b). We have therefore carried out ab initio pseudopotential calculations⁷ on the molecular and electronic structures of ScCp_2^+ and LaCp_2^+ and, for comparison, on MH_2^+ and MF_2^+ (M = Sc, La). While the isolated MCp_2^+ cations are not known experimentally, such moieties are of considerable interest as fragments of the important Cp_2MX systems (e.g. X = halogen, hydride, alkyl, etc.).^{8,9}

Figure 2 shows the bending potentials obtained for

(7) (a) Hartree-Fock gradient geometry optimizations and partial optimizations at the MP2 level of theory have been carried out with the Gaussian 90 program (Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian 90, Revision F; Gaussian, Inc., Pittsburgh, PA, 1990). For MCp_2^+ , the SCF ring geometry obtained for the linear (D_{3d}) metallocene structure was kept fixed in the partial optimizations of M-ring distances and ring-M-ring angles (within C_2 symmetry) at the SCF and MP2 levels. MH_2^+ and MF_2^+ have been fully optimized within C_{2v} and D_{3h} symmetry. (b) Quasirelativistic 11-valence-electron pseudopotentials and extended valence spd basis sets have been used for Sc and La, augmented by one f function in MP2 calculations (Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* 1987, 86, 866. Dolg, M.; Stoll, H.; Savin, A.; Preuss, H. *Theor. Chim. Acta* 1989, 75, 173. Dolg, M.; Stoll, H. *Theor. Chim. Acta* 1989, 75, 369). Pseudopotentials and DZ valence basis sets have been used for C and F, with diffuse and polarization functions added on F (Igel-Mann, G.; Stoll, H.; Preuss, H. *Mol. Phys.* 1988, 65, 1321. Dolg, M. Dissertation, Stuttgart, Germany, 1989. Kaupp, M.; Stoll, H.; Preuss, H. *J. Comput. Chem.* 1990, 11, 1029. Cf. ref 6c for the fluorine basis.). A (4s)/[2s] hydrogen basis (Dunning, T. H.; Hay, P. J. In *Methods of Electronic Structure Theory*. *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 3) was employed, with one p function ($\alpha = 1.0$) added for MH_2^+ .

(8) See, e. g.: Evans, W. J. *Adv. Organomet. Chem.* 1985, 24, 131.

Table II. Other Geometry Parameters^a Calculated for MCp_2^+ (M = Sc, La)⁷

M	R-MC	R-CC	R-CH	φ
Sc	2.477	1.411	1.065	4.3
La	2.880	1.410	1.066	6.0

^aDistances in Å and φ in deg. The SCF results were obtained for linear (D_{3d}) geometries. Cf. Figure 1 for the internal coordinates.

MCp_2^+ .⁷ Table I gives the X-M-X angles, the linearization energies, and the M-X distances for MX_2^+ . Table II summarizes the Cp ligand geometry. Obviously, all of these species are bent. As electron correlation is important for the quantitative evaluation of the angles and linearization energies (as well as for the M-ring distances in the metallocenes⁵), we will discuss only the MP2 results: The linearization energies for a given metal decrease along the series X = H, F, Cp, in agreement with an increasing π -bonding character of the ligand.^{5,6d,10} However, even the MCp_2^+ cations are considerably bent, in contrast to the floppy neutral MCp_2 species (M = Ca, Sr, Ba, Sm, Eu, Yb).⁵ The La systems are generally more strongly bent than the cations containing the smaller Sc.

Table III shows that π bonding dominates the covalent bonding contributions in the MCp_2^+ systems (cf., for example, metal d_{xz} and d_{yz} populations). However, the σ populations (s and totally symmetric $d_{z^2} + d_{x^2-y^2}$ populations) are by no means negligible. More importantly, the $d_{z^2} + d_{x^2-y^2}$ populations increase considerably upon bending, leading to larger overall covalent bonding contributions (the average Sc-C Wiberg bond order increases from 0.166 to 0.173). The π populations change only very little. Thus, the σ -bonding contributions are responsible for the bent metallocene structures, even though they represent only a minor fraction of the total covalent bonding. This conclusion is likely to apply to the only slightly bent, more ionic MCp_2 systems (e.g. M = Ba, Sm)⁵ as well. Other cationic d^0 MCp_2^+ (M = Y, Ln(III)) species are expected to adopt angles and linearization energies intermediate between ScCp_2^+ and LaCp_2^+ .

One aspect that could not be quantified in the present study is the magnitude of the ring-ring repulsion. While the smaller size of the group 3 trications compared to that of the group 2 and lanthanide(II) dications will increase the repulsion (and the polarization) of the rings, the smaller negative ligand charge in the MCp_2^+ systems (e.g., the NPA charges are ca. 0.5 electron per Cp ring in ScCp_2^+ compared to ca. 0.9 electron in CaCp_2^5) will reduce it. As the square of the charges enters a Coulomb-type interaction law, the net effect probably is a reduction of the in-

(9) Semiempirical EHMO calculations predict a small preference for a bent structure in SmCp_2^+ : Ortiz, J. V.; Hoffmann, R. *Inorg. Chem.* 1985, 24, 2095.

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Table III. Metal Valence Populations^a for ScCp₂⁺ in Different Geometries^b

$\angle\text{CpScCp}$, deg	s	p _x	p _y	p _z	d _{xy}	d _{zz}	d _{yz}	d _{x²-y² + d_{z²}}	d _{tot}
180	0.134	0.016	0.016	0.003	0.005	0.379	0.379	0.062	0.826
160	0.133	0.015	0.012	0.004	0.015	0.377	0.382	0.100	0.874

^a Natural population analysis was employed.¹¹ ^b The yz plane contains the Cp ring midpoints and the metal.

ter-ring repulsion. This will also contribute to the more bent structures for the MCp₂⁺ cations studied here compared to the neutral MCp₂ systems.

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