(γ in this case) may depend much more strongly on chain length than does λ_{max}.[1]

The fact that a catalyst and conditions have been found to effect the living polymerization of 1 suggests that it may be possible to polymerize other $HC{\equiv}CCH_2XCH_2C{\equiv}CH$ derivatives. It is important to note that the initiator employed here is one of the members of a class of well-characterized initiators employed for ring opening of norbornenes and substituted norbornadienes[28] and therefore that it should be possible to synthesize other well-defined block copolymers relatively routinely and to prepare microphase-separated materials from them. Further studies in these directions are under way.

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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 temperatures[2] 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 = halogen, H, CH_3, NH_2, OH). The latter show significantly bent structures (except for the lighter metal Ca).[6a-e] Covalent σ-MX-bonding contributions (involving 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]

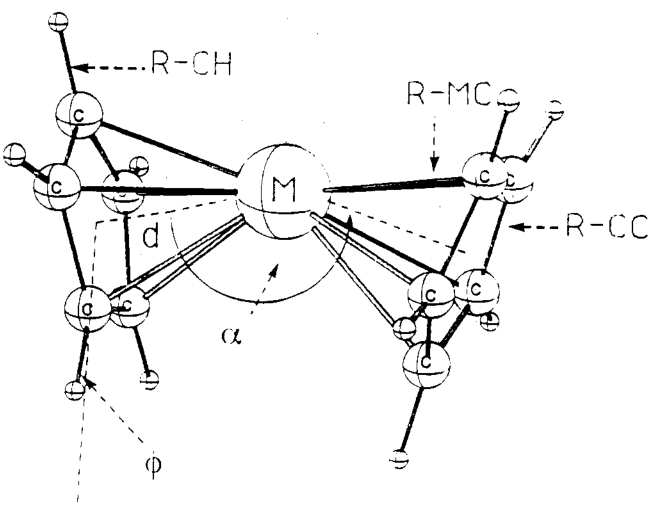

Figure 1. Definition of internal coordinates for MCp_2 and MCp_2^+.

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

	SCF				MP2			
	R-MX	ΔR_l	XMX	ΔE_l	R-MX	ΔR_l	XMX	ΔE_l
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

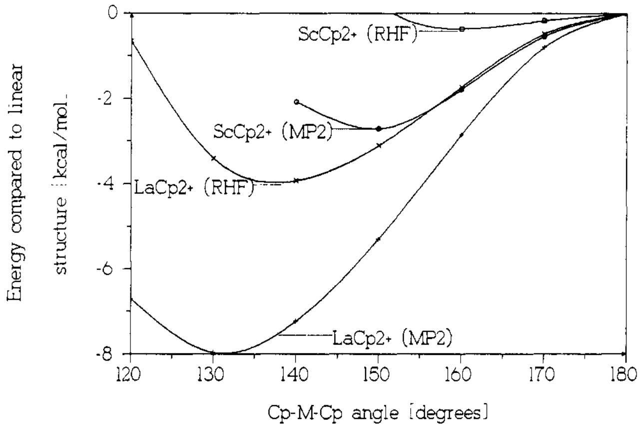

Figure 2. Bending potentials for MCp_2^+ (M = Sc, La) obtained by SCF and MP2 single-point calculations, respectively.[7]

(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 calculations[7] 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 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 metallocenes[5]), 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 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

[a] Distances in Å and φ in deg. The SCF results were obtained for linear (D_{5d}) geometries. Cf. Figure 1 for the internal coordinates.

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-

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(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_{5d}) metallocene structure was kept fixed in the partial optimizations of M–ring distances and ring–M–ring angles (within C_s symmetry) at the SCF and MP2 levels. MH_2^+ and MF_2^+ have been fully optimized within C_{2v} and $D_{\infty h}$ 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 (α = 1.0) added for MH_2^+.

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Table III. Metal Valence Populations[a] for $ScCp_2^+$ in Different Geometries[b]

∠CpScCp, deg	s	p_x	p_y	p_z	d_{xy}	d_{xz}	d_{yz}	$d_{x^2-y^2} + d_{z^2}$	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 MCp_2^+ cations studied here compared to the neutral MCp_2 systems.

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Articles

Unusual Low-Valent Dirhodium Complexes Bridged by Bis(dimethylphosphino)methane Ligands

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The low-valent complex $[Rh_2(CO)_3(dmpm)_2]$ (1) (dmpm = $Me_2PCH_2PMe_2$) is prepared by the reaction of *trans*-$[RhCl(CO)(dmpm)]_2$ with aqueous NaOH and CO. Under a CO atmosphere 1 is in equilibrium with the labile tetracarbonyl species $[Rh(CO)(\mu\text{-}CO)(dmpm)]_2$ (2). The structure of 1 is believed to be unsymmetrical having a trans arrangement of diphosphine ligands at one metal and a cis arrangement at the other, and a mixed-valence Rh(1+)/Rh(1−) formulation, while 2 is symmetric having the bridging diphosphines cis at both metals, and a corresponding Rh(0)/Rh(0) formulation. Reduction of $[Rh_2Cl_2(CO)_2(\mu\text{-}RC{\equiv}CR)(dmpm)_2]$ (R = CO_2Me, CF_3) yields $[Rh_2(CO)_2(\mu\text{-}RC{\equiv}CR)(dmpm)_2]$ (**3**, **4**), which can also be obtained by alkyne addition to 1. The alkyne ligands are apparently bound perpendicular to the Rh–Rh axes in both species. Protonation of 1 with $HBF_4{\cdot}OEt_2$ yields $[Rh_2(CO)_3(\mu\text{-}H)(dmpm)_2][BF_4]$, and under carbon monoxide this yields $[Rh_2(CO)_4(\mu\text{-}H)(dmpm)_2][BF_4]$. Protonation of 3 yields $[Rh_2(CO)_2(\mu\text{-}DMAD)(\mu\text{-}H)(dmpm)_2][BF_4]$, whereas protonation of 4 yields $[Rh_2(CO)_2(CF_3C{=}C(H)CF_3)(dmpm)_2][BF_4]$, which apparently has a σ, π-vinylic moiety. Reaction of this vinyl complex with CO gives $[Rh_2(CO)_3(CF_3C{=}C(H)CF_3)(\mu\text{-}CO)(dmpm)_2][BF_4]$ in which the vinyl group is σ bound to only one metal.

Introduction

Oxidative-addition reactions are of fundamental importance in organometallic chemistry and are of enormous practical significance since oxidative addition represents one of the key steps in the mechanisms of most homogeneous catalysts.[1] As the term implies, the oxidative-addition reaction proceeds with an increase in coordination number and oxidation state of the metal center(s) involved. Coordinatively unsaturated, electron-rich metal complexes are therefore well suited to such processes. Our recent interest in oxidative-addition reactions[2-10] has centered around *dppm*-bridged complexes involving Rh or Ir (dppm = bis(diphenylphosphino)methane) in efforts to obtain an improved understanding about the functions of the adjacent metals in the oxidative-addition step(s), about the subsequent ligand rearrangements that occur, and about the possibility of coupling organic fragments on the adjacent metals. It was surmised that low-valent binuclear complexes of Rh(0) or Rh(I), bridged by the closely related

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