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Molecular Structures of Alkaline-Earth-Metal Metallocenes: Electron Diffraction and ab Initio Investigations

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The *thermal average* molecular structures of $Sr(C_5Me_5)_2$ and $Ba(C_5Me_5)_2$ have been determined by gas electron diffraction. For both compounds the experimental data are consistent with molecular models where the C_5Me_5 rings are approximately η^5-bonded to the metals and with ring centroid–metal–ring centroid angles close to 150°. The metal–carbon bond distances are r_a(Sr–C) = 275.0 (8) pm and r_a(Ba–C) = 289.8 (10) pm (mean values). The experimental results are compared to calculations on the model compounds $Mg(C_5H_5)_2$ and $Ca(C_5H_5)_2$ in a discussion of the bonding and structure of alkaline-earth-metal metallocenes.

Introduction

The alkaline-earth-metal dicyclopentadienyl compounds have been known for some time.[1] While no quantitative structural information has been available for the heavier alkaline-earth metals strontium and barium,[2] the lighter alkaline-earth-metal dicyclopentadienyls have been structurally characterized; bis(cyclopentadienyl)beryllium, $Be(C_5H_5)_2$, has in the solid state one cyclopentadienyl ring η^5-bonded and the other η^1-bonded to the beryllium atom.[3] In the gas phase the structure is similar, but due to the low scattering power of light atoms in the gas electron diffraction experiment, the bonding mode of the second cyclopentadienyl ring is uncertain, and a second investigation of the compound concludes that the second cyclopentadienyl ring is more or less η^3-bonded to the beryllium atom.[4] Bis(cyclopentadienyl)magnesium or magnesocene, $Mg(C_5H_5)_2$, has a monomeric, regular sandwich structure where the cyclopentadienyl rings are parallel and are η^5-bonded to the magnesium atom in both the gas and the crystalline phases.[5,6] Bis(cyclopentadienyl)calcium, $Ca(C_5H_5)_2$, has a polymeric solid-state structure, with each calcium atom surrounded by four cyclopentadienyl rings in a $\eta^5,\eta^5,\eta^3,\eta^1$ fashion.[7] This polymeric compound has a low vapor pressure, and attempts to obtain electron diffraction patterns of $Ca(C_5H_5)_2$ for a determination of the molecular gas-phase structure have failed.[8] The base-free bis(cyclopentadienyl) compounds of strontium and barium are also expected to be polymers in the solid state on the basis of their high temperatures of sublimation, ~260 °C (Ca), 360–440 °C (Sr), and 420–460 °C (Ba) at "hochvacuum", respectively, their low solubility, and their IR spectra, which are similar to those of the Ca analogue.[1]

The sterically bulky pentamethylcyclopentadienyl ligand has been employed successfully in order to prevent polymerization and thus increase the vapor pressure of compounds compared to those of their nonmethylated cyclopentadienyls.[9,10] We have recently determined the molecular structures of $Mg(C_5Me_5)_2$, $Ca(C_5Me_5)_2$, and $Yb(C_5Me_5)_2$ in the gas phase.[9] The *thermal average* structures of $Ca(C_5Me_5)_2$ and $Yb(C_5Me_5)_2$ were somewhat surprisingly found to be bent sandwich structures with ring centroid–metal–ring centroid angles of 154 (3) and 158 (4)° respectively, while $Mg(C_5Me_5)_2$ has a regular sandwich structure as found in the nonmethylated analogue. Also $Sr(C_5Me_5)_2$ and $Ba(C_5Me_5)_2$ have recently been prepared,[11] and the temperatures needed to sublime these compounds, 100–110 and 130–140 °C at 10^{-3} mmHg, respectively, indicate that these compounds are much more volatile than their nonmethylated analogues. Indeed, the vapor pressures were high enough to permit an investigation by gas electron diffraction (GED). The main results of this investigation have been presented previously in a short communication.[12] Since that time the crystal structure of $Ba(C_5Me_5)_2$ has been reported,[13] as have the X-ray structures of the tetrahydrofuran adduct $Sr(C_5H_3(SiMe_3)_2)_2(thf)$.[14] These four structures are, as far as we know, the only organostrontium and -barium structures that have been reported.

Theoretical calculations for heavier metallocene compounds have been plagued by notorious difficulties, as shown in a series of calculations by Almlöf and co-workers,[15] which conclude that due to d-shell correlation effects a post-Hartree–Fock treatment is required to account qualitatively for the molecular structure. This fact and

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[1] Wilkinson, G.; Cotton, F. A. *Chem. Ind. (London)* **1954**, *11*, 307. Fischer, E. O.; Hofmann, H. P. *Chem. Ber.* **1959**, *92*, 482. Fischer, E. O.; Stölzle, G. *Chem. Ber.* **1961**, *94*, 2187.

[2] This statement is not strictly true; the only available information about interatomic distances in organostrontium or -barium compounds was that from an absorption and emission spectral investigation of bis(fluorenyl)barium in tetrahydrofuran (thf) and tetrahydropyran (thp) solutions. That investigation indicated that the distances from one fluorenyl center to the other are approximately 450 and 470 pm and that the angles between the planes defined by the fluorenyl ligands are about 79 and 67° in thf and thp, respectively. The tilting of the fuorenyl ligands may in these cases be a consequence of solvent coordination to the barium atom. See: Hogen-Esch, T. E., Plodinec, M. J. *J. Chem. Phys.* **1976**, *80*, 1085.

[3] Nugent, K. W.; Beattie, J. K.; Hambley, T. W.; Snow, M. R. *Aust. J. Chem.* **1984**, *37*, 1601.

[4] Almenningen, A.; Haaland, A.; Lusztyk, J. *J. Organomet. Chem.* **1979**, *170*, 271.

[5] Haaland, A.; Lusztyk, J.; Brunvoll, J.; Starowieyski, K. B. *J. Organomet. Chem.* **1975**, *85*, 279.

[6] Bünder, W.; Weiss, E. *J. Organomet. Chem.* **1975**, *92*, 1.

[7] Zerger, R.; Stucky, G. *J. Organomet. Chem.* **1974**, *80*, 7.

[8] Haaland, A. Personal communication.

[9] Andersen, R. A.; Boncella, J. M.; Burns, C. J.; Blom, R.; Haaland, A.; Volden, H. V. *J. Organomet. Chem.* **1986**, *312*, C49. Andersen, R. A.; Blom, R.; Boncella, J. M.; Burns, C. J.; Volden, H. V. *Acta Chem. Scand.* **1987**, *A41*, 24.

[10] Blom, R.; Haaland, A.; Weidlein, J. *J. Chem. Soc., Chem. Commun.* **1985**, 266. Blom, R.; Boersma, J.; Budzelaar, P. H. M.; Fischer, B.; Haaland, A.; Volden, H. V.; Weidlein, J. *Acta Chem. Scand.* **1986**, *A40*, 113.

[11] Burns, C. J.; Andersen, R. A. *J. Organomet. Chem.* **1987**, *325*, 31.

[12] Andersen, R. A.; Blom, R.; Burns, C. J.; Volden, H. V. *J. Chem. Soc., Chem. Commun.* **1987**, 768.

[13] Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1045.

[14] Engelhardt, L. M.; Junk, P. C.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1988**, 1500.

[15] Lüthi, H. P.; Ammeter, J. H.; Almlöf, J.; Faegri, K., Jr. *J. Chem. Phys.* **1982**, *77*, 2002. Almlöf, J.; Faegri, K., Jr.; Schilling, B. E. R.; Lüthi, H. P. *Chem. Phys. Lett.* **1984**, *106*, 266. Lüthi, H. P.; Siegbahn, P. E. M.; Almlöf, J.; Faegri, K., Jr.; Heiberg, A. *Chem. Phys. Lett.* **1984**, *111*, 1.

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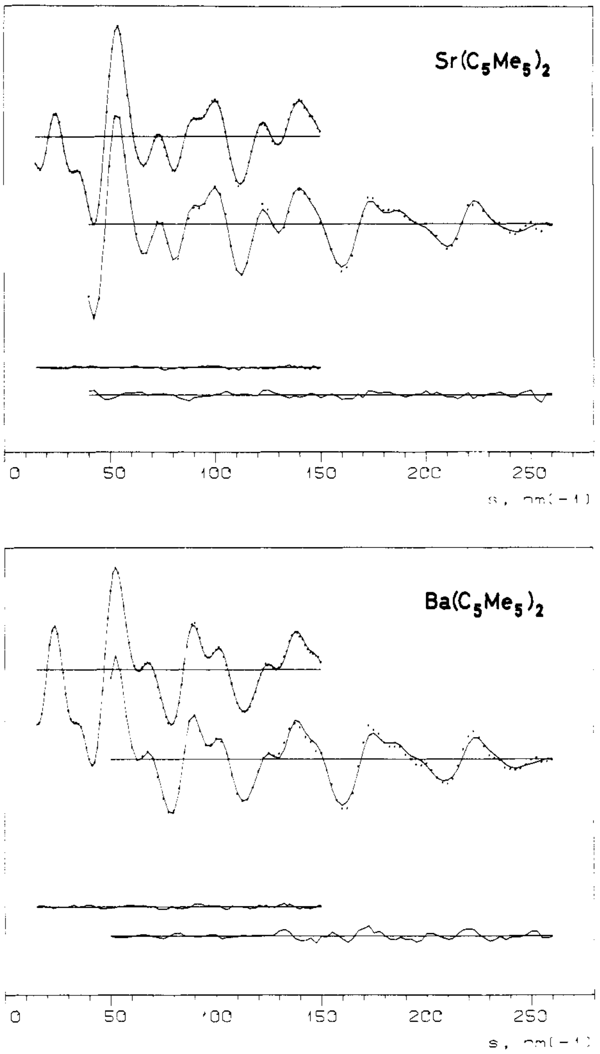

Figure 1. Theoretical molecular intensity curves with experimental points for $Sr(C_5Me_5)_2$ (top) and $Ba(C_5Me_5)_2$ (bottom). The differences between experimental and theoretical curves for the best models are drawn in the lower part for each compound.

their rather large size effectively place the strontium and barium compounds out of reach of a thorough theoretical investigation. However, magnesocene appears to fall outside this rather unsuccessful trend; high-quality Hartree–fock ab initio calculations reproduce the experimental metal–ring distance to within 2 pm[16] and provide a reasonable interpretation of the IR and Raman spectra. To our knowledge, no corresponding theoretical studies of bis(cyclopentadienyl)calcium exists. It therefore appeared worthwhile to perform high-quality Hartree–Fock calculations on the model compounds $Mg(C_5H_5)_2$ and $Ca(C_5H_5)_2$ to further elucidate the effects that influence the molecular structures of the alkaline-earth-metal metallocenes.

In the present paper we report the full gas-phase structures of bis(pentamethylcyclopentadienyl)strontium and -barium, $Sr(C_5Me_5)_2$ and $Ba(C_5Me_5)_2$, respectively, and ab initio calculations on the two model compounds $Mg(C_5H_5)_2$ and $Ca(C_5H_5)_2$.

Experimental Section

General and Electron Diffraction Data. The ether complexes $(C_5Me_5)_2Sr(OEt_2)$ and $(C_5Me_5)_2Ba(thf)_2$ were prepared from the metal diiodides and NaC_5Me_5 in OEt_2 (Sr) and thf (Ba) as described by Andersen et al.[11] The base-free compounds were obtained by the "toluene reflux" method.[17] The GED patterns of $Sr(C_5Me_5)_2$ (I) and $Ba(C_5Me_5)_2$ (II) were recorded on a Balzers Eldigraph KD-G2 instrument[18] with an accelerating potential of 42 kV. The electron wavelength was calibrated against diffraction patterns of benzene (r_a(C–C) = 139.75 pm), with an estimated uncertainty of 0.1%. In order to keep the temperature at a minimum, and thus minimize the thermal decomposition, we used a torus-shaped nozzle,[19] which permits the diffraction patterns to be recorded with a vapor pressure of approximately 1 mmHg. The nozzle and reservoir temeratures were 200 (5) °C for I and 270 (5) °C for II. Because of the high temperatures needed to obtain the desired vapor pressure of the compounds, Teflon O-rings were used in the inlet system. Exposures were made with nozzle-to-plate distances of about 50 and 25 cm. For compound I five plates at 50 cm and four plates at 25 cm were exposed, with s ranging from 15.0 to 150.0 nm^{-1} with Δs = 1.25 nm^{-1} (50 cm) and from 40.0 to 260.0 nm^{-1} with Δs = 2.5 nm^{-1} (25 cm). For compound II the numbers of plates were five at 50 cm and three at 25 cm, with s ranging from 15.0 to 150.0 nm^{-1} with Δs = 1.25 nm^{-1} (50 cm) and from 50.0 to 260.0 nm^{-1} with Δs = 2.5 nm^{-1} (25 cm). The plates were subjected to photometry and the optical densities processed by standard procedures.[20] The experimental backgrounds were computer-drawn by a least-squares fit of the sum of a polynomial and a theoretical molecular intensity curve to the leveled experimental intensity curve. The degree of the polynomial was 6 for the 50-cm data and 8 for the 25-cm data. The curves for each nozzle-to-plate distance were averaged, but the average curves were not connected during the least-squares refinements. Complex atomic scattering factors, $f'(s)$, were calculated from an analytical representation of the atomic Hartree–Fock–Slater potentials for C[21] and from a bonded potential for H.[22] Tabulated scattering factors were used for Sr and Ba.[23]

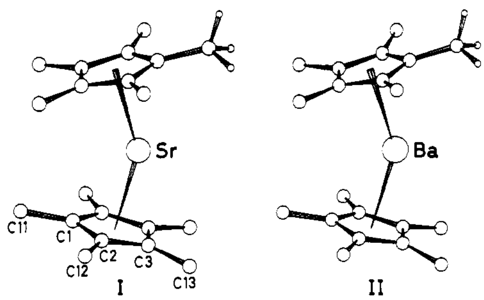

Figure 2. Molecular models of $Sr(C_5Me_5)_2$ and $Ba(C_5Me_5)_2$. The numberings of the carbon atoms are shown. Most of the hydrogen atoms are omitted for clarity.

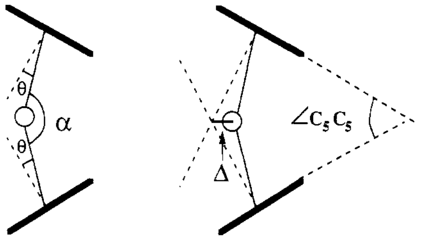

Figure 3. Definitions of α, θ, Δ, and $\angle C_5C_5$.

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(16) Faegri, K., Jr.; Almlöf, J.; Lüthi, H. P. *J. Organomet. Chem.* **1983**, *249*, 303.

(17) Coates, G. E.; Glockling, F. *J. Chem. Soc.* **1954**, 22.

(18) Zeil, W.; Haase, J.; Wegmann, L. *Z. Instrumentenkd.* **1966**, *74*, 84. Bastiansen, O.; Graber, R.; Wegmann, L. *Balzers' High Vacuum Report* **1969**, *25*, 1.

(19) Ashby, E. C.; Fernholt, L.; Haaland, A.; Seip, R.; Smith, R. S. *Acta Chem. Scand.* **1980**, *A34*, 213; Annual Report of the Norwegian Electron Diffraction Group, 1980.

(20) Andersen, B.; Seip, H. M.; Strand, T. G.; Stølevik, R. *Acta Chem. Scand.* **1969**, *23*, 3224.

(21) Strand, T. G.; Bonham, R. A. *J. Chem. Phys.* **1964**, *40*, 1686. Yates, A. C. *Comput. Phys. Commun.* **1971**, *2*, 175.

(22) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(23) *International Tables for X-Ray Crystollography*; Kynoch Press: Birmingham, 1974; Vol. 4, Section 2.5.

Table I. Correlation between the Main Parameters (×100) for the Two Different Choices of Independent Parameters As Described in the Text[a]

	scheme A							scheme B					
	σ_{ls}	d	α	θ	l_1	l_2		σ_{ls}	d	Δ	$\angle C_5C_5$	l_1	l_2
							$Sr(C_5Me_5)_2$						
d	0.18	...					d	0.58	...				
α	1.01	-30	...				Δ	2.30	95	...			
θ	0.47	-22	74	...			$\angle C_5C_5$	0.66	11	16	...		
l_1	0.23	-42	43	63	...		l_1	0.28	68	78	1	...	
l_2	0.54	-25	23	50	50	...	l_2	0.52	33	43	31	46	...
							$Ba(C_5Me_5)_2$						
d	0.19	...					d	1.13	...				
α	2.02	-2	...				Δ	4.41	97	...			
θ	1.01	-10	50	...			$\angle C_5C_5$	1.61	3	16	...		
l_1	0.54	-10	26	85	...		l_1	0.41	68	73	40	...	
l_2	0.78	-7	67	74	53	...	l_2	0.70	74	71	-21	35	...

[a] Scheme A gave the correlation when the bend angle, α, and the tilt angle, θ, were chosen as independent parameters. Scheme B gene the correlation when $\angle C_5C_5$ and the displacement of the metal atom away from the intersection of the C_5 axis of the two cyclopentadienyl rings, Δ, were used as independent parameters. σ_{ls} is the standard deviation from least squares. l_1 is l(M–C) and l_2 is l(M···C(Me)).

The molecular intensities were modified by multiplication by $s/|f'_C||f'_M|$ (M = Sr or Ba).

Structure Refinements. The structure refinements of I and II were carried out as previously described for the Ca and Yb analogues.[9] The molecular models are shown in Figure 2. It was assumed that the C_5Me_5 ligands have C_{5v} symmetry and that the C–CH_3 fragments have local C_{3v} symmetry with the hydrogen atoms fixed in positions with two pointed toward and one pointed away from the metal atom as shown in Figure 2. The best fits between experimental and theoretical molecular intensity curves were for both compounds obtained with the rings in the *staggered* conformation with overall molecular C_s symmetry. The mirror plane is defined by the metal atom and the C1–C11 bond. With these assumptions each molecular geometry is described by eight independent geometrical parameters: the metal–ring centroid distance (d), the bond distances C–C (in ring), C–C(Me), and C–H, the angle between the C_5 ring plane and the C–C(Me) bond ($\angle C_5$, C–C(Me)), the valence angle $\angle$CCH, and two parameters describing the relative orientation of the cyclopentadienyl rings.

Two different choices of parameters were used to describe the nonparallel cyclopentadienyl rings; one scheme uses a bend angle, α, and a tilt angle, θ, as independent parameters, where θ is defined as positive as shown in Figure 3. This choice is called scheme A. Scheme B uses the angle between the two ring planes, $\angle C_5C_5$, and a parameter, Δ, that describes the displacement of the metal atom in the C_s plane away from the intersection of the two C_5 axes of the cyclopentadienyl rings as independent parameters. Δ is defined as positive as drawn in Figure 3. In Table I, the correlations between the main independent parameters are shown for the two different choices of parameters. As seen in the Table, Scheme A appears to be a somewhat better choice of parameters because the correlation is smeared over a larger number of parameters. The structural parameters obtained with the two different schemes were of course equal within the least-squares standard deviations.

In addition to these eight geometrical parameters, 12 (I) and 11 (II) root-mean-square amplitudes of vibration (l values) were refined. These are indicated in Table II with their estimated standard deviations in parentheses. Nonrefined l values were taken from the previous GED study of $Ca(C_5Me_5)_2$.[9] The theoretical molecular intensity curves calculated for the best molecular models of $Sr(C_5Me_5)_2$ and $Ba(C_5Me_5)_2$ and the corresponding experimental points are drawn in Figure 1, and the corresponding radial distribution curves (RD curves) are drawn in Figure 4.

Computational Details. All calculations were carried out by using the DISCO program, which takes full advantage of the molecular symmetry.[24] Calculations were carried out on $Mg(C_5H_5)_2$ and $Ca(C_5H_5)_2$. Initial calculations were performed on molecular models of D_{5d} symmetry, and the metal–ring centroid distances were varied to yield an optimum energy for each basis set. The ring geometries were assumed to have local D_{5h} symmetry in all calculations with r(C–C) = 142.7 pm and r(C–H) = 108.0 pm. In addition, a series of calculations have been carried out where the ring centroid–metal–ring centroid angle has been varied at fixed metal–ring centroid distances, retaining the local ring geometries above. The bent molecules were assumed to have overall C_s symmetry. Two different sets of basis functions were used for

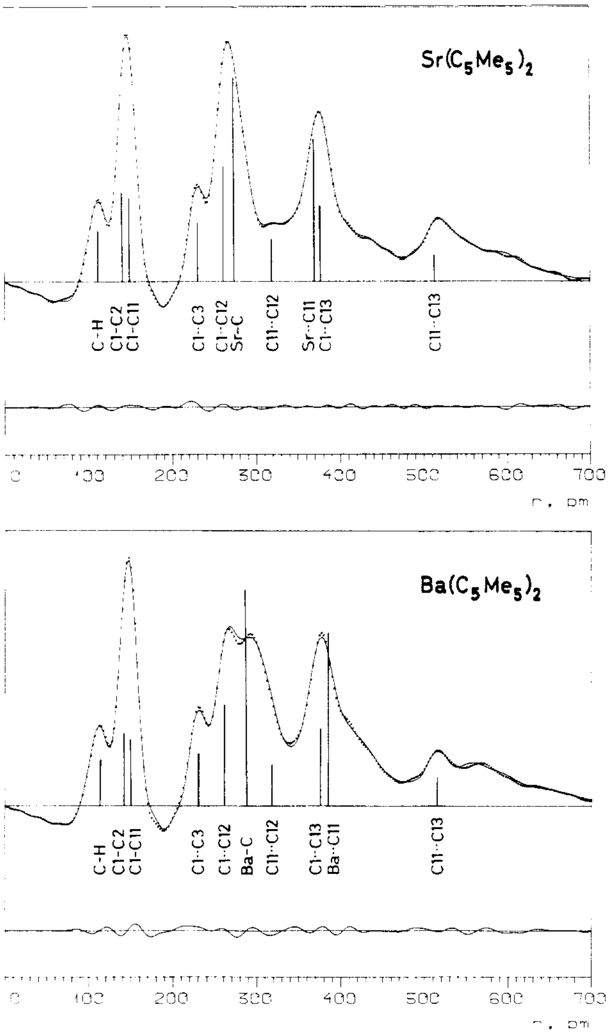

Figure 4. Experimental RD curves for $Sr(C_5Me_5)_2$ (top) and $Ba(C_5Me_5)_2$ (bottom). The most important distances are indicated with bars of height approximately proportional to the area under the corresponding peak. The differences between experimental and theoretical RD curves for the best model are drawn in the lower part for each compound. The artificial damping constant, k, is 20 pm^2.

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(24) Almlöf, J.; Faegri, K., Jr.; Korsell, K. *J. Comput. Chem.* **1982**, *3*, 385.

Table II. Geometrical Parameters and Rms Amplitudes of Vibration (*l* Values) for Bis(pentamethylcyclopentadienyl)strontium(II), $Sr(C_5Me_5)_2$, and Bis(pentamethylcyclopentadienyl)barium(II), $Ba(C_5Me_5)_2$[a]

Distances/pm

	$Sr(C_5Me_5)_2$		$Ba(C_5Me_5)_2$	
	r_a	l	r_a	l
M–C range (M = Sr, Ba)	270–280		284–296	
mean M–C	275.0 (8)	10.5 (7)	289.8 (10)	14.8 (16)
d^b	246.9 (6)		263.1 (6)	
C1–C2	142.8 (3)	4.7^d	142.9 (4)	4.7^d
C1–C11	150.6 (4)	5.2^d	151.1 (5)	5.2^d
C–H	110.1 (5)	8.4 (6)	110.5 (6)	8.5 (7)
M···C(Me)	370^c	25 (2)	385^c	24 (3)
M···H long	469^c	17 (5)	484^c	18^d
M···H short	394^c	21 (4)	408^c	41 (15)
C1···C3	231	5.8 (9)	231	6.3 (10)
C1···C12	261	7.9 (7)	261	8.9 (7)
C1···C13	376	7.6 (6)	377	9.0 (8)
C11···C12	318	13.1^d	319	13.6^d
C11···C13	515	9.5 (17)	516	8.1 (18)
C(Cp)···C′(Cp) range	435–534	14–16 (3)[e]	461–571	26–28 (8)[e]
C(Cp)···C′(Me) range	441–640	43–45 (6)[e]	468–668	43–45 (11)[e]
C(Me)···C′(Me) range	414–727	30–32 (11)[e]	445–754	31–33 (14)[e]
Δ^b	−12 (7)		−11 (13)	

Angles/deg

	$Sr(C_5Me_5)_2$	$Ba(C_5Me_5)_2$		$Sr(C_5Me_5)_2$	$Ba(C_5Me_5)_2$
$\angle C_5$–C–C(Me)	−2.3 (10)	−4.7 (10)	θ^b	−2.9 (15)	−3 (3)
∠CCH	121 (2)	120 (2)	$\angle C_5C_5{}^b$	25 (3)	26 (6)
α^b	149 (3)	148 (6)			

[a] Refined parameters are listed with estimated standard deviations ($3\sigma_{ls}$) in parentheses in units of the last digit(s). Numbering of the C atoms is shown in Figure 2. [b] See text or Figure 3 for definition. [c] Mean values. [d] Fixed values. [e] Large groups of similar *l* values.

Table III. Main Geometrical Parameters of the $M(C_5H_5)_2$ and $M(C_5Me_5)_2$ (M = Mg, Ca, Sr, Ba) Compounds in the Gas Phase[a]

	r_a(M–C)/pm	bonding modes	α/deg	θ/deg	$\angle C_5C_5$/deg	Δ/pm	ref
$Be(C_5H_5)_2$	190.3 (8)[b]	η^5,η^3					4
$Mg(C_5H_5)_2$	233.9 (4)	η^5,η^5	0^c	0^c	0^c	0^c	5
$Mg(C_5Me_5)_2$	234.1 (6)	η^5,η^5	0^c	0^c	0^c	0^c	9
$Ca(C_5Me_5)_2$	260.9 (6)	η^5,η^5	154 (3)	−1.4 (9)	20 (2)	-6^d	9
$Sr(C_5Me_5)_2$	275.0 (8)	η^5,η^5	149 (3)	−2.9 (15)	25 (3)	−12 (7)	
$Ba(C_5Me_5)_2$	289.8 (10)	η^5,η^5	148 (6)	−3 (3)	26 (6)	−11 (13)	

[a] Definitions of the parameters are given in Figure 3. [b] To the η^5-bonded cyclopentadienyl ring. [c] Best fixed values. [d] Calculated from the α and θ parameters.

each molecule: The M basis set is a 10s6p 1 d primitive basis set contracted to 6s4p1d for magnesium,[25] 12s7p4d contracted to 9s5p2d for calcium,[26] 7s3p contracted to 4s2p for carbon,[27] and a 4s basis set contracted to 2s for hydrogen.[28] The L basis set is a 12s9p2d basis set contracted to 7s5p2d for magnesium,[29] 15s11p5d contracted to 10s7p3d for calcium,[30] 9s5p1d contracted to 4s2p1d for carbon,[31] and a 4s basis set contracted to 2s for hydrogen.

Results and Discussion

The values of the geometrical parameters and root-mean-square amplitudes of vibration (*l* values) obtained for the best molecular models of $Sr(C_5Me_5)_2$ and $Ba(C_5Me_5)_2$ are listed in Table II. In parentheses are the least-squares standard deviations multiplied by a factor of 3 to compensate for errors introduced by the systematic errors. The geometrical parameters and *l* values of the pentamethylcyclopentadienyl ligand are equal to those found for other permethylated cyclopentadienyl compounds.[32] in Table III the main geometrical parameters obtained for the $M(C_5H_5)_2$ and $M(C_5Me_5)_2$ compounds of the alkaline-earth metals in the gas phase are shown.

In the gas phase both $Sr(C_5Me_5)_2$ and $Ba(C_5Me_5)_2$ have *thermal average* molecular structures that are *bent* sandwich structures with bend angles (α) of 149 (3) and 148 (6)°, respectively, and mean metal–carbon bond distances r(Sr–C) = 275.0 (8) pm and r(Ba–C) = 289.8 (10) pm. $Ba(C_5Me_5)_2$ exhibits a bent sandwich structure in the solid state as well,[13] but this bending may be rationalized as a consequence of intermolecular interaction; each bar-

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(25) 10s4p from: Roos, B.; Siegbahn, P. *Theor. Chim. Acta* **1970**, *17*, 209. Two additional sets of p orbitals (ξ = 0.45, 0.07) and a set of d orbitals (ξ = 0.1) were taken from ref 16.

(26) 12s6p from: Roos, B.; Veillard, A.; Vinot, G. *Theor. Chim. Acta* **1971**, *20*, 1. A set of diffuse p orbitals (ξ = 0.12) and d orbitals (ξ = 11.890159, 2.8731701, 0.813352, and 0.2168254 with coefficients 0.0382865, 0.1943, 0.430411, and 1.0 respectively) was also used.

(27) Dunning, T. H., Jr. *J. Chem. Phys.* **1971**, *55*, 716.

(28) Dunning, T. H., Jr. *J. Chem. Phys.* **1970**, *53*, 2823.

(29) 12s9p from: McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639. Two sets of d orbitals (ξ = 0.70 and 0.167) were taken from ref 16.

(30) 14s9p basis from: Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033. One diffuse s (ξ = 0.01) and two diffuse 4p-like functions (ξ = 0.074979 and 0.026927) were taken from: Bauschlichher, C. W., Jr.; Langhoff, S. R.; Partridge, H. *J. Chem. Phys.* **1986**, *84*, 901. The d orbitals were the same as for the M basis, but an additional set of diffuse d orbitals was added (ξ = 0.0611571).

(31) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823. A set of d orbitals with ξ = 0.6 was taken from ref 16.

(32) $Fe(C_5Me_5)_2$: Almenningen, A.; Haaland, A.; Samdal, S.; Brunvoll, J.; Robbins, J. L.; Smart, J. C. *J. Organomet. Chem.* **1979**, *173*, 293. $Mn(C_5Me_5)_2$: Fernholt, L.; Haaland, A.; Seip, R.; Robbins, J. L.; Smart, J. C. *J. Organomet. Chem.* **1980**, *194*, 351. $Ge(C_5Me_5)_2$: Fernholt, L.; Haaland, A.; Jutzi, P.; Kohl, F. X.; Seip, R. *Acta Chem. Scand.* **1984**, *A38*, 211. $In(C_5Me_5)$: Beachley, O. T., Jr.; Blom, R.; Churchill, M. R.; Faegri, K., Jr.; Fettinger, J. C.; Pazik, J. C.; Victoriano, L. *Organometallics* **1989**, *8*, 346.

Table IV. Structural Trends of the Alkali-Earth-Metal Bis(pentamethylcyclopentadienyl), Diiodo, Dichloro, and Difluoro Compounds[a]

M	$M(C_5Me_5)_2$	MI_2	MCl_2	MF_2[e]
Mg	180[b]	(lin)[e]	(lin)[e]	(lin)
Ca	154 (3)[c]	149,[f] 180,[g] (lin)[e]	180,[g,h] (lin)[e]	(bent)
Sr	149 (3)[d]	144,[f] (lin)[e]	142,[h] (bent)[e]	(bent)
Ba	148 (6)[d]	138,[f] 148,[h] (bent)[e]	127,[h] (bent)[e]	(bent)

[a] *Thermal average* (r_a) or *equilibrium* (r_e) bend angles in degrees from gas-phase electron diffraction studies are shown. Entries in parentheses are results from gas-phase molecular beam electron deflection studies; lin = linear. [b] Best fixed value.[9] [c] Reference 9. [d] This study. [e] Reference 34. [f] r_a structures.[35] [g] r_e structures.[36] [h] r_e structures.[37]

ium atom interacts with a methyl group of the neighboring molecule with a short barium–carbon distance of 334.9 (5) pm. The mean Ba–C bond distance found in the solid state is 298.7 (18) pm, which is about 10 pm longer than the distance found in the gas phase. The elongation observed in the solid is probably a consequence of the additional intermolecular barium–methyl interaction and of the increased intramolecular inter-ring methyl–methyl repulsions caused by the smaller ring centroid–barium–ring centroid angle in the solid state, 131° compared to 148 (6)° in the gas phase.

The bis(pentamethylcyclopentadienyl) compounds of the group 14 elements Ge, Sn, and Pb have *bent* sandwich structures in both the gas and the solid state.[33] For these compounds the bending can easily be rationalized as a consequence of repulsions between the nonbonding lone pair on the group 14 element and the negatively charged cyclopentadienyl rings. In addition to the bending ($\alpha < 180°$), the tilt angle, θ, of the rings is quite large and has a positive sign for these compounds, which probably is caused by the same repulsions that cause the bending. For the heavier group 2 bis(pentamethylcyclopentadienyl) compounds, α is larger or is of the same magnitude as those found for the group 14 analogues, and θ is zero or small with a negative sign. Since the group 2 metals do not have a lone pair that could rationalize this bending, it is tempting to use the polarized-ion model previously used to describe the structural trend of the group 2 dihalides.[34-37] The observed structures of the group 2 dihalides indicate that a bent structure is favored if the cation has a large ionic radius and the halide has a small ionic radius and is strongly electronegative.[38] In this way the difluorides CaF_2, SrF_2, and BaF_2 are bent in the gas phase, while of the diiodine compounds, only BaI_2 is bent. This structural trend is favored by ab initio calculations on CaF_2 and by CNDO/2 calculations by including diffuse d orbitals on the group 2 metals.[39,40] However, some of the ab initio calculations with larger basis sets yield a linear configuration for CaF_2.[41] A comparison of gas-phase results for the group 2 dihalides and bis(pentamethylcyclopentadienyl) compounds is presented in Table IV.

Table V. Optimal Metal-Ring Centroid Distance (d) and Corresponding Energies for $Mg(C_5H_5)_2$, $Ca(C_5H_5)_2$, and $Ca(C_5Me_5)_2$ with Molecular Symmetries D_{5d} from ab Initio Calculations[a]

	$Mg(C_5H_5)_2$	$Ca(C_5H_5)_2$	$Ca(C_5Me_5)_2$
	Experimental Data		
d_{exp}/pm	200.8 (4)		231.2 (6)
	M Basis		
d/pm	207.5	240.0	239.0
E/au	−583.588180	−1060.733304	−1450.541850
	L Basis		
d/pm	202.8	240.0	
E/au	−584.160600	−1061.334188	

[a] d_{exp} is the experimental metal–ring centroid distance in the gas phase.

The polarizability of the group 2 elements increases down the group, and the bent structures of the bis(pentamethylcyclopentadienyl) compounds of calcium, strontium, and barium may be rationalized as a consequence of the large polarizability of these elements compared to that of magnesium. Dipoles may easily be induced on these atoms (ions) by the negatively charged cyclopentadienyl rings. The polarized-ion model assumes 100% ionic character of the metal–ligand bonds, and then the charge–charge, charge–induced-dipole, and induced-dipole–induced-dipole interactions as well as the work of formation of the induced dipoles are analyzed as functions of the molecular structure. Such an analysis has quantitatively been performed by Guido and Gigli for all the group 2 dihalides,[38] and the model may qualitatively be used to explain the structural trend of the group 2 metallocenes as well: When one goes from a linear to a slightly bent configuration, the charge–charge interactions and the work of formation of the induced dipoles will tend to *increase* the total energy of the molecule, while the charge–induced-dipole and induced-dipole–induced-dipole interactions will *decrease* the total molecular energy. If the decrease in energy by the last two terms is larger than the increase caused by the first two terms, a bent sandwich structure will be favored. Since the negative part of the polarized central atom takes less space than a lone pair, the tilt (θ) of the pentamethylcyclopentadienyl rings is for the bent group 2 metallocenes not positive, as it is for the group 14 metallocenes, but rather small and negative. A negative tilt may be a consequence of methyl–methyl repulsions between the two pentamethylcyclopentadienyl rings.

The ab initio calculations on $Mg(C_5H_5)_2$ and $Ca(C_5H_5)_2$ were undertaken in order to investigate in terms of molecular orbitals why the former has an *average* molecular structure with parallel cyclopentadienyl rings (regular sandwich structure) while the latter has a bent sandwich structure in the monomeric permethylated derivatives. In the calculations we used two different sets of basis functions for each compound as described in the previous section.

As seen in Table V, the equilibrium magnesium–ring centroid distance, d, is reduced from 207.5 to 202.8 pm

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[33] Jutzi, P.; Kohl, F.; Hofmann, P.; Krüger, C.; Tsay, Yi-H. *Chem. Ber.* **1980**, *113*, 757. Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1981**, 925. Fernholt, L.; Haaland, A.; Jutzi, P.; Kohl, F. X.; Seip, R. *Acta Chem. Scand.* **1984**, *A38*, 211.

[34] Electric deflection experiments: Wharton, L.; Berg, R. A.; Klemperer, W. *J. Chem. Phys.* **1963**, *39*, 2023. Büchler, A.; Stauffer, J. L.; Klemperer, W. *J. Am. Chem. Soc.* **1964**, *86*, 4544.

[35] Kasparov, V. V.; Ezhov, Tu. S.; Rambidi, N. G. *J. Struct. Chem. (Engl. Transl.)* **1979**, *20*, 285.

[36] Vajda, E.; Hargittai, M.; Hargittai, I.; Tremmel, J.; Brunvoll, J. *Inorg. Chem.* **1987**, *26*, 1171.

[37] Spiridonov, V. P.; Gershikov, A. G.; Altman, A. B.; Romanov, G. V.; Ivanov, A. A. *Chem. Phys. Lett.* **1981**, *77*, 41. Spiridonov, V. P.; Altman, A. B.; Gershikov, A. G.; Ramanov, G. V. Presented at the 2nd Conference on Determination of Molecular Structure by MW Spectroscopy and Electron Diffraction, Tübingen, FRG, 1980.

[38] Guido, M.; Gigli, G. *J. Chem. Phys.* **1976**, *65*, 1397. Drake, M. C.; Rosenblatt, G. M. *J. Elecrochem. Soc.* **1979**, *126*, 1387.

[39] Gole, L. J.; Siu, K. Q.; Hayes, E. F. *J. Chem. Phys.* **1973**, *58*, 857. Coulson, C. A. *Isr. J. Chem.* **1973**, *11*, 683.

[40] CNDO/2: Hase, Y.; Takahata, Y. *An. Acad. Bras. Cienc.* **1982**, *54*, 501. Hase, Y.; Takahata, Y. *An. Acad. Bras. Cienc.* **1983**, *55*, 23.

[41] Yarkony, D. R.; Hunt, W. J.; Schaefer, H. F., III. *Mol. Phys.* **1973**, *26*, 941.

Table VI. Molecular Orbital Energies for $Mg(C_5H_5)_2$ and $Ca(C_5H_5)_2$ of D_{5d} Symmetry along with Orbital Energies for the $(C_5H_5)_2$ Skeleton and the Metal Atoms[a]

orbital	Mg	$Mg(C_5H_5)_2$	$(C_5H_5)_2$	$Ca(C_5H_5)_2$	Ca	character
$3e_{1g}$		−8.16	−8.16	−8.41		ligand π + metal $d_{xz,yz}$ (Ca)
$3e_{1u}$		−9.00	−8.16	−8.15		ligand π + metal $p_{x,y}$ (Mg)
$3a_{2u}$		−14.07	−13.22	−13.51		ligand π + metal p_z
$2e_{2g}$		−14.13	−14.32	−13.97		C–H
$2e_{2u}$		−14.14	−14.32	−13.97		C–H
$2e_{1g}$		−14.88	−14.87	−14.69		C–H
$2e_{1u}$		−14.89	−14.87	−14.68		C–H
$3a_{1g}$	−6.88	−14.98	−13.22	−14.11	−5.32	ligand π + metal s
$2a_{2u}$		−19.08	−19.00	−18.90		C–C
$2a_{1g}$		−19.13	−19.00	−18.93		C–C
$1e_{2u}$		−19.99	−19.96	−19.86		C–C
$1e_{2g}$		−20.03	−19.96	−19.88		C–C
$1e_{1g}$		−25.91	−25.89	−25.71		C–C
$1e_{1u}$		−25.95	−25.89	−25.67		C–C
$1a_{2u}$		−31.56	−31.62	−30.94		C–C
$1a_{1g}$		−31.65	−31.62	−31.26		C–C
				−35.16	−36.47	Ca 3p
				−59.39	−61.05	Ca 3s
	−62.05	−62.24				Mg 2p
	−102.41	−102.40				Mg 2s
		−305.66	−306.20	−305.49		C 1s
				−369.13	−370.77	Ca 2p
				−455.80	−457.46	Ca 2s
	−1333.75	−1334.26				Mg 1s
				−4062.75	−4062.79	Ca 1s

[a] The energies are in eV.

when d orbitals are included on the carbon atoms. The latter value is in satisfactory agreement with the experimental value of 200.8 (4) pm.[4] Such a reduction of the metal–ring centroid distance is consistent with the previous calculations on magnesocene by Almlöf and co-workers[16] and has also been observed in recent large-basis calculations on $Li(C_5H_5)$.[42] For $Ca(C_5H_5)_2$ such a reduction is *not* achieved by including d orbitals on the carbons; the calcium–ring centroid distance is 240.0 pm with both the M and L basis sets, which is approximately 9 pm longer than the experimental distance observed in $Ca(C_5Me_5)_2$ of 231.2 (6) pm. As seen in Table V, the introduction of 10 methyl groups on the cyclopentadienyl ring reduces the calcium–ring centroid distance by only 1 pm, so the omission of the methyl groups in the calculations cannot account for the large discrepancy between the calculations and experiment. This failure to reproduce the metal–ring centroid distance is similar to that observed in previous large-scale Hartree–Fock calculations on the third-row transition-metal metallocenes. The distances are consistently calculated too long within this theoretical model. The failure to reproduce the calcium–ring centroid distance in $Ca(C_5H_5)_2$ may have the same origin as that of the transition-metal metallocenes and may be connected to the tendency for these metals to be bonded to the cyclopentadienyl rings through the metal d orbitals.

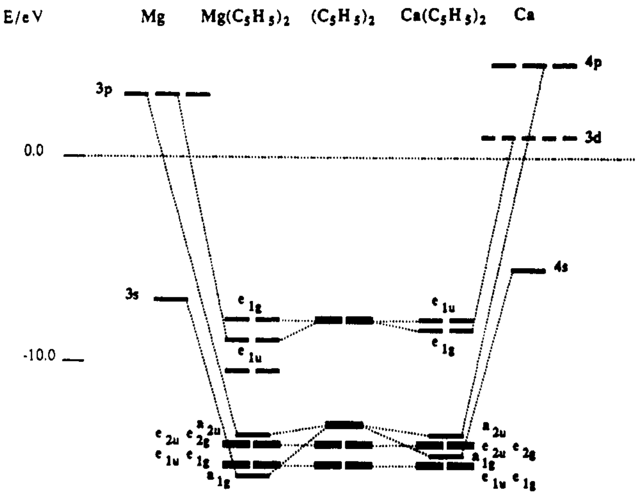

Figure 5. Schematic drawing of the highest molecular orbitals of $Mg(C_5H_5)_2$ and $Ca(C_5H_5)_2$ along with those of the $(C_5H_5)_2$ skeleton and the atomic orbitals of Mg and Ca. All orbitals with negative orbital energies are filled.

In Table VI and Figure 5 the MO energies obtained for $Mg(C_5H_5)_2$ and $Ca(C_5H_5)_2$ are shown along with those of the $(C_5H_5)_2$ skeleton and the free metal atoms. The main difference between the magnesium and calcium analogues is that the latter has empty low-lying d orbitals that can be used for bonding. For both compounds the highest metal s orbital combines with an a_{1g} orbital of the $(C_5H_5)_2$ skeleton. For $Mg(C_5H_5)_2$ there is additional bonding between the $p_{x,y}$ and p_z orbitals on magnesium and the e_{1u} and a_{2u} orbitals of the rings. For $Ca(C_5H_5)_2$, the picture is different: The p_z orbital on the calcium atom is involved in metal–ring bonding, but to a lesser extent than for the magnesium analogue, and as seen in Table V, the highest e_{1g} orbital of the $(C_5H_5)_2$ skeleton is stabilized by 0.25 eV by interaction with the d_{xz} and d_{yz} orbitals of the calcium atom.

The total energies as a function of α are shown in Figure 6 for the two different basis sets and different metal–ring centroid distances, *d*. The curves for $Mg(C_5H_5)_2$ indicate that this molecule has a global energy minimum for α = 180° for both the M and L basis sets. The potential curves for $Ca(C_5H_5)_2$ are flatter around α = 180°, and whether the *equilibrium* structure comes out bent or linear is strongly dependent on the basis sets and on the metal–ring centroid distance used in the calculations. The calculations with the optimal metal–ring centroid distance for the M basis yield a local energy maximum for α = 180°. The α value that corresponds to a minimum energy in these calculations is approximately 174°, much larger than the experimental *average* angle of 154 (3)°. However, the other calculations on $Ca(C_5H_5)_2$ with shorter metal–ring centroid distances and those using the larger L basis yield a global

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(42) Faegri, K., Jr.; Blom, R. To be submitted for publication.

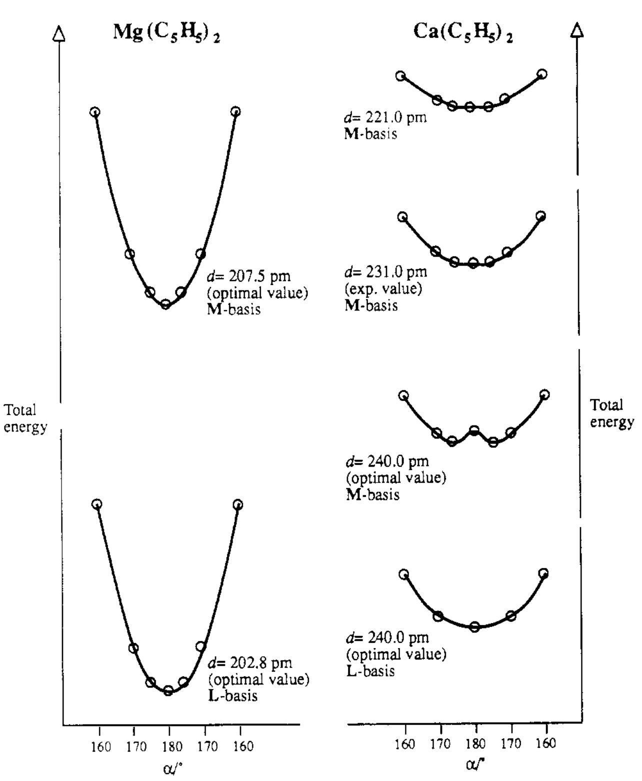

Figure 6. Total Hartree–Fock energies as a function of bend angle, α, for $Mg(C_5H_5)_2$ and $Ca(C_5H_5)_2$ obtained with the M basis (medium basis) and L basis (large basis). The scale of the relative energy axis is equal for all the curves.

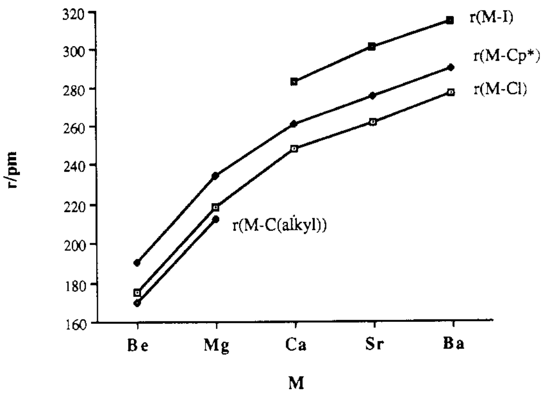

Figure 7. Group 2 metal-to-element bond distances in MI_2, MCp^*_2 ($Cp^* = C_5Me_5$), MCl_2, and $M(alkyl)_2$ compounds.

minimum for α = 180°. The energy difference obtained between 180 and 160° is approximately 3.5 kJ mol^{-1} in these calculations, which is only one-fourth of the energy needed to bend $Mg(C_5H_5)_2$ the same amount. The strong basis set dependence on the bending is similar to the results obtained for CaF_2, and it is here interesting to note that our L basis, which gives a nonbent *equilibrium* structure for $Ca(C_5Me_5)_2$, is based on the same primitive Gaussian basis that gives a linear CaF_2 structure.[41] Ab initio calculations also fail to reproduce the bending observed in $Ge(C_5H_5)_2$,[43] and quasi-relativistic Xα–scattered-wave calculations on $Yb(C_5H_5)_2$ cannot explain the bent structure observed for $Yb(C_5Me_5)_2$ in the gas phase.[44]

We find it difficult to rationalize the bent sandwich structure observed for $Ca(C_5Me_5)_2$ (and for the strontium and barium analogues) in terms of molecular and atomic orbitals, but part of the explanation is probably the availability of low-lying d orbitals for bonding. For $Mg(C_5H_5)_2$ the molecular orbitals that are most destabilized on bending are the bonding $3a_{2u}$ orbital and the C–H orbitals $2e_{2g}$, $2e_{2u}$, $2e_{1g}$, and $2e_{1u}$. These orbitals are all destabilized by 0.05–0.07 eV when bending 20°. The reason for the destabilizations seem to be an inter-ring antibonding interaction, and the destabilizations are not observed for $Ca(C_5H_5)_2$ due to the 60 pm longer inter-ring distance in this compound. Thus, in terms of orbital energies it appears easier to explain why $Mg(C_5H_5)_2$ does not bend than to explain why $Ca(C_5H_5)_2$ has a bent structure. However, if the electron diffraction results, the theoretical results, and evidence from X-ray studies of similar compounds[45] are considered, we feel that it is highly probable that the bis(pentamethylcyclopentadienyl) compounds of calcium, strontium, and barium have *equilibrium* structures that are bent. The failure of even high-quality ab initio Hartree–Fock calculations to predict correct metal–ring distances in transition-metal sandwich compounds is attributed to an inadequate description of d-shell correlation. This same inadequacy may also be responsible for the failure to describe the *bent* calcocene structure—the missing correlation of the d shell will certainly also be of importance for a proper description of the polarized-ion effect. It is noteworthy that calcium, which normally has no d electrons, still is affected by the low-lying empty d orbitals in the same manner as the transition-metal compounds, although not so dramatically.

In Figure 7, the trends of the M–C bond distances of the $M(C_5Me_5)_2$ compounds of the group 2 elements have been drawn (for Be, the Be–C bond distance of the η^5-bonded fragment of $Be(C_5H_5)_2$ has been used, 190.3 pm, since $Be(C_5Me_5)_2$ is unknown). Also M–C(alkyl) and M–X (X = halogen) bond distances in the bivalent compounds have been drawn for comparison. All lines are quite parallel and reflect the different sizes of the group 2 elements. Because of the regular trend of the M–X lines in the figure, covalent radii for the group 2 elements have previously been calculated by using the Schomaker–Stevenson equation and established radii of the halides.[46] Unfortunately, these radii are not proper to estimate bond lengths between group 2 elements and main-group elements other than the halides, and attempts to calculate metal radii for the group 1 and 2 elements simultaneously with other main-group elements in addition to the halides have not been successful.[47] This is probably a consequence of dative p_π–p_π bonding between the halides and group 2 metals, which makes the metal–halogen bonds shorter than expected if they were pure single bonds.[48] For other main-group elements such as carbon, no lone pairs are available for dative p_π–p_π bonding. The Be–C and Mg–C bonds will for this reason be underestimated by more than 10 pm when the Schomaker–Stevenson equation and the reported radii of Be and Mg[49] are used.

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(43) Almlöf, J.; Fernholt, L.; Faegri, K., Jr.; Haaland, A.; Schilling, B. E. R.; Seip, R.; Taugbøl, K. *Acta Chem. Scand.* **1983**, *A37*, 131.

(44) Green, J. C.; Hohl, D.; Rösch, N. *Organometallics* **1987**, *6*, 712.

(45) $Sm(C_5Me_5)_2$ and $Eu(C_5Me_5)_2$ are bent in the solid state: Evans, W. L.; Hughes, L. A.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1285.

(46) Akishin, P. A.; Spiridonov, V. P. *Kristallografiya* **1957**, *2*, 475; *Sov. Phys.—Crystallogr. (Engl. Transl.)* **1957**, *2*, 472.

(47) Blom, R.; Haaland, A. *J. Mol. Struct.* **1985**, *128*, 21. Blom, R. Unpublished results.

(48) Haaland, A. *J. Mol. Struct.* **1983**, *97*, 115.

(49) The Schomaker–Stevenson equation with a carbon radius of 77 pm and Pauling electronegativities gives r_{calc}(Be–C) = 156 pm and r_{calc}(Mg–C) = 198 pm. The M–C bond distances of $BeMe_2$ and $Mg(CH_2CMe_3)_2$ are 169.8 and 212.6 pm, respectively: Almenningen, A.; Haaland, A.; Morgan, G. L. *Acta Chem. Scand.* **1969**, *23*, 2921. Ashby, E. C.; Fernholt, L.; Haaland, A.; Seip, R.; Smith, R. S. *Acta Chem. Scand.* 1980, *A34*, 213.

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Synthesis and NMR Spectroscopy of Cyclopalladated Tertiary Phosphite Complexes. X-ray Crystal Structure of $Pd(\eta^5\text{-}C_5H_5)(P(OPh)_2(OC_6H_4))$

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A series of cyclopalladated tertiary phosphite complexes of structure $[Pd(\mu\text{-}Cl)(P(OR^1)_2(OC_6H_3R^2))]_2$ (2), with R^1 being either Ph or Et, has been prepared and studied with use of ^{31}P, ^{13}C, and ^1H NMR methods. For **2a** (R^1 = Ph, R^2 = H) there are two isomers that have been assigned to the sym-cis and sym-trans structures and that are in equilibrium as shown by ^{31}P 2-D exchange NMR spectroscopy. For the platinum analogue of **2a**, the exchange can be shown to be intramolecular, again via 2-D exchange NMR spectroscopy. An analysis of the ^{13}C NMR characteristics for **2** and some mononuclear derivatives obtained with use of PPh_3, $AsPh_3$, $C{\equiv}NBu^t$, diphos, CH_3CN, and $\eta^5\text{-}C_5H_5$ suggests that the low-field shift of the palladated carbon arises from the nature of the Pd–C bond and not a ring effect. Various approaches to the syntheses of **2** are discussed, and cyclopalladation of $P(OEt)_2(NMePh)$ is presented. The molecular structure of $Pd(\eta^5\text{-}C_5H_5)(P(OPh)_2(OC_6H_4))$ has been determined by X-ray diffraction. The complex crystallized in the space group $P2_12_12_1$, with a = 9.197 (4) Å, b = 10.807 (3) Å, c = 20.718 (3) Å, V = 2059 (2) Å^3, and Z = 4. The structure was refined to R = 0.045. Relevant bond distances (Å) and angles (deg) are as follows: Pd–P = 2.150 (2), Pd–C(2) = 2.026 (6), Pd–C(19) = 2.347 (9), Pd–C(20) = 2.301 (7), Pd–C(21) = 2.346 (7), Pd–C(22) = 2.283 (7), Pd–C(23) = 2.300 (7); P–Pd–C(2) = 80.2 (2). The dihedral angle between the P–Pd–C(2) and $\eta^5\text{-}C_5H_5$ planes is 87.1°.

Introduction

Cyclopalladation is now a widely recognized reaction[1] with potential applications for organic synthesis.[2-5] Our interest in the cyclopalladation[6,7] of benzylideneanilines and their eventual conversion to ortho-substituted aldehyde derivatives has prompted us to extend our studies to phenol-related ligands, with specific emphasis on phosphites. There is relatively sparse literature concerned with the cyclometalation of phosphites involving Pd(II) and Pt(II)[8] and also a few Fe(II),[9] Ru(II),[10] Mn(I),[11] and Os(II)[12] derivatives. Normally, for the Pd(II) chemistry, yields were modest and the spectroscopic possibilities limited. We report here our initial studies on the cyclometalation and characterization of complexes derived from $P(OPh)_3$ and $P(OEt)_2(OPh)$, with the latter ligand selected so that after cyclometalation and subsequent transformation (e.g., carbonylation), hydrolysis would readily yield the ortho-

Scheme I

$$cis\text{-}PdCl_2(P(OPh)_3)_2 + Ag(CF_3SO_3) \xrightarrow[-60\ ^\circ C]{\text{solvent}} AgCl + cis\text{- and } trans\text{-}[PdCl(\text{solvent})(P(OPh)_3)_2]^+CF_3SO_3^-$$

solvent = MeOH, acetone

For MeOH: $\delta(^{31}P)_{cis}$ = 83.1, 70.8, $^2J(P,P)$ = 50 Hz; $\delta(^{31}P)_{trans}$ = 86.8; trans:cis ca. 1:20

for acetone: $\delta(^{31}P)_{cis}$ = 81.8, 72.8, $^2J(P,P)$ = 52 Hz; $\delta(^{31}P)_{trans}$ = 84.4; trans:cis ca. 1:8

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[1] Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327. Omae, I. *Chem. Rev.* **1979**, *79*, 287.

[2] Maasarani, F.; Pfeffer, M.; Le Borne, G. *Organometallics* **1987**, *6*, 2029, 2043.

[3] Horino, H.; Inoue, H. *J. Org. Chem.* **1981**, *46*, 4416.

[4] Horino, H.; Inoue, N. *Teterahedron Lett.* **1979**, *26*, 2403.

[5] Murahashi, S.; Tamba, Y.; Yamamura, M.; Yoshimura, N. *J. Org. Chem.* **1978**, *43*, 4099.

[6] Pregosin, P. S.; Rüedi, R. *J. Organomet. Chem.* **1984**, *273*, 401.

[7] Albinati, A.; Pregosin, P. S.; Rüedi, R. *Helv. Chim. Acta* **1985**, *68*, 2046.

[8] Ahmad, N.; Ainscough, E. W.; James, T. A.; Robinson, S. D. *J. Chem. Soc., Dalton Trans.* **1973**, 1148, 1151.

[9] Stewart, R. R., Jr.; Isbrandt, L. R.; Benedict, J.; Palmer, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 3215.

[10] Lewis, L. N. *Inorg. Chem.* **1985**, *24*, 4433; *J. Am. Chem. Soc.* **1986**, *108*, 743.

[11] Stewart, R. P., Jr.; Isbrandt, L. R.; Benedikt, J. *Inorg. Chem.* **1976**, *15*, 2011.

[12] Ainscough, E. W.; James, T. A.; Robinson, S. D.; Wingfield, J. N. *J. Chem. Soc., Dalton Trans.* **1974**, 2384.

0276-7333/90/2309-0379$02.50/0