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The Molecular Structures of Bis(pentamethylcyclopentadienyl)Calcium
and -Ytterbium in the Gas Phase ; Two Bent Metallocenes.

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Gas electron diffraction studies show that while the ligand rings in $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mg}$, $\text{Me}=\text{CH}_3$, are essentially parallel, the thermal average structures of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ca}$ and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Yb}$ are bent, the opening angle between the ligand ring planes being $20(3)^\circ$ in both.

Dicyclopentadienylmagnesium, Cp_2Mg , has a regular sandwich structure with D_{5d} symmetry in the solid phase¹ and D_{5d} or D_{5h} symmetry in the gas phase². Dicyclopentadienylcalcium is polymeric in the solid phase; each Ca atom (ion) appears to have bonding interactions with four Cp rings, and each ring to two Ca atoms³. Only one base-free dicyclopentadienyllanthanide has been characterized structurally: Evans and coworkers have synthesized Cp_2^*Sm ($\text{Cp}^* = \text{C}_5\text{Me}_5$, $\text{Me} = \text{CH}_3$), and determined the crystal structure⁴. Somewhat unexpectedly, the two η^5 -bonded rings were found to be non-parallel; the ring-centroid to Sm to ring-centroid angle is 140° . The average Sm-C bond distance is 279(1)pm. Further, a methyl carbon atom from an adjacent molecule is approaching the Sm atom with a Sm...C contact distance of 322(1)pm. The question thus arises whether this contact is the cause of, or the consequence of, the bent structure. The question could presumably be answered by determining the molecular structure in the gas phase. We found, however, that the vapor pressure / thermal stability was too low to allow a study by gas electron diffraction (GED)⁵.

Recently we have been able to prepare base free Cp_2^*Yb and Cp_2^*Eu ⁶. Crystals of these compounds are isomorphous with those of the Sm analogue, and the molecular structures of the three compounds are therefore similar.

The colourless Cp_2^*Ca , m.p. $207\text{--}210^\circ\text{C}$, was prepared from CaI_2 and NaCp^* in a manner similar to that used to prepare Cp_2^*Yb ⁶. The metallocene sublimes at 75°C and 10^{-3} mm and gives a M^+ in the mass spectrum. The Cp_2^*Mg was prepared from $(\text{Me}_3\text{CCH}_2)_2\text{Mg}$ and $\text{Me}_5\text{C}_5\text{H}$ and purified by sublimation⁷. We now report the gas phase structures of Cp_2^*Yb , Cp_2^*Ca and (for comparison) Cp_2^*Mg as determined by GED.

The electron diffraction data were recorded with nozzle temperatures of about 160°C (Mg and Ca) and 190°C (Yb). The data sets for Ca and Yb extend from $s=15\text{ nm}^{-1}$ to 260 nm^{-1} . The data for Mg extend from $s=15\text{ nm}^{-1}$ to 150 nm^{-1} . This is, however, the range that carries information

about the relative position of the ligands, i.e. information as to whether the molecular structure is linear or bent.

A molecular model of Cp_2^*Ca is shown in Fig.1. The two $(\eta^5\text{-C}_5\text{Me}_5)\text{Ca}$ fragments were assumed to be identical and to have C_{5v} symmetry (H atoms excluded). The molecular symmetry was assumed to be C_s with staggered ligand rings as indicated in the Figure. The molecular structure is then determined by eight parameters; the bond distances M-C, C-C (in ring), C-C(Me) and C-H, the angle between the C-C(Me) bonds and the C_5 ring planes, the valence angle $\angle\text{CCH}$, a methyl group torsion angle, and the angle between the two ring planes, $\angle\text{C}_5\text{C}_5$.

The eight structure parameters and five r.m.s. amplitudes of vibration (1) were refined by least-squares calculations on the intensity data with a diagonal weight matrix. The values obtained for the most important structure parameters are listed in the Table. Estimated standard deviations have been multiplied with a factor of three to compensate for data correlation and uncertainty introduced by non-refined vibrational amplitudes.

Both Cp_2^*Ca and Cp_2^*Yb come out significantly bent, the opening angle between the ring planes in each molecule being $\angle\text{C}_5\text{C}_5 = 20(3)^\circ$, corresponding to a ring-centroid metal ring-centroid angle of $160(3)^\circ$. Cp_2^*Mg by contrast comes out linear; when $\angle\text{C}_5\text{C}_5$ is refined, it fluctuates between 3 and 8° , but does not converge. Refinements with $\angle\text{C}_5\text{C}_5$ fixed at 0° and 5° yield equally good agreement ($R_2 = 5.3\%$). Refinements carried out with $\angle\text{C}_5\text{C}_5$ fixed at 20° yield significantly poorer agreement ($R_2 = 7.9\%$ after appropriate background modification); such a model can be ruled out.

It might be objected that our molecular model is inappropriate, and that the non-parallel nature of the rings is due to ring tilting rather than ring-metal-ring bending. Ring tilting would leave the ring-centroid metal ring-centroid angle at 180° , and reduce the

symmetry of each $(C_5Me_5)M$ fragment to C_5 . However, comparison of the values obtained for the M-C vibrational amplitudes in Cp_2^*Ca , $\perp(Ca-C) = 10.8(4)pm$, Cp_2^*Yb , $\perp(Yb-C) = 9.0(3)pm$, and Cp_2Mg , $\perp(Mg-C) = 10.3(3)pm$, show that the metal-carbon distances in the Ca and Yb derivatives also must be very nearly equal.

The values obtained for the angle between the ring planes in Cp_2^*Ca and Cp_2^*Yb are thermal average values and have not been corrected for the effect of ring-metal-ring bending vibrations. Such corrections could reduce the value of $\langle C_5C_5 \rangle$, but it seems unlikely that the equilibrium conformation is one in which the rings are parallel.

The angle between the ring planes in Cp_2^*Ca and Cp_2^*Yb is similar to the angle found in $Cp_2^*Ge^8$, $\langle C_5C_5 \rangle = 22(2)^\circ$. In the latter molecule the driving force for bending is probably provided by anti-bonding interactions between a metal-centered electron lone pair and the ring π -orbitals⁹.

Neither quasirelativistic X α -SW calculations nor the observed photoelectron spectrum provide an explanation for the bent structure of Cp_2^*Yb in terms of molecular orbital energies¹⁰.

It may be recalled, however, that monomeric CaF_2 is nonlinear in the gas phase¹¹, and that the dihalides of several lanthanides are found to be bent in the gas phase¹², and inert gas metrices¹³. The non-linearity of these species have been rationalized in terms of the polarizable ion model¹⁴. In this context it may also be significant that the shortest inter-ligand contact between methyl groups in both Cp_2^*Ca and Cp_2^*Yb is about 400pm, which correspond to twice the accepted van der Waals radius of methyl groups. In Cp_2^*Mg , where no bending is observed, the perpendicular metal-to-ring distance, h , is such that inter-ligand methyl-methyl contact are about 400pm when the rings are parallel.

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Table: Selected structure parameters of $(C_5Me_5)_2M$, M= Mg, Ca, and Yb.

M :	Mg	Ca	Yb
R(M-C)/pm	236(2)	260.4(5)	261.7(4)
$\underline{l}$ (M-C)/pm	15(2)	10.8(4)	9.0(3)
$\underline{h}^A$ /pm	203(3)	230.8(5)	232.1(4)
$\angle C_5C_5^B$ /deg.	0^D	20(3)	20(3)
R_2^C /%	5.3	4.7	4.2

^A $\underline{h}$ = perpendicular metal-to-ring distance. ^B Opening angle between C_5 -ring planes. ^C $R_2 = \sqrt{[w(I_{obs} - I_{calc})^2 / wI_{obs}^2]}$.

^D Fixed value, see comment in text.

Figure Captions:

Fig.1: Molecular model of $(C_5Me_5)_2Ca$.

Fig.2: Dots; experimental radial distribution (RD) curve for $(C_5Me_5)_2Ca$. Full line; theoretical RD curve calculated for best model. Inter-ligand C...C distances are indicated by bars. Insert; corresponding curve for best model with parallel ligand rings. Artificial damping constant, $k = 20\text{pm}^2$.

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