

### Preliminary communication

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## THE MOLECULAR STRUCTURES OF BIS(PENTAMETHYLCYCLOPENTADIENYL)-CALCIUM AND -YTTERBIUM IN THE GAS PHASE; TWO BENT METALLOCENES

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### Summary

Gas electron diffraction studies show that whereas the ligand rings in  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mg}$ , 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 ring-centroid–metal–ring-centroid angles being  $154(3)^\circ$  and  $158(4)^\circ$ , respectively.

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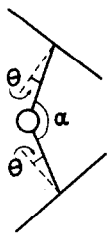
Dicyclopentadienylmagnesium,  $\text{Cp}_2\text{Mg}$ , has a regular sandwich structure with  $D_{5d}$  symmetry in the solid phase [1] and  $D_{5d}$  or  $D_{5h}$  symmetry in the gas phase [2]. Dicyclopentadienylcalcium is polymeric in the solid phase; each Ca atom (ion) appears to have bonding interactions with four Cp rings, and each ring to two Ca atoms [3]. Only one base-free dicyclopentadienyllanthanide has been structurally characterized: Evans and his co-workers have synthesized  $\text{Cp}_2^*\text{Sm}$  ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ), and determined the crystal structure [4]. Somewhat unexpectedly, the two  $\eta^5$ -bonded rings were found to be non-parallel, the ring-centroid to Sm to ring-centroid angle being  $140^\circ$ ; the average Sm–C bond distance is 279(1) pm. Further, a methyl carbon atom from an adjacent molecule approaches the Sm atom with a Sm...C contact distance of 322(1) pm. The question thus arises of 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  $\text{Cp}_2^*\text{Yb}$  and  $\text{Cp}_2^*\text{Eu}$  [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  $\text{Cp}_2^*\text{Ca}$ , m.p. 207–210°C, was prepared from  $\text{CaI}_2$  and  $\text{NaCp}^*$  by a procedure similar to that used to prepare  $\text{Cp}_2^*\text{Yb}$  [6]. The metallocene sublimes at 75°C and  $10^{-3}$  mmHg and gives a  $M^+$  in the mass spectrum. The  $\text{Cp}_2^*\text{Mg}$  was prepared from  $(\text{Me}_3\text{CCH}_2)_2\text{Mg}$  and  $\text{Me}_5\text{C}_5\text{H}$  and purified by sublimation [7]. We now report the gas phase structures of  $\text{Cp}_2^*\text{Yb}$ ,  $\text{Cp}_2^*\text{Ca}$  and (for comparison)  $\text{Cp}_2^*\text{Mg}$  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 to 260  $\text{nm}^{-1}$ . The data for Mg extend from  $s$  15 to 250  $\text{nm}^{-1}$ , and are for some reason of lower quality than for Ca and Yb.

A molecular model of  $\text{Cp}_2^*\text{Ca}$  is shown in Fig. 1. It may be obtained from a model of  $C_{2v}$  symmetry and eclipsed ligand rings by rotating one ring 36° into the staggered arrangement. The  $\text{C}_5\text{Me}_5$  fragments were assumed to have  $C_{5v}$  symmetry (H atoms excluded). The molecular structure is then determined by nine parameters; the bond distances C–C (in ring), C–C(Me) and C–H, the angle between the C–C(Me) bonds and the  $\text{C}_5$  ring planes, the valence angle CCH, a methyl group torsion angle, the M–ring centroid distance  $d$ , the ring-centroid–M–ring-centroid angle  $\alpha$ , and the tilt angle  $\theta$ :



The nine structure parameters and twelve r.m.s. amplitudes of vibration ( $l$ ) were refined by least-squares calculations on the intensity data with a diagonal weight

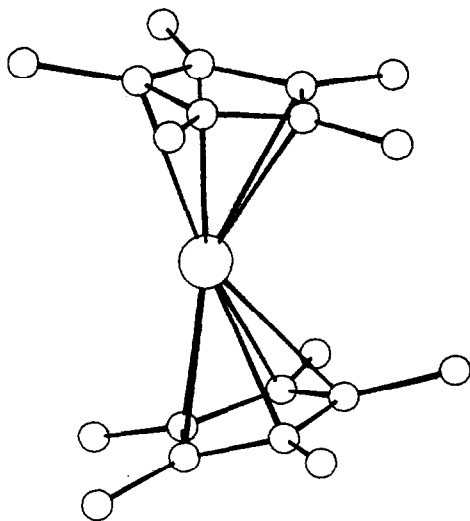


Fig. 1. Molecular model of  $(\text{C}_5\text{Me}_5)_2\text{Ca}$  with H atoms omitted.

TABLE 1  
SELECTED STRUCTURE PARAMETERS FOR  $(C_5Me_5)_2M$  ( $M = Mg, Ca, Yb$ )

	Mg	Ca	Yb
$d$ (pm)	201.9(9)	231.3(6)	232.6(5)
$\alpha$ (deg)	0 <sup>a</sup>	154(3)	158(4)
$\theta$ (deg)	0 <sup>a</sup>	-3(1 <sub>5</sub> )	-1(2 <sub>5</sub> )
$R(M-C)$ (pm)			
Mean value	234.8(9)	260.9(6)	262.1(6)
Range	-	255-267	261-263
$l(M-C)$ (pm)	13(2)	9.9(4)	9.4(5)
$R_2$ <sup>b</sup> (%)	4.9	3.4	3.6

<sup>a</sup> Fixed value, see comment in text. <sup>b</sup>  $R_2 = \sqrt{[\sum w(I_o - I_c)^2 / \sum w I_o^2]}$ .

matrix. The values obtained for the most important structure parameters are listed in Table 1. 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 ring-centroid-M-ring-centroid angles being  $154(3)^\circ$  and  $158(4)^\circ$ .  $Cp_2^*Mg$  by contrast comes out linear; when  $\alpha$  is fixed at  $180^\circ$   $R_2$  4.9%, when  $\alpha$  is fixed at lower values,  $R_2$  increases.  $\alpha$   $160^\circ$  yields  $R_2$  6.0% (after appropriate background modification); such a model can be ruled out.

The values obtained for the ring-centroid-M-ring-centroid angles ( $\alpha$ ) in  $Cp_2^*Ca$  and  $Cp_2^*Yb$  are thermal average values and have not been corrected for the effect of

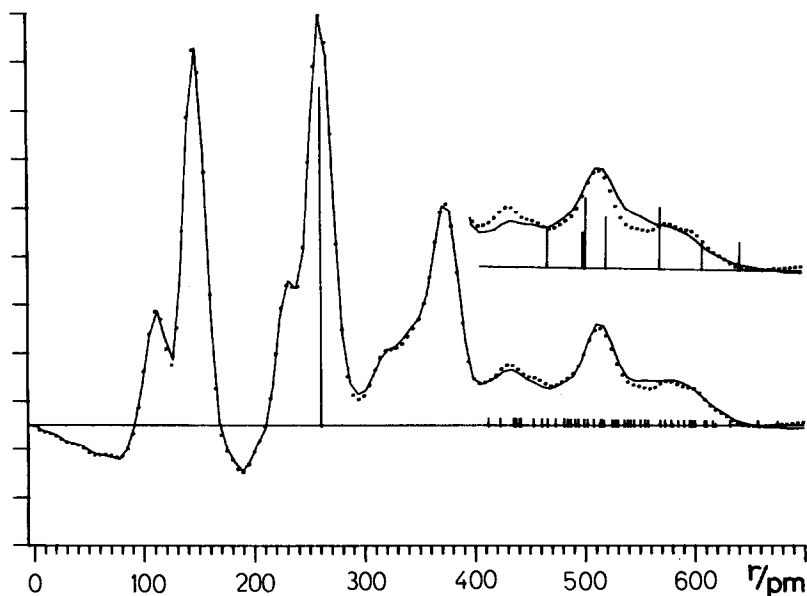


Fig. 2. Dots; experimental radial distribution (RD) curve for  $(C_5Me_5)_2Ca$ . Full line; theoretical RD curve calculated for best model. Inter-ligand C...C distances are indicated by bars. Insert; corresponding curve for best model with parallel ligand rings. Artificial damping constant,  $k$  20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

ring-metal-ring bending vibrations. Such corrections are expected to increase  $\alpha$ , and linear ( $\alpha 180^\circ$ ) equilibrium structures cannot be ruled out. If, however, the equilibrium conformations are linear, the energies required to bend the molecule  $20^\circ$  must be less than the thermal energies available,  $4 \text{ kJ mol}^{-1}$ .

Neither quasi-relativistic  $X\alpha$ -SW calculations nor the observed photoelectron spectrum provides an explanation for the bent structure of  $\text{Cp}_2^*\text{Yb}$  in terms of molecular orbital energies [8].

It may be recalled, however, that monomeric  $\text{CaF}_2$  is nonlinear in the gas phase [9], and that the dihalides of several lanthanides are found to be bent both in the gas phase [10] and inert gas matrices [11]. The non-linearity of these species have been rationalized in terms of the polarizable ion model [12]. In this context it may also be significant that the shortest inter-ligand contact between methyl groups in both  $\text{Cp}_2^*\text{Ca}$  and  $\text{Cp}_2^*\text{Yb}$  is about 410 pm, which corresponds to twice the accepted Van der Waals radius of methyl groups. In  $\text{Cp}_2^*\text{Mg}$ , where no bending is observed, the metal-to-ring distance is such that inter-ligand methyl-methyl contacts are about 410 pm when the rings are parallel.

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