The Thermal Average Molecular Structures of Bis(pentamethylcyclopentadienyl)magnesium(II), -calcium(II) and -ytterbium(II) in the Gas Phase

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The *thermal average* molecular structures of the three compounds $Mg(C_5Me_5)_2$, $Ca(C_5Me_5)_2$ and $Yb(C_5Me_5)_2$ (Me = CH_3) have been determined by gas phase electron diffraction (GED). $Mg(C_5Me_5)_2$ has a *regular* sandwich structure where the predominant conformer is found to be eclipsed (D_{5h} symmetry), but a model with staggered conformation (D_{5d} symmetry) cannot be ruled out. In contrast, $Ca(C_5Me_5)_2$ and $Yb(C_5Me_5)_2$ can best be decribed as *bent* sandwich molecules in which the angle between the two ring planes, $<C_5C_5$, is found to be 20(3)° in both cases. The major cause of the non-zero angle seems to be bending of the molecule rather than ring tilting. The latter two molecules are best described by models of C_s symmetry in which the rings have staggered conformation. It must be emphasized that the *bent* structures are *thermal average* structures and that the *equilibrium* structures may still be *regular* sandwich. If this is the case the molecules undergo large amplitude motion. Important structural parameters are: r(Mg–C) = 234.1(6) pm with l(Mg–C) = 11.9(13) pm, mean r(Ca–C) = 260.9(6) pm with l(Ca–C) = 9.9(11) pm and mean r(Yb–C) = 262.2(6) pm with l(Yb–C) = 9.3(5) pm.

The dicyclopentadienyl compounds of Group IIa metals show some interesting structural features. In the crystalline and the gas phase, $Be(C_5H_5)_2$ is monomeric with one cyclopentadienyl ring η^5-bonded and one peripherally bonded to the Be atom.[1,2] $Mg(C_5H_5)_2$ has a *regular* sandwich structure (parallel rings bonded η^5 to the Mg atom) in both the crystalline[3] and the gas phase.[4] The conformation is found to be staggered (D_{5d} symmetry) in the crystal. In the gas phase the predominant conformation is eclipsed (D_{5h} symmetry), but the authors could not definitely rule out the occurrence of the staggered conformation.[4] Crystalline $Ca(C_5H_5)_2$ is polymeric; each Ca atom is attached to four cyclopentadienyl rings bonded in an $(\eta^5\text{–}C_5H_5)_2(\eta^3\text{–}C_5H_5)(\eta^1\text{–}C_5H_5)$ fashion.[5] The compound is not volatile enough to be investigated by gas phase electron diffraction (GED).

The base-free cyclopentadienyllanthanide compounds $M(C_5H_5)_2$ (M = Eu or Yb)[6] and $Yb(C_5H_4SiMe_3)_2$[7] are known. They are insoluble in hydrocarbon solvents, but form coordination complexes with ethers, amines, etc. The base-free compounds are doubtless polymeric, with structures possibly similar to that of $Ca(C_5H_5)_2$.[5] One way to prevent polymerisation, and thus increase the vapor pressure, is to use sterically bulky ligands. The use of the pentamethylcyclopentadienyl ligand has in this way proved very successful.[8–11]

Only one base-free dicyclopentadienyllanthanide compound has previously been character-

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ized structurally; the X-ray investigation of $Sm(C_5Me_5)_2$ shows that the two C_5Me_5 rings are *non*-parallel.[12] The angle between the ring planes is found to be approximately 40°, but the shortest Sm···C contact distance to a neighbouring molecule is 322(1) pm. The neighbouring methyl group does not approach the metal from the sterically most open "front" part of the bent metallocene, but rather from the side. The question arises as to whether this contact is a consequence of, or the cause of, the bent structure. This question could presumably be answered by determining the gas phase structure of the compound. Unfortunately, $Sm(C_5Me_5)_2$ is not volatile enough to be studied by GED.

Ca(II) and Yb(II) metallocenes are known to have isostructural tendencies; the IR spectra of $Ca(C_5H_5)_2$ and $Yb(C_5H_5)_2$ indicate similar structures,[6,13] and the similar X-ray patterns and identical IR spectra of crystalline dimethoxyethane adducts of $K_2Ca(C_8H_8)_2$ and $K_2Yb(C_8H_8)_2$ show these to be isostructural.[14] The ionic radii of Ca^{2+} and Yb^{2+} for coordination number four have been proposed to be similar, viz. 100 and 102 pm, respectively.[15]

We have been able to synthesize the three compounds bis(pentamethylcyclopentadienyl)-magnesium(II), $Mg(C_5Me_5)_2$, bis(pentamethylcyclopentadienyl)calcium(II), $Ca(C_5Me_5)_2$ and bis(pentamethylcyclopentadienyl)ytterbium(II), $Yb(C_5Me_5)_2$. They are all sufficiently volatile to be investigated by GED. The crystals of $Yb(C_5Me_5)_2$ [and $Eu(C_5Me_5)_2$] are isomorphous with the Sm analogue,* and the molecular structures of the three compounds are therefore similar in the solid state.

$Mg(C_5Me_5)_2$ was included in this study for the purpose of comparison. It is also interesting to see what structural consequences the introduction of ten methyl groups in the two cyclopentadienyl rings has, and which conformer is predominant.

Experimental

Synthesis. All manipulations were carried out under nitrogen. Analyses were performed by the microanalytical laboratory at the University of California, Berkeley. The NMR spectra of samples dissolved in deuterated benzene were recorded on a JEOL FX-90Q instrument operating at 89.56 MHz for proton and 22.50 MHz for carbon. All chemical shifts are in δ-units relative to tetramethylsilane. Mass spectra were recorded on a AEI-MS-12 instrument equipped with a direct inlet. $Yb(C_5Me_5)_2$ was prepared as previously described.[9]

$Mg(C_5Me_5)_2$. Pentamethylcyclopentadiene (10.4 g, 12.0 ml, 0.077 mol) was added slowly to dibutylmagnesium[16] (60 ml of a 0.64 M heptane solution, 0.038 mol) and the solution was heated under reflux for 12 h. The solution was cooled to room temperature and then kept at −80 °C for two days. The white prisms were collected by filtration and dried under reduced pressure. The yield was 9.0 g (89 %). The compound sublimed at 100–110 °C/10^{-2} mm. The physical properties were identical to those previously described.[17]

$(C_5Me_5)_2Ca(OEt_2)$. Calcium iodide[18] (3.24 g, 11.0 mmol) was slurried with NaC_5Me_5 (3.35 g, 21.2 mmol) in 200 ml of diethyl ether and the suspension was stirred for 24 h. The ether solution was filtered and the volume of the filtrate was reduced to 80 ml. The solution was cooled to −25 °C, producing large white needles. A second batch of crystals was obtained from the mother liquor by concentrating and cooling. The total yield was 2.82 g (69.2 %), m.p. 186–191 °C. Anal. $C_{24}H_{40}OCa$: C,H. IR (nujol): 2722(m), 1650 (wbr), 1440(s), 1417(m), 1301(vw), 1286(w), 1177(sh), 1162(sh), 1146(s), 1068(vs), 1040(s), 1017(m), 971(sh), 924(m), 912(sh), 837(s), 815(w), 738(sh), 720(w), 625(w), 613(w), 588(m), 545(wbr), 526(sh), 512(w), 438(m), 409 (sh), 354(wsh), 333(vsbr), 279(s) cm^{-1}. ^1H NMR (C_6D_6, 30 °C): δ 2.92 (4H, q, $^3J_{HH} = 7$ Hz), 2.05 (30 H,s), 0.80 (6H,t, $^3J_{HH} = 7$ Hz). ^{13}C NMR (C_6D_6, 30 °C): δ 113.1 (C_5Me_5, s), 66.20 (OCH_2, t, $^1J_{CH} = 143$ Hz), 13.35 (OCH_2CH_3, q, $^1J_{CH} = 126$ Hz), 11.38 ($C_5(CH_3)_5$, q, $^1J_{CH} = 124$ Hz).

$Ca(C_5Me_5)_2$. The compound $(C_5Me_5)_2Ca(OEt_2)$ (2.50 g, 6.50 mmol) was dissolved in 200 ml of toluene. The solution was heated to 100 °C and the solvent was removed slowly under vacuum. An additional 200 ml of toluene was added and the process was repeated. The light yellow residue

*The cell dimensions of $Yb(C_5Me_5)_2$ as determined from precession photographs are: $a = 980$ pm, $b = 1240$ pm, $c = 1490$ pm, $\beta = 95°$ and $V = 1.8 \cdot 10^9$ pm^3. Space group $P2_1/n$.

was extracted with 180 ml of hexane, and the hexane extract was concentrated to a volume of 50 ml and cooled to −25 °C, producing large colorless blocks. Further batches of crystals were obtained by concentrating and cooling the mother liquor. The total yield was 1.83 g (90.6 %), m.p. 207–210 °C. The compound sublimed at 75 °C/10^{-4} mm. Anal. $C_{20}H_{30}Ca$: C,H. IR (nujol): 2721(m), 1653(wbr), 1441(s), 1418(sh), 1162(w), 1058(w), 1019(s), 950(vw), 891(vw), 723(m), 665(w), 628(w), 594(w), 539(wbr), 462 (shbr), 399(wsh), 367(vs), 291(s), 276(sh) cm^{-1}. ^1H NMR (C_6D_6, 31 °C): δ 1.90(s). ^{13}C NMR (C_6D_6, 31 °C): δ 114.3 (C_5Me_5, s), 10.27 ($C_5CH_3)_5$, q, $^1J_{CH}$ = 124 Hz). The EI mass spectrum at the lowest possible temperatures showed M^+ (310) as well as sequential ring loss and fragmentation of the rings (base peak = 136, C_5Me_5H). At higher temperatures, higher cluster fragments were visible, corresponding to $Ca_2(C_5Me_5)_2$, $Ca_2(C_5Me_5)_3$, $Ca_2(C_5Me_5)_4$ and even $Ca_3(C_5Me_5)_4$ (base peak = 175, CaC_5Me_5).

Electron diffraction. Electron diffraction patterns were recorded on a Balzers Eldiograph KD-G2.[19] The electron wavelength was calibrated against diffraction patterns of gaseous benzene [r(C–C) = 139.75 pm], and its estimated uncertainty is 0.1 %. In order to keep the temperature at a minimum, and thus minimize thermal decomposition, we used a torus-shaped nozzle[20] which permits the scattering pattern to be recorded with a reservoir vapor pressure of about 1 mmHg. Nozzle and reservoir temperatures were approx. 160 °C (Mg and Ca) and 190 °C (Yb). Exposures were made with two nozzle-to-plate distances, 50 and 25 cm. For the Mg compound we exposed 6 plates at 50 cm and 4 plates at 25 cm, but owing to inconsistency we used data from only 3 plates of each set in the final refinements, with s ranging from 25.0 to 145 nm^{-1} with Δs = 1.25 nm^{-1} (50 cm), and from 35 to 250 nm^{-1} with Δs = 2.5 nm^{-1} (25 cm). For the Ca compound we used 6 plates of each set, with s ranging from 15 to 150 nm^{-1} with Δs = 1.25 nm^{-1} (50 cm), and from 40 to 260 nm^{-1} with Δs = 2.5 nm^{-1} (25 cm). For the Yb compound we used 5 and 6 plates of each set, with s ranging from 15 to 140 nm^{-1} with Δs = 1.25 nm^{-1} (50 cm), and from 45 to 260 nm^{-1} with Δs = 2.5 nm^{-1} (25 cm).

The plates were subjected to photometry and the optical densities processed by standard procedures.[21] The backgrounds were computer drawn by least-squares fitting of the sum of a polynomial and a theoretical molecular intensity curve to the experimental levelled 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 of the two nozzle-to-plate distances were averaged, but the average curves were not connected.

Complex atomic scattering factors, $f'(s)$, for

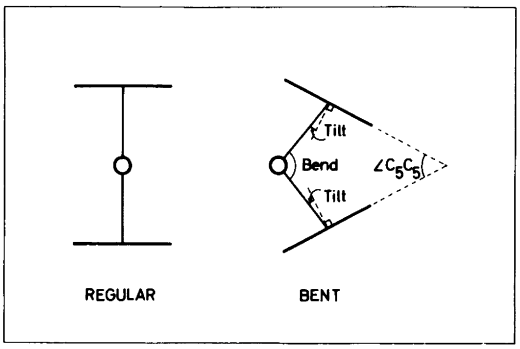

Fig. 1. The two main molecular models considered in this study: The *regular* sandwich and the *bent* sandwich. The bend and tilt angles are defined. The tilt angles are defined as negative as drawn in the figure.

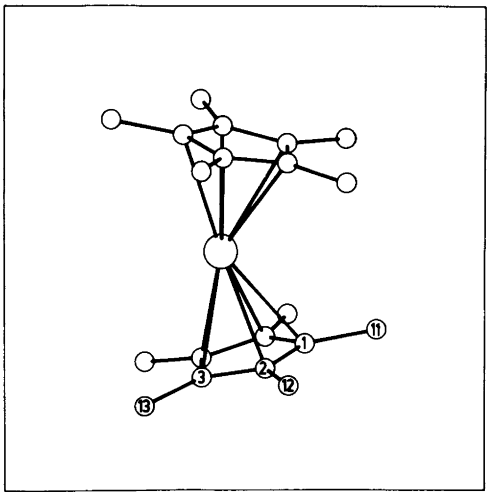

Fig. 2. The *bent* sandwich molecular model. The molecule has a staggered conformation of C_s symmetry. Numbering of the C atoms in the rings is shown. The hydrogen atoms are omitted for clarity.

C, H and Mg were calculated from an analytical representation of the atomic potential,[22] using a program written by Yates.[23] For Ca and Yb (scales Hf factors) they were taken from Ref. 24. The molecular intensities were modified by multiplication by $s/|f'_C||f'_M|$ (M = Mg, Ca or Yb).

Structure refinement

Throughout this study the C_5Me_5 fragments were assumed to be of C_{5v} symmetry and the C–CH_3 fragments to be of C_{3v} symmetry.

Fig. 1 shows the two main models considered: (*i*) a *regular* sandwich in which the bend angle is fixed at 180° and the tilt angle at 0°, i.e. the two rings are parallel ($<C_5C_5 = 0°$) and the MC_5Me_5 fragments have C_{5v} symmetry (H's excluded), and (*ii*) a *bent* sandwich where the bend angle is <180° and/or the tilt angle ≠0°.

The molecular geometry is described by nine independent parameters, viz. the bond distances C1–C2, C1–C11, C–H and M–C (M = Mg, Ca or Yb), the angles $<C_5$,C–C(Me) (defined as positive when the methyl groups are bent *towards* the metal atom), <CCH, the bend angle, the tilt angle and a torsion angle τ(CCCH) indicating the rotation of the methyl groups. The root-mean-square amplitudes of vibration (*l*) that were refined are listed with their estimated standard deviations in Table 1. Non-refined *l*-values and the difference between *l*-values refined in-group were taken from GED investigations of $Fe(C_5Me_5)_2$[25] and $Mn(C_5Me_5)_2$[26] (*l*-values in the same group have constant differences and obtain the same shift in the least-squares refinement).

Attempts were made to determine the relative orientation of the rings, i.e. whether the rings rotate freely, are predominantly staggered or are eclipsed. For the *bent* sandwich model we considered two different staggered conformations, viz. one with C_2 symmetry and one with C_s symmetry. A molecular model in which the rings have the latter conformation is shown in Fig. 2. All hydrogen atoms are ignored when molecular symmetry classifications are used.

Experimental intensity curves with the difference between the experimental and theoretical curves for the best model for each compound are drawn in Figs. 3a, 3b and 3c.

Experimental radial distribution (RD) curves for the three compounds are drawn in Figs. 4a, 4b and 4c. The two curves below each RD curve are the difference between the experimental and theoretical RD curves obtained for A, a *regular* sandwich model, and B, a *bent* sandwich model (the bend angle is fixed at 160°, no tilt). The background was re-drawn, and the same parameters were refined in the least-squares refinement of the two models, with the following exceptions: When we refined the *regular* sandwich model for the Ca and Yb compounds, the *inter*-ring *l*-values were fixed at the values obtained for the *regular* sandwich model for the Mg compound. When we tried to refine these *l*-values they grew intolerably large. The R_2-values[27] that were obtained for the theoretical intensity curves used to calculate A and B in Fig. 4 (the conformer found to give best fit to the experimental data is noted in parentheses) were 4.9 % and 6.0 % for $Mg(C_5Me_5)_2$ (eclipsed), 6.6 % and 3.5 % for $Ca(C_5Me_5)_2$ (staggered), and 7.5 % and 3.6 % for $Yb(C_5Me_5)_2$ (staggered), respectively.

Bis(pentamethylcyclopentadienyl)magnesium(II). Initial refinements were made on a *regular* sandwich model with an eclipsed conformation (D_{5h} symmetry). This model yielded a R_2 factor of 4.9 %. In order to test the validity of the assumptions inherent in this model, namely $<C_5C_5 = 0$ and C_{5v} symmetry of the MgC_5Me_5 fragment, we introduced the bend and tilt angles in the refinements. In this model, which leads to different Mg–C bond lengths, the *l*-values for the Mg–C bond distances were assumed to be equal. The same assumptions were made for the Mg···C (Me) and Mg···H distances. A slightly bent model with the bend angle fixed at values >175° or the tilt angle fixed at values <2.5° did not give significantly poorer fit to the experimental data than the *regular* sandwich model, but by increasing $<C_5C_5$ more by bending or tilting the molecular model the R_2 factor increased; a bend angle of 160° yielded $R_2 = 6.0$ %, and a 5° tilt angle yielded $R_2 = 5.5$ % after appropriate background modification. Attempts were made to refine the bend and tilt angles as independent parameters. When the tilt angle was fixed at 0° and the bend angle refined, it fluctuated between 178° and 182° and did not converge properly. When the bend angle was fixed at 180° and the tilt angle refined, it fluctuated between −1.0° and 1.0°. When both the bend and tilt angles were refined simultaneously, the bend angle fluctuated between 177 and 181° and the tilt angle between −3 and 1° in

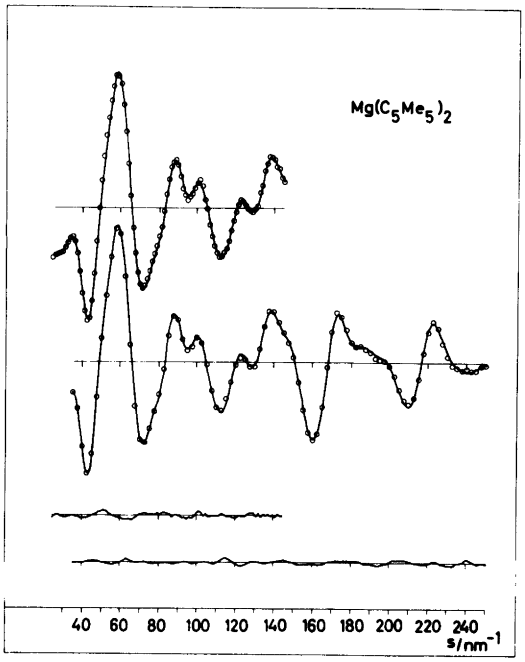

Fig. 3a. Theoretical molecular intensity curves with experimental points for bis(pentamethylcyclopentadienyl)magnesium(II), $Mg(C_5Me_5)_2$. The differences between experimental and theoretical curves for the best model are drawn in the lower part of the figure.

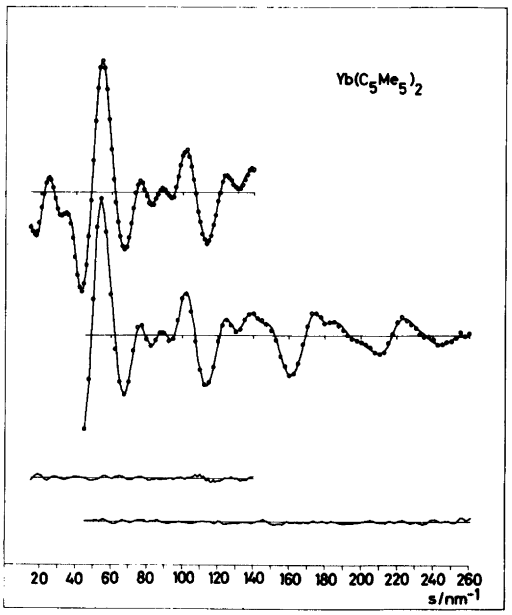

Fig. 3c. Theoretical molecular intensity curves with experimental points for bis(pentamethylcyclopentadienyl)ytterbium(II), $Yb(C_5Me_5)_2$. The differences between experimental and theoretical curves for the best model are drawn in the lower part of the figure.

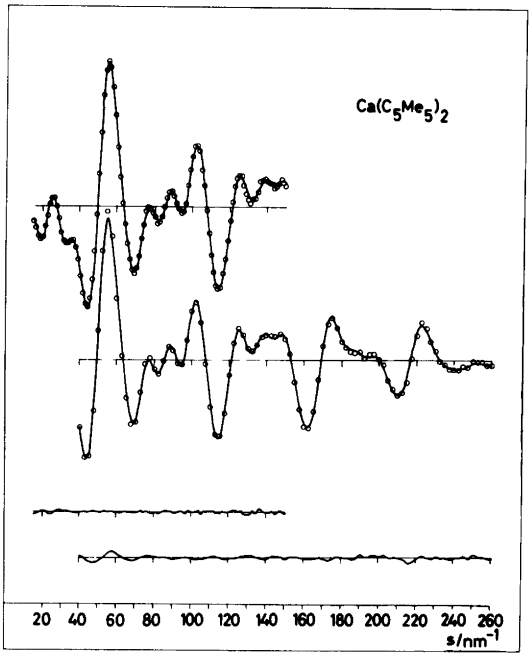

Fig. 3b. Theoretical molecular intensity curves with experimental points for bis(pentamethylcyclopentadienyl)calcium(II), $Ca(C_5Me_5)_2$. The differences between experimental and theoretical curves for the best model are drawn in the lower part of the figure.

such a manner as to maintain $<C_5C_5$ at values between 1.0 and $-1.0°$. These three refinements had to be carried out with large damping of the least-squares shifts. The inclusion of additional independent parameters did not lead to improved fits to the experimental data. We have, in spite of the fact that the Mg atom on average may be displaced about 9 pm from the point where the C_5 axes of the two rings intersect (corresponding to a tilt angle of 2.5°), chosen to fix the Mg atom at the C_5 axes of the rings and $<C_5C_5$ at 0°. In the following refinements only the *regular* sandwich model was considered.

Refinements on a rigid eclipsed and a rigid staggered model yielded R_2-values of 4.9% and

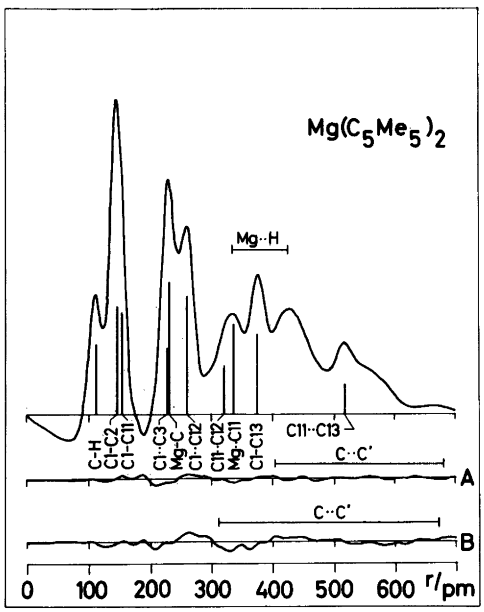

Fig. 4a. Experimental RD curve for bis(pentamethylcyclopentadienyl)magnesium(II), $Mg(C_5Me_5)_2$. The most important distances are indicated by bars of height approx. proportional to the area under the corresponding peak. The differences between the experimental and the theoretical RD curves obtained for A, a *regular* sandwich model (bend angle fixed at 180°, no tilt) with eclipsed conformation (D_{5h} symmetry), and B, a *bent* sandwich model (bend angle fixed at 160°, no tilt) with eclipsed conformation (C_2 symmetry), are drawn in the lower part of the figure. Artificial damping constant, *k*, is 20 pm^2.

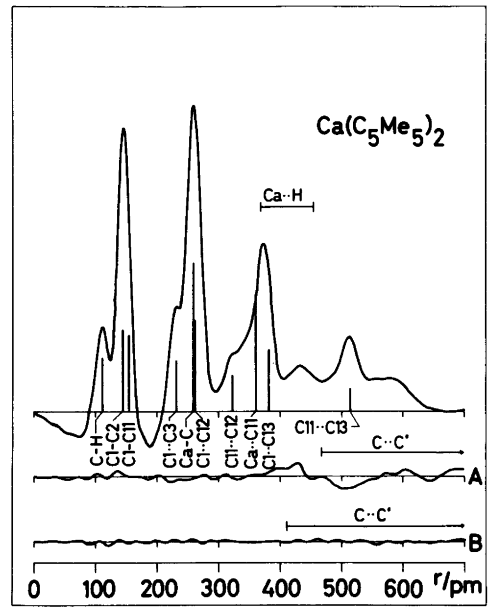

Fig. 4b. Experimental RD curve for bis(pentamethylcyclopentadienyl)calcium(II), $Ca(C_5Me_5)_2$. The most important distances are indicated by bars of height approx. proportional to the area under the corresponding peak. The differences between the experimental and the theoretical RD curves obtained for A, a *regular* sandwich model (bend angle fixed at 180°, no tilt) with staggered conformation (D_{5d} symmetry), and B, a *bent* sandwich model (bend angle fixed at 160°, no tilt) with staggered conformation (C_s symmetry), are drawn in the lower part of the figure. Artificial damping constant, *k*, is 20 pm^2.

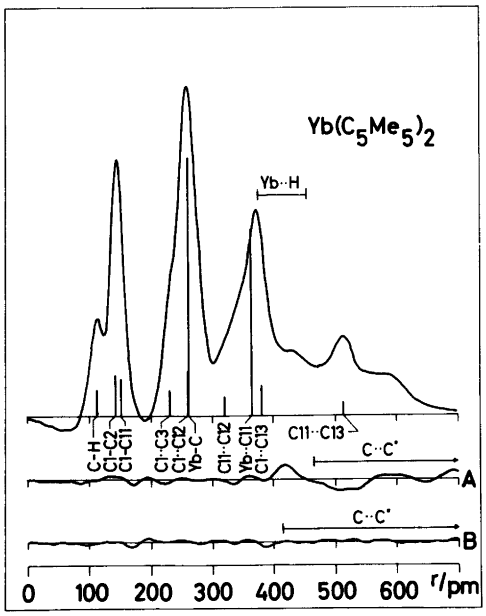

Fig. 4c. Experimental RD curve for bis(pentamethylcyclopentadienyl)ytterbium(II), $Yb(C_5Me_5)_2$. The most important distances are indicated by bars of height approx. proportional to the area under the corresponding peak. The differences between the experimental and the theoretical RD curves obtained for A, a *regular* sandwich model (bend angle fixed at 180°, no tilt) with staggered conformation (D_{5d} symmetry), and B, a *bent* sandwich model (bend angle fixed at 160°, no tilt) with staggered conformation (C_s symmetry), are drawn in the lower part of the figure. Artificial damping constant, *k*, is 20 pm^2.

5.5 %, respectively.* In addition, the *inter*-ring *l* (C(Me)···C(Me)) for the rigid staggered model was very large and uncertain with a value of 89 (50) pm, in contrast to the value of 27(8) pm obtained with the rigid eclipsed model. A free rotation model yielded a R_2-value of 5.3 %. Up to this point in the refinements we used the "full" data set with s ranging from 15 to 250 nm^{-1}. In the final refinements the data for $s < 25$ nm^{-1} were omitted. For the purpose of determining the energy difference between the eclipsed and staggered conformer we used a dynamic model as described for the structure determination of decamethylferrocene.[25] The energy difference between the two conformers correlated to some extent with the chosen difference between the *inter*-ring *l*-values refined in-group, but the eclipsed conformer was consistently predominant. The mean energy difference between the two conformers ($E_{eclipsed}$–$E_{staggered}$) was $\Delta E = -10(9)$ kJ mol^{-1}. We have chosen to present the structural parameters obtained for this dynamic model in Table 1.

Bis(pentamethylcyclopentadienyl)calcium(II) and -ytterbium(II). Initial refinements were made on a *regular* sandwich model. However, inspection of the part of the RD curve that contained information about the C···C distances between one ring and the other (from about 400 to 600 pm; see Figs. 4b and 4c) indicated that the theoretical curve obtained for a *regular* sandwich model had too great an area between 520 and 570 pm, and too small an area between 400 and 460 pm. One way to compensate for this discrepancy was to increase the angle between the ring planes, $<C_5C_5$. By increasing the angle to 20°, the average *inter*-ring C···C distance is shortened by about 10 pm and these distances show greater spreading.

The molecular bending can occur either by tilting or by bending the two rings towards each other. The bent model could easily be brought into agreement with the data for both compounds. Since a bent model with no tilt assumes C_{5v} symmetry of the MC_5Me_5 fragments, we included the tilt angle in the refinements in order to test the validity of this assumption. In this model, which leads to different M–C bond lengths, the *l*-values for the M–C bond distances were assumed to be equal. The same assumptions were made for the M···C(Me) and M···H distances. When the bend angle was fixed at 180°, the tilt angle converged towards 0° and a R_2 factor of 6.7 (i.e. a *regular* sandwich). In Table 2 we show some results of refinements in which the tilt angle and bend angle were fixed at different values so as to maintain the angle between the ring planes ($<C_5C_5$) at 20°. The *l*-values obtained for the extremely tilted models are omitted because they became unreasonably low (partly negative); as the R_2-values show, there was considerable discrepancy between the experimental and theoretical intensity curves for these models. The most serious discrepancies in the RD curves were observed for the peaks corresponding to the M–C and M···C(Me) distances, i.e. at about 260 and 360 pm, respectively, for the Ca and the Yb compounds. In these refinements the *intra*-ring C···C *l*-values were fixed.

We also carried out refinements in which both the tilt angle and the bend angle were refined; the values converged towards $-3(1_5)°$ and 154(3)° for the Ca compound, and $-1(2_5)°$ and 158(4)° for the Yb compound, respectively, the sign of the tilt angle being such as to render the ring planes more parallel. These values correspond to an angle of 20° between the ring planes in both molecules. The Ca–C bond distances ranged from 255 to 267 pm, with an average of 260.9(6) pm and *l*(Ca–C) of 9.9(11) pm, which may be compared to the values obtained for the *non*-tilted model of 260.8(6) pm and 10.5(11) pm, respectively. The Yb–C bond distances ranged from 261 to 263 with an average of 262.2 pm and *l*(Yb–C) of 9.3 pm, which may be compared to the values obtained for the *non*-tilted model of 262.1(6) pm and 9.6(5) pm, respectively. All the other structural parameters and *l*-values were equal to those found for the *non*-tilted molecular models. The correlation between the tilt angle and the bend angle was 90 and 86 % for the two calculations, respectively. However, the introduction of the tilt angle did not lead to a significantly better fit to the experimental data; the only result was a reduction in the R_2 factor by 0.1 for Ca, with no re-

*Using Hamilton's significance test one obtains $R = 1.122$. The number of intensity values is 196, and the number of refined parameters is 19. The staggered conformation is rejected at a significance level of 0.05 if the hypothesis has a dimension of less than about 20. Any conclusions should be drawn with caution, since the intensity data are not uncorrelated and the dimension of the hypothesis is not obvious.

duction for the Yb compound. We have, nevertheless, chosen to present the structural parameters and *l*-values obtained for the tilted molecular model for both $Ca(C_5Me_5)_2$ and $Yb(C_5Me_5)_2$ in Table 1.

For both bis(pentamethylcyclopentadienyl)-calcium(II) and -ytterbium(II), the theoretical intensity curves calculated for rigid staggered models of C_s symmetry gave a better fit to the experimental curves than those for the rigid eclipsed model of C_2 symmetry, the rigid staggered model of C_2 symmetry or the free rotation model. This former conformer is the one used in the final structure refinement (see Fig. 2).

Discussion

The values of the geometrical parameters and root-mean-square amplitudes of vibration (*l*-values) obtained for the best model for each compound are listed in Table 1. In parentheses are the standard deviations from the least-squares refinement multiplied by a factor of 3 to compensate for the errors introduced by uncertainties in the assumptions and by systematic errors.

Bis(pentamethylcyclopentadienyl)magnesium(II). $Mg(C_5Me_5)_2$ is best described as a *regular* sandwich molecule. The Mg–C bond distance and *l*-

Table 1. Geometrical parameters and r.m.s. amplitudes of vibration (ℓ) for the three compounds bis(pentamethylcyclopentadienyl)magnesium(II), $Mg(C_5Me_5)_2$, bis(pentamethylcyclopentadienyl)calcium(II), $Ca(C_5Me_5)_2$, and bis(pentamethylcyclopentadienyl)ytterbium(II), $Yb(C_5Me_5)_2$. Refined parameters are listed with estimated standard deviations in parentheses in units of the last digit. Numbering of the C atoms is shown in Fig. 2.

	$Mg(C_5Me_5)_2$[a]		$Ca(C_5Me_5)_2$		$Yb(C_5Me_5)_2$	
	r_a/pm	ℓ/pm	r_a/pm	ℓ/pm	r_a/pm	ℓ/pm
M–C (M = Mg, Ca or Yb)	234.1(6)	11.9(13)	260.9(6)[d]	9.9(11)	262.2(6)[d]	9.4(5)
d[b]	201.1(8)	–	231.2(6)	–	232.6(5)	–
C1–C2	142.8(3)	4.6[c]	142.7(3)	5.2(5)[e]	142.8(4)	4.1(7)[e]
C1–C11	152.0(5)	5.1[c]	150.6(4)	5.7(5)[e]	151.1(5)	4.6(7)[e]
C–H	111.6(5)	7.5(4)	110.7(4)	8.3(5)	111.6(5)	7.9(5)
M···C(Me)	340	16(1)	357[d]	19(2)	361[d]	19(2)
M···H range	342–427	46(30)	366–454	21(6)	372–459	26(9)
C1···C3	230	6.4(13)	231	6.3(7)	231	6.7(7)
C1···C12	262	7.4(5)	261	7.1(9)	261	6.4(4)
C1···C13	377	8.2(5)	376	7.7(5)	376	7.5(5)
C11···C12	320	13.6[c]	318	12.3(13)	319	13.8(24)
C11···C13	518	9.8(13)	515	8.3(15)	516	10.5(33)
Interligand parameters						
C(ring)···C(ring) range	402–465	20–22(4)	423–517	14–16(4)	423–520	11–13(5)
C(ring)···C(Me) range	440–562	44–46(13)	435–619	36–38(7)	437–623	37–39(9)
C(Me)···C(Me) range	416–681	26–28(8)	411–711	16–18(6)	415–717	19–21(10)
Angles/°						
$<C_5$,C–C(Me)	−5(2)	–	−1.4(9)	–	−3(2)	–
<CCH	115(2)	–	119(2)	–	121(2)	–
Bend	0[c]		154(3)		158(4)	
Tilt	0[c]		$-3(1_5)$		$-1(2_5)$	
$<C_5C_5$	0[c]	–	20(2)	–	20(3)	–
τ(CCCH)	31(12)	–	8(6)	–	11(8)	–

[a]The dynamic model with $E_{eclipsed}$–$E_{staggered}$ = −10(9) kJ mol^{-1} is presented. [b]The distance from the metal atom to the centre of the C_5Me_5 ring. [c]Fixed values (see text). [d]Mean values. [e]These values were refined in-group.

Table 2. R_2- and ℓ-values for $Ca(C_5Me_5)_2$ and $Yb(C_5Me_5)_2$ obtained when the tilt angle and bend angle (see Fig. 1 for definitions of these angles) are fixed at different values maintaining the angle between the ring planes ($<C_5C_5$) at 20°.

Tilt Bend	10° 180°	5° 170°	0° 160°	−5° 150°	−10° 140°
$Ca(C_5Me_5)_2$					
ℓ-(Ca–C)/pm	–	7.7(7)	10.4(4)	8.2(7)	–
ℓ(Ca···C(Me))/pm	–	17(2)	20(1)	17(2)	–
ℓ(Ca···H)/pm	–	23(9)	23(4)	17(5)	–
R_2[a]/%	12.7	4.0	3.5	4.0	13.7
$Yb(C_5Me_5)_2$					
ℓ(Yb–C)/pm	–	4.4(9)	9.0(4)	4.8(9)	–
ℓ(Yb···C(Me))/pm	–	15(2)	19(1)	15(2)	–
ℓ(Yb···H)/pm	–	26(20)	28(12)	56(24)	–
R_2[a]/%	17.2	4.7	4.0	4.7	16.7

[a] $R_2 = \sqrt{[w(I_{obs}-I_{calc})^2/wI_{obs}^2]}$, see Ref. 27.

value obtained are 234.1(6) and 11.9(13) pm, respectively. The values found for gaseous $Mg(C_5H_5)_2$ are 233.9(4) and 10.3(3) pm, respectively.[4] The larger *l*-value obtained for $Mg(C_5Me_5)_2$ may indicate that introduction of CH_3 groups destabilises the Mg–C bond.* It may also be a consequence of lower symmetric and asymmetric ring tilt frequencies in $Mg(C_5Me_5)_2$ than in $Mg(C_5H_5)_2$. For the latter molecule, the line at 207 cm^{-1} in the Raman spectrum is assigned to the symmetric ring tilt (e_{1g}) and the line at 524 cm^{-1} in the IR spectrum is assigned to the asymmetric ring tilt (e_{1u}).[29] The IR spectrum of $Mg(C_5Me_5)_2$ has been reported[17] but no assignments have been made. The C–C and C–H distances and *l*-values for the ligands are normal for this kind of compound.

*When $Mg(C_5H_5)_2$ and $Mg(C_5Me_5)_2$ are considered as three "atom" molecules, $(C_5H_5)-Mg-(C_5H_5)$ and $(C_5Me_5)-Mg-(C_5Me_5)$, respectively, the connection between l^2 of the bond between metal and ring and its force constant, *f*, of a diagonal force field may be written approximately as $l^2 = kT(f^{-1}) + C(m_A^{-1} + m_B^{-1})$. *C* is a positive constant and m_A and m_B are the masses of the metal and the ring, respectively. It is easy to see that the larger *l*-value found for the $Mg-(C_5Me_5)$ bond necessarily leads to a smaller force constant for this bond than for the $Mg-(C_5H_5)$ bond. For more details see Ref. 28.

The conformation of $Mg(C_5H_5)_2$ in the gas phase was found to be eclipsed, but a model with a staggered conformation could not be ruled out.[4] The barrier to rotation has been found by *ab initio* calculations[30] to be as low as 0.12 kJ mol^{-1} (cf. the rotational barrier found in ferrocene by GED of 3.8(13) kJ mol^{-1},[31] and by *ab initio* calculations of 2.5 kJ mol^{-1} [32]). It is not possible to determine such a low barrier accurately in a relatively large molecule like $Mg(C_5Me_5)_2$ by GED. The energy difference between the eclipsed and staggered conformation which we have calculated is very inaccurate. We cannot, on the basis of our experiment, completely exclude the presence of a larger number of molecules in the staggered conformation. Even the conclusion that the predominant conformer is eclipsed must here be drawn with caution. A predominance of the eclipsed conformer may be rationalized as follows: In ferrocene, the predominant conformer in the gas phase is eclipsed, whereas in decamethylferrocene it is staggered because of repulsion between the methyl groups. Bis(pentamethylcyclopentadienyl)magnesium(II) can maintain the electronically favorable eclipsed conformation because the distance between the methyl groups of the two rings is greater than 400 pm (this is the Pauling van der Waals radius of the methyl groups[33]) and maximum van der Waals attraction is obtained when the rings have eclipsed conforma-

tion. The shortest *inter*-ring C(Me)···C(Me) distance is reduced from 451 to 416 pm when rotating from the staggered to the eclipsed conformation. Our very uncertain energy difference between the two conformers of 10(9) kJ mol^{-1} certainly cannot be fully explained by van der Waals interaction between the methyl groups; our value is probably too high.

Bis(pentamethylcyclopentadienyl)calcium(II) and -ytterbium(II). $Ca(C_5Me_5)_2$ and $Yb(C_5Me_5)_2$ are best described as *bent* sandwich molecules. The mean Ca–C bond distance is found to be 260.9(6) pm. This is 14 pm shorter than the mean Ca–C bond distance (to the nearest η^5-bonded ring) found in crystalline $Ca(C_5H_5)_2$.[5] The larger distance found in the latter may be due to higher coordination number and steric effects; each Ca atom is attached to four C_5H_5 rings in a $(\eta^5-C_5H_5)_2(\eta^3-C_5H_5)(\eta^1-C_5H_5)$ fashion. The mean Yb–C bond distance of 262.2(5) pm is about 4 pm smaller than the mean Yb–C bond distance in crystalline $(Me_5C_5)_2Yb(THF)$, 266(2) pm.[11] This reduction is about half that obtained on removing *two* THF molecules from $(Me_5C_5)_2Sm(THF)_2$: the mean Sm–C bond distance is reduced from 286(3) to 279(1) pm.[12,34] The difference between the Yb–C and Ca–C bond distances is the same as the difference in the ionic radii of Ca^{2+} and Yb^{2+} suggested by Shannon[15] for coordination number six. The coordination number is defined as the number of electron pairs involved in ligand-to-metal coordination.[35]

The *l*-values obtained, $l(Ca–C) = 9.9(11)$ pm and $l(Yb–C) = 9.3(5)$ pm, are as expected for this kind of compound: In $Fe(C_5Me_5)_2$ $l(Fe–C) = 6.6(2)$ pm,[25] and in $Mg(C_5Me_5)_2$ $l(Mg–C) = 11.9(13)$ pm (this work). The geometrical parameters that describe the shape of the ligands, and the *l*-values, are found to be normal for this kind of compound; exceptions are the angles <CCH at the methyl groups which seem somewhat large, viz. 119(2)° and 121(2)° for the two compounds, respectively. It is not clear whether the values are representative for this kind of compound or why the GED experiment failed to determine these angles properly.

The angle between the ring planes is found to be 20(3)° for both $Ca(C_5Me_5)_2$ and $Yb(C_5Me_5)_2$. This is about the same as in gaseous $Ge(C_5Me_5)_2$, 22(3)°,[36] but smaller than the angle found in crystalline $Sm(C_5Me_5)_2$, 40°.[12] In the latter compound, each Sm atom interacts with a methyl group of a neighbouring molecule (the shortest intermolecular Sm···Me distance is 322(1) pm). On the other hand, in $Ge(C_5H_4Me)_2$ the angle between the ring planes is found to be 34(7)°.[37] The relatively small angle found in $Ge(C_5Me_5)_2$ may be a consequence of *inter*-ligand methyl···methyl repulsion.

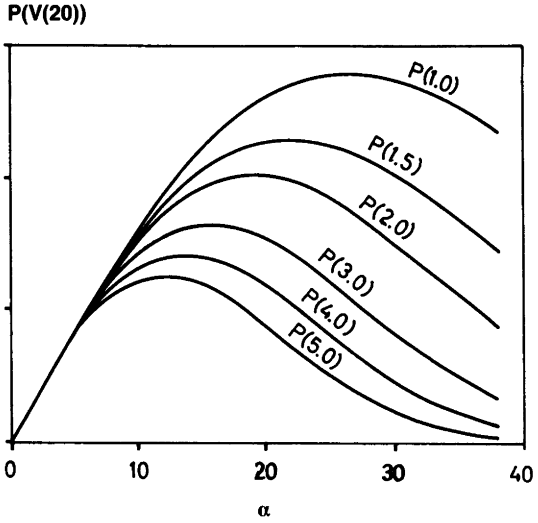

Fig. 5. The probability of finding a molecule with $<C_5C_5 = \alpha$ (only bending considered) for different values of $V(20)$ (in kJ mol^{-1}). $V(\alpha)$ is assumed parabolic with minimum point at (0,0). The probabilities are calculated from the equation $P = \sin(\alpha)\exp[-V(\alpha)/RT]$.

For both molecules, the angle between the two ring planes, $<C_5C_5$, is determined with satisfactory accuracy and the major cause of the non-zero angle is bending of the molecule rather than ring tilting. The position of the metal atom with respect to the rings is inaccurately determined; it may be displaced by as much as 20 pm from the point where the C_5 axes of the two rings intersect (corresponding to a tilt angle of 5°).

It must be remembered that the structures are *thermal average* structures and that the data are not corrected for ring–metal–ring bending vibrations or ring–tilt vibrations (shrinkage effects). Such corrections are expected to decrease the bend and tilt angles. The observed bending in $Ca(C_5Me_5)_2$ and $Yb(C_5Me_5)_2$ may therefore be a consequence of large amplitude motion; the *equi-*

librium geometry may be the *regular* sandwich, but if the energy needed to bend the molecule more than 20° is less than about 1.9 kJ/mol^{-1} ($RT/2$), the *thermal average* structure will be found to be bent for statistical reasons. A bent model has several possible positions of the rings on a sphere, whereas the regular model has only one. A consequence of this is a higher entropy for the bent structure. The probability of finding a molecule within $d\alpha$ is $P(\alpha)d\alpha \sim \sin(\alpha) \exp[-V(\alpha)/RT]d\alpha$, where $V(\alpha)$ is the energy difference between $<C_5C_5 = \alpha$ and $<C_5C_5 = 0$. Even if $<C_5C_5 = 0$ is the *equilibrium* angle, i.e. $V(0)$ is a minimum, $P(\alpha)$ will have a maximum at some angle $\alpha > 0$ dependent on $V(\alpha)$. In Fig. 5 we have drawn $P(\alpha)$ for different values of $V(20)$ [$V(0) = 0$]. The chosen form of $V(\alpha)$ is simply parabolic with minimum point at (0,0), $V(\alpha) = a\alpha^2$. This form is not expected to be useful at high values of α, where the inter-ring Me···Me distances are shorter than about 400 pm, but it is illustrative as a qualitative picture. It may be recalled that *ab initio* calculations on $Ge(C_5H_5)_2$ yield an *equilibrium* structure that is *not* bent, and the calculated energy required to bend the molecule 20° is only 1.0 kJ mol^{-1}.[37]

If the *equilibrium* geometries are *bent* sandwich, the cause of the bending can be rationalised in two ways (one does not exclude the other): (*i*) Polarisation of the central atom, as in the model used to rationalise the structural trends in metal halides.[38] The attraction between a negatively charged C_5Me_5 ring and an induced metal dipole is directly proportional to the polarizability of the central atom, and when the attractive energy is greater than the repulsions caused by bringing the rings closer together, the *equilibrium* geometry will be bent. (*ii*) Van der Waals interaction between the methyl groups of the ligands. The shortest Me··Me distances found in $Ca(C_5Me_5)_2$ and $Yb(C_5Me_5)_2$ are 411(8) and 415(10) pm, which are not much different from twice the van der Waals radius for the methyl group proposed by Pauling.[33] If the bending energy is small, the energy gained by maximizing the van der Waals attraction between the methyl group of the two C_5Me_5 rings may make the *equilibrium* geometry bent.

In addition, it should be noted that neither quasi-relativistic Xα–SW calculations nor the observed photoelectron spectrum of $Yb(C_5Me_5)_2$ provide any explanation for the bent structure in terms of molecular orbital energies.[39]

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