Molecular Structures of Dicyclopentadienylmagnesium and Dicyclopentadienylchromium by Gas-phase Electron Diffraction

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Summary The molecular structures of $(C_5H_5)_2Mg$ and $(C_5H_5)_2Cr$ have been determined by gas-phase electron diffraction; the C–H bonds in $(C_5H_5)_2Cr$ are bent 2·9(1·1)° out of the plane of the C_5 ring towards the metal atom.

THE electron scattering pattern from gaseous $(C_5H_5)_2Mg$ from $s = 1{\cdot}25$ to $31{\cdot}00$ Å^{-1} was recorded with a nozzle temperature of *ca.* 125°; the scattering pattern from $(C_5H_5)_2Cr$ was recorded from $s = 1{\cdot}50$ to $30{\cdot}00$ Å^{-1} with a nozzle temperature of *ca.* 145°.

Least-squares refinements[1] were carried out on both eclipsed (D_{5h}) and staggered (D_{5d}) models. Both models are characterized by four independent parameters, *e.g.* the C–H, C–C, and M–C bond distances and the angle, $\angle$ (C_5,H), between the C–H bonds and the C_5 plane. This angle is defined as positive when the C–H bonds are bent *towards* the metal atom. Perpendicular amplitude corrections were calculated from a molecular force-field, and the refinements carried out under the constraints of a geometrically consistent r_α-structure. Ten vibrational amplitudes were refined; the remaining C $\cdots$ H and H $\cdots$ H amplitudes were fixed at the values calculated from the molecular force-fields.

For both molecules better agreement was obtained with the eclipsed than with the staggered models. For $(C_5H_5)_2Cr$, R_3 was 11·95 for the staggered model and 11·49 for the eclipsed model.[1] For $(C_5H_5)_2Mg$ the corresponding values were 8·59 and 8·23 respectively. Hence an eclipsed equilibrium conformation is probable for both molecules, but we do not feel that a staggered equilibrium conformation can be ruled out. In any event the large vibrational amplitudes (*ca.* 0·2 Å) obtained for the distances between atoms in different C_5H_5 rings indicate that the barriers to internal rotation are less than the thermal energy available, 0·8 kcal mol^{-1}.

The bond distances (r_a) and their estimated standard deviations obtained by refinement on the eclipsed models are given in the Table. While no significant deviation from planarity is found for the C_5H_5 rings in $(C_5H_5)_2Mg$, the C–H bonds in $(C_5H_5)_2Cr$ are bent 2·9° out of the plane of the C_5

TABLE

	$(C_5H_5)_2Mg$	$(C_5H_5)_2Cr$
C–H	1·116(7) Å	1·108(7) Å
C–C	1·423(2) Å	1·431(2) Å
M–C	2·339(4) Å	2·169(4) Å
h^a	2·008(4) Å	1·798(4) Å
∠(C_5,H)	−1·0(1·6)°	2·9(1·1)°

[a] The distance from the metal atom to the centre of the C_5 rings.

ring towards the Cr atom. This deviation is significant at the 2% level.

Several years ago Bohn and Haaland in a gas-phase electron diffraction investigation of $(C_5H_5)_2Fe$ found that the value obtained for the Fe · · · H distance was 0·054(11) Å smaller than the distance calculated under the assumption that the H atoms lie in the plane of the C_5 ring.[2] This corresponds to an angle ∠ (C_5,H) = 4·6(0·9)°. However, since shrinkage had been neglected, the authors concluded that the result should be taken as an indication rather than a demonstration of nonplanarity. Recently the perpendicular amplitude corrections have been calculated from a molecular force-field by Schäfer and his co-workers.[3] These coefficients lead to a calculated shrinkage of the Fe · · · H distance of only 0·010 Å. The angle ∠ (C_5,H) corrected for shrinkage is then 3·7(0·9)°.

In $(C_5H_5)_2Be$ the metal atom is situated on the five-fold symmetry axis of the molecule, but closer to one ring than to the other, the perpendicular distances being 1·47 and 1·90 Å respectively. No indication is found for a similar asymmetry in $(C_5H_5)_2Mg$. The Mg–C vibrational amplitude obtained by refinement on a symmetrical model, l(Mg–C) 0·103(3) Å, is unexceptional.

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