Molecular Structure of Dimethyl(cyclopentadienyl)aluminium Monomer in the Gas Phase by Electron Diffraction

By D. A. DREW and ARNE HAALAND*

(*Department of Chemistry, University of Oslo, Blindern, Oslo* 3, *Norway*)

Summary The cyclopentadienyl ring in gaseous monomeric $AlMe_2(C_5H_5)$ is bound to the metal atom in an asymmetric *polyhapto* fashion.

THE ^1H n.m.r. spectrum of dimethyl(cyclopentadienyl)-aluminium, $AlMe_2(C_5H_5)$, in benzene solution at room temperature contains only one line due to the five ring protons.[1] It was assumed that the compound contains σ-bonded rings, and the ^1H n.m.r. spectrum was interpreted as evidence for non-rigid behaviour of the (C_5H_5) ring. Later, however, Haaland and Weidlein have interpreted the i.r. and Raman spectra of solid $AlMe_2(C_5H_5)$ as evidence for the presence of π-bonded rings in that phase and have suggested that the rings remain π-bonded in solution and in the gas phase.[2]

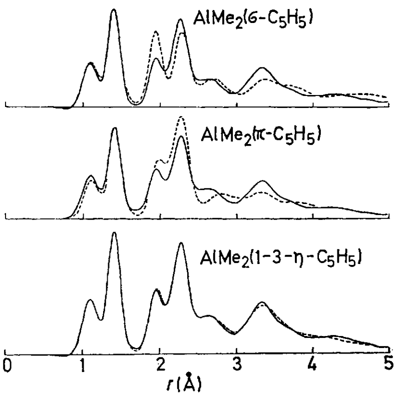

Figure 1.

Since $AlMe_2(C_5H_5)$ is only weakly associated in solution,[2] it is most probably monomeric in the gas phase. We have recorded the electron scattering pattern from gaseous $AlMe_2(C_5H_5)$ from $s = 1{\cdot}50$—$39{\cdot}00$ Å^{-1} with the reservoir at 105° and the nozzle at 110° and 130°. There are no significant differences between the data collected at the two nozzle temperatures. $AlMe_2(C_5H_5)$ is thermally stable up to 145°.[2] Until now, structure refinement has been based on the data collected with a nozzle temperature of 130°. Radial distribution curves confirm that $AlMe_2(C_5H_5)$ is monomeric in the gas phase under the experimental conditions.

The two upper curves in Figure 1 show experimental radial distribution curves (full line) along with theoretical radial distribution curves (dashed line) calculated for models containing σ-bonded and π-bonded rings. Both models lead to serious disagreement between experimental and calculated curves in the region around $r = 2{\cdot}0$ Å, *i.e.* in the region containing the Al–C bond distances, and may confidently be ruled out.

Satisfactory agreement is obtained with the model of C_s symmetry containing 1—3-η-bonded rings shown in Figure 2. A theoretical radial distribution curve (dashed line) calculated for this model is shown at the bottom of Figure 1 along with an experimental curve (full line). The main structure parameters obtained by least-squares refinement of this model are given in the Table.

Preliminary refinements have been carried out on three other models of C_s symmetry containing *polyhapto* rings. In one of these the methyl group C atoms remain in the mirror plane, but the Al atom has been displaced towards the midpoint of the C(3)–C(3′) bond. In the two last models the line connecting the methyl group C atoms is perpendicular to the mirror plane and the Al atom has been displaced towards C(1) or the midpoint of the C(3)–C(3′) bond, respectively. The refinements indicate that these models may be brought into nearly as good agreement with the experimental data as the model shown in Figure 2 and more work is required before any of them can be ruled out. The values obtained for the C–C and Al–C(Me) bond distances, the perpendicular distance from Al to the ring, Al–o, and the distance from the Al atom to the (approximate) fivefold symmetry axis of the ring, o–p, are, however, similar to the values quoted in the Table.

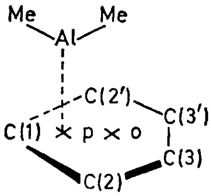

Figure 2.

Table

C–C (mean)	1·413(3) Å
Al–C(Me)	1·943(5) Å
Al–p	2·13(1) Å
o–p	0·96(5) Å
∠C(Me)–Al–C(Me)	117(2)°
Al–C(1)	2·14(1) Å
Al–C(2)	2·48(2) Å
Al · · · C(3)	2·96(4) Å

We would suggest that the asymmetric structure of monomeric $AlMe_2(C_5H_5)$ is due to the fact that the (C_5H_5) ring need function only as a three-electron ligand for the Al atom to be surrounded by an octet of electrons. As a simplification the model in Figure 2 may be regarded as a π-allyl-type complex. Rapid rotation of the ring would render all ring protons equivalent on the n.m.r. time scale.

(*Received*, 16*th October* 1972; *Com.* 1769.)

---

[1] W. R. Kroll and W. Naegele, *Chem. Comm.*, 1969, 246.

[2] A. Haaland and J. Weidlein, *J. Organometallic Chem.*, 1972, **40**, 29.