ACTA CHEMICA SCANDINAVICA 27 (1973) 3735–3745

On the Molecular Structure of Monomeric Dimethyl(cyclopentadienyl)aluminium, $(CH_3)_2Al(C_5H_5)$

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The electron scattering pattern from gaseous monomeric $(CH_3)_2$-$Al(C_5H_5)$ has been recorded from $s = 1.50$ Å^{-1} to $s = 30.00$ Å^{-1}. The data rule out models containing *monohapto* (σ-bonded) or *pentahapto* (symmetrically π-bonded) C_5H_5 rings.

The four possible models of C_s symmetry containing *polyhapto* (asymmetrically π-bonded) rings were refined by least squares calculations on the intensity data, and satisfactory agreement was obtained for all four. The values obtained for the perpendicular distances from the Al atom to the plane of the C_5H_5 ring and to the (approximate) fivefold symmetry axis of the ring ranged from 2.05 to 2.20 Å and from 0.9 to 1.4 Å, respectively.

CNDO/2 calculations indicate that the equilibrium conformation of monomeric $(CH_3)_2Al(C_5H_5)$ is as model (I) in Fig. 5, that the barrier to internal rotation of the C_5H_5 ring is of the order of 5 kcal mol^{-1} or less, and that the barrier to exchange of the methyl groups is between 10 and 20 kcal mol^{-1}.

The most important structure parameters obtained by refinement of model (I) are: Perpendicular distance from the Al atom to the ring: 2.10 (2) Å, perpendicular distance from the Al atom to the symmetry axis of the ring: 0.99(10) Å. C – C = 1.422(2) Å, Al – C(Me) = 1.952 (3) Å.

The nature of the bonding is discussed.

The first cyclopentadienyl-aluminium compound, Et_2AlCp ($Et = C_2H_5$, $Cp = C_5H_5$), was synthesized by Giannini and Cesca in 1961.[1] Since the compound is partly associated in freezing benzene and since it forms a 1:1 complex with diethylether, Giannini and Cesca suggested that it contains *monohapto*, or σ-bonded, cyclopentadienyl rings and that dimerization occurs through ethyl bridges.

Several years later, Kroll and Naegele reported the ^1H NMR spectra of Me_2AlCp ($Me = CH_3$), Et_2AlCp and Bu^i_2AlCp ($Bu^i = iso$-C_4H_9).[2] In each compound the five ring protons gave rise to only one line in the ^1H NMR spectrum, and this line remained unsplit when Et_2AlCp in cyclopentane was cooled to – 60° or when Bu^i_2AlCp in cyclopentane was cooled to – 91°. It was therefore suggested that the Cp rings undergo rapid 1 – 2 or 1 – 3 shifts which render the ring protons equivalent on the NMR time scale.

Kroll and coworkers subsequently synthesized and investigated the analogous dialkyl(methylcyclopentadienyl) derivatives.[3] The ^1H NMR spectrum of $Me_2Al(C_5H_4Me)$ in cyclopentane at +10° consisted of two singlets arising from the four ring protons, one singlet arising from the ring Me group and one singlet from the Me groups bonded to the metal. Cooling to –40° produced no change except broadening. The spectrum therefore seemed to be in agreement with a model in which the Al atom and the Me group are bonded to the same atom in the Cp ring. Furthermore it was pointed out that this compound too is associated. That the Me group bonded to Al gives only a singlet in the ^1H NMR spectrum at –40° would therefore seem to imply that either bridge-terminal exchange is more rapid than in Me_6Al_2 or that the Cp rings occupy the bridging position.

More recently Haaland and Weidlein have recorded the IR and Raman spectra of solid Me_2AlCp.[4] The spectra provided strong evidence against the presence of bridging Me groups and σ-bonded Cp groups. Haaland and Weidlein therefore proposed that solid Me_2AlCp contains π-bonded Cp rings of approximate D_{5h} symmetry. In view of the low solubility and volatility and the high melting point of the compound they further proposed a polymeric structure with bridging *pentahapto* Cp rings as shown schemativally in Fig. 1 A. Such bridging Cp groups have been found in crystalline InCp [5] and $PbCp_2$.[6] Finally it was suggested that the polymer is broken down to a mixture of monomeric and oligomeric species in solution and in the gas phase, and that the Cp rings remain π-bonded in the monomer.

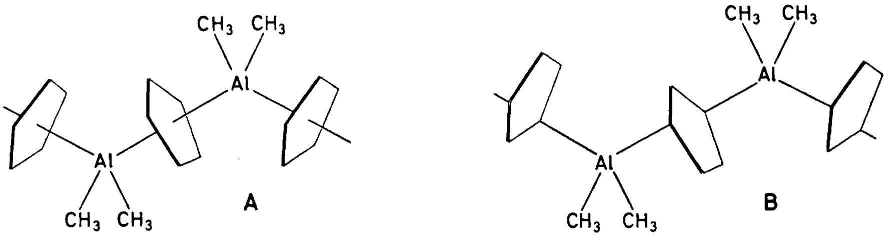

Fig. 1. A. Structure model of solid Me_2AlCp proposed by Haaland and Weidlein.[4] B. Revised model of solid Me_2AlCp.

We now report the result or a gas phase electron diffraction investigation of monomeric Me_2AlCp. A preliminary account has appeared elsewhere.[7]

EXPERIMENTAL AND CALCULATION PROCEDURE

Me_2AlCp was prepared from NaCp and Me_2AlCl as described by Kroll and Naegele.[2] The electron scattering pattern was recorded on the Oslo electron diffraction unit [8] with the sample reservoir at 105° and nozzle temperatures of 110° and 130°. Me_2AlCp is thermally stable up to 145°.[4] There were no significant differences between the data collected at the two temperatures. The structure refinement was carried out on the data collected at 130°. Exposures had been made with nozzle to photographic plate distances of 48 cm and 20 cm. The optical densities of five plates from the first set were recorded at $\Delta s = 0.125$ Å^{-1} intervals, the optical densities of five plates from the last were recorded at $\Delta s = 0.250$ Å^{-1} intervals. (The scattering parameter $s = (4\pi/\lambda)$ sin $(\theta/2)$ where λ is the electron wavelength and θ the diffraction angle). The optical densities were converted into intensities and the data prosessed in the usual way.[9]

Every second of the modified molecular intensity points obtained from the 48 cm plates is shown in Fig. 2 A and the modified intensity points obtained from the 20 cm plates are shown in Fig. 3 A.

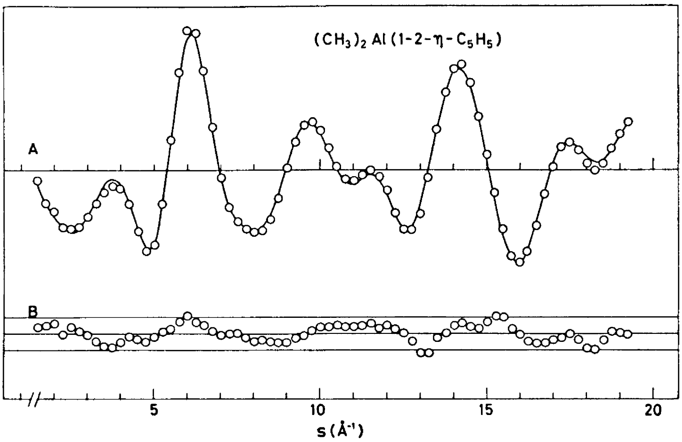

Fig. 2. A. O; Experimental modified molecular intensity points from $s = 1.50$ to 19.25 Å^{-1}. Full line; theoretical modified molecular intensity curve calculated for model (I) and parameter set P.A. B. O; Difference points. The two full lines indicate the estimated uncertainty (three standard deviations) of the experimental intensity points. *Note:* The scale of B is twice that of A.

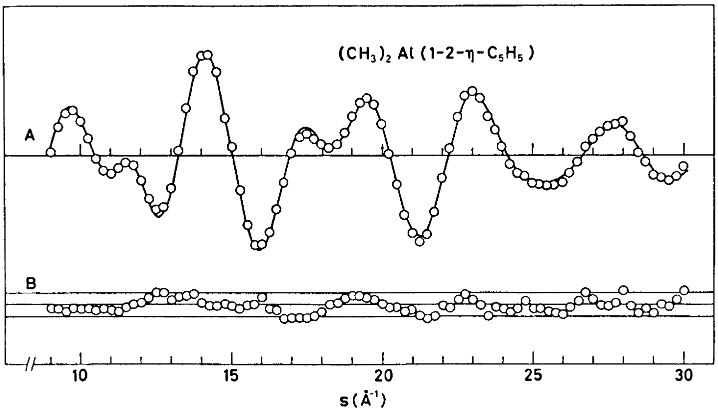

Fig. 3. A. O; Experimental modified molecular intensity points from $s = 9.00$ Å^{-1} to 30.00 Å^{-1}. Full line; theoretical modified molecular intensity curve calculated for model (I) and parameter set PA. B. O; Difference points. The two full lines indicate the estimated uncertainty (three standard deviations) of the experimental intensity points. *Note:* The scale of B is twice that of A.

Theoretical intensity curves were calculated from:

$$I^{\mathrm{AlC}}(s) = \sum_{\mathrm{i}\neq \mathrm{j}} \frac{|f_{\mathrm{i}}(s)||f_{\mathrm{j}}(s)|}{|f_{\mathrm{Al}}(s)||f_{\mathrm{C}}(s)|} \cos\left[\eta_{\mathrm{i}}(s) - \eta_{\mathrm{j}}(s)\right] \frac{\sin(R_{\mathrm{ij}}s)}{R_{\mathrm{ij}}} \exp(-\tfrac{1}{2}l^2_{\mathrm{ij}}s^2)$$

The sum extends over all atom pairs i,j in the molecule. R_{ij} is the internuclear distance, l_{ij} the root mean square amplitude of vibration. $f_{\mathrm{j}}(s) = |f_{\mathrm{j}}(s)| \exp[\mathrm{i}\eta_{\mathrm{j}}(s)]$ is the complex atomic scattering factor of atom j. It has been calculated for Al, C, and H by the partial wave approximation with a program written by Peacher.[10] The scattering potentials of Al and C have been found by non-relativistic Hartree-Fock calculations.[11,12]

Radial distribution functions were calculated by Fourier inversion of experimental and theoretical intensity curves after multiplication with the artificial damping function $\exp(-ks^2)$. The experimental intensity functions obtained with different nozzle-to-plate distances were then first spliced to each other and to the theoretical curve calculated for the best model below $s = 1.50$ Å^{-1}.

The molecular structure was refined by least-squares calculations on the intensity data with a non-diagonal weight matrix and a separately refined scale factor for the intensity data obtained for each nozzle to plate distance.[13]

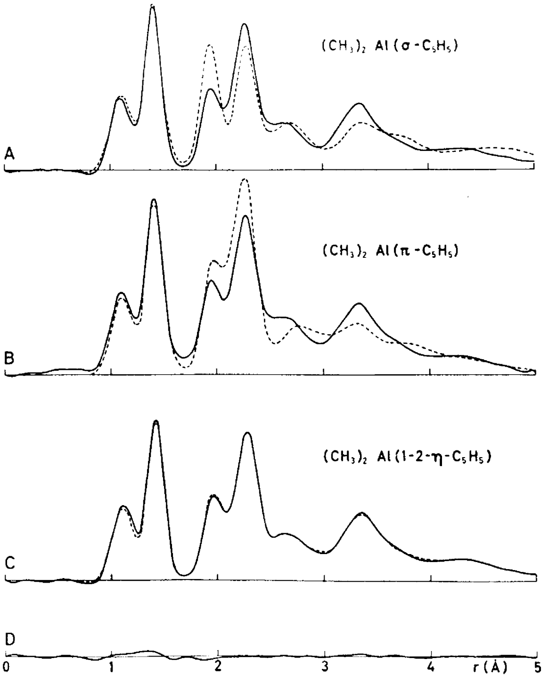

Fig. 4. A, B and C. Full line; experimental RD curves. A. Stipled line; theoretical RD curve calculated for model containing σ-bonded Cp ring. B. Stiplet line; theoretical RD curve calculated for model containing symmetrically π-bonded Cp ring. C. Stipled line: theoretical RD curve calculated for model containing asymmetrically π-bonded [model (I), parameter set PA] Cp ring. D. Difference between the two RD curves in C. Artificial damping constant $k = 0.002$ Å^2.

STRUCTURE ANALYSIS

In Fig. 4 A and B the experimental RD-curve for Me_2AlCp (full line) is compared to theoretical RD-curves (stipled lines) calculated for models containing *monohapto*, or σ-bonded, and *pentahapto*, or symmetrically π-bonded, cyclopentadienyl rings. Both models lead to serious disagreement between experimental and calculated curves in the region around $r = 2.0$ Å, *i.e.* in the region containing the $Al-C$ bond distances, and may confidently be ruled out.

The four possible models of Me_2AlCp with C_s symmetry and the numbering of the C atoms in each model are shown in Fig. 5. The H atoms were given the same number as the C atoms to which they are bonded. For all models the following assumptions were made:

(i) The Cp rings have D_{5h} symmetry. The point at which the fivefold axis intersects the ring plane is denoted by o.

(ii) The Me_2Al fragment has C_{2v} symmetry. The projection of the Al atom onto the ring plane is denoted by p. The distance $o-p$ is therefore equal to the perpendicular distance from the Al atom to the fivefold symmetry axis.

(iii) The Me groups have C_{3v} symmetry with the threefold axes coinciding with the $Al-C$ bonds, and are oriented in such a way that one C_6-H_6 bond is *anti* to the $Al-C_7$ bond.

The four models shown in Fig. 5 are closely related and may be regarded as rotational isomers: Model (II) may be obtained from model (I) by rotating the Cp ring 36° about its fivefold symmetry axis. Model (III) can be obtained from model (I) by rotating the Me_2Al fragment 90° about its twofold symmetry axis. Model (IV) can be obtained from model (III) by a 36° rotation of the Cp ring or from model (II) by a 90° rotation of the Me_2Al fragment.

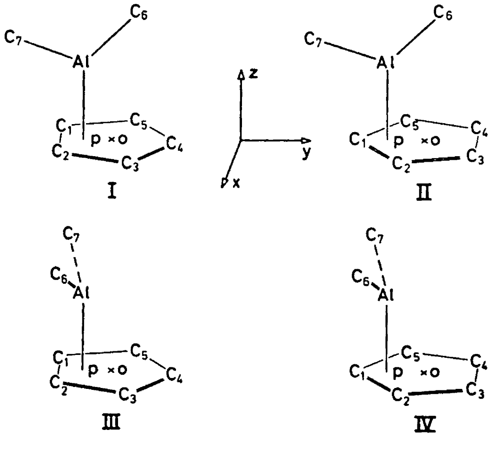

Fig. 5. Molecular models of Me_2AlCp.

Specifically the models differ in the values assigned to the angle between the AlC_6C_7 plane and the $y-z$ plane [0° for models (I) and (II), 90° for (III) and (IV)] and the value assigned to the angle between o-C_4 and the y-axis [0° for models (I) and (III), 36° for (II) and (IV)].

After the assumptions (i) to (iii) regarding the local symmetry have been made, the structure of each of the four models is completely determined by the same nine parameters, *i.e.* by the C_1-H_1, C_1-C_2, $Al-C_6$, and C_6-H_6 bond distances, the $\angle C_6-Al-C_7$ and $\angle Al-C_6-H_6$ valence angles, the perpendicular distance from Al to the ring, $Al-p$, the distance from Al to the fivefold axis of the ring, $o-p$, and finally the angle between the fivefold axis of the ring and the twofold symmetry axis of the Me_2Al fragment. The latter angle was denoted as α and was defined as positive when C_6 and C_7 are moved towards the negative part of the y-axis; hence all models as shown in Fig. 5 have α greater than zero.

It should be emphasized that models containing σ-bonded or symmetrically π-bonded Cp rings only are special cases of the four models in Fig. 5: Values of $o-p$ and α close to or equal to zero would correspond to a symmetrically π-bonded ring, while a value of $o-p$ equal to about 2.20 Å, of $Al-p$ equal to about 1.65 Å (which together would give $Al-C_1 = 1.95$ Å) and of α equal to about 30° for models (II) and (IV) would correspond to a σ-bonded ring.

For each model the nine structure parameters were refined by least-squares calculations on the intensity data along with the root-mean-square vibrational amplitudes of all bond distances as well as all non-bonded Al···C and C···C distances except $C_6 \cdots C_7$. The amplitude of the latter distance was fixed at $l = 0.133$ Å, the value found in monomeric $(CH_3)_3Al$.[14]

It was found that all models could be brought into satisfactory agreement with the electron diffraction data. The generalized R-factors[13]

$$R_3 = 100\left[\sum_k \sum_l P_{kl}V_kV_l / \sum \sum P_{kl}I_kI_l\right]$$

obtained were 15.6, 15.8, 16.3, and 14.9, respectively. Since we have made assumptions about local symmetry, since not all vibrational amplitudes have been refined, and since shrinkage has been neglected, we do not feel that these numbers are significantly different.

The most important parameter values obtained for each model are shown in Table 1 along with their estimated standard deviations. The four sets of structure parameters have been denoted as PA, PB, PC, and PD. The amplitudes of the C(Me)···C(Cp) distances are not listed. For each model they ranged from 0.1 to 0.4 Å with estimated standard deviations ranging from 0.02 to 0.2 Å. Theoretical intensity curves calculated for model (I) with parameter set PA are compared to the experimental intensity data in Fig. 2 and Fig. 3. The corresponding RD curve is compared to the experimental RD-curve in Fig. 4 C and D. The agreement is seen to be satisfactory. The theoretical curves calculated for the best models (II), (III), and (IV) do not differ significantly from those shown.

At the first glance it is surprising that four models that should differ so much in the non-bonded C(Me)···C(Cp) distances all can be brought into agreement with the electron diffraction data. Inspection of Table 1 shows that this has been possible only with very different values for some structure parameters, particularly $Al-p$, $o-p$, α, and $\angle C_6-Al-C_7$.

Table 1. Structure parameters for Me_2AlCp obtained by least-squares refinement on the four models shown in Fig. 5. Estimated standard deviations are given in parantheses in the units of the last digit.

Model Parameter set	I PA R (Å)	II PB R (Å)	III PC R (Å)	IV PD R (Å)
C_1-C_2	1.422(2)	1.422(2)	1.421(2)	1.421(2)
$C_1\cdots C_3$	2.300(2)	2.300(3)	2.300(3)	2.300(3)
C_1-H_1	1.06(2)	1.08(3)	1.12(2)	1.13(2)
$Al-C_1$	2.21(2)	2.20(3)	2.19(2)	2.16(1)
$Al-C_2$	–[b]	2.55(4)	–[b]	2.63(8)
$Al\cdots C_3$	2.75(5)	3.03(7)	2.84(4)	3.24(17)
$Al\cdots C_4$	3.04(7)	–[c]	3.18(6)	–[c]
$Al\cdots p$	2.10(2)	2.19(3)	2.06(2)	2.16(2)
$o\cdots p$	0.99(10)	0.99(9)	1.21(6)	1.33(22)
$Al-C_6$	1.952(3)	1.957(4)	1.953(3)	1.957(3)
C_6-H_6	1.14(2)	1.14(3)	1.09(2)	1.10(2)
$\angle C_6-Al-C_7$	124(3)°	117(4)°	109(3)°	109(6)°
$\angle Al-C_6-H_6$	113(2)°	118(2)°	116(3)°	116(3)°
α[a]	13(2)°	1(2)°	–9(4)°	–19(9)°
	l (Å)	l (Å)	l (Å)	l (Å)
C_1-C_2	0.049(2)	0.051(2)	0.049(2)	0.051(2)
$C_1\cdots C_3$	0.060(2)	0.060(3)	0.062(2)	0.053(3)
$C_1\cdots H_1$	0.06(2)[d]	0.07(2)[d]	0.07(1)[d]	0.08(1)[d]
$Al-C_1$	0.130(8)	0.092(10)	0.120(17)	0.060(8)
$Al-C_2$	–	0.35(7)	–	0.28(4)
$Al\cdots C_3$	0.29(6)	0.31(6)	0.26(4)	0.31(12)
$Al\cdots C_4$	0.28(12)	–	0.30(24)	–
$Al-C_6$	0.064(3)	0.067(3)	0.065(3)	0.063(3)
C_6-H_6	0.06(2)[d]	0.07(2)[d]	0.07(1)[d]	0.08(1)[d]

[a] α is the angle between the line bisecting the $\angle C_6-Al-C_7$ angle and the $Al-p$ vector. For definition of sign see text. [b] By symmetry equal to $Al-C_1$. [c] By symmetry equal to $Al\cdots C_3$. [d] $l(C_1-H_1)$ and $l(C_6-H_6)$ were assumed equal.

Table 2. Binding energies (in atomic units) and energies in excess of model (I) (in kcal mol^{-1}) obtained by CNDO/2 calculations on the four models in Fig. 5 with various parameter sets (see Table 1). (1 atomic unit = 627.13 kcal mol^{-1}).

Parameter set	Basis	I	II	III	IV
PA	(*sp*)	BE = –7.4483 ΔE = 0	BE = –7.4417 ΔE = 4.1	BE = –7.4212 ΔE = 17.0	BE = –7.4200 ΔE = 17.7
PB	(*sp*)	BE = –7.4874 ΔE = 0	BE = –7.4835 ΔE = 2.5		
PC	(*sp*)	BE = –7.4464 ΔE = 0		BE = –7.4242 ΔE = 13.9	
PD	(*sp*)	BE = –7.4515 ΔE = 0			BE = –7.4449 ΔE = 4.2
PA	(*spd*)	BE = –8.2913 ΔE = 0	BE = –8.2813 ΔE = 6.2	BE = –8.2747 ΔE = 10.4	BE = –8.2758 ΔE = 9.7

MOLECULAR ORBITAL CALCULATIONS

A series of CNDO/2 molecular orbital calculations[15,16] were carried out on the four models with various sets of structure parameters. Calculations were carried out with both (*sp*) and (*spd*) bases. The binding energies obtained are listed in Table 2.

It is seen that for parameter set PA model (I) gives lower energy than the three other models, and that for each of the three parameter sets PB, PC, and PD model (I) gives lower energy than the model for which the parameter set was obtained. The calculations therefore suggest that the equilibrium conformation of Me_2AlCp is (I) but that the barrier to rotation of the Cp ring *via* (II) is of the order of 5 kcal mol^{-1} or less, and that the barrier to exchange of the two Me groups *via* (III) or (IV) is between 10 and 20 kcal mol^{-1}.

The atomic charges on Al and C atoms obtained by calculations on model (I) with parameter set PA and the (*sp*) basis are listed in Table 3. Very similar charges were obtained in the other calculations.

Table 3. Atomic charges (in 0.01 electron units) obtained by CNDO/2 calculations on model (I) with parameter set PA and (*sp*) basis. $\mu = 2.23$ Debye.

	q		q
C_1	−7	C_5	−3
C_2	−7	Al	+75
C_3	−3	C_6	−23
C_4	−9	C_7	−24

DISCUSSION

The close agreement obtained between experimental and calculated RD curves (Fig. 4 C and D) shows that Me_2AlCp indeed is monomeric under the experimental conditions: In associated species the ratio of nonbonded to bonded distances would be greater than for the monomeric unit. Hence if the gas jet had contained significant amounts of associated species, the integrated area under the outer part of the experimental RD-curve would have been greater than the area under the theoretical curve calculated for any model of the monomeric unit.

The electron diffraction data rule out models for the monomeric unit containing σ-bonded or symmetrically π-bonded Cp rings. Unfortunately, however, the data do not allow a distinction to be made between the four models of C_s symmetry shown in Fig. 5.

The Al – C bridge bond in dimeric Me_3Al determined by electron diffraction is 2.140(4) Å.[14] In $B_9C_2H_{11}AlEt$ where the Al atom occupies a corner of a distorted icosahedron and is bonded to three B atoms and two C atoms within the icosahedral unit, the two Al – $C(B_9H_2H_{11})$ distances are 2.173(7) Å.[17] Inspection of Table 1 therefore suggests that there is appreciable bonding between Al and C_1 and C_2 in models (I) and (III). These models may therefore be described as containing *dihapto* Cp rings. The Al – C(Cp) distances obtained by refinement of models (II) and (IV) suggest appreciable bonding only between Al and C_1, though there probably is some additional bonding between Al and C_2 and C_5. These models may perhaps best be described as containing *trihapto* rings.

Since the distance from o to the center of the C_1-C_2 bond is 0.98 Å, the Al atom in model (I) is actually situated directly above the center of this bond, while in model (III) the metal atom is situated 0.2 Å *outside* the edge of the ring. Since the distance $o-C_1$ is 1.21 Å the Al atom is situated 0.2 Å inside the ring in model (II), 0.1 Å outside in model (IV).

In $(CH_3)Be(C_5H_5)$ the Be atom is situated at the fivefold symmetry axis of the ring.[18] It has been suggested that the Be atom is (sp) hybridized, bonding with hybrid orbitals to the methyl C atom and to the a_1 π-orbital of the ring. The two unhybridized $2p$ orbitals on Be overlap with the e_1 π-orbitals of the ring forming two degenerate bonding molecular orbitals. The Cp ring serves as a five-electron ligand and the Be atom is surrounded by an octet of electrons. The assymetric structure of Me_2AlCp is probably due to the fact that in this compound the Cp ring only need function as a three-electron ligand for the Al atom to be surrounded by an octet of electrons: After the two Al – C(Me) bonds have been formed, the Al atom is left with one electron and two atomic orbitals to effect bonding to the ring. One of these orbitals is $2p_x$, the other an (sp) type hybrid pointing towards a point near p.

The molecular orbital calculations show that the a_1 and the two e_1 π-orbitals of the ring interact with the atomic orbitals on Al. For model (I) and parameter set PA the resulting molecular orbitals are approximately:

$$\psi_1 = 0.43z_1 + 0.43z_2 + 0.39z_3 + 0.38z_4 + 0.39z_5 + 0.18s_{Al} - 0.17z_{Al}$$
$$\psi_2 = -0.38z_1 + 0.38z_2 + 0.54z_3 - 0.54z_5 + 0.31x_{Al}$$
$$\psi_3 = 0.41z_1 + 0.41z_2 - 0.23z_3 - 0.60z_4 - 0.23z_5 - 0.17z_{Al} + 0.14y_{Al}$$

where s_{Al}, x_{Al}, y_{Al}, and z_{Al} are the $3s$, $3p_x$, $3p_y$, and $3p_z$ orbitals on Al and z_1 to z_5 the $2p_z$ orbitals of the five carbon atoms in the ring.

It is therefore clear that the four models are best described as π-complexes, albeit asymmetric. Furthermore it should be noted that allthough the metal atom is bonded to the ring *via* two or three C atoms, the bonding molecular orbitals are not restricted to Al and the C atoms in question, but are delocalized over the entire ring.

Since model (I) has two Al – C(Cp) bond distances near 2.20 Å while model (II) has only one, it might be thought that the bonding between Al and Cp is stronger in (I) than in (II). The molecular orbital calculations indicate that the effect is small: The energy of the three Al to Cp bonding orbitals change only slightly, and the total binding energy for (II) calculated with parameter set PA is only 4.1 kcal mol^{-1} higher than the binding energy of (I).

It might further be thought that model (I) is more favorable than models (III) or (IV) since it allows for effective overlap between the $3p_x$ orbital on Al and the appropriate e_1 π-orbital on the ring. This hypothesis receives support from the molecular orbital calculations: When calculations are carried out on models (III) or (IV) with parameter set PA, the energy of ψ_2 rises significantly and the total binding energies obtained are 17 kcal mol^{-1} higher than for model (I).

The molecular orbital calculations therefore indicate that the equilibrium structure of Me_2AlCp is (I). This model is moreover, when the two Me groups are replaced by *pentahapto* Cp rings, entirely analogous to the structure of $(C_5H_5)_3Ti$ as recently determined by X-ray diffraction.[19]

The CNDO calculations also indicate that the barrier to internal rotation of the Cp ring *via* (II) is only a few kcal mol^{-1}. This is in agreement with the large vibrational amplitudes obtained for the Al – C(Cp) distances (see Table 1). Neither, of course, is this low barrier or the moderate barrier obtained for exchange of the Me groups in disagreement with the ^1H NMR spectrum of Me_2AlCp in benzene solution at ambient temperature which concists of one singlet corresponding to the six Me protons and another singlet corresponding to the five Cp protons.[2] It must be kept in mind, however, that Me_2AlCp is partly associated in benzene and that there therefore may be other mechanisms of exchange.

The atomic charges on Al and C atoms obtained by CNDO calculations on model (I) are listed in Table 3. All H atoms were found to carry small (less than 0.02 e.u.) charges. Very similar charges were obtained by calculations on the other models. The Me group C atoms carry the same charge as in monomeric Me_3Al,[20] -0.23 e.u. The Al atom carries a larger positive charge than in Me_3Al, $+0.63$ e.u. The negative charge on the ring is fairly uniformly distributed.

The Al – C(Me) bond distances in Me_2AlCp are not significantly different from the terminal Al – C bonds in dimeric Me_3Al or dimeric Me_2AlH, 1.957(3) Å [14] and 1.949(3) [21] Å, respectively, as determined by gas phase electron diffraction.

The $C_1 - C_2$ bond distance is very similar to the C – C bond distance in MeBeCp, 1.420(1) Å.[18] The values obtained for the vibrational amplitude of the C – C bond in the two molecules, 0.051(1) Å in MeBeCp and 0.049(2) in Me_2AlCp are also very similar. This indicates that the five C – C bonds in Me_2AlCp must be very nearly equal.

After Haaland and Weidlein published their spectroscopic evidence against σ-bonded Cp rings in solid Me_2AlCp, Einstein, Gilbert and Tuck have determined the crystal structure of $InCp_3$.[22] This compound is polymeric in the solid phase. Each In atom is σ-bonded to two terminal Cp rings and is linked to two bridging Cp rings. The latter show small, though definite, deviations from fivefold symmetry. Each bridging Cp group is bonded to two In atoms that are lying on opposite sides of the ring. Only two contacts, $In - C_1$ and $C_3 - In'$ are short enough to indicate appreciable bonding. We believe that the model for solid Me_2AlCp should be modified to contain similar bridging groups as shown schematically in Fig. 1 B.

Conversely we would propose that monomeric $InCp_3$ has a structure analogous to that of monomeric Me_2AlCp, *i.e.* that the bridging Cp rings become assymetrically π-bonded in the monomer. The ^1H NMR spectrum or the degree of association of $InCp_3$ in inert solvents have not been reported. The ^1H NMR spectra of $InCp_3$ in $CDCl_3$ down to $-70°$ or in CH_2Cl_2 down to $-90°$ consists of one narrow line only.[23] If the compound is monomeric in these solvents and if the structure of the monomer is not influenced, the ^1H NMR spectra would indicate rapid exchange of the σ- and asymmetrically π-bonded rings.

Acknowledgement. We are grateful to the *Norwegian Research Council for Science and the Humanities* and to the *National Science Foundation* (grant GP 24090) for financiel support, and to cand. real. Arne Almenningen for help in recording the electron diffraction data.

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Received July 4, 1973.