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SPECTROSCOPIC EVIDENCE FOR *pentahapto*-CYCLOPENTADIENYL GROUPS IN SOLID DIMETHYL(CYCLOPENTADIENYL)-ALUMINIUM

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SUMMARY

The IR and Raman spectra indicate that solid dimethyl(cyclopentadienyl)aluminium contains *pentahapto*-cyclopentadienyl rings of approximate D_{5h} symmetry.

INTRODUCTION

The synthesis of diethyl(cyclopentadienyl)aluminium, $(C_2H_5)_2Al(C_5H_5)$, was reported by Giannini and Cesca in 1961[1]. Since the compound was found to be associated in freezing benzene (the degree of association decreasing from 1.95 in a 0.56 *M* solution to 1.22 in a 0.065 *M* solution) and since it forms a 1/1 complex with diethylether, Giannini and Cesca suggested that the compound contains *monohapto* (*i.e.* σ-bonded) cyclopentadienyl rings, and that dimerization occurs through formation of ethyl bridges.

Several years later, Kroll and Naegele reported the PMR spectra of dimethyl(cyclopentadienyl)aluminium, diethyl(cyclopentadienyl)aluminium and diisobutyl(cyclopentadienyl)aluminium in benzene solution[2]. It was found that for all three compounds the five ring protons gave rise to only one line in the PMR spectrum, and that this line remained unchanged when $(C_2H_5)_2Al(C_5H_5)$ was cooled to $-60°$ or $(C_4H_9)_2Al(C_5H_5)$ was cooled to $-91°$. It was therefore suggested that the cyclopentadienyl rings undergo rapid 1–2 or 1–3 shifts, which render the ring protons equivalent on the PMR time scale. Such valence tatutomerism has been shown to occur, for example, in cyclopentadienylmercury[3–5] and cyclopentadienylsilicon[6] compounds.

In the hope of slowing down the rearrangement sufficiently to allow it to be seen on the PMR time scale, Kroll and coworkers synthesized and investigated the analogous dialkyl(methylcyclopentadienyl) derivatives[7]. They found that while the four ring protons in $(CH_3)_2Al(C_5H_4CH_3)$ and $(C_2H_5)_2Al(C_5H_4CH_3)$ gave only a singlet at ambient temperatures, cooling to $+10°$ converted this singlet into two singlets of ratio 1/1. Further cooling to $-40°$ produced no further change, except broadening of these singlets and of the singlet corresponding to the ring methyl group.

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The signals from the methyl or ethyl groups bonded to aluminium were not split by cooling to −40°. The PMR spectra therefore seemed to be in agreement with a structure in which the aluminium atom was bonded to the same carbon atom in the cyclopentadienyl ring as the methyl groups. Furthermore it was pointed out that these compounds, too, were associated, and that the invariance of the spectra of the alkyl protons with temperature indicated that either bridge-terminal exchange is more rapid than in $(CH_3)_3Al$ or $(C_2H_5)_3Al$ or that the cyclopentadienyl ring occupies the bridging position.

PREPARATION AND PROPERTIES

Following Kroll and Naegele[1], we prepared $(CH_3)_2Al(C_5H_5)$ from $Na(C_5H_5)$ and $(CH_3)_2AlCl$. The compound is a colorless solid which melts without decomposition at 138° (uncorrected). Above 145° thermal decomposition becomes rapid. The compound sublimes at 60° and about 0.001 mm. It is almost insoluble in pentane, and poorly soluble in benzene. In a 0.025 *M* solution in freezing benzene the degree of association is 1.4 ± 0.1.

RESULTS AND DISCUSSION

IR and Raman spectral data for solid $(CH_3)_2Al(C_5H_5)$ are listed in Table 1. In dimeric $(CH_3)_3Al$ and in dimeric $(C_2H_5)_3Al$ the ring breathing vibration (ν_2) gives rise to a very strong line in the Raman spectrum near 450 cm^{-1} [8]. The complete absence of lines in the Raman spectrum between 350 and 550 cm^{-1} must be regarded as strong evidence against the presence of bridging methyl groups—and to a lesser extent against bridging *monohapto*-cyclopentadienyl (h^1-Cp) groups—in solid $(CH_3)_2Al(C_5H_5)$. The spectra are, on the contrary, in excellent agreement with the presence of two terminal methyl groups on each aluminium atom: All the lines expected for an $Al(CH_3)_2$ fragment[8] can easily be assigned, in particular the strong band at 580 cm^{-1} ($\nu_s(AlC_2)$) and the medium bands at 690 cm^{-1} ($\nu_{as}(AlC_2)$) and 1207 cm^{-1} ($\nu_s[CH_3(Al)]$) in the Raman spectrum and the corresponding medium intensity bands at 586 and 1192 cm^{-1} in the IR spectrum.

An h^1-Cp ring of C_s symmetry would have 24 normal vibrations, all of which would be both IR and Raman active[9]. A *pentahapto*-cyclopentadienyl (h^5-Cp) ring of symmetry D_{5h} would have fourteen normal vibrations of which four would be IR and seven Raman active[9]. However, since the molecular and crystal site symmetry must be lower than D_{5h} one may expect a few additional lines to appear, and intermolecular coupling may lead to doubling of some lines. Nevertheless the spectra remaining after the $Al(CH_3)_2$ bands have been assigned, are much too simple to be consistent with the presence of h^1-Cp rings. On the contrary, they are very similar to those obtained from *pentahapto* or from ionic cyclopentadienyl metal compounds.

It has been pointed out by Davison and Rakita[6] that the IR spectrum in the region above 3000 cm^{-1}, that is in the region of olefin–hydrogen stretching frequencies, allows a clear distinction to be made between h^1-Cp and h^5-Cp rings: The former should exhibit four lines in this region, and the latter only one. Thus the IR spectrum of $(CH_3)_3(h^1\text{-}Cp)Si$ contains three resolved bands at 3075, 3094 and 3121 cm^{-1} [6], while the spectrum of solid $Mg(h^5\text{-}Cp)_2$ contains one band at 3063 cm^{-1} [10]. The IR

TABLE 1

IR AND RAMAN SPECTRA (cm^{-1}) OF SOLID $(CH_3)_2Al(C_5H_5)$

IR	*Raman*	*Assignment*[a]
	3122 ms	ν_s(CH(Cp))
	3100 ms	ν_{as}(CH(Cp))
3040 vw	3040 s	ν_{as}(CH(Cp))
2940 m	2945 m	$\nu_{as}(CH_3)$
2900 w	2895 m	$\nu_s(CH_3)$
2840 w(sh)	2825 w(br)	$2 \times \delta_{as}(CH_3)$
1660 vw		Overtone
1485 mw	1475 vw	Overtone
1440 w		$\delta_{as}(CH_3)$
1415 m		
	1380 mw	ν_{as}(C–C(Cp))
	1370	
1362 w		ν_{as}(C–C(Cp))
1192 m	1207 m	$\delta_s(CH_3)$
1180 (sh)	1195 w	δ_{as}(CH$\parallel$(Cp))
	1130 vs	ν_{puls}(C–C(Cp))
	1090 w	δ_{as}(CH$\perp$(Cp))
1075 w	1075 ms	
1008 w		δ_{as}(CH$\parallel$(Cp))
997 s		
878 m	875 w	δ_{as}(C–C$\parallel$(Cp))
	860 mw	
848 w	850 w	δ_{as}(CH$\perp$(Cp))
	845 mw	
825 w		
810 m		
781 s	790 w	δ_s(CH$\perp$(Cp))
752 m		
695 w(sh)	690 m	$\nu_{as}(AlC_2)$
672 s		$\rho(CH_3)$
	635 w	δ(C–C$\perp$(Cp))
586 m	580 s	$\nu_s(AlC_2)$
561 m		$\rho(Al\text{–}Cp_2)$(?)
	345 m(br)	$\delta_s(AlC_2)$
	210 m	$\nu(Al\text{–}Cp_2)$ (?)
	123 s	$\tau(CH_3)$, $\delta(AlC_2)$

[a] $\parallel$ And $\perp$ define the direction of nuclear displacement with respect to the plane of the C_5 ring.

spectrum of solid $(CH_3)_2Al(C_5H_5)$ contains one band at 3040 cm^{-1}. The three other bands expected in the IR spectrum of a Cp ring of D_{5h} symmetry are found in the expected range and with the expected intensity[5]: 1362 cm^{-1} (ν_{as}(C–C)), 997 cm^{-1} (δ_{as}(C–H$\parallel$)) and 781 cm^{-1} (δ_s(C–H)). The latter appears to have been split by intermolecular coupling. The remaining bands are easily assigned by comparison with ferrocene[11,12] and with $MgCp_2$[10] or as overtones.

On the basis of the published Raman spectra of ferrocene[11,12], $MgCp_2$[10] and KCp[13], the seven bands expected in the Raman spectrum of a Cp ring of D_{5h} symmetry may be summarized as follows:

(*i*). Two bands of variable intensity above 3000 cm^{-1} (ν(CH)).
(*ii*). One medium to weak band near 1360 cm^{-1} (ν_{as}(C–C)).
(*iii*). One band of variable intensity near 1180 cm^{-1} (δ_{as}(CH)).
(*iv*). One strong or very strong band near 1100 cm^{-1} (ν_{puls}(C–C)).
(*v*). One medium to weak band near 900 cm^{-1} (δ_{as}(C–C$\|$)).
(*vi*). One band of variable intensity of the region around 800 cm^{-1} (δ_{as}(CH$\perp$)).

All these lines are found in the Raman spectrum of $(CH_3)_2Al(C_5H_5)$ in the expected region and with the expected intensity. Several of them are split. The remaining bands are easily assigned by comparison with ferrocene and $MgCp_2$ or as overtones.

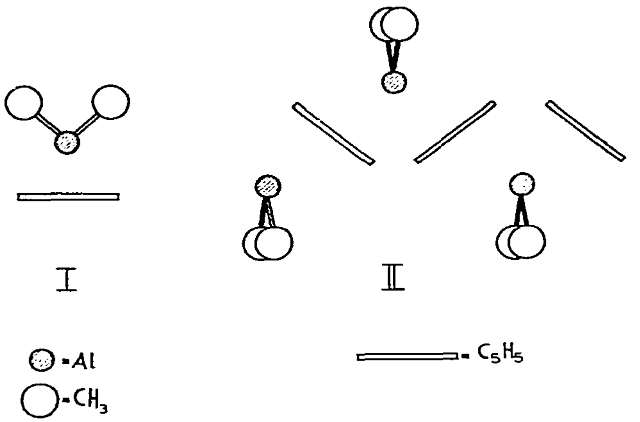

Fig. 1. Proposed structures for monomeric (I) and polymeric (II) $(CH_3)_2Al(C_5H_5)$.

Note should be made of the fact that the IR and Raman spectra contain a total of six bands in the region 750 to 850 cm^{-1}. A Cp ring of D_{5h} symmetry would have only two normal modes in this region, the a_2'' and e_1'' out of plane CH deformation vibrations. It would appear that the latter mode has been split by the low molecular or crystal site symmetry, and that all lines subsequently have been doubled by intermolecular coupling. A similar multiplicity of lines in this region has been found in the IR spectra of solid $SnCp_2$ and $PbCp_2$[14].

The IR and Raman spectra would therefore seem to be in agreement with molecular structure (I), but we do not believe this to be the structure in the solid phase: $(CH_3)_2Al(C_5H_5)$ is associated in benzene, and the low solubility and volatility and the high melting point indicate that it is highly associated in the crystal. We would therefore propose a polymeric structure with bridging h^5-Cp rings, (II), analogous to that of crystalline InCp[15] and $PbCp_2$[16]. This polymer would be broken down to a mixture of monomeric and oligomeric species in solution and in the vapor. In our view this model is in agreement with the PMR spectra of $(CH_3)_2Al(C_5H_5)$ and related compounds described above.

A gas-phase electron diffraction investigation has been initiated.

EXPERIMENTAL

The IR spectra of suspensions of solid $(CH_3)_2Al(C_5H_5)$ in Nujol/Hostaflon between CsI plates prepared under dry nitrogen[17] were recorded on a Beckman IR 12 spectrophotometer. The Raman spectrum of the solid was recorded on a Coderg PHO Spectrophotometer, with the 4880 Å line of an Ar/Kr laser as exciting radiation.

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