Evidence for Non-rigid Behaviour of Aluminium–Cyclopentadienyl Groups in Dialkylaluminium Cyclopentadienyls

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ALTHOUGH a stable dialkylaluminium cyclopentadienyl has been reported[1] no spectral data for this compound were given. We have prepared and examined the n.m.r. spectra of several dialkylaluminium cyclopentadienyls,[2] since we are interested in the effect of an unsaturated ligand on the chemistry and exchange reactions of organoaluminium compounds.

We were particularly concerned to see whether the protons of the cyclopentadienyl ring would exhibit the complex n.m.r. pattern typical for localized, σ-bonded metal–cyclopentadienyls since our initial work[2] with cyclopentadienyldi-isobutylaluminium had shown, unexpectedly, only one signal (a feature commonly observed for ionic- or π-bonded cyclopentadienyls).

In order to eliminate possible accidental collapse of the ring proton signals due to solvent effects, the results were checked by using both different inert solvents and also different concentrations. As shown in the Table these compounds (all prepared by halogen-interchange reaction from sodium cyclopentadienyl and the corresponding dialkylaluminium chloride†) exhibited only a singlet.

We have also studied the n.m.r. spectrum (60 as well as 100 MHz) of cyclopentadienyldi-isobutylaluminium in pentane at temperatures as low as −91°. Again only a singlet was observed. A similar result was obtained with cyclopentadienyldiethylaluminium although here we were limited to −60° as the lowest temperature, owing to the solubility problems. Cyclopentadienyldimethylaluminium was not investigated at low temperatures owing to its low solubility. Recent work on dicyclopentadienylmercury[3] indicated that, among many solvents tried, only liquid SO_2 at −70° gave the expected σ-bonded pattern. Our choice of solvents for the cyclopentadienyldialkylaluminiums is limited owing to to their great reactivity.

Chemical shift of $R_2AlC_5H_5$*

R	C_5H_5	R
Me	+4·65, s	−2·23, s
Et	+4·80, s	−1·81, q; −0·43, t
Bu^i	+4·78, s	−1·54, d; +0·20, m; −0·50, d

* All spectra (60 MHz) obtained at room temperature from solutions *ca.* 15% (w/w) in benzene [except in the case of $Me_2AlC_5H_5$ with *ca.* 3% (w/w) in benzene]. The chemical shifts are given in p.p.m. relative to internal cyclopentane. Shifts upfield from C_5H_{10} negative, shifts downfield positive.

Our observation of a single signal for the ring protons of $R_2AlC_5H_5$ does not agree with the localized σ-bonded structure suggested by Giannini.[1] That all the protons of the ring have the same chemical shift may be explained in

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† All compounds were distilled and gave satisfactory elemental analysis.

terms of the dissociation of the compounds into ions; physical data for these compounds (*e.g.* solubility and volatility) however argue against this suggestion. The presence of ion-pair intermediates cannot be excluded however. An alternative explanation for the n.m.r. data assumes predominant bonding between the aluminium and a carbon atom of the ring. Owing to rapid 1,2- or 1,3-rearrangement only one signal is observed. Such a migration of the metal around the ring was first postulated by Wilkinson[4] in connection with an n.m.r. study of dicyclopentadienylmercury. Later more examples of such "stereochemically non-rigid organometallic compounds" have been discovered and discussed by Cotton and Pettit. Our data show for the first time evidence for non-rigid behaviour of organoaluminium compounds containing a cyclopentadienyl ligand. The fact that we could not slow down this rearrangement sufficiently at −91° to observe the typical σ-metallocene n.m.r. pattern indicates that the activation energy for this process must be very low.

Shchembelov[5] has recently calculated the energy of activation for the migration of metal–carbon bonds in σ-bonded metal cyclopentadienyls. His calculations indicate that the activation energy for such a migration in cyclopentadienylalanes is very low or zero. This means that the theoretical considerations for such a dynamic system are in agreement with evidence obtained by n.m.r. studies.

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