

THE NMR SPECTRA OF CH_3AlCl_2 . DONOR COMPLEXES
IN THE PRESENCE OF A SMALL EXCESS OF $[\text{CH}_3\text{AlCl}_2]_2$ OR DONOR

A.C.M. Wanders and E. Konijnenberg

Central Laboratory, Staatsmijnen/DSM, Geleen, The Netherlands

(Received 22 March 1967)

Recently Zambelli e.a. (1,2) published an extensive study on the interaction between aluminiumalkylchlorides and various Lewis bases. The systems were analysed by IR and NMR spectroscopy. In a "coda" to their second paper (2) the authors note that the methyl-signal in the PMR spectrum of $\text{CH}_3\text{AlCl}_2\cdot\text{TPP}^*)$ is split into a doublet as a consequence of P-H coupling, and that this spin-spin splitting shows up only when a (slight) excess of aluminiumalkylchloride is present. The authors leave this latter point unexplained, however.

The NMR spectra of complexes of aluminiumalkyls with ethers have been studied extensively in this laboratory (3), and as to the influence of small excess amounts of the acceptor or the donor component on the spectra results similar to those of Zambelli e.a. have been found.

The NMR spectrum of a mixture of $\text{CH}_3\text{AlCl}_2\cdot\text{IPE}^{**})$ and $\text{AlCl}_3\cdot\text{IPE}^{**})$ in benzene solution is shown in FIG. 1a. The spectra obtained from this mixture after addition of a slight excess of $[\text{CH}_3\text{AlCl}_2]_2$ or IPE are given in FIG. 1b and FIG. 1c, respectively. The latter spectrum (c) shows the characteristic pattern of one isopropylgroup, though three chemically different species of IPE molecules are present in the mixture, viz. IPE bonded to CH_3AlCl_2 IPE

*) TPP = triphenylphosphine

***) IPE = diisopropylether

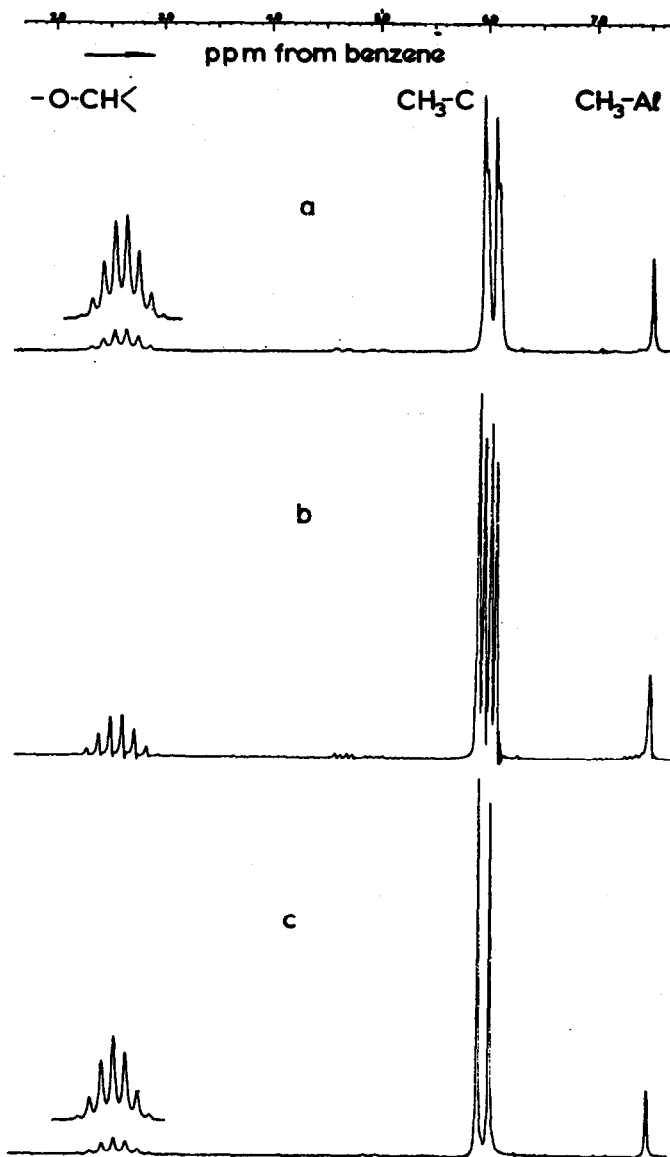


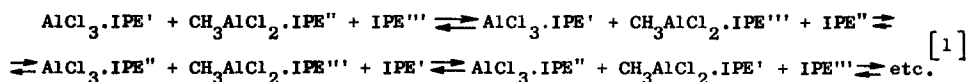
FIG. 1

Proton MR spectra at 30 °C in benzene of:

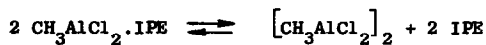
- a. 1 M CH₃AlCl₂·(i-Pr)₂O and 1 M AlCl₃·(i-Pr)₂O
- b. 1 M CH₃AlCl₂·(i-Pr)₂O and 1 M AlCl₃·(i-Pr)₂O + .025 M(CH₃AlCl₂)₂
- c. 1 M CH₃AlCl₂·(i-Pr)₂O and 1 M AlCl₃·(i-Pr)₂O + .05 M(i-Pr)₂O

bonded to AlCl_3 , and "free" (i.e. solvated) IPE molecules^{*}). The spectrum of the mixture in which a small excess of $[\text{CH}_3\text{AlCl}_2]_2$ is present, clearly shows a superposition of two isopropyl signals with the chemical shift between the tertiary H septets just equal to the proton-proton coupling constant (6.6 c.p.s.). (This interpretation can be confirmed from the spectra of the solutions in toluene in which two nicely separated septets can be distinguished.) The PMR spectrum of the mixture of $\text{CH}_3\text{AlCl}_2\cdot\text{IPE}$ and $\text{AlCl}_3\cdot\text{IPE}$ as such (FIG. 1a) mostly resembles that of FIG. 1b. The signals are broadened, however, and the separation between the isopropyl signals is somewhat smaller.

The FIGS. 1a and 1b indicate a net exchange of IPE molecules between the two complexes in the case of FIG. 1a. However, comparison with FIG. 1c strongly suggests that the presence of "free" IPE molecules is imperative for the exchange reaction to occur. Schematically this may be explained as follows:



This interpretation assumes that the exchange of complexed and "free" ether molecules goes much faster than the direct exchange of ether molecules between two complexes. Hence, the mixture in which excess aluminiumalkyl is present shows two sharp isopropyl signals because of the absence of "free" IPE. On the other hand, the mixture to which a slight excess of IPE was added has only one isopropyl signal owing to the rapid exchange of ether molecules. The exchange of the mixture without any additions may be accounted for either by reaction of the complexes with a slight amount of impurities, which might liberate some ether, or by a possible dissociation according to:



^{*}) Obviously, the signal from the non-complexed ether would have been hardly detectable as the added excess is small.

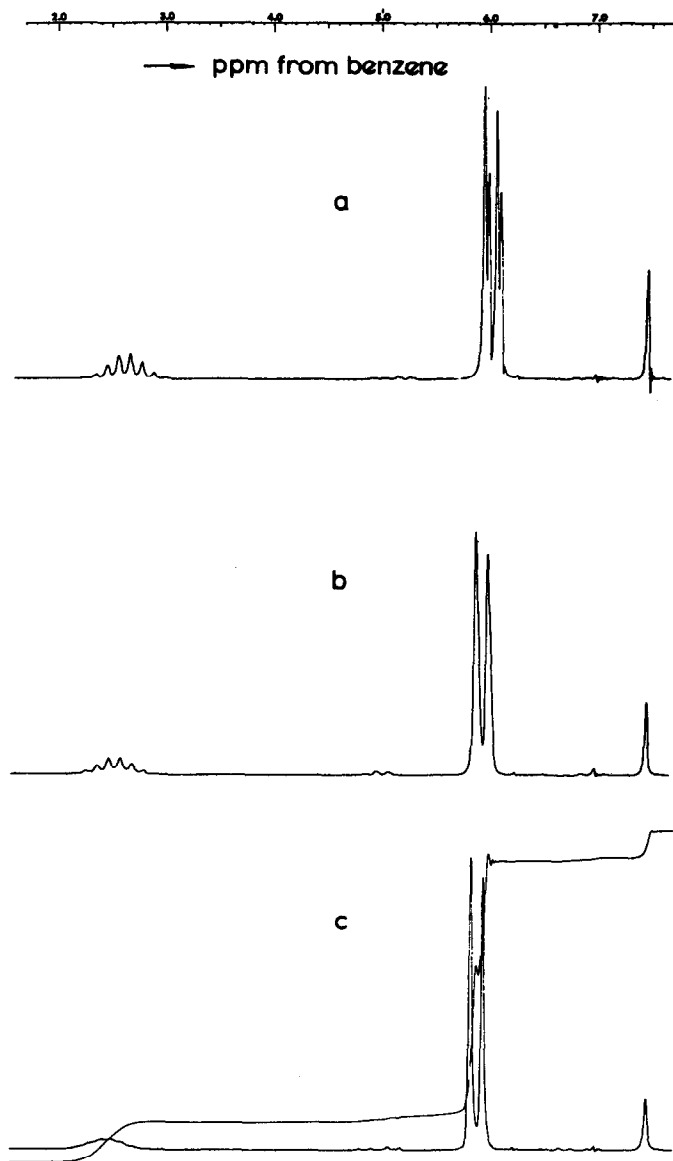


FIG. 2

Proton MR spectra of 1 M $\text{CH}_3\text{AlCl}_2 \cdot (\text{i-Pr})_2\text{O}$ and 1 M $\text{AlCl}_3 \cdot (\text{i-Pr})_2\text{O}$ in benzene at
(a) 10 °C, (b) 50 °C, (c) 75 °C

The latter explanation does not seem very plausible to us, since it is known that this kind of complexes are very stable (4, 5, 6).

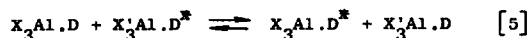
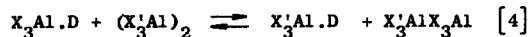
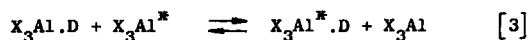
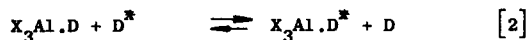
The assumption of exchange of ether molecules is nicely confirmed by the temperature dependence of the NMR spectrum of FIG. 1a as shown in FIG. 2. At elevated temperature the isopropyl doublets completely coalesce, giving only one doublet, whereas the two septets, lying originally further apart, have broadened and moved towards each other. At lower temperatures the rate of exchange decreases, as appears from the increased separation and sharpness of the isopropyl signals. The shifts between the doublets and between the septets being 3 and 6.6 c.p.s. respectively, we may infer from spectrum 2b that under the present conditions at 50 °C, the mean life time of an ether molecule bonded to either of the aluminium compounds is between .03 and .08 sec (7).

The observation of Zambelli et al. (1, 2) on the NMR spectra of $\text{CH}_3\text{AlCl}_2\cdot\text{TPP}$ may be explained in a similar way. In this case the exchange will also manifest itself in the behaviour of the $\text{CH}_3\text{-Al}$ -proton signal which is a doublet owing to P-H coupling, if there is no exchange of TPP molecules. Coalescence of the doublet may be expected to show up as a consequence of exchange of TPP, which seems to be favoured by the same conditions as those for the exchange of ether molecules.

The influence of chemical exchange on the PMR spectra of the donor molecules has, to our knowledge, not received much attention so far.

The influence on the ^{27}Al - and ^1H -magnetic resonance spectra of the aluminiumalkyl constituent has been reported on by Swift et al. (8) and by Mole et al. (9), respectively. The ^{27}Al studies indicate a rapid exchange of tri-ethylaluminium between the complexed and the uncomplexed state with $\tau < 3 \cdot 10^{-4}$ sec. in hexane at room temperature. Mole et al. found an exchange of CH_3 and phenyl groups with a life time between 10^{-1} and 10^2 sec. in ether at 40 °.

In view of these results and ours quite a variety of exchange mechanisms must be taken into account:



Moreover, exchange mechanisms in which a direct exchange of the X groups is involved may be visualized (9).

From our results where X denotes CH_3 and/or Cl, we may conclude that reaction [2] is fast compared with [4] and [5] (the case given in FIG. 1b). Also, if $\text{X} = \text{X}'$, reaction [5] is slow, as is shown by Zambelli's results (2) on the P-H spin-spin coupling in the case where D is TPP. Reaction [3] may be important if the $(\text{X}_3\text{Al})_2$ dimer is dissociated to a sufficiently high degree; this may explain e.g. Swift's results on the exchange of tri-ethylaluminium between the complexed and uncomplexed state (8) which, at first sight, seem to conflict with the observations on the methylaluminiumchlorides.

In order to obtain more insight into this field, we thought it worthwhile to investigate reaction [2] more thoroughly. Experiments on the kinetics of this reaction are in progress in this laboratory.

*) An asterisk is used to distinguish between molecules of the same species. X is used for both halogen and alkyl. A prime denotes a chemically different group.

R E F E R E N C E S

1. A. Zambelli, A.L. Segre, A. Marinangeli and G. Gatti, Chim. Ind. (Milan), 48, 1 (1966).
2. A. Zambelli, G. Gatti, A. Marinangeli, F. Cabassi, and I. Pasquon, Chim. Ind. (Milan), 48, 333 (1966).
3. E.H. Adema, E. Konijnenberg, W. van Raaijen, A.J.J.M. Teunissen, and A.C.M. Wanders, unpublished results.
4. K. Ziegler, Organometallic Chemistry, H. Zeiss ed., p. 194, Reinhold Publishing Corp. New York (1960).
5. R. Köster and P. Binger, Adv. Inorg. Chem. Radiochem. 7, 263 (1965).
6. H.M.J.U.A. de Mooy, A.J.J.M. Teunissen and A.C.M. Wanders unpublished results.
7. J.A. Pople, W.G. Schneider and H.J. Bernstein, High-resolution Nuclear Magnetic Resonance, chapter 10, Mc Graw-Hill New York (1959).
8. H.E. Swift, C.P. Poole, Jr. and J.F. Itzel, Jr., J. Chem. Phys. 68, 2509 (1964).
9. T. Mole and J.R. Surtees, Austral. J. Chem. 17, 310 (1964).