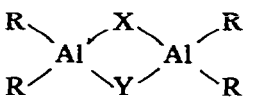
Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

Mixed-bridged alkylaluminium compounds

M. FISHWICK, C.A. SMITH and M.G.H. WALLBRIDGE
Department of Chemistry, The University, Sheffield S3 7HF (Great Britain)
(Received November 10th, 1969)

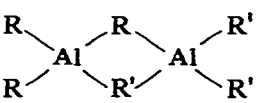
In view of two recent reports[1,2] which have presented evidence from NMR results for the existence of alkylaluminium compounds containing different bridging groups, (I), we wish to report our observations which considerably extend the examples of this type of compound.

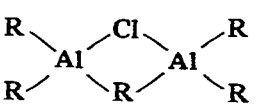


(I)

(R = Me, X = Me, Y = NPh_2; R = Me, X = Me, Y = $OC(Me)Ph_2$)

We have identified two types of compounds: (i) Those which are labile and cannot be isolated as a distinct mixed-bridged species. (ii) Those which are formed irreversibly, and exist as stable compounds of type (I). Other workers[3,4] have suggested the presence of labile mixed-bridged species in mixtures of trialkylalanes and dialkylaluminium halides *e.g.*:





although such compounds have not yet been positively identified. In a 1/1 molar mixture of dimethylaluminium chloride and bromide only one alkyl signal is observed in the ^1H NMR spectrum indicating a rapid halogen and/or alkyl exchange. If halogen exchange is occurring the mixture would contain $(Me_2AlCl)_2$, $(Me_2AlBr)_2$ and $(Me_2AlClBrAlMe_2)$, and we have confirmed the presence of the mixed halide from the mass spectrum of the mixture. Thus the mass spectra of the two individual halides at 70 eV show that the highest *m/e* value observed corresponds to $(\text{molecular ion}-CH_3)^+$, the bromide showing a triplet at *m/e* values of 261, 259 and 257 (from $Me_3Al_2{}^{81}Br_2{}^+$, $Me_3Al_2{}^{81}Br^{79}Br^+$, etc.) with an intensity ratio of 1/2/1, and the chloride a triplet at *m/e* values of 173, 171 and 169 (from $Me_5Al_2{}^{37}Cl_2{}^+$, $Me_3Al^{37}Cl^{35}Cl^+$, etc.) with an intensity ratio of 1/6/9. The mass spectrum of the 1/1 mixture shows both the above triplets and in addition a further triplet at *m/e*

values of 217, 215 and 213 (217 = $Me_3Al_2{}^{81}Br^{37}Cl^+$, 215 = $Me_3Al_2{}^{81}Br^{35}Cl^+$ + $Me_3Al_2{}^{79}Br^{37}Cl^+$, etc.) with an intensity ratio of 1/4/3. This can only be rationalised by assuming the presence of the mixed-bridged compound $Me_2AlClBrAlMe_2$. Moreover, the relative total intensities of the sets of triplets from the bromide, mixed-bridged, and chloride compounds is 1/2/1 respectively showing a statistical distribution of halogens within the mixture. Therefore, while the labile mixed-bridged compound cannot be separated in this case the above results show it to be present in the mixture.

The mixed-bridged compounds can be isolated when one of the bridging groups is less labile than alkyl or halogen *e.g.* dialkylamino or ethoxide. For example the ^1H NMR spectrum of a 1/1 molar mixture of diethyl aluminium–chloride and –dimethylamino at 25° shows two ethylaluminium signals corresponding to the pure compounds (Fig.1a, b, c).

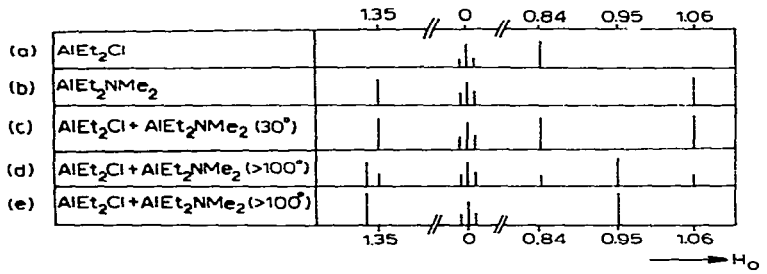
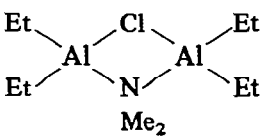


Fig.1. For simplicity the quartet, which appears to high field of the triplet, is represented as a single line placed at the centre of the two most intense signals.

Heating the mixture to above 100° causes the quartets (arising from the ethyl groups) to diminish in intensity, and a new quartet of intermediate internal shift ($\Delta(CH_2)$–$\Delta(CH_3)$ = 0.95 ppm, the average of the quartets from the pure compounds) to appear. Simultaneous with these changes the NMe_2 singlet decreases, and a new NMe_2 singlet appears at about 0.1 ppm to low field Fig.1d. The final spectrum contains only the intermediate quartet and the low field NMe_2 singlet Fig.1e, and remains unchanged on cooling to 25°. Since all the ethyl groups are now in an identical environment the NMR spectra are consistent with the mixture containing a mixed-bridged compound.

$$(Et_2AlCl)_2 + (Et_2AlNMe_2)_2 \rightarrow$$



The product melts at -137 ± 5° while a 1/1 molar mixture of the components softens at -95° and finally melts at -12°. Although this compound does not undergo rapid exchange with either the pure chloro or dialkylamino compounds at 25°, it does react with trimethylamine forming the chloro adduct, and the dialkylamino compound.

$$2\,Et_2AlCl(NMe_2)AlEt_2 + 2\,NMe_3 \rightarrow 2\,Et_2AlCl \cdot NMe_3 + (Et_2AlNMe_2)_2$$

Several other mixed-bridged compounds may be formed in a similar manner, and these are summarised in Table 1 together with the temperature required for the reaction.

TABLE 1

MIXED-BRIDGED COMPOUNDS OF THE TYPE $Et_2AlXYAlEt_2$

X	NMe_2	NMe_2	NEt_2	NMe_2	OEt	NMe_2[a]
Y	Br	I	Br	OEt	Br	SMe
Temp. (°C)	120	120	120	190	100	140

[a] Mixed-bridged compound formed in equilibrium with components.

We have not yet been successful in forming a mixed-bridged compound for X = Et, Y = NMe_2 since the diethylaluminium compounds, $Et_3Al + Et_2AlNMe_2$, do not undergo any exchange at 25°, and the ^1H spectrum remains unchanged after heating of the mixture at 120° for 1 h.

REFERENCES

1 M. Kawai, T. Ogawa and K. Hirota, *Bull. Chem. Soc. Japan*, 37 (1964) 1302.
2 E.C. Ashby, J. Laemmle and G.E. Parris, *J. Organometal. Chem.*, 19 (1969) P24.
3 K. Ziegler, W.R. Kroll, W. Larbig and O.W. Stendel, *Ann. Chem.*, 629 (1960) 53.
4 K. Ziegler and W.R. Kroll, *Ann. Chem.*, 629 (1960) 167.