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

Preliminary communication

Stable mixed alkoxy-alkyl bridged organoaluminum compounds

E.C. ASHBY, J. LAEMMLE and G.E. PARRIS
School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332 (U.S.A.)

(Received August 7th, 1960)

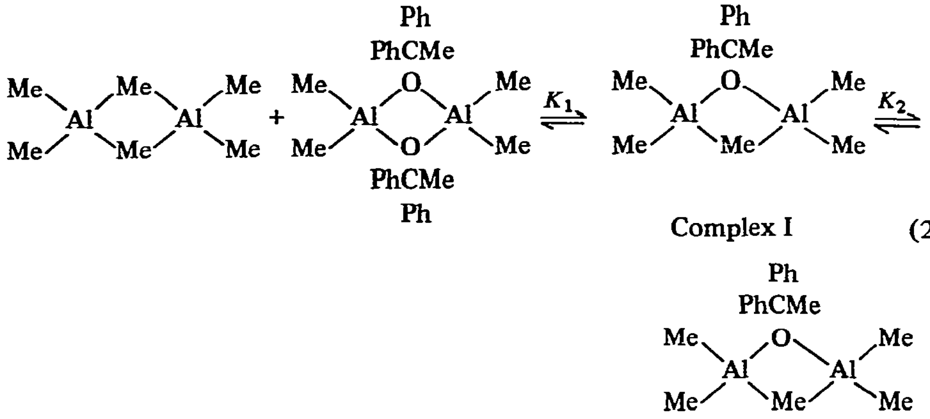
Recently we have reported on the mechanism of trimethylaluminum (Me_3Al) addition to benzophenone in benzene[1]. Interpretation of the kinetic data for this reaction demanded that each molecule of the product ($Me_2AlOCPh_2Me$) should be complexed to one molecule of Me_3Al. Product studies and ultraviolet spectra of reacting mixtures of Me_3Al with benzophenone in 1/1 ratio also provided additional evidence for complexation between the product and Me_3Al. Although the complex was believed to be a mixed alkoxy-alkyl bridged organoaluminum compound, it remained for low temperature NMR studies

$$2\,Me_3Al + 2\,Ph_2C{=}O \rightarrow Me_2AlOCPh_2Me \cdot Me_3Al + Ph_2C{=}O \qquad (1)$$

to prove this point. We would like to report now conclusive evidence for our original suggestion concerning a mixed bridge compound and further report that alkyl exchange in the complex is intramolecular rather than intermolecular as reported for Me_3Al[2].

Mixtures of Me_3Al with $Me_2AlOCPh_2Me$ were prepared by adding appropriate amounts of trimethylaluminum to benzophenone in toluene and allowing the solution to warm to 80° in sealed flasks for two hours. Portions of the samples were hydrolyzed and GLPC analysis using 9-fluorenone as an internal standard gave a 100% yield of 1,1-diphenylethanol. Samples were placed in tightly capped NMR tubes using tetramethylsilane as internal standard. The NMR spectra were obtained within 24 hours of preparation of the compounds. Solution concentrations were 0.2 *M* in $Me_2AlOCPh_2Me$ and 0.2 and 0.4 *M* in Me_3Al. No evidence of exchange of any species with TMS was observed. The NMR scans commenced + 50 cycles downfield from TMS to higher fields so that all signals represent protons on methyl groups bonded to aluminum.

Interpretation of the NMR spectra at 35°, 0°, −10°, −30° and −65° for toluene solutions of the following: (1) Me_3Al, (2) $Me_2AlOCPh_2Me$, (3) $Me_2AlOCPh_2Me + Me_3Al$ and (4) $Me_2AlOCPh_2Me + 2\,Me_3Al$, is consistent with the formation of a mixed alkoxy-alkyl bridge system as represented by Eq.2.



Complex I (2)

Complex II

The room temperature (+35°) spectra of the four systems studied are illustrated in Fig.1. The top spectrum is that of Me_3Al which shows a single proton signal at −21.4 cycles upfield from TMS. The second spectrum is that of $Me_2AlOCPh_2Me$ and shows a single proton signal −50 cycles upfield from TMS. The third spectrum is that of a 1/1 mixture of $Me_2AlOCPh_2Me$ and Me_3Al and shows a broad peak with a chemical shift −30 cycles above TMS. This represents the complex of $Me_2AlOCPh_2Me$ and Me_3Al. The two small signals at −22 and −50 cycles upfield from TMS represent equilibrium amounts of Me_3Al and $Me_2AlOCPh_2Me$. An equilibrium constant at 35° for this equilibrium is calculated to be 625. The fourth spectrum is that of a 1/2 mixture of $Me_2AlOCPh_2Me$ and Me_3Al. The characteristic peak for Me_3Al appears at −21.4 cycles (3.2 H), the peak for the complex appears at −30 cycles upfield from TMS (5 H) and a very small peak for $Me_2AlOCPh_2Me$ appears at −50 cycles indicating that the equilibrium has been driven toward the complex by the addition of excess Me_3Al. The fact that the actual integration ratio of Me_3Al to $Me_2AlOCPh_2Me \cdot Me_3Al$ (3.2/5) is so close to the expected ratio (3/5) demonstrates that $Me_2AlOCPh_2Me$ binds only one equivalent of Me_3Al. It should also be noted that the unbound Me_3Al shows no tendency to exchange with the complex since the chemical shift of Me_3Al in the 1/2 mixture is the same as that of free Me_3Al and the integration, as previously noted, shows that a full equivalent of Me_3Al is unaffected by the presence of $Me_2AlOCPh_2Me$.

Figure 2 shows the spectra of the same four solutions at −65°. The first spectrum is that of Me_3Al which shows two peaks, one at −1.8 cycles (2 H) and the other at −35.8 cycles (4 H). This spectrum is characteristic of Me_3Al dimer showing both the bridging and terminal methyl groups as previously reported[2,3]. The second spectrum is that of $Me_2AlOCPh_2Me$ which shows only a single peak at −44.8 cycles. Although the peak appears somewhat broadened, temperatures as low as −80° failed to resolve this peak indicating that no methyl bridging occurs. Single or double alkoxy bridges apparently hold this species together since association studies show this compound to be a dimer over a wide concentration range[4]. The third spectrum is that of $Me_2AlOCPh_2Me \cdot Me_3Al$. No peaks are visible for free Me_3Al or $Me_2AlOCPh_2Me$ showing that at −65° the equilibrium (K_1) is shifted so far to the complex that the NMR cannot detect free Me_3Al or $Me_2AlOCPh_2Me$. The interesting feature of this spectrum is the fact that the complex

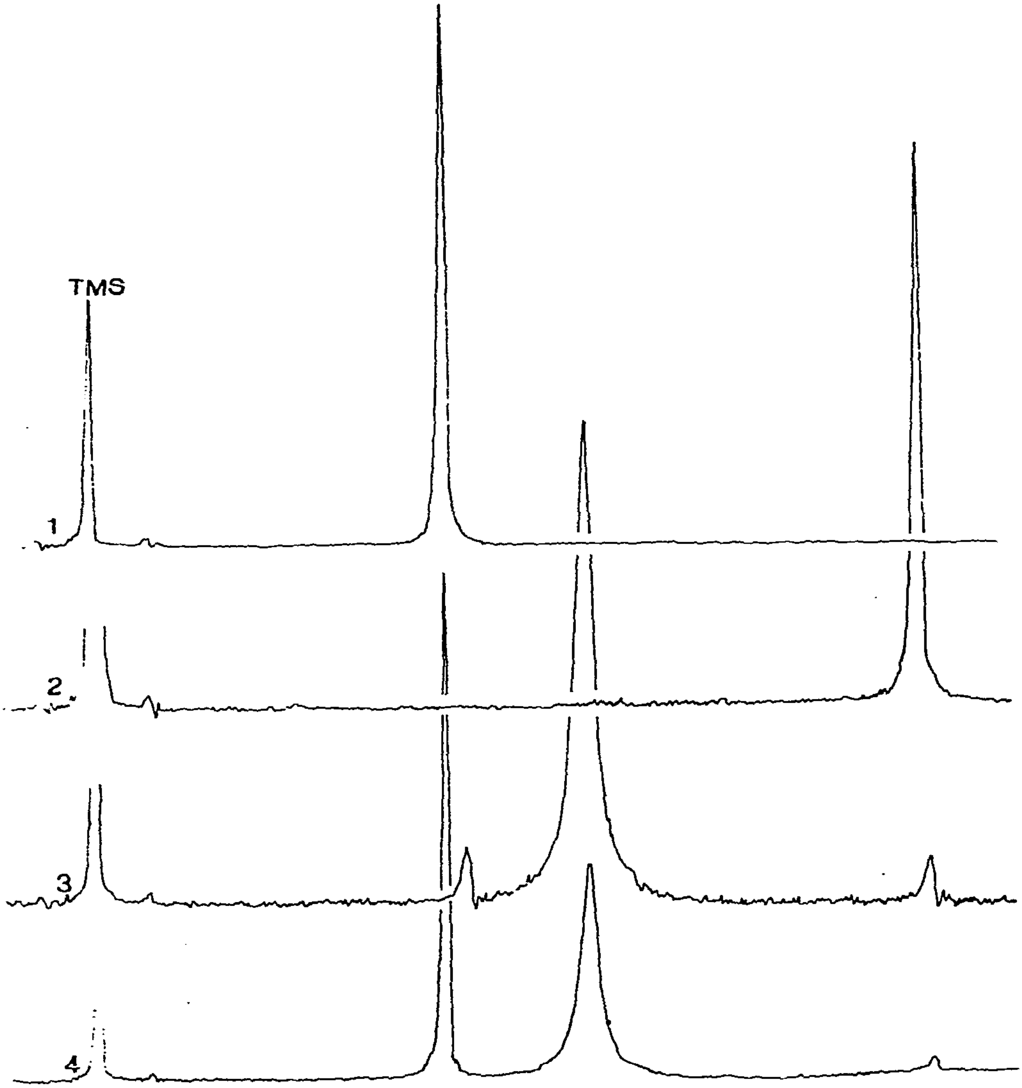


Fig.1. NMR spectra in toluene at 35° for: (1) Me_3Al; (2) $Me_2AlOCPh_2Me$; (3) $Me_2AlOCPh_2Me + Me_3Al$; (4) $Me_2AlOCPh_2Me + 2(Me_3Al)$.

splits into two peaks. One peak occurs at 5.2 cycles downfield from TMS (1 H) and the second at −37.2 cycles upfield from TMS (5.26 H), indicating two different types of methyl protons. If the only species in solution were the complex II the ratio of bridging to terminal methyl protons would be 1/4. The actual ratio is 1/5.26 showing that an equilibrium occurs (K_2 = 4) containing an appreciable amount of complex I. Complex II is the first example, of a stable alkoxy-alkyl bridge species.

The fact that only one signal is observed at room temperature for the complex and two signals are found at −65° shows that rapid exchange of terminal and bridging

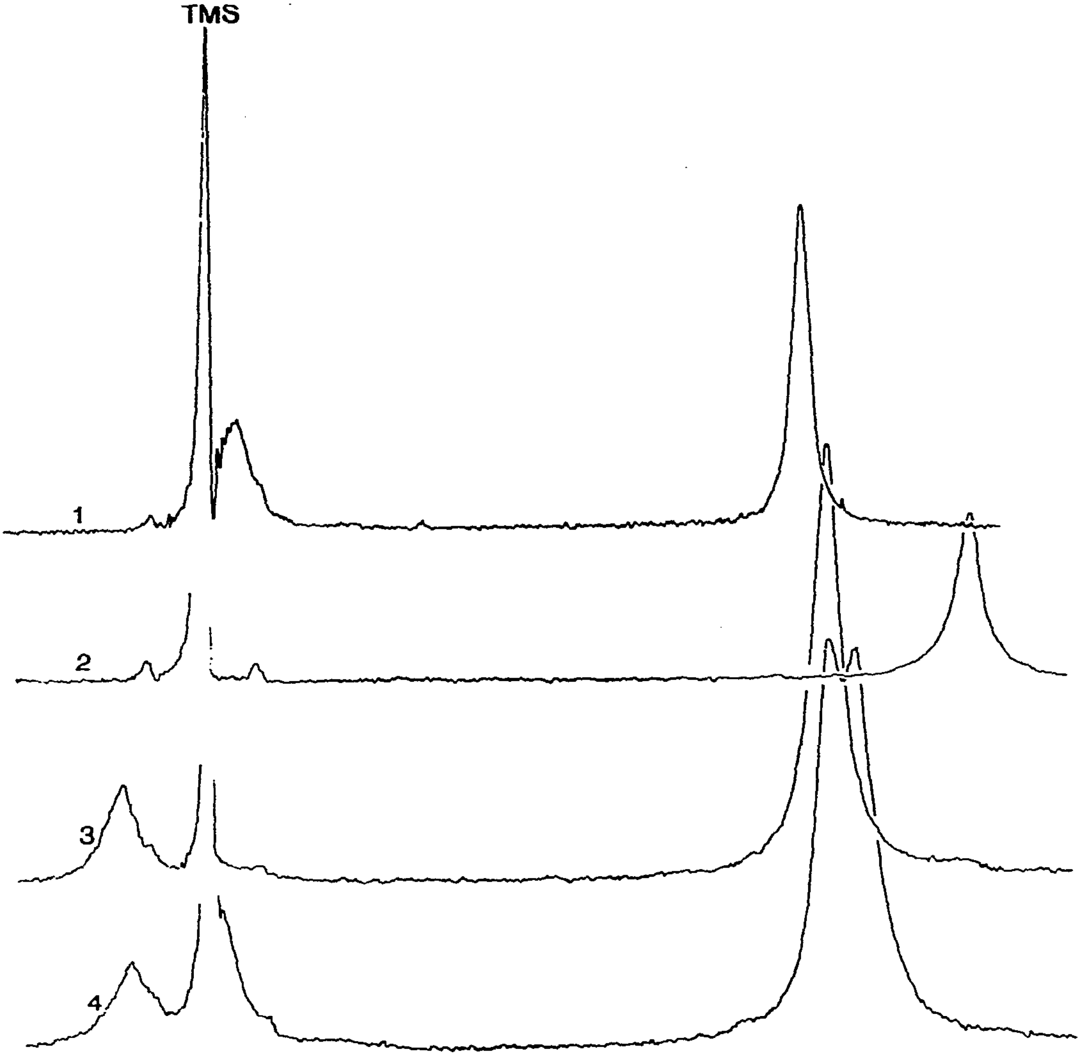


Fig.2. NMR spectra in toluene at −65° for: (1) Me_3Al; (2) $Me_2AlOCPh_2Me$; (3) $Me_2AlOCPh_2Me + Me_3Al$; (4) $Me_2AlOCPh_2Me + 2(Me_3Al)$.

methyl groups are occurring at room temperature. At −65° the exchange is slowed enough to see both types of methyl groups. Because Me_3Al does not exchange with the complex at any temperature below 35°, the exchange (Eq. 2) must be intramolecular.

The fourth spectrum is a mixture of $Me_2AlOCPh_2Me$ and $2(Me_3Al)$ and exhibits the same pattern as that of the complex plus an additional mole of Me_3Al[★]. This spectrum is further indication of the intramolecular exchange exhibited in Eq. 2.

[★] The fact that the terminal methyl signals for $Me_2AlOCPh_2Me + 2\ Me_3Al$ at −65° do not line up exactly with those of Me_3Al and $Me_2AlOCPh_2Me + Me_3Al$ at the same temperature is due to our inability to control the temperature of the NMR probe accurately at −65°. The recorded temperatures are ± 2°.

Molecular association studies on $Me_2AlOCPh_2Me$ show this compound to be dimeric in benzene. Similar studies on a 1:1 mixture of $Me_2AlOCPh_2Me$ and Me_3Al show this mixture to be dimeric. These results are consistent with the description of the mixed bridged species as shown in Eq. 2 eliminating the representation as trimeric, tetrameric, polymeric, etc. species.

We are attempting to define the scope of the mixed bridge phenomena in both aluminum and magnesium compounds involving not only alkoxy–alkyl systems, but dialkylamino–alkyl, alkoxy–halogen etc. systems as well.

ACKNOWLEDGMENTS

We are indebted to the National Science Foundation (Grant GP-7994) for support of this work.

REFERENCES

1 E.C. Ashby, J. Laemmle and H.M. Neumann, *J. Amer. Chem. Soc.*, 90 (1968) 5179.
2 K.C. Williams and T.L. Brown, *ibid.*, 88 (1966) 5460.
3 N. Muller and P.E. Pritchard, *ibid.*, 82 (1960) 248.
4 E.C. Ashby and J.T. Laemmle, unpublished data.