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# COMPLEXES OF CARBONYL COMPOUNDS WITH $R_nAlX_{3-n}$ COMPOUNDS

## IV *. THE EVIDENCE FOR THE FORMATION OF CYCLIC COMPLEXES WITH CHLOROALUMINIUM COMPOUNDS

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## Summary

Reasonably stable 1 : 2 complexes are formed by carbonyl compounds with chloroaluminium compounds, usually in equilibrium with a 1 : 1 complex, however with trimethylaluminium only a 1 : 1 complex is formed. In the case of complexes with an excess of $MeAlCl_2$, a disproportionation reaction occurs. Possible structures are discussed in light of PMR and IR spectroscopy, dipole moments and molecular weight determination. The previously proposed cyclic six-membered ring is the most reliable structure for the 1 : 2 complex.

## Introduction

Carbonyl compounds form strong complexes of the donor—acceptor type with organoaluminium compounds. Many of them undergo rapid rearrangement [1] or disproportionation reactions [2] even at room temperature. Some stable complexes were investigated and it was found that a complex with a 1 : 2 ratio (C=O/Al) can be formed as well as a 1 : 1 complex [3—6]. However, its structure is still not established.

Reinheckel et al. [3] proposed for the 1 : 2 complexes of γ-lactones with ethylaluminium chlorides, a structure with two monomeric organoaluminium molecules complexed through the carbonyl- and ether-oxygen atom. They did not observe the formation of a 1 : 2 complex with triethylaluminium, unlike ethylaluminium chlorides and explained this fact by considering different changes in the electronegativity of the aluminium atom when complexed. Romm et al. [6] investigated complexes of ketones with aluminium bromide. They determined the presence of a 1 : 2 complex only for aromatic and heteroaromatic ketones

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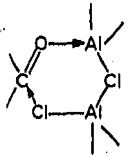
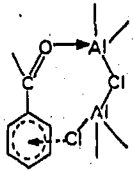
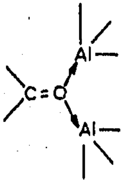
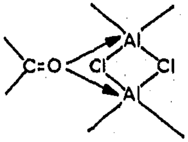
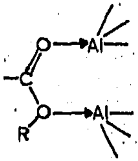
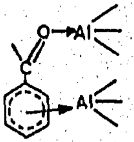
* For part III see ref. 5.

TABLE 1

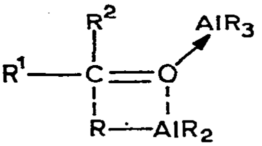
EVIDENCE FOR THE FORMATION OF 1 : 2 COMPLEXES AND CORRELATION OF STRUCTURES PROPOSED WITH DATA OBTAINED

| Method | Existence of 1 : 2 complex with | | Structures proposed for 1 : 2 complexes | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Chloro-aluminium cpds. | $R_3Al$ | <br>(III) | <br>(IV) | <br>(V) | <br>(VI) | <br>(VII)[a] | <br>(VIII)[b] |
| PMR: | | | | | | | | |
| splitting of the signals at −70° [c] | +[h] | ——[k] | 0[g] | 0 | 0 | 0 | 0 | 0 |
| chemical shifts at room temp. [d] | + | —[j] | + | — | — | — | — | — |
| internal chemical shift | + | n.i. [l] | + | 0 | — | — | — | 0 |
| Dipole moments | ++[i] | —— | 0 | —— | 0 | 0 | —— | —— |
| IR [e] | + | n.i. | 0 | 0 | 0 | 0 | —— | 0 |
| Solubility of $AlCl_3$ | ++ | | + | — | 0 | 0 | —— | — |
| Molecular weight | + | 0 | 0 | — | 0 | 0 | — | — |
| Heat of mixing [f] | + | n.i. | 0 | 0 | — | — | 0 | 0 |

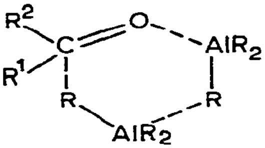
[a] Ref. 3. [b] Ref. 6. [c] See also ref. 4. [d] See also refs. 4, 5. [e] See also ref. 12. [f] Ref. 4. [g] 0, Do not exclude. [h] +, Agree with proposed structure. [i] ++, Strongly support. [j] —, Rather exclude. [k] ——, Strongly exclude. [l] n.i., Not investigated.

and proposed that the second $AlBr_3$ molecule was attached to the 1 : 1 complex by means of π-bonding between the aromatic ring and the aluminium atom. Complexes of 1 : 2 stoichiometry were also formed by substituted pyridines with alkylaluminium chlorides. Matsubayashi et al. [7,8] proposed the presence of two types of 1 : 2 complex; donor—acceptor and ionic. Only the 1 : 1 complex was formed by the same donors with trialkylaluminiums.

Nearly all complexes of organoaluminium compounds with carbonyl compounds undergo further reaction. So, the knowledge of the structure of the complexes which are obligatory intermediates, and conditions of their formation, is necessary in order to solve the reaction mechanism. The first step of the reaction between ketones and trialkylaluminiums is the formation of the 1 : 1 complex. The next step of the reaction, with an excess of organoaluminium compound, is complexation with the next molecule of $R_3Al$. There are two possibilities for the transition state with an excess of $R_3Al$; four-centered I, proposed by Jeffery and Mole [1], and six-centered II, proposed by Pasynkiewicz et al. [9] and Ashby et al. [10]. However, there is no conclusive evidence for either of these structures.



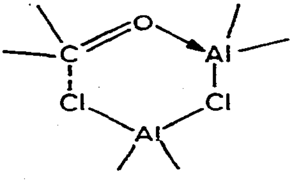
(I)



(II)

Recently, Ashby [11] proposed for the six-centered transition state a more detailed structure, in which the bridging aluminium atom is adjacent to the carbonyl oxygen atom. Such a structure, with reasonable bond distances and angles, is more advantageous energetically, due to the interaction between oxygen and the bridging aluminium.

In the previous papers [4,5] the presence of a 1 : 2 complex was suggested for esters and ketones with chloroaluminium compounds, and a plausible cyclic structure was proposed (III).



(III)

This work is carried out in order to obtain further evidence for the structure of stable 1 : 2 complexes on the basis of data obtained for the series of complexes of carbonyl compounds with organoaluminium compounds and aluminium chloride.

## Results and discussion

Possible structures of 1 : 2 complexes are compiled in Table 1. The results (including ones given in previous papers in this series [4,5,12]) are examined in order to prove or exclude the proposed structures.

*PMR spectroscopy*

*(i) Complexes of $Me_2AlCl$.* Formation of a 1 : 2 complex was proposed on the basis of the splitting of signals at low temperature for the system PhCOOMe/$Me_2AlCl$, indicating two complexes present in solution [4]. At room temperature the chemical shift of the $—OCH_3$ signal for the 1 : 2 ratio is situated between the shifts of free ester and the 1 : 1 complex. Complexes of *p*-methyl toluate with dimethylaluminium chloride display a similar feature; greater upfield shift of $—OCH_3$ protons for a 1 : 1 than for a 1 : 2 ratio (Fig. 1) *. Only structures III and IV (Table 1) seem to agree with these results. However, information drawn from these data is not very significant. A better approach, less dependent on the influence of solvent, is the investigation of the internal chemical shift of the

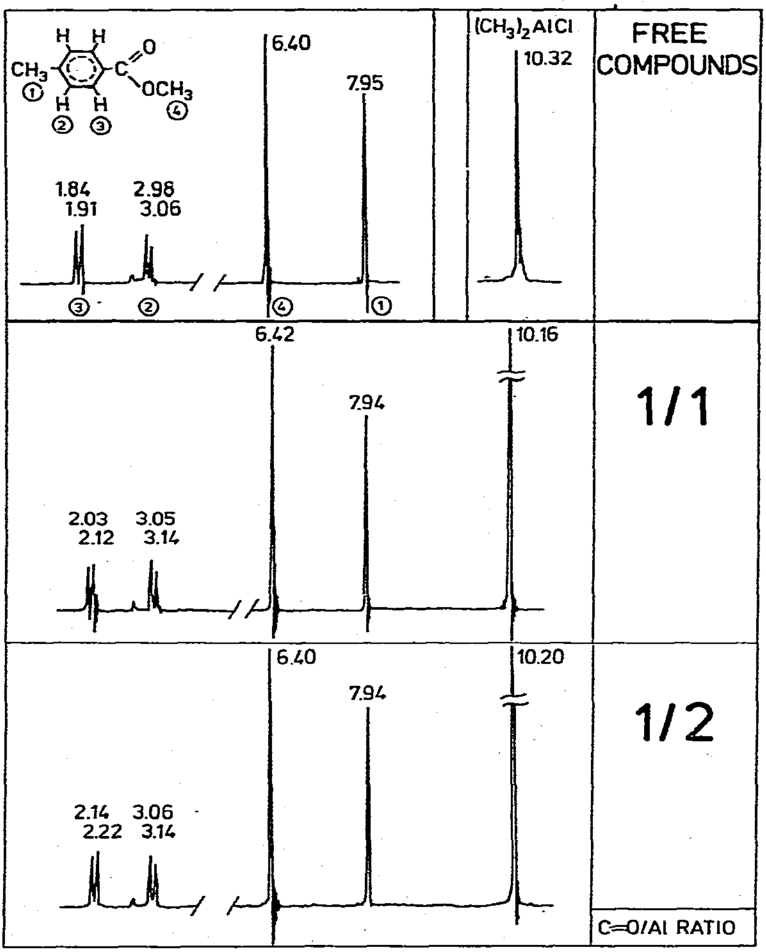


Fig. 1. PMR spectra of the system $p\text{-}CH_3C_6H_4COOCH_3/(CH_3)_2AlCl$ in $C_6D_6$ at room temperature. Chemical shifts in τ-scale (ppm) are given near the signals.

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* A similar effect was also observed for the $—OCH_3$ signal in the PhCOOMe/$AlCl_3$ system [13] and for the $—\overset{//}{C}—CH_3$ signal in the $MeC_6H_4COMe/AlCl_3$ system [5].

ethyl group, which gives direct information about the electronegativity of the atom bonded to this group [14]. The data obtained (Table 2) confirm the lower electronegativity of the carbonyl carbon for a 1 : 2 than for a 1 : 1 ratio, which is in agreement with structures III and IV.

In the previous paper [5], discussion of the chemical shifts of aromatic protons for the system $MeC_6H_4COMe/AlCl_3$ was carried out, and conclusions were drawn, proving structure III. Chemical shifts of the aromatic protons in the complexes of methyl toluate with dimethylaluminium chloride display a similar trend; the upfield shift of the ring protons caused by complexation is greater for a 1 : 2 than for a 1 : 1 ratio (Fig. 1). This fact can be explained by the removal of coplanarity of the ester molecule after complexation, which decreases the conjugation between the aromatic ring and the carbonyl group. Such a steric effect was observed by Chevrier et al. for 1 : 1 complexes of toluic acid chlorides [15] and is even more reasonable for a 1 : 2 complex. However, the chemical shifts of the aromatic protons in such complexes strongly depend on the solvent and its concentration. Belen'ky et al. [16] observed for similar complexes a downfield shift of ring protons in chlorinated hydrocarbons. Watson and Eastham [17] suggested an essential contribution of aromatic solvent to the formation of complexes between amine and ethylaluminium chlorides. Hence, these data do not produce very strong arguments in favour of either one of the structures.

*(ii) Complexes of $Me_3Al$.* The spectra of the system $PhCOOMe/Me_3Al$ are shown in Fig. 2. At room temperature there are always two signals due to the $—OCH_3$ and $Al—CH_3$ protons. At low temperatures the $Al—CH_3$ proton signal splits into three peaks, only in excess of trimethylaluminium. The chemical shifts of these signals correspond to a 1 : 1 complex and the free and bridging group in trimethylaluminium dimer. There is always one single peak for $—OCH_3$ protons, which indicates that only the 1 : 1 stable complex is formed.

*(iii) Complexes of $MeAlCl_2$.* Complexes of the system $PhCOOMe/MeAlCl_2$ show unexpected splitting of the $—OCH_3$ protons signals at room temperature and broadening of the $Al—CH_3$ signal (Fig. 3). This can be explained by the formation of two steric isomers of the 1 : 2 complex (only in the case of $MeAlCl_2$ each aluminium atom in ring structure III has two different substituents; $—CH_3$ and $—Cl$) or by a disproportionation reaction. The second hypothesis is more likely because disproportionation occurs easily for an excess of organoaluminium compound with alkylaluminium dichlorides but not with dialkylaluminium chlorides [17,18], which agrees with the results obtained. Both PhCOOMe/Me-

TABLE 2

INTERNAL CHEMICAL SHIFTS OF THE ETHYL GROUP OF THE SYSTEM $\mathrm{Et}\overset{\overset{O}{\|}}{\mathrm{C}}\mathrm{—OPh/Me_2AlCl}$, IN BENZENE

| C=O/Al molar ratio | τ (ppm) | | Δ($CH_3 — CH_2$) (ppm) |
|---|---|---|---|
| | $—CH_2—$ | $—CH_3$ | |
| 1 : 1 | 7.46 | 8.99 | 1.53 |
| 1 : 2 | 7.47 | 8.97 | 1.50 |
| ester | 7.78 | 8.99 | 1.20 |

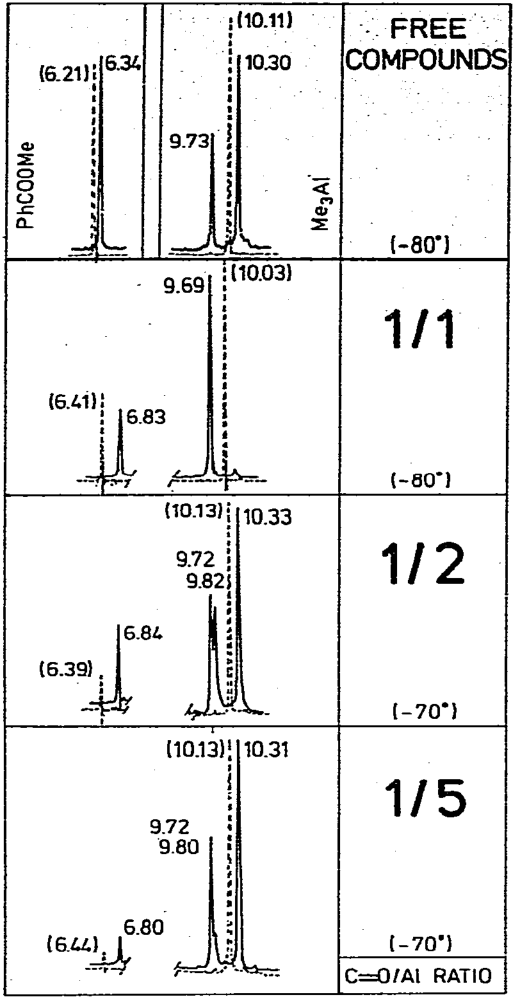

Fig. 2. PMR spectra of the system $PhCOOMe/Me_3Al$ in toluene - - - - - - 20°C, ——— −70°C or −80°C. Chemical shifts in τ-scale (ppm) are given near the signals (in parentheses for room temperature spectra).

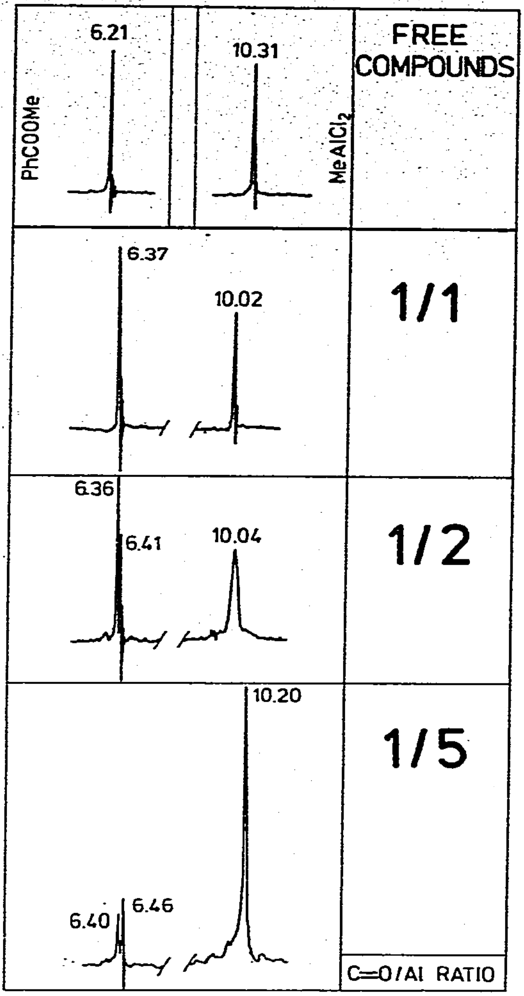

Fig. 3. PMR spectra of the system $PhCOOMe/MeAlCl_2$ in benzene at room temperature. Chemical shifts in τ-scale (ppm) are given near the signals.

$AlCl_2$ and $PhCOOMe/Me_2AlCl$ were examined from the disproportionation point of view by analysis of solution, as described later.

### *Dipole moments*

Dipole moment data are summarized in Table 3. Formation of the complex causes a strong increase in the value of the dipole moment relative to the free carbonyl compound. Addition of a second mol of aluminium compound causes a further increase of about 2D for all chlorine-containing aluminium compounds. The only system, which does not show this increase, is the $PhCOOMe/Me_3Al$ system.

TABLE 3

DIPOLE MOMENTS OF RR'CO/Me$_n$AlX$_{3-n}$ SYSTEMS AND OF FREE DONORS, IN BENZENE AT 25°C

| System | C=O/Al molar ratio (D) | | free donor (D) |
|---|---|---|---|
| | 1 : 1 | 1 : 2 | |
| PhCOOMe/Me$_3$Al [a] | 4.8 | (3.5) [b] | 1.9 |
| PhCOOMe/Me$_2$AlCl | 6.0 | 7.7 | 1.9 |
| EtCOOMe/Me$_2$AlCl | 4.7 | 7.1 | 1.7 |
| PhCOMe/AlCl$_3$ [c] | 8.0 | 10.2 [d] | 3.0 |

[a] Reaction was observed. [b] See discussion. [c] Obtained only from dielectric constant data. [d] Obtained for the highest amount of dissolved AlCl$_3$.

The experimental values of the dielectric constant and refractive index do not fit a straight line equation if plotted against weight fraction of the solute. This discrepancy is observed for the complexes and is greater for a 1 : 2 ratio in the PhCOOMe/Me$_3$Al system and for a 1 : 1 ratio in other systems. The maximal error in dipole moment computing caused by this discrepancy is not higher than 0.5 D. This is caused by the equilibrium, occuring in solution, leading to intricate interactions. The discrepancies are observed, because the data computed are based on the existence of only one complex in each case (1 : 1 or 1 : 2). The most significant information from dipole moment data is the very similar increase of dipole moments for the 1 : 2 complexes of ketones, aliphatic and aromatic esters with chloroaluminium compounds, which suggests similar structures for these complexes. Because a similar 1 : 2 complex is formed by compounds without an aromatic ring (EtCOOMe) or without an alkoxy group (PhCOMe), as with PhCOOMe investigated earlier, the structure with a contribution from the aromatic ring or alkoxy oxygen to 1 : 2 complex formation is unlikely for all these compounds and structures IV, VII and VIII can be excluded.

*IR and Raman spectroscopy*

The IR and Raman spectra show a characteristic shift of the stretching frequency of the C=O group towards lower values, and of $\overset{//}{\mathrm{C}}$—O—C towards higher frequencies (Table 4). In the range of 700—1800 cm$^{-1}$ for a 1 : 1 and 1 : 2 ratio the spectra look very similar, which excludes the structure VII. One of the bands which differs in position both in IR and Raman is $\nu$(C=O) (3—10 cm$^{-1}$) *. $\nu$-($\overset{//}{\mathrm{C}}$—O—C) differs only in Raman of about 8 cm$^{-1}$. In Raman spectra one can see for a 1 : 2 ratio two new bands at 335 and 715 cm$^{-1}$, which are not observed for a 1 : 1 ratio.

The spectra confirm the existence of two complexes by the presence of different C=O bands for the 1 : 1 and 1 : 2 ratio. The similar value for $\nu$(C=O) and $\nu$($\overset{//}{\mathrm{C}}$—O—C) in the complex, irrespective of differences between the values of the

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* Both for a 1 : 1 and a 1 : 2 ratio two $\nu$(C=O) bands are present (as a main band and a shoulder). In Table 4 the frequency of the most intensive band is given, neglecting the weaker band. For the exact shape of the bands see refs. 4 and 5.

TABLE 4

$\nu(C{=}O)$ AND $\nu(\overset{//}{C}{-}O{-}C)$ FREQUENCIES OF DONORS, 1 : 1 AND 1 : 2 COMPLEXES IN IR AND RAMAN SPECTRA

| Carbonyl compound | Aluminium compound | $\nu(C{=}O)$ ($cm^{-1}$) free | complex | $\Delta\nu$ | $\nu(\overset{//}{C}{-}O{-}C)$ ($cm^{-1}$) free | complex | $\Delta\nu$ |
|---|---|---|---|---|---|---|---|
| | | *IR spectra* | | | | | |
| PhCOOMe | | 1730 | | | 1280 | | |
| | $Me_2AlCl$ | | 1645 [a] | 85 | | 1355 | 75 |
| | | | (1635) [b] | (95) | | | |
| | $MeAlCl_2$ | | 1635 | 95 | | 1360 | 80 |
| | | | (1633) | (97) | | | |
| | $AlCl_3$ | | 1620 | 110 | | 1365 | 85 |
| | | | (1615) [c] | (115) | | | |
| EtCOOMe | | 1745 | | | 1206 | | |
| | $Me_2AlCl$ | | 1645 | 100 | | 1360 | 154 |
| | | | (1642) | (103) | | | |
| | $AlCl_3$ | | 1618 | 127 | | 1370 | 164 |
| | | | (1616) [c] | (129) | | | |
| PhCOMe | | 1690 | | | — | | |
| | $AlCl_3$ | | 1570 | 120 | | — | |
| | | | (1560) [c] | (130) | | | |
| | | *Raman spectra* | | | | | |
| PhCOOMe | | 1725 | | | 1280 | | |
| | $Me_2AlCl$ | | 1643 | 82 | | 1350 | 70 |
| | | | (1637) | (88) | | (1358) | (78) |

[a] Values for 1 : 1 ratio, see discussion. [b] Values in parentheses for 1 : 2 ratio, see discussion. [c] Obtained for the highest amount of dissolved $AlCl_3$.

free groups bands in the aromatic and aliphatic esters, is observed. This suggests a similar structure of complexes formed by these compounds. The bands 335 and 715 $cm^{-1}$ in Raman spectra may correspond to a 1 : 2 complex or to the $Me_2AlCl$ dimer present in the solution because of the equilibrium of complex formation [19].

*Composition of the solution of the complexes*

*(i) Solubility of $AlCl_3$.* Since the 1 : 2 complex exists in equilibrium with the 1 : 1 complex and the organoaluminium compound dimer (eq. 1), most of the

$$\mathrm{Base/2R_nAlX_{3-n}} \rightleftharpoons \mathrm{Base/R_nAlX_{3-n}} + 0.5\ (\mathrm{R_nAlX_{3-n}})_2 \tag{1}$$

methods (e.g. PMR at room temperature, dipole moments molecular weight determination) give the mean value for all the forms present in solution. The solubility of $AlCl_3$ in a benzene solution of various carbonyl compounds provides proof of the presence of the 1 : 2 complex ($AlCl_3$ is insoluble in benzene). The data obtained (Table 5) show, that the solubility never exceeds 2 mol of $AlCl_3$ per 1 mol of carbonyl group. It is greater for ketones than for esters, for aliphatic species than for aromatic ones and greater for compounds containing an electron-attracting rather than an electron-donating group attached to the carbonyl carbon. Equilibrium of the formation of the complex with interaction of the terminal chlorine atom with the carbonyl carbon (III) should be shifted

TABLE 5

SOLUBILITY OF ALUMINIUM CHLORIDE IN 10% BENZENE SOLUTION OF DONORS

| Carbonyl compound | Mols of $AlCl_3$ per one mol of donor |
|---|---|
| PhCOMe | 1.88 |
| $Ph_2CO$ | 1.74 |
| PhCOOMe | 1.44 |
| $CCl_3COOEt$ | 1.51 |

towards a higher amount of 1 : 2 complex in the case of a carbonyl compound, whereas in the 1 : 1 complex there is a greater positive charge on the carbonyl carbon atom. The observed solubility of $AlCl_3$ is consistent with this order of charge (eq. 2).

$$\begin{aligned}&Ph_2CO/AlCl_3 < PhCOMe/AlCl_3 \text{ (a)}\\&EtCOOMe/AlCl_3 < CCl_3COOMe/AlCl_3 \text{ (b)}\\&PhCOOMe/AlCl_3 < PhCOMe/AlCl_3 \text{ (c)}\end{aligned} \qquad (2)$$

*(ii) Disproportionation ability of the complexes.* Analysis of the complexes, separated by addition of n-heptane to benzene solution, shows that disproportionation occurs with an excess of organoaluminium compound in the case of the $PhCOOMe/MeAlCl_2$ system, but not in the case of the $PhCOOMe/Me_2AlCl$ system; in the former case a greater Cl/Al ratio in the separated complex was found compared to that in benzene/heptane solution.

### *Molecular weight*

Molecular weight data, calculated and found for the 1 : 1 or 1 : 2 complex of carbonyl compounds with aluminium compounds are listed in Table 6. The molecular weights obtained for the 1 : 2 ratio are greater than those calculated for 1 : 1 complexes. The deviation from the value calculated for the 1 : 2 ratio is

TABLE 6

MOLECULAR WEIGHT DATA, OBTAINED CRYOMETRICALLY IN CA. 1% BENZENE SOLUTIONS

| System | C=O/Al molar ratio | Mol.wt. found ($M_f$) (calcd. ($M_c$)) | $\frac{M_f}{M_c}$ |
|---|---|---|---|
| $PhCOOMe/Me_3Al$ | 1 : 1 | 224 (208) [a] | 1.08 |
| | 1 : 2 | 213 (280) [a] | 0.76 |
| $PhCOOMe/Me_2AlCl$ | 1 : 1 | 241 (229) | 1.05 |
| | 1 : 2 | 251 (321) | 0.78 |
| $PhCOOMe/AlCl_3$ | 1 : 1 | 295 (269) | 1.10 |
| | 1 : 1.44 [b] | 354 (403) | 0.88 |
| $EtCOOMe/Me_2AlCl$ | 1 : 1 | 191 (181) | 1.06 |
| | 1 : 2 | 227 (273) | 0.83 |
| $PhCOMe/AlCl_3$ | 1 : 1 | 256 (254) | 1.01 |
| | 1 : 1.88 [b] | 350 (387) | 0.91 |

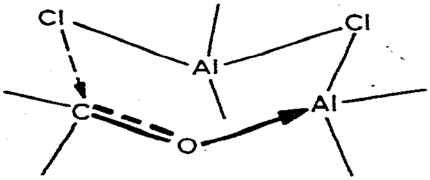
[a] Results uncertain. Alkylation reaction was observed and great dispersion of results was obtained. [b] The highest amount of dissolved $AlCl_3$.

greater for esters than for ketones, which agrees with the order of electric charge, discussed above (eq. 2a). The increase of molecular weight obtained for a 1 : 1 ratio related to the calculated value can be caused by dipole association in solution or by non-ideality of the system [20].

## Conclusions

(i) Reasonably stable 1 : 2 complexes are formed by carbonyl compounds (ketones and esters: aliphatic and aromatic) with chloroaluminium compounds.

(ii) The most likely structure of a 1 : 2 complex is III. The six-membered ring is closed by formation of a donor—acceptor bond O→Al and by interaction of the terminal chlorine with the carbonyl carbon, while one chlorine bridge between aluminium atoms remains unbroken. More detailed examination of the molecular model with reasonable bond distances and angles leads to the non-planar structure IIIa *.



(IIIa)

(iii) The 1 : 2 complex exists in solution in equilibrium with the 1 : 1 complex and organoaluminium chloride dimer. The amount of 1 : 2 complex is greater when the positive charge on the carbonyl carbon in the 1 : 1 complex increases.

(iv) Trimethylaluminium does not form such stable complexes. Similar structures for trialkylaluminiums correspond to the alkylation reaction transition state II, and its presence cannot be determined by the methods used for the investigation of stable complexes.

(v) Complexes with an excess of methylaluminium dichloride easily undergo disproportionation reaction. This was not observed for the complexes of dimethylaluminium chloride.

## Experimental

### *Materials*

Methylaluminium compounds were obtained by conventional methods from methylaluminium sesquichloride (from aluminium and methyl chloride). Aluminium chloride (BDH, Laboratory Reagent, England) was purified by sublimation in a vacuum through a layer of aluminium turnings. Acetophenone (Sojuzchimexport, USSR), methyl benzoate (Argon, Poland) and other donors were dried over molecular sieves 4A and distilled in a nitrogen atmosphere. Methyl

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* According to Ashby [11], in a similar structure there is a possibility of interaction between the oxygen atom with the second aluminium atom, which can be energetically favorable.

propionate, phenyl propionate and methyl trichloroacetate were obtained by conventional methods from acid and methanol or phenol. Methyl toluate was obtained from *p*-tolunitrile (Merck, Germany) and methanol. Benzene, deuterobenzene and toluene were dried over molecular sieves 4A, heated with a potassium/benzophenone complex to obtain a blue colour, and distilled off from the complex.

### *Techniques*

Complexes were prepared in a nitrogen atmosphere. Organoaluminium compounds were vapour-transferred using a high-vacuum line to the vessel, which was weighed and a suitable amount of solvent and donor were added. Reactive complexes of trimethylaluminium were prepared at low temperatures, and low temperature spectra were recorded first. The NMR spectra were run on a JEOL 100 MHz spectrometer, using sealed tubes, filled in the vacuum line. The IR spectra were recorded on a Zeiss-UR-10 spectrophotometer, using a liquid cell, adapted to be filled in a nitrogen atmosphere. Raman spectra were recorded on a Coderg spectrometer with a neon-helium laser, using sealed tubes. The molecular weights were measured cryoscopically in benzene. Dipole moments were computed, using the Guggenheim method [21], from dielectric constants and refractive index values, which were measured by a Dipolmeter DM-01 and Abbe refractometer, adapted to work in a nitrogen atmosphere. Aluminium and chlorine contents were determined by volumetric analysis, after hydrolysis with methanol and a diluted solution of nitric acid of a known amount of the complex.

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