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

EXCHANGE OF ALKYL GROUPS AND CHLORINE BETWEEN TETRAMETHYLLEAD AND ORGANOALUMINIUM COMPOUNDS

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(Received February 2nd, 1971)

SUMMARY

Exchange reactions involving alkyl groups and chlorine between tetramethyllead and organoaluminium compounds (Et_3Al, Me_2AlCl and $MeAlCl_2$), and between tetramethyllead and organoaluminium/benzonitrile complexes ($Me_2AlCl \cdot PhCN$, $MeAlCl_2 \cdot PhCN$), have been investigated. The reaction mechanism, and the effect of Lewis acid strength on the reactivity of the organoaluminium compound, has been established. A slow exchange of alkyl groups was found to occur between trialkylaluminium or dialkylaluminium chloride and tetramethyllead, *viz.*,

$$R_4Pb + R'R_2Al \rightleftarrows R_3PbR' + R_3Al$$

With alkylaluminium dichloride as the reactant the alkyl group exchange was accompanied by a rapid exchange of chlorine:

$$R_4Pb + RAlCl_2 \rightleftarrows R_3PbCl + R_2AlCl$$

In the presence of a Lewis base in equimolar proportions to the organoaluminium compound the above exchange was hindered. The reactions were followed through NMR spectral observations and by quantitative analyses of the products.

INTRODUCTION

Ethylaluminium and methylaluminium compounds R_nAlX_{3-n} (R = Me, Et; X = Cl, Br, I) react with certain lead salts to produce tetraalkyllead, the yield being governed by numerous factors including subsequent reactions involving the product.

Tetraalkyllead has been reported to exchange its alkyl groups readily for chlorine in reactions with some Group IIIa element chlorides (BCl_3[1], $AlCl_3$[2]) which may be considered as acids in the Lewis sense.

According to Calingaert[3] and Russel[4,5] the reaction of tetraalkyllead with aluminium chloride is likely to yield trialkyllead chloride and alkylaluminium dichloride,

$$R_4Pb + AlCl_3 \rightleftarrows R_3PbCl + RAlCl_2$$

These authors, however, assume that the subsequent reactions following the synthesis of tetraalkyllead from organoaluminium compounds include one involving the exchange of groups between the product and the organoaluminium reactants added or formed in the system concerned.

No reactions between alkyllead and organoaluminium compounds have hitherto been reported and the purpose of this work was to study such reactions with particular reference to the exchange of alkyl groups and chlorine between tetramethyllead and organoaluminium compounds.

EXPERIMENTAL

Reactants

Organolead compounds Me_nPbEt_{4-n} ($n \leqslant 4$), trimethyllead chloride, and dimethyllead dichloride were prepared by conventional methods[6,8]. The alkyllead compounds were purified by distillation under reduced pressure; the alkyllead chlorides being purified by repeated crystallization from ethanol or water.

Liquid organoaluminium compounds, prepared by conventional means, were distilled before use and methylaluminium dichloride was crystallized from benzene.

The solvents, benzene, toluene, xylene, and cyclohexane were distilled from sodium in a nitrogen atmosphere. Methylene chloride was dried over magnesium sulphate, and redistilled in a nitrogen atmosphere.

Benzonitrile (FOCh, Gliwice, Poland) was dried over a type 4a molecular sieve, and distilled in a nitrogen atmosphere immediately prior to use.

Potassium chloride (FOCh, Gliwice) was ground and dried for 24 h at 150–200°.

Analysis

Organoaluminium compounds were estimated by hydrolysis followed by determination of aluminium by titration with sodium versenate at pH 4.5–5.0, and of chlorine by analysis (at pH 6.3–10.5) using the modified Mohr method[9].

Tetramethyllead was estimated using Newman's iodometric technique[10]. In the presence of organoaluminium compounds tetramethyllead was determined after a 5-ml sample had been hydrolyzed with diluted (1/9) hydrochloric acid and extracted repeatedly with small volumes of xylene.

With the $Me_3PbCl \cdot MeAlCl_2$ complex lead was determined gravimetrically as $PbSO_4$ and aluminium titrimetrically with sodium versenate.

NMR studies

NMR spectra were recorded on a JNM-60-H (JEOL, Tokyo) spectrometer using 5–15% solutions with toluene as a solvent (methyl group), and with methylene chloride and heavy water as the internal standards. The solutions were prepared and sampled in a purified nitrogen atmosphere.

Reaction of tetramethyllead with methylaluminium dichloride and with $MeAlCl_2 \cdot KCl$ complex

To a nitrogen-flushed three-necked flask equipped with a stirrer and cold trap, 1.755 g (0.0155 mole) methylaluminium dichloride, 13 ml xylene, and finally 4.961 g (0.0185 mole) tetramethyllead were added. During this addition the temperature of the flask and its contents increased only slightly. The flask and contents were thermostatted at 135°, and after 10 min. the first sample (1 ml) was taken for analysis. For the first 2 h samples were withdrawn at 30-min intervals and later every 1 h. The reaction was continued for 6 h 40 min.

After the reaction had been completed tetramethyllead was determined in the reaction mixture, and a tetramethyllead balance was prepared (Table 3).

The $MeAlCl_2 \cdot KCl$ complex was prepared in a three-necked flask through the addition of reactants in equimolar (0.124 mole) amounts. The resulting mixture was heated for 2 h with vigorous stirring. Upon cooling, 22 ml xylene and 0.0262 mole tetramethyllead were added, the mixture thoroughly stirred and sampled, and the flask thermostatted at 135°. The reaction was continued for 5 h during which period samples were withdrawn at 30-min intervals for tetramethyllead analysis. The residue was also analyzed for tetramethyllead and a balance prepared (Table 3).

Synthesis of trimethyllead chloride methylaluminium dichloride complex

Trimethyllead chloride followed by a solution of methylaluminium dichloride in benzene was added dropwise to a nitrogen-flushed three-necked flask equipped with a magnetic stirrer, dropping funnel and cold trap connected to a liquid seal. The mole ratio of the reactants was $MeAlCl_2/Me_3PbCl$ 1/1.2. Most of the trimethyllead chloride dissolved rapidly and the temperature of the mixture increased considerably. The solution was decanted and the benzene evaporated to yield a crystalline solid which upon hydrolysis was found to contain Al/Pb = 1.04/1.00. The NMR spectrum is presented in Fig. 3 and Table 1.

RESULTS AND DISCUSSION

Exchange reactions between tetramethyllead and organoaluminium compounds, including trimethylaluminium, triethylaluminium, dimethylaluminium

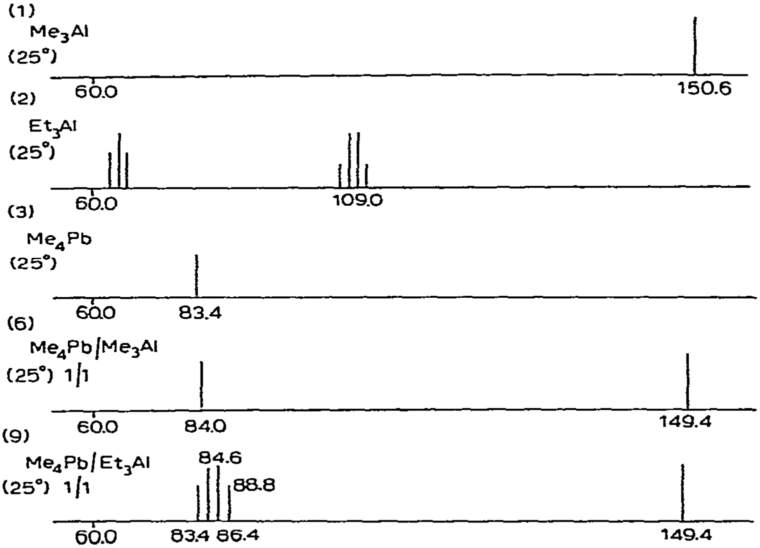


Fig. 1. Chemical shifts of CH_3Pb and CH_3Al protons in the NMR spectra of the products of the reaction of Me_4Pb with the Me_3Al and Et_3Al.

TABLE 1

CHEMICAL SHIFTS OF CH_3Pb AND CH_3Al BANDS IN THE NMR SPECTRA OF THE PRODUCTS OF THE REACTION OF TETRAMETHYLLEAD WITH ORGANOALUMINIUM COMPOUNDS

Solvent and internal reference: toluene (methyl group).

Spectrum No.	Reactants	Mole ratio	Chemical shift (Hz)		Temp. (°C)
			CH_3Pb	CH_3Al	
Series I					
1	Me_3Al			150.6	25
2	Et_3Al^a				25
3	Me_4Pb		83.4		25
4	$Me_3PbC_2H_5$		84.6		25
5	Me_2PbEt_2		86.4		25
6	Me_4Pb/Me_3Al	1/1	84.0	149.4	25
7		1/1	88.2	154.2	100
8		1/2	84.6	150.6	25
9	Me_4Pb/Et_3Al	1/1	83.4; 84.6 86.4; 88.8		25
Series II					
10	Me_2AlCl			148.8	25
11	Me_2AlCl : PhCN			140.4	25
12	Me_4Pb		83.4		25
13	Me_4Pb/Me_2AlCl	2/1	83.4	149.4	25
14	Me_4Pb/Me_2AlCl/PhCN	2/1/1	83.4	139.2	25
15	Me_4Pb/Me_2AlCl	1/1	84.0	148.8	25
16	Me_4Pb/Me_2AlCl/PhCN	1/1/1	84.0	141.0	25
17	Me_4Pb/Me_2AlCl	1/2	83.4	150.0	25
18	Me_4Pb/Me_2AlCl/PhCN	1/2/2	83.4	141.0	25
Series III					
19	$MeAlCl_2$			147.6	25
20	Me_4Pb		83.4		25
21	Me_3PbCl		50.0		25
22	$Me_3PbCl : AlMeCl_2$		21.0	139.0	25
23	$Me_4Pb/MeAlCl_2$	2/1	71.4	141.0	25
24		2/1	80.4; 25.8	136.2	−65
25		1/1	61.2	147.6	25
26		1/1	80.4; 27.0	135.6	−70
27		1/2	25.2	147.0	25
28		1/2	23.4	129.0; 141.0	−71
29		1/3	24.6	147.0	25
30		1/3	21.6	129.0; 142.2	−71
31		1/4	23.4	146.0	25
32		1/4	23.4	129.6; 144.0	−66
Series IV					
33	$MeAlCl_2 \cdot$ PhCN			130.2	25
34	Me_4Pb		84.0		25
35	$Me_4Pb/MeAlCl_2 \cdot$ PhCN	2/1	83.4	132.6	25
36		2/1	85.2	136.2	68
37		1/1	82.8	128.4	25
38		1/1	84.6	134.4	70
39		1/2	85.8	133.8	25
40		1/2	87.6	138.0	68

[a] Chem. shift of CH_2Al 109.0 Hz, CH_3CAl 62.4 Hz.

chloride, methylaluminium dichloride, and a methylaluminium dichloride/benzonitrile complex, have been investigated. The reactions were followed through the change in the NMR spectra of the systems and through quantitative analyses of the products.

The NMR spectra of the products in the reaction of tetramethyllead with trimethylaluminium are presented in Table 1, series I. The chemical shifts of the protons of the methyl group combined with the aluminium and lead atoms are identical with those observed in the pure reactants (Table 1, series I, spectra 1 and 3, Fig. 1). This fact suggests that a rapid exchange of the alkyl groups occurs but does not entirely rule out a slow exchange as a possibility.

Spectrum 9 of the products of the reaction of tetramethyllead with triethylaluminium proves that a slow exchange of alkyl groups occurs between the aluminium and the lead atoms. This suggests that the reaction should yield a mixture of methylethyllead and methylethylaluminium compounds according to eqn. (1).

$$Me_4Pb + Et_3Al \rightarrow Me_3PbEt + Me_2PbEt_2 + MePbEt_3 + Et_4Pb + Et_2AlMe + EtAlMe_2 + Me_3Al \qquad (1)$$

Actually, spectrum 9 exhibits four peaks in the positions corresponding to CH_3Pb methyl protons, and these are attributable to the alkyllead compounds (Me_4Pb, Me_3PbEt, Me_2PbEt_2, $MePbEt_3$) occurring in eqn. (1).

Additional proof of this exchange is provided by the peak assignable to the CH_3Al methyl group and by the peaks attributable to C_2H_5Pb ethyl groups which have been omitted in Table 1. The occurrence of a single CH_3Al peak in the spectrum for methylaluminium compounds Me_3Al, Me_2AlEt, and $MeAlEt_2$ is due to the rapid exchange of alkyl groups in the organoaluminium compounds.

Modification of the mole ratio of reactants and increase of the reaction temperature to 100° increases the reaction rate only slightly (spectra 6–8).

On reaction with tetramethyllead dimethylaluminium chloride also exchanges its alkyl groups. The exchange is slow. In this system chlorine is not exchanged (Table 1, Fig. 2). The exchange may be represented by the eqn. (2).

$$Me_3PbMe^* + Me_2AlCl \rightleftarrows Me_4Pb + Me^*AlMeCl \qquad (2)$$

On varying the reactant mole ratio no chemical shifts of the aluminium (CH_3Al) and the lead (CH_3Pb) methyl groups protons as compared with standards (spectra 13 ,15, 17, 10, and 12) were observed. Broadening of the peaks due to the aluminium (CH_3Al) and lead (CH_3Pb) methyl groups (Fig. 2) confirms that reaction (2) occurs. A strong Lewis base (*e.g.* benzonitrile) when added in equimolar proportions to the mixture of dimethylaluminium chloride and tetramethyllead stops the exchange completely. The peaks narrow to the widths exhibited by the pure standards (Table 2, Fig. 2).

The spectra of the products of the reaction of tetramethyllead with dimethylaluminium chloride (Table 1, series II) exhibit no peaks which may be attributed to protons of methyllead chloride compounds, and for this reason chlorine exchange should be ruled out, for otherwise chemical shifts characteristic of these derivatives would have been observed. The shift of the methyl group, e.g. in Me_3PbCl, is about 30 Hz compared with the methyl in tetramethyllead.

Methylaluminium dichloride reacts with tetramethyllead in a different manner

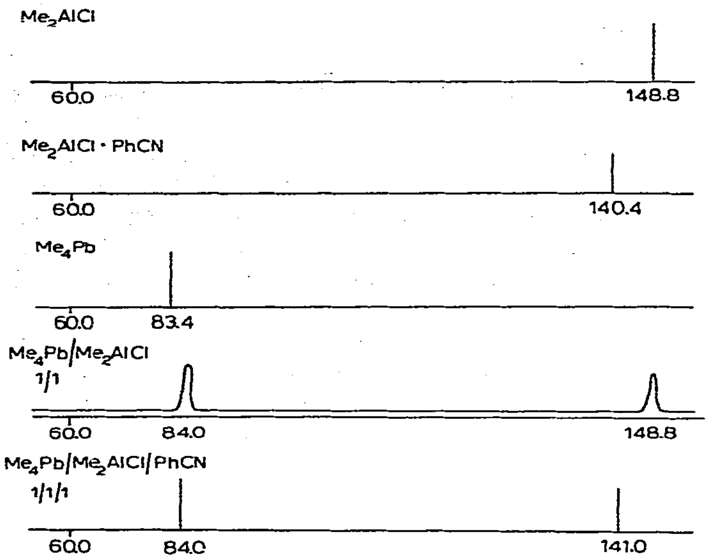


Fig. 2. Chemical shifts of CH_3Pb and CH_3Al protons of the products of the reaction of Me_4Pb with Me_2AlCl and $Me_2AlCl : PhCN$.

TABLE 2

CHANGES IN WIDTH OF THE CH_3Pb AND CH_3Al PEAKS IN THE SPECTRUM OF PRODUCTS OF THE REACTION OF TETRAMETHYLLEAD WITH DIMETHYLALUMINIUM CHLORIDE, MOLE RATIO 1/1, IN COMPARISON WITH THOSE FOR THE STANDARDS

Spectrum[a] No.	Reactants[b]	Peak width, Δν 1/2 (Hz)	
		CH_3Pb	CH_3Al
10	Me_2AlCl	2.0	
11	$Me_2AlCl \cdot PhCN$	1.5	
12	Me_4Pb		1.5
15	Me_4Pb/Me_2AlCl	5.0	4.5
16	$Me_4Pb/Me_2AlCl \cdot PhCN$	1.5	1.7

[a] cf. Table 1. [b] The chemical shifts of CH_3Al and CH_3Pb are listed in Table 1, series II.

from that exhibited by trialkylaluminium and dimethylaluminium chloride. In this case two simultaneous reactions appear to occur: a slow exchange of alkyl groups and a rapid exchange of chlorine. The exchange of chlorine gives rise to the formation of trimethyllead chloride and to organoaluminium chloride compounds other than the original methylaluminium dichloride reactant. This chlorination of tetramethyllead may be represented by eqn. (3). The resulting trimethyllead chloride yields a donor–acceptor complex with methylaluminium dichloride, in which the chlorine atom attached to the lead donates, and the aluminium atom accepts, electrons.

$$Me_4Pb + MeAlCl_2 \rightarrow Me_3PbCl + Me_2AlCl \tag{3}$$

$$Me_3PbCl + MeAlCl_2 \rightarrow \underset{(I)}{Me_3PbCl{:}AlMeCl_2} \tag{4}$$

Reaction (4) prevents precipitation of toluene-insoluble trimethyllead chloride.

The postulated chlorine exchange between tetramethyllead and methylaluminium dichloride is supported by quantitative analyses (Table 3) and NMR spectral evidence (Table 1, series III).

TABLE 3

TETRAMETHYLLEAD MATERIAL BALANCE AND CONDITIONS FOR REACTIONS OF TETRAMETHYLLEAD WITH METHYLALUMINIUM DICHLORIDE AND WITH METHYLALUMINIUM DICHLORIDE POTASSIUM CHLORIDE COMPLEX

Reaction conditions	Reaction			
	$Me_4Pb/MeAlCl_2$		$Me_4Pb/MeAlCl_2 \cdot KCl$	
Reactant mole ratio	1.2/1		1/5	
CH_3AlCl_2 added (mole)	0.0155		0.131	
Temp. (°C)	135°		135°	
Time (h)	$6\frac{2}{3}$		5	
Me_4Pb balance	(mole)	(%)	(mole)	(%)
$[Me_4Pb]$ before reaction	0.0185	100	0.0262	100
$[Me_4Pb]$ found (during and after reaction)	0.0112	60.52	0.0255	97.29
$[Me_4Pb]$ decrease (converted)	0.0073	39.48	0.0007	2.71

The decrease in the tetramethyllead concentration during the reaction of tetramethyllead with methylaluminium dichloride (*cf. Experimental*) is considerable and equilibrium is set up very quickly. This decrease is 0.0073 mole (Table 3) and eqn. (3) implies that 0.0073 mole of methylaluminium dichloride also react to yield trimethyllead chloride in an equimolecular amount. The unconverted dichloride is 0.0155 (before reaction)−0.0073 (converted) = 0.0082 mole, giving a mole ratio of the resulting trimethyllead chloride to the unconverted methylaluminium dichloride of 0.0073/0.0082, in good agreement with that of the constituents of complex (I) where $Me_3PbCl/AlMeCl_2 = 1/1$.

Further studies of the reaction of tetramethyllead with methylaluminium dichloride were made through the use of NMR spectra (Table 1, series III). The spectrum of products exhibits two broad peaks which are attributable to the aluminium (CH_3Al) and the lead (CH_3Pb) methyl groups protons. At 25° the positions of the CH_3Pb peaks are related to the mole ratio of the reactants. The observed changes in the chemical shift of CH_3Pb are presented graphically in Fig. 4.

As the $MeAlCl_2/Me_4Pb$ mole ratio is raised from 0.5 to 2, the CH_3Pb peak moves downfield, but a futher increase in the proportion of methylaluminium dichloride in the system does not change its position. However, above a ratio of 2/1 the peak becomes sharper (enhanced resolution) (Fig. 3, spectrum 27). The experimental data comply with the over-all reaction as represented by the collective eqn. (5).

$$Me_4Pb + 2\ MeAlCl_2 \rightleftarrows Me_3PbCl + MeAlCl_2 + Me_2AlCl \longrightarrow Me_3PbCl{:}AlMeCl_2 + Me_2AlCl \quad (5)$$

At mole ratios higher than 2/1 the reaction mixture contains only the complex (I), in addition to the organoaluminium compounds. Below a 2/1 ratio tetramethyllead

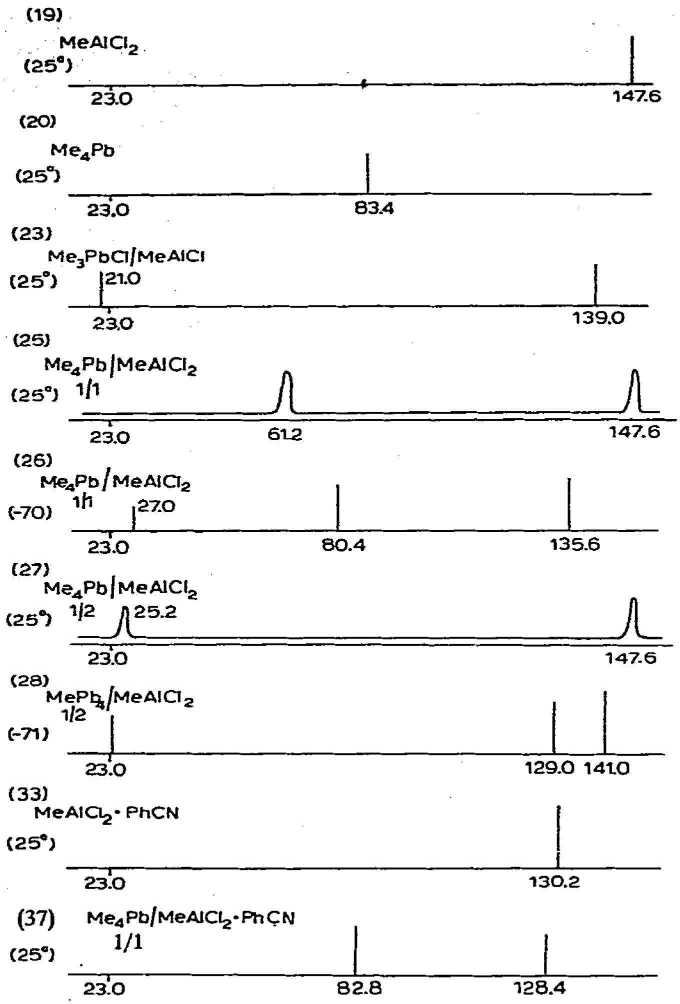


Fig. 3. Chemical shifts of CH_3Pb and CH_3Al protons of the products of the reaction of Me_4Pb with $MeAlCl_2$ and $MeAlCl_2:PhCN$.

also exists. The broad CH_3Pb peak which appears in an intermediate position with respect to the chemical shifts of CH_3Pb in tetramethyllead and in complex (I) confirms the rapid exchange of alkyl groups which occurs between organolead compounds. This peak changes its position depending on the tetramethyllead-to-complex (I) concentration ratio.

On decreasing the temperature to about −70° the broad peak due to CH_3Pb methyl groups resolves into two sharp peaks corresponding to the chemical shifts for pure tetramethyllead and complex (I) (Table 1, Fig. 3).

At room temperature the occurrence of broad diffuse CH_3Al peaks (Table 1, Fig. 3) indicates: (1) that the exchange of alkyl groups between aluminium and lead proceeds slowly enough for the peaks due to CH_3Pb and CH_3Al to be observable; and (2) that a rapid exchange of the alkyl groups combined with the aluminium atoms

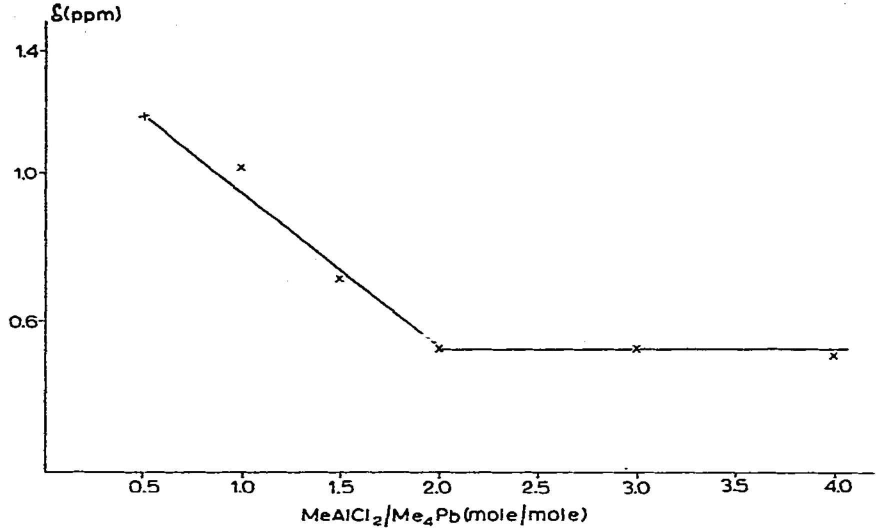
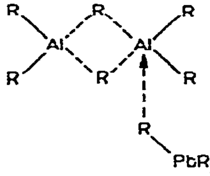


Fig. 4. Change of the chemical shift of CH$_3$Pb protons in the NMR spectra of the products of the reaction of Me$_4$Pb with MeAlCl$_2$, as a function of the reactant mole ratio.

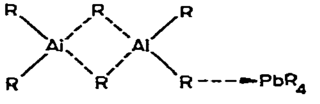
occurs between the organoaluminium compounds (MeAlCl$_2$, Me$_2$AlCl, Me$_3$PbCl:AlMeCl$_2$) present in the reaction mixture. At low temperatures the exchange of the methyl groups combined with aluminium is hindered and this results in the NMR spectrum exhibiting two peaks (Table 1, series III).

Addition of a Lewis base to the reaction mixture stops the exchange of chlorine and alkyl groups completely, as is evident from the NMR spectral and quantitative analytical data. A study of the reaction system involving tetramethyllead, methylaluminium dichloride and benzonitrile, over a wide range of temperatures (25–70°) and reactants mole ratios (Table 1, series IV), revealed no signs of chlorine exchange. Similarly, in a system involving tetramethyllead, methylaluminium dichloride and potassium chloride, the tetramethyllead concentration remains constant despite the presence of a large excess of complex and an increase in the reaction temperature to 135° (Table 3).

The above data provide conclusive evidence regarding the mechanism of the exchange of chlorine and alkyl groups between tetramethyllead and organoaluminium compounds. The exchange begins trhough an attack of the alkyl group combined with the lead atom on the aluminium atom. This is represented as (I) in the scheme. In case (I) the tetracoordinated aluminium atom and the alkyl group initially united with the lead atom are the acceptor and donor, respectively, while in case (II) the CH$_3$Pb and the CH$_3$Al alkyl groups are the acceptor and donor, respectively.

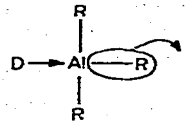


(I) Yes



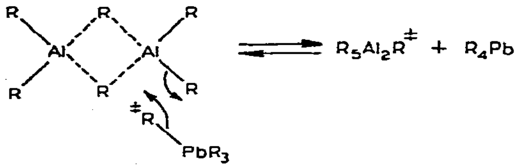
(II) No

If the reaction occurred through the attack of the alkyl group attached to aluminium atom (II), the complex of the organoaluminium compound with a strong Lewis base would be more active than the free organoaluminium compound, *i.e.*:



leading to facile abstraction. In actual fact addition of a Lewis base to the reaction mixture completely inhibits the exchange.

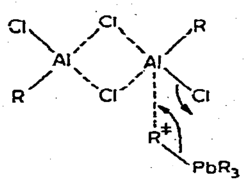
It follows, therefore, that the reacting system may be represented as:



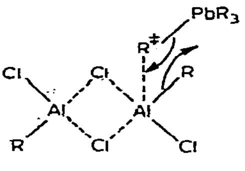
This reaction proceeds slowly, principally because of the weak acceptor properties of the tetracoordinate aluminium atom and the low polarity of the R–Pb bond. Despite the overall low rate of exchange of alkyl groups the observed changes in peak width (resolution) and in chemical shifts of the CH_3Al groups lead to the conclusion that the rate of alkyl group exchange depends on the acceptor properties of the organoaluminium compound and increases as:

$$R_3Al < R_2AlCl < RAlCl_2$$

In the presence of methylaluminium dichloride which possesses more strongly pronounced acceptor properties the exchange is faster and involves the terminal chlorine atoms.

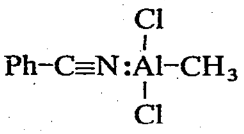


R —► Cl exchange



R —► R exchange

Addition of a Lewis base to this system leads to the formation of a complex



$$\text{Ph–C}\equiv\text{N:}\underset{\text{Cl}}{\overset{\text{Cl}}{\text{Al}}}\text{–CH}_3$$

in which the aluminium atom, though tetracoordination as in the pure dimer, has little or no acceptor properties. For these reasons, in the presence of a Lewis base the exchange of both alkyl groups and chlorine atoms must become hindered.

In summary, it may be concluded that in the systems studied several simultaneous reactions occur, *viz.*:

1. Exchange of alkyl groups between organoaluminium and organolead compounds.
2. Chlorination of tetramethyllead by methylaluminium dichloride.
3. Formation of the $Me_3PbCl:AlMeCl_2$ complex.
4. Exchange of alkyl groups between organoaluminium compounds.
5. Exchange of alkyl groups in the organolead compounds.

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