*Journal of Organometallic Chemistry*, 92 (1975) 175—180

# REDISTRIBUTION OF ALKYL GROUPS IN ORGANOLEAD COMPOUNDS IN THE PRESENCE OF METHYLALUMINIUM DICHLORIDE WITH TRIMETHYLLEAD CHLORIDE, DIMETHYLLEAD DICHLORIDE, AND LEAD CHLORIDE

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(Received January 14th, 1975)

## Summary

The redistribution reaction of alkyl groups between tetramethyl- and tetraethyl-lead catalysed by methylaluminium dichloride complexes with trimethyllead chloride, dimethyllead dichloride, and lead chloride has been studied.

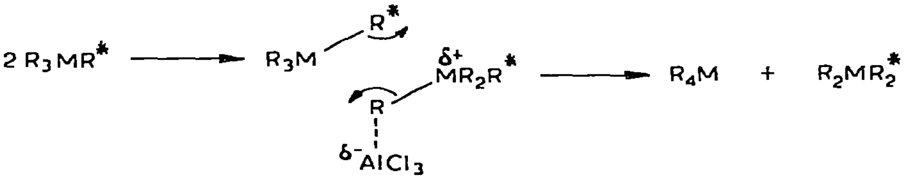
On the basis of the results obtained the active catalytic complex has been defined, and a reaction mechanism for the redistribution is proposed.

## Introduction

Many authors have studied the exchange reaction of alkyl groups in organolead compounds. Calingaert [1,2] ascertained that the exchange reaction yields a few mixed alkyls. The quantities of individual compounds are in line with Gauss's distribution curve.

In the case of the catalytic redistribution reaction of alkyl groups between tetramethyl- and tetraethyl-lead proceeding in the presence of small amounts of aluminium chloride, methylaluminium dichloride, or dimethylaluminium chloride, besides methylethyllead compounds also trialkyllead chloride and lead chloride (products of the reaction between the catalyst and tetraalkyllead) are obtained [3].

In 1959 Russell [4,5] proposed the following mechanism for the redistribution reaction (eqn. 1):



$$2\,R_3MR^* \longrightarrow R_3M \overset{R^*}{\cdots} \overset{\delta+}{M}R_2R^* \underset{\overset{\delta-}{AlCl_3}}{\overset{R}{\cdots}} \longrightarrow R_4M + R_2MR_2^* \qquad (1)$$

Pollard, Nickless and Uden [6] studied the exchange reaction of alkyl groups between organometallic compounds of the Group IV elements in the presence of catalytic quantities of aluminium chloride using chromatographic methods. They proposed an exchange reaction mechanism in line with Russell's proposition.

The purpose of the present work was to identify the active catalytic complex and to study the mechanism of the redistribution of alkyl groups in organolead compounds in the presence of organoaluminium compounds.

## Results and discussion

From our previous studies it was found that one of the products of the reaction between tetramethyllead and methylaluminium chloride compounds is the trimethyllead chloride—methylaluminium dichloride complex [7] (compound III, see eqns. 2 and 4). In the quoted work [7] it is also asserted that organoaluminium compounds containing a halogen atom catalyze the rapid exchange reaction of alkyl groups in organolead compounds.

In the present work in the course of direct synthesis we obtained methylaluminium dichloride complexes with trimethyllead chloride [8], dimethyllead dichloride, and lead chloride [9]. The redistribution reaction of methyl and ethyl groups between tetramethyl- and tetraethyl-lead in the presence of small quantities of methylaluminium dichloride, dimethylaluminium chloride, and of the complexes mentioned above has been studied. It has also been established that the redistribution reaction does not occur in the presence of trimethylaluminium (Table 4).

The results obtained show that the redistribution reaction between tetramethyl- and tetraethyl-lead proceeds with almost quantative yields ($\approx 95$ mol.%) in the presence of methylaluminium dichloride complexes with trimethyllead chloride (Table 1), dimethyllead dichloride (Table 2), and lead chloride (Table 3) at room temperature with a reaction time of 10-30 min.

A variation in the composition of the product mixture may be obtained by changing the reactant molar ratio $Me_4Pb/Et_4Pb$ from 0.5 to 2. An excess of the reactants (tetramethyl- or tetraethyl-lead) of more than 1.5/1 molar ratio causes an increased content of these derivatives in the product mixture; the component occurring in a lesser quantity reacts almost completely. Methylaluminium dichloride complexes with trimethyllead chloride, dimethyllead dichloride, and lead chloride show similar catalytic activities.

In the light of these data the reaction mechanism of alkyl group redistribution between tetramethyl- and tetraethyl-lead in the presence of methylaluminium chloride compounds may be represented by the following equations:

$$R_4Pb + CH_3AlCl_2 \rightleftharpoons \underset{(I)}{R_3PbCl} + R(CH_3)AlCl \qquad (2)$$

$$R_3PbCl + CH_3AlCl_2 \rightleftharpoons \underset{(II)}{R_2PbCl_2} + R(CH_3)AlCl \qquad (3)$$

An organoaluminium compound containing a chlorine atom, e.g. $(CH_3)_2AlCl$ or $CH_3AlCl_2$, exchanges methyl groups and chlorine atoms with tetraalkyllead, yielding trialkyllead chloride (I, eqn. 2) and dialkyllead dichloride (II, eqn. 3).

TABLE 1

COMPOSITION OF THE PRODUCTS OF THE REDISTRIBUTION REACTION PROCEEDING IN THE PRESENCE OF COMPLEX III AS A FUNCTION OF TEMPERATURE

Molar ratio $(CH_3)_4Pb/(C_2H_5)_4Pb$ 1/1; reaction time 10 min

| Quantity of catalyst III (mol) per mol Pb | Reaction temperature (°C) | Composition of reaction products (mol. %) | | | | |
|---|---|---|---|---|---|---|
| | | $Me_3PbEt$ | $Me_2PbEt_2$ | $MePbEt_3$ | $Me_4Pb$ | $Et_4Pb$ |
| 0.0166 | 20 | 17.17 | 16.89 | 23.08 | 23.56 | 19.22 |
| 0.05 | 20 | 20.41 | 52.97 | 19.08 | 3.40 | 4.14 |
| 0.05 | 40 | 28.30 | 46.25 | 18.92 | 2.85 | 3.69 |
| 0.05 | 60 | 26.38 | 48.72 | 19.38 | 2.71 | 2.82 |

TABLE 2

COMPOSITION OF THE PRODUCTS OF THE REDISTRIBUTION REACTION PROCEEDING IN THE PRESENCE OF COMPLEX IV AS A FUNCTION OF THE MOLAR RATIO OF THE REACTANTS

Reaction temperature 20°C; reaction time 10 min; complex IV (mol)/Pb (mol) 0.05

| Molar ratio $Me_4Pb/Et_4Pb$ | Composition of reaction products (mol. %) | | | | |
|---|---|---|---|---|---|
| | $Me_3PbEt$ | $Me_2PbEt_2$ | $MePbEt_3$ | $Me_4Pb$ | $Et_4Pb$ |
| 1/2 | 6.16 | 42.80 | 41.12 | 0.18 | 9.74 |
| 1/1 | 27.58 | 52.55 | 14.81 | 3.63 | 1.45 |
| 2/1 | 47.50 | 30.02 | 3 94 | 18.30 | |
| 2/1[a] | 46.75 | 29.30 | 6.72 | 17.21 | |

[a] Reaction time 30 min.

TABLE 3

COMPOSITION OF THE PRODUCTS OF THE REDISTRIBUTION REACTION PROCEEDING IN THE PRESENCE OF COMPLEX V AS A FUNCTION OF THE MOLAR RATIO OF THE REACTANTS

Reaction temperature 20°C; reaction time 10 min; complex V (mol)/Pb (mol) 0.05

| Molar ratio $Me_4Pb/Et_4Pb$ | Composition of reaction products (mol. %) | | | | |
|---|---|---|---|---|---|
| | $Me_3PbEt$ | $Me_2PbEt_2$ | $MePbEt_3$ | $Me_4Pb$ | $Et_4Pb$ |
| 1/1 | 4.86 | 41.25 | 42.55 | 0.23 | 10.62 |
| 1/1.5 | 9.00 | 40.15 | 44.35 | | 6.42 |
| 1/1 | 26.00 | 50.00 | 18.68 | 3.02 | 2.32 |
| 2/1 | 45.00 | 34.82 | 3.53 | 16.59 | |

TABLE 4

COMPOSITION OF THE PRODUCTS OF THE REDISTRIBUTION REACTION PROCEEDING IN THE PRESENCE OF VARIOUS CATALYSTS

Reaction temperature 20°C, reaction time 10 min; molar ratio $(CH_3)_4Pb/(C_2H_5)_4Pb$ 1/1; catalyst (mol)/Pb (mol) 0.05

| Catalyst | Composition of reaction products (mol. %) | | | | |
|---|---|---|---|---|---|
| | $Me_3PbEt$ | $Me_2PbEt_2$ | $MePbEt_3$[a] | $Me_4Pb$ | $Et_4Pb$ |
| $MeAlCl_2$ | 26.81 | 47.65 | 20.40 | 2.81 | 2.58 |
| $Me_2AlCl$ | 23.62 | 48.20 | 20.10 | 3.06 | 5.00 |
| $Me_3Al$ | | | | 49.80 | 50.20 |

Further chlorination of dialkyllead dichloride (II) yields lead chloride. Calingaert and Soroos [3] isolated trimethyllead chloride and lead chloride in the reaction of tetramethyllead with methylaluminium dichloride. The trialkyllead chloride, dialkyllead dichloride and lead chloride obtained in the reactions described above form complexes III, IV, V with methylaluminium dichloride according to eqns. 4-6:

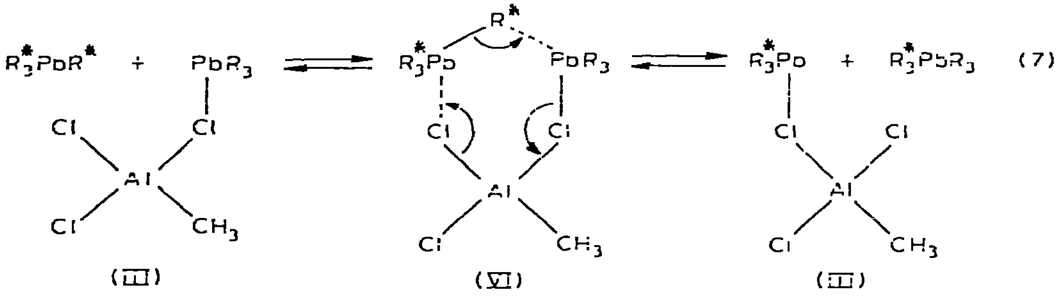
$$R_3PbCl + CH_3AlCl_2 \rightarrow \underset{(III)}{R_3PbCl \cdot Al(CH_3)Cl_2} \qquad (4)$$

$$R_2PbCl_2 + 2CH_3AlCl_2 \rightarrow \underset{(IV)}{R_2PbCl_2 \cdot 2\,Al(CH_3)Cl_2} \qquad (5)$$

$$PbCl_2 + 2\,CH_3AlCl_2 \rightarrow \underset{(V)}{PbCl_2 \cdot 2\,Al(CH_3)Cl_2} \qquad (6)$$

Our studies show that complexes III-V act as catalysts in the alkyl group redistribution.

The mechanism of the redistribution reaction in the presence of complex III, for example, may be represented by eqn. 7:



As a result of reaction 7 an exchange of alkyl groups in organolead compounds and regeneration of the catalyst takes place. The stages leading to the formation of the active complex VI are rapid. Due to this a small quantity of complexes III, IV and V assure a complete exchange of alkyl groups in line with Gauss's function. Reaction 7 should be regarded as dynamic, in which the methyl group from the organoaluminium compound will be in a position convenient for a rearrangement. As a result of this reaction, among others, aluminium chloride is formed, which immediately reacts with the organolead compound according to eqn. 8 and then to eqns. 2-6, reproducing catalysts III-V.

The role of methylaluminium dichloride or dimethylaluminium chloride in the redistribution reaction is that in the first stage they react with tetraalkyllead yielding trialkyllead chloride, dialkyllead dichloride and lead chloride, and afterwards form with them complexes III-V. In these complexes a partition of charge between the aluminium and lead atoms takes place with the formation of a partial positive charge on the lead atom and a negative one on the aluminium atom. Such a charge partition facilitates the formation of active complex

VI in which a synchronous displacement of the alkyl and chloride groups with electron pairs takes place.

The proposed reaction mechanism confirms Russell's studies [4,5], in which he used aluminium chloride as the catalyst. He ascertained the presence of organoaluminium compounds in the reaction mixture (eqn. 8):

$$R_4Pb + AlCl_3 \rightarrow R_3PbCl + RAlCl_2 \qquad (8)$$

Our observation that trimethylaluminium does not catalyze the exchange reaction of alkyl groups in organolead compounds (Table 4) is in line with the proposed mechanism.

## Experimental

### *Synthesis of the methylaluminium dichloride—trimethyllead chloride complex $(CH_3)_3PbCl \cdot CH_3AlCl_2$ (III)*

To a nitrogen-flushed three-necked flash equipped with a stirrer, cold trap, and dropping funnel, were introduced trimethyllead chloride and methylaluminium dichloride with the molar ratio 1/1 in benzene. The reactants were stirred and heated until the precipitate dissolved. The post-reaction mixture was filtered and concentrated under reduced pressure. The crystalline complex was recrystallized from benzene and creamy-yellow crystals (m.p. 52-58°C) were obtained. Analysis found: Pb, 49.1; Al, 6.7; molar ratio Pb/Al = 1/1.02. $(CH_3)_3PbCl \cdot CH_3AlCl_2$ calcd.: Pb, 51.7; Al, 6.7.

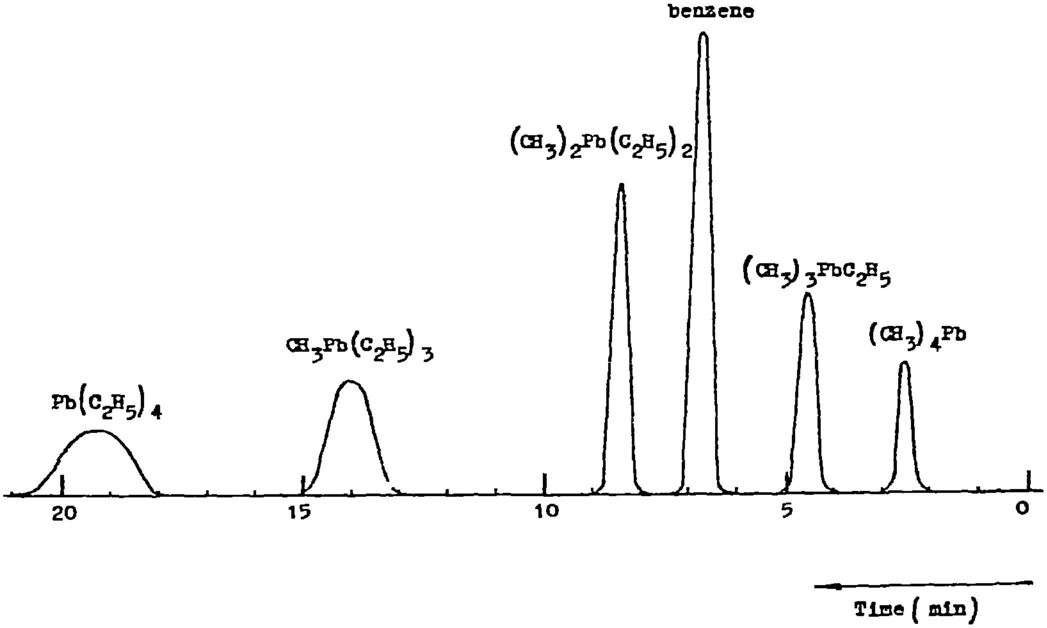


Fig. 1. A typical chromatogram of the mixture after the reaction is completed. Length of column: 3 m; i.d. 4 mm; packing: 10% glycol 1500 on diatomite CQ. Operating conditions: temp. 80°C; $p_{Ar}$ 2 atm.

### *Synthesis of the methylaluminium dichloride—dimethyllead dichloride complex* $(CH_3)_2PbCl_2 \cdot 2\, CH_3AlCl_2$ *(IV).*

This was obtained as above but the molar ratio methylaluminium dichloride/dimethyllead dichloride was 2/1. The crystal complex has a m.p. 85-95°C. Analysis found: Pb, 39.1; Al, 9.94; molar ratio Pb/Al = 1/1.97. $(CH_3)_2PbCl_2 \cdot 2\, CH_3AlCl_2$ calcd.: Pb, 38.8; Al, 10.1.

### *Synthesis of the methylaluminium dichloride—lead chloride complex* $PbCl_2 \cdot 2\, CH_3AlCl_2$ *(V)*

This was obtained as for compound IV. White crystals (m.p. 135-140°C (dec.) were obtained. Analysis found: Pb, 39.8; Al, 10.5; molar ratio Pb/Al = 1/2.01. $PbCl_2 \cdot 2\, CH_3AlCl_2$ calcd.: Pb, 41.1; Al, 10.7.

### *Studies of the catalytic redistribution of alkyl groups*

Complex III, IV or V was placed in the reactor under nitrogen. Then benzene solutions of tetramethyl- and tetraethyl-lead with the determined molar ratio were added. The reactor and its contents were thermostatted at the required temperature. After the reaction was complete the mixture was hydrolyzed and the organic layer separated. After drying, the organolead compounds in the organic layer were determined chromatographically using a Gas Chromatograph G CH F 18.3 (Willy Gide) apparatus. A typical chromatogram is given in Fig. 1.

Aluminium was determined by sodium versenate in acid. Lead was determined gravimetrically as $PbSO_4$.

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