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

SYNTHESIS OF ORGANOLEAD COMPOUNDS
V. DIFFICULTIES IN THE SYNTHESIS OF TETRANEOPENTYLLEAD

KENNETH C. WILLIAMS
Ethyl Corporation, Baton Rouge, Louisiana 70821 (U.S.A.)

(Received March 19th, 1970)

SUMMARY

The reaction of neopentylmagnesium chloride with lead chloride in tetrahydrofuran as solvent gives a reddish-brown solution which is characteristic of trineopentylplumbylmagnesium chloride. The role of this complex in earlier unsucessful attempts to prepare tetraneopentyllead has been investigated and elucidated.

INTRODUCTION

Recent reports from this laboratory have described a method of preparation of trialkylplumbylmagnesium chlorides from lead(II) salts and Grignard reagents in tetrahydrofuran solution[1,2]:

$$3\,\mathrm{RMgCl} + \mathrm{PbX_2} \xrightarrow{\mathrm{THF}} \mathrm{R_3PbMgCl} + \mathrm{MgCl_2} + \mathrm{MgX_2} \qquad (1)$$

These complexes are relatively stable and highly reactive toward alkyl chlorides:

$$\mathrm{R_3PbMgCl} + \mathrm{R^1Cl} \xrightarrow{\mathrm{THF}} \mathrm{R_3R^1Pb} + \mathrm{MgCl_2} \qquad (2)$$

The above reactions can be carried out in one step by addition of the lead(II) salt to a mixture of Grignard reagent and alkyl halide to give tetraalkyllead compounds in high yields without formation of by-product lead metal:

$$3\,\mathrm{RMgCl} + \mathrm{R^1Cl} + \mathrm{PbX_2} \rightarrow \mathrm{R_3R^1Pb} + 2\,\mathrm{MgCl_2} + \mathrm{MgX_2} \qquad (3)$$

Normally, the reaction of a Grignard reagent with lead chloride proceeds according to:

$$4\,\mathrm{RMgCl} + 2\,\mathrm{PbCl_2} \rightarrow \mathrm{R_4Pb} + \mathrm{Pb} + 4\,\mathrm{MgCl_2} \qquad (4)$$

Previous attempts to prepare tetraneopentyllead from lead chloride have been unsuccessful. Zimmer and Homberg[3], and Singh[4] attempted to prepare tetraneopentyllead from the reaction of neopentylmagnesium chloride with lead chloride; however, the only organolead compounds which were isolated from the reaction were hexaneopentyldilead and trineopentyllead chloride. Zimmer and Homberg[3] were also unsuccessful in an attempt to prepare tetraneopentyllead by the reaction of neopentylmagnesium chloride with trineopentyllead iodide; the only product obtained was hexaneopentyldilead. In an earlier investigation we attempted to prepare tetraneopentyllead by the reaction of neopentylmagnesium chloride and lead tetraacetate; however, this reaction gave only hexaneopentyldilead and a trace of trineopentyllead chloride[5].

Singh[6] has recently reported the preparation of tetraneopentyllead in almost quantitative yield from the reaction of neopentylmagnesium chloride with trineopentyllead bromide in diethyl ether/tetrahydrofuran mixed solvent.

$$[(CH_3)_3CCH_2]_3PbBr + (CH_3)_3CCH_2MgCl \rightarrow [(CH_3)_3CCH_2]_4Pb + MgBrCl \quad (5)$$

In view of the earlier difficulties that were encountered in the synthesis of tetraneopentyllead from lead chloride and the ease of formation of tetrakis[(trimethylsilyl)methyl]lead[2,7], an investigation was begun to study these phenomena. Some interesting reactions were discovered and the synthesis of tetraneopentyllead from an inorganic lead(II) salt was accomplished.

DISCUSSION

When lead chloride is added to neopentylmagnesium chloride in tetrahydrofuran a reddish-brown solution is obtained, which is due to formation of trineopentylplumbylmagnesium chloride. This conclusion is consistent with previous results obtained for reaction of alkyl-Grignard reagents with lead(II) salts and was readily shown by reaction of the reddish-brown solution with (chloromethyl)trimethylsilane. In this latter reaction a new silicon substituted organolead compound was formed in high yield.

$$[(CH_3)_3CCH_2]_3PbMgCl + ClCH_2Si(CH_3)_3 \rightarrow [(CH_3)_3CCH_2]_3[(CH_3)_3SiCH_2]Pb + MgCl_2 \quad (6)$$

Trineopentyl[(trimethylsilyl)methyl] lead is a white crystalline solid which melts at 79–82°.

In a similar reaction, an attempt was made to react trineopentylplumbylmagnesium chloride with neopentyl chloride; however, the only lead products obtained were hexaneopentyldilead and lead metal. These products were probably formed by thermal decomposition of trineopentylplumbylmagnesium chloride:

$$[(CH_3)_3CCH_2]_3PbMgCl \rightarrow [(CH_3)_3CCH_2]_2Pb + RMgCl \quad (7)$$

$$3\,[(CH_3)_3CCH_2]_2Pb \rightarrow [(CH_3)_3CCH_2]_6Pb_2 + Pb \quad (8)$$

These equations would result in two-thirds of the lead chloride being converted to hexaneopentyldilead, which is consistent with the 65% conversion found experimentally. The lack of formation of tetraneopentyllead can be attributed to the unreactive nature of neopentyl chloride. On the other hand, the reaction of trineopentylplumbylmagnesium chloride with neopentyl iodide gave essentially a quantitative yield (98%) of hexaneopentyldilead without any lead metal being formed. These results indicate that a metal–halogen exchange occurs which results in hexaneopentyldilead being formed via a coupling reaction.

$$[(CH_3)_3CCH_2]_3PbMgCl + (CH_3)_3CCH_2I \rightarrow [(CH_3)_3CCH_2]_3PbI + (CH_3)_3CCH_2MgCl \quad (9)$$

$$[(CH_3)_3CCH_2]_3PbMgCl + [(CH_3)_3CCH_2]_3PbI \rightarrow [(CH_3)_3CCH_2]_6Pb_2 + MgICl \quad (10)$$

A metal–halogen exchange process involving Grignard reagents has been postulated for other systems[8], and the above scheme readily accounts for the formation of hexaneopentyldilead and the lack of formation of lead metal. A small amount of metal–halogen exchange would also account for the formation of trineopentyllead chloride in the reaction of neopentylmagnesium chloride and lead chloride[3].

Reaction of trineopentylplumbylmagnesium chloride with neopentyl bromide in tetrahydrofuran gave hexaneopentyldilead (64%), tetraneopentyllead (11%), and a small amount of lead metal. The relatively high yield of hexaneopentyldilead with only a small amount of lead metal being produced indicates that metal–halogen exchange followed by coupling occurred together with some thermal decomposition of the complex. The tetraneopentyllead may have been formed as expected:

$$[(CH_3)_3CCH_2]_3PbMgCl + (CH_3)_3CCH_2Br \rightarrow [(CH_3)_3CCH_2]_4Pb + MgBrCl \quad (11)$$

or by metal–halogen exchange followed by reaction with the Grignard reagent:

$$[(CH_3)_3CCH_2]_3PbMgCl + (CH_3)_3CCH_2Br \rightarrow [(CH_3)_3CCH_2]_3PbBr + (CH_3)_3CCH_2MgCl \quad (12)$$

$$[(CH_3)_3CCH_2]_3PbBr + (CH_3)_3CCH_2MgCl \rightarrow [(CH_3)_3CCH_2]_4Pb + MgBrCl \quad (13)$$

Reaction (13) was reported by Singh[6] to give tetraneopentyllead in almost quantitative yield in diethyl ether/tetrahydrofuran; when repeated in this study using tetrahydrofuran as solvent, a 91% yield was obtained.

Zimmer and Homberg[3] attempted to prepare tetraneopentyllead from the reaction of trineopentyllead iodide and neopentylmagnesium chloride in tetrahydrofuran at relatively high temperature (addition at ambient temperature followed by tetrahydrofuran reflux). The only lead product isolated by these investigators was hexaneopentyldilead. These results are consistent with the metal–halogen exchange postulated above [eqn. (9)] for the reaction of trineopentylplumbylmagnesium chloride with neopentylmagnesium iodide; however, in this experiment the exchange occurred in the opposite direction. Therefore, eqn. (9) should probably be written as an equilibrium reaction:

$$[(CH_3)_3CCH_2]_3PbI + (CH_3)_3CCH_2MgCl \rightleftarrows [(CH_3)_3CCH_2]_3PbMgCl + (CH_3)_3CCH_2I \quad (14)$$

The reaction of trineopentyllead iodide with neopentylmagnesium chloride in tetrahydrofuran at −10° gave tetraneopentyllead in 54% yield. At this low temperature the metal–halogen exchange is slowed sufficiently to allow the reaction between trineopentyllead iodide and neopentylmagnesium chloride to proceed in the desired manner.

TABLE 1

PROTON MAGNETIC RESONANCE DATA[a]

Compound	τ (ppm)				$J(^{207}Pb\text{-}H)$ (Hz)		
	$(CH_3)_3Si$	CH_2Si	$(CH_3)_3C$	CH_2C	CH_2Si	$(CH_3)_3C$	CH_2C
$[(CH_3)_3CCH_2]_4Pb$			8.99	8.26		5.0	34.0
$[(CH_3)_3CCH_2]_3[(CH_3)_3SiCH_2]Pb$	9.96	9.57	8.97	8.25	64.0	5.0	37.0

[a] The spectra were taken in 10% CCl_4 solutions with TMS as an internal standard.

Table 1 contains a tabulation of the observed PMR data for tetraneopentyllead and trineopentyl[(trimethylsilyl)methyl]lead. The data for tetraneopentyllead are consistent with that previously reported by Singh[6]. No long range coupling constant ($^{207}Pb\text{-}C\text{-}Si\text{-}C\text{-}H$) in trineopentyl[(trimethylsilyl)methyl]lead was observed. The long range coupling constant in this compound is probably small and not resolved, which is consistent with the small value reported for (trimethylplumbyl)(trimethylsilyl)methane[9]. Singh reported the melting point of tetraneopentyllead to be 139–141° when purified by sublimation. We found that after several sublimations, tetraneopentyllead gave a rather broad melting range from 137–141°, but after several recrystallizations from acetone a sharp melting point of 145–147° was obtained.

EXPERIMENTAL

All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride before use. The PMR spectra were recorded using a Varian Associates A-60 spectrometer. Molecular weights were determined by the differential vapor pressure technique in benzene solution at 37° using a Mechrolab Model 302 vapor pressure osmometer.

The reactions were performed in a 500 ml or 1000 ml three-necked, round-bottom flask equipped with condenser (Dewar filled with dry ice/acetone) and magnetic or paddle stirrer. The lead salt was added from a 50 ml round-bottom flask connected to the reaction vessel by a short piece of Gooch tubing. Neopentylmagnesium chloride was prepared from magnesium turnings and a slight excess of neopentyl chloride. The reaction was initiated with ethylene dibromide at 60°; it was found that continued heating was necessary to complete the reaction. Under these conditions no problem was encountered in the preparation. Other investigators have had difficulty in preparing neopentylmagnesium chloride[10].

Lead contents of the new organolead derivatives were determined as previously described[2]. Hexaneopentyldilead was identified by comparison of its PMR spectrum with that previously reported[3].

All yields are reported as the percent conversion of lead chloride to the organolead product.

1. *Preparation of trineopentylplumbylmagnesium chloride*

Neopentylmagnesium chloride was prepared from 4.0 g (0.167 g-atom) of magnesium turnings and an equivalent amount of neopentylchloride in 300 ml of

THF. The Grignard solution was treated slowly at 5° with 13.9 g (0.05 mole) of lead chloride. A dark reddish-brown, homogeneous solution of the complex was obtained. Derivatives of the compound were prepared as described below.

2. *Reaction of trineopentylplumbylmagnesium chloride with (chloromethyl)trimethylsilane*

Trineopentylplumbylmagnesium chloride was prepared using the quantities and procedure described above. To the complex was added 10.0 g (0.075 mole) of (chloromethyl)trimethylsilane and the solution was slowly warmed to room temperature. After 30 min the mixture was heated at 50° for 10 min; the color disappeared, and a small amount of lead metal was formed (0.2 g). After hydrolysis the THF was removed by distillation. A heavy yellow oil which separated from the aqueous phase was extracted into petroleum ether (b.p. 37–54°). Fractional crystallization from petroleum ether gave a yellow fraction (2.3 g) which was identified as hexaneopentyldilead and a white fraction (16.0 g or 63.3% yield) which was identified as $[(CH_3)_3CCH_2]_3$-$[(CH_3)_3SiCH_2]Pb$. This new organolead compound melted at 79–82°. (Found: C, 44.99; H, 8.55; Pb, 40.65; mol.wt., 520. $C_{19}H_{44}PbSi$ calcd.: C, 44.93; H, 8.73; Pb, 40.79%; mol.wt., 508.)

3. *Reaction of trineopentylplumbylmagnesium chloride with neopentyl chloride*

Trineopentylplumbylmagnesium chloride was prepared from 13.9 g (0.05 mole) of lead chloride in 400 ml of THF. To the complex was added 20 ml of neopentyl chloride over a 15 min period. The mixture was slowly warmed to 60° and stirred for 2½ h; during which time the color disappeared and a small amount of lead metal was formed. The mixture was hydrolyzed and more lead metal was formed. The THF was removed by distillation and the yellow solid which floated on the aqueous phase was extracted into petroleum ether (b.p. 37–54°). Evaporation of the petroleum ether yielded 13.8 g (64.8% yield) of hexaneopentyldilead (m.p. 204–205°).

4. *Reaction of trineopentylplumbylmagnesium with neopentyl iodide*

Trineopentylplumbylmagnesium chloride was prepared from 27.8 g (0.1 mole) of lead chloride in 500 ml of THF. To the reddish-brown complex was added dropwise 20.0 g (0.1 mole) of neopentyl iodide; the reddish-brown color of the complex disappeared within 15 min. The solution was warmed to ambient temperature and hydrolyzed. The THF was removed by distillation, and the yellow solid was extracted into petroleum ether. Evaporation of the ether yielded 41.5 g (97.5% yield) of hexaneopentyldilead.

5. *Reaction of trineopentylplumbylmagnesium chloride with neopentyl bromide*

Trineopentylplumbylmagnesium chloride was prepared from 13.9 g (0.05 mole) of lead chloride in 300 ml of THF. To the complex was added 15 ml of neopentyl bromide at −15°. The cold bath was removed and the mixture was allowed to slowly warm to ambient temperature with stirring. The mixture was stirred at ambient temperature for 15 min, and then heated at reflux for 15 min; the solution retained some of its reddish-brown color and a small amount of lead metal was formed. The solution was hydrolyzed and the THF was removed by distillation. The yellow product was extracted into petroleum ether (b.p. 37–54°). Fractional crystallization from petroleum ether gave 13.3 g (64%) of hexaneopentyldilead and 2.6 g (11%) of tetraneopentyllead. The more soluble tetraneopentyllead was identified by comparison (melting point, NMR spectrum) with a sample prepared as described by Singh[6].

6. *Reaction of neopentylmagnesium chloride with trineopentyllead iodide*

To a stirred solution of 12.0 g (0.0145 mole) of hexaneopentyldilead in 250 ml of THF was added one percent iodine solution in THF until the yellow color of the lead compound was discharged. The resulting trineopentyllead iodide solution was added dropwise to a Grignard solution prepared from 1.5 g (0.062 g-atom) of magnesium and an equivalent amount of neopentyl chloride (0.062 mole) in 100 ml of THF at −10°. The mixture was heated to 60° and stirred for 10 min. After hydrolysis the THF was removed by distillation and the yellow organolead product was extracted into petroleum ether. After several fractional crystallizations from petroleum ether gave 3.2 g of a white fraction (least soluble) and 7.6 g of a light yellow fraction. The white product was identified as trineopentyllead iodide, and the light yellow fraction was identified as tetraneopentyllead (54% yield) containing a trace of hexaneopentyldilead.

ACKNOWLEDGEMENT

The author gratefully acknowledges Dr. M. B. Smith for the molecular weight determinations, Mr. S. R. Henderson and W. J. Easley for elemental analyses and Dr. D. W. Imhoff for the PMR spectra.

REFERENCES

1 K. C. Williams, *J. Organometal. Chem.*, 22 (1970) 141.
2 K. C. Williams, *J. Organometal. Chem.*, 23 (1970) 465.
3 H. Zimmer and O. A. Homberg, *J. Org. Chem.*, 31 (1967) 947.
4 G. Singh, *J. Org. Chem.*, 31 (1967) 949.
5 K. C. Williams, *J. Org. Chem.*, 32 (1968) 4062.
6 G. Singh, *J. Organometal. Chem.*, 11 (1968) 133.
7 D. Seyferth and W. Freyer, *J. Org. Chem.*, 26 (1961) 2604.
8 N.K. Patel and H. J. Harwood, *J. Org. Chem.*, 32 (1967) 2999.
9 H. Schmidbaur, *Chem. Ber.*, 97 (1964) 270.
10 F. M. Rossi, P. A. McCusker and G. F. Hennion, *J. Org. Chem.*, 32 (1967) 1233.