

INVESTIGATIONS ON ORGANOLEAD COMPOUNDS V*. LEAD-LEAD BOND CLEAVAGE REACTIONS OF HEXAPHENYLDI- LEAD**

L. C. WILLEMSSENS AND G. J. M. VAN DER KERK

Institute for Organic Chemistry TNO, Utrecht (The Netherlands)

(Received July 6th, 1968)

SUMMARY

It has been shown that a number of nucleophilic and weakly electrophilic reagents (organolithium and organomagnesium compounds, metallic lithium, potassium permanganate, sodium ethoxide, diaryl disulphides, sulphur, ozone, hypochlorous acid and iodine/iodide) selectively cleave the lead-lead bond of hexaphenyldilead. No lead-phenyl bond cleavage occurs with these reagents. The reactions with lithium, potassium permanganate, diaryl disulphides, ozone, hypochlorous acid and iodine/iodide form useful synthetic procedures for the preparation of triphenyllead derivatives from the readily available hexaphenyldilead.

INTRODUCTION

In compounds of the type $R_3Pb-PbR_3$ two kinds of relatively labile bonds are present, viz. lead-carbon and lead-lead. These bonds are readily broken, as appears from numerous reactions of organolead compounds^{3,4,5}.

It is generally assumed that the lead-lead bond is still more readily cleaved than the lead-carbon bond. Thus, in hexaalkyldilead compounds cleavage of the lead-lead bond is always the first step, e.g., halogenation produces trialkyllead halides^{2b}.

On the other hand, we have found that with hexaphenyldilead both kinds of cleavage can occur depending on the reagent used. Thus, strongly electrophilic reagents (halogens, hydrogen halides) cleave the lead-phenyl bond as well as the lead-lead bond^{2c}, followed by very complex secondary reactions which are not yet completely clear. This paper deals only with reactions in which exclusively the lead-lead bond is cleaved.

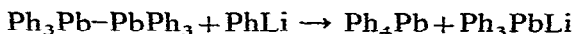
Since hexaphenyldilead is readily accessible from lead dichloride and phenylmagnesium bromide (see *experimental*), selective lead-lead bond cleavage reactions are useful for the preparation of triphenyllead derivatives (see Table 1).

* For Part IV see ref. 1.

** Partly described in dissertation of L. C. Willemsens, Utrecht, 1965; see also ref. 2a.

RESULTS AND DISCUSSION

It has been reported⁶ that hexaphenyldilead is cleaved by phenyllithium to produce tetraphenyllead and triphenylplumbyllithium

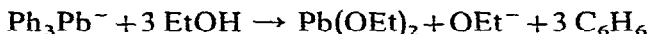
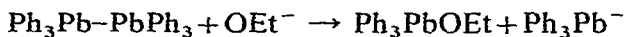


In agreement with this result we found that the addition of phenyllithium to an excess of hexaphenyldilead in tetrahydrofuran at room temperature results in a rapid reaction (immediate precipitation of tetraphenyllead and a negative Gilman test⁷ after 5 min). Subsequent treatment with benzyl chloride yielded 92% of tetraphenyllead and 83% of benzyltriphenyllead (based on phenyllithium). The corresponding reaction with phenylmagnesium bromide proceeds slower and even more slowly in diethyl ether.

From hexaphenyldilead and lithium in tetrahydrofuran triphenylplumbyllithium is formed⁸, a reaction which constitutes a convenient method for preparing this reagent^{2d}.

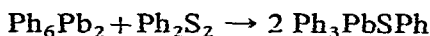
Potassium permanganate in acetone quantitatively cleaves the Pb-Pb bond of hexaphenyldilead to give bis(triphenyllead) oxide⁹. Clearly the first reaction step is a nucleophilic attack of the permanganate anion on the lead-lead bond.

Another nucleophilic reagent which gives rise to selective lead-lead bond cleavage is sodium ethoxide in benzene/ethanol. Lead diethoxide and triphenyllead ethoxide (both determined as the corresponding acetates) are formed in equimolar amounts. The following reaction equations account for the result:



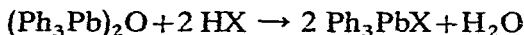
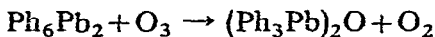
The intermediate triphenyllead anion is solvolyzed to give inorganic bivalent lead and benzene, analogous to the hydrolysis of triphenylplumbyllithium^{2c}.

All reagents so far discussed are nucleophiles. However, two successful cleavage reactions were found with reagents which in general do not show pronounced nucleophilic character. First, hexaphenyldilead reacts with a diaryl disulphide in refluxing wet benzene to give an (aryltio)triphenyllead, possibly via a four-centre transition state.



This cleavage is considerably aided by the presence of water. In dry benzene diphenyl disulphide cleaves only 23% of hexaphenyldilead, whereas under comparable conditions in wet benzene a yield of 75.5% of (phenylthio)triphenyllead is obtained.

The second case is the reaction of hexaphenyldilead with ozone, which produces bis(triphenyllead) oxide quantitatively¹⁰. With acids the oxide readily yields triphenyllead salts, and thus this reaction is a convenient method for the preparation of these salts (see Table 1).

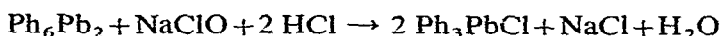


One may consider a radical mechanism for these last two cases. It should, however, be noted that the formation of triphenyllead radicals from hexaphenyl-

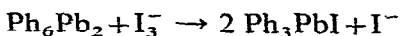
dilead, though often proposed in the literature because of its obviousness, has never been demonstrated unequivocally.

The reactions of hexaphenyldilead with sulphur and with dimethyl disulphide were also studied. The former reaction has been reported¹¹ to give a yield of 59% bis(triphenyllead) sulphide. We found that in these reactions the temperature must be so high (> 100°) that serious thermal decomposition of hexaphenyldilead occurs as a side-reaction (producing eventually tetraphenyllead and lead sulphide). From the reaction with sulphur without solvent at 140°, bis(triphenyllead) sulphide was isolated in 53% yield (plus 28% of tetraphenyllead). Refluxing hexaphenyldilead with dimethyl disulphide in benzene for 3 h gave only 10% of (methylthio)triphenyllead. During this period 20% of the hexaphenyldilead had decomposed to give tetraphenyllead and lead.

As already stated, strongly electrophilic reagents simultaneously cleave the lead-lead as well as the lead-phenyl bond in hexaphenyldilead, which results in a considerable decrease of the yield of the triphenyllead derivative (in some cases this could not be isolated in the pure state at all). However, with related reagents of lower electrophilicity, exclusive cleavage of the lead-lead bond occurs. Thus, hypochlorous acid (as a substitute for chlorine) produces triphenyllead chloride in nearly quantitative yield¹²:



Similarly, hexaphenyldilead reacts with iodine to produce only triphenyllead iodide, provided that excess potassium iodide is present during the reaction (in this way iodine reacts as the I_3^- ion):



It can be readily understood why for an exclusive lead-lead bond cleavage of hexaphenyldilead the reagent should not be strongly electrophilic. As a result of the electron-withdrawing properties of the phenyl groups and the electropositive nature of the lead atoms, the lead-phenyl bond is polarized as follows: $\text{Pb}^{\delta+}-\text{C}^{\delta-}$. Consequently, nucleophilic reagents only attack the lead-lead bond, but strongly electrophilic reagents may attack the negatively charged carbon atom preferentially which results in cleavage of the stronger lead-phenyl bond as well. In hexaalkyldileads the lead-carbon bond certainly is less polarized, and so in this case only the lead-lead bond is cleaved, even by strong electrophiles.

EXPERIMENTAL

Preparation of hexaphenyldilead

The following procedure is a modification of that of Krause and Reissaus¹³. A Grignard solution was prepared from 314 g of bromobenzene (2 moles) and 45 g of magnesium turnings in 1 l of dry diethyl ether in a 3-l three-necked flask fitted with an efficient stirrer, reflux condenser and dropping funnel. To this solution 278 g of lead dichloride (1 mole) was added in portions through a hopper with vigorous stirring within about 5 to 10 min. Some cooling was applied to keep the temperature between 20 and 35°. The mixture rapidly turned dark-brown and soon separation of metallic lead started, which sometimes rendered the mixture difficult to stir. Hereupon the

mixture was refluxed for 4 h with continuous vigorous stirring. After cooling down, the mixture was hydrolyzed by adding 1.5 kg of crushed ice as rapidly as possible, followed by stirring. If this operation was carried out properly, the temperature sank below 0° because of the formation of a freezing mixture of ice and magnesium salts. If not enough ice is added or if the ice is added too slowly, a vigorous exothermal reaction sets in which is difficult to control (hydration of magnesium salts).

After hydrolysis the ether layer was separated and discarded. The resulting grayish-black mass was filtered off, air-dried and extracted with three portions of 300 ml each of hot chloroform. The combined extracts were concentrated to 600 ml and placed overnight in a refrigerator to allow any tetraphenyllead present to crystallize. This was filtered off (12.9 g, 5%) and 1 l of ethanol was added to the filtrate whereupon 210 g of pure, slightly creme-coloured hexaphenyldilead (72%) crystallized. On the Kofler Heizbank it decomposed at ca. 170° under transient melting and resolubilization with blackening, a behaviour which is typical for hexaphenyldilead.

Reaction of hexaphenyldilead with phenyllithium⁶ or phenylmagnesium bromide

Hexaphenyldilead (25.0 g, 0.0285 mole) was dissolved in 100 ml of dry tetrahydrofuran in a nitrogen atmosphere. A tetrahydrofuran solution of phenyllithium (25 ml 0.80 M, 0.02 mole) was added at once at room temperature with stirring. A precipitate of tetraphenyllead rapidly formed. The temperature rose from 22 to 33°. After 5 min the Gilman test⁷ was negative. The mixture was cooled to 5° and 3.6 g of benzyl chloride (0.0285 mole) was added. After stirring for 2 h the precipitated tetraphenyllead was filtered off: yield 9.5 g (92% based on phenyllithium). The filtrate was concentrated *in vacuo* and taken up in chloroform/water (to remove lithium chloride). The chloroform layer was concentrated and boiled with 200 ml of ethanol to give 7.1 g of insoluble unchanged hexaphenyldilead (95% of the amount added in excess). From the hot filtrate 8.8 g of benzyltriphenyllead (83% based on phenyllithium) crystallized.

A similar reaction with *phenylmagnesium bromide* in tetrahydrofuran (treatment with benzyl chloride after standing for 17 h) gave 78% of tetraphenyllead and 21% of benzyltriphenyllead. The recovery of hexaphenyldilead (22% plus the added excess) indicated that the reaction had progressed for 78%. In diethyl ether, after 8 h of reflux, the reaction had taken place for only about 5% (based on the isolation of 5% of tetraphenyllead).

Reaction of hexaphenyldilead with lithium. Preparation of triphenylplumbyllithium

Hexaphenyldilead (87.7 g, 0.1 mole) was dissolved in 250 ml of tetrahydrofuran (carefully dried on sodium) in an atmosphere of pure nitrogen. The solution was cooled to about -20° and 1.5 g of lithium shavings (0.214 mole) were added. The mixture was stirred for 24 h at -20° under nitrogen. The lithium slowly disappeared and a dark solution, containing a black sludge, resulted. It was filtered through dried Filtrapid under nitrogen into a storage bottle. The yellow to brown filtrate was added up with tetrahydrofuran to 300 ml.

The concentration of the triphenylplumbyllithium solution can be determined in two ways: (1) by complete oxygen-free hydrolysis^{2e} ($\text{Ph}_3\text{PbLi} + 2 \text{H}_2\text{O} \rightarrow \text{PbO} + \text{LiOH} + 3 \text{C}_6\text{H}_6$) followed by titration of the inorganic lead formed^{2f}; and (2) by reaction with benzyl chloride¹⁴ followed by the isolation of the benzyltriphenyllead

formed. The two methods give values which are in close agreement.

(1). An aliquot of the above triphenylplumbylithium solution (25 ml) was cooled to -30° . About 50 ml of water (freed from oxygen by boiling) was added dropwise with stirring. The temperature was allowed to rise slowly to about 20° . An orange-red turbid organic layer formed, from which cream-coloured lead oxide slowly precipitated with simultaneous decoloration. After about 2 h the orange-red colour had disappeared. The organic solvent was removed *in vacuo*. Acetic acid was added until the mixture reacted weakly acid; nearly all of the precipitate dissolved. Filtration gave a trace of hexaphenyldilead and/or tetraphenyllead. The lead (Pb^{2+}) content of the filtrate was determined by volumetric titration^{2f}, yield 90%.

(2). To another 25 ml of the above triphenylplumbylithium solution was added excess of benzyl chloride at once at about -25° . The mixture was allowed to attain room temperature with stirring in about 1.5 h. Hydrolysis with ice produced two almost colourless layers. Diethyl ether was added. The ethereal layer was separated, dried on sodium sulphate and concentrated to a small volume. Sometimes a trace of hexaphenyldilead crystallized which was filtered off. Addition of ethanol to the filtrate caused benzyltriphenyllead to precipitate almost quantitatively. It was filtered off, dried and weighed. Yield 88%. M.p. 93° (mixed m.p.).

Reaction of hexaphenyldilead with potassium permanganate⁹. Preparation of triphenyllead hydroxide and triphenyllead salts

To a suspension of 87.7 g of hexaphenyldilead (0.1 mole) in 500 ml of acetone was added dropwise at room temperature a 0.1 M solution of potassium permanganate in acetone. A brown-black precipitate of $\text{K}_2\text{O} \cdot 2\text{MnO}_2$ formed. Evolution of heat was hardly perceptible. After 700 ml had been added the mixture was checked for the presence of unreacted permanganate by allowing the precipitate to settle. This procedure was repeated after each addition of a 20-ml aliquot until after the addition of in total 780 ml (17% excess) the solution became pink-coloured. The mixture was filtered through Filtrapid and the residue washed with warm acetone. The combined filtrate and washings were concentrated to about 0.5 l and 15 ml of water was added. After standing overnight in a refrigerator the crystals were collected on a filter (57.6 g). After adding more water to the filtrate another 2.6 g of crude product separated. The $\text{K}_2\text{O} \cdot 2\text{MnO}_2$ cake was extracted with hot ethanol to give another 24.1 g. The total yield was 84.3 g of triphenyllead hydroxide (93%), decomposing at $138-144^{\circ}$. (Found: Pb, 45.46. $\text{C}_{18}\text{H}_{16}\text{OPb}$ calcd.: Pb 45.48%.)

A few triphenyllead salts were prepared by adding an equivalent of acid instead of water to the acetone solution (see Table 1).

Reaction of hexaphenyldilead with sodium ethoxide

Five ml of a solution of 0.002 mole of sodium ethoxide in absolute ethanol was added to a solution of 8.8 g of hexaphenyldilead (0.01 mole) in 100 ml of dry benzene. After 2 h reflux no visible change had taken place. To the slightly yellow solution 2.0 g of acetic acid (0.033 mole) and 100 ml of water were added, the final pH being 5-6. The mixture was warmed up until the two layers were clear. In the aqueous layer (100 ml) lead diacetate was determined (0.0776 M, yield 78%)^{2f}. The benzene layer was concentrated whereupon 3.8 g of triphenyllead acetate (78%) crystallized. From the mother liquor 1.9 g of hexaphenyldilead (21%) was precipitated with ethanol.

Reaction of hexaphenyldilead with diaryl disulphides. Preparation of (aryltio)-triphenyllead compounds

A solution of 8.8 g of hexaphenyldilead (0.01 mole) and 2.2 g of diphenyl disulphide in 125 ml of benzene was refluxed for 3 h with 5 ml of water. After about 0.5 h the system became turbid. At the end 0.3 g of insoluble material was filtered off and discarded (lead oxide). The filtrate was concentrated and 0.7 g of tetraphenyllead (7%) crystallized out. Upon further concentration 8.25 g of (phenylthio)triphenyllead (75.5%) was isolated, m.p. 105–106° (mixed m.p.).

A similar experiment in dry benzene gave 0.5 g of insoluble material and 1.7 g of tetraphenyllead (16.5%). Concentration of the filtrate gave 3.65 g of unchanged hexaphenyldilead (42%). The mother liquor was evaporated to dryness and the residue recrystallized from 25 ml of acetone to give 2.55 g of (phenylthio)triphenyllead (23%).

(*p*-Chlorophenylthio)triphenyllead was prepared similarly (see Table 1).

TABLE I

TRIPHENYLLEAD DERIVATIVES PREPARED FROM HEXAPHENYLDILEAD

Ph ₃ Pb derivative	Reagent	Recrystd. from	Yield (%)	M.p. (°C)	Lit. m.p. (°C)
Ph ₃ PbLi	Li		90		
Ph ₃ PbOH	KMnO ₄	Acetone	93	138-44 dec.	
	O ₃		94		
Ph ₃ PbCl	KMnO ₄	Acetone	71	210	206 (ref. 3)
	O ₃		76		
	HClO		95		
Ph ₃ PbBr	KMnO ₄	Acetone	70	166	166 (ref. 3)
Ph ₃ PbI	I ₃ ⁻	Chloroform/ ethanol	92	143	139 (ref. 13)
Ph ₃ PbOAc	KMnO ₄	Acetone	76	204-6	206-7 (ref. 3)
	O ₃		97		
(Ph ₃ Pb) ₂ S	S	Cyclohexane	53	137-9	137-9 (ref. 11)
Ph ₃ PbSPh	Ar ₂ S ₂	Ethanol	76	105-6	106-7 (ref. 15)
	O ₃		66		
Ph ₃ PbSC ₆ H ₄ Cl- <i>p</i>	Ar ₂ S ₂	Ethanol	80	102.5	102 (ref. 16)

Reaction of hexaphenyldilead with ozone. Preparation of triphenyllead hydroxide and triphenyllead salts

Hexaphenyldilead (8.8, 0.01 mole) was dissolved in 75 ml of chloroform. A stream of oxygen containing a few percent of ozone was passed for 5 min through this solution (not enough ozone to convert all of the hexaphenyldilead). After addition of 1 ml of water the mixture was shaken, dried, filtered and evaporated to dryness. Extraction with hot ethanol left behind 2.7 g of starting material. The alcoholic extract was treated with activated charcoal. The triphenyllead hydroxide was precipitated with water. Yield 5.9 g (94% based on converted hexaphenyldilead).

In other experiments the ozone was passed through until all of the hexaphenyldilead had been converted. The end-point was determined by testing a sample of the reaction mixture with a few drops of a dilute solution of potassium permanganate in

acetone: if hexaphenyldilead was still present, the colour changed from violet to brown.

Addition of one equivalent of acid gave the corresponding triphenyllead salt (see Table 1). If the acid does not react readily with hexaphenyldilead or ozone, it may already be added to the mixture before the ozonization. This has the advantage that the end-point is roughly visible (decoloration of the yellow solution). Thus, 8.8 g of hexaphenyldilead plus 1.2 g of acetic acid gave upon ozonization a chloroform solution from which triphenyllead acetate was isolated in a yield of 97%.

Reaction of hexaphenyldilead with sulphur¹¹

Hexaphenyldilead (8.8 g, 0.01 mole) and 0.32 g of sulphur (0.01 g-atom) were thoroughly mixed and heated 1.5 h at *ca.* 140° with occasional stirring. A thick black mass resulted which solidified upon cooling. Extraction with 100 ml of hot chloroform left behind 0.7 g of black residue (PbS, 15%). The chloroform extract was concentrated and placed overnight in a refrigerator to allow tetraphenyllead to crystallize. Filtration gave 2.9 g of tetraphenyllead (28%). The filtrate was evaporated to dryness and the residue recrystallized from 15 ml of cyclohexane. The yield was 4.8 g of bis(triphenyllead) sulphide (53%); m.p. 137–139° (mixed m.p.).

Reaction of hexaphenyldilead with hypochlorous acid. Preparation of triphenyllead chloride

To a solution of 8.8 g of hexaphenyldilead (0.01 mole) in 100 ml tetrahydrofuran was added 10 ml of a 1 M aqueous solution of sodium hypochlorite. Hydrochloric acid (1 N) was added dropwise with efficient mixing until pH 4 was reached. More hypochlorite and acid were used until a drop of the reaction mixture no longer caused any discoloration of a dilute solution of potassium permanganate in acetone. Chloroform was added, and the chloroform layer was separated, dried on Na₂SO₄, and concentrated whereupon triphenyllead chloride crystallized out. Yield 95%.

Reaction of hexaphenyldilead with iodine

(a). *In the presence of potassium iodide. Preparation of triphenyllead iodide.* To a solution of 8.8 g of hexaphenyldilead (0.01 mole) in 100 ml of tetrahydrofuran and 10 ml of water was added dropwise at 5° a solution of 2.6 g of iodine (0.01 mole) and 8.3 g of potassium iodide (50 mmole) in 50 ml of tetrahydrofuran plus 10 ml of water. A light-yellow solution remained. During warming at 50° for 1 h a little yellow precipitate formed which redissolved at the end. The tetrahydrofuran was stripped off and the residue taken up in chloroform/water. Insoluble lead diiodide (0.2 g) was filtered off. The chloroform layer was separated, dried and concentrated. Practically white triphenyllead iodide (10.35 g, 91.5%) was precipitated by adding ethanol. The compound gave a clear, colourless melt at 143°. This proves the absence of hexaphenyldilead since its presence, even in tiny amounts, causes a yellow, turbid melt, which rapidly solidifies.

A similar experiment in dry peroxide-free 1,2-dimethoxyethane with sodium iodide without water gave a yield of 90% of triphenyllead iodide.

(b). *Without potassium iodide.* A similar reaction was carried out in aqueous tetrahydrofuran without potassium iodide. The reaction mixture was evaporated to dryness in vacuum. The residue was extracted with hot chloroform. The remainder

was dissolved in aqueous base, and lead and iodide were determined volumetrically: found: lead diiodide, 1.5 mmole; lead oxide, 0.7 mmole. From the chloroform extract tetraphenyllead was allowed to crystallize (0.5 g, 1.0 mmole). The filtrate was evaporated to dryness. The residue was washed with ethanol and proved to be a yellow unseparable mixture of hexaphenyldilead and triphenyllead iodide (8.6 g). From an iodine analysis (17.50%) the respective amounts were calculated: triphenyllead iodide, 11.9 mmole (59.5%); hexaphenyldilead, 2.2 mmole (22%).

ACKNOWLEDGEMENTS

This work was sponsored by the International Lead Zinc Research Organization (Director: Dr. SCHRADER F. RADTKE). Thanks are due to Dr. G. M. VAN DER WANT for his interest and stimulating discussions. We are much indebted to Mr. H. J. H. VAN DER MAAS for capable assistance in the experimental work.

REFERENCES

- 1 L. C. WILLEMSSENS AND G. J. M. VAN DER KERK, *J. Organometal. Chem.*, 13 (1968) 357.
- 2 L. C. WILLEMSSENS AND G. J. M. VAN DER KERK, *Investigations in the Field of Organolead Chemistry*, Inst. Org. Chem. TNO, Utrecht, ILZRO, New York, 1965, (a) p. 24: (b) p. 66: (c) p. 56: (d) p. 33: (e) p. 34: (f) p. 84.
- 3 R. W. LEEPER, L. SUMMERS AND H. GILMAN, *Chem. Rev.*, 54 (1954) 101.
- 4 L. C. WILLEMSSENS, *Organolead Chemistry*, Inst. Org. Chem. TNO, Utrecht, 1964.
- 5 L. C. WILLEMSSENS AND G. J. M. VAN DER KERK, in A. G. MACDIARMID (Ed.), *Organometallic Compounds of the Group IV elements*, Vol. 1, Part 2, Dekker, New York, 1968, p. 191-229.
- 6 E. BINDSCHADLÉR AND H. GILMAN, *Proc. Iowa Acad. Sci.*, 48 (1941) 273; *Chem. Abstr.*, 36 (1942) 1595.
- 7 H. GILMAN AND F. SCHULZE, *J. Amer. Chem. Soc.*, 47 (1925) 2002.
- 8 C. TAMBORSKI, F. E. FORD, W. L. LEHN, G. J. MOORE AND E. J. SOLOSKI, *J. Org. Chem.*, 27 (1962) 619.
- 9 G. BÄHR, *Z. Anorg. Chem.*, 253 (1947) 330.
- 10 TNO, *Dutch Patent Application*, 66/18311, filed Dec. 29, 1966.
- 11 A. W. KREBS AND M. C. HENRY, *J. Org. Chem.*, 28 (1963) 1911.
- 12 TNO, *Dutch Patent Application* 68/03766, filed March 15, 1968.
- 13 E. KRAUSE AND G. G. REISSAUS, *Ber.*, 55 (1922) 888.
- 14 H. GILMAN, L. SUMMERS AND R. W. LEEPER, *J. Org. Chem.*, 17 (1952) 630.
- 15 M. C. HENRY AND A. W. KREBS, *J. Org. Chem.*, 28 (1963) 225.
- 16 W. E. DAVIDSON, K. HILLS AND M. C. HENRY, *J. Organometal. Chem.*, 3 (1965) 285.

J. Organometal. Chem., 15 (1968) 117-124