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

Preliminary communication

The chemistry of bis(triphenyllead)dichloromethane. Some reactions of Ph_3PbCCl_2Li

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(Received May 21st, 1970)

Whereas the study of reactions of halomethylmetal (*e.g.* R_3SiCX_2R[1,2] and Me_3SnCF_3 [3]) and halomethyldimetal (e.g. $Ph_3SiCCl_2SiPh_3$ [4] and $Me_3SnCCl_2SnMe_3$ [1,3]) derivatives of silicon and tin recently have received considerable attention, very little has been reported concerning the chemistry of polyhaloorganolead compounds[5,6]. Because of the recent interest in IVth group halomethylmetal derivatives as precursors for organometal-substituted lithium reagents[1,2] or carbenes[3] we present in preliminary form some related results obtained in a study of the chemistry of bis(triphenyllead)dichloromethane (I).

At its melting point of 214–216° (I), which is readily obtained by the 1/2 reaction of CCl_4 and Ph_3PbLi in THF[5,6], undergoes α-elimination to give triphenyllead chloride, lead chloride and other, unidentified, products. When a benzene solution of Ph_3PbCCl_3 [5,6] is heated in a sealed tube at 140° for 7 h, triphenyllead chloride is formed in 78% yield; heating at 115° for 7 h in the presence of cyclohexene affords dichloronorcarane in 70% yield[7]. However, upon heating in refluxing xylene for 24 h (I) was recovered in better than 70% yield. As it is conceivable that an equilibrium (1) involving the divalent species (II) may have been established, (I) was refluxed in xylene in the presence of tri-*p*-tolyllead chloride. However, after 17 h the NMR spectrum of the crude reaction product gave no evidence for the reaction of tri-*p*-tolyllead chloride with II.

$$\underset{\text{(I)}}{(Ph_3Pb)_2CCl_2} \rightleftharpoons Ph_3PbCl + \underset{\text{(II)}}{[Ph_3Pb\overset{\bullet}{\underset{\bullet}{C}}Cl]} \qquad (1)$$

Compound (I) is stable to silver acetate in acetone/benzene/water at room temperature for 90 h and even with silver nitrate only minor decomposition occurs. The reaction of I with n-butyllithium in THF at −75° results in a quantitative yield of triphenylleaddichloromethyllithium (III) and compound (IV), indicating that this reaction proceeds exclusively via transmetalation, with no halogen–metal exchange. This result is noteworthy when compared with our recent results obtained with mixed metal dichloromethanes[8].

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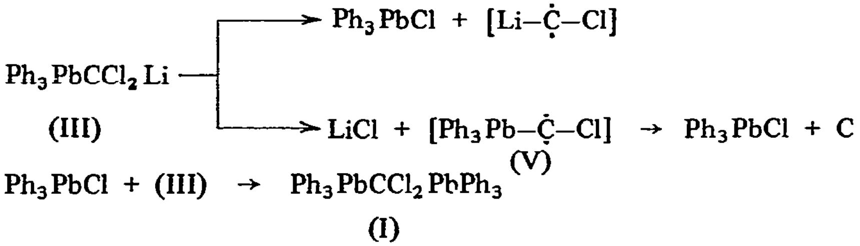
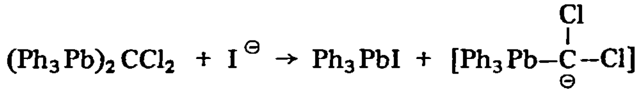
$$\underset{\text{(I)}}{(Ph_3Pb)_2CCl_2} + n\text{-}BuLi \rightarrow \underset{\text{(III)}}{Ph_3PbCCl_2Li} + \underset{\text{(IV)}}{Ph_3Pb(n\text{-}Bu)} \qquad (2)$$

The hydrolysis of III at -75° affords triphenylleaddichloromethane [$\delta(CCl_2H)$, 6.25 ppm; $J(^{207}Pb{-}^1H)$, 60 Hz] in quantitative yield (based on I). As compared with Me_3MCCl_2Li (M = Si and Sn)[1] and halomethyllithium reagents[9] in general which have to be prepared at very low temperatures (~ -125°) the relative stability of III at -75° is noteworthy. However, if a solution of (III) in THF is allowed to warm up to room temperature, the colour changes from yellow to black and, surprisingly, upon hydrolysis 16% of (I) is isolated along with some triphenyllead chloride. This was not unreacted starting material since hydrolysis at -75° of a sample from the same preparation of (III) indicated that the transmetalation reaction (2) had gone to completion. Two alternative possible reaction routes can be proposed as follows:

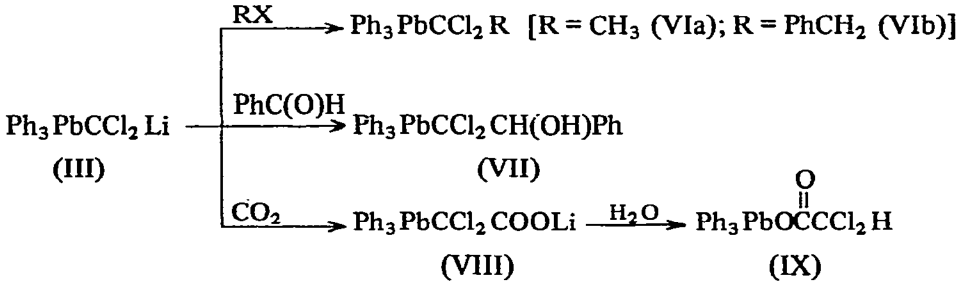


Attempts to trap (V) with cyclohexene (*cf.* ref.3) or to isolate a dimer or trimer of (V) so far have been unsuccessful. Treatment of I with sodium iodide in refluxing 1,2-dimethoxyethane was investigated as an alternative route to (V) (*cf.* refs. 10 and 11). Reaction for 25 h gave 79% recovery of (I), triphenyllead iodide (12%), lead iodide (4%) and several as yet unidentified products. These results would be consistent with formation of a carbene precursor (*cf.* ref. 3).



$$(Ph_3Pb)_2CCl_2 + I^{\ominus} \rightarrow Ph_3PbI + [Ph_3Pb{-}\overset{\displaystyle Cl}{\underset{\ominus}{C}}{-}Cl]$$

Triphenylleaddichloromethyllithium very cleanly undergoes the usual coupling reactions of organolithium reagents to give the expected products in good yield:



The alcohol (VII), the first example of an α,α-dihalo-β-hydroxyorganolead compound, should have an interesting chemistry of its own. The addition of (III) to carbon dioxide followed by hydrolysis affords triphenyllead dichloroacetate (IX). Our results suggest that III has added in the usual manner to give VIII.

In the course of this work two interesting spectroscopic observations were made. The values of $J(^{207}Pb-\beta-^{1}H)$ observed in the ^{1}H NMR spectrum of VIa and VIb are about 60 Hz, which contrasts with values of about 160 Hz observed for a series of unsubstituted alkyl triphenyllead compounds, *e.g.* $J(^{207}Pb-\beta-^{1}H)$ for $Ph_3PbCH_2CH_3$ is 168 Hz[7]. The mass spectra of all α,α-dihaloorganolead compounds show $Ph_2PbCl^{\oplus}$ as one of the major fragments, an observation that may be useful in identifying α-halo-organolead compounds.

Further work concerned with the preparative application of organolead-methyllithium reagents is in progress, and full details will be reported at a later date.

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