Bis(triphenyl-lead)dichloromethane: a Dichloromethylene Transfer Reagent

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Summary Starting from $(Ph_3Pb)_2CCl_2$ compounds of the type $R_nM^1CCl_2Li$ and $R_nM^1CCl_2M^2R_m$ can be prepared.

IN our investigation[1] of the chemistry of bis(triphenyl-lead)-dichloromethane, (I), its reaction with n-butyl-lithium has been found to provide a potential general method for the preparation of metal- and semi-metal-substituted dichloromethanes $R_nM^1CCl_2Li$ and $R_nM^1CCl_2M^2R_m$ (where M^1 and M^2 may be the same or different). We report our initial results in view of the current interest in these types of compounds as possible precursors for organometallic-substituted carbenes[2] and the lack of a suitable general method for their preparation (*cf.* ref. 3).

The method which we have developed is illustrated by Equations (1)—(5). All of the reactions were carried out

$$\underset{(I)}{(Ph_3Pb)_2CCl_2} + Bu^nLi \rightarrow \underset{(II)}{Ph_3PbCCl_2Li} + Ph_3PbBu^n \qquad (1)$$

$$(II) + \underset{(III)}{R_nM^1X} \rightarrow \underset{(IV)}{Ph_3PbCCl_2M^1R_n} + LiX \qquad (2)$$

$$(IV) + Bu^nLi \rightarrow \underset{(V)}{R_nM^1CCl_2Li} + Ph_3PbBu^n \qquad (3)$$

$$(V) \left[\begin{array}{ll} \xrightarrow{R_mM^2X} \underset{(VI)}{R_nM^1CCl_2M^2R_m} + LiX & (4) \\ \xrightarrow{PhHgCl} \underset{(VII)}{R_nM^1CCl_2HgPh} + LiCl & (5) \end{array} \right.$$

in dry tetrahydrofuran at −75°. Representative examples of the compounds prepared are (IV) [$MR_n = Ph_3Sn$ (a); Ph_3Ge (b); Me_3Ge (c); Ph_3Si (d)], $Ph_3GeCCl_2SnPh_3$ (VIa), and Ph_3PbCCl_2HgPh (VIIa).

It would seem that this reaction sequence offers a general method for transferring a dichloromethylene group by a non-carbene route from (I) to other organometallic compounds. The key reactions are those illustrated by Equations (1) and (3). Reaction (1) is essentially quantitative, the n.m.r. spectrum of the crude reaction product after hydrolysis indicating the exclusive presence of Ph_3PbCCl_2H and Ph_3PbBu^n. No halogen–metal exchange was observed. This is not unexpected as organic chlorides are relatively unsusceptible to undergoing exchange reactions with alkyl-lithium compounds.[4] On the other hand, organolead compounds readily take part in transmetalation reactions.[5]

However, the mixed-metal dichloromethanes (IV) react with Bu^nLi to give, dependent on the nature of M, transmetalation, involving either the Pb–C [Equation (3)] or M–C bond, and halogen–metal exchange. Starting with $(Ph_3Pb)_2CCl_2$, (I), the reaction sequence (1), (2), and (3) was carried out under identical conditions with Ph_3MCl [Equation (2); M = Si, Ge, Sn]. The crude reaction product obtained after hydrolysis at the completion of step (3) was investigated by n.m.r. spectroscopy ($CDCl_3$ solution). Each of the major products gives a characteristic spectrum: Ph_3MCCl_2H [CCl_2H, δ (p.p.m.) (M): 6·2 (Pb); 5·9 (Sn); 6·0 (Ge);[6] 5·9 (Si)[6]] and $Ph_3PbCClHSiPh_3$ [CClH δ 4·7 p.p.m. $J(^{207}Pb\text{–}^1H)$ 61 Hz]. The products obtained in these experiments are given in the Table.

With respect to the transmetalation reactions of $Ph_3PbCCl_2MPh_3$ (IV) there is essentially no selectivity between Pb–C and Sn–C cleavage in (IVa) whereas with the Ge (IVb) and Si (IVd) analogues the Pb–C bond is selectively cleaved. In contrast, the reaction between Bu^nLi and the

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Pb–Hg compound (VIIa) results in exclusive attack on the Hg–C bond as shown by n.m.r. spectroscopy and isolation of Ph_3PbCCl_2H. With respect to halogen–metal exchange only the silicon compound (IVd) reacts appreciably by this route. If the stabilization of the product of halogen–metal exchange, $Ph_3PbCCl(Li)MPh_3$, is important in determining the extent of this reaction, then our results reflect the current thoughts[7] that the ability of M to stabilize negative charge on adjacent carbon decreases in the order Si > Ge > Sn > Pb. Whether the order of addition of reagents in reaction (3) effects the yields of the various products is under investigation.

TABLE

		Yield(%)[a]	
R_nMX	Ph_3PbCCl_2H	Ph_3MCCl_2H	$Ph_3PbCClHMPh_3$
Ph_3SnCl	60	40	—
Ph_3GeCl	—	80	20
Ph_3SiCl	—	33	67[b]

[a] Yield based on integration of the n.m.r. spectrum; in all cases the appropriate amount of Ph_3PbBu^n was found.

[b] M.p. 155—158° with satisfactory analytical data.

Some of the advantages of the present method are as follows. Compound (I) is readily prepared from Ph_3PbLi and CCl_4,[8] a method that is not suitable for the preparation of the analogous silicon[9] or germanium[10] compounds. The organometallic halides, (III), are readily available. High yields can be obtained in specific cases without the isolation of intermediates. For example, in the preparation of (VIa) which involves four separate reactions, a 75% yield was obtained. For the reactions studied so far, very low temperatures requiring multiple solvent mixtures which are usually used for the preparation of polyhalogeno-organolithium reagents,[11] are not required.

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