ORGANOMETALLIC COMPOUNDS OF GROUP III, IV, AND V

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ABSTRACT

The preparation and reactions of a number of organometallic compounds has been studied. The organolithium compounds under investigation are Ph_2CHLi, Ph_3CLi, Ph_3SnLi, Ph_3GeLi, Ph_3PbLi, Ph_2PLi and Ph_2NLi. Also included in this series is Ph_2NNa. The reactions of these organometallics with various compounds as carbon dioxide, water, alkyl halides, aryl halides, aralkyl halides, metallic halides and esters has been studied.

A research program has recently been initiated on organometallic chemistry of certain elements of group III, IV and V of the periodic table. This program has two objectives; the first is the synthesis and evaluation of physical and chemical properties of a class of perarylated compounds indicated by the general structure RnMM'Rn. In most cases, R is a phenyl group (Ph); M or M' is either B, Al, C, Si, Ge, Sn, Pb, P and N; $M = \text{or} \neq M'$ and n is either 2 or 3 depending on the valence of M. The second objective, which is the subject of this report, is the study of the synthesis and reactions of the intermediate organometallics (R_nM-metal) necessary for the preparation of the perarylated $R_nMM'R_n$ compounds.

A series of compounds possessing various combinations of elements, $R_nMM'R_n$, will offer a convenient manner of studying some chemical reactions as, for example, hydrolysis and oxidation on simple structures. The preparation of compounds containing M-M' bonds can be accomplished by various means. The following examples illustrate a few of the various methods which have been reported in the literature.

Symmetrical $Ph_3M\text{-}M'Ph_3$

$$2Ph_3CCl + Zn \longrightarrow Ph_3C\text{-}CPh_3 + ZnCl_2 \tag{1}$$
$$2Ph_3SiCl + 2Na \longrightarrow Ph_3SiSiPh_3 + 2NaCl \tag{2}$$
$$2Ph_3SiCl + Mg \longrightarrow Ph_3SiSiPh_3 + MgCl \tag{3}$$
$$3PbCl_2 + 6PhMgX \longrightarrow Ph_3PbPbPh_3 + 6MgCl + Pb \tag{4}$$
$$3PbCl_2 + 6PhLi \longrightarrow Ph_3PbPbPh_3 + 6LiCl + Pb \tag{5}$$
$$PhMgX(\text{large excess}) + GeCl_4 \longrightarrow Ph_3GeGePh_3 \tag{6}$$
$$2Ph_2PCl + 2Na \longrightarrow Ph_2P\text{-}PPh_2 + NaCl \tag{7}$$

Unsymmetrical $Ph_3MM'Ph_3$

The unsymmetrical $Ph_3MM'Ph_3$ compounds require a two-step process. This involves the preparation of an intermediate organometallic, Ph_nM-metal, which is then further reacted with a $Ph_nM'X$ compound to yield the desired unsymmetrical product. The preparation of the intermediate Ph_nM-metal has been studied quite extensively. A few specific examples for its preparation reported in the literature are the following:

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14. ABSTRACT

The preparation and reactions of a number of organometallic compounds has been studied. The organolithium. compounds under investigation are Ph2CHLi Ph3CLi, Ph3SnLi, Ph3GeLi, Ph3PbLi, Ph2PU and Ph2NLi. Also included in this serie 8 is Ph2NNa. The reactions of these organometallics with various compounds as carbon dioxide, water, alkyl halides, aryl halides, aralkyl halides, metallic halides and esters has been studied.

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$$Ph_3CCl + 2Li \xrightarrow{THF} Ph_3CLi + LiCl \qquad (8)$$

$$Ph_3CH + NaNH_2 \xrightarrow{NH_3} Ph_3CNa + NH_3 \qquad (9)$$

$$Ph_3SiCl + 2Li \xrightarrow{THF} Ph_3SiLi + LiCl \qquad (10)$$

$$Ph_3GeH + Na \xrightarrow{NH_3} Ph_3GeNa + 1/2H_2 \qquad (11)$$

$$Ph_2Sn + PhLi \longrightarrow Ph_3SnLi \qquad (12)$$

$$Ph_4Pb + Na \xrightarrow{NH_3} Ph_3PbNa + PhH + NaNH_2 \qquad (13)$$

$$Ph_3SiSiPh_3 + 2Li \xrightarrow{THF} 2Ph_3SiLi \qquad (14)$$

The subsequent reaction of the intermediate Ph_nM-metal with an arylmetallic halide $Ph_nM'X$ has been studied extensively by Gilman (1) in a series of six publications.

$$Ph_nM\text{-metal} + Ph_nM'X \qquad Ph_nMM'Ph_n + \text{metal halide} \qquad (15)$$

Most of the above reactions (1 through 15) are not of a general nature which can be applied to all the elements of interest in groups III, IV and V. A reaction which is successful for the tin compound may not necessarily work for the lead analog. Gilman (2) has however indicated that the reaction reported in equation 10 may be of a general nature and applicable for other metals or metalloids.

In our studies on the synthesis of M-M' compounds, essentially three different methods thus far have been used to synthesize the organometallic intermediates.

Direct Method

$$R_nMCl + 2Li \longrightarrow LiCl + R_nMLi \qquad (16)$$

Cleavage Method

$$R_nMMR_n + 2Li \longrightarrow 2R_nMLi \qquad (17)$$

Metal-Hydrogen Exchange

$$Ph_2NH + C_4H_9Li \longrightarrow C_4H_{10} + Ph_2NLi \qquad (18)$$
$$Ph_2NH + NaH \longrightarrow H_2 + Ph_2NNa \qquad (19)$$

Each method of synthesis and its reactions will be discussed in greater detail separately.

Direct Method

The direct method of preparing triphenylsilyllithium (Ph_3SiLi) from chlorotriphenylsilane and lithium metal in tetrahydrofuran (THF) was first reported by Gilman (2). Using this procedure, this reaction has now been extended to include the preparation of diphenylmethyllithium, triphenylgermyllithium, triphenyltinlithium, triphenylleadlithium and diphenylphosphinolithium. The metallic chlorides readily react with lithium in THF to yield the desirable organolithium compounds in good yields. When subjected to Color Test I (3) all the organolithium compounds produced a positive color test indicating the presence of the M-Li bond. This Color Test I was useful in following the course of a reaction to determine the presence or absence of the organometallic reagents. An indication of the yield of organometallic reagent was obtained by derivatization with benzyl chloride. The values obtained in all cases do not indicate the true yields of the organometallic reagent since no attempt was made at maximizing yields. The benzyl derivatives as shown in Table I were characterized by mixture melting point determinations and comparison of the infrared curves with benzyl derivatives which were synthesized by an alternate route as shown in equation 20.

$$Ph_nMCl + C_6H_5CH_2MgCl \longrightarrow MgCl_2 + Ph_nMCH_2C_6H_5 \qquad (20)$$

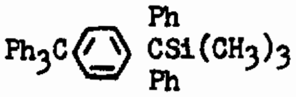
TABLE I

$Ph_nM^{n+1}Li$	Benzyl Derivative	M.P. [e]	% Yield
Ph_3CLi [a]	Ph_3CCH_2Ph	143.5-145	67
---	Ph_3CCH_2Ph [c]	141.0-142.0	75
Ph_3SiLi [a]	Ph_3SiCH_2Ph	98.5-99.5	39
---	Ph_3SiCH_2Ph [c]	96.0-97.0	65
Ph_3GeLi [a]	Ph_3GeCH_2Ph	85.0-86.5	60
Ph_3GeLi [b]	Ph_3GeCH_2Ph	85.0-87.0	75
Ph_3SnLi [a]	Ph_3SnCH_2Ph	90.0-91.0	77
Ph_3SnLi [b]	Ph_3SnCH_2Ph	91.0-92.0	72
---	Ph_3SnCH_2Ph [c]	91.0-92.0	80
Ph_3PbLi [a]	Ph_3PbCH_2Ph	95.0-96.0	76
Ph_3PbLi [b]	Ph_3PbCH_2Ph	95.0-97.0	87
---	Ph_3PbCH_2Ph [c]	94.0-95.0	67
Ph_2PLi [a]	$Ph_2P(O)CH_2Ph$ [d]	193.0-194.0	80
Ph_2PLi [b]	$Ph_2P(O)CH_2Ph$	193-194	83
---	$Ph_2P(O)CH_2Ph$ [c]	192.0-193.5	64

(a) Prepared by the direct method. (b) Prepared by cleavage of Ph_nMMPh_n.
(c) Prepared by the reaction of the benzyl Grignard with the Ph_nMCl.
(d) Benzyl substituted phosphine compounds are easily air oxidized to the phosphine oxide. Since the purification of the benzyl phosphine derivative was done with no precaution to exclude atmospheric oxygen, the phosphine was readily converted to the phosphine oxide. (e) Melting points are uncorrected.

Some other reactions carried out on the individual organolithium compounds are shown in Table II.

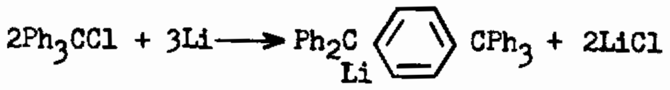
TABLE II

	Ph_nMLi	Reactant	Product	% Yield
1.	Ph_3CLi	$(CH_3)_3SiCl$	$Ph_3CSi(CH_3)_3$ +	37
				12
2.	Ph_3CLi	CO_2	Ph_3CCOOH	80
3.	Ph_2CHLi	Ph_3SnCl	$Ph_2CHSnPh_3$	63
4.	Ph_2CHLi	Ph_3SiCl	$Ph_2CHSiPh_3$	81
5.	Ph_2CHLi	Ph_2SiCl_2	$(Ph_2CH)_2SiPh_2$	78
6.	Ph_2CHLi	$PhSiCl_3$	$(Ph_2CH)_3SiPh$	28
7.	Ph_2CHLi	$(CH_3)_3SiCl$	$Ph_2CHSi(CH_3)_3$	66
8.	Ph_2CHLi	CO_2	$Ph_2CHCOOH$	91
9.	Ph_3SnLi	Ph_3SiCl	$Ph_3SnSiPh_3$	ca. 20
10.	Ph_3SnLi	$(CH_3)_3SiCl$	$Ph_3SnSnPh_3$	69
11.	Ph_3SnLi	$PhBr$	Ph_4Sn	62
12.	Ph_3SnLi	C_2H_5I	$Ph_3SnC_2H_5$	87
13.	Ph_3SnLi	$(C_4H_9O)_3PO$	$Ph_3SnC_4H_9$	70
14.	Ph_3SnLi	CO_2	$Ph_3SnSnPh_3$	85
15.	Ph_3SnLi	H_2O	Ph_3SnH	74
16.	Ph_2PLi	CH_2Cl_2	$Ph_2PCH_2PPh_2$	59

Ph_3CLI and Ph_2CHLi

Triphenylmethyllithium was not used extensively to synthesize Ph_3CMPh_n type compounds because of difficulties encountered in the isolation of the desired product. Tomboulian (4) describes the formation of two different species of organolithium compounds in the direct method preparation of triphenylmethyllithium.

$$Ph_3CCl + 2Li \longrightarrow LiCl + Ph_3CLi \qquad (21)$$



(22)

In addition to the formation of two organometallic species, Ph_3CLi undergoes another undesirable side reaction very readily. When Ph_3CLi is derivatized with Ph_nMCl it readily undergoes a metal-halogen interchange.

$$Ph_3CLi + Ph_nMCl \longrightarrow Ph_3CCl + Ph_nMLi \qquad (23)$$

This reaction further complicates the use of Ph_3CLi as an organometallic reagent for the synthesis of M-M' compounds. The other Ph_nMLi organometallics that were studied also undergo metal-halogen interchange, however, to an apparently lesser extent. In addition, in no case was any other product formed indicative of a reaction similar to that shown in equation 22.

Since Ph_3CLi caused many undesirable by products, it was of interest to see if the analogy would be carried over to the Ph_2CHLi organometallic. The diphenylmethyl derivative Ph_3MCPh_2H could also be converted to compounds possessing a $\equiv MC(Ph_2)M'\equiv$ bonding if such structure should become of interest.

$$Ph_2CHLi + Ph_nMCl \qquad Ph_nMCPh_2H + LiCl \qquad (24)$$

$$Ph_nMCPh_2H + C_4H_9Li \qquad C_4H_{10} + Ph_nMCPh_2Li \qquad (25)$$

$$Ph_nMCPh_2Li + Ph_nM'Cl \qquad LiCl + Ph_nMCPh_2M'Ph_n \qquad (26)$$

Diphenylmethyllithium was prepared very readily by use of the direct method. Some of its reaction products are shown in Table II. Unlike triphenylmethyllithium, diphenylmethyllithium does not appear to form side reaction as shown in equation 22 and 23.

Ph_3SnLi

Triphenyltinlithium has been prepared previously and described in literature by Wittig (5).

$$(C_6H_5)_2Sn + C_6H_5Li \longrightarrow (C_6H_5)_3SnLi \qquad (27)$$

Gilman (6) later modified the preparation according to the following reaction.

$$3C_6H_5Li + SnCl_2 \longrightarrow 2LiCl + (C_6H_5)_3SnLi \qquad (28)$$

By use of the direct method of synthesis, Ph_3SnLi can readily be prepared in high yields. It undergoes various reactions as shown in Table II. Unfortunately, it also undergoes metal-halogen interchange when used for the preparation of Ph_3SnMPh_n compounds. The degree of interchange appears to be less than in the Ph_3CLi reactions.

Cleavage Method

In the course of preparing the various organolithium compounds via the direct method, it appeared that an intermediate compound is formed prior to the formation of the organolithium compound. This assumption is based on the following observations: (1) shortly after the clear THF solution of the chloride is added to the lithium, a white cloudiness appears with most metallic halides (7). At this stage Color Test I is negative. With further reaction the white cloudiness disappears with the formation of a dark colored solution which gives a positive Color Test I; (2) by-product of this reaction usually found in small quantities is the coupled product $(C_6H_5)_nM^{n+1}M^{n+1}(C_6H_5)_n$; (3) the by-product $(C_6H_5)_nM^{n+1}M^{n+1}(C_6H_5)_n$ can readily be cleaved by lithium in THF to produce excellent yields of $(C_6H_5)_nM^{n+1}Li$. Gilman (8) and co-workers in the direct preparation of triphenylsilyllithium noted similar observations and proposed the following series of reactions.

$$(C_6H_5)_3SiCl + 2Li \qquad (C_6H_5)_3SiLi + LiCl \tag{29}$$
$$(C_6H_5)_3SiLi + (C_6H_5)_3SiCl \qquad (C_6H_5)_3SiSi(C_6H_5)_3 + LiCl \tag{30}$$
$$(C_6H_5)_3SiSi(C_6H_5)_3 + 2Li \qquad 2(C_6H_5)_3SiLi \tag{31}$$

To verify our observations, hexaphenylditin, hexaphenyldigermanium, hexaphenyldilead and tetraphenylbiphosphine were all subjected to lithium cleavage in THF and produced excellent yields of the organolithium compound. No attempts were made to optimize the yields of the organolithium compounds prepared either by the direct method or the cleavage of the Ph_nMMPh_n compounds. The organolithium reagent was derivatized with benzyl chloride to produce the benzyl derivatives as shown in Table I. The same benzyl derivatives were synthesized by an alternate route (see equation 20) so that mixed melting points and comparisons of their infrared spectra could be made. The various benzyl derivatives were characterized by elemental analysis, mixture melting points and comparison of the infrared curves of each benzyl derivative made by the three synthesis routes.

Of the two methods used for the preparation of the organolithium compounds, the cleavage of Ph_nMMPh_n method offers some advantage in that the starting material can be obtained in a higher degree of purity and the yields are somewhat higher (see Table I). For the preparation of the various Ph_nMLi compounds, it is felt however that either one of these two methods is preferable to those reported in literature (5,6) since only one species of organolithium compound is present and thus offers a cleaner reaction.

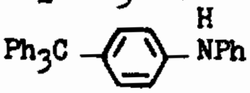
Metal-Halogen Exchange

The preparation and reactions of lithium and sodium diphenylamine was studied. These organometallic compounds were prepared by a metal-hydrogen exchange reaction.

$$Ph_2NH + C_4H_9Li \longrightarrow C_4H_{10} + Ph_2NLi \tag{32}$$
$$Ph_2NH + NaH \longrightarrow H_2 + Ph_2NNa \tag{33}$$

The reactions of these organometallics with various halides is shown in Table III.

TABLE III

	Ph_2N	Reactant	Product	Yield
1.	Ph_2NLi	Ph_3CCl	Ph_2NCPh_3 +	70
				3.2
2.	Ph_2NNa	Ph_3CCl	Ph_2NCPh_3	66
3.	Ph_2NLi	Ph_3SiCl	Ph_2NSiPh_3	68
4.	Ph_2NNa	Ph_3SiCl	Ph_2NSiPh_3	56
5.	Ph_2NLi	Ph_3GeCl	Ph_2NGePh_3	23
6.	Ph_2NNa	Ph_3GeCl	Ph_2NGePh_3	40
7.	Ph_2NLi	Ph_2PCl	Ph_2NPPh_2	58
8.	Ph_2NNa	Ph_2PCl	Ph_2NPPh_2	70

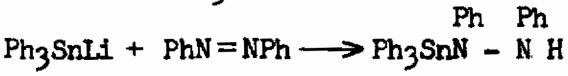
$$Ph_2NNa \text{ or } (Li) + Ph_nMCl \longrightarrow NaCl + Ph_2NMPh_n \qquad (34)$$

In all cases the normal expected product was obtained. In the reaction of Ph_2NLi and Ph_3CCl, however, an additional para isomer was obtained in low yields. Some preliminary acid hydrolysis studies on Ph_3SiNPh_2 have shown that the Si-N bond in such structures is easily cleaved.

$$Ph_3SiNPh_2 + HOH \longrightarrow Ph_3SiOSiPh_3 + Ph_2NH \qquad (35)$$

The properties of the other Ph_nMNPh_2 compounds are presently being investigated.

Attempts to prepare the Ph_3SnNPh_2 compound by reaction 34 has been unsuccessful. Addition of Ph_3SnLi to azobenzene was also unsuccessful.



$$Ph_3SnLi + PhN{=}NPh \longrightarrow Ph_3Sn\overset{Ph}{N} - \overset{Ph}{N}H \qquad (36)$$

Apparently the Sn-N bond is very hydrolytically unstable.

$$Ph_3SnNPh_2 + HOH \longrightarrow Ph_3SnOSnPh_3 + Ph_2NH \qquad (37)$$

In both reactions that failed to yield a Sn-N compound, one of the reaction products identified was $Ph_3SnOSnPh_3$. The desired product containing the Sn-N bond was apparently cleaved during the work up of the reaction. By use of extremely anhydrous conditions it is believed that the Sn-N compound can be isolated.

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3. H. Gilman and F. Schulze, J. Am. Chem. Soc., 47, 2002 (1925).

4. P. Tomboulian, J. Org. Chem., 24, 229 (1959).

5. G. Wittig, Angew. Chem., 62, 231 (1950).

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7. The cloudiness which appears is probably due to the low solubility of the intermediate $(C_6H_5)_nM^{n+1}M^{n+1}(C_6H_5)_n$ in the quantity of solvent used.

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