

ORGANOMETALLIC COMPOUNDS OF GROUP III, IV, AND V

C. Tamborski  
Aeronautical Systems Division

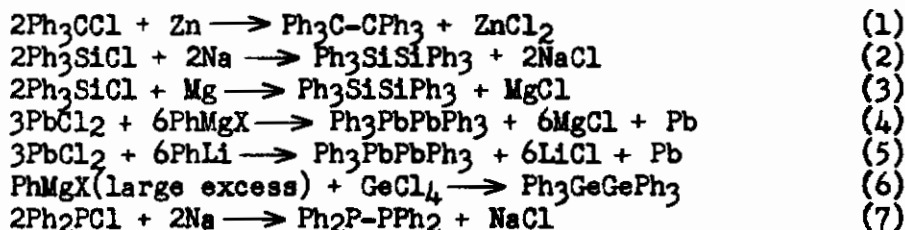
ABSTRACT

The preparation and reactions of a number of organometallic compounds has been studied. The organolithium compounds under investigation are  $\text{Ph}_2\text{CHLi}$ ,  $\text{Ph}_3\text{CLi}$ ,  $\text{Ph}_3\text{SnLi}$ ,  $\text{Ph}_3\text{GeLi}$ ,  $\text{Ph}_3\text{PbLi}$ ,  $\text{Ph}_2\text{PLi}$  and  $\text{Ph}_2\text{NLi}$ . Also included in this series is  $\text{Ph}_2\text{NNa}$ . 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  $\text{R}_n\text{MM}'\text{R}_n$ . 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 = 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 ( $\text{R}_n\text{M-metal}$ ) necessary for the preparation of the perarylated  $\text{R}_n\text{MM}'\text{R}_n$  compounds.

A series of compounds possessing various combinations of elements,  $\text{R}_n\text{MM}'\text{R}_n$ , 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.

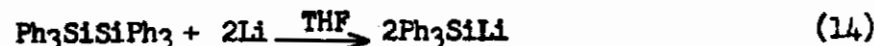
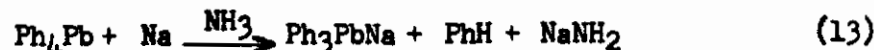
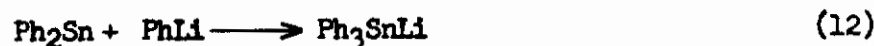
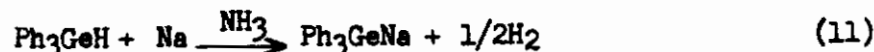
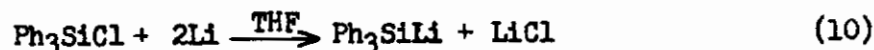
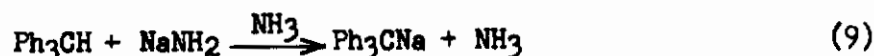
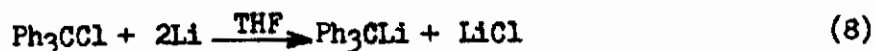
Symmetrical  $\text{Ph}_3\text{M-M}'\text{Ph}_3$



Unsymmetrical  $\text{Ph}_3\text{MM}'\text{Ph}_3$

The unsymmetrical  $\text{Ph}_3\text{MM}'\text{Ph}_3$  compounds require a two-step process. This involves the preparation of an intermediate organometallic,  $\text{Ph}_n\text{M-metal}$ , which is then further reacted with a  $\text{Ph}_n\text{M}'\text{X}$  compound to yield the desired unsymmetrical product. The preparation of the intermediate  $\text{Ph}_n\text{M-metal}$  has been studied quite extensively. A few specific examples for its preparation reported in the literature are the following:

# Contrails



The subsequent reaction of the intermediate  $\text{Ph}_n\text{M}$ -metal with an arylmetallic halide  $\text{Ph}_n\text{M}'\text{X}$  has been studied extensively by Gilman (1) in a series of six publications.



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  $\text{M-M}'$  compounds, essentially three different methods thus far have been used to synthesize the organometallic intermediates.

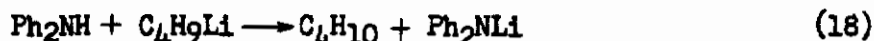
## Direct Method



## Cleavage Method



## Metal-Hydrogen Exchange



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

## Direct Method

The direct method of preparing triphenylsilyllithium ( $\text{Ph}_3\text{SiLi}$ ) 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 diphenylmethylithium, 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.

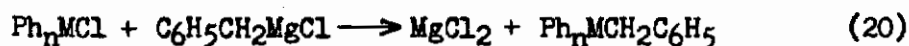


TABLE I

$\text{Ph}_n\text{M}^{n+1}\text{Li}$	Benzyl Derivative	M.P. °	% Yield
$\text{Ph}_3\text{CLi}^a$	$\text{Ph}_3\text{CCH}_2\text{Ph}$	143.5-145	67
---	$\text{Ph}_3\text{CCH}_2\text{Ph}^c$	141.0-142.0	75
$\text{Ph}_3\text{SiLi}^a$	$\text{Ph}_3\text{SiCH}_2\text{Ph}$	98.5-99.5	39
---	$\text{Ph}_3\text{SiCH}_2\text{Ph}^c$	96.0-97.0	65
$\text{Ph}_3\text{GeLi}^a$	$\text{Ph}_3\text{GeCH}_2\text{Ph}$	85.0-86.5	60
$\text{Ph}_3\text{GeLi}^b$	$\text{Ph}_3\text{GeCH}_2\text{Ph}$	85.0-87.0	75
$\text{Ph}_3\text{SnLi}^a$	$\text{Ph}_3\text{SnCH}_2\text{Ph}$	90.0-91.0	77
$\text{Ph}_3\text{SnLi}^b$	$\text{Ph}_3\text{SnCH}_2\text{Ph}$	91.0-92.0	72
---	$\text{Ph}_3\text{SnCH}_2\text{Ph}^c$	91.0-92.0	80
$\text{Ph}_3\text{PbLi}^a$	$\text{Ph}_3\text{PbCH}_2\text{Ph}$	95.0-96.0	76
$\text{Ph}_3\text{PbLi}^b$	$\text{Ph}_3\text{PbCH}_2\text{Ph}$	95.0-97.0	87
---	$\text{Ph}_3\text{PbCH}_2\text{Ph}^c$	94.0-95.0	67
$\text{Ph}_2\text{PLi}^a$	$\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{Ph}^d$	193.0-194.0	80
$\text{Ph}_2\text{PLi}^b$	$\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{Ph}$	193-194	83
---	$\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{Ph}^c$	192.0-193.5	64

- (a) Prepared by the direct method. (b) Prepared by cleavage of  $\text{Ph}_n\text{MMPh}_n$ .  
 (c) Prepared by the reaction of the benzyl Grignard with the  $\text{Ph}_n\text{MCl}$ .  
 (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.

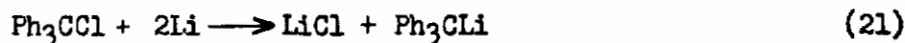
Some other reactions carried out on the individual organolithium compounds are shown in Table II.

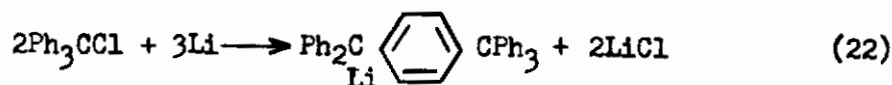
TABLE II

$\text{Ph}_n\text{MLi}$	Reactant	Product	% Yield
1. $\text{Ph}_3\text{CLi}$	$(\text{CH}_3)_3\text{SiCl}$	$\text{Ph}_3\text{CSi}(\text{CH}_3)_3 +$	37
		$\text{Ph}_3\text{C} \begin{array}{c} \text{Ph} \\ \text{CSi}(\text{CH}_3)_3 \\ \text{Ph} \end{array}$	12
2. $\text{Ph}_3\text{CLi}$	$\text{CO}_2$	$\text{Ph}_3\text{CCOOH}$	80
3. $\text{Ph}_2\text{CHLi}$	$\text{Ph}_3\text{SnCl}$	$\text{Ph}_2\text{CHSnPh}_3$	63
4. $\text{Ph}_2\text{CHLi}$	$\text{Ph}_3\text{SiCl}$	$\text{Ph}_2\text{CHSiPh}_3$	81
5. $\text{Ph}_2\text{CHLi}$	$\text{Ph}_2\text{SiCl}_2$	$(\text{Ph}_2\text{CH})_2\text{SiPh}_2$	78
6. $\text{Ph}_2\text{CHLi}$	$\text{PhSiCl}_3$	$(\text{Ph}_2\text{CH})_3\text{SiPh}$	28
7. $\text{Ph}_2\text{CHLi}$	$(\text{CH}_3)_3\text{SiCl}$	$\text{Ph}_2\text{CHSi}(\text{CH}_3)_3$	66
8. $\text{Ph}_2\text{CHLi}$	$\text{CO}_2$	$\text{Ph}_2\text{CHCOOH}$	91
9. $\text{Ph}_3\text{SnLi}$	$\text{Ph}_3\text{SiCl}$	$\text{Ph}_3\text{SnSiPh}_3$	ca. 20
10. $\text{Ph}_3\text{SnLi}$	$(\text{CH}_3)_3\text{SiCl}$	$\text{Ph}_3\text{SnSnPh}_3$	69
11. $\text{Ph}_3\text{SnLi}$	$\text{PhBr}$	$\text{Ph}_4\text{Sn}$	62
12. $\text{Ph}_3\text{SnLi}$	$\text{C}_2\text{H}_5\text{I}$	$\text{Ph}_3\text{SnC}_2\text{H}_5$	87
13. $\text{Ph}_3\text{SnLi}$	$(\text{C}_4\text{H}_9\text{O})_3\text{PO}$	$\text{Ph}_3\text{SnC}_4\text{H}_9$	70
14. $\text{Ph}_3\text{SnLi}$	$\text{CO}_2$	$\text{Ph}_3\text{SnSnPh}_3$	85
15. $\text{Ph}_3\text{SnLi}$	$\text{H}_2\text{O}$	$\text{Ph}_3\text{SnH}$	74
16. $\text{Ph}_2\text{PLi}$	$\text{CH}_2\text{Cl}_2$	$\text{Ph}_2\text{PCH}_2\text{PPh}_2$	59

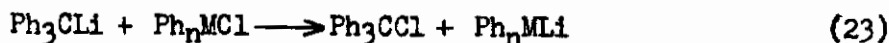
$\text{Ph}_3\text{CLi}$  and  $\text{Ph}_2\text{CHLi}$

Triphenylmethyllithium was not used extensively to synthesize  $\text{Ph}_3\text{CPh}_n$  type compounds because of difficulties encountered in the isolation of the desired product. Tombouliau (4) describes the formation of two different species of organolithium compounds in the direct method preparation of triphenylmethyllithium.



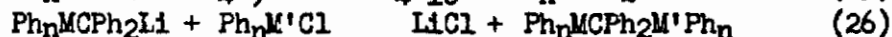
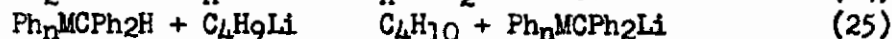
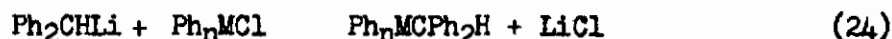


In addition to the formation of two organometallic species,  $\text{Ph}_3\text{CLi}$  undergoes another undesirable side reaction very readily. When  $\text{Ph}_3\text{CLi}$  is derivatized with  $\text{Ph}_n\text{MCl}$  it readily undergoes a metal-halogen interchange.



This reaction further complicates the use of  $\text{Ph}_3\text{CLi}$  as an organometallic reagent for the synthesis of  $\text{M-M'}$  compounds. The other  $\text{Ph}_n\text{MLi}$  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.

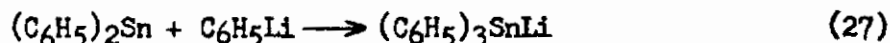
Since  $\text{Ph}_3\text{CLi}$  caused many undesirable by products, it was of interest to see if the analogy would be carried over to the  $\text{Ph}_2\text{CHLi}$  organometallic. The diphenylmethyl derivative  $\text{Ph}_2\text{MCPH}_2\text{H}$  could also be converted to compounds possessing  $\text{a} \equiv \text{MC}(\text{Ph}_2)\text{M}' \equiv$  bonding if such structure should become of interest.



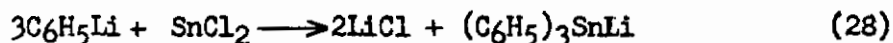
Diphenylmethyl lithium was prepared very readily by use of the direct method. Some of its reaction products are shown in Table II. Unlike triphenylmethyl lithium, diphenylmethyl lithium does not appear to form side reaction as shown in equation 22 and 23.

### $\text{Ph}_3\text{SnLi}$

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



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

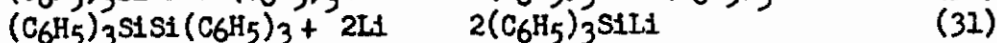
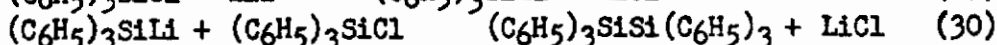
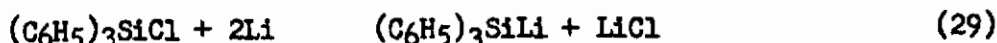


By use of the direct method of synthesis,  $\text{Ph}_3\text{SnLi}$  can readily be prepared in high yields. It undergoes various reactions as shown in Table II. Unfortunately, it also undergoes metal-halogen interchange when used for the preparation of  $\text{Ph}_3\text{SnMPh}_n$  compounds. The degree of interchange appears to be less than in the  $\text{Ph}_3\text{CLi}$  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.



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  $Ph_nMMPPh_n$  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  $Ph_nMMPPh_n$  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.



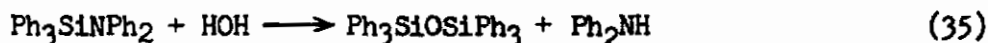
The reactions of these organometallics with various halides is shown in Table III.

TABLE III

Ph <sub>2</sub> N	Reactant	Product	Yield
1. Ph <sub>2</sub> NLi	Ph <sub>3</sub> CCl	Ph <sub>2</sub> NCPPh <sub>3</sub> + Ph <sub>3</sub> C -  - NPh	70 3.2
2. Ph <sub>2</sub> NNa	Ph <sub>3</sub> CCl	Ph <sub>2</sub> NCPPh <sub>3</sub>	66
3. Ph <sub>2</sub> NLi	Ph <sub>3</sub> SiCl	Ph <sub>2</sub> NSiPh <sub>3</sub>	68
4. Ph <sub>2</sub> NNa	Ph <sub>3</sub> SiCl	Ph <sub>2</sub> NSiPh <sub>3</sub>	56
5. Ph <sub>2</sub> NLi	Ph <sub>3</sub> GeCl	Ph <sub>2</sub> NGePh <sub>3</sub>	23
6. Ph <sub>2</sub> NNa	Ph <sub>3</sub> GeCl	Ph <sub>2</sub> NGePh <sub>3</sub>	40
7. Ph <sub>2</sub> NLi	Ph <sub>2</sub> PCL	Ph <sub>2</sub> NPPH <sub>2</sub>	58
8. Ph <sub>2</sub> NNa	Ph <sub>2</sub> PCL	Ph <sub>2</sub> NPPH <sub>2</sub>	70

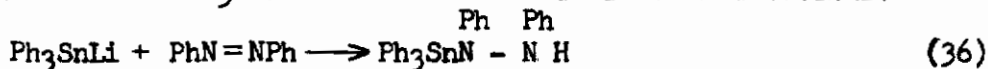


In all cases the normal expected product was obtained. In the reaction of Ph<sub>2</sub>NLi and Ph<sub>3</sub>CCl, however, an additional para isomer was obtained in low yields. Some preliminary acid hydrolysis studies on Ph<sub>3</sub>SiNPh<sub>2</sub> have shown that the Si-N bond in such structures is easily cleaved.

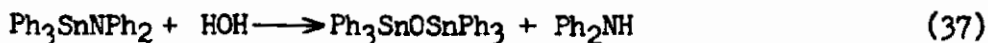


The properties of the other Ph<sub>n</sub>MNPh<sub>2</sub> compounds are presently being investigated.

Attempts to prepare the Ph<sub>3</sub>SnNPh<sub>2</sub> compound by reaction 34 has been unsuccessful. Addition of Ph<sub>3</sub>SnLi to azobenzene was also unsuccessful.



Apparently the Sn-N bond is very hydrolytically unstable.



In both reactions that failed to yield a Sn-N compound, one of the reaction products identified was Ph<sub>3</sub>SnOSnPh<sub>3</sub>. 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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