A New General Method for the Synthesis of Unsubstituted Phosphino-silanes and -germanes

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A general method for the synthesis of unsubstituted phosphino-silanes and -germanes, *i.e.* PH_2-substituted derivatives, has been much investigated. Although Me_3SiPH_2 can be prepared from the reaction of $LiPH_2$ with Me_3SiCl,[1] the analogous reactions between KPH_2 and SiH_3Br,[2] GeH_3Br,[3] and dihalogeno-silanes and -germanes[4] do not yield the desired products. Recently, we reported a new method for the synthesis of GeH_3PH_2 which involves the phosphination of germyl bromide with lithium tetrakis(dihydrogenphosphido)aluminate, $LiAl(PH_2)_4$.[5] Based on subsequent studies of the reactions of $LiAl(PH_2)_4$ with a variety of other halogeno-silanes and -germanes, we now report a possible general method for the preparation of mono- and bis-phosphino-silanes and -germanes.

The results of some typical reactions between $LiAl(PH_2)_4$ and halogeno-silanes and -germanes are shown in the Table. In each case, $LiAl(PH_2)_4$ in diglyme [bis(2-methoxyethyl)ether], prepared essentially as described by Finholt *et al.*,[6] reacted smoothly with the appropriate halide under the stated conditions to yield the desired phosphino-substituted products.

$$LiAl(PH_2)_4 + 4\,MX \rightarrow LiX + AlX_3 + 4\,MPH_2$$

$$LiAl(PH_2)_4 + 2\,M'X_2 \rightarrow LiX + AlX_3 + 2\,M(PH_2)_2$$

$$M = SiH_3,\ Si_2H_5,\ Me_3Si,\ Me_3Ge$$

$$M' = Me_2Si,\ Me_2Ge;\ X = Cl \text{ or } Br$$

The product(s) of the reaction mixtures were separated by low temperature fractional distillation. Each component was characterized by i.r., ^1H and ^{31}P n.m.r., and mass spectral techniques. The physical and spectral properties of the SiH_3PH_2, $Si_2H_5PH_2$, and Me_3SiPH_2 prepared in these reactions were in complete agreement with the published values. Trimethylgermyl phosphine, $Me_2Si(PH_2)_2$ and $Me_2Ge(PH_2)_2$ were prepared for the first time

Summary of data for typical phosphination reactions

Silyl- or germyl halide	Mole ratio halide: $LiAl(PH_2)_4$	Reaction time (temp. °c)	Product (% yield)
SiH_3Br	3·1 : 1·0	20 min. (−45)	SiH_3PH_2 (82)
Si_2H_5Br	3·4 : 1·0	20 min. (−45)	$Si_2H_5PH_2$ (52)
Me_3SiBr	3·0 : 1·0	15 min. (−10)	Me_3SiPH_2 (58)
Me_2SiCl_2	1·5 : 1·0	20 min. (−10)	$Me_2Si(PH_2)_2$ (57)
Me_3GeBr	3·1 : 1·0	20 min. (−23)	Me_3GePH_2 (69)
Me_2GeCl_2	1·4 : 1·0	15 min. (−23)	$Me_2Ge(PH_2)_2$ (46)

and a complete description of these compounds is being reported in detail elsewhere. Small quantities of PH_3 and the parent hydrides (*i.e.* SiH_4 from the SiH_3Br reaction) were also obtained from the phosphination reactions. The source of the PH_3 has not been firmly established yet; however, it appears that the parent silanes or germanes are formed by reduction of the halogeno-silane or -germane by small quantities of residual Al–H-containing material which is inevitably present in the $LiAl(PH_2)_4$ solutions.

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