

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

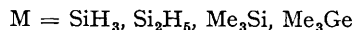
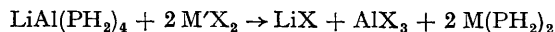
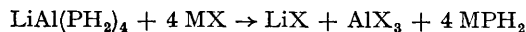
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A general method for the synthesis of unsubstituted phosphino-silanes and -germanes, *i.e.* PH_2 -substituted derivatives, has been much investigated. Although Me_3SiPH_2 can be prepared from the reaction of LiPH_2 with Me_3SiCl ,¹ the analogous reactions between KPH_2 and SiH_3Br ,² GeH_3Br ,³ and dihalogeno-silanes and -germanes⁴ 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(dihydrogen-phosphido)aluminate, $\text{LiAl}(\text{PH}_2)_4$.⁵ Based on subsequent studies of the reactions of $\text{LiAl}(\text{PH}_2)_4$ 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 $\text{LiAl}(\text{PH}_2)_4$ and halogeno-silanes and -germanes are shown in the Table. In each case, $\text{LiAl}(\text{PH}_2)_4$ 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.



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 , $\text{Si}_2\text{H}_5\text{PH}_2$, and Me_3SiPH_2 prepared in these reactions were in complete agreement with the published values. Trimethylgermyl phosphine, $\text{Me}_2\text{Si}(\text{PH}_2)_2$ and $\text{Me}_2\text{Ge}(\text{PH}_2)_2$ were prepared for the first time

Summary of data for typical phosphination reactions

| Silyl- or germyl halide | Mole ratio halide: $\text{LiAl}(\text{PH}_2)_4$ | Reaction time (temp. °C) | Product (% yield) |
|--|--|-----------------------------|--|
| SiH_3Br | 3:1:1:0 | 20 min. (-45) | SiH_3PH_2 (82) |
| $\text{Si}_2\text{H}_5\text{Br}$ | 3:4:1:0 | 20 min. (-45) | $\text{Si}_2\text{H}_5\text{PH}_2$ (52) |
| Me_3SiBr | 3:0:1:0 | 15 min. (-10) | Me_3SiPH_2 (58) |
| Me_2SiCl_2 | 1:5:1:0 | 20 min. (-10) | $\text{Me}_2\text{Si}(\text{PH}_2)_2$ (57) |
| Me_3GeBr | 3:1:1:0 | 20 min. (-23) | Me_3GePH_2 (69) |
| Me_2GeCl_2 | 1:4:1:0 | 15 min. (-23) | $\text{Me}_2\text{Ge}(\text{PH}_2)_2$ (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 $\text{LiAl}(\text{PH}_2)_4$ solutions.

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