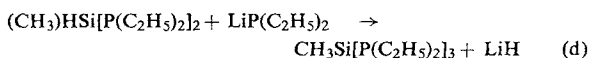
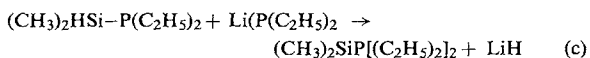
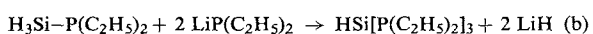
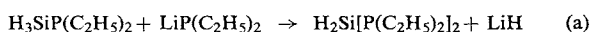


Reactions of Silylphosphines. — Formation of Lithium Tris(diethylphosphinyl)silicide

By G. Fritz and G. Becker[*]

Chlorosilanes such as HSiCl_3 which contain SiH groups react with $\text{LiP}(\text{C}_2\text{H}_5)_2$ to give large amounts of $(\text{C}_2\text{H}_5)_2\text{PH}$ together with silylphosphines. $(\text{C}_2\text{H}_5)_2\text{P}-\text{P}(\text{C}_2\text{H}_5)_2$ is formed from chlorosilanes such as SiCl_4 which do not contain SiH groups, provided that an excess of $\text{LiP}(\text{C}_2\text{H}_5)_2$ is present^[1]. In addition, red polymers containing Si-Si groups are formed. These side reactions are almost completely suppressed if an excess of the chlorosilane is maintained during the whole reaction, as can be done by adding dropwise an ethereal solution of the phosphide to the chlorosilane^[2]. Thence it can be assumed that a silylphosphine formed as intermediate is reactive towards the strongly nucleophilic phosphide. We have therefore prepared silyl- and methylsilyl-phosphine and have studied their behavior towards $\text{LiP}(\text{C}_2\text{H}_5)_2$ in diethyl ether. The course of the reaction was followed by measurement of the NMR spectrum.

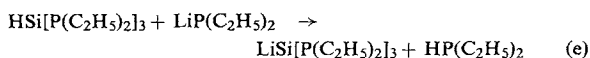
We found that $(\text{CH}_3)_3\text{Si}-\text{P}(\text{C}_2\text{H}_5)_2$ and $\text{LiP}(\text{C}_2\text{H}_5)_2$ do not react with each other, even during a long period. However, SiH-containing silylphosphines do react, giving phosphorylated products:



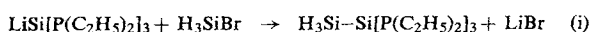
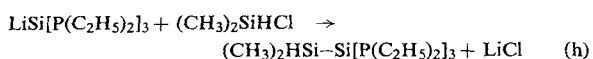
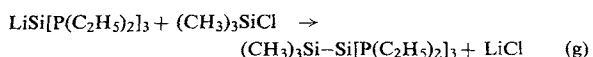
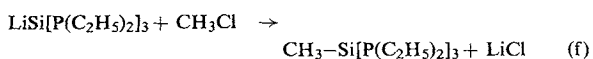
Since reaction (a) is the fastest, it is understandable why the compounds $\text{H}_2\text{Si}[\text{P}(\text{C}_2\text{H}_5)_2]_2$ and $\text{HSi}[\text{P}(\text{C}_2\text{H}_5)_2]_3$ always occur as by-products in the preparation of $\text{H}_3\text{Si}-\text{P}(\text{C}_2\text{H}_5)_2$ from H_3SiBr and $\text{LiP}(\text{C}_2\text{H}_5)_2$. Reaction of LiH with H_3SiBr gives SiH_4 .

Reactions (c) and (d) are appreciably slower. Reaction (d), the slowest, requires several days for completion.

$\text{HSi}[\text{P}(\text{C}_2\text{H}_5)_2]_3$ and $\text{LiP}(\text{C}_2\text{H}_5)_2$ react quite differently. If the two compounds are mixed in ether in an NMR tube and the NMR spectrum is measured immediately, the following observations can be made: The quartet of the SiH resonance, which arises by spin-spin coupling with the three phosphorus atoms, has almost disappeared and simultaneously the multiplet of the phosphorus-hydrogen resonance of diethylphosphine appears. After about 2 hours the Si-H resonance can hardly be seen at all in the spectrum. The color of the ethereal solution has changed from pale yellow to bright red. The reaction occurs in accordance with



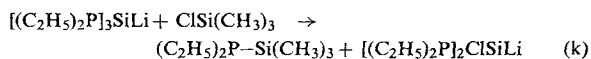
The diethylphosphine formed can be distilled off with the solvent in a vacuum and oxidized by iodine solution to diethylphosphinous acid. This analysis shows 80% of the $\text{HP}(\text{C}_2\text{H}_5)_2$ expected for the complete reaction.



Lithium tris(diethylphosphinyl)silicide, $\text{LiSi}[\text{P}(\text{C}_2\text{H}_5)_2]_3$, cannot be isolated in crystalline form. It is obtained as a red resinous substance which redissolves completely in ether. It reacts with CH_3Cl , $(\text{CH}_3)_3\text{SiCl}$, $(\text{CH}_3)_2\text{SiHCl}$, and H_3SiBr according to equations (f)–(i). In reaction (f) a Si-C bond is formed, but in (g)–(i) phosphinyl derivatives of disilane are obtained.

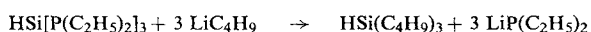
Experimental: $\text{HSi}[\text{P}(\text{C}_2\text{H}_5)_2]_3$ was mixed with the stoichiometric amount of $\text{LiP}(\text{C}_2\text{H}_5)_2$ in ether, then kept at 20°C for about 5 h, after which the diethylphosphine was pumped off with the solvent. There remained the red resinous $\text{LiSi}[\text{P}(\text{C}_2\text{H}_5)_2]_3$, which dissolved without residue on renewed addition of ether. The halogen compound was condensed on to the frozen solution, in which it dissolved at about -90°C. Reaction occurs only between -50° and -60°C, the solution being decolorized and the appropriate amount of lithium halide precipitated. The products were isolated by distillation. Yields are 30–40%.

The products indicated in equations (f)–(i) are accompanied by less volatile products containing Si-Si bonds and by simple silylphosphines such as diethyl(trimethylsilyl)phosphine, which is formed by reaction of $\text{LiSi}[\text{P}(\text{C}_2\text{H}_5)_2]_3$ with $(\text{CH}_3)_3\text{SiCl}$. Thus substitution of the lithium [eq. (g)] is accompanied by fission of the Si-P bond by the halogen compound [eq. (k)].



This product, which contains lithium and halogen on the same Si atom, gives substances of high molecular weight with loss of LiCl.

In contrast to reaction (e), $\text{HSi}[\text{P}(\text{C}_2\text{H}_5)_2]_3$ and butyllithium in pentane do not react with metalation of the Si atom:



Metalation in accord with equation (e) occurs only with $\text{HSi}[\text{P}(\text{C}_2\text{H}_5)_2]_3$. If either one or two $(\text{C}_2\text{H}_5)_2\text{P}$ groups are attached to the Si atom, then reaction occurs with formation of LiH [eq. (a)–(d)]. Apparently the Si-H hydrogen loses its hydride character as the number of $(\text{C}_2\text{H}_5)_2\text{P}$ on the Si atom increases, so that the exchange for lithium becomes understandable in the case of $\text{HSi}[(\text{C}_2\text{H}_5)_2]_3$. Similar conclusions can be drawn from the NMR spectra of the SiH-containing compounds of this series.

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[1] G. Fritz, G. Poppenburg, and M. Rocholl, *Naturwissenschaften* 49, 449 (1962); G. Fritz and G. Poppenburg, *Angew. Chem.* 75, 297 (1963); *Angew. Chem. internat. Edit.* 2, 262 (1963).

[2] G. Fritz, *Angew. Chem.* 78, 80 (1966); *Angew. Chem. internat. Edit.* 5, 53 (1966).