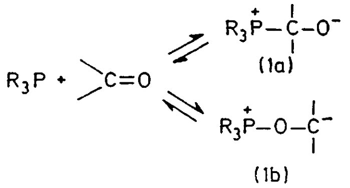
Novel Reaction of Silylaminophosphines with Ketones

By Robert H. Neilson* and Donald W. Goebel
(*Department of Chemistry, Texas Christian University, Fort Worth, Texas* 76129)

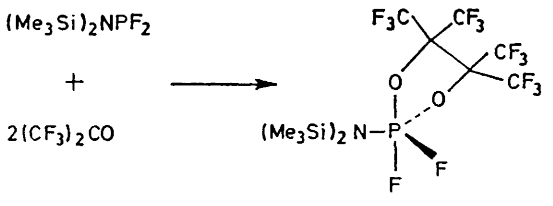
Summary In a process which involves a [1,5] silyl migration from nitrogen to oxygen, treatment of $(Me_3Si)_2NPMe_2$ with hexafluoroacetone or acetone itself affords the P–C bonded phosphine imines $Me_3SiN{=}PMe_2[CR_2(OSiMe_3)]$ ($R = CF_3$ or Me).

Usually the addition of neutral trivalent phosphorus compounds to isolated carbonyl groups is highly reversible with the equilibrium [equation (1)] lying well to the left.[1]



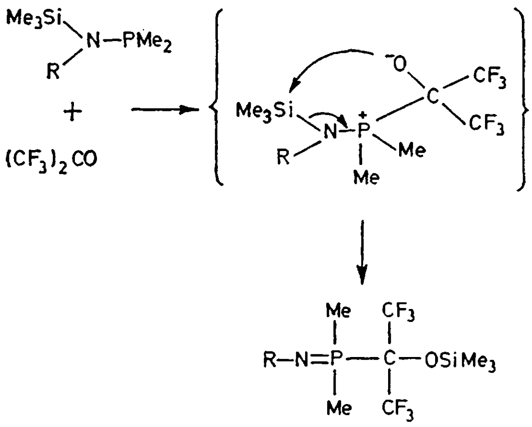
(1)

With hexafluoroacetone, however, a net reaction occurs in which the betaine (**1b**) attacks a second molecule of the carbonyl compound to generate a stable pentacovalent compound.[1,2] Schmutzler *et al.*[3] have observed this type of reaction [equation (2)] for a difluorophosphine bearing a silicon–nitrogen substituent.



(2)

In striking contrast to these earlier studies, we find that the reaction of *P*-methylated silylaminophosphines[4] with hexafluoroacetone takes a more novel course [equation (3)] involving 1 : 1 stoicheiometry and a [1,5] silyl shift from nitrogen to oxygen.



(3)

(2); R = Me₃Si
(3); R = Bu^t

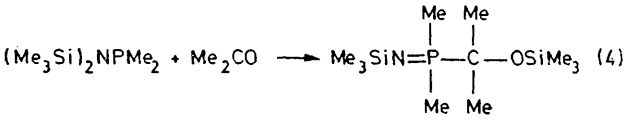
In a typical experiment, an excess of gaseous $(CF_3)_2CO$ (18·6 mmol) was introduced into an evacuated flask containing $(Me_3Si)_2NPMe_2$ (9·3 mmol) which was being stirred at 0 °C. An exothermic reaction ensued in which only 1 equiv. of $(CF_3)_2CO$ was consumed. Distillation gave a colourless liquid (89% yield, b.p. 39—40 °C at 0·2 Torr) identified as the phosphine imine (**2**) by ^1H and ^{13}C n.m.r. spectroscopy (Table). Similarly, the t-butyl analogue (**3**) was prepared in 81% yield. Satisfactory elemental analyses confirm the 1 : 1 stoicheiometry of the reaction. More-

Table. ^1H and ^{13}C n.m.r. data for (**2**).

Signal	$\delta(^1H)$	$\delta(^{13}C)$	J/Hz
Me_3SiO	0·03	1·14	
Me_3SiN	0·30	3·51	P–C 3·1
Me_2P	1·55	17·77	P–H 12·5, P–C 72·6
$(\mathit{CF}_3)_2\mathrm{C}$		123·10	F–C 289·9
$(\mathrm{CF}_3)_2\mathit{C}$		77·48	P–C 70·8 F–C 28·1

over, the method of mixing reagents is not a critical factor since comparable yields of (**2**) and (**3**) were obtained when the reactants were condensed together and allowed to warm slowly from −196 °C.

The alternative structure $\mathrm{RN{=}PMe_2[OC(CF_3)_2(SiMe_3)]}$ was considered but rejected since the ^{13}C n.m.r. spectrum contains a doublet of septets for the quaternary $C(\mathrm{CF_3})_2$ carbon with the large value of J_{PC} (*ca.* 70 Hz) being indicative of a phosphorus–carbon bond.[5,6] Attack at the carbonyl carbon rather than oxygen is further illustrated by the fact that acetone itself reacts similarly, but more slowly with $\mathrm{(Me_3Si)_2NPMe_2}$ [equation (4)]. A J_{PC} value of 96·4 Hz ($\mathrm{P}C\mathrm{Me_2}$) was obtained for compound (**4**) which was isolated in 80% yield after reaction for 3 days in $\mathrm{CH_2Cl_2}$ solution.



$$\mathrm{(Me_3Si)_2NPMe_2 + Me_2CO \longrightarrow Me_3SiN{=}\overset{Me}{\underset{Me}{P}}{-}\overset{Me}{\underset{Me}{C}}{-}OSiMe_3} \qquad (4)$$

(4)

Clearly, these reactions demonstrate that the nucleophilic character of the phosphine centre can be utilized in combination with the high reactivity of the Si–N bond in silylaminophosphines to effect the synthesis of new types of functionalized organophosphorus compounds.

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