A New Synthetic Route to λ^3-Iminophosphines involving Nucleophilic Displacement Reactions on Aminoiminophosphines

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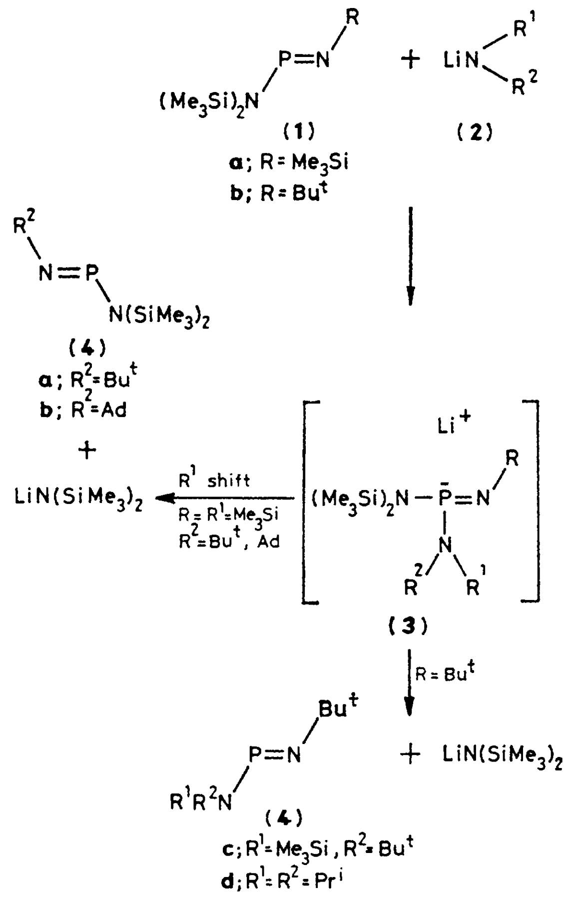
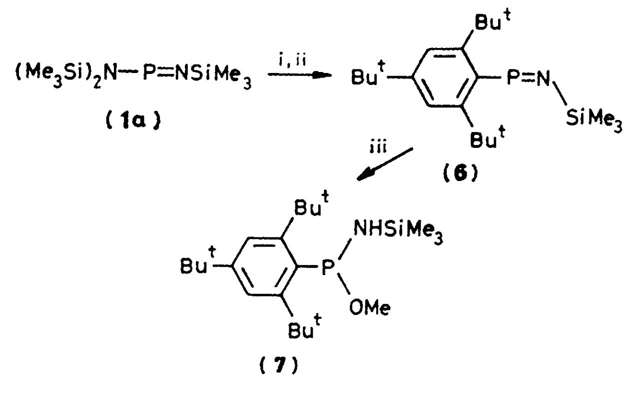
Aminoiminophosphines undergo transamination when treated with highly hindered lithium amides; this observation is exploited in the synthesis of $Bu^t_3C_6H_2P{=}NSiMe_3$, the first thermally stable dico-ordinated phosphorus compound based on the skeleton C–P=N.

Thermal elimination of small, energetically stable molecules XY (X = Me_3Si, Li; Y = halogen) from the crowded phosphorus–nitrogen bond –P(Y)–N(X)– has so far been the only synthetic route to λ^3-iminophosphines.[1] Our interest in



Scheme 1



Scheme 2. *Reagents:* i, 2,4,6-tri-t-butylphenyl-lithium; ii, 2,2,6,6-tetramethylpiperidine hydrochloride; iii, methanol, hexane, 3 h at 0 °C.

the reactions of aminoiminophosphines (**1**) with a variety of nucleophiles has led us to elaborate a novel route to λ^3-iminophosphines *via* nucleophilic displacement at the dico-ordinated phosphorus atom in the aminoiminophosphine series (Schemes 1 and 2).

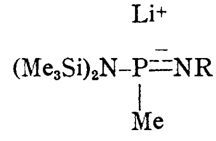
Treatment of (**1a**) with $LiN(SiMe_3)Bu^t$ (1 equiv.) in tetrahydrofuran (THF) at 20 °C gives (**4a**) in quantitative yield. Analogously, the reaction of (**1a**) with $LiN(SiMe_3)Ad$ (Ad = 1-adamantyl) results in the exclusive formation of the respective adamantyl substituted aminoiminophosphine (**4b**). Transformations (**1b**)→(**4c**) and (**1b**)→(**4d**) were also quantitative at room temperature. The results of these reactions are summarized in Table 1.

Table 1. Results of the reactions of the aminoiminophosphines (**1**) with lithium amides (**2**).[a]

Starting aminoimino-phosphine (1)	Lithium amide (2)[b]	Product[c]	%Yield of product[d,e]
(**1a**)	$LiN(SiMe_3)Bu^t$	(**4a**)[f]	100(86)
(**1a**)	$LiN(SiMe_3)Ad$	(**4b**)[f]	100(75)
(**1b**)	$LiN(SiMe_3)Bu^t$	(**4c**)	100(89)
(**1b**)	$LiNPr^i_2$	(**4d**)	100(86)

[a] All reactions and manipulations were carried out under an argon atmosphere. [b] 1.0 equiv. with respect to (**1**). [c] All compounds were identified by comparison with authentic samples prepared by published procedures (*cf.* ref. 1) [d] Determined by ^{31}P n.m.r. spectroscopy. [e] The figures in parentheses show the isolated yield after distillation. [f] Reactions of the aminoiminophosphine (**1a**) with $LiN(SiMe_3)Bu^t$ and $LiN(SiMe_3)Ad$ involve an irreversible [1,3]silyl migration in the N–P–N system. The $(Me_3Si)_2N$-substituted iminophosphines (**4a**) and (**4b**) are both thermodynamically stable isomers (*cf.* refs. 1a, b).

We recently showed that addition of methyl-lithium to the aminoiminophosphines (**1**) results in the formation of the ionic species (**5**) in which the methyl group is directly attached



$$\begin{array}{c} Li^+ \\ (Me_3Si)_2N\text{-}\overset{-}{P}\text{=}NR \\ | \\ Me \end{array}$$

(**5**)

to phosphorus.[2] We now report that the reactions of aminoiminophosphines with hindered organolithium compounds provide a pathway to derivatives of dico-ordinated phosphorus based on the skeleton C–P=N.† The λ^3-iminophosphine (**6**), the first thermally stable compound of the C–P=N type, has been synthesised by a nucleophilic displacement reaction between the aminoiminophosphine (**1a**) and 2,4,6-tri-t-butylphenyl-lithium (Scheme 2). The detailed procedure was as follows: (**1a**) (0.03 mol) in THF (30 ml) was added to a stirred solution of 2,4,6-tri-t-butylphenyl-lithium[3] (0.03 mol) in THF (180 ml) at −78 °C under an argon atmosphere and stirred at this temperature for 1 h and then at 20 °C for 0.5 h. Then the mixture was cooled to −30 °C and 2,2,6,6-tetramethylpiperidine hydrochloride (0.03 mol) was added. After 20 min the mixture was warmed to room temperature with stirring, filtered, and concentrated. Distillation of the residue afforded (**6**) (55%), b.p. 110 °C at 0.001 mmHg, as an orange-red liquid extremely sensitive to hydrolysis; *m/z* 363 (11%, M^+), cryoscopic molar mass (in C_6H_6) 350; ^1H n.m.r. δ (C_6D_6) 7.27 (s, 2H, aromatic), 1.41 (s, 18H, *o*-Bu^t), 1.25 (s, 9H, *p*-Bu^t), 0.14 (s, 9H, Me_3Si). Noteworthy of (**6**) is its ^{31}P n.m.r. signal which appears at extremely low field (476 p.p.m. in THF). Reaction of (**6**) with methanol at 0 °C gives (**7**) in 70% yield after distillation (b.p. 122—124 °C, 0.02 mmHg); *m/z* 395 (14%, M^+); ^1H n.m.r. δ(C_6D_6) 7.30 (s, 2H, aromatic), 3.24 (d, *J* 13.6 Hz, 3H, POMe), 1.67 (s, 18H, *o*-Bu^t), 1.28 (s, 9H, *p*-Bu^t), and 0.10 (s, 9H, Me_3Si); ^{31}P n.m.r. δ (hexane) 118.7 p.p.m., ^3J(HP) 13.6 Hz.

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† The first example of this class of compound described in the literature was $Bu^tN{=}PBu^t$ obtained from $Bu^tN(Li){-}P(F)Bu^t$,[1c] which was characterised by n.m.r. spectroscopy. It dimerizes at a temperature higher than −40 °C.

Clearly, the above transformations demonstrate that nucleophilic substitution in aminoiminophosphines can be utilized for the synthesis of new types of functionalized dicoordinated phosphorus compounds.

Received, 15th September 1982; Com. 1099

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