Structures and Reactions of Iminophosphoranide Anions

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It is demonstrated that iminophosphoranide anions are formed when the aminoiminophosphine $(Me_3Si)_2N-P=N(SiMe_3)$ is treated with $LiAlH_4$ or $MeLi$; their structures and reactions have been investigated.

Proton abstraction from secondary aminophosphines followed by treatment with active halides has been shown to be a useful approach to the synthesis of novel P- and N-containing compounds.[1,2] However, the structures of the implied anionic intermediates are not clear and cannot be deduced from the identities of the products because of the possibility of sigmatropic rearrangement(s). Addition of H^- to $R_2N-P=NR$ or deprotonation of $R_2N-PH-NHR$ could, in principle, result in phosphide (1), amide (2), or iminophosphoranide (3) anions. We present evidence which indicates that the preferred structure is (3) when R = Me_3Si.

Treatment of the aminoiminophosphine, $(Me_3Si)_2N-P=N(SiMe_3)$ (4),[3] with $LiAlH_4$ in diethyl ether solution at 0 °C, followed by quenching of the reaction mixture with D_2O results in the mono-deuteriated secondary aminophosphines, (5a, b). The [31]P n.m.r. spectrum of (5a, b) indicates the presence

of P–H and P–D bonds in equal abundances at $+33.8$ p.p.m.,† (J_{PH} 219.7 Hz, J_{PD} 33.0 Hz). The i.r. spectrum of a liquid film of (5a, b) exhibits P–H and P–D, and N–H and N–D stretching vibrations of approximately equal intensities at 2245, 1640, 3350, and 2480 cm^{-1}, respectively. Reduction of (4) with $LiAlD_4$ in diethyl ether solution at 0 °C, followed by
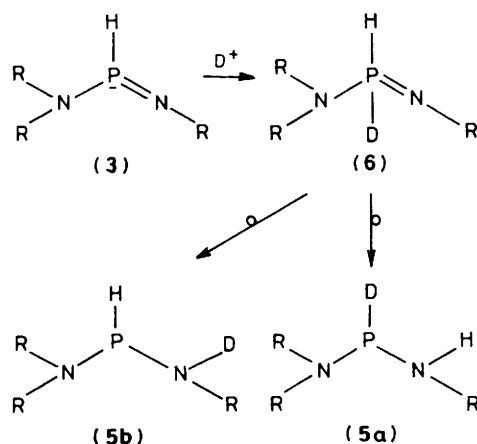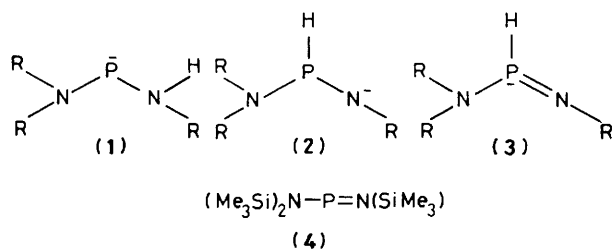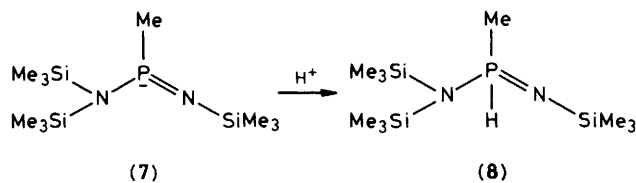

(3)　　　(6)

(5b)　　　(5a)

$(Me_3Si)_2N-P=N(SiMe_3)$

(4)

H_2O quenching of the reaction mixture, results in a material with spectral properties identical to those of (5a, b). The deuteriation experiments rule out anion structures (1) and (2) because in e.g. the $LiAlH_4$–D_2O experiment, anion (1) should give 100% of the P–D bonded aminophosphine, (5a), and (2) should produce exclusively the N–D compound, (5b). Only the iminophosphoranide structure (3) is consistent with the observed 50/50 mixture of N–H/N–D and P–H/P–D bonds in aminophosphines, (5a, b).‡ The final product arises by e.g. D^+ attack on anion (3) to give the iminophosphorane, (6), which rearranges to (5a) or (5b) via hydrogen or deuterium shift, respectively. The phosphoranide anion, (3), also results from the deprotonation of $(Me_3Si)_2NP(H)N(H)(SiMe_3)$ (5) because treatment of the latter with an equimolar quantity of Bu^nLi in n-hexane solution at $-78\,°C$, followed by D_2O quench, produces (5a, b).

The intermediacy of the iminophosphorane, (6), is supported by analogous methylation experiments. Thus, (4) reacts readily with MeLi in diethyl ether solution at $-78\,°C$. Hydrolysis of the reaction mixture produces the iminophosphorane, (8), presumably via anion (7). Compound (8) can also be produced by treatment of (5) with Bu^nLi followed by MeI. The constitution of (8), which can be regarded as the product of oxidative addition of CH_4 to $(Me_3Si)_2N-P=N(SiMe_3)$, is established by n.m.r. spectroscopy: ^1H (90.0 MHz) $NSiMe_3$ (δ 0.11, 9H, s), $N(SiMe_3)_2$ (δ 0.34, 18H, s), PMe (δ 1.68,

(7)　　　　　　　　　　　　(8)

3H, dd, J_{PCH} 13.3, J_{HPCH} 3.0 Hz); $^{13}C\{^1H\}$ (20.0 MHz) (p.p.m., Me_4Si) δ 1.77 ($NSiMe_3$, d, J_{PNSiC} 6.2 Hz), 5.24 [$N(SiMe_3)_2$, d, J_{PNSiC} 8.5 Hz], and 25.4 (PMe, d, J_{PC} 20.4 Hz); ^{31}P (36.43 MHz) -13.6 p.p.m.† (d, J_{PH} 463.4 Hz). The presence of both Me and H groups on phosphorus is demonstrated inter alia by the large values of J_{PH} and J_{PCH} and by the ^{13}C n.m.r. parameters for the PMe group.[4]

References

1 E. Niecke and G. Ringel, Angew. Chem., Int. Ed. Engl., 1977, 16, 486.

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3 E. Niecke and W. Flick, Angew. Chem., Int. Ed. Engl., 1973, 12, 585.

4 For ^{13}C parameters of other PMe compounds, see A. H. Cowley, J. E. Kilduff, and J. C. Wilburn, J. Am. Chem. Soc., 1981, 103, 1575.

‡ In principle, this result could also arise from an equilibrium between (1) and (2) for which $K = 1$. However, we consider this possibility unlikely.