Spontaneous Formation of a Dicoordinate Iminophosphine from a Tricoordinate Triaminophosphine *via* a Tetracoordinate Phosphorane

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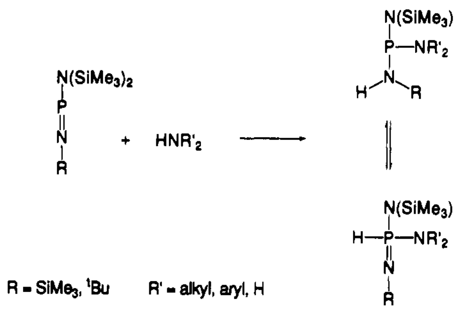
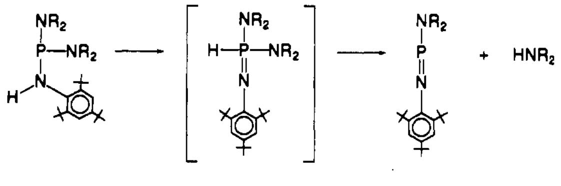
Received April 29, 1993

Dicoordinate environments for phosphorus are generally considered unstable with respect to compounds involving higher coordination numbers.[1] For example, iminophosphines (one of the more extensive series of compounds containing dicoordinate phosphorus)[2] are observed to dimerize unless prevented by steric shielding.[3] Iminophosphines also readily undergo addition reactions,[4–6] as illustrated for reactions with primary or secondary amines in eq 1,[4] giving three- or four-coordinate phosphorus (tautomer stability is dependent upon the substituents).[4,7]



(1)

Here we report the first examples of the spontaneous reverse reaction, the elimination of a secondary amine from a triaminophosphine (eq 2), indicating thermodynamic preference for the dicoordinate phosphine over the tricoordinate phosphine. The process is enforced by the extreme steric influences of the 2,4,6-tri-*tert*-butylphenyl (Mes*) substituent but, interestingly, proceeds *via* a four-coordinate iminophosphorane. To confirm the potential for four coordination at phosphorus under such sterically demanding circumstances, the first structural characterization of a ((2,4,6-tri-*tert*-butylphenyl)imino)phosphorane is also presented.



(2)

1 **2** **3**

a: $NR_2 = NMe_2$; **b**: $NR_2 = NEt_2$; **c**: NR_2 = piperidino; **d**: $NR_2 = N^iPr_2$

Dicoordinate phosphine derivatives are most commonly generated using reactions that are apparently driven by the exothermic precipitation of a salt or elimination of a halosilane.[1,2] We have now realized the surprising analogous reaction for derivatives of $(NR_2)_2P$–N(H)Mes* (**1**). These compounds eliminate HNR_2 under ambient conditions to give the corresponding iminophosphines NR_2–P=NMes* (**3**) (known compounds),[8] in high or quantitative yield as shown by NMR spectroscopy.[9] A ^{31}P NMR study of compound **1b** (75% ^{15}N labeled at NMes*)[10] with time shows the appearance of a signal at −17.7 ppm, coincident with the decrease in intensity of the signal at 116 ppm (**1b**) and prior to the appearance of the signal at 230 ppm corresponding to **3b**. On the basis of ^1H NMR data (specifically a doublet of doublets $^1J_{HP} = 565$ Hz and $^2J_{HN} = 8$ Hz[4] for the phosphorus-bound H) and IR data (P–H stretch at 2197 cm^{-1}), we conclude that the intermediate (−17.7 ppm) is the isomeric iminophosphorane **2b**, the result of a tautomerism of **1b** effecting hydrogen transfer from nitrogen to phosphorus and perhaps facilitating elimination.

Preliminary studies clearly indicate that the rates of elimination follow the trend **1a** > **1b** > **1c** > **1d**, with **1d** apparently stable and **3d** only evident after a few weeks, possibly due to a sterically imposed unfavorable conformation for the tautomeric hydrogen

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(9) A solution of LiNHMes* was prepared by the addition of nBuLi in hexanes to an equimolar quantity of (2,4,6-tri-*tert*-butylphenyl)amine (0.5 g, 1.9 mmol) in diethyl ether (40 mL) under an atmosphere of dry nitrogen. This was added to an equimolar quantity of R_2PCl ($R = NMe_2$, NEt_2, piperidino, N^iPr_2) in diethyl ether (30 mL) at 0 °C with stirring. The solution was allowed to warm to room temperature, and the solvent was quickly removed *in vacuo*. The reaction mixture was redissolved in deuterated solvent ($CDCl_3$ or CD_2Cl_2), and ^{31}P and ^1H NMR spectra were obtained at regular intervals. **a** [$NR_2 = NMe_2$ (CD_2Cl_2)]: **1a** not observed; **2a**, ^{31}P −18 ppm [$^1J_{PN} = 49$ Hz], ^1H 7.22 ppm (dd, 1H) [$^2J_{HN} = 10$ Hz, $^1J_{HP} = 577$ Hz]; **3a**, ^{31}P 211 ppm (cf. 203 in C_6D_6).[8] **b** [$NR_2 = NEt_2$ ($CDCl_3$)]: **1b**, ^{31}P 116 ppm [$^1J_{PN} = 76$ Hz], ^1H 7.14 ppm (s, 2H), 4.55 ppm (dd, 1H) [$^1J_{HN} = 72$ Hz, $^2J_{HP} = 4$Hz], 2.92 ppm (m, 8H), 1.47 ppm (s, 18H), 1.25 ppm (s, 9H), 0.89 ppm (t, 12H) [$^3J_{HH} = 7$ Hz]; **2b** appeared after 1 h, ^{31}P −17.7 ppm [$^1J_{PN} = 46$ Hz] {**2b** exhibits ^1H NMR similar to that of **4b**, except for 7.27 ppm (dd, 1H) [$^1J_{HP} = 565$ Hz, $^2J_{HN} = 8$ Hz][4]}; subsequently, **3b** appeared, ^{31}P 230 ppm (cf. 225 in C_6D_6).[8] A solution IR study of **1b** with time shows the appearance and disappearance of a band at 2197 cm^{-1} (ν_{P-H}). **c** [NR_2 = piperidino (CD_2Cl_2)]: **1c**, ^{31}P 109 ppm [$^1J_{PN} = 76$ Hz]; ^1H 7.28 ppm (s, 2H), 4.54 ppm (dd, 1H) [$^1J_{HN} = 74$ Hz, $^2J_{HP} = 5$Hz], 3.11–2.87 ppm (m, 8H), 1.67–1.34 ppm (m, 12H), 1.54 ppm (s, 18H), 1.33 ppm (s, 9H); **2c** formed within 2 h, ^{31}P −22 ppm [$^1J_{PN} = 51$ Hz]; **3c** formed within hours, ^{31}P 214 ppm (cf. 207 in C_6D_6).[8] **d** [$NR_2 = N^iPr_2$ ($CDCl_3$)]: **1d**, ^{31}P 91 ppm [$^1J_{PN} = 76$ Hz]; ^1H 7.25 ppm (s, 2H), 4.51 ppm (d, 1H) [$^1J_{HN} = 74$ Hz, $^2J_{HP} = 2$ Hz], 3.41 ppm (m, 4H), 1.48 ppm (s, 18H), 1.23 ppm (s, 9H), 1.20 ppm (d, 6H), 1.17 ppm (d, 6H), 1.09 ppm (d, 6H), 0.93 ppm (d, 6H) [$^3J_{HH} = 7$ Hz]; intermediate **2d** not observed; **3d** first appeared after 2 weeks as part of a complex spectrum, ^{31}P 269 ppm (cf. 268 in C_6D_6).[8]

(10) Burgers, J.; Hoefnagel, M. A.; Verkade, P. E.; Viser, H.; Webster, B. M. *Recl. Trav. Chim.* **1958**, *77*, 491. Incomplete (75%) nitration of 2,4,6-tri-*tert*-butylbenzene by 95% enriched $H^{15}NO_3$ was completed by addition of excess HNO_3.

0020-1669/93/1332-4988$04.00/0

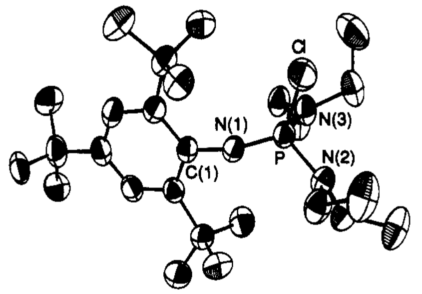

Figure 1. ORTEP view of $(NEt_2)_2P(Cl){=}NMes^*$ (**4b**). Selected metrical values: P–Cl = 2.100(1) Å; P–N(1) = 1.492(2) Å; P–N(1)–C(1) = 161.5(2)°.

transfer. The tautomerism has been reported between less sterically substituted aminophosphine and iminophosphorane derivatives ($=NSiMe_3$),[4] and thermodynamic preference for the phosphorane is interpreted in terms of a P–H bond (in the tetracoordinate phosphorane) being less stereochemically demanding than a nonbonding pair (in the tautomeric tricoordinate phosphine).[4] Tetracoordination at phosphorus in the presence of the (2,4,6-tri-*tert*-butylphenyl)imino substituent has not been reported. Therefore, we have prepared the thermally stable chloro derivative of **2b** (**4b**)[11] by the facile reaction of **1b** with CCl_4[12] and confirmed the structure by X-ray crystallography (Figure 1).[13]

It is generally thought that low-coordinate environments for non-metal elements are kinetically stabilized by bulky substituents.[14] In this context, the Mes* substituent has been employed to prevent dimerization or oligomerization of a diphosphene,[15] an aluminum aryloxide,[16] an iminoborane,[17] and group 13 halides,[18] for example. Observation of spontaneous generation of an acyclic[19] dicoordinate phosphine by elimination from the tricoordinate phosphine **1** demonstrates, for the first time, the thermodynamic consequences of this sterically imposing substituent. In addition, we conclude that thermodynamically favorable coproducts, such as $MgCl_2$,[2] are perhaps redundant in the synthesis of Mes*-substituted iminophosphines, and therefore, the process offers a simpler and cleaner means of preparation.[20]

We note that (phenylamino)phosphines [e.g. $(PhNH)_3P$] have been reported to decompose on heating *via* amine elimination and oligomerization.[21] On the basis of our observations, it is likely that eliminations from the phenyl derivatives proceed in a fashion similar to that of the derivatives of **1**; however, the derivatives of **3** presented above are sterically prevented from further reaction and oligomerization.

Acknowledgment. We thank the Natural Sciences and Engineering Council of Canada (N.B.), the donors of the Peteroleum Research Fund. administered by the American Chemical Society (N.B.), and the NSF (equipment grant) and NSF/EPSCOR program (J.F.R.) for financial support, the Atlantic Region Magnetic Resonance Centre for use of the instrumentation, and Professor Rod Wasylishen for providing $H^{15}NO_3$ used in the preparation of $Mes^{15}NH_2$.

Supplementary Material Available: Tables of crystal data, atomic positional and thermal parameters, bond distances and angles, and anisotropic thermal parameters (7 pages). Ordering information is given on any current masthead page.

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(11) Carbon tetrachloride (0.56 mL, 5.7 mmol) was added to a solution of **1b**, obtained *in situ* as described above. The reaction mixture was stirred at room temperature for 4 h, then the LiCl was removed by filtration, and slow removal of the solvent *in vacuo* yielded colorless crystals of **4b** (0.60 g, 67%), mp. 65–67 °C. NMR ($CDCl_3$): ^{31}P –21 ppm [$^1J_{PN}$ = 78 Hz]; ^1H 7.17 ppm (s, 2H), 3.06 ppm (m, 8H), 1.33 ppm (s, 18H), 1.21 ppm (s, 9H), 1.03 ppm (t, 12H) [$^3J_{HH}$ = 7 Hz]. Anal. Calcd: C, 66.4; H, 10.5; N, 8.9%. Found: C, 66.2; H, 10.5; N, 8.8%. ^{31}P NMR spectrum of the reaction mixture indicated quantitative formation of **4b** (single signal at –21 ppm).

(12) Hudson, R. F.; Searle, R. J. G.; Devitt, F. H. *J. Chem. Soc. C* **1976**, 1001.

(13) Crystal data for compound **4b**: $C_{26}H_{49}ClN_3P$, M = 470.13, space group = $P\bar{1}$, a = 11.480(2) Å, b = 13.812(4) Å, c = 9.480(2) Å, α = 100.06(2)°, β = 94.03(2)°, γ = 104.25(2)°, V = 1424.4 Å^3, Z = 2, D_c = 1.10 g cm^{-3}, $F(000)$ = 516, λ(Mo Kα) = 0.710 73 Å, μ = 2.0 cm^{-1}, T = 23 °C, crystal dimensions = 0.30 × 0.45 × 0.55 mm, Enraf-Nonius CAD-4 diffractometer, ω–2θ scan, number of reflections with $I > 3\sigma(I)$ = 3250, parameters = 304, Lorentz–polarization correction, R = 0.047, R_w = 0.049. Further details of the crystal structure may be obtained as supplementary material.

(14) See, for example: Weber, L. *Chem. Rev.* **1992**, *92*, 1839.

(15) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587.

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(19) Cyclic iminophosphines (heterophospholes) are readily formed by elimination (Schmidpeter, A.; Karaghiosoff, K. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Theime: New York, 1990; p 258) but have relative stabilities associated with π-electron delocalization.

(20) A solution of **1b**, obtained *in situ* as described above, was stirred at room temperature for 8 h, and the solvent was removed *in vacuo* to give yellow crystals of **3b** (0.43 g, 62%): ^{31}P ($CDCl_3$), 230 ppm [$^1J_{PN}$ = 80 Hz] (cf. 225 ppm, 84 Hz).[8]

(21) Thompson, M. L.; Tarassoli, A.; Haltiwanger, R. C.; Norman, A. D. *Inorg. Chem.* **1987**, *26*, 684. Tarassoli, A.; Haltiwanger, R. C.; Norman, A. D. *Inorg. Chem.* **1982**, *21*, 2684.