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Metallation-induced migration of phosphorus from nitrogen to carbon in 1-oxo-2,8-diphenyl-2,5,8-triaza-1λ^5-phosphabicyclo[3.3.0]octane: unusual bonding parameters of the double migration product

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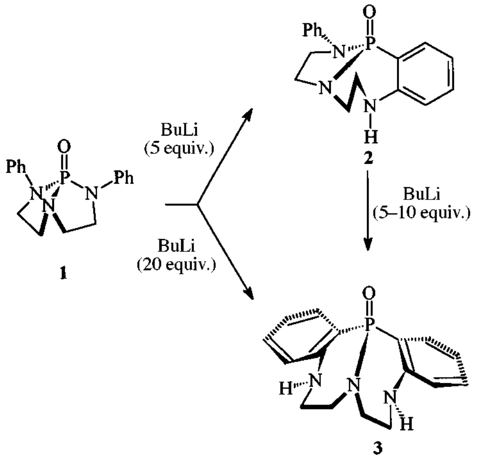
The title compound undergoes lithiation-induced rearrangement, first to a bicyclic phosphonic diamide, and next to a bicyclic phosphinic amide; for the latter product an unusually long phosphoryl bond was observed.

Recently we reported the regioselective cleavage of one P–N bond in the title compound **1** leading to either the eight-membered (2,5,8-triaza-1λ^5-phosphacyclooctane) or the five-membered (1,3,2λ^5-diazaphospholidine) monocyclic product.[1] We present here another transformation of substrate **1** induced by treatment with BuLi. We reported before the LDA-induced migration of phosphorus from nitrogen to aromatic carbon for simple phosphoric *N*-phenylamides,[2] but for **1** the reaction, involving a bicyclic substrate, leads to the formation of new bicyclic systems. Because of the presence of two N–Ph groups in **1**, lithiation can induce single or double N → C migration of the P atom, leading to the bicyclic phosphonic diamide **2** or the bicyclic, symmetrical phosphinic amide **3**, depending on the excess of BuLi.† The product of single migration **2** can be also converted to **3** upon further treatment with BuLi (Scheme 1). The structures of products **2** and **3** were deduced from their NMR (^{31}P, ^{1}H, ^{13}C) spectra, but the unambiguous structural evidence was obtained from the crystal structures of both products (Figs. 1 and 2).‡ Since the crystal structure of **1** was determined before,[3] we could compare the molecular parameters of all three bicyclic compounds. The comparison revealed some interesting structural changes that take place at the phosphorus centre during the transformation **1** → **2** → **3** leading to some unusual bonding parameters of the phosphoryl function in the final product **3** (Table 1). The P–C bond distance in **2** has a typical value,§ but for **3** the differences in the P–C distances within each of the crystallographically independent molecules are worth noting as they lead to the effective loss of the molecular symmetry for **3**. The P–N bond distances in all three compounds are typical for the amides of P^{IV} acids,[5] with the possible exception of the unusually long bond in one of the two molecules of **3**. Dramatic variations have however been



Scheme 1

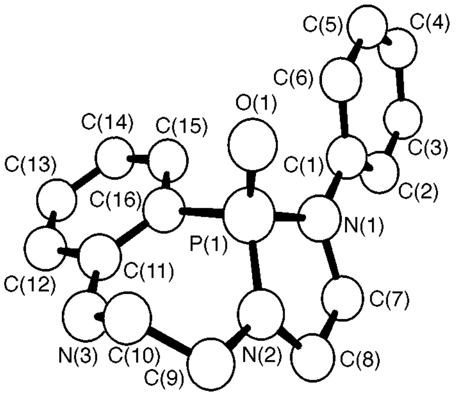


Fig. 1 ORTEP[11] plot of the structure of **2**.

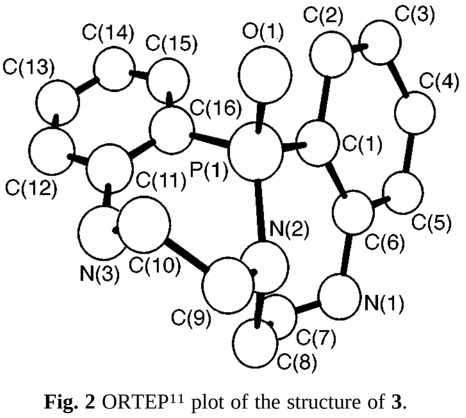


Fig. 2 ORTEP[11] plot of the structure of **3**.

Table 1 Structural data for amides **1**–**3**

Compound	P=O/Å	P–N/Å	P–C/Å
1[a]	1.437(5)	1.653(6)	
		1.661(6)	
		1.676(6)	
2	1.479(2)	1.675(2)[b]	1.816(3)
		1.630(3)[c]	
3	1.641(3)[d]	1.785(4)[d]	1.608(4)[e]
	1.578(3)[d]	1.664(4)[d]	1.750(4)[e]
			1.607(4)[e]
			1.959(5)[e]

[a] Taken from ref. 3. [b] P–N(Ph) bond. [c] P–N(CH$_2$)$_2$ bond. [d] For two crystallographically independent molecules. [e] Each pair for one of the two crystallographically independent molecules.

observed within the series **1**, **2**, **3** for the distance parameter of the phosphoryl group. It is well known that the P–O bond distance in the phosphoryl function is insensitive to its molecular environment or external effects; for example, although the P=O group can accept up to three hydrogen bonds, its length seems to be little affected.[6] The average P=O bond length in phosphates is given as 1.462 Å, with the extreme range of 1.38–1.56 Å observed for 82 compounds studied.[7] The phosphoryl group in **1** represents a typical, average case of the P=O bond distance. The rearrangement to the structure **2** results in some increase of the P=O bond length, but still within the typical range. It is, however, the 7/7-membered fused ring system **3**, in which a dramatic elongation of the P=O bond takes place. In fact, the values of 1.578 and 1.641 Å locate the function within the typical range for a *single* P–O bond (1.56–1.64 Å[7]), thus indicate the dipolar resonance notation, $P^+–O^-$. Since **3** belongs to the class of *N*,*N*-disubstituted diarylphosphinic amides, it could be compared with the simplest analogue $Ph_2P(O)NMe_2$. The P=O bond distance in the latter was determined as 1.47 Å;[8] for **3** the average value is 0.14 Å greater, indicating *ca.* 10% elongation of the phosphoryl bond. A Cambridge Crystallographic Data File search revealed the distribution of the P=O bond distances for phosphinic amides [C(C)P(O)N structural unit, 44 structures], as shown in Fig. 3, showing that the P=O distance in **3** lies beyond the usual range, particularly in view of the fact that the few cases with the P=O distance greater than 1.49 Å concern complexes with Lewis acids, *i.e.* when a decrease in the P=O bond order is expected. The elongation of the P–O distance in **3** is not a consequence of any unusual 'back donation' effect of the amide nitrogen, as there is not only no shortening of the P–N bond in **3**, but the amide bond is slightly longer than the typical value for the related systems. The change in the nature of the P=O bond in **3** was confirmed by IR spectroscopy. The characteristic bands for the P=O stretching vibrations occur in the range of 1200–1400 cm^{-1}.[9] For **1** the ν_{PO} = 1234 cm^{-1}, similar to that of 1209 cm^{-1} reported for HMPA.[9] The change of **1** to **2** is followed by a bathochromic shift to ν_{PO} = 1185 cm^{-1}; for **3** the absorption occurs at 1162 cm^{-1}, beyond the usual range for the phosphoryl compounds and approaching the range typical for a single P–O bond stretching vibration.

In the solid state the molecules of **3** are interconnected *via* a network of hydrogen bonds between the phosphoryl oxygens and the N–H amine functions. Because of the packing pattern, there are three types of N–H···O=P bonds, each characterized by the following values of the N···O distance and the N–H···O angle: (i) 2.495(6) Å, 163(4)°; (ii) 3.478(6) Å, 167(3)°; (iii) 2.866(5) Å, 175(5)°. Those values are similar to the parameters observed for other phosphoric amides,[5] and do not indicate any particularly strong bonding that might be responsible for the unusually long P–O distance. It seems therefore that the observed bonding parameters are a consequence of the specific steric effects operating in the highly rigid skeleton of the molecule. This in turn suggested that the reactivity of the amide bond in **3** should differ from that observed for simple phosphinic amides, as well as from the reactivity of the precursors **2** and **1**. The reactivity of **3** is currently being studied in our laboratory.

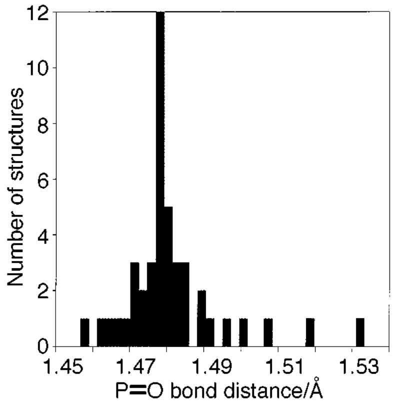


Fig. 3 Distribution of the P=O bond distances in phosphinic amides.[12]

Notes and references

† BuLi-induced rearrangement of **1**: A solution of **1** (0.60 g, 2.0 mmol) in anhydrous THF (100 ml) was cooled to −78 °C under an atmosphere of dry nitrogen. The required amount of BuLi (1.6 M solution in hexane) was added by means of a syringe with stirring and cooling. The solution was stirred at −78 °C for 1 h, warmed to room temperature and stirred for the required period. MeOH (1–2 ml) was added, followed by $CHCl_3$ (200 ml), and the solution was washed with water, dried (Na_2SO_4) and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, $CHCl_3$–acetone, 1 : 1). *Selected data* for **2** (prepared using BuLi (5 equiv.), 2 h of stirring at room temp., 0.51 g, 85%): mp 236.4–237.7 °C (from THF); δ_H(300 MHz, $CDCl_3$) 3.05–3.25 (2H, m), 3.40–3.68 (4H, m), 3.70–3.82 (1H, m), 3.96 (1H, m), 4.32 (1H, br s), 6.55–6.64 (2H, m), 7.00 (1H, t, *J* 6.8), 7.09 (1H, t, *J* 6.7), 7.29 (3H, m), 7.43 (2H, d, *J* 6.4); δ_C(CD_3OD) 47.1 (s), 48.2 (d, *J* 9.1), 49.5 (d, *J* 10.3), 52.8 (d, *J* 6.3), 120.2 (s), 120.4 (s), 120.7 (s), 120.8 (d, *J* 11.6), 124.9 (s), 131.9 (s), 132.4 (d, *J* 7.6), 134.2 (s), 146.3 (d, *J* 6.3), 154.4 (d, *J* 7.8); δ_P($CDCl_3$) 23.7 (Found: C, 64.61; H, 6.17; N, 14.08. $C_{16}H_{18}N_3OP$ requires: C, 64.21; H, 6.06; N, 14.04%). For **3** (prepared using BuLi (20 equiv.), 10 h of stirring at room temp., 0.30 g, 50%): mp 253.6–254.3° (decomp.); δ_H($CDCl_3$) 3.12 (2H, m), 3.41 (2H, m), 3.63 (4H, m), 4.06 (2H, br s), 6.67 (2H, dd, *J* 5.4, 1.0), 6.83 (2H, dd, *J* 5.5, 1.1), 7.23 (2H, m), 7.41 (2H, ddd, *J* 14.3, 7.7, 1.6); δ_C(CD_3OD) 49.6 (s), 56.4 (d, *J* 3.6), 121.1 (s), 121.3 (s), 121.4 (d, *J* 9.8), 135.1 (s), 135.8 (d, *J* 9.3), 155.0 (d, *J* 5.0); δ_P($CDCl_3$) 33.1 (Found: C, 64.28; H, 6.06; N, 13.81%).

‡ *Crystal data* for **2**: $C_{16}H_{18}N_3OP$, *M* = 299.30, monoclinic, space group $P2_1/n$ (No. 14), *a* = 8.201 (3), *b* = 9.054 (2), *c* = 20.266 (2) Å, β = 91.65 (2)°, *U* = 1504 (1) $Å^3$, *F*(000) = 632, λ(Mo-Kα) = 0.7107 Å, μ(Mo-Kα) = 0.185 mm^{-1}, *T* = 295 (1) K, *Z* = 4, D_c = 1.32 g cm^{-3}, 4659 reflections measured on a diffractometer in the range $3 \leqslant \theta \leqslant 30°$, ($R_{int}$ = 0.018). The structure was solved by different methods and refinement, based on F^2, was by full-matric least-squares methods (ref. 10) to *R*1 = 0.078, *wR*2 = 0.183, $w = 1/[\sigma^2(F_o^2) + (0.0584P)^2 + 0.8458P]$ where $P = (F_o^2 + 2F_c^2)/3'$ for 194 parameters using 2899 unique reflections with $I > 2\sigma(I)$. For **3**: $C_{16}H_{18}N_3OP$, *M* = 299.30, monoclinic, space group $P2_1/n$ (No. 14), *a* = 13.959 (30), *b* = 13.773 (2), *c* = 16.077 (4) Å, β = 113.44 (3)°, *U* = 2836 (1) $Å^3$, *F*(000) = 1264, λ(Mo-Kα) = 0.7107 Å, μ(Mo-Kα) = 0.196 mm^{-1}, *T* = 293 (2) K, *Z* = 8, D_c = 1.402 g cm^{-3}. Data were collected on a diffractometer in the range $1 \leqslant \theta \leqslant 30°$ (5169 reflections). The structure was solved by direct methods and refinement (ref. 10), based on F^2, was by full-matrix least-squares to *R*1 = 0.060, *wR*2 = 0.146, $w = 1/[\sigma^2(F_o^2) + (0.0916P)^2]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$ for 416 parameters using 2479 unique reflections with $I > 2\sigma(I)$. There are two independent molecules in the asymmetric unit. CCDC 182/1208. Crystallographic data are available in .cif format from the RSC website, see http://www.rsc.org/suppdata/cc/1999/853/

§ Emsley and Hall reported the value of 1.84 Å as average P–C bond length (ref. 4).

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