PERKIN 1 COMMUNICATION

# One pot synthesis of a chiral *N*-phosphine substituted iminophosphorane: X-ray structure and *in situ* NMR study

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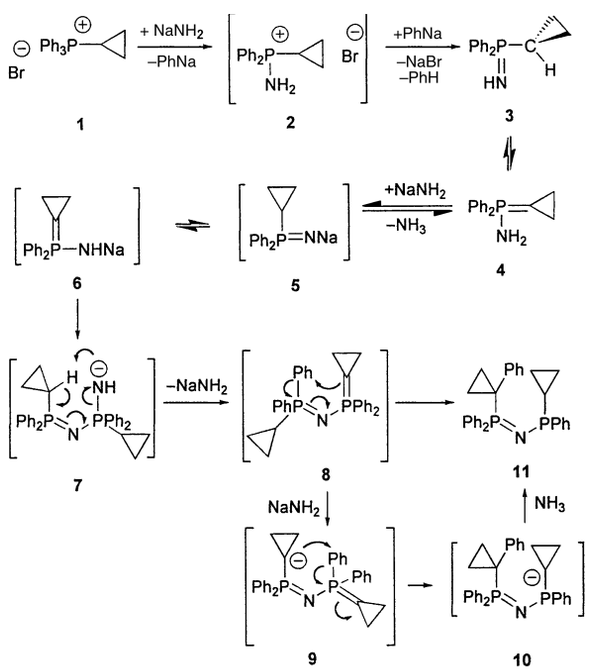
**An X-ray crystal structure reveals that the attempted deprotonation of cyclopropyl(triphenyl)phosphonium bromide with sodium amide affords a chiral *N*-phosphine substituted iminophosphorane *via* an unusual mechanism that has been investigated by multi-nuclear and variable temperature *in situ* NMR spectroscopy.**

During our recent investigations into the interactions of s-block and main group metals with phosphonium ylides[1] and iminophosphoranes,[2] we attempted to synthesise triphenylphosphonium cyclopropylide by the deprotonation of its parent phosphonium salt **1**. Using sodium amide as base in THF, a standard method of ylide formation but not one that has been previously reported using **1**,[3,4] we isolated a crystalline compound whose $^{31}$P NMR spectrum precluded the simple cyclopropylide as the product and instead suggested that a compound containing two phosphorus centres had been isolated.§ A single crystal X-ray diffraction study¶ revealed the product to be a chiral *N*-phosphine substituted iminophosphorane **11** (Fig. 1). Further NMR, including *in situ* studies‖ of the reaction mechanism, and chemical analysis confirmed **11** as the bulk product which was isolated in good yield.

Whilst **11** is not the first example of an *N*-phosphine-substituted iminophosphorane,[5–8] previous examples have been synthesised *via* markedly different routes, often involving coupling reactions using reagents such as Li[N(PPh$_2$)$_2$].[6] The serendipitous synthesis reported here poses several interesting mechanistic questions which we have addressed by *in situ* variable temperature NMR studies. Scheme 1 represents one possible mechanism which is consistent both with our NMR results and with previous work.

Initially, nucleophilic attack at phosphorus of **1** [$\delta$($^{31}$P) 31.22] by nitrogen gives the aminophosphonium salt **2** and PhNa. **2** and the PhNa thus formed react rapidly, eliminating benzene (analogous to loss of hydrocarbon which occurs during the hydrolysis of phosphorus ylides)[9] to yield the cyclopropyl-(diphenyl)iminophosphorane **3** as a first identifiable intermediate [$\delta$($^{31}$P) 27.84]. The transformation is very slow below 0 °C, but is completed after 30 min at ambient temperature. The presence of the cyclopropyl moiety is deduced from the $^{13}$C NMR data: $\delta$ 9.09 (CH, $^1J_{PC}$ 103.8 Hz), 4.3 (CH$_2$, $^2J_{PC}$ 3.6 Hz). By allowing the sample to stand at 25 °C, the iminophosphorane **3** equilibrates with the aminophosphonium cyclopropylide **4** [characterised through the $^1$H, $^{13}$C, and $^{31}$P NMR spectra: $\delta$ ($^1$H) 0.88 (CH$_2$, $^3J_{PH}$ 27.2 Hz), $\delta$ ($^{13}$C) 8.72 (CH$_2$, $^2J_{PC}$ 8.3 Hz), $\delta$ ($^{31}$P) 16.7 ppm].** After approximately 2 h at 25 °C, a 1:1 equilibrium is established between both species. At −20 °C, the iminophosphorane **3** predominates over the aminoylide tautomer (60:40), whereas this ratio is reversed




**Scheme 1**

at 60 °C. The iminophosphorane–aminoylide tautomerism is precedented[10] and recently it has been claimed to be involved in the synthesis of enaminecyclopentenones mediated by alkyldiphenyliminophosphoranes.[2c]

During the equilibration process between **3** and **4** at ambient temperature the $^{31}$P spectrum shows the appearance of two phosphorus doublets, corresponding to the final product **11** ($\delta$ 23.2 and 55.7, $^2J_{PP}$ 94 Hz) together with a broad signal at 38.7 ppm (this broad signal shows no correlation to either $^{31}$P nucleus of **11** and its intensity significantly increases with ageing, suggesting it corresponds to decomposition or hydrolysed products). The intensity of both groups of signals (assigned to **11**) increases with the concomitant decrease in the intensity of the signals of **3**/**4**. On heating the sample at 60 °C for 5 hours **3** completely disappears. Further reaction at ambient temperature is slow in a sealed NMR tube, but the aminoylide **4** completely transforms to **11** after five days.

We suggest that deprotonation of **3**/**4** by a second equivalent of sodium amide affords the *N*-sodiated iminophosphorane **5** and aminoylide **6**. The existence of **5** (analogous to R$_3$PNLi)[11] has previously been proposed by Schmidbaur and Fuller, as an intermediate in the formation of a phosphonium ylide-substituted iminophosphorane.[12] In the absence of any starting

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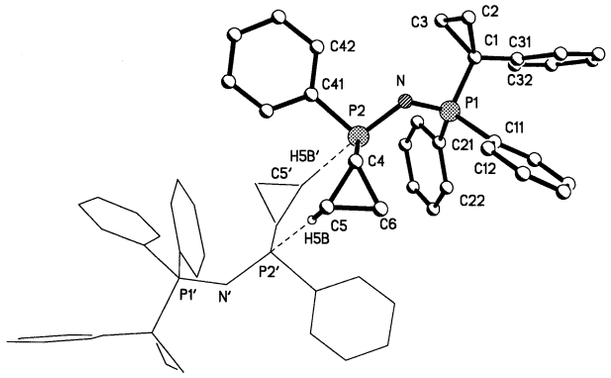


**Fig. 1** Molecular structure of **11**, showing intermolecular H···P contacts. Atoms related *via* inversion centre, are primed. For clarity, H atoms other than those involved in hydrogen bonding are omitted. Selected bond lengths (Å): P(1)–N 1.572(3), P(2)–N 1.689(3), P(1)–C(1) 1.819(3), P(1)–C(11) 1.816(4), P(1)–C(21) 1.822(3), P(2)–C(4) 1.828(4), P(2)–C(41) 1.839(4), C(5)···P(2′) 4.103(4).

material available, the formation of **11** may then proceed by nucleophilic attack of **5/6** on the neutral intermediates **3/4**, yielding the metallated iminophosphorane **7**. Intramolecular abstraction of the methine proton of **7** affords the imino-phosphorane-substituted ylide **8**, which is deprotonated in the basic medium to give the anion **9**. This can rearrange to **10** *via* a process resembling the Sommelet–Hauser rearrangement.[13] Subsequent neutralisation of **10** leads to the final *N*-phosphino iminophosphorane **11**.

Alternatively, a direct route from **8** to **11** could be achieved by invoking a Stevens' rearrangement. The thermal phospha-Stevens' rearrangements of phosphonium ylides is known to proceed under forcing conditions.[14] However, the conjugation of the P=C linkage in **8** with the iminophosphorane moiety may allow the rearrangement to occur at ambient temperature.[15]

Unambiguous characterisation of **11** was achieved *via* a single crystal X-ray structure.¶ The molecular geometry of **11** is unremarkable: the P–N distances and the P–N–P angle are similar to those found in other substituted iminophosphoranes,[4–7] and the conformations of the cyclopropyl groups are usual.[16] The crystal packing of **11** is characterised by H···P(III) contacts between inversion-related molecules (see Fig. 1). The P···H distance, 3.13 Å for the observed H position (C–H 0.98(4) Å) or 3.01 Å for the idealised one, is longer than in $(Ph_3PMe)^+$ $\{[C_6H_2(CF_3)_3\text{-}2,4,6]_2P\}^-$ (2.79 Å)[17] and close to the sum of the van der Waals radii (3.07 Å from crystallographic data,[18] 3.24 Å from *ab initio* calculations[19]). Thus the contact cannot be regarded as a hydrogen bond proper, as in $Ph_2PC(Ph)=CBu^nB(OH)CBu^n{}_2NBu^tCMe$ (with the OH···P distance of 2.30 Å),[20] but neither is it likely to be merely incidental, given the acidity of the cyclopropyl hydrogen atom and its pointing almost exactly towards the lone electron pair of the P(2) atom. The existence of an H···P contact, rather than an H···N interaction such as was previously found[21] in $Ph_3P=NH$, can be explained by steric overcrowding of **11**, wherein the N atom lone pair is almost entirely masked by the H atoms at C(2) and C(42), which lie at 2.69 and 2.57 Å from the N atom and close to its $sp^2$ plane. This is a feature of **11** that we also expect to be significant in its coordination chemistry.

Although the mechanism described above is speculative, the first intermediates involved have been identified by NMR and overall this route emphasises the strong involvement of metallic base interactions in organic/inorganic transformations involving organophosphorus species, even under such mild conditions as these. This is, for example, known to be a factor in the stereochemical outcome of Wittig reactions, but is still little understood.[22]

We hope to extend our knowledge in this area through further studies on these and related systems, including their potential use as ligands to main group and transition metals.





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## Notes and references

§ Synthesis of **11**: A suspension of (triphenyl)cyclopropylphosphonium bromide, **1** (10.1 g, 26.4 mmol) and sodium amide (1.1 g, 28 mmol) in 50 mL dry THF was stirred at ambient temperature under Ar for 24 hours. Removal of a white precipitate from the orange solution by filtration was followed by removal of approximately 40 mL solvent *in vacuo* and addition of dry hexane (10 mL) which precipitated **11** as a yellow solid (2.8 g, 46%). For the X-ray study, **11** was recrystallised from a hexane–toluene mixture at −30 °C. Mp 144–145 °C (Found: C 75.2, H 6.3, N 2.5, P 14.0; Calc. for $C_{30}H_{29}NP_2$: C 77.4, H 6.3, N 3.0, P 13.3%); $^1$H NMR (300 MHz, $C_6D_6$): $\delta_H = 0.58$ (1H, m, H6), 0.62 (2H, overlapping m, H5), 0.74 (1H, m, H6), 1.02 (1H, m, H4), 1.06 (2H, overlapping m, H2, 3β), 2.24 (3H, overlapping m, H2, 3α, H4), 6.8–7.25 (11HAr, overlapping m), 7.75 (2H, m, H12, 16), 7.82 (2H, m, H22, 26), 7.32 (1H, m, H44), 7.48 (2H, m, H43, 45), 8.20 (2H, m, H42, 46); $^{13}$C NMR (75.5 MHz, $C_6D_6$): $\delta_C = 2.69$ (d, $^2J_{PC}$ 13.9 Hz, C6), 4.04 (d, $^2J_{PC}$ 11.6 Hz, C5), 10.95 (d, $^2J_{PC}$ 1.1 Hz, C2/3), 11.35 (t, $^2J_{PC} = {}^4J_{PC}$ 1.1 Hz, C2/3), 17.58 (dd, $^1J_{PC}$ 17.6, $^3J_{PC}$ 9.7 Hz, C4), 24.82 (d, $^1J_{PC}$ 103.1, C1), 126.74 (d, $^4J_{PC}$ 2.8 Hz, C44), 129.75 (d, $^2J_{PC}$ 18.9 Hz, C41), 130.86 (d, $^1J_{PC}$ 92.0 Hz, C11/C21), 131.09 (d, $^1J_{PC}$ 97.6 Hz, C21/C11), 133.17 (dd, $^2J_{PC}$ 9.0, $^4J_{PC}$ 2.3 Hz, C12, 16/22, 26), 133.30 (dd, $^2J_{PC}$ 6.9, $^4J_{PC}$ 0.9 Hz, C12, 16/22, 26), 127.4–132.74 (13 CAr), 139.42 (dd, $^2J_{PC}$ 4.6, $^4J_{PC}$ 0.9 Hz, C31), 149.96 (dd, $^1J_{PC}$ 16.6, $^3J_{PC}$ 14.8 Hz, C41); $^{31}$P NMR (121.49 MHz, $C_6D_6$): $\delta_P = 22.5$ (d, $^2J_{PP}$ 89 Hz, P1), 56.0 (d, $^2J_{PP}$ 89 Hz, P2). All assignments refer to Fig. 1 (α and β refer to protons above and below the plane of the cyclopropyl rings as depicted in Fig. 1).

¶ Crystal data for **11**: $C_{30}H_{29}NP_2$, $M = 465.5$, monoclinic, space group $P2_1/c$ (No. 14), at $T = 150$ K, $a = 9.555(1)$, $b = 10.182(1)$, $c = 25.711(2)$ Å, $\beta = 98.75(1)°$, $U = 2472.3(4)$ Å$^3$, $Z = 4$, $D_x = 1.25$ g cm$^{-3}$, $\lambda$ (Mo-Kα) = 0.71073 Å, $\mu = 2.0$ cm$^{-1}$. 14385 data (4252 unique) with $2\theta \leq 50°$ were measured with a SMART CCD area detector; least squares refinement of 334 variables on $F^2$ (ref. 23) gave $R = 0.062$ [for 3030 data with $F^2 > 2\sigma(F^2)$] and $wR(F^2) = 0.134$.

CCDC reference number 207/492. See http://www.rsc.org/suppdata/p1/b0/b005816p/ for crystallographic files in .cif format.

‖ *In situ* NMR studies were performed on a 0.1 mmol scale in a $d_8$-toluene solution (a relatively dilute sample was used because of the reduced solubility of the starting materials). The temperature range covered by the study was −90 °C to +60 °C, in 20 °C incremental steps from −90 °C to −30 °C, then 10 °C steps thereafter once progress of the reaction was evident. $^1$H and $^{31}$P{$^1$H} were recorded for all temperatures, while $^{13}$C{$^1$H} APT, DEPT, $^2$D $^1$H, $^{13}$C gHMQC and gHMBC were measured for selected temperatures. A $^1$H, $^{15}$N gHMQC spectrum acquired at −20 °C showed only the $^{15}$N signal corresponding to the $NaNH_2$ ($\delta$ −387 ppm).

** The ylidic carbon of **4** could not be identified by APT or HMBC NMR experiments. This may be due to very slow relaxation and broadening due to solution dynamics.

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