

The synthesis of novel trisphosphoranylphosphine and its oxide

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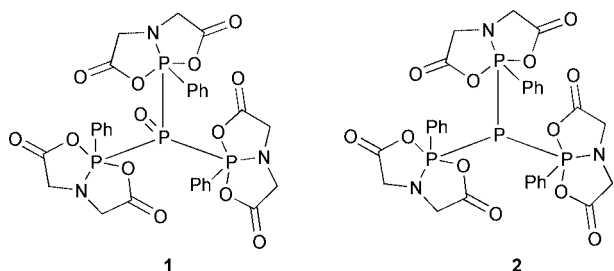
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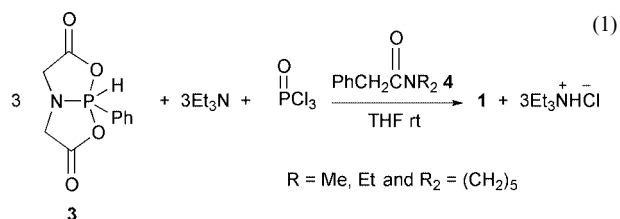
A new trisphosphoranylphosphine oxide **1** bearing three $\sigma^5\lambda^5\text{P}-\sigma^4\lambda^3\text{P}$ bonds was synthesized through an efficient method in which *N,N*-dialkylphenylacetamide played an important role. Chloroform reduced the phosphine oxide **1** to the corresponding phosphine **2**. The crystal structure of **2** was determined.

Organophosphorus compounds containing only one phosphorus-phosphorus bond with pentacoordinate phosphorus atoms have attracted much interest in the past two decades.¹ Most of these compounds were synthesized using phosphines, or halophosphoranes as starting materials. Lamande and Munoz synthesized some of these compounds and also a new kind of phosphorane bearing two P-P bonds by the reaction of hydridophosphoranes.² However, trisphosphoranylphosphines and their oxides have never been reported. As part of our research on reactivity of hydridophosphoranes we have synthesized the new trisphosphoranylphosphine oxide **1** and the corresponding phosphine **2**, bearing three $\sigma^5\lambda^5\text{P}-\sigma^4\lambda^3\text{P}$



$\sigma^5\lambda^5\text{P}-\sigma^3\lambda^3\text{P}$ bonds respectively, by the reaction of hydridophosphorane **3**. Compounds **1** and **2** have been characterized by ¹H NMR, ³¹P NMR, and quantitative elemental analyses, ESMS or FABMS spectroscopy. In addition, the crystal structure of **2** was determined.

In order to obtain compound **1**, we firstly reacted **3** with phosphorus oxychloride using triethylamine as acid acceptor in absolute THF at room temperature. But the yield was very poor and the purification of the product was very difficult. Later we found that in the presence of phenylacetamide **4** the reaction afforded compound **1** smoothly within 30 minutes. Treating an absolute THF solution of **4** and phosphorus oxychloride with a solution of hydridophosphorane **3** and excess triethylamine in absolute THF at room temperature under nitrogen gives **1** in 58–63% yield (eqn. 1). Compound **1** is stable in both air and



moisture with thermal decomposition taking place only at temperatures over 240 °C.

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For the formation of compound **1**, we suggested the mechanism shown in Scheme 1. Phenylacetamide **4** reacts with phosphorus oxychloride to produce phosphoryliminium chloride **5**.³ Hydridophosphorane **3** is easily transformed into phosphorane anion **6** under the action of triethylamine.⁴ Nucleophilic phosphorane anion **6** attacks the phosphorus atom of **5** to give **7** with the elimination of hydrogen chloride and phenylacetamide **4**. Then, **7** reacts with two equivalents of **6** to give compound **1**. The re-formed **4** has been examined by TLC and ¹H NMR spectroscopy.

We surprisingly found that compound **1** could be reduced into **2**, with the $\sigma^4\lambda^5$ phosphorus atom being reduced to a $\sigma^3\lambda^3$ phosphorus atom, using pure chloroform at room temperature (eqn. 2).



Many reagents, for example, LiAlH₄, Ca(AlH₄)₂, CaH₂, silanes, boranes and alanes, have been successfully used to reduce tertiary phosphine oxides to the corresponding tertiary phosphines.⁵ Experimental evidence has proven that chloroform cannot reduce common phosphine oxides (like Ph₃PO, Bu₃PO) to phosphine. We believe that the ease of reduction of **1** using chloroform may be closely related to the presence of three P-P bonds. Owing to the three direct P-P bonds, the nucleophilic reactivity of the P=O oxygen atom in **1** may be stronger than that in ordinary phosphine oxides. Therefore a possible mechanism is shown in Scheme 2. The oxygen atom of P=O attacks the carbon atom of CHCl₃ with elimination of Cl⁻ to give the intermediate **9**, which gives **2** with elimination of phosgene. This pathway is different to that in the reduction reaction of tertiary phosphine oxide by trichlorosilane.⁶

Like the ³¹P NMR spectrum of [(EtO)₂P]₃P (¹J_{PP} = 158 Hz)⁷ and that of (F₂P)₃P (¹J_{PP} = 323 Hz)⁸, both the ³¹P NMR spectra of **1** and **2** show AB₃ spin patterns (see Experimental section and Fig. 1). Since the J_{PP} values are relatively small compared with the Δδ value between the chemical shift of $\sigma^5\lambda^5\text{P}$ and the central phosphorus atoms (J/Δδ ≈ 0.06), the ³¹P NMR spectra are complex but consistent with the theoretical calculation of AB₃ spin systems described by Corio.⁹ Notable are the similar values for the ³¹P chemical shifts and ¹J_{PP} couplings of **1** and **2**, which is abnormal for phosphines and their corresponding oxides. However, the crystal structure of **2** (Fig. 2) clearly shows that the central phosphorus atom is a $\sigma^3\lambda^3$ phosphorus atom and that the geometry is pyramidal.¹⁰

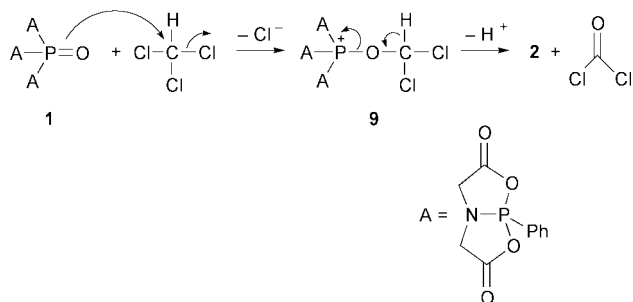
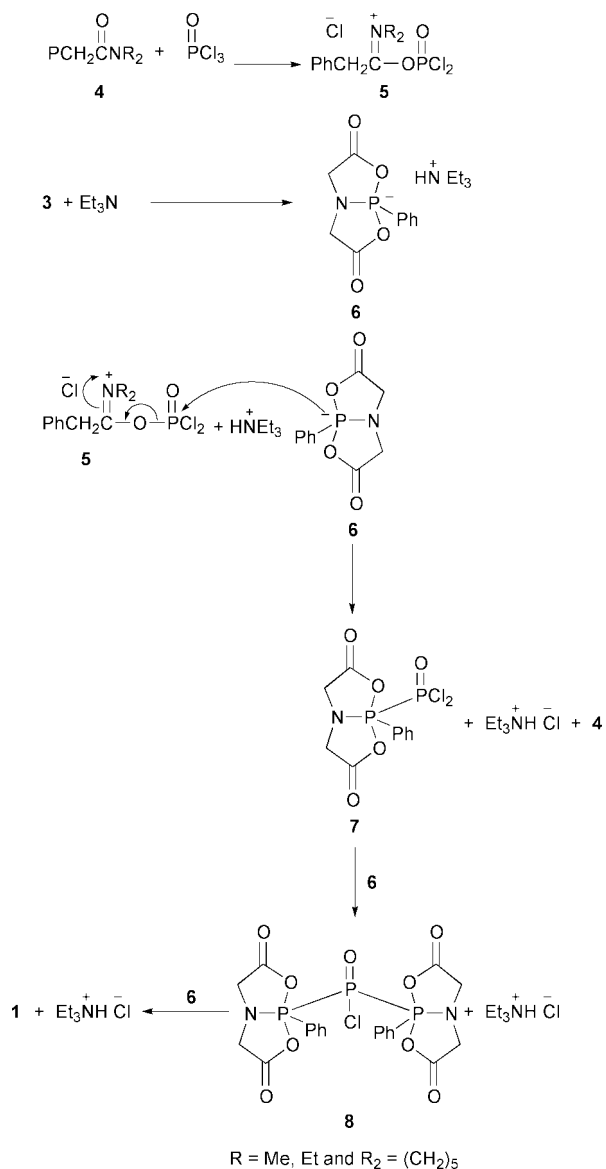
Studies on the synthesis of compounds similar to **1** but having different pentacoordinate phosphorus atoms are underway. Further investigations including the mechanism of the formation of **2** are also in progress.

In summary, the first trisphosphoranylphosphine oxide **1** bearing three direct $\sigma^5\lambda^5\text{P}-\sigma^4\lambda^3\text{P}$ bonds has been synthesized. Oxide **1** can be converted to the corresponding phosphine **2** using chloroform.

Experimental

Melting points were determined with a Thomas-Hoover

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melting point apparatus and the thermometer was not standardized. ¹H NMR spectra were recorded with a Bruker AC-P200 spectrometer using tetramethylsilane as an internal standard. ³¹P NMR spectra were determined by a Bruker AC-P200 spectrometer using 85% H₃PO₄ as an external standard. ES mass spectra were obtained with an HP5988A mass spectrometer. FAB mass spectra were obtained on a VG ZAB-BS mass spectrometer. Elemental analyses were carried out with a Yanaco CHN Corder MT-3 elemental analyzer.

Preparation of compound 1

A mixture of 2.1 mmol phenylacetamide and 0.33 g (2.1 mmol) phosphorus oxychloride in 15 ml of absolute THF was stirred at room temperature under N₂ for 1 hour. Then an absolute

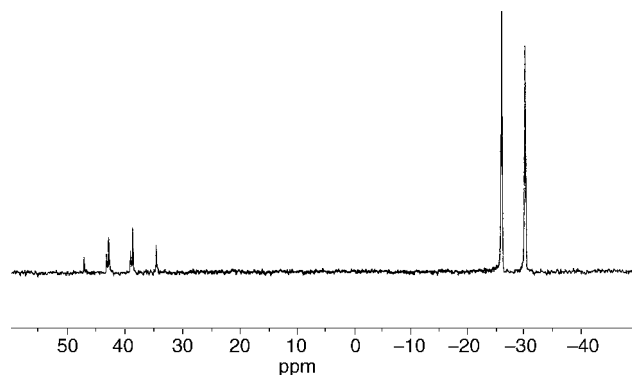


Fig. 1 The ³¹P NMR spectrum of **2**.

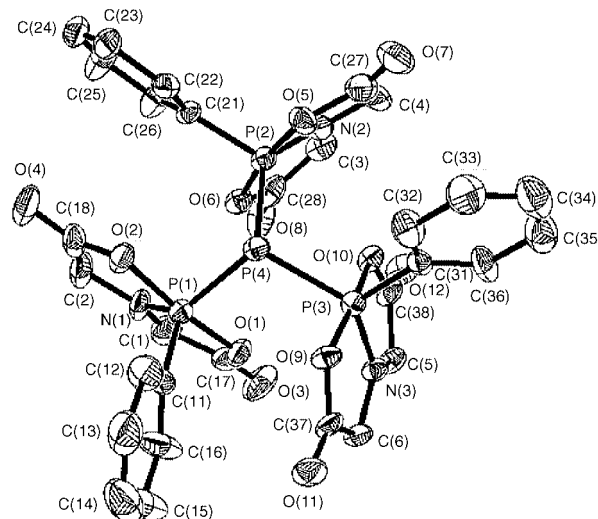


Fig. 2 Crystal structure of **2**. The hydrogen atoms are omitted for clarity. Selective bond distances (Å) and angles (°): P(1)–P(4) = 2.245(3), P(2)–P(4) = 2.244(2), P(3)–P(4) = 2.244(3), P(1)–N(1) = 1.646(5), P(2)–N(2) = 1.646(6), P(3)–N(3) = 1.648(5), P(1)–C(11) = 1.813(4), P(2)–C(21) = 1.809(4), P(3)–C(31) = 1.790(4); P(3)–P(4)–P(2) = 105.72(10), P(3)–P(4)–P(1) = 104.76(10), P(2)–P(4)–P(1) = 105.36(10).

THF solution of 0.5 g (2.1 mmol) of hydridophosphorane **3** and 0.63 g (6.3 mmol) of triethylamine were added to the mixture while cooling in an ice–water bath. The reaction mixture was then stirred at room temperature for 30 min and filtered. The filtrate was concentrated under vacuum and the residue was dissolved in 20 ml of dichloromethane, washed with water, dried over magnesium sulfate and filtered. The volatile components were distilled under reduced pressure. Recrystallization of the residue with dichloromethane–ether afforded compound **1** (0.30–0.34 g, 58–63%, based on **3**) as a white powder, mp 240 °C (decomp.) (Found: C, 47.04; H, 3.50; N, 5.33. C₃₀H₂₇N₃O₁₃P₄ requires C, 47.32; H, 3.57; N, 5.52%); δ_H (200 MHz; DMSO-d₆; Me₄Si) 3.64–4.28 (12H, br s, CH₂), 7.51–7.72 (15H, m, Ph); δ_P (200 MHz; DMSO-d₆; 85% H₂SO₄) –23.67 (σ⁵λ⁵P, m, ¹J_{P-P} = 329.7 Hz), +37.88 (σ⁴λ⁵P, m, ¹J_{P-P} = 329.7 Hz); *m/z* (ESMS) 762 [(M + 1)⁺].

Preparation of compound 2

100 mg of **1** was dissolved in 5 ml of chloroform in a 50 ml round-bottomed flask and the flask was left for 30 minutes. Then 5 ml of ether was added and colorless crystals of **2** were precipitated gradually. After 24 hours the crystals of **2** were filtered and dried under a nitrogen atmosphere. Yield of **2**: 45 mg, 46%; mp 216 °C (decomp. sealed, N₂) (Found: C, 48.42; H, 3.47; N, 5.41. C₃₀H₂₇N₃O₁₂P₄ requires C, 48.30; H, 3.65; N, 5.63%); δ_H (200 MHz; CDCl₃; Me₄Si) 3.34–4.53 (12H, m, CH₂), 7.48–7.73 (15H, m, Ph); δ_P (200 MHz; CDCl₃; 85% H₂SO₄) –28.16 (σ⁵λ⁵P, m, ¹J_{P-P} = 341.3 Hz), +40.85 (σ³λ³P, m, ¹J_{P-P} = 341.3 Hz); *m/z* (FABMS) 746 [(M + 1)⁺].

Acknowledgements

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References and notes

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- A solution of 3 mmol *N,N*-dimethylphenylacetamide and 3 mmol phosphorus oxychloride in absolute THF was stirred at room temperature under nitrogen for 30 min, then the solvent was evaporated under vacuum. The ³¹P NMR spectrum showed a new single sharp peak at -2.29 ppm, corresponding to phosphoryliminium chloride **5**. See also: J. C. Tebby and S. E. Willetts, *Phosphorus and sulfur*, 1987, **30**, 293; D. Qian, X. Shi, X. Zeng, R. Cao and L. Liu, *Heteroat. Chem.*, 1999, **10**, 21.
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- Crystal data for **2**: colorless crystals. C₃₀H₂₇N₃O₁₂P₄, *M* = 745.43, orthorhombic, *P*2₁2₁2₁, *T* = 293(2) K, *a* = 9.4387(11), *b* = 18.424(2), *c* = 19.358(2) Å, *α* = *β* = *γ* = 90°, *V* = 3366.57(7) Å³, *Z* = 4, *D*_c = 1.471 mg m⁻³, *μ* = 0.291 mm⁻¹, 14177 reflections collected, 5946 independent reflections, *R*₁ = 0.0598 [for *I* > 2σ(*I*)], *wR*₂ = 0.0758. CCDC reference number 207/424. See <http://www.rsc.org/suppdata/p1/b0/b001917h/> for crystallographic files in .cif format.