



# Synthesis and X-ray crystal structure of a novel long chain acyclic phosphazene, $N,N'$ -{dimethyl-bis(diphenylphosphino)iminophosphorane}ethylenediamine $\{(\text{PhO})_2\text{P}(\text{O})\text{N}=\text{PN}(\text{CH}_3)\text{CH}_2\}_2$ , obtained via a Staudinger reaction

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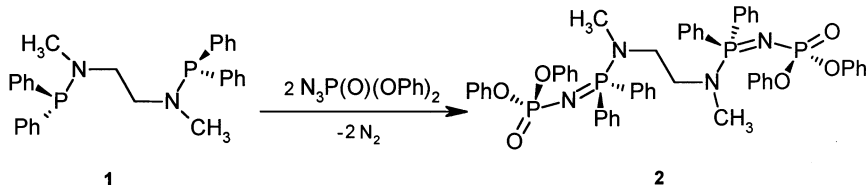
**Abstract**—The title compound was synthesized by the reaction of  $N,N'$ -dimethyl- $N,N'$ -bis(diphenylphosphino)ethylenediamine with phosphoryl azide and characterized by mass spectrometry, microanalysis, and  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectroscopy and the structure was confirmed by single crystal X-ray studies. © 2001 Elsevier Science Ltd. All rights reserved.

Since the utilization of the well-known Staudinger reaction in the clean synthesis of phosphinimines, a large number of mono- and bis(phosphines) have been effectively converted into the corresponding iminophosphoranes,<sup>1</sup> which were found to be excellent reagents in bridging the main group elements with transition elements.<sup>2,3</sup> The versatility of phosphinimines in the synthesis of heterocycles embedded with high-valent transition metals is well documented.<sup>4</sup> The partial oxidation of phosphorus centers in bidentate or tridentate ligands with organic azides has led to very useful heterofunctional systems, which have created a host of new coordination and organometallic complexes.<sup>5–8</sup>

We report here a new member of this class of compounds, the first example of an acyclic bis(iminophosphorane) derivative of  $N,N'$ -dimethylethylenediamine having as many as 12 atoms in the chain with as many as six donor atoms. This compound was synthesized by the direct reaction of  $N,N'$ -dimethyl- $N,N'$ -bis(diphenylphosphino)ethylenediamine<sup>9</sup> with a phosphoryl

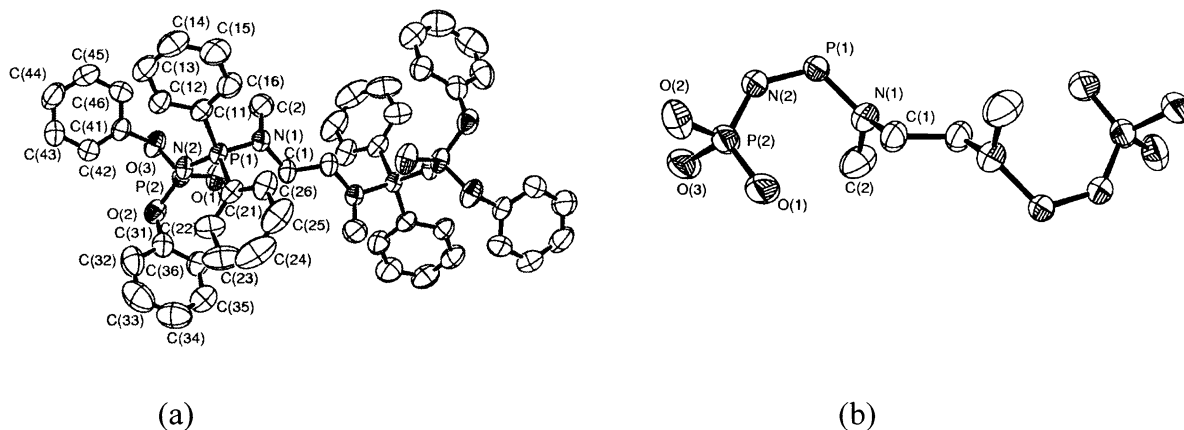
azide and isolated as an air-stable white crystalline solid in quantitative yield.<sup>10</sup> The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2** shows two doublets as expected for the phosphinimine and phosphoryl centers at  $\delta$  23.8 and 9.0, respectively, with a  $^2J_{\text{PP}}$  value of 32 Hz. The  $^1\text{H}$  NMR spectrum of **2** shows a doublet at  $\delta$  2.28 for the methyl protons and a multiplet at  $\delta$  2.98 for the ethylene protons. Further evidence comes from microanalysis and the high-resolution mass spectrum (HRMS), which shows a mass corresponding to a molecular weight of 951. The structure of compound **2** was confirmed by a single crystal X-ray structure determination.<sup>11</sup>

The ORTEP<sup>12</sup> plot (Fig. 1) establishes the presence of crystallographically imposed centrosymmetry. The core looks like a diphenyl molecule opened on opposite sides, resembling an unlocked ‘handcuff’. The P(1)–N(1) bond distance of 1.651(2) Å is slightly shorter than that of a diphosphine ( $\text{Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{CH}_2\text{CH}_2(\text{PhCH}_2)\text{NPPH}_2$ : 1.680(2) Å), which is similar to the parent diphosphine **1** but with different sub-



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**Figure 1.** (a) Molecular structure of **2** (perspective view) and (b) the core of **2** displaying only the skeleton atoms. For clarity hydrogen atoms are omitted. Selected bond distances (Å) and bond angles (°): P(1)–N(1) 1.651(2), P(1)–N(2) 1.572(2), P(1)–C(21) 1.803(3), P(1)–C(11) 1.810(3), P(2)–O(1) 1.475(2), P(2)–N(2) 1.579(2), P(2)–O(3) 1.595(2), P(2)–O(2) 1.601(2), N(1)–C(1) 1.474(3), N(1)–C(2) 1.474(4), N(2)–P(1)–N(1) 118.92(11), P(2)–N(2)–P(1) 133.94(14), P(1)–N(1)–C(2) 118.65(19), P(1)–N(1)–C(1) 118.44(18), N(2)–P(2)–O(1) 120.04(12).

stituents on the amine nitrogen.<sup>9</sup> The structure of the parent diphosphine is not known. The P(1)–N(2) (1.572(2) Å) and P(2)–N(2) (1.579(2) Å) bond distances are quite comparable although the former is a double bond. This may be due to the strong  $\pi$ -acceptor nature of phosphoryl group that has a doubly bonded oxygen atom beside two electron-withdrawing phenoxy groups. The P(2)–N(2)–P(1) bond angle is 133.94(14)° whereas the total bond angles around the amine nitrogen are 350°, which indicates that the planar geometry around the amine nitrogen is slightly distorted.

The compound described here represents the first example of a long chain acyclic phosphazene that can be a potential multidentate ligand due to the presence of six donor atoms with a relatively flexible backbone. Further utilization of this compound in coordination chemistry of transition metals, as well as f-block elements, and in polymerization studies is currently in progress.

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### References

- Gololobov, Y. G.; Kaushkin, L. F. *Tetrahedron* **1992**, *48*, 1353–1406.
- Imhoff, P.; Nefkens, S. C. A.; Elsevier, C. J.; Goubtiz, K.; Stam, C. H. *Organometallics* **1991**, *10*, 1421–1431.
- Imhoff, P.; Asselt, R. V.; Ernsting, J. M.; Vreize, K.; Elsevier, C. J. *Organometallics* **1993**, *12*, 1523–1536.
- Witt, M.; Roesky, H. W. *Chem. Rev.* **1994**, *94*, 1163–1181.
- Balakrishna, M. S.; Santarsiero, B. D.; Cavell, R. G. *Inorg. Chem.* **1994**, *33*, 3079–3084.
- Grim, S. O.; Kettler, P. B. *J. Chem. Soc., Chem. Commun.* **1991**, 979–980.
- Katti, K. V.; Cavell, R. G. *Comments Inorg. Chem.* **1990**, *10*, 53–73.
- Reed, R. W.; Santarsiero, B.; Cavell, R. G. *Inorg. Chem.* **1996**, *35*, 4292–4300.
- Balakrishna, M. S.; Abhyankar, R. M.; Mague, J. T. *J. Chem. Soc., Dalton Trans.* **1999**, 1407–1412.
- Compound **2**: Yield 96%, mp 188–190°C. Anal. calcd for C<sub>52</sub>H<sub>50</sub>N<sub>4</sub>O<sub>6</sub>P<sub>4</sub>: C, 65.69; H, 5.30; N, 5.89. Found: C, 65.62; H, 5.30; N, 5.81%. MS (EI, *m/z*): 951. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): phenyl region, 7.65, 7.50, 7.32, 7.16 (m, 40H); *N*-methyl,  $\delta$  2.28 (d, 6H, <sup>3</sup>*J*<sub>PH</sub> = 3.6 Hz); ethylene, 2.98 (m, 4H). <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta$  P<sub>(N)</sub>, 23.80 (d); P<sub>(O)</sub>, 9.00 (d); (<sup>2</sup>*J*<sub>PP</sub> = 32 Hz). The compound did not give any X-ray quality crystals in dry solvents but precipitated out as a microcrystalline material without any evidence of water molecules by microanalysis and <sup>1</sup>H NMR data. However, when air was bubbled for a few seconds through a dichloromethane–hexane (1:1) solution, X-ray quality crystals were obtained with water of solvation and are located in the diffraction map.
- Crystal data*: C<sub>52</sub>H<sub>50</sub>N<sub>4</sub>O<sub>6</sub>P<sub>4</sub>·2H<sub>2</sub>O, *M* = 986.87, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 9.5356(14), *b* = 12.9818(13), *c* = 21.0894(18) Å,  $\beta$  = 102.235(10)°, *V* = 2551.3(5) Å<sup>3</sup>, *T* = 293(2) K, *Z* = 2, *D*<sub>calcd</sub> = 1.285 g cm<sup>-3</sup>, *F*(000) = 1036,  $\mu$  = 2.05 cm<sup>-1</sup>, *R* = 0.0612, *R*<sub>w</sub> = 0.0682. Full details are provided as Supporting Information. CCDC reference no. 150232.
- Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *32*, 565.