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A versatile synthesis of a new bisiminophosphorane

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ABSTRACT

The iminophosphorane $CH_2CH_2[P\{=NP(=O)(OPh)_2\}Ph_2]_2$ is synthesized in high yields (80–97%) via a very convenient procedure using diphenylphosphoryl azide (DPPA) and 1,2-bis(diphenylphosphino)ethane.

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Since the discovery of the imination reaction of phosphines with azides, the Staudinger reaction,[1] a large number of mono- and bis-phosphines have been converted effectively into the corresponding iminophosphoranes or bis(iminophosphoranes).[2]

It is known that iminophosphoranes are important reagents and intermediates in organic synthesis.[3,4] Recently, their use for the introduction of imine units[5] in the synthesis of nitrogen heterocycles via inter- and intramolecular aza-Wittig reactions has been developed.[3a,4a] Successful methods include N-thiophosphorylated and N-phosphorylated iminophosphoranes as models for dendrimers.[6]

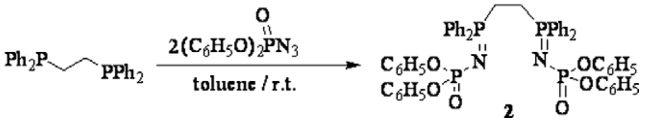
Organic azides have assumed an important position at the interface between chemistry, biology, medicine, and materials science.[7] Diphenylphosphoryl azide has been used extensively as a peptide coupling reagent,[8] in the transformation of alcohols into amines,[9] in the transformation of the oxo-function of quinoline/pyridine/quinazolin-4-ones to form 4-azido-derivatives,[10] in the transformation of acids into acyl azide intermediates,[11,12] and in the synthesis of ruthenium complexes containing iminophosphorane ligands.[13] To our knowledge, the reactivity of DPPA toward 1,2-bis(diphenylphosphino)ethane has not been investigated.

We were interested in the preparation of iminophosphoranes starting from diphenylphosphoryl azide (DPPA) and tertiary phosphines because these species seem to have been less studied and they are important as intermediates in organic synthesis and as ligands in organometallic chemistry, especially with gold or silver.

Monoimination and bisimination of bis(diphenylphosphino)methane (DPPM) with azides have been successfully applied for the preparation of several iminophosphorane-phosphine ligands $[Ph_2PCH_2P(=NR)Ph_2]$.[14,15]

The bisimination of 1,2-bis(diphenylphosphino)ethane (DPPE)[16] (Scheme 1) has been studied recently in our laboratory. The reaction proceeds in the presence of excess diphenylphosphoryl azide in toluene at room temperature. In this case, the final product was purified by slow diffusion of hexane in which the corresponding iminophosphorane **2** is not soluble.

The thermal behavior of the solid iminophosphorane **2** was studied by differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis. The TG measurements proved that no solvent or water remained with the crystals. The change in weight was complete in two steps, but the phases were highly delimited, maybe because of the symmetry of the molecule. This compound began to lose weight at 270 °C and reached the first maximum rate of weight loss at 355 °C when 30% of the compound had decomposed. The second maximum rate of weight loss was at 390 °C when 58% of the compound had decomposed. The total weight loss



2

Scheme 1. Synthesis of bis(iminophosphorane)ethane $\{CH_2CH_2[P\{=NP(=O)(OPh)_2\}Ph_2]_2\}$.

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between 0 and 600 °C was 88%. The DSC shows that two endothermic and one exothermic processes occur. The melting point of the sample was attributed to the endothermic processes at 133 °C.

The structure of compound **2** was determined by X-ray diffraction measurements (CCDC 694483), representative bond lengths and angles are presented in Table 1.

Figure 1 shows the molecular structure of compound **2**, where the P–N single bond length is 1.58(3) Å and the P–N double bond distance is 1.57(3) Å, being typical values for iminophosphorane moieties. The lengths of the P–O bonds are 1.54(5) Å for the double bond and 1.56(5) Å and 1.50(5) Å, respectively, for the single bonds. The angle C14–O2–P2 is 117.60(4)° and that of P2–O3–C20 is 116.50(4)°, while the torsion angles are as follows: C14–O2–P2–O3, 162.1(4)°, and C20–O3–P2–O2, 52.0(5)° (probably due to weak O···H intermolecular interactions between the O3 atom and the hydrogen atoms of the neighboring aromatic rings). The angle C7–P1–N1 has a value of 114.77(2)° and that of the torsion angle C7–P1–N1–P2 is 65.5(3)°.

The molecular structure of **2** is directed by weak O···H intermolecular interactions (2.557 Å, 2.635 Å, and 2.595 Å which are close to the sum of the van der Waals radii) due to the packing effect. The structure contains a disordered toluene solvent molecule and edge-face interactions between one of the phenyl rings and the solvent (d1 = 5.324 Å and d2 = 3.189 Å) are present, Figure 2. However, no π-π stacking was observed.

In conclusion, an efficient method for the synthesis of the novel iminophosphorane $\{CH_2CH_2[P\{=NP(=O)(OPh)_2\}Ph_2]_2\}$ has been developed. The product was isolated in high yield and characterized from melting point, IR, ^1H NMR, ^{13}C NMR, ^{31}P NMR, UV, and X-ray data. The advantages of the present method are that the reaction can be monitored by TLC and the evolution of nitrogen is easily observed. Compound **2** is an air-stable white solid, soluble in chlorinated solvents, acetonitrile, and ethyl acetate, and is insoluble in non-polar solvents such as hexane or pentane. Further studies on the reactivity of this iminophosphorane are in progress.

Table 1
Selected bond lengths (Å) and angles (°) for compound **2**

Bond length (Å)		Angle (°)	
C1–P1	1.79(4)	C1–P1–C7	106.87(2)
C7–P1	1.80(4)	C1–P1–C13	107.43(2)
C13–P1	1.80(4)	C14–O2–P2	117.60(4)
C14–O2	1.52(7)	P2–O3–C20	116.50(4)
C20–O3	1.58(9)	O3–P2–O1	107.30(3)
N1–P1	1.57(3)	O3–P2–O2	102.70(3)
N1–P2	1.58(3)	O1–P2–O2	109.90(3)
O3–P2	1.50(5)	O3–P2–N1	115.70(2)
O1–P2	1.58(3)	O1–P2–N1	114.30(2)
O2–P2	1.54(5)	O2–P2–N1	106.30(2)
		P1–N1–P2	129.90(2)

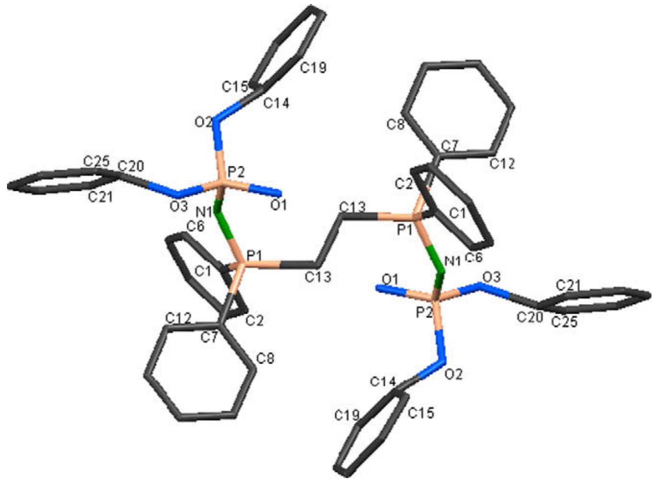

Figure 1. Molecular structure of compound **2**; hydrogen atoms are omitted for clarity.

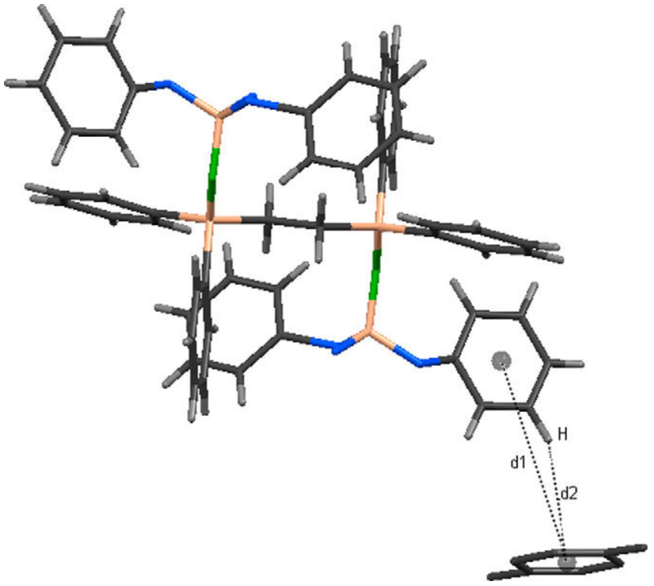

Figure 2. Intramolecular aromatic edge-to-face interactions with a disordered toluene solvent molecule (d1 = 5.324 Å and d2 = 3.189 Å).

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.07.112.

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16. Synthesis of $CH_2CH_2[P\{{=}NP({=}O)(OPh)_2\}Ph_2]_2$. A solution of 1,2-bis(diphenylphosphino)ethane (0.700 g, 1.77 mmol) in toluene (15 ml) was treated dropwise, at room temperature, with a solution of diphenylphosphoryl azide (1 ml, 4.62 mmol) in toluene (5 ml). After 1 h (TLC), the solvent was removed under reduced pressure to give a colorless oil. A microcrystalline white solid was obtained by slow diffusion of hexane. Characterization data for **2**: yield: 97% (1.53 mg); mp = 135–137 °C (CH_3CN) (DSC 133 °C); IR (KBr, cm^{-1}) v 3050 (m), 3048 (m), 2956 (m), 2912 (m), 1590 (m), 1487 (m), 1438 (m), 1327 (s), 1202 (vs), 915 (vs), 821 (m), 746 (s), 692 (s), 512 (s); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 2.96$ (s, 4H, CH_2CH_2), 7.05–7.73 (m, 40H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 21.6$, 22.0, 120.7, 123.8, 128.3, 128.9, 129.3, 131.2, 132.3, 152.4; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): $\delta = -6.7$ (dd, $^2J_{PP} = 36.5$ Hz, $^3J_{PP} = 12.9$ Hz, 2P, $(PhO)_2P{=}O$), 18.4 (dd, $^2J_{PP} = 36.5$ Hz, $^3J_{PP} = 12.9$ Hz, 2P, $Ph_2P{=}N$); UV (CH_2Cl_2) λ_1 243 nm, λ_2 277 nm, % of P content: theoretical 13.88; experimental[17] 13.79.
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