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# An efficient entry to monoiminophosphoranes derived from 1,2-bis(diphenylphosphino)ethane: new bidentate P,N ligands

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**Abstract**—Base-catalyzed Michael-type addition of diphenylphosphane to *P*,*P*,*P*-diphenylvinyl iminophosphoranes yielded monoiminophosphoranes derived from 1,2-bis(diphenylphosphino)ethane, heteroditopic P,N-donor ligands which are not easily available by the direct monoimination of the parent bis(phosphane). © 2001 Elsevier Science Ltd. All rights reserved.

Oxidation at only one phosphorus atom of a bis(phosphane) creates heteroditopic phosphane ligands with contrasting (e.g. hard/soft) reactivities of their two donor centers. A number of mono-oxidized bis(phosphane) derivatives have proven to be efficient ligands in coordination and organometallic chemistry,[1] and their complexes are appreciated as valuable catalysts.[2] The heteroatom at the phosphorus(V) center in these P(III),P(V) bidentate ligands is typically O, S, Se or N.

Despite its great potential and anticipated diversity, the coordination and catalytic chemistry of mono-oxidized bis(phosphanes) still remains scarcely explored due to the lack of good general methods for their synthesis. Mono-oxidation of bis(phosphanes) is not easily controlled. Most reagents readily oxidize both phosphorus atoms, a result which generally prevails with identically substituted phosphane units.

In this context, the selective monoimination of bis(diphenylphosphino)alkanes with azides via the Staudinger reaction[3] has been successfully applied to the preparation of several monoiminophosphoranes derived from bis(diphenylphosphino)methane (dppm).[4] The high selectivity of these reactions probably lies on the proximity of the two phosphane groups, which results in the failure of the imination at the second phosphorus atom by steric reasons. With other bis(diphenylphosphino)alkanes of longer chain, such as bis(diphenylphosphino)ethane (dppe), propane (dppp) and butane (dppb), the monoimination only could be achieved in good yield by the particularly unreactive trimethylsilylazide.[5]

In the course of a program devoted to the preparation of new heteroditopic bis(phosphane)-based ligands[6] we directed our attention to the monoiminophosphoranes derived from dppe. When we tested the selective monoimination of dppe with *p*-tolylazide, under the reaction conditions we had established as optimal for dppm (1 equiv of azide, slow addition over the phosphane, in acetonitrile, rt),[6] we obtained low levels of selectivity (2:1, mono:bis iminophosphoranes, as measured by $^1H$ and $^{31}P$ NMR analysis of the crude). Moreover, the tedious separation of the components of the final mixture by column chromatography resulted in poor isolated yield of the desired monoiminophosphorane (always lower than 30%, in several runs) due to extensive hydrolysis of its P=N function to give the phosphane oxide dppeO and *p*-toluidine.

As an alternative to the not practicable monoimination of dppe, we here report a general and efficient method for the preparation of monoiminophosphoranes derived from that bis(phosphane), in two high-yielding steps, starting from the commercially available diphenylvinylphosphane.

It has been reported that the C=C bond of diphenylvinylphosphane and its chalcogenides (oxide and sulfide) is reactive in Michael-type additions of a variety of nucleophilic reagents, such as phosphanes,[7] alcohols[8] and amines.[9] By contrary to the oxide and sulfide $Ph_2P(=X)CH=CH_2$ ($X = O$, S), the *P*,*P*,*P*-diphenylvinyl iminophosphoranes $Ph_2P(=NR)CH=CH_2$ are poorly known species whose chemistry remains almost unexplored.[10] We envisaged that the Michael-type additions of secondary phosphanes (e.g. $Ph_2PH$) to these species could be a potential source of the elusive dppe monoiminophosphoranes.

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To this end we prepared a number of iminophosphoranes **1** by reacting diphenylvinylphosphane with a range of aryl, acyl and phosphoryl azides under the standard conditions of the Staudinger reaction (Scheme 1).

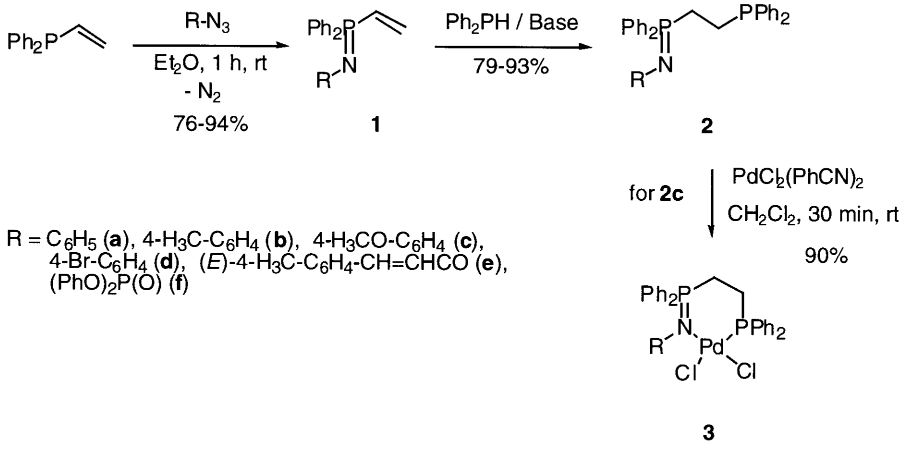
Compounds **1** were isolated after a simple work-up and obtained as crystalline solids in good yields (76–94%). The characterization of **1** was straightforward following their analytical and spectral data. The $^{31}$P NMR (121.4 MHz, $CDCl_3$) spectra of **1a–d** showed a singlet in the range −0.77 to −1.03 ppm, whereas that of **1e** appeared at 18.06 ppm. Two doublets ($^2J_{PP}=32.5$ Hz) at −7.31 and 9.80 ppm were observed for **1f**. In their $^1$H NMR spectra, the signals attributed to the vinylic protons appeared as the ABM portion of an ABMX system, due to their coupling with the phosphorus nucleus.

We were pleased to find that the base-catalyzed Michael addition of diphenylphosphane to the *P*,*P*,*P*-diphenylvinyl iminophosphoranes **1** led to the dppe monoiminophosphoranes **2** in excellent yields (Table 1).

The catalytic activity of three different bases (phosphazene base $P_4$-*t*-Bu,[11] $KN(TMS)_2$ and *t*-BuOK) in combination with two reaction solvents was checked, and we found no relevant differences in terms of efficiency. These reactions were completed in less than 30 min at room temperature and their yields, estimated by NMR analysis, were nearly quantitative. Compounds **2** could be further purified by flash chromatography on deactivated (5% $Et_3N$) silica gel column, eluting with ethyl acetate/hexane (1:1, v:v). They could be also crystallized from $CH_2Cl_2/Et_2O$ providing this operation was carried out rapidly (in less than 3 h), otherwise partial hydrolysis of the P=N function occurred to yield crystals contaminated by dppeO.

Analytical and spectral data of **2** were consistent with their presumed structures.[12] The $^{31}$P NMR spectra of the *N*-aryl derivatives **2a–d** in $CDCl_3$ showed two well-separated doublets ($^3J_{PP}=46.5$–$46.7$ Hz) near −12 and 7 ppm, attributed to the phosphane and iminophosphorane functions respectively, the P(III) nucleus lying typically upfield from the P(V) one. The presence of the ethylene fragment in **2** was ascertained by their $^1$H and $^{13}$C NMR spectra.

With ligands **2** in hand, we carried out a first test of their ability to coordinate metal ions. Reaction of **2c** with dichlorobis(benzonitrile)palladium(II) in dichloromethane at room temperature afforded complex **3** in 90% yield. Elemental analysis, $^1$H and $^{13}$C NMR, and FAB-MS data of **3** are in accord with the proposed structure. The $^{31}$P NMR spectrum of **3** in $CDCl_3$ showed two doublets ($^3J_{PP}=11.4$ Hz) at 24.72 and 21.93 ppm, notably shifted downfield when compared with those of the free ligand **2c** (−12.61 and 6.62 ppm), as expected for the coordination in a σ-N and



**Scheme 1.**

**Table 1.** Compounds **2** prepared by Michael-type addition of $Ph_2PH$ to **1**

| R | Base[a] | Solvent | Yield (%)[b] | R | Base[a] | Solvent | Yield (%)[b] |
|---|---|---|---|---|---|---|---|
| $C_6H_5$ | $P_4$-*t*-Bu | Toluene | 90 | 4-Br-$C_6H_4$ | $P_4$-*t*-Bu | Toluene | 86 |
| $C_6H_5$ | $KN(TMS)_2$ | Toluene | 89 | 4-Br-$C_6H_4$ | $KN(TMS)_2$ | Toluene | 92 |
| $C_6H_5$ | *t*-BuOK | THF | 93 | 4-Br-$C_6H_4$ | *t*-BuOK | THF | 93 |
| 4-$H_3C$-$C_6H_4$ | *t*-BuOK | THF | 91 | (*E*)-4-$H_3C$-$C_6H_4$-CH=CHCO | $KN(TMS)_2$ | Toluene | 78 |
| 4-$H_3CO$-$C_6H_4$ | $P_4$-*t*-Bu | Toluene | 90 | (*E*)-4-$H_3C$-$C_6H_4$-CH=CHCO | *t*-BuOK | THF | 80 |
| 4-$H_3CO$-$C_6H_4$ | $KN(TMS)_2$ | Toluene | 93 | $(PhO)_2P(O)$ | *t*-BuOK | THF | 79 |
| 4-$H_3CO$-$C_6H_4$ | *t*-BuOK | THF | 93 | | | | |

[a] 0.1 equivalents.

[b] Isolated pure products after flash column chromatography.

σ-P chelate mode. We are currently engaged in further studies of ligands **2**, in an attempt to systematize their coordinating abilities.

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11. Available as 1 M *n*-hexane solution from Fluka Chemie AG.
12. **2c**: yellow needles (dichloromethane/diethyl ether). Mp 125–127°C; IR (Nujol) 1500, 1456 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$) $\delta$ 2.18 [m, 2H, CH$_2$P(III)], 2.47 [m, 2H, CH$_2$P(V)], 3.71 (s, 3H, OCH$_3$), 6.62 (d, 2H, $^{3}J_{\mathrm{HH}}=9.3$ Hz, H$_{\mathrm{arom}}$), 6.63 (d, 2H, $^{3}J_{\mathrm{HH}}=9.3$ Hz, H$_{\mathrm{arom}}$), 7.23–7.25 (m, 10H, Ph), 7.39–7.51 (m, 6H, Ph), 7.65–7.72 (m, 4H, Ph); $^{13}$C NMR (CDCl$_3$) $\delta$ 19.33 [dd, $^{1}J_{\mathrm{CP(III)}}=14.8$, $^{2}J_{\mathrm{CP(V)}}=3.8$ Hz, CH$_2$P(III)], 24.31 [dd, $^{1}J_{\mathrm{CP(V)}}=64.9$, $^{2}J_{\mathrm{CP(III)}}=16.8$ Hz, CH$_2$P(V)], 55.68 (OCH$_3$), 114.49 (C-3), 123.60 (d, $^{3}J_{\mathrm{CP}}=17.4$ Hz, C-2), 128.60 (d, $^{3}J_{\mathrm{CP(III)}}=6.4$ Hz, C$_m$), 128.82 (d, $^{3}J_{\mathrm{CP(V)}}=11.0$ Hz, C$_m$), 128.90 (C$_p$), 129.78 (d, $^{1}J_{\mathrm{CP(V)}}=109.5$ Hz, C$_i$), 131.64 (d, $^{4}J_{\mathrm{CP(V)}}=2.3$ Hz), 131.65 (d, $^{2}J_{\mathrm{CP(V)}}=9.2$ Hz, C$_o$), 132.75 (d, $^{2}J_{\mathrm{CP(III)}}=18.6$ Hz, C$_o$), 137.39 (d, $^{1}J_{\mathrm{CP(III)}}=13.3$ Hz, C$_i$), 144.70 (C-1), 152.01 (C-4); $^{31}$P NMR (CDCl$_3$) $\delta$ −12.61 [d, $^{3}J_{\mathrm{PP}}=46.7$ Hz, P(III)], 6.62 [d, $^{3}J_{\mathrm{PP}}=46.7$ Hz, P(V)]; MS *m*/*e* (EI) 519 (90, M$^{+}$), 182 (100). Anal. calcd for $C_{33}H_{31}NOP_2$: C, 76.29; H, 6.01; N, 2.70. Found: C, 76.35; H, 5.92; N, 2.65.