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Addition of secondary phosphines to *N*-vinylpyrroles

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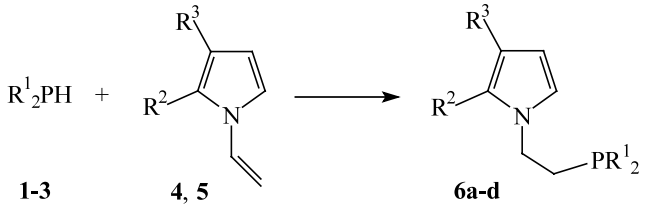
Abstract—Secondary phosphines **1**–**3** react readily with *N*-vinylpyrroles **4** and **5** under radical initiation to give regiospecifically anti-Markovnikov adducts, diorganyl-2-(1-pyrrolyl)ethylphosphines **6a**–**d**, highly reactive building blocks for organic synthesis, in 88–91% yields.

P,*N*-Ligands are being extensively investigated in the design of a new generation of metal complex catalysts.[1] Tertiary phosphines bearing nitrogen-containing heterocyclic substituents,[2] including pyrrolyls,[2a] have been successfully applied as ligands in a variety of transition metal-catalyzed reactions (hydrogenation of olefins and arenes,[2a,b] allylic substitution,[2c] isomerization of alkenes,[2d] etc.). Therefore, the search for new convenient approaches to the synthesis of prospective polydentate ('hemilabile') *P*,*N*-ligands remains an important synthetic task.



Scheme 1.

The present letter reports the first examples of the hydrophosphination of readily available *N*-vinylpyrroles[3] with secondary phosphines, now easily prepared directly from elemental phosphorus and electrophiles in superbase systems.[4]

Secondary phosphines **1**–**3** add to *N*-vinylpyrroles **4** and **5** regio- and chemospecifically in the presence of azaisobutyronitrile (AIBN) at 65–70°C or under UV irradiation to form the corresponding tertiary diorganyl-2-(1-pyrrolyl)ethylphosphines **6a**–**d** in high yields[5] (Scheme 1, Table 1).

Table 1. Synthesis of phosphines **6**[a]

	Reactants (mmol)					Initiation	Time (h)	Product **6**, yield (%)[b]
	R^1			R^2	R^3			
1	*n*-Bu	(0.75)	**5**	$(CH_2)_4$	(0.76)	AIBN	30	**6a**, 91
2	$Ph(CH_2)_2$	(0.50)	**4**	*n*-Pr	Et (0.50)	UV	13	**6b**, 91
2	$Ph(CH_2)_2$	(0.50)	**4**	*n*-Pr	Et (0.51)	AIBN	41	**6b**, 89
2	$Ph(CH_2)_2$	(0.58)	**5**	$(CH_2)_4$	(0.60)	UV	2	**6c**, 91
2	$Ph(CH_2)_2$	(0.96)	**5**	$(CH_2)_4$	(0.98)	AIBN	41	**6c**, 88
3	2-$Py(CH_2)_2$	(1.83)	**5**	$(CH_2)_4$	(1.84)	AIBN	40	**6d**, 90

[a] All experiments were carried out under an argon atmosphere.
[b] Isolated yields.

Keywords: secondary phosphines; *N*-vinylpyrroles; addition; radical initiation; functional tertiary phosphines.
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Some preliminary information concerning the properties of the polyfunctional compounds synthesized has been obtained. Thus, methylation of **6d** with MeI (ether, room temperature, 1 h) proceeds regiospecifically at the phosphorus atom (even with a three-fold molar excess of MeI) to afford phosphonium iodide **7** in 93% yield (Scheme 2). Phosphine **6d** is quantitatively oxidized in air to the phosphine oxide **8** (Scheme 2).

Deactivation of the pyridine nucleus in the molecule **7** is likely due to its coordination to the phosphorus atom with partial positive charge transfer to the pyridine nitrogen and the pyrrole moiety (structures **9**–**11**) (Scheme 3).

Table 2. Spectroscopic data for compounds **6**–**8**

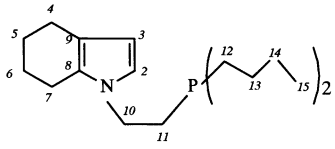
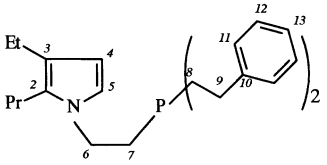
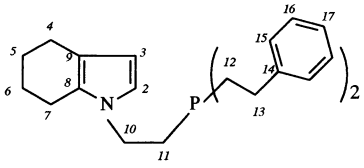
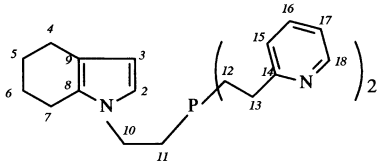
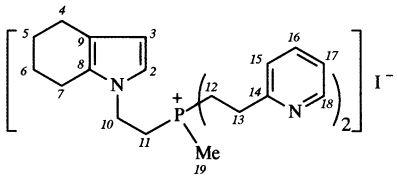
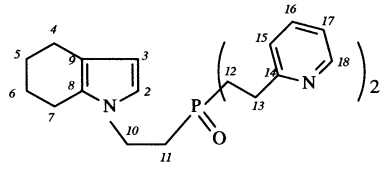
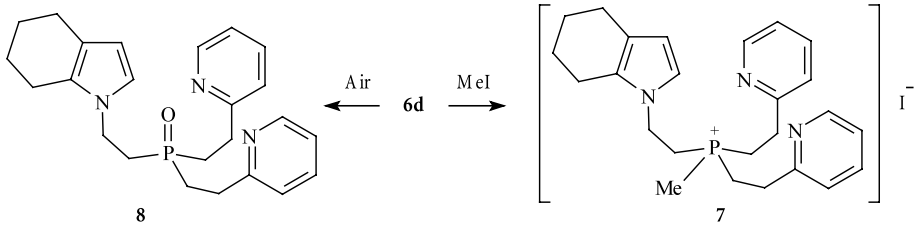
Product [a]	Formula	NMR ($CDCl_3$, δ, ppm); ^1H (400 MHz); ^{13}C (100 MHz); ^{31}P (161.98 MHz)		
		^1H	^{13}C	^{31}P
6a		0.94 (*t*, 6H, $^3J_{14,15}$=7.0 Hz, H-15), 1.40 (*m*, 8H, H-13,14), 1.70-1.90 (*m*, 10H, H-5,6,11,12), 2.54 (*m*, 4H, H-4,7), 3.90 (*q*, 2H, $^3J_{10,11}$=8.1 Hz, H-10), 5.91 (*d*, 1H, $^3J_{2,3}$=2.8 Hz, H-3), 6.54 (*d*, 1H, H-2)	13.52 (C-15), 21.69, 22.85, 23.14, 23.38 (C-4-7), 23.59 (*d*, $^1J_{P,C}$=12.5 Hz, C-12), 24.14 (*d*, $^2J_{P,C}$=11.1 Hz, C-13), 26.43 (*d*, $^1J_{P,C}$=15.5 Hz, C-11), 24.54 (*d*, $^3J_{P,C}$=11.0 Hz, C-14), 43.50 (*d*, $^3J_{P,C}$=14.0 Hz, C-10); 106.17 (C-3), 117.89 (C-2,9), 126.91 (C-8)	–33.23
6b		0.96 [*t*, 3H, $^3J_{H,H}$=7.3 Hz, Me(Et)], 1.18 [*t*, 3H, $^3J_{H,H}$=7.4 Hz, Me(Pr)], 1.53 [*m*, 2H, β-CH_2(Pr)], 1.74 (*m*, 4H, H-8), 1.89 (*t*, 2H, $^3J_{6,7}$=8.3 Hz, H-7), 2.43 [*q*, 2H, CH_2(Et)], 2.51[*t*, 2H, $J_{H,H}$=8.0 Hz, α–CH_2(Pr)], 2.76 (*m*, 4H, H-9), 3.93 (*q*, 2H, $^3J_{P,H}$=8.1 Hz, H-6), 6.02 (*d*, 1H, $^3J_{4,5}$=2.6 Hz, H-4), 6.54 (*d*, 1H, H-5), 7.21 (*m*, 6H, H-11,13,15), 7.31 (*m*, 4H, H-12,14)	14.16 [CH_3(Et)], 15.81 [CH_3(Pr)], 19.45 [β-CH_2(Pr)], 24.15 [CH_2(Et)] and [α-CH_2(Pr)], 26.36 (*d*, $^1J_{P,C}$=16.0 Hz, C-7), 30.02 (*d*, $^1J_{P,C}$=13.5 Hz, C-8), 32.33 (*d*, $^2J_{P,C}$=15.1 Hz, C-9), 44.18 (*d*, $^2J_{P,C}$=23.0 Hz, C-6), 106.93 (C-4), 118.05 (C-5), 122.28 (C-3), 126.16 (C-13), 128.10, 128.56, 128.39 (C-2,11,12,14,15), 142.60 (*d*, $^3J_{P,C}$=9.5 Hz, C-10)	–30.84
6c		1.70-2.00 (*m*, 10H, H-5,6,11,12), 2.56 (*m*, 4H, H-4,7), 2.76 (*m*, 4H, H-13), 3.92 (*q*, 2H, $^2J_{P,H}$ = 3.9 Hz, H-10), 5.98 (*d*, 1H, $^3J_{2,3}$=2.8 Hz, H-3), 6.55 (*d*, 1H, H-2), 7.26 (*m*, 6H, H-15,17,19), 7.34 (*m*, 4H, H-16,18)	21.64, 22.87, 23.02, 23.26 (C-4-7), 28.60 (*d*, $^1J_{P,C}$=13.7 Hz, C-12), 29.13 (*d*, $^1J_{P,C}$=15.7 Hz, C-11), 31.91 (*d*, $^2J_{P,C}$=11.4 Hz, C-13), 43.38 (*d*, $^2J_{P,C}$=22.0 Hz, C-10), 106.16 (C-3), 117.90 (C-2,9), 125.74 (C-17), 126.24 (C-8), 127.77, 128.15, 128.39 (C-15,16,18,19), 142.00 (*d*, $^3J_{P,C}$=8.5 Hz, C-14)	–30.79
6d		1.70-2.00 (*m*, 10H, H-5,6,11,12), 2.50 (*m*, 4H, H-4,7), 2.93 (*m*, 4H, H-13), 3.91 (*q*, 2H, $^3J_{10,11}$=8.1 Hz, $^3J_{P,H}$=8.1 Hz, H-10), 5.92 (*d*, 1H, $^3J_{2,3}$=2.8 Hz, H-3), 6.55 (*d*, 1H, H-2), 7.12 (*dd*, 2H, $^3J_{16,17}$=8.0 Hz, $^3J_{17,18}$=4.8 Hz, H-17), 7.15 (*d*, 2H, $^3J_{15,16}$= 8.0 Hz, H-15), 7.59 (*t*, 2H, H-16), 8.53 (*d*, 2H, H-18)	21.72, 22.98, 23.13, 23.28 (C-4-7), 26.51 (*d*, $^2J_{P,C}$=13.5 Hz, C-13), 29.21 (*d*, $^1J_{P,C}$=15.8 Hz, C-11), 34.21 (*d*, $^1J_{P,C}$=14.5 Hz, C-10), 43.48 (*d*, $^2J_{P,C}$=21.9 Hz, C-12), 106.15 (C-3), 117.29 (C-9), 118.03, 122.41 (C-15,17), 125.95 (C-8), 136.27 (C-17), 148.98 (C-18), 161.53 (*d*, $^3J_{P,C}$=11.0 Hz, C-14)	–30.52

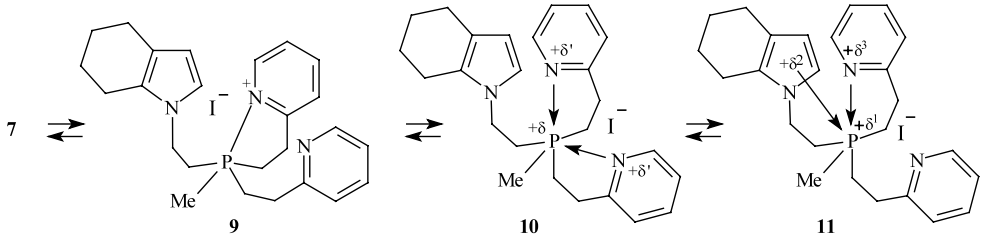
Table 2. (*Continued*)

7		1.61-1.77 (*m*, 4H, H-5,6), 1.87 (*d*, 2H, $^{2}J_{P,H}$=13.6 Hz, H-19), 2.36-2.53 (*m*, 4H, H-4,7), 2.81-2.86 (*m*, 4H, H-12), 3.17-3.26 (*m*, 6H, H-11,13), 4.19-4.27 (*m*, 2H, H-10), 5.86 (*d*, 1H, H-3), 6.56 (*d*, 1H, H-2), 7.16 (*dd*, 2H, H-17), 7.34 (*d*, 2H, H-15), 7.63 (*t*, 2H, H-16), 8.44 (*d*, 2H, H-18)	6.56 (*d*, $^{1}J_{P,C}$=50.9 Hz, C-19), 20.51 (*d*, $^{1}J_{P,C}$=49.7 Hz, C-12), 22.08, 22.96, 23.17, 23.28 (C-4-7), 24.24 (*d*, $^{1}J_{P,C}$=48.1 Hz, C-11), 29.84 (*d*, $^{2}J_{P,C}$=3.9 Hz, C-13), 39.58 (*d*, $^{2}J_{P,C}$=2.0 Hz, C-10), 107.66 (C-3), 118.90 (C-9), 118.99 (C-2), 122.27 and 123.46 (C-15,17), 127.20 (C-8), 137.01 (C-16), 147.81 (C-18), 157.39 (*d*, $^{3}J_{P,C}$=8.5 Hz, C-14)	32.28
8		1.21-1.24 (*m*, 4H, H-5,6), 1.65-1.80 (*m*, 4H, H-12), 2.09-2.18 (*m*, 4H, H-4,7), 2.42-2.59 (*m*, 4H, H-10,11), 3.02-3.08 (*m*, 4H, H-13), 4.08-4.14 (*m*, 2H, H-10), 5.88 (*d*, 1H, H-3), 6.50 (*d*, 1H, H-2), 7.10 (*dd*, 2H, H-17), 7.13 (*d*, 2H, H-15), 7.15 (*t*, 2H, H-16), 7.59 (*d*, 2H, H-18)	21.84, 23.12, 23.28, 23.49 (C-4-7), 28.00 (*d*, $^{1}J_{P,C}$=64.4 Hz, C-12), 29.73 (*d*, $^{2}J_{P,C}$=14.9 Hz, C-13), 30.53 (*d*, $^{1}J_{P,C}$=61.1 Hz, C-11), 39.26 (C-10), 107.03 (C-3), 117.99 (C-9), 118.41 (C-2), 121.66 (C-17), 122.84 (C-15), 127.33 (C-8), 136.67 (C-16), 149.29 (C-18), 159.80 (*d*, $^{3}J_{P,C}$=12.8 Hz, C-14)	45.67

[a] Compounds **6a-d**, **8** are oils, iodide **7** is a crystalline substance of yellow-brown color, mp 30-31 °C (ether). Elemental analyses of compounds **6-8** correspond to the calculated values.



Scheme 2.



Scheme 3.

In summary, the addition of secondary phosphines to *N*-vinylpyrroles presents a new convenient approach to C–P bond formation and the synthesis of new polyfunctional phosphines.

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5. *General procedure*: An equimolar mixture of the secondary phosphine and the *N*-vinylpyrrole was irradiated (200 W mercury arc lamp) in a quartz ampoule or heated at 65–70°C in the presence of AIBN (0.5–1.5 mass% of the reactant's mass) in a sealed ampoule. The crude product, a viscous undistillable liquid, was purified by Al_2O_3 column chromatography (diethyl ether) to give phosphine **6** (Table 1). Spectral characteristics of phosphines **6a–d** are presented in Table 2.