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A convenient access to new phosphine and diphosphine ligands from phosphinic acids

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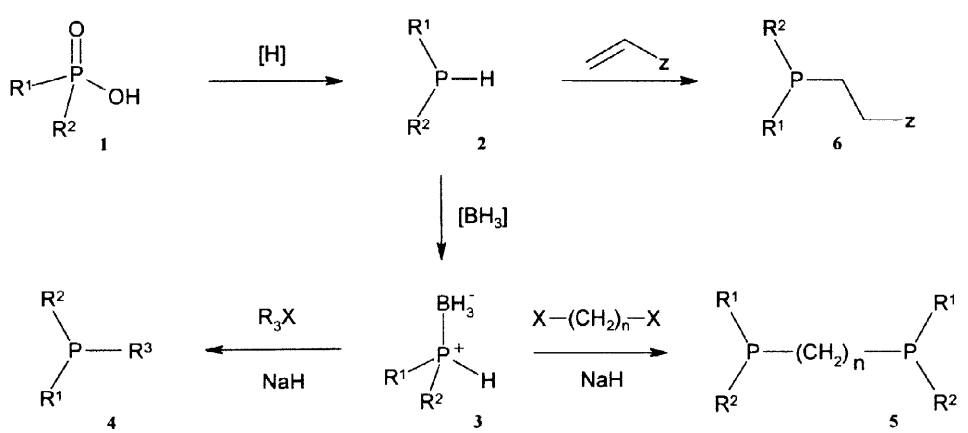
Abstract : Phosphinic acids are convenient starting materials for a two-steps route to a large variety of phosphines and polyphosphines.

Phosphine ligands play a central role in coordination chemistry[1] and homogeneous catalysis[2], and there is an increasing need for easy to handle methods affording new ligands with specific properties. A recently described general access to a variety of phosphinic acids **1** from commercial hypophosphorous acid via a bis(trimethylsilyl)phosphonite intermediate[3] prompted us to consider their reduction as a convenient way to various secondary phosphine synthons **2**[4] which could be easily converted into[1] tertiary mono and diphosphines via their P-BH_3 complexes **3** (scheme 1).



Scheme 1

Phosphinic acids **1a-f** were synthetized from the corresponding halides according to Boyd's procedure (**1a** and **1b** were described by Boyd[3d], **1c** described as a by-product in the

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thermal cyclisation of arenylphosphonic acids[7], **1e** and **1f**, not previously described, as far as we know, with 70 (**1c**), 90 (**1d**), 100 (**1e**) and 100% (**1f**) yields respectively).

Silanes $C_6H_5SiH_3$ or $(C_6H_5)_2SiH_2$, or lithium aluminum hydride reduced cleanly[8] phosphinic acids **1a-f** into the corresponding secondary phosphines **2a-f** (table 1, all new, except **2d**, of course, and **2a** previously synthetized from o-xylylenediphosphinic acid by cyclisation, followed by esterification, then reduction[9]).

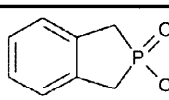
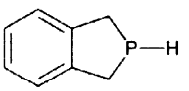
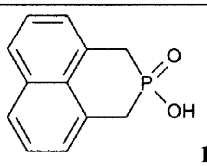
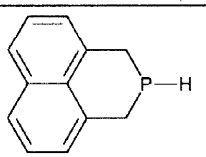
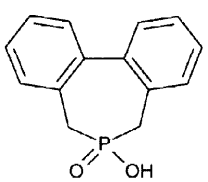
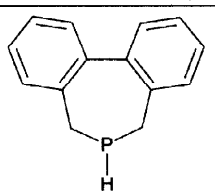
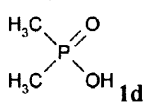
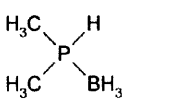
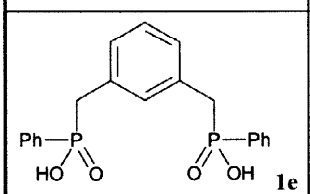
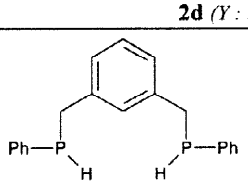
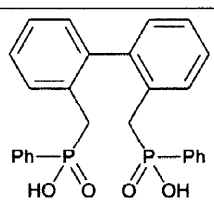
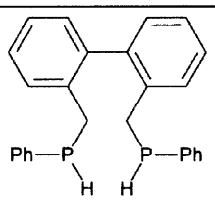
Phosphinic acid	Reducing agent	Phosphine	^{31}P NMR	^{13}C NMR selected Cα-P
 **1a**	$PhSiH_3$	 **2a** *(Y : 60%)*	δ -59.7 $^1J_{P-H}$: 190 Hz	δ 27.6 $^1J_{P-C}$: 10 Hz
 **1b**	$PhSiH_3$	 **2b** *(Y : 70%)*	δ -82.7 $^1J_{P-H}$: 190 Hz	δ 23.5 $^1J_{P-C}$: 10 Hz
 **1c**	$PhSiH_3$	 **2c** *(Y : 70%)*	δ -31.8 $^1J_{P-H}$: 254 Hz	δ 23
 **1d**	$PhSiH_3$	 **2d** *(Y : 50%)*	δ -29.8 $^1J_{P-H}$: 364 Hz	δ 6.8 $^1J_{P-C}$: 39 Hz
 **1e**	$LiAlH_4$	 **2e** *(Y : 46%)*	δ -40.2; -40.3 $^1J_{P-H}$: 203 Hz	δ 31.2 $^1J_{P-C}$: 20 Hz
 **1f**	$LiAlH_4$	 **2f** *(Y : 54 %)*	δ -45.5; -46.5 $^1J_{P-H}$: 210 Hz	δ 29.4; 29.2 $^1J_{P-C}$: 16 Hz

Table 1

As expected, these phosphines **2a-f** are sensitive to oxidation. They may be used as such in Michael additions on activated alkenes (phosphine **6**). In most cases, it is preferable to complex them into more stable borane adducts **3**. This can be made readily by reacting

phosphines with BH_3-THF overnight at room temperature, leading to air-stable crystalline solids (**3a-c**, table 2).

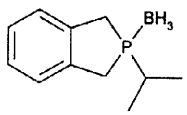
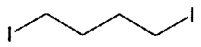
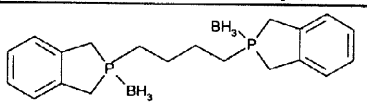
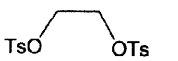
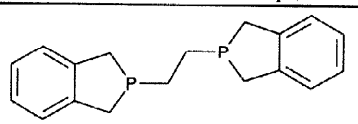
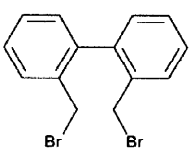
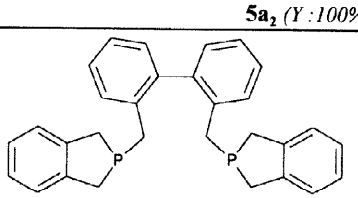
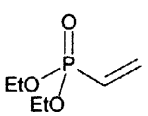
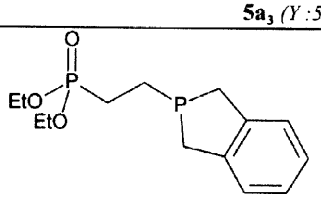
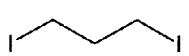
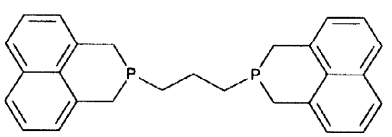
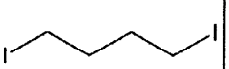
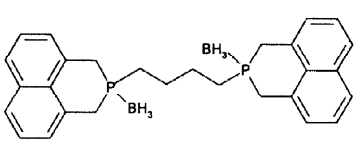
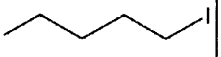
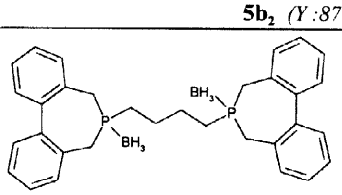
Phosphine or phosphine-borane adduct	Reactant	Phosphine	^{31}P NMR	^{13}C NMR selected C_α-P
3a		 **$4a_1$** *(Y :93%)*	δ 32.3	δ 29.2 $^1J_{P\text{-}C}$: 33 Hz
		 **$5a_1$** *(Y :79%)*	δ 35.6	δ 31.2. $^1J_{P\text{-}C}$: 34 Hz
		 **$5a_2$** *(Y :100%)*	δ -14.2	δ 32.9 $^1J_{P\text{-}C}$: 7 Hz
		 **$5a_3$** *(Y :56%)*	δ -8.9	δ 33.3; 32.8 $^1J_{P\text{-}C}$: 16 Hz
2a		 **6** *(Y :70%)*	δ 31.8; -13.4 $^3J_{P\text{-}P}$: 54 Hz	δ 32.7 $^1J_{P\text{-}C}$: 14 Hz
3b		 **$5b_1$** *(Y :78%)*	δ -55.9	δ 29.4 $^1J_{P\text{-}C}$: 13 Hz
		 **$5b_2$** *(Y :87%)*	δ -2.2	δ 28.2 $^1J_{P\text{-}C}$: 34 Hz
3c		 **5c** *(Y :100%)*	δ 43.7	δ 29.6; 28.9 $^1J_{P\text{-}C}$: 32 Hz

Table 2

In spite of this protective effect, the P-H bond of these adducts remained – as expected[11,12,13,14] – very reactive. By addition of one equivalent of NaH to a mixture of the secondary phosphine-borane adduct and an alkyl halide (1eq) or dihalide or ditosylate (0.5 eq), the mono and diphosphines-BH_3 adducts were isolated[16], from which the free phosphines could easily be liberated - if needed - by the Livingshouse's procedure (i.e. deprotection by $HBF_4.OMe_2$)[15]. Phosphines obtained by this procedure are gathered in table 2 with some pertinent NMR data. Phosphines $\mathbf{5a_3}$ and **6** are particularly noteworthy : $\mathbf{5a_3}$ is an analogue of BISBI[17], an excellent ligand of Rh for selective hydroformylation and **6** is a potent hemilabile ligand[18]. Other examples and applications to catalysis are presently under investigation from this laboratory.

Aknowledgements : The authors thank Dr R. Pichon and N. Kervarec for valuable NMR assistance and the MENRT for a grant (E.S.).

References and notes

1 for a review, see G.Bertrand ed., special issue on phosphorus chemistry, *Chem. Rev.*, **1994**, *94*, 1161.

2 Cornils, B.; Hermann, W.A.; "*Applied homogeneous catalysis with organometallic compounds*", VCH, **1996**.

3 (a) Boyd, E.A.; Corless, M.; James, K.; Regan, A.C.; *Tetrahedron Lett.*, **1990**, *31* (20), 2933-2936.
(b) Boyd, E.A.; Regan, A.C.; James, K.; *Tetrahedron Lett.*, **1992**, *33* (6), 813-816.
(c) Boyd, E.A.; Regan, A.C.; James, K.; *Tetrahedron Lett.*, **1994**, *35* (24), 4223-4226.
(d) Boyd, E.A.; Boyd, M.E.K.; Kerrigan, F.; *Tetrahedron Lett.*, **1996**, *37* (30), 5425-5426.

4 some examples of such reductions of phosphinic acids by silanes[5] or $LiAlH_4$ (generally via their P(O)Cl intermediates[6]) are known.

5 see for examples (a) Fritzsche, H.; Hasserodt, U.; Korte, F ; *Chem. Ber.*, **1965**, *98*, 1681-1687.
(b) De Koe, P.; Van Veen, R.; Bickelhaupt, F.; *Angew. Chem. Int. Ed.*, **1968**, *7* (6), 465-466.
(c) Toulhoat, C.; Vidal, M.; Vincens, M.; *Phosphorus, Sulfur and Silicon*, **1992**, *71* (1), 127-138.

6 see for examples (a) Hays H.R.; Logan, T.J.; J.Org.Chem., **1966**, *31*, 3391-3394.
(b) De Graaf, H.G.; Dubbeldam, J.; Vermeer, H.; Bickelhaupt, F.; *Tetrahedron Lett.*, **1973**, (26), 2397-2400.

7 Robinson, C.N.; Pettit, W.A.; *Tetrahedron Lett.*, **1972**, (49), 4977-4978.

8 In a typical experiment - *reduction by silane* : a mixture of phosphinic acid and phenylsilane (1 eq.) is stirred at 100°C for 2 to 12 hrs under N_2. The phosphine is distilled under reduced pressure.
- *reduction by $LiAlH_4$* : the diphosphinic acids **1e** and **1f** are converted into their chlorides with an excess $SOCl_2$ in CH_2Cl_2, which, in turn, are reduced to the phosphines with $LiAlH_4$ (x mg, 2.5 eq.) in THF (RT, overnight). Hydrolysis (x µl H_2O, x µl 15%NaOH, 3x µl H_2O) then filtration and evaporation gave diphosphines **2e** and **2f**.

9 Robinson, C.N.; Lewis, R.C.; *J. Heterocyclic Chem.*, **1973**,*10*, 395-397.

10 Schmidbaur, H.; *J. Organomet. Chem.*, **1980**, *200*, 287-306.

11 Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K.; *J. Am. Chem. Soc.*, **1990**, *112*, 5244-5252.

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13 Brisset, H.; Gourdel, Y.; Pellon, P.; Le Corre, M.; *Tetrahedron Lett.*, **1993**, *34* (28), 4523-4526.

14 (a) Bourumeau, K.; Gaumont, A.C.; Denis, J-M.; *Tetrahedron Lett.*, **1997**, *38* (11), 1923-1926.
(b) Bourumeau, K.; Gaumont, A.C.; Denis, J-M.; J. Organomet. Chem., **1997**, *529*, 205-213.

15 (a) Mc Kinstry, L ; Livinghouse, T.; *Tetrahedron Lett.*, **1994**, *35* (50), 9319-9322.
(b) Mc Kinstry, L ; Livinghouse, T.; *Tetrahedron*, **1995**, *51* (28), 7655-7666.

16 In a typical experiment : a suspension of NaH (1 mmole) in THF (5 mL) was added to a mixture of phosphine-borane (1 mmole) and alkyl halide (1 mmole) in THF (10 mL) at 0°C. The mixture was stirred at room temperature until the reaction was complete. THF was removed in vacuo, and dry dichloromethane added. The mixture was treated with diluted HCl and extracted with dichloromethane.

17 Devon, T.J.; Phillips, G.W.; Puckette, T.A.; Stavinoha, J.L.; Vanderbilt, J.J.; *U.S. Patent* 4,694,109.

18 Bader, A.; Lindler, E.; *Coord. Chem. Rev.*, **1991**, *108*, 27-110.