Stabilization of Parent Phosphinous Acid and Some of its Derivatives by P-Complexation with Tungsten Pentacarbonyl

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A stable phosphinous acid complex, $H_2P(OH)W(CO)_5$, was prepared by $LiAlH_4$ reduction followed by acid hydrolysis of the corresponding diethylaminodichlorophosphine complex.

Phosphinous acid H_2POH, the phosphorus analogue of hydroxylamine, is still unknown today. According to recent theoretical calculations,[1] it is slightly lower in energy than the isomeric phosphine oxide H_3PO. Thus, its postulated intermediacy in the reaction of $POBr_3$ with LiH at low temperature giving $(PH)_n$[2] appears very likely but its stability is obviously very low. Nevertheless, some of its derivatives have been either characterized (*e.g.* PH_2I in the reaction of PI_3 with PH_3[3]) or isolated in the pure state [*e.g.* $(Me_3Si)_2NPH_2$[4]]. On the other hand, P-complexation seems to be a very powerful tool for stabilizing this kind of compound as demonstrated by the isolation of stable complexes like $(ROPH_2)BH_3$[2] and $[RP(H)A]W(CO)_5$, A = OH, NH_2, Cl, Br, I.[5] In view of these results, the synthesis of H_2POH was attempted in the co-ordination sphere of tungsten.

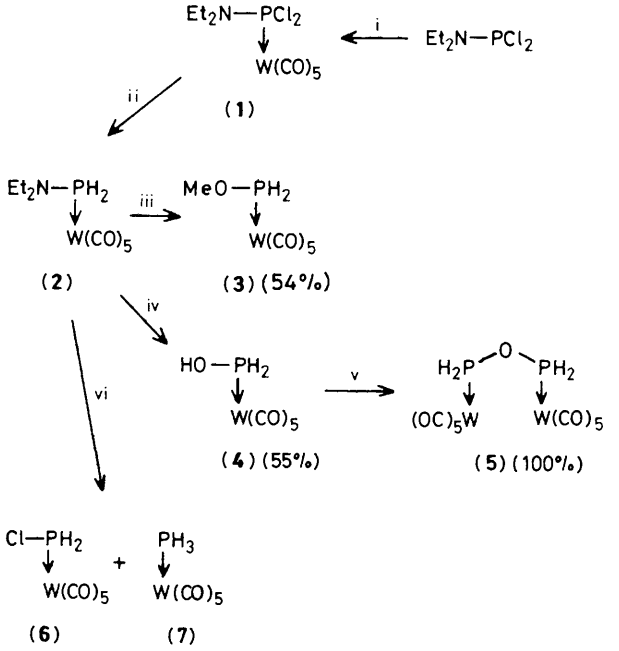
The diethylaminodichlorophosphine complex (**1**) ($\delta\ ^{31}P$ +120 p.p.m. in C_6D_6) was first synthesized by allowing a slight excess (*ca.* 20%) of the corresponding free phosphine to react with $W(CO)_5(THF)$ (THF = tetrahydrofuran) at room temperature and purified by chromatography on a short silica gel column with diethyl ether (72% yield). Complex (**1**) was reduced using a large excess of $LiAlH_4$ in Et_2O at room temperature with vigorous stirring. The unreacted metal hydride was destroyed by adding acrylonitrile to the reaction mixture. The *N,N*-diethyl phosphinamide complex (**2**) was recovered in the pure state by simply filtering and evaporating the Et_2O solution (60% yield).

Methanolysis of (**2**) was performed in the presence of acetic acid. After methanolysis, the crude organic residue was recrystalized in hexane to afford the *O*-methyl phosphinite complex (**3**) as stable white crystals (m.p. 62°C). Similarly, the hydrolysis of (**2**) was promoted by acetic acid. The crude

Table 1. N.m.r. data of $(APH_2)W(CO)_5$ complexes.[a]

A		$\delta(^{31}P)$	$^1J(^{31}P-^{183}W)$	$^1J(P-H)$	$\delta(PH)$	$\delta(A)$
Et_2N-	(**2**)	−17.9	244	342	5.81	Me : 0.70, $^3J(H-H)$ 7.1 CH_2 : 2.57, $^3J(H-P)$ 12.9
MeO-	(**3**)	54.5	273	343	6.13	2.75, $^3J(H-P)$ 12.9
HO-	(**4**)	29.4	269	353	6.63	4.71
-O-	(**5**)[b]	62.1	244	356	6.17	—
Cl-	(**6**)	−24	264	368	5.61	—

[a] N.m.r. spectra were recorded in C_6D_6 solutions; δ in p.p.m., + ve for downfield shifts and *J* in Hz; Me_4Si as internal standard for ^1H and 85% H_3PO_4 as external reference for ^{31}P. [b] Simulation of the AA'BB'XX' spectrum gave $^3J(H-P)$ 5 Hz and $^2J(P-P)$ *ca.* 60 Hz.



Reagents and conditions: i, $W(CO)_5(THF)$, THF, 20 °C, 3 h; ii, $LiAlH_4$, Et_2O, 20 °C, 0.5 h; iii, MeOH (excess) + 5% $MeCO_2H$, Et_2O, 20 °C, 0.5 h; iv, H_2O (excess) + 5% $MeCO_2H$, Et_2O, 20 °C, 0.5 h; v, heat, $-H_2O$; vi, dry HCl, C_6H_6, 20 °C, 5 min.

phosphinous acid complex (**4**) was purified by chromatography on silica gel with benzene–ethyl acetate (50/50). This acid shows a great tendency to dehydrate and gives quantitatively the corresponding anhydride (**5**) (m.p. 129 °C) by recrystallization in hexane–benzene (95/5). Complex (**5**) can be reconverted into (**4**) by chromatography on silica gel. Finally, the bubbling of dry gaseous HCl through a benzene solution of complex (**2**) afforded the unstable chlorophosphine complex (**6**). In this case, it was impossible to prevent the formation of some of the phosphine complex (**7**) (δ ^{31}P −189 p.p.m.).

With the exception of complex (**6**), all the products described here were obtained in the pure state and fully characterized by ^1H n.m.r., ^{31}P n.m.r., i.r. and [for (**3**) and (**5**)] elemental analysis. The most significant n.m.r. data are given in Table 1.

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