Synthesis of Di- or Trisubstituted Phosphonic and Phosphonothioic Di- or Trihydrazides

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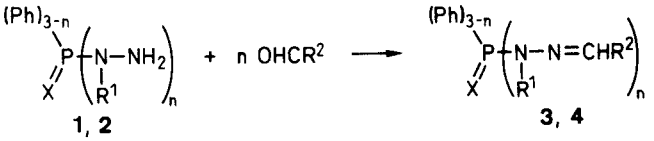
2,2′ disubstituted phosphonothioic or phosphonic dihydrazides **3a–p** or **3a′–g′** and 2,2′,2″ trisubstituted phosphonothioic or phosphonic trihydrazides **4a–e, 4i–l** or **4a′–h′** were prepared in high yields by reacting phosphonothioic or phosphonic di- or trihydrazides **1a,a′,b** or **2a,a′** with various aldehydes. The structure of one of these compounds **4a′** was solved by X-ray analysis.

Phosphodihydrazides $RP(X)(NNH_2)_2$ **1** (X = O,S) have been used for a long time as ligands for the complexation of a variety of transition metals.[1] They are also excellent starting materials for the preparation of a large number of phosphorus containing macrocycles arising from [1+1], [2+2], [3+3] or even [4+4] cyclocondensation reactions, involving compounds **1** and various dialdehydes.[2] Some of these macrocycles possess interesting complexation properties[2] due to the presence of a number of heteroatom donors (P,S,O,N) and some additional groups like P=S, P=O, OH, N=C.

Phosphodi- or trihydrazones of the general formula $R_{3-n}P(X)(NR^1N=CHR^2)_n$ **3** (n = 2) or **4** (n = 3) might also exhibit powerful complexation properties. Indeed, in a preliminary communication we have already demonstrated that compounds **3f′** and **4a′** were isolated and fully characterized by X-ray diffraction studies as the unexpected complexes of the type L_2Ni_3.[3] These observations prompted us to prepare different phosphodi- or trihydrazones possessing free functional groups such as OH, CO_2H which might help to diversify complexation properties of these derivatives not only towards alkaline or transition metals, rare earths but also towards anions or neutral molecules.

We report here the easy formation of some of these new ligands as well as the X-ray structure determination of one of these compounds, namely, the 2,2′,2″tris[(2-hydroxyphenyl)methylene]-1,1′,1″trimethyl-*P*-phenylphosphonothioic trihydrazide (**4a′**). Phosphodihydrazides $PhP(X)[N(R)\text{-}NH_2]_2$ **1a,a′,b** (**1a**, X = O, R = Me; **1a′**, X = S, R = Me; **1b**, X = O, R = H) or phosphotrihydrazides $(X)P\text{-}(NMeNH_2)_3$ **2a,a′** (**2a**, X = O, **2a′**, X = S) react respectively with 2 or 3 equivalents of aldehyde to give after purification the phosphodi- or trihydrazones **3** or **4** in high yield (68–93%) (Scheme). These reactions were carried out under the same experimental conditions in different solvents (see experimental) at room temperature and allowed the isolation of white or yellow air-stable powders. The structure of these new derivatives were deduced from ^1H, ^{31}P, ^{13}C NMR, IR, MS spectral data and microanalyses (Table 1). For example, IR spectroscopy showed the disappearance of the ν_{NH_2} band and the appearance of a new one corresponding to the imine functions HC=N (from 1620 to 1670 cm^{-1}). ^{13}C NMR spectra clearly indicated the presence of a doublet for HC=N groups ($^3J_{CP}$ from 11.3 to 13.3 Hz). An expected deshielding effect was observed in ^{31}P NMR when going from compounds **1** or **2** to **3** or **4**.



1, **3** n = 2
2, **4** n = 3

Phosphodihydrazones (n = 2)

3	R^1	R^2	X	3	R^1	R^2	X
a	Me	2-HOC_6H_4	O	**a′**	Me	2-HOC_6H_4	S
b	Me	3-HOC_6H_4	O	**b′**	Me	3-HOC_6H_4	S
c	Me	4-HOC_6H_4	O	**c′**	Me	4-HOC_6H_4	S
d	Me	3,5-*t*-Bu,4-HOC_6H_2	O	**d′**	Me	3,5-*t*-Bu,4-HOC_6H_2	S
e	Me	2,3-HOC_6H_3	O	**e′**	Me	2,3-HOC_6H_3	S
f	Me	2,4-HOC_6H_3	O	**f′**	Me	2,4-HOC_6H_3	S
g	Me	3,4-HOC_6H_3	O	**g′**	Me	3,4-HOC_6H_3	S
h	Me	CO_2H	O				
i	Me	2-$HO_2CC_6H_4$	O				
j	Me	4-$HO_2CC_6H_4$	O				
k	Me	2-HO-5-$HO_2CC_6H_3$	O				
l	Me	2-$NaO_2CC_6H_4$	O				
m	Me	2-$NaO_3SC_4H_2O$	O				
n	H	2-$HO_2CC_6H_4$	O				
o	H	4-$HO_2CC_6H_4$	O				
p	H	2-$NaO_3SC_4H_2O$	O				

Phosphotrihydrazones (n = 3)

4	R^1	R^2	X	4	R^1	R^2	X
a	Me	2-HOC_6H_4	O	**a′**	Me	2-HOC_6H_4	S
b	Me	3-HOC_6H_4	O	**b′**	Me	3-HOC_6H_4	S
c	Me	4-HOC_6H_4	O	**c′**	Me	4-HOC_6H_4	S
d	Me	2,3-HOC_6H_3	O	**d′**	Me	2,3-HOC_6H_3	S
e	Me	2,4-HOC_6H_3	O	**e′**	Me	2,4-HOC_6H_3	S
				f′	Me	3,4-HOC_6H_3	S
				g′	Me	2,5-HOC_6H_3	S
				h′	Me	3,5-MeO,4-HOC_6H_2	S
i	Me	CO_2H	O				
j	Me	2-$HO_2CC_6H_4$	O				
k	Me	4-$HO_2CC_6H_4$	O				
l	Me	2-$NaO_3SC_4H_2O$	O				

Scheme

Suitable crystals for X-ray analysis were obtained for **4a′**. Classical bond lengths were observed for the imine functions (Table 2). N(1)PN(3), N(1)PN(5) and N(3)PN(4) angles are very close [from 104.7 (1) to 106.4 (1)°] as well as SPN(1), SPN(3) and SPN(5) angles [from 111.29 (7) to 116.00(9)°]. The main feature of the structure is the existence of hydrogen bonds between the OH groups and the N(2), N(4) and N(6) nitrogen atoms of the imine functions with the formation of three six-membered rings (Figure).

Table 1. Compounds **3** and **4** Prepared

Product[a]	Yield (%)	mp (°C)	IR (KBr) (cm^{-1}) $\nu_{C=N}$	$\nu_{P=O}$	$\nu_{P=S}$	$\nu_{C=O}$	^1H NMR (solvent/TMS)[b] δ, J (Hz)	^{13}C NMR (solvent/TMS)[b] δ, J (Hz)	^{31}P NMR (solvent)[b], δ
3a	44	173–174	1645 (w)	1260 (s)			3.31 (d, $^3J_{HP}$ = 7.2, 6H, CH_3), 6.83–8.13 (m, 13H, C_6H_5, C_6H_4), 8.13 (br s, 2H, HC=N), 10.25 (br s, 2H, OH)	31.5 (d, $^2J_{CP}$ = 7.6, CH_3), 102.8–133.0 (m, C_6H_5, C_6H_4), 137.9 (d, $^3J_{CP}$ = 13.1, HC=N), 156.9 (s, COH)	22.5 (s)
3b	80	194–195	1645 (w)	1260 (s)			3.22 (d, $^3J_{HP}$ = 6.5, 6H, CH_3), 6.82–8.12 (m, 17H, C_6H_5, C_6H_4, HC=N, OH)	30.8 (d, $^2J_{CP}$ = 7.2, CH_3), 112.6–132.8 (m, C_6H_5, C_6H_4), 137.2 (d, $^3J_{CP}$ = 12.9, HC=N), 156.1 (s, COH)	22.4 (s)
3c	94	176–177	1640 (w)	1274 (s)			3.21 (d, $^3J_{HP}$ = 7.5, 6H, CH_3), 6.71–8.01 (m, 15H, C_6H_5, C_6H_4, HC=N), 9.72 (br s, 2H, OH)	30.7 (d, $^2J_{CP}$ = 8.0, CH_3), 116.1–133.6 (m, C_6H_5, C_6H_4), 137.5 (d, $^3J_{CP}$ = 11.5, HC=N), 157.3 (s, COH)	22.7 (s)
3d	62		1642 (w)	1282 (s)			1.34 (s, 36H, CH_3C), 3.18 (d, $^3J_{HP}$ = 9.7, 6H, CH_3N), 7.27–8.10 (m, 13H, C_6H_5, C_6H_2, HC=N, OH)	29.7 (br s, $\underline{C}H_3C$), 30.7 (d, $^2J_{CP}$ = 8.8, CH_3N), 34.0 (s, CH_3C), 122.5–135.3 (m, C_6H_5, C_6H_2), 137.4 (d, $^3J_{CP}$ = 13.1, HC=N), 154.7 (s, COH)	25.7 (s)
3e	77	151–152	1642 (w)	1265 (s)			3.35 (d, $^3J_{HP}$ = 7.2, 6H, CH_3), 6.61–8.14 (m, 11H, C_6H_5, C_6H_3), 8.14 (s, 2H, HC=N), 8.9–9.8 (m, 4H, OH)	30.6 (d, $^2J_{CP}$ = 7.6, CH_3), 117.3–131.9 (m, C_6H_5, C_6H_3), 139.2 (d, $^3J_{CP}$ = 11.5, HC=N), 145.5 (s, COH), 144.6 (s, COH)	23.1 (s)
3f	89		1655 (w)	1270 (s)			3.25 (d, $^3J_{HP}$ = 7.3, 6H, CH_3), 6.30–8.04 (m, 13H, C_6H_5, C_6H_3, HC=N), 10.10 (br s, 4H, OH)	–	22.4 (s)
3g	43		1638 (w)	1270 (s)			3.20 (d, $^3J_{HP}$ = 7.1, 6H, CH_3), 6.72–8.12 (m, 13H, C_6H_5, C_6H_3, HC=N), 9.11 (br s, 4H, OH)	–	21.7 (s)
3h	93	187–188	–				3.15 (d, $^3J_{HP}$ = 7.0, 6H, CH_3), 7.13 (s, 2H, HC=N), 7.68–8.09 (m, 5H, C_6H_5), 12.5 (br s, 2H, CO_2H)	–	21.9 (s)
3i	95	169–170		1245 (s)		1710 (s)	3.30 (d, $^3J_{HP}$ = 7.0, 6H, CH_3), 7.49–9.36 (m, 15H, C_6H_5, C_6H_4, HC=N), 13.1 (br s, 2H, CO_2H)	–	23.7 (s)
3j	98	206–207		1250 (s)		1685 (s)	3.31 (d, $^3J_{HP}$ = 7.0, 6H, CH_3), 7.64–8.17 (m, 15H, C_6H_5, C_6H_4, HC=N), 12.8 (br s, 2H, CO_2H)	31.0 (d, $^2J_{CP}$ = 7.6, CH_3), 125.1–133.4 (m, C_6H_5, C_6H_4), 136.7 (d, $^3J_{CP}$ = 14.1, HC=N), 139.6 (s, CCO_2H), 166.9 (s, CO_2H)	23.7 (s)
3k	94		–				3.24 (d, $^3J_{HP}$ = 7.0, 6H, CH_3), 9.90–8.08 (m, 13H, C_6H_5, C_6H_3, HC=N), 12.4 (br s, 4H, CO_2H, COH)	–	23.9 (s)
3l	85	155–156	–				3.23 (d, $^3J_{HP}$ = 7.0, 6H, CH_3), 7.23–9.03 (m, 15H, C_6H_5, C_6H_4, HC=N)	–	22.4 (s)
3m	90	118–119	–				3.01 (d, $^3J_{HP}$ = 7.0, 6H, CH_3), 6.43 (d, $^3J_{HH}$ = 4.0, 2H, CHCH), 6.61 (d, $^3J_{HH}$ = 4.0, 2H, CHCH), 7.43–7.78 (m, 7H, C_6H_5, HC=N)	–	25.0 (s)
3n	95	115–116	–				7.65–8.92 (m, 15H, C_6H_5, C_6H_4, HC=N), 9.99 (d, $^2J_{HP}$ = 25, 2H, NH), 12.8 (br s, 2H, CO_2H)	–	16.6 (s)
3o	97			1285 (s)		1687 (s)	7.69–8.21 (m, 15H, C_6H_5, C_6H_4, HC=N), 10.00 (d, $^2J_{HP}$ = 25, 2H, NH), 12.8 (br s, 2H, CO_2H)	126.1–137.5 (m, C_6H_5, C_6H_4), 139.0 (s, $\underline{C}CO_2H$), 142.8 (d, $^3J_{CP}$ = 17.7, HC=N), 166.9 (s, CO_2H)	11.2 (s)

Table 1. (continued)

Product[a]	Yield (%)	mp (°C)	IR (KBr) (cm^{-1}) $\nu_{C=N}$	$\nu_{P=O}$	$\nu_{P=S}$	$\nu_{C=O}$	^1H NMR (solvent/TMS)[b] δ, J (Hz)	^{13}C NMR (solvent/TMS)[b] δ, J (Hz)	^{31}P NMR (solvent)[b], δ
3p	89	112–113	–				6.46 (d, $^3J_{HH}$ = 4.0, 2H, CHCH), 6.61 (d, $^3J_{HH}$ = 4.0, 2H, CHCH), 7.40–8.31 (m, 7H, C_6H_5, HC=N)		15.3 (s)
3a′	82	130–131	1645 (w)		730 (s)		3.36 (d, $^3J_{HP}$ = 9.4, 6H, CH_3), 6.75–8.15 (m, 13H, C_6H_5, C_6H_4), 8.16 (br s, 2H, HC=N), 10.21 (br s, 2H, OH)	30.5 (d, $^2J_{CP}$ = 7.8, CH_3), 102.4–133.1 (m, C_6H_5, C_6H_4), 140.8 (d, $^3J_{CP}$ = 12.7, HC=N), 157.1 (s, COH)	78.8 (s)
3b′	88	89–90	1645 (w)		730 (s)		3.36 (d, $^3J_{HP}$ = 9.7, 6H, CH_3), 6.77–8.23 (m, 15H, C_6H_5, C_6H_4, HC=N), 9.60 (br s, 2H, OH)	30.4 (d, $^2J_{CP}$ = 9.6, CH_3), 111.6–133.2 (m, C_6H_5, C_6H_4), 136.0 (d, $^3J_{CP}$ = 12.7, HC=N), 155.5 (s, COH)	77.2 (s)
3c′	76	96–97	1642 (w)		725 (s)		3.27 (d, $^3J_{HP}$ = 10.1, 6H, CH_3), 6.74–8.01 (m, 15H, C_6H_5, C_6H_4, HC=N), 9.72 (br s, 2H, OH)	30.9 (d, $^2J_{CP}$ = 8.7, CH_3), 115.4–133.2 (m, C_6H_5, C_6H_4), 138.3 (d, $^3J_{CP}$ = 11.3, HC=N), 158.1 (s, COH)	76.9 (s)
3d′	68		1645 (w)		720 (s)		1.37 (s, 36H, CH_3C), 3.23 (d, $^3J_{HP}$ = 9.7, 6H, CH_3N), 7.12–8.30 (m, 13H, C_6H_5, C_6H_2, HC=N, OH)	29.8 (br s, $\underline{C}H_3C$), 30.6 (d, $^2J_{CP}$ = 9.6, CH_3N), 33.8 (s, $\underline{C}CH_3$), 123.1–135.6 (m, C_6H_5, C_6H_2), 137.6 (d, $^3J_{CP}$ = 13.3, HC=N), 154.0 (s, COH)	79.4 (s)
3e′	72	176–177	1645 (w)		730 (s)		3.34 (d, $^3J_{HP}$ = 9.6, 6H, CH_3), 6.70–8.14 (m, 15H, C_6H_5, C_6H_3, OH), 8.14 (s, 2H, HC=N)	31.1 (d, $^2J_{CP}$ = 8.8, CH_3), 116.5–132.5 (m, C_6H_5, C_6H_3), 141.3 (d, $^3J_{CP}$ = 12.1, HC=N), 144.8 (s, COH), 145.4 (s, COH)	76.9 (s)
3f′	84		1645 (w)		740 (s)		3.29 (d, $^3J_{HP}$ = 9.7, 6H, CH_3), 6.29–7.99 (m, 11H, C_6H_5, C_6H_3), 8.05 (br s, 2H, HC=N), 9.85 (s, 2H, OH), 10.38 (s, 2H, OH)	30.7 (d, $^2J_{CP}$ = 7.8, CH_3), 102.4–132.2 (m, C_6H_5, C_6H_3), 141.3 (d, $^3J_{CP}$ = 12.9, HC=N), 157.9 (s, COH), 159.6 (s, COH)	76.5 (s)
3g′	92	127–128	1645 (w)		725 (s)		3.29 (d, $^3J_{HP}$ = 9.9, 6H, CH_3), 6.91–8.46 (m, 13H, C_6H_5, C_6H_3, HC=N), 9.19 (s, 2H, OH), 9.30 (s, 2H, OH)	–	76.8 (s)
4a	79	205–206	1645 (w)	1278 (s)			3.30 (d, $^3J_{HP}$ = 7.3, 9H, CH_3), 6.85–7.62 (m, 12H, C_6H_4), 8.16 (s, 3H, HC=N), 10.70 (br s, 3H, OH)	30.6 (d, $^2J_{CP}$ = 9.1, CH_3), 112.1–133.4 (m, C_6H_4), 138.4 (d, $^3J_{CP}$ = 12.8, HC=N), 156.1 (s, COH)	10.7 (s)
4b	66	245–246	1645 (w)	1260 (s)			3.20 (d, $^3J_{HP}$ = 7.4, 9H, CH_3), 6.83–7.88 (m, 12H, C_6H_4), 7.82 (s, 3H, HC=N), 9.48 (br s, 3H, OH)	31.5 (d, $^2J_{CP}$ = 8.5, CH_3), 116.4–137.1 (m, C_6H_4), 140.1 (d, $^3J_{CP}$ = 12.3, HC=N), 158.1 (s, COH)	12.8 (s)
4c	70	216–217	1645 (w)	1265 (s)			3.21 (d, $^3J_{HP}$ = 7.4, 9H, CH_3), 6.76 (d, $^3J_{HH}$ = 8.3, 6H, C_6H_4), 7.52 (d, $^3J_{HH}$ = 8.3, 6H, C_6H_4), 7.77 (s, 3H, HC=N), 9.60 (br s, 3H, OH)	32.3 (d, $^2J_{CP}$ = 7.8, CH_3), 116.8–127.8 (m, C_6H_4), 136.4 (d, $^3J_{CP}$ = 11.6, HC=N), 157.5 (s, COH)	12.8 (s)
4d	77	218–219	1645 (w)	1260 (s)			3.31 (d, $^3J_{HP}$ = 7.4, 9H, CH_3), 6.68–7.00 (m, 9H, C_6H_3), 8.14 (s, 3H, HC=N), 10.24 (br s, 6H, OH)	31.1 (d, $^2J_{CP}$ = 8.8, CH_3), 115.8–133.0 (m, C_6H_3), 140.8 (d, $^3J_{CP}$ = 11.9, HC=N), 144.7 (s, COH), 145.5 (s, COH)	10.1 (s)
4e	78		1645 (w)	1265 (s)			3.29 (d, $^3J_{HP}$ = 7.3, 9H, CH_3), 6.29–7.19 (m, 9H, C_6H_3), 7.90 (s, 3H, HC=N), 9.39 (s, 3H, OH), 10.60 (s, 3H, OH)	–	10.6 (s)
4i	93	155–156	–				3.18 (d, $^3J_{HP}$ = 7.0, 9H, CH_3), 7.15 (s, 3H, HC=N), 12.5 (br s, 3H, CO_2H)	–	9.1 (s)

Table 1. (continued)

Product[a]	Yield (%)	mp (°C)	IR (KBr) (cm^{-1}) $\nu_{C=N}$	$\nu_{P=O}$	$\nu_{P=S}$	$\nu_{C=O}$	^1H NMR (solvent/TMS)[b] δ, J (Hz)	^{13}C NMR (solvent/TMS)[b] δ, J (Hz)	^{31}P NMR (solvent)[b], δ
4j	88	127–128		1250 (s)		1705 (s)	3.31 (d, $^3J_{HP}$ = 7.0, 9H, CH_3), 7.37–8.68 (m, 15H, C_6H_4, HC=N), 12.9 (s, 3H, CO_2H)	32.9 (d, $^2J_{CP}$ = 7.5, CH_3), 128.2–133.2 (m, C_6H_4), 137.8 (s, $\underline{C}CO_2H$), 139.4 (d, $^3J_{CP}$ = 15.4, HC=N), 170.5 (s, CO_2H)	12.7 (s)
4k	93	250 <	–				3.33 (d, $^3J_{HP}$ = 7.0, 9H, CH_3), 7.70–8.01 (m, 15H, C_6H_4, HC=N), 12.7 (s, 3H, CO_2H)	32.3 (d, $^2J_{CP}$ = 7.6, CH_3), 126.2–130.4 (m, C_6H_4), 137.0 (d, $^3J_{CP}$ = 14.2, HC=N), 139.6 (s, $\underline{C}CO_2H$), 170.5 (s, CO_2H)	12.5 (s)
4l	87		–				3.19 (d, $^3J_{HP}$ = 6.8, 9H, CH_3), 6.65 (m, 6H, CHCH), 7.80 (s, 3H, HC=N)	32.8 (d, $^2J_{CP}$ = 7.3, CH_3), 110.1 (br s, CHCH), 129.8 (d, $^3J_{CP}$ = 14.7, HC=N), 149.9, 156.9 (s, CSO_3 and $\underline{C}CH$)	10.0 (s)
4a′	86	196–197	1640 (w)		738 (s)		3.37 (d, $^3J_{HP}$ = 8.8, 9H, CH_3), 6.87–7.62 (m, 12H, C_6H_4), 8.18 (s, 3H, HC=N), 10.64 (br s, 3H, OH)	30.3 (d, $^2J_{CP}$ = 8.1, CH_3), 102.1–130.2 (m, C_6H_4), 138.5 (d, $^3J_{CP}$ = 12.1, HC=N), 155.3 (s, COH)	71.2 (s)
4b′	86	132–133	1640 (w)		730 (s)		3.35 (d, $^3J_{HP}$ = 8.6, 9H, CH_3), 6.83–7.15 (m, 12H, C_6H_4), 7.84 (s, 3H, HC=N), 9.32 (br s, 3H, OH)	30.6 (d, $^2J_{CP}$ = 9.1, CH_3), 112.1–133.4 (m, C_6H_4), 138.4 (d, $^3J_{CP}$ = 12.8, HC=N), 156.1 (s, COH)	72.5 (s)
4c′	78	170–171	1648 (w)		735 (s)		3.32 (d, $^3J_{HP}$ = 9.0, 9H, CH_3), 6.76 (d, $^3J_{HH}$ = 8.3, 6H, C_6H_4), 7.53 (d, $^3J_{HH}$ = 8.3, 6H, C_6H_4), 7.81 (s, 3H, HC=N), 9.69 (br s, 3H, OH)	31.1 (d, $^2J_{CP}$ = 8.5, CH_3), 115.8–132.9 (m, C_6H_4), 139.1 (d, $^3J_{CP}$ = 12.0, HC=N), 158.1 (s, COH)	72.1 (s)
4d′	73	182–183	1635 (w)		720 (s)		3.38 (d, $^3J_{HP}$ = 9.2, 9H, CH_3), 6.78–7.11 (m, 9H, C_6H_3), 8.18 (s, 3H, HC=N), 9.17 (s, 3H, OH), 10.37 (s, 3H, OH)	31.1 (d, $^2J_{CP}$ = 8.8, CH_3), 115.8–133.0 (m, C_6H_3), 140.8 (d, $^3J_{CP}$ = 11.9 Hz, HC=N), 144.7 (s, COH), 145.5 (s, COH)	71.5 (s)
4e′	81		1648 (w)		728 (s)		3.21 (d, $^3J_{HP}$ = 8.7, 9H, CH_3), 6.73–7.92 (m, 9H, C_6H_3), 8.09 (s, 3H, HC=N), 9.6 (br s, 3H, OH), 10.6 (br s, 3H, OH)		71.4 (s)
4f′	83	141–142	1645 (w)		730 (s)		3.31 (d, $^3J_{HP}$ = 9.0, 9H, CH_3), 6.70–7.19 (m, 9H, C_6H_3), 7.74 (s, 3H, HC=N), 9.13 (br s, 6H, OH)		72.7 (s)
4g′	45	110–111	1635 (w)		735 (s)		3.36 (d, $^3J_{HP}$ = 9.2, 9H, CH_3), 6.76–7.02 (m, 9H, C_6H_3), 8.09 (s, 3H, HC=N), 8.93 (s, 3H, OH), 9.97 (s, 3H, OH)	–	71.4 (s)
4h′	91	176–177	1640 (w)		730 (s)		3.35 (d, $^3J_{HP}$ = 8.8, 9H, CH_3), 3.64 (s, 18H, CH_3O), 6.94 (s, 6H, C_6H_2), 7.83 (s, 3H, HC=N), 8.55 (br s, 3H, OH)	–	73.4 (s)

[a] Satisfactory microanalysis obtained: C ± 0.30, H ± 0.23, N ± 0.28.

[b] The following solvents were used for NMR spectroscopic measurements. ^1H NMR: DMSO-d_6 for **3a, b, c, e–l, n, o, 3a′–c′, e′–g′, 4a′–h′**; $CDCl_3$ for **3d, d′**; CD_3OD for **3m, p**. ^{13}C NMR: DMSO-d_6 for **3a–c, e, j, o; 3a′–c′, e′, f′, 4a–d, 4k–l, 4a′–d′**; $CDCl_3$ for **3d, d′**; CD_3OD for **4j**; CH_2Cl_2 for **3b**, CD_3OD for **3m, p**. ^{31}P NMR: DMSO-d_6 for **3e, f, g–i, l, o, 3b′, c′, e′, f′, 4a–c, 4e–l, 4a′–d′**, $CDCl_3$ for **3d, 3a′, d′**; THF for **3a–c, j, k, n, 3g′, 4d, 4e′–g′**.

Phosphodihydrazones 3a–c, e–h, k, n, o, 3a′–c′, e′–g′; Typical Procedure:

To a solution of aldehyde (20 mmol) in CH_2Cl_2 (100 mL) at r.t. was added phosphodihydrazide **1a, a′** or **1b** (10 mmol) as a powder. The resulting mixture was stirred for 3 h. The solvent was evaporated and the crude product was washed with petroleum ether (bp 40—70 °C) to give either pale yellow or white powders.

Table 2. Selected Bond Distances and Angles for Compound **4a'**

Bond Distances (Å)		Bond Angles (°)	
P-N(1)	1.670(2)	SPN(1)	116.00(9)
P-N(3)	1.671(2)	SPN(3)	111.29(7)
P-N(5)	1.669(2)	SPN(5)	112.61(8)
N(2) C(2)	1.282(3)	N(1) PN(3)	104.7(1)
N(4) C(4)	1.285(4)	N(1) PN(5)	105.08(9)
N(6) C(6)	1.285(3)	N(3) PN(5)	106.4(9)
O(1) ... N(2)	2.611(3)		
H(O1) ... N(2)	1.79(2)		
O(2) ... N(4)	2.645(2)		
H(O2) ... N(4)	1.80(2)		
O(3) ... N(6)	2.661(4)		
H(O3) ... N(6)	1.82(4)		

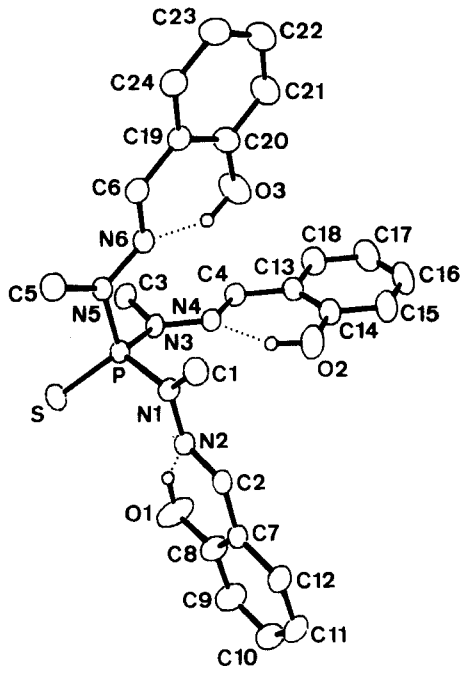


Figure Ortep Diagram of **4a'**

Phosphodihydrazones 3d, 3d':
To a solution of phosphodihydrazide **1a** (2.782 g, 13 mmol) or **1a'** (2.990 g, 13 mmol) in THF (20 mL) was added a solution of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (6.09 g, 2.6 mmol) in CH_2Cl_2 (20 mL) at r.t. After stirring for 7d, the solvent was evaporated. The residue was washed with MeCN (20 mL) and dried in vacuum to give a white powder.

Phosphodihydrazones 3i, 3j:
To a solution of *ortho*- or *para*-carboxybenzaldehyde (0.660 g, 4.4 mmol) in EtOH (10 mL) was added a solution of phosphodihydrazide $PhP(O)(NMeNH_2)_2$ (0.460 g, 2.15 mmol) in EtOH (10 mL). The solution became quickly yellow and a precipitate was formed. The resulting mixture was stirred at r.t. for 2 h and filtered. The precipitate was washed with EtOH (2 × 10 mL) to give a white powder.

Phosphodihydrazone 3l:
To a solution of phosphodihydrazone **3i** (0.478 g, 1 mmol) in water (20 mL) was added NaOH (0.080 g, 2 mmol). Evaporation of water afforded **3l** as a white powder.

Phosphodihydrazones 3m, 3p:
To a solution of 5-formyl-2-furansulfonic acid sodium salt (0.450 g, 2.27 mmol) in MeOH (10 mL) was added a solution of phosphodihydrazide $PhP(O)(NHNH_2)_2$ (**1a**; 0.230 g, 1.07 mmol or **1b**; 0.200 g, 1.07 mmol) in MeOH (5 mL). The heterogenous solution was stirred for 2 h till the solution became homogeneous. Evaporation of the solvent followed by washing of the precipitate with MeOH (10 mL) and THF (10 mL) gave **3m** or **3p** as a white powder.

Phosphotrihydrazones 4; Typical Procedure:
To a solution of aldehyde (30 mmol) in THF (50 mL) was added the phosphotrihydrazide **2a** or **2a'** (10 mmol) as a powder at r.t. The resulting mixture was stirred overnight. Evaporation of the solvent followed by washing of the residue with petroleum ether (bp 40–70 °C) gave pale yellow or white powders.

X-ray Structural Analysis of Compound 4a':
A single crystal of $C_{24}H_{27}N_6O_3PS \cdot 0.5C_6H_{12}$ of 0.45 × 0.15 mm dimensions was mounted on an Enraf-Nonius CAD4 diffractometer. Cell constants were obtained from a least-squares fit of the setting angles of 25 reflections in the range $11.5° < \theta < 13.4°$. The compound crystallizes in the tricyclic system, space group $P\bar{1}$ (N°2) with a = 11.238 (1), b = 13.348 (2), c = 10.275 (1) Å; α = 109.76 (2), β = 104.95 (2), γ = 76.36 (2)°, V = 1393.4 (7) Å^3, Z = 2; F(000) = 584, d calcd. = 1.317 g. cm^{-3}. 4905 reflections were recorded (2 θ max = 50°), using MoKα radiation (λ = 0.71073 Å), θ–2θ scan mode. The structure was solved by direct methods using SHELXS-86 program. Successive Fourier maps and least-squares refinement cycles with SHELX-76 program, using 3713 reflections having $Fo^2 \geq 3\sigma(Fo^2)$, revealed the positions of all missing non-hydrogen atoms and the presence of crystallization solvent, i.e. cyclohexane. The final full-matrix least-squares refinement converged to R = 0.036 and Rw = 0.035 ($w = 1/\sigma^2$ (Fo)). All non-hydrogen atoms were refined anisotropically.[4]

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(4) Crystallographic data were deposited at Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW England and are available from there. Table of atomic parameters, bond geometry and structure factors are available on request from the authors.