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Synthesis of tetraphenylphosphonium (thio)phosphorylthiobenzamides and hydrolytic degradation to $Ph_3P{=}O$, H_2S and phosphoryl(thio)benzamides: A route for crystal design of $PhC(X)NHP(O)(OiPr)_2$ (X=S, O)

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ABSTRACT

Reactions of the sodium salts of $PhC(S)NHP(Y)(OiPr)_2$ (Y=S, **HL^I**; O, **HL^II**) with PPh_4Br in 96% aqueous EtOH leads to the corresponding compounds **$PPh_4L^{I,II}$**. The structures of these compounds were investigated by IR, ^1H, $^{31}P\{^1H\}$ NMR spectroscopies; their compositions were examined by microanalysis. Recrystallization of **$PPh_4L^{I,II}$** from $EtOH/H_2O$ solution (1:1, v/v) leads to the formation of **HL^{II}** and $PhC(O)NHP(O)(OiPr)_2$ (**HL^{III}**), respectively. The crystal structures of **$HL^{II,III}$** are reported and compared with the previously reported polymorphs.

N-(Thio)phosphorylated (thio)ureas and (thio)amides $RC(X)NHP(Y)(OR')_2$ (X, Y=O, S) are easily deprotonated under the influence of bases in aqueous alcohol medium [1–3]. Accordingly salts with alkaline metal cations are easily formed. In the literature there is so far only one crystal structure of a salt of *N*-(thio)phosphorylthioureas ($[K(Me_2CO)](PhNHC(S)NP(S)(OiPr)_2)$) [4]. The structures of similar compounds, salts of *N*-(thio)phosphorylamides and thioamides $[M(CCl_3C(O)NP(O)(OMe)_2)]$, $M = Na^+$ or Rb^+ [5]; $[K(Me_2CO)](PhC(S)NP(S)(OiPr)_2)$ [6], $[K(MeOH)](PhC(O)NP(S)Ph_2)$ [7,8] have also been investigated. Salts of *N*-phosphorylamides and thioamides with the alkaline metal cation being complexed by crown ether molecules $[M(crown)](PhC(Y)NP(X)(OiPr)_2)$ (X, Y=O, S; $M=Na^+$, K^+; crown = 18-crown-6, dibenzo-18-crown-6, 1,10-diaza-18-crown-6) are also described [1]. Furthermore, a number of salts of imidodiphosphinate ligands $R_2P(X)NHP(Y)R'_2$ were isolated and structurally characterized [9–11]. Phosphonium salts of $RC(O)NHP(O)(OR')_2$ are also of interest, since they might exhibit a variety of structures [1,5].

The X-ray diffraction data for crystal modifications of each *N*-(diisopropoxyphosphoryl)(thio)benzamides $PhC(S)NHP(O)(OiPr)_2$ [12,13] and $PhC(O)NHP(O)(OiPr)_2$ were reported earlier [14,15].

Herein we present data about the tetraphenylphosphonium salts of $PhC(S)NHP(Y)(OiPr)_2$ (Y=S, **HL^I**; O, **HL^{II}**) (Scheme 1). Recrystallization of **$PPh_4L^{I,II}$** from $EtOH/H_2O$ solution (1:1, v/v) leads to the formation of **HL^{II}** and $PhC(O)NHP(O)(OiPr)_2$ (**HL^{III}**), respectively. The crystal structures of **$HL^{II,III}$** are reported and compared with the previously reported polymorphs.

The tetraphenylphosphonium salts **$PPh_4L^{I,II}$** were prepared by the following procedure: the ligand was *in situ* converted to the sodium salt, followed by interaction with PPh_4Br (Scheme 1) [16]. The obtained compounds are solids, which are soluble in H_2O and slightly soluble in EtOH and most polar solvents.

The IR spectra of **$PPh_4L^{I,II}$** contain an intense absorption band for the conjugated S⋯C⋯N group at about 1560 cm^{-1}. There is a weak absorption band of the P=S group at 608 cm^{-1} in the spectrum of **PPh_4L^I**, while a band for the P=O group in the spectrum of **PPh_4L^{II}** was observed at 1192 cm^{-1}. The strong band at 996–1008 cm^{-1} corresponds to the POC group. No NH group bands were found in the IR spectra of **$PPh_4L^{I,II}$**.

In the $^{31}P\{^1H\}$ NMR spectrum of **PPh_4L^I** the resonance at 61.8 ppm corresponds to the phosphorus atom of the thiophosphoryl group [1], while the singlet signal of the phosphoryl group in the spectrum of **PPh_4L^{II}** was found at 11.4 ppm [1]. These signals are low-field shifted relative to those in the spectra of **$HL^{I,II}$**, respectively [1]. The signal of the phosphorus atom of PPh_4^+ was found at 22.3–23.9 ppm. The ^1H NMR spectra of **$PPh_4L^{I,II}$** contain only signals, which correspond to the proposed structures. The spectra contain a set of signals for the *i*Pr protons: signals for the CH_3 protons at 1.08–1.18 ppm and a signal for the CH protons at 4.57–4.74 ppm. The signals for the phenyl protons in the spectra were observed at 6.21–7.82 ppm.

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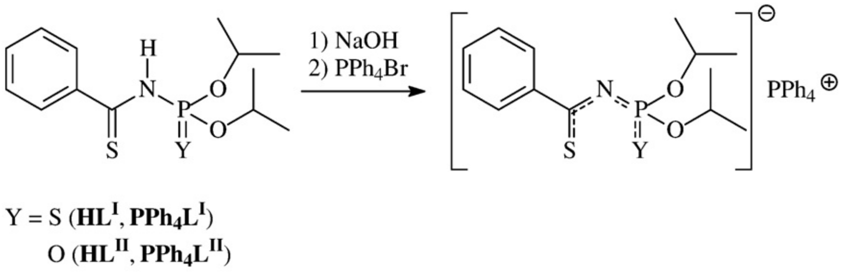

Scheme 1.

The ES (electrospray method) mass spectra were measured in the positive and negative ion regime. In the mass spectra of **$PPh_4L^{I,II}$** besides the $[PPh_4]^+$ peak there are characteristic peaks for the molecular ions $[PPh_4Lig + H]^+$ and, in addition, peaks for the $[PPh_4Lig + PPh_4]^+$ and $[(PPh_4)_2Lig_2 + H]^+$ cations; some of them containing additional solvent molecules (alcohol and/or water). Negative ES mass spectra of **$PPh_4L^{I,II}$** revealed peaks of $[Lig]^-$ but again also the peaks of the composition as $[PPh_4Lig + solv + Lig]^-$ and $[(PPh_4)_2Lig_2 + solv + Lig]^-$ (solv = H_2O or CH_3OH).

Unfortunately, we were not successful to obtain X-ray-suitable crystals of **$PPh_4L^{I,II}$** even though attempting a number of different solvents for crystallization. However, recrystallization of **$PPh_4L^{I,II}$** from an aqueous EtOH solution (1:1, v/v) leads to the formation of **HL^{II}** and **HL^{III}**, respectively. After several days, yellow needles of **HL^{II}** or colorless plates of **HL^{III}** were deposited and then isolated by decantation. The structures of **$HL^{II,III}$** were proven by means of ^1H, $^{31}P\{^1H\}$ NMR spectroscopy and microanalysis. The mother liquor was left for one day and afterwards the fine-crystalline solid of $Ph_3P{=}O$ ($\delta_P = 29.9$ ppm [17]) was formed. The hydrolysis of the thiophosphoryl and thiocarbonyl groups was most likely caused by the presence of H_2O as well as the presence of the PPh_4^+ ion. We assume, that binding of PPh_4^+ to L^{I-} or L^{II-} through the sulfur atom of the thiopho-

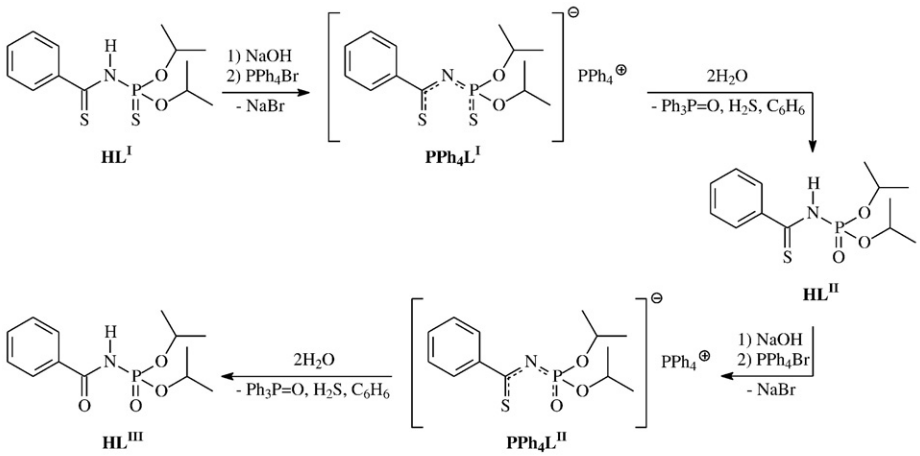

Chart 1.

Table 1
Crystal data and data collection details for **HL^{II}** and **HL^{III}**.

	HL^{II}		**HL^{III}**	
	Polymorph **HL^{II}**{**1**}	Polymorph **HL^{II}**{**2**} [13]	Polymorph **HL^{III}**{**1**}	Polymorph **HL^{III}**{**2**} [14]
Empirical formula	$C_{13}H_{20}NO_3PS$	$C_{13}H_{20}NO_3PS$	$C_{13}H_{20}NO_4P$	$C_{13}H_{20}NO_4P$
Formula weight	301.33	301.33	285.27	285.28
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$	$C2/c$	$P2_1/c$
a/Å	23.694 (2)	9.497 (1)	22.831 (2)	15.573(4)
b/Å	9.0823 (8)	18.972 (2)	8.8312(9)	9.546 (2)
c/Å	14.8961 (15)	8.937 (1)	14.9842 (15)	21.897 (3)
β/°	91.696 (8)	95.30 (1)	91.025 (2)	100.94 (2)
V/Å^3	3204.2 (5)	1603.4 (3)	3020.7 (5)	3196 (6)
Z	8	4	8	8
D_{calc}/g cm^{-3}	1.25	1.25	1.26	1.19
T/K	173 (2)	293 (2)	100 (2)	293 (2)
μ/mm^{-1}	0.3 (Mo $K\alpha$)	2.8 (Cu $K\alpha$)	0.2 (Mo $K\alpha$)	1.7 (Mo $K\alpha$)
Reflections collected	10,491	3492	8551	7528
Unique reflections	2988	3295	3068	2290
Observed reflections	2270 ($R_{int} = 0.0511$)	3030 ($R_{int} = 0.012$)	2646 ($R_{int} = 0.024$)	1506 (R_{int} = not given)
Final R indices [I > 2sigma(I)]	$R_1 = 0.0594$, $wR_2 = 0.1730$	$R_1 = 0.041$, $wR_2 = 0.112$	$R_1 = 0.0487$, $wR_2 = 0.1217$	$R_1 = 0.044$, $wR_2 = 0.053$

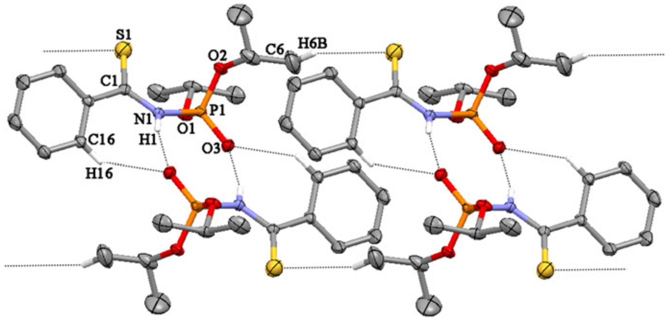

Fig. 1. Displacement ellipsoid representation of **HL**$^{\mathrm{II}}$. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms not involved in H-bonding are omitted for clarity.

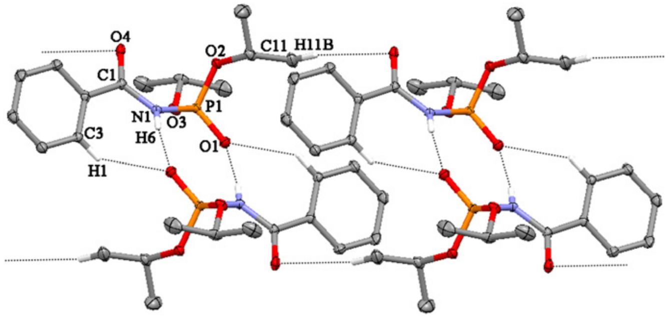

Fig. 2. Displacement ellipsoid representation of **HL**$^{\mathrm{III}}$. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms not involved in H-bonding are omitted for clarity.

sphoryl or the thiocarbonyl group, respectively, might provoke the hydrolysis of the P=S group in **PPh$_4$L$^{\mathrm{I}}$** and the C=S group in **PPh$_4$L$^{\mathrm{II}}$** (Chart 1). It should be noted, that recrystallization of **HL**$^{\mathrm{I,II}}$ or their sodium salts from an EtOH/H$_2$O solution (1:1, v/v) does not lead to the hydrolysis products.

The crystal structures of **HL**$^{\mathrm{II,III}}$ were elucidated by single-crystal X-ray diffraction [18] and are compared with the previously reported structures [12–15]. It is noteworthy that the X-ray suitable crystals of the recently published structures of **HL**$^{\mathrm{II,III}}$ were obtained from the slow evaporation of their solutions in the chloroform–ethanol (1:1, v/v) and benzene–diethyl ether (1:2, v/v) mixtures, respectively [12–15]. Results of the structure solutions and refinements are collected in Table 1. The representative structures are shown in Figs. 1 and 2, bonding parameters are collected in Table 2.

The crystal structures of **HL**$^{\mathrm{II,III}}$ reveal to be polymorphs of the previously reported structures [13,14]. In view of the fact that the structures of these polymorphs (**HL**$^{\mathrm{II}}${**1**} and **HL**$^{\mathrm{III}}${**1**}) have been established we discuss in the following the structural parameters of these polymorphs in comparison with the recently established second polymorphs **HL**$^{\mathrm{II}}${**2**} and **HL**$^{\mathrm{III}}${**2**}.

The polymorphs **HL**$^{\mathrm{II}}${**1**} and **HL**$^{\mathrm{III}}${**1**} crystallize in the monoclinic space group $C2/c$ ($Z=8$), while the polymorphs **HL**$^{\mathrm{II}}${**2**} and **HL**$^{\mathrm{III}}${**2**} crystallize in the space groups $P2_1/n$ ($Z=4$) [13] and $P2_1/c$ ($Z=8$) [14], respectively (Table 1). The polymorph **HL**$^{\mathrm{III}}${**2**} contains two independent molecules in the crystal [14]. The parameters of the C=S, C–N, P–N and P=O distances observed in the molecular structures of the polymorphs **HL**$^{\mathrm{II,III}}${**1**} and **HL**$^{\mathrm{II,III}}${**2**} (Table 2) are in the typical range for *N*-phosphorylated (thio)amides [1]. The P–N–C=X moieties in **HL**$^{\mathrm{II,III}}${**1**} and **HL**$^{\mathrm{II,III}}${**2**} exhibit an *E*-conformation (Figs. 1 and 2) [13,14], and are significantly flattened (torsion angle is −9.4(4)° in **HL**$^{\mathrm{II}}${**1**}, 7.5(2)° in **HL**$^{\mathrm{II}}${**2**}, −12.1(3)° in **HL**$^{\mathrm{III}}${**1**}, and 4.8° and 11.8° in **HL**$^{\mathrm{III}}${**2**}, respectively) and rotated towards the phenyl group.

In the crystal modifications **HL**$^{\mathrm{II,III}}${**1**} and **HL**$^{\mathrm{II,III}}${**2**} the molecules are linked into identical centrosymmetric or pseudocentrosymmetric dimers by a pair of intermolecular hydrogen bonds N–H···O=P$^{\#1}$, formed between the hydrogen atom of the NH group and the oxygen atom of the P=O group of a neighboring molecule (Figs. 1 and 2, Table 3). Furthermore, in the polymorphs **HL**$^{\mathrm{II,III}}${**1**} a centrosymmetric dimer is additionally stabilized by two H-bonding contacts C–H(Ph)···O=P$^{\#1}$, formed between the hydrogen atom of the *ortho* CH unit of the phenyl group and the oxygen atom of the P=O group of a further molecule (Figs. 1 and 2, Table 3). These dimers in **HL**$^{\mathrm{II,III}}${**1**} are packed into stacks along the *b* axis by intermolecular C–H(*i*Pr)···S=C$^{\#2}$ or C–H(*i*Pr)···O=C$^{\#2}$ interactions, respectively, formed between the methyl hydrogen atoms of the *i*Pr groups and the sulfur (**HL**$^{\mathrm{II}}${**1**}) or oxygen (**HL**$^{\mathrm{III}}${**1**}) atoms of the C=S or C=O groups of further dimers (Figs. 1 and 2, Table 3). The crystal packing in the modification **HL**$^{\mathrm{II}}${**1**} is similar to that in **HL**$^{\mathrm{II}}${**2**} (Table 1), while the crystal packing in the polymorph **HL**$^{\mathrm{III}}${**1**} differs markedly compared with the crystallographic modification **HL**$^{\mathrm{III}}${**2**} (Table 1). This is also evident in the difference of density (0.07 g cm^{-3}) of the polymorphs.

It should be noted, that the differences in the polymorphs are not apparently due to the hydrogen bonding. Thus, compounds **HL**$^{\mathrm{II,III}}${**1**} and **HL**$^{\mathrm{II,III}}${**2**} can be considered as a good example to stress the importance of the entire crystal packing arrangement to the overall energy and stability of a certain crystal form [29,30].

Table 2
Selected bond lengths (Å) and bond angles (°) for **HL**$^{\mathrm{II}}$ and **HL**$^{\mathrm{III}}$.

	Polymorph **HL**$^{\mathrm{II}}${**1**}	Polymorph **HL**$^{\mathrm{II}}${**2**} [13]	Polymorph **HL**$^{\mathrm{III}}${**1**}	Polymorph **HL**$^{\mathrm{III}}${**2**} [14]
Bond lengths				
P–O	1.561 (2), 1.569 (2)	1.545 (1), 1.557 (1)	1.5553 (15), 1.5647 (14)	1.544 (4), 1.546 (4), 1.559 (5), 1.560 (5)
P=O	1.471 (2)	1.465 (1)	1.4654 (15)	1.440 (4), 1.463 (4)
P–N	1.677 (3)	1.675 (1)	1.6633 (17)	1.649 (6), 1.670 (5)
X=C	1.591 (3)	1.650 (2)	1.309 (2)	1.200 (7), 1.229 (7)
N–C	1.366 (4)	1.365 (2)	1.374 (2)	1.356 (8), 1.388 (8)
Bond angles				
O=P–O	115.22 (13), 115.30 (13)	114.73 (7), 114.96 (7)	114.60 (8), 115.90 (8)	116.1 (3), 116.3 (3), 116.4 (3)
O–P–O	103.81 (12)	104.94 (6)	103.54 (8)	98.1 (2), 101.9 (3)
O=P–N	107.52 (13)	107.05 (7)	108.48 (8)	107.8 (3), 110.4 (3)
O–P–N	105.08 (13), 109.37 (12)	105.61 (7), 109.09 (7)	104.42 (8), 109.29 (8)	101.6 (3), 108.9 (3), 109.1 (3)
C–N–P	126.7 (2)	128.4 (1)	124.44 (14)	126.8 (5)
N–C=X	122.6 (2)	123.2 (1)	122.05 (17)	120.4 (7)
Torsion angles[a]				
O=P–N–C	−176.3 (2)	174.5 (1)	−174.98 (15)	174.9, 179.6
O–P–N–C	−53.1 (3), 57.8 (3)	51.9 (2), −60.5 (2)	−50.82 (17), 59.42 (18)	47.9, 55.5, −51.5, −58.2
P–N–C=X	−9.4 (4)	7.5 (2)	−12.1 (3)	4.8, 11.8

[a] Torsion angles must be compared by their magnitudes.

Table 3
Hydrogen bond lengths (Å) and angles (°) for $\mathbf{HL^{II}}$ and $\mathbf{HL^{III}}$.

		D–H···A	*d* (D–H)	*d* (H···A)	*d* (D···A)	∠ (DHA)
$\mathbf{HL^{II}}$	Polymorph $\mathbf{HL^{II}}\{\mathbf{1}\}$[a]	N(1)–H(1)···O(3)$^{\#1}$	0.83 (4)	2.04 (4)	2.849 (4)	165 (3)
		C(16)–H(16)···O(3)$^{\#1}$	0.95	2.60	3.239 (4)	125
		C(6)–H(6B)···S(1)$^{\#2}$	0.98	2.81	3.705 (6)	152
	Polymorph $\mathbf{HL^{II}}\{\mathbf{2}\}$[b] [13]	N(1)–H(1)···O(3)$^{\#1}$	0.87 (2)	1.95 (2)	2.805 (2)	165 (2)
$\mathbf{HL^{III}}$	Polymorph $\mathbf{HL^{III}}\{\mathbf{1}\}$[c]	N(1)–H(6)···O(1)$^{\#1}$	0.80 (3)	2.04 (3)	2.836 (2)	172 (3)
		C(3)–H(1)···O(1)$^{\#1}$	0.95	2.58	3.254 (2)	128
		C(11)–H(11B)···O(4)$^{\#2}$	0.98	2.68	3.615	159
	Polymorph $\mathbf{HL^{III}}\{\mathbf{2}\}$ [14]	N–H(1)···O(1)′	0.89 (6)	1.96 (8)	2.837 (7)	162 (5)
		N′–H(1)′···O(1)	0.84 (6)	1.99 (6)	2.811 (7)	164 (6)

[a] Symmetry transformations used to generate equivalent atoms: #1 $1/2-x$, $1/2-y$, $1-z$; #2 x, $-1+y$, z.
[b] Symmetry transformations used to generate equivalent atoms: #1 $1-x$, $-y$, $-z$.
[c] Symmetry transformations used to generate equivalent atoms: #1 $3/2-x$, $3/2-y$, $1-z$; #2 x, $-1+y$, z.

In summary, the tetraphenylphosphonium salts $\mathbf{PPh_4L^{I,II}}$ have been synthesized and characterized by means of IR, ^{1}H, ^{31}P{^{1}H} NMR spectroscopy, ES mass spectrometry and microanalysis. Recrystallization of $\mathbf{PPh_4L^{I,II}}$ from an aqueous EtOH solution (1:1, v/v) leads to the formation of $\mathbf{HL^{II,III}}$, respectively. The crystal structures of $\mathbf{HL^{II,III}}$ reveal to be polymorphs to the previously reported structures. Single crystal X-ray diffraction studies showed that $\mathbf{HL^{II,III}}$ form intermolecular hydrogen bonds leading to the centrosymmetric dimer formation.

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Appendix A. Supplementary material

CCDC 767460 ($\mathbf{HL^{II}}$) and 767909 ($\mathbf{HL^{III}}$) contain the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at doi:10.1016/j.inoche.2012.02.041.

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[16] *Physical measurements*: IR spectra were recorded with Bruker IFS66νS or Specord M-80 spectrometers in the range 400–3600 cm^{-1}. NMR spectra ($CDCl_3$) were obtained on Bruker Avance 300 MHz or Varian Unity-300 NMR spectrometers at 25 °C. ^{1}H and ^{31}P{^{1}H} spectra were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to $SiMe_4$ (^{1}H) and 85% H_3PO_4 (^{31}P{^{1}H}). Electrospray ionization mass spectra were measured with a Finnigan-Mat TCQ 700 mass spectrometer on a 10^{-6} M solution in CH_3OH. The speed of sample submission was 2 μL/min. The ionization energy was 4.5 kV. The capillary temperature was 200 °C. Elemental analyses were performed on a Perkin–Elmer 2400 CHN microanalyser. *Synthesis of* $\boldsymbol{PPh_4L^{I,II}}$: A suspension of $\mathbf{HL^{I,II}}$ (0.317 or 0.301 g, respectively; 1.0 mmol), in 96% aqueous EtOH (10 mL) was mixed with a 96% aqueous EtOH (10 mL) solution of sodium hydroxide (0.044 g, 1.1 mmol, 10% excess). A 96% aqueous EtOH (10 mL) solution of PPh_4Br (0.419 g, 1.0 mmol) was added dropwise under vigorous stirring to the resulting sodium salt. The mixture was stirred at room temperature for a further 3 hours and left overnight. The white precipitate of NaBr was filtered off, and the solvent was removed *in vacuo*. A yellow ($\mathbf{PPh_4L^{II}}$) or colorless precipitate ($\mathbf{PPh_4L^{II}}$) was isolated from a H_2O/EtOH mixture (1:1, v/v). $\boldsymbol{PPh_4L^{I}}$: Yield 0.525 g (80%). IR ν (cm^{-1}): 608 (P=S), 996 (POC), 1562 (S···C···N). ^{1}H NMR δ (ppm): 1.14 (d, $^3J_{H,H}=6.2$ Hz, 6H, CH_3, *i*Pr), 1.18 (d, $^3J_{H,H}=6.1$ Hz, 6H, CH_3, *i*Pr), 4.57 (d sept, $^3J_{POCH}=9.4$ Hz, $^3J_{H,H}=6.2$ Hz, 2H, OCH), 6.38–7.82 (m, overlapped with the solvent signal, Ph). ^{31}P{^{1}H} NMR δ (ppm): 23.9 (1P, PPh_4), 61.8 (1P, NPS). ES–MS positive ion *m/z* (%): 339.4 (100) $[PPh_4]^+$, 657.1 (81.8) $[PPh_4Lig+H]^+$, 1013.4 (28.9) $[PPh_4Lig+H_2O+PPh_4]^+$, 1041.7 (17.4) $[PPh_4Lig+EtOH+PPh_4]^+$, 1330.8 (10.9) $[(PPh_4)_2Lig_2+H_2O+H]^+$. ES–MS negative ion *m/z* (%): 316.2 (62.1) $[Lig]^-$, 972.4 (85.3) $[PPh_4Lig+Lig]^-$, 1646.8 (38.6) $[(PPh_4)_2Lig_2+H_2O+Lig]^-$. Anal. for $C_{37}H_{39}NO_2P_2S_2$ (655.79): calcd. C 67.77, H 5.99, N 2.14; found C 67.64, H 6.04, N, 2.09. $\boldsymbol{PPh_4L^{II}}$: Yield 0.569 g (89%). IR ν (cm^{-1}): 1008 (POC), 1192 (P=O), 1557 (S···C···N). ^{1}H NMR δ (ppm): 1.08 (d, $^3J_{H,H}=6.0$ Hz, 6H, CH_3, *i*Pr), 1.14 (d, $^3J_{H,H}=6.2$ Hz, 6H, CH_3, *i*Pr), 4.74 (d sept, $^3J_{POCH}=9.0$ Hz, $^3J_{H,H}=6.0$ Hz, 2H, OCH), 6.21–7.76 (m, overlapping with the solvent signal, Ph). ^{31}P{^{1}H} NMR δ (ppm): 11.4 (1P, NPO), 22.3 (1P, PPh_4). ES–MS positive ion *m/z* (%): 339.1 (100) $[PPh_4]^+$, 641.3 (70.2) $[PPh_4Lig+H]^+$, 979.6 (44.1) $[PPh_4Lig+PPh_4]^+$, 1312.0 (27.4) $[(PPh_4)_2Lig_2+CH_3OH+H]^+$. ES–MS negative ion *m/z* (%): 300.3 (48.2) $[Lig]^-$, 972.7 (13.6) $[PPh_4Lig+CH_3OH+Lig]^-$. Anal. for $C_{37}H_{39}NO_3P_2S$ (639.73): calcd. C 69.47, H 6.14, N 2.19; found: C 69.32, H 6.18, N 2.13.

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[18] The X-ray data for $\mathbf{HL^{II}}\{\mathbf{1}\}$ were collected on a Stoe IPDS-II diffractometer with graphite-monochromatized Mo *Kα* radiation generated by fine-focus X-ray tube operated at 50 kV and 40 mA. The images were indexed, integrated and scaled using the X-Area data reduction package [19]. Data were corrected for absorption using the PLATON program [20]. The structures were solved by Direct Method using the SHELXS-97 program [21] and refined on F^2 with full-matrix least-squares using SHELXL-97 [22]. Hydrogen atoms were revealed from $\Delta\rho$ maps and those bonded to C were refined using a riding model. The H atoms bonded to N were freely refined. The X-ray data for $\mathbf{HL^{III}}\{\mathbf{1}\}$ were collected on a Bruker SMART Apex CCD difractometer with graphite-monochromatized Mo *Kα* radiation. Data reduction was carried out using the software package Bruker *SAINT* [23]. Empirical corrections were performed with *SADABS* [24]. The structure was solved by Direct Methods, while the remainder of the atomic positions were found using difference Fourier methods. All non-hydrogen atoms were refined anisotropically (with appropriate restraints using SIMU and ISOR) by blocked full-matrix least squares calculations on F^2 using SHELX-97 [25] within the X-seed environment [26,27]. Hydrogen atoms were added to the structure model on calculated positions and were refined as riding atoms. Figures were generated using the program Mercury [28].

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