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Phenylmercury(II) derivatives of tetraorganodichalcogenoimidodiphosphorus acids. Crystal and molecular structure of $[PhHg\{(OPR_2)(SPPh_2)N\}]_2$ (R = Me, Ph)

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Abstract

The reactions between PhHgCl or PhHgAc and $M[(XPR_2)(YPR'_2)N]$ (M = Na, K; X, Y = O, S; R, R′ = Me, Ph, OEt), in 1:1 molar ratio, have been investigated. $PhHg[(XPR_2)(YPR'_2)N]$ derivatives were isolated as microcrystalline powders and were characterised using IR and NMR (^1H, ^{13}C and ^{31}P) spectroscopy and mass spectrometry. The molecular structure of $PhHg[(OPR_2)(SPPh_2)N]$ [R = Me (**1**), Ph (**2**)] was investigated by X-ray diffraction. In the monomeric unit, $PhHg[(OPR_2)(SPPh_2)N]$, the mercury atom forms the primary bonds with the carbon of the phenyl group and the sulfur atom of the phosphorus ligand [Hg(1)–S(1) 2.405(1) Å for **1**, 2.398(2) Å for **2**]. These primary bonds are significantly deviated from the expected linear arrangement [C(1)–Hg(1)–S(1) 166.4(2)° for **1**, 165.0(2)° for **2**]. Both compounds exhibit dimeric associations in the crystal through *S*,*O*-bridging organophosphorus ligands [Hg(1)–O(1) 2.556(4) Å for **1**, 2.588(4) Å for **2**], thus resulting in a distorted T-shaped arrangement of the CHgSO coordination core.. The formation of a 12-membered $Hg_2O_2S_2P_4N_2$ ring with different conformation in **1** and **2**, respectively, results in different additional chalcogen atoms being in the proximity of the metal atom. Weak transannular Hg···O [2.753(4) Å] are also established in **1**, leading to a tricyclic ladder structure with a planar central Hg_2O_2 ring.

Keywords: Crystal structures; Organophosphorus ligands; Phenylmercury(II) derivatives

1. Introduction

The large bite and high flexibility of the tetraorganodichalcogenoimidodiphosphorus anions make them versatile ligands towards metallic and organometallic centers. A variety of structures has been reported for complexes of Main Group elements, including Group 12 metals, due to the coordination opportunities offered both by metals and ligands [1]. Only a few mercury(II) compounds containing imidodiphosphorus ligands, i.e. inorganic $Hg[(SPPh_2)_2N]_2$, $HgCl[(SPPh_2)_2N]$ [2], $Hg[(SePPh_2)_2N]_2$ [3], and organometallic derivatives, i.e. $PhHg[\{OP(OPh)_2\}_2N]$ [4,5], are known. The inorganic species $Hg[(SePPh_2)_2N]_2$ was found to exhibit a spiro $NP_2Se_2HgSe_2P_2N$ core with tetrahedral coordinated metal center due to the expected *Se*,*Se*-chelating nature of the ligand moieties [3]. By contrast, unusual *N*,*O*-bridging imidodiphosphorus ligands led to dimeric species in the crystal of $PhHg[\{OP(OPh)_2\}_2N]$ (Fig. 1a). The reaction of HgO with $[OP(OPh)_2]_2NH$ or $(OPEt_2\}[OP(OPh)_2]NH$ resulted in *ortho*-mercuration of a phenoxy group and isolation of dinuclear compounds, $Hg_2[(OPR_2)\{OP(OPh)(OC_6H_4\text{-}2)\}N]_2$ (R = Et [6], OPh [4]) (Fig. 1b). The second covalence at the mercury atom is achieved through a Hg-N bond which involves the nitrogen of a neighboring mercurated imidodiphosphoric ligand, thus resulting in the formation of a 12-

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membered $Hg_2C_4O_2P_2N_2$ ring with almost linear N–Hg–C fragments.

In the context of our interest in the coordination chemistry of imidodiphosphorus ligands [1], we decided to investigate the influence of the nature of the chalcogen atoms in organomercury(II) derivatives containing ligands of the type $[(XPR_2)(YPR'_2)N]^-$. We report here on the synthesis and spectroscopic characterization of some phenylmercury(II) compounds, $PhHg[(XPR_2)(YPR'_2)N]$, as well as the crystal and molecular structure of $PhHg[(OPR_2)(SPPh_2)N]$ [R = Me, Ph].

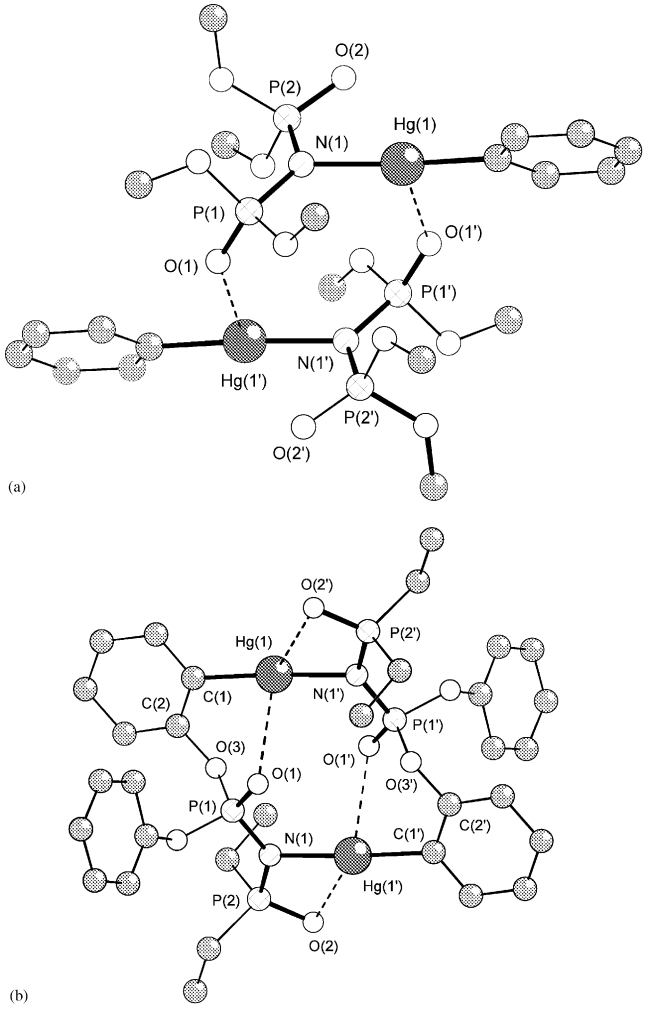
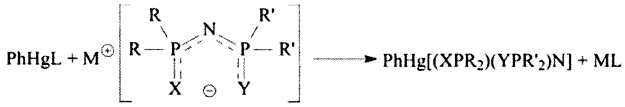


Fig. 1. (a) Dimeric association in the crystal of $PhHg[\{OP(OPh)_2\}_2N]$ [5] (for clarity, only carbons bound to oxygen atoms in the ligand moiety are shown); (b) the structure of dinuclear complex $Hg_2[(OPEt_2)\{OP(OPh)(OC_6H_4\text{-}2)\}N]_2$ [4].

2. Results and discussion

2.1. Preparation

The title compounds were prepared according to Eq. (1), by reacting stoichiometric amounts of either phenylmercury(II) chloride or acetate and the alkali salt of the appropriate tetraorganodichalcogenoimidodiphosphorus ligand:



		X	Y	R	R'
L = Cl	**1**	O	S	Me	Ph
L = CH_3COO	**2**	O	S	Ph	Ph
	3	O	S	OEt	Ph
	4	O	O	OEt	Ph

(1)

All compounds were isolated as air-stable, colorless crystalline products. They were characterized by multinuclear (^1H, ^{13}C and ^{31}P) NMR and IR spectroscopy and mass spectrometry. The crystal and molecular structures of $PhHg[(OPMe_2)(SPPh_2)N]$ (**1**) and $PhHg[(OPPh_2)(SPPh_2)N]$ (**2**) were determined by single crystal X-ray diffraction.

2.2. IR spectra

IR bands were assigned for $\nu_{as}(P_2N)$, $\nu(PO)$ and $\nu(PS)$ stretching vibrations by comparison with the free $(XPR_2)(YPR'_2)NH$ acids and their alkali salts [7–9]. The presence of strong absorptions in the region 1290–1200 cm^{-1}, assigned to $\nu_{as}(P_2N)$ stretching vibration, and the absence of strong absorptions characteristic for the free acids around 2700–2600 [$\nu(NH)$] and 950–900 cm^{-1} [$\nu_{as}(P_2NH)$], indicates that the imidodiphosphorus moieties are coordinated to the metal center in the deprotonated form.

2.3. NMR spectra

The ^1H- and ^{13}C-NMR spectra of compounds **1**–**4** show the expected resonances and suggest that the organic groups attached to the same phosphorus atom are equivalent on the NMR time scale at room temperature. In all cases the lower field resonance in the ^1H-NMR spectra (δ ca. 8 ppm) is due to the *ortho* protons of the $P–C_6H_5$ group. The expected splitting pattern due to phosphorus–proton and phosphorus–carbon couplings were observed. Satellites due to $^{199}Hg–^{13}C$ coupling surround the ^{13}C resonances assigned to the *ortho* and *meta* carbons of the phenyl group on the metal atom.

The ^{31}P-NMR spectra of compounds **1**–**4** exhibit two resonances, as is expected in the presence of the non-equivalent phosphorus atoms in a ligand moiety. Only in the case of **3** is a resolved doublet pattern due to phosphorus–phosphorus coupling observed for both ^{31}P signals. The magnitude of the chemical shifts suggests that both calcogen atoms of the ligand unit are involved in coordination to the metal center, e.g. δ 21.1 (P_O), 28.8 (P_S) for **2**, compared to 28.9 (P_O), 41.8 (P_S) for Me–O–PPh_2=N–PPh_2=S and 13.3 (P_O), 26.7 (P_S) for O=PPh_2–N=PPh_2–S–Me esters, respectively [10].

2.4. Mass spectra

The mass spectra of compounds **1**–**3** exhibit highly abundant [M^++H] fragments, which represent the molecular ion for compounds **2** and **3** in the FAB-MS. In addition, the DCI-MS spectrum of **1** and the FAB-MS spectra of **2** and **3** show higher *m*/*z* ions corresponding to [M_2^++H] (**1**) and [M_2^+] (**2**) as well as [M_2^+ − Ph+2H] (**3**). This supports the dimeric association established by the single-crystal X-ray diffraction studies for **1** and **2**.

2.5. Crystal and molecular structure of $PhHg[(OPMe_2)(SPPh_2)N]$ (1) and $PhHg[(OPPh_2)(SPPh_2)N]$ (2)

Crystals suitable for single-crystal X-ray diffraction analysis were obtained for compounds **1** and **2** from a mixture of chloroform and hexane (1/4, v/v). In both cases the crystals consist of discrete dimeric units separated by normal van der Waals distances. The ORTEP diagrams for compounds **1** and **2** with the atom numbering scheme are depicted in Figs. 2 and 3,

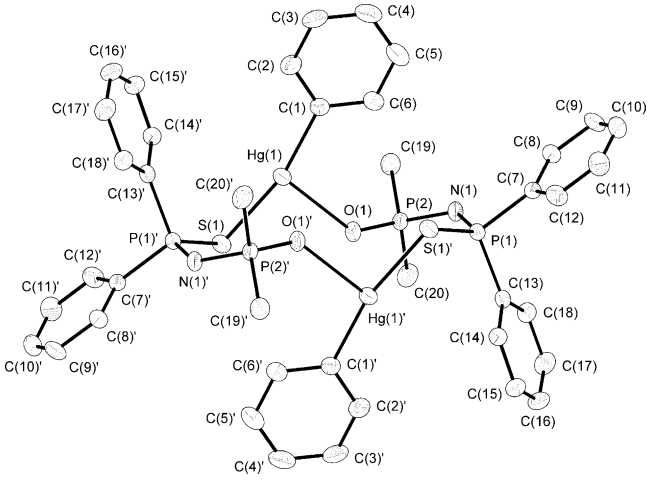


Fig. 2. ORTEP plot of the discrete dimer in the crystal of **1**. The atoms are drawn with 25% probability ellipsoids. Hydrogen atoms are omitted for clarity.

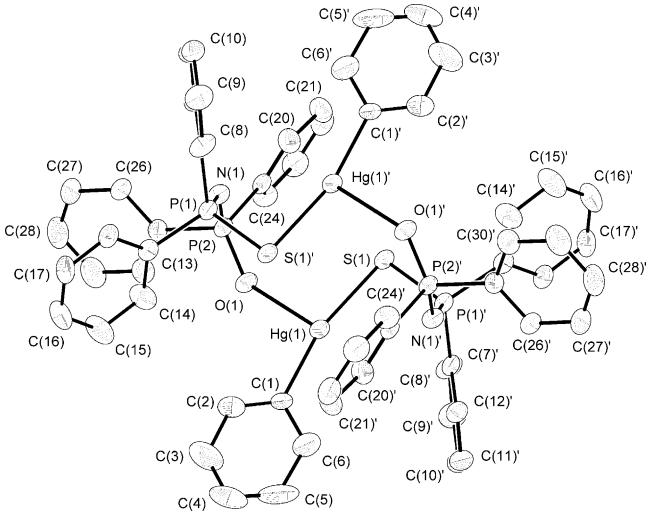


Fig. 3. ORTEP plot of the discrete dimer in the crystal of **2**. The atoms are drawn with 20% probability ellipsoids. Hydrogen atoms are omitted for clarity.

respectively. Selected interatomic distances and angles are listed in Table 1.

There are some common structural features for both compounds:

i) in the monomeric unit, $PhHg[(OPR_2)(SPPh_2)N]$, the mercury atom forms the primary bonds with the

Table 1
Selected interatomic distance (Å) and bond angles (°) in **1** and **2** [a]

	1	**2**
Bond lengths		
Hg(1)–C(1)	2.076(6)	2.058(7)
Hg(1)–S(1)	2.405(1)	2.398(2)
Hg(1)–O(1)	2.556(4)	2.588(4)
P(1)–S(1′)	2.048(2)	2.060(2)
P(1)–N(1)	1.587(4)	1.574(5)
P(2)–N(1)	1.610(4)	1.602(6)
P(2)–O(1)	1.509(4)	1.494(5)
Hg(1)···X(1′) [b]	2.753(4)	3.313(2)
Hg(1)···Hg(1′)	3.872(1)	4.197(1)
O(1)···S(1′)	3.471(4)	3.899(5)
Bond angles		
C(1)–Hg(1)–S(1)	166.4(2)	165.0(2)
C(1)–Hg(1)–O(1)	104.9(2)	99.2(2)
S(1)–Hg(1)–O(1)	85.91(8)	94.5(1)
Hg(1′)–S(1′)–P(1)	97.18(6)	92.67(8)
S(1′)–P(1)–N(1)	118.6(2)	115.8(2)
P(1)–N(1)–P(2)	131.1(3)	134.7(4)
O(1)–P(2)–N(1)	116.9(2)	119.6(3)
Hg(1)–O(1)–P(2)	136.7(2)	133.7(3)
X(1′)···Hg(1)–C(1) [b]	104.3(2)	101.3(2)
X(1′)···Hg(1)–S(1) [b]	84.30(8)	86.77(5)
X(1′)···Hg(1)–O(1) [b]	86.4(1)	94.5(1)
Hg(1)···X(1′)–Hg(1′) [b]	93.6(1)	93.2(1)

[a] Symmetry equivalent position given by a 'prime' for **1** ($-x+1$, $-y+1$, $-z+1$) and for **2** ($-x$, $-y$, $-z$), respectively.
[b] X(1′) = O(1′) for **1** and S(1′) for **2**.

carbon of the phenyl group [Hg(1)–C(1) 2.076(6) Å for **1**, 2.058(7) Å for **2**] and the sulfur atom of the phosphorus ligand [Hg(1)–S(1) 2.405(1) Å for **1**, 2.398(2) Å for **2**]. These primary bonds are significantly deviated from the expected linear arrangement [C(1)–Hg(1)–S(1) 166.4(2)° for **1**, 165.0(2)° for **2**]. Their magnitude is comparable with those observed, for example, in $[PhHg\{S(S)PEt_2\}]_n$ [Hg–C 2.062(11) Å, Hg–S 2.375(4) Å] [11].

ii) the monomeric units are associated into discrete dimers, $[PhHg\{(OPR_2)(SPPh_2)N\}]_2$, through *S*,*O*-bridging monothioimidodiphosphinato ligands. The mercury–oxygen interactions within the twelve-membered $Hg_2O_2S_2P_4N_2$ ring thus formed [Hg(1)–O(1) 2.556(4) Å for **1**, 2.588(4) Å for **2**] are considerably shorter than the sum of the van der Waals radii for the corresponding atoms [Σ_{vdW}(Hg,O) 3.0 Å] [12]. These interatomic interactions are stronger than the intra- [Hg···O 2.897(4) Å] or inter-dimer [Hg···O 2.831(3) Å] interactions observed in the ribbon-like structure of $[MeHg\{S(O)PPh_2\}]_n$ [13]. They are also shorter than the Hg–O bond in the dimeric association based on *N*,*O*-bridging ligand which was described for the related derivative $PhHg[\{OP(OPh)_2\}_2N]$ [Hg–O 2.684(5) Å] [5].

iii) the CHgSO cores exhibit a distorted T-shaped coordination geometry; the sum of the bond angles around the mercury atom being closed to 360°, i.e. 357.2° for **1**, and 358.7° for **2**.

iv) the bond lengths within the SPNPO skeleton are consistent with *S*-covalent bonded bridging ligands, i.e. single phosphorus–sulfur bonds [P(1)–S(1′) 2.048(2) Å for **1**, 2.060(2) Å for **2**] and considerable double bond character for the phosphorus–oxygen bonds [P(2)–O(1) 1.509(4) Å for **1**, 1.494(5) Å for **2**] (cf. $[2\text{–}(Me_2NCH_2)C_6H_4]Te\text{–}S\text{–}PPh_2{=}N\text{–}PPh_2{=}S$ [14]: P–S 2.057(1), P=S 1.945(1) Å; $Ph_2P(=O)OH$ [15]: P–O 1.526(6), P=O 1.486(6) Å). Accordingly, the lengths of the phosphorus–nitrogen bonds (Table 1) are consistent with some delocalization within the Hg–S–P=N–P=O→Hg fragment (cf. $[2\text{-}(Me_2NCH_2)C_6H_4]Te\text{–}S\text{–}PPh_2{=}N\text{–}PPh_2{=}S$ [14]: P–N 1.612(3), P=N 1.557(3) Å).

There are also significant differences between the dimeric units found in the crystals of **1** and **2**, mainly related to the conformation of the twelve-membered inorganic rings (Fig. 4). The bond angles within the $Hg_2O_2S_2P_4N_2$ rings of the dimeric associations (Table 1) are of the same magnitude, but the rings are twisted to bring the second oxygen atom in **1** or the second sulfur atom in **2** into the proximity of the mercury atom. The transannular metal-chalcogen distances indicate significant secondary bonding in **1** [Hg(1)···O(1′) 2.753(4) Å], while in **2** [Hg(1)···S(1′) 3.313(2) Å] they are at the limit

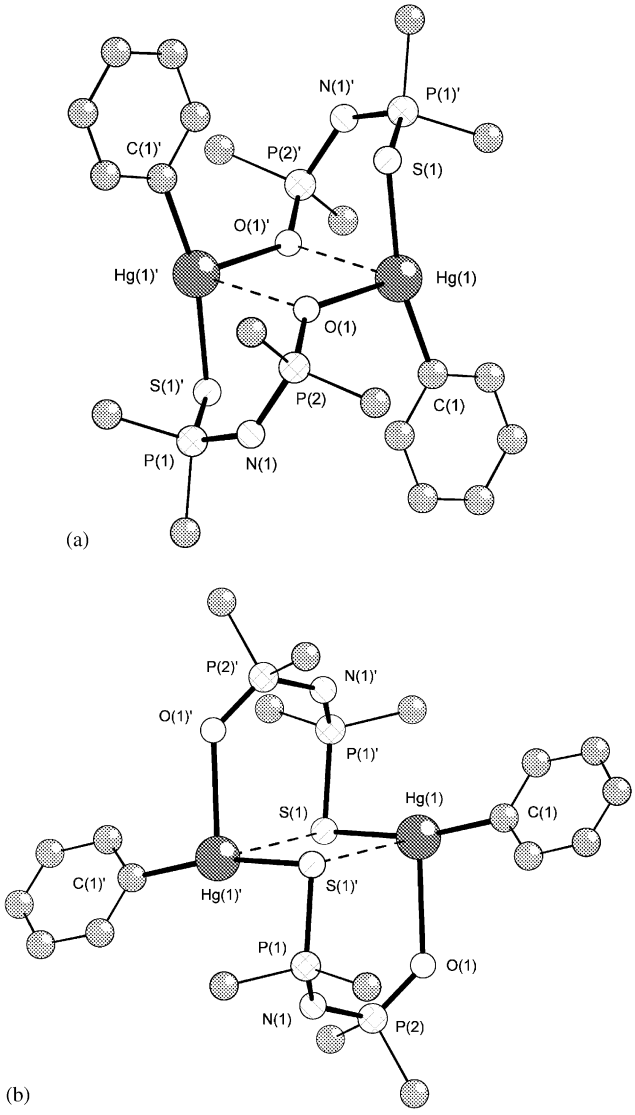


Fig. 4. Conformation of the 12-membered $Hg_2O_2S_2P_4N_2$ inorganic rings in the dimeric associations of compounds **1** and **2**.

of the sum of the van der Waals radii [Σ_{vdW}(Hg,O) 3.0 Å, Σ_{vdW}(Hg,S) 3.3 Å] [12]. If these weak interatomic contacts are considered, the overall tricyclic system features a ladder structure with SPNP and OPNP fragments for **1** and **2**, respectively, placed on opposite sides of the central planar Hg_2X_2 core (X = O, S). The magnitude of the Hg(1)···Hg(1′) distances [3.872(1) Å for **1** and 4.197(1) Å for **2**] within the Hg_2X_2 cores is consistent with the absence of any interactions between the metal atoms. The external cyclic $HgOSP_2N$ systems exhibit distorted chair conformation in **1**, with Hg and N atoms in the apices, and distorted boat conformation in **2**, with O and P atoms in the apices [the dihedral angle between the best O(1)Hg(1)S(1a)P(1) and O(1)P(2)N(1)P(1) planes is 142.4°]. The orientation of the phenyl groups attached to mercury atoms is also different: they are *trans* with respect to the Hg_2O_2

system in **1** (Fig. 4a), while the *ipso* carbons of the aromatic groups are basically coplanar with the Hg_2S_2 system in **2** (Fig. 4b).

3. Conclusions

New PhHg[$(XPR_2)(YPR'_2)$N] (X, Y = O, S; R, R′ = Me, Ph, OEt) derivatives were prepared and characterized using IR and NMR (^{1}H, ^{13}C and ^{31}P) spectroscopy and mass spectrometry. Evidence for the presence of dimeric associations was obtained from MS data. The molecular structure of PhHg[$(OPR_2)(SPPh_2)$N] [R = Me (**1**), Ph (**2**)] was investigated by X-ray diffraction. Both compounds exhibit dimeric associations in the crystal through *S*,*O*-bridging organophosphorus ligands, resulting in 12-membered inorganic rings and distorted T-shaped CHgSO cores with the sulfur atom *trans* to the aromatic *ipso* carbon. The $Hg_2O_2S_2P_4N_2$ rings are twisted in different ways to bring an additional oxygen and sulfur atoms in **1** and **2**, respectively, into the proximity of the metal, thus leading to overall tricyclic ladder structures with central Hg_2O_2 and Hg_2S_2 planar cores.

4. Experimental

4.1. Materials and procedures

The starting materials were prepared according to literature methods: Na[$(OPMe_2)(SPPh_2)$N], [8] K[$(OPPh_2)(SPPh_2)$N] [7], K[{$OP(OEt_2)$}$(SPPh_2)$N], [9] K[{$OP(OEt_2)$}$(OPPh_2)$N] [9], PhHgCl and $PhHgO(O)CCH_3$ [16]. Solvents were dried on potassium (toluene) and sodium (*n*-hexane) and freshly distilled prior to use. Infrared spectra were recorded in the range 4000–250 cm^{-1} as KBr pellets on a Jasco FT/IR-615 instrument. The ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on a VARIAN GEMINI 300S instrument operating at 299.5, 75.4 and 121.4 MHz, respectively, at room temperature, in $CDCl_3$. The chemical shifts are reported in ppm relative to TMS and H_3PO_4 85%, respectively. Mass spectra were recorded on a VG Autospec.3. spectrometer.

4.2. Preparation of the title compounds, PhHg[$(XPR_2)(YPR'_2)$N] (Table 2)

Mixtures of either PhHgCl or $PhHgOCOCH_3$ and the appropriate alkali salt, M[$(XPR_2)(YPR'_2)$N] (1:1 molar ratio) in 40 ml toluene were refluxed for 18 h and then filtered to remove the resulting alkali metal salt. The filtrate was evaporated under reduced pressure and an oily product was obtained. After stirring for 30 min. with *n*-hexane, a white solid was deposited. This was separated by filtration, washed with *n*-hexane and dried in vacuum. Details of the preparations and melting points are given in Table 2. Microanalysis (C, H, N) and NMR spectra are consistent with the given composition of the isolated products.

4.2.1. PhHg[$(OPMe_2)(SPPh_2)$N] (**1**)

Anal. Found: C, 40.7; H, 3.5; N, 2.5. Calc. for $C_{20}H_{21}HgNOP_2S$: C, 41.0; H, 3.6; N, 2.4%. IR (cm^{-1}): 1210vs [$\nu_{as}(P_2N)$], 1107vs [ν(PO)], 560s [ν(PS)]. ^{1}H-NMR: δ 1.55dd (6H, P–CH_3, $^2J_{PH}$ 13.9, $^4J_{PH}$ 1.6 Hz), 7.22tt (1H, Hg–C_6H_5-*para*, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.5 Hz), 7.32dd (2H, Hg–C_6H_5-*meta*, $^3J_{HH}$ 7.5 Hz), 7.45m (8H, P–C_6H_5-*meta*+*para*, Hg–C_6H_5-*ortho*), 7.94ddd (4H, P–C_6H_5-*ortho*, $^3J_{PH}$ 14.0, $^3J_{HH}$ 7.9, $^4J_{HH}$ 1.6 Hz). ^{13}C-NMR: δ 21.31dd (P–CH_3, $^1J_{PC}$ 92.7, $^3J_{PC}$ 4.6 Hz), 128.41s (Hg–C_6H_5-*para*), 128.61d (P–C_6H_5-*meta*, $^3J_{PC}$ 13.7 Hz), 128.73s (Hg–C_6H_5-*meta*, $^3J_{HgC}$ 190.1 Hz), 130.85d (P–C_6H_5-*ortho*, $^2J_{PC}$ 11.5 Hz), 131.67d (P–C_6H_5-*para*, $^4J_{PC}$ 2.3 Hz), 136.94s (Hg–C_6H_5-*ortho*, $^2J_{HgC}$ 116.8 Hz), 137.84dd (P–C_6H_5-*ipso*, $^1J_{PC}$ 111.1, $^3J_{PC}$ 4.6 Hz), 156.82s (Hg–C_6H_5-*ipso*). ^{31}P-NMR: δ 25.8s, br (Me_2PO), 36.8s, br (Ph_2PS). MS [DCI_{pos}, NH_3, 8 mA s^{-1}, *m*/*z* (%)]: 1173 (7) [M_2^+ + H], 864 (5) [M_2^+ − L], 819 (28) [M_2^+ −PhHg + H], 588 (76) [M^+ + H], 310 (100) [$PhMeHg^+ + NH_3$], 296 (78) [$PhHg^+ + NH_3$].

4.2.2. PhHg[$(OPPh_2)(SPPh_2)$N] (**2**)

Anal. Found: C, 50.4; H, 3.8; N, 1.8. Calc. for $C_{30}H_{25}HgNOP_2S$: C, 50.7; H, 3.6; N, 2.0%. IR (cm^{-1}): 1272vs [$\nu_{as}(P_2N)$], 1146vs [ν(PO)], 555vs [ν(PS)]. ^{1}H-NMR: δ 7.48–7.22m (15H, P–C_6H_5-*meta*+*para*, Hg–C_6H_5-*meta*+*para*), 7.52d (2H, Hg–C_6H_5-*ortho*, $^3J_{HH}$ 6.9 Hz), 7.92m (8H, P–C_6H_5-*ortho*). ^{13}C–NMR: δ 128.02d (P–C_6H_5-*meta*, $^3J_{PC}$ 12.6 Hz), 128.38s (Hg–C_6H_5-*para*), 128.52d (P–C_6H_5-*meta*, $^3J_{PC}$ 13.7 Hz), 128.65s (Hg–C_6H_5-*meta*, $^3J_{HgC}$ 190.2 Hz), 130.32d (P–C_6H_5-*para*, $^4J_{PC}$ 2.3 Hz), 130.94d (P–C_6H_5-*ortho*, $^2J_{PC}$ 11.4 Hz), 131.22d (P–C_6H_5-*ortho*, $^2J_{PC}$ 10.3 Hz), 131.60d (P–C_6H_5-*para*, $^4J_{PC}$ 3.4 Hz), 137.04s (Hg–C_6H_5-*ortho*, $^2J_{HgC}$ 116.8 Hz), 137.47dd [P(S)–C_6H_5-*ipso*, $^1J_{PC}$ 112.2, $^3J_{PC}$ 4.6 Hz], 138.58dd [P(O)–C_6H_5-*ipso*, $^1J_{PC}$ 132.2, $^3J_{PC}$ 4.6 Hz], 157.07s (Hg–C_6H_5-*ipso*). ^{31}P-NMR: δ 21.1s (Ph_2PO, $^1J_{PC}$ 128.7 Hz), 28.8s (Ph_2PS, $^1J_{PC}$ 117.0 Hz). MS [FAB_{pos}, *m*/*z* (%)]: 1420 (3) [M_2^+], 988 (8) [M_2^+ − L], 712 (100) [M^+ + H], 634 (45) [M^+ − Ph].

4.2.3. PhHg[{$OP(OEt)_2$}$(SPPh_2)$N] (**3**)

Anal. Found: C, 40.7; H, 3.6; N, 2.1. Calc. for $C_{22}H_{25}HgNO_3P_2S$: C, 40.9; H, 3.9; N, 2.2%. IR (cm^{-1}): 1290s, 1260s [$\nu_{as}(P_2N)$], 1190vs, 1102s [ν(PO)], 1037vs [ν(POC)], 565s [ν(PS)]. ^{1}H-NMR: δ 1.29t (6H, P-OCH_2CH_3, $^3J_{HH}$ 6.9 Hz), 4.07dq (4H, P–OCH_2CH_3, $^3J_{PH}$ 7.1, $^3J_{HH}$ 7.1 Hz), 7.23t (1H, Hg–C_6H_5-*para*, $^3J_{HH}$

Table 2
Preparation data and m.p. for PhHg[(XPR$_2$)(YPR$'_2$)N] derivatives

Starting materials		Product [yield: g (%)]	m.p. (°C)
PhHgL (g mmol^{-1})	M[(XPR$_2$)(YPR$'_2$)N] (g mmol^{-1})		
PhHgCl 0.313/1.00	Na[(OPMe$_2$)(SPPh$_2$)N] 0.331/1.00	PhHg[(OPMe$_2$)(SPPh$_2$)N] (**1**) 0.378 (65)	138
PhHgOCOCH$_3$ 0.337/1.00	K[(OPPh$_2$)(SPPh$_2$)N] 0.471/1.00	PhHg[(OPPh$_2$)(SPPh$_2$)N] (**2**) 0.506 (71)	116–118
PhHgOCOCH$_3$ 0.337/1.00	K[{OP(OEt$_2$)}(SPPh$_2$) N] 0.407/1.00	PhHg[{OP(OEt$_2$)}(SPPh$_2$) N] (**3**) 0.497 (77)	92 (dec.)
PhHgOCOCH$_3$ 0.337/1.00	K[{OP(OEt$_2$)}(OPPh$_2$) N] 0.391/1.00	PhHg[{OP(OEt$_2$)}(OPPh$_2$) N] (**4**) 0.327 (52)	130–132 (dec.)

7.2 Hz), 7.32dd (2H, Hg–C$_6$*H*$_5$-*meta*, $^3J_{HH}$ 7.2 Hz), 7.46m (8H, P–C$_6$*H*$_5$-*meta*+*para*, Hg–C$_6$*H*$_5$-*ortho*), 8.00ddd (4H, P–C$_6$*H*$_5$-*ortho*, $^3J_{PH}$ 14.3, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.5 Hz). ^{13}C-NMR: δ 16.38d (P–OCH$_2$*C*H$_3$, $^3J_{PC}$ 8.0 Hz), 61.86d (P-O*C*H$_2$CH$_3$, $^2J_{PC}$ 5.7 Hz), 128.52s (Hg–*C*$_6$H$_5$-*para*), 128.53d (P–*C*$_6$H$_5$-*meta*, $^3J_{PC}$ 13.7 Hz), 128.70s (Hg–*C*$_6$H$_5$-*meta*, $^3J_{HgC}$ 190.1 Hz), 130.99d (P–*C*$_6$H$_5$-*ortho*, $^2J_{PC}$ 11.5 Hz), 131.79d (P–*C*$_6$H$_5$-*para*, $^4J_{PC}$ 3.5 Hz), 136.88s (Hg–*C*$_6$H$_5$-*ortho*, $^2J_{HgC}$ 113.4 Hz), 137.00dd (P–*C*$_6$H$_5$-*ipso*, $^1J_{PC}$ 113.4, $^3J_{PC}$ 6.9 Hz), 156.74s (Hg–*C*$_6$H$_5$-*ipso*). ^{31}P-NMR: δ 4.49d [(EtO)$_2$*P*O, $^2J_{PP}$ 21.4 Hz], 30.4d (Ph$_2$*P*S, $^2J_{PP}$ 21.4 Hz). MS [FAB$_{pos}$, *m*/*z* (%)]: 1217 (15) [$M_2^+ - Ph + 2H$], 648 (100) [$M^+ + H$], 570 (17) [$M^+ - Ph$].

4.2.4. PhHg[{OP(OEt)$_2$}(OPPh$_2$)N] (**4**)

Anal. Found: C, 41.7; H, 3.9; N, 2.1. Calc. for C$_{22}$H$_{25}$HgNO$_4$P$_2$: C, 41.9; H, 4.0; N, 2.2%. IR (cm^{-1}): 1260s [ν_{as}(P$_2$N)], 1183vs, 1120m [ν(PO)], 1042vs [ν(POC)]. ^{1}H-NMR: δ 1.03t (6H, P–OCH$_2$C*H*$_3$, $^3J_{HH}$ 7.0 Hz), 3.82dq (4H, P–OC*H*$_2$CH$_3$, $^3J_{PH}$ 7.0, $^3J_{HH}$ 7.0 Hz), 7.28m (11H, P–C$_6$*H*$_5$-*meta*+*para*, Hg–C$_6$*H*$_5$), 7.88ddd (4H, P–C$_6$*H*$_5$-*ortho*, $^3J_{PH}$ 12.3, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.4 Hz). ^{13}C-NMR: δ 16.04d (P–OCH$_2$*C*H$_3$, $^3J_{PC}$ 6.8 Hz), 62.21d (P–O*C*H$_2$CH$_3$, $^2J_{PC}$ 5.7 Hz), 127.98s (P–*C*$_6$H$_5$-*meta*, $^3J_{PC}$ 12.6 Hz), 128.97s (Hg–*C*$_6$H$_5$-*para*), 129.20s (Hg–*C*$_6$H$_5$-*meta*), 130.85s (P–*C*$_6$H$_5$-*para*), 131.68d (P–*C*$_6$H$_5$-*ortho*, $^2J_{PC}$ 11.1 Hz), 136.62s (Hg–*C*$_6$H$_5$-*ortho*), 136.57d (P–*C*$_6$H$_5$-*ipso*, $^1J_{PC}$ 129.4 Hz), 146.36s (Hg–*C*$_6$H$_5$-*ipso*). ^{31}P-NMR: δ 5.0d [(EtO)$_2$*P*O, $^2J_{PP}$ 11.7 Hz], 20.3s,br (Ph$_2$*P*O).

4.3. X-ray structure determination

Block crystals of **1** and **2** were mounted on glass fibres. Data were collected on an Enraf–Nonius KappaCCD area detector diffractometer, with φ and ω scans chosen to give a complete asymmetric unit. Cell refinement [17] gave cell constants corresponding to a monoclinic (for **1**) and orthorhombic (for **2**) cells whose dimensions are given in Table 3 along with other experimental parameters. An absorption correction was applied [18]. The structures were solved by direct methods [19] and the structure was refined using the WINGX version [20] of SHELX-97 [21]. All of the non-hydrogen atoms were treated anisotropically. The phenyl ring attached to Hg displays considerable disorder and can be modelled but with no significant influence on

Table 3
X-ray crystal data and structure refinement for **1** and **2**

	1	**2**
Empirical formula	C$_{40}$H$_{42}$O$_2$N$_2$P$_4$S$_2$Hg$_2$	C$_{60}$H$_{50}$O$_2$N$_2$P$_4$S$_2$Hg$_2$
Formula weight	1171.94	1420.20
Temperature (K)	299(2)	299(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pbca$
Unit cell dimensions		
a (Å)	9.057(2)	23.176(5)
b (Å)	11.905(2)	9.641(2)
c (Å)	19.799(4)	24.947(5)
β (°)	97.93(3))	
V (Å^3)	2114.4(7)	5574(2)
Z	2	4
D_{calc} (g cm^{-3})	1.841	1.692
Absorption coefficient (mm^{-1})	7.538	5.736
F(000)	1128	2768
Crystal size (mm^3)	0.20 × 0.15 × 0.10	0.40 × 0.15 × 0.15
θ Range for data collection (°)	2.92–30.33	2.40–27.48
Reflections collected	14747	28099
Independent reflections	5199 [$R_{int} = 0.0513$]	6360 [$R_{int} = 0.0811$]
Data/restraints/parameters	5199/0/237	6360/0/325
Goodness-of-fit on F^2	1.018	1.005
Final R indices [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.0416$, $wR_2 = 0.0866$	$R_1 = 0.0480$, $wR_2 = 0.1003$
R indices (all data)	$R_1 = 0.0714$, $wR_2 = 0.0978$	$R_1 = 0.1089$, $wR_2 = 0.1197$
Largest difference peak and hole (e Å^{-3})	1.364 and −1.863	0.902 and −0.984

the overall refinement. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The final cycle of full-matrix least-squares refinement was based on 5199 for **1** and 6360 for **2** observed reflections [3694 for **1** and 3571 for **2** for $F^2 > 2\sigma(F^2)$] and 237 for **1** and 325 for **2** variable parameters and converged (largest parameter shift was 0.001 times its esd).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 197677 and 197678 for compounds **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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