Novel Mercury Phosphanylamides

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The reactions of bis(pentafluorophenyl)mercury, bis(diphenylphosphanyl)amine and neodymium or erbium metal in toluene yielded the subvalent mercury(1.33) complex $[Hg_3\{\mu_2\text{-}(Ph_2P)_2N\}_4]\cdot 3\,C_7H_8$ (**1**$\cdot 3\,C_7H_8$) as a toluene solvate. The complex was also prepared in high yield from $Hg(C_6F_5)_2$, $(PPh_2)_2NH$ and mercury metal in toluene at room temperature. From reaction of $Hg(C_6F_5)_2$ and $HN(PPh_2)_2$ in toluene with no added metal, $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_2\{(Ph_2P)(OPPh_2)N\}_2]\cdot 2\,C_7H_8$ (**3**$\cdot 2\,C_7H_8$) has been obtained, and **3**$\cdot 2\,C_4H_{10}O_2$ has also been isolated in low yield. From a related reaction, a solution of the product in $CDCl_3$ deposited $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_3Cl]\cdot 3/2\,CDCl_3$ (**4**$\cdot 3/2\,CDCl_3$). The structure of **1**$\cdot 3\,C_7H_8$ contains a Hg–Hg bonded Hg_3 triangle with adjacent metals bridged (P,P′) by either one or two phosphanylamide ligands. One mercury is four coordinate, and the other two are five coordinate. In $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_2\{(Ph_2P)(OPPh_2)N\}_2]\cdot 2\,S$ [S = C_7H_8 or $C_4H_{10}O_2$ (1,2-dimethoxyethane)], the mercury atoms are bridged (P,P′) by two phosphanylamide ligands, whilst the hemi-oxidised ligands are chelating (O,P) in a *transoid* disposition to each other leading to four coordination. There is unsymmetrical ligation in $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_3Cl]\cdot 3/2\,CDCl_3$ (**4**$\cdot 3/2\,CDCl_3$) with one mercury four coordinate and the other three. Three phosphanylamide ligands bridge (P,P′) the metals with a non-bonding Hg···Hg separation of 3.0042(7) Å. Each HgP_3 array has a triangular arrangement, little affected in one case by the attachment of a chloride approximately normal to HgP_3.

Introduction

In recent years the bidentate bis(diphenylphosphanyl) amine (Hdppa) ligand has received considerable attention.[1] This interest partly emanates from the electronic and structural similarity to the widely used and hugely successful bis(diphenylphosphanyl)methane (dppm) ligand,[2] which gives a wide range of binuclear and metal cluster complexes with transition metals.[3] Such diphosphane ligands are attractive due to their ability to bridge or flexibly chelate (for dppm an aspect furnished by distortion of the central sp^3 hybridised methylene PCP angle), offering coordination geometries that can be tailored to the metal at hand. This often permits short metal–metal contacts, thereby increasing the likelihood of high nuclearity metal complexes.[2,4] Deprotonation of bis(diphenylphosphanyl) amine is readily achieved by treatment with group 1 alkyls (e.g. butyllithium) or alkoxides.[5] The resulting bis(diphenylphosphanyl)amide ligand is an isoelectronic analogue of dppm that has so far demonstrated an ability to bridge, chelate or act as a terminal ligand for transition metals[5–7] and, more recently, lanthanoid metals by coordination through the amide and the phosphorus donor sets.[1b,8]

Another interesting feature of the bis(diphenylphosphanyl)amine ligand is the ability of the phosphorus atoms to be sequentially oxidised by selected chalcogen elements (E = O, S, Se), thereby forming the new derivatives $(PPh_2)[P(E)Ph_2]NH$ and $[P(E)Ph_2]_2NH$.[7] The neutral ligands, or their anionic forms generated by deprotonation,[1a] can also behave as unidentate N/P/E-bonded, E,E/P-chelating or E,E/P-bridging ligands. This class of ligand is capable of acting simultaneously as both a hard and soft Lewis base donor.[1c] Herein we report the synthesis and structures of some unusual and unexpected mercury complexes resulting initially from redox transmetallation/ligand exchange reactions involving lanthanoid metals, bis(pentafluorophenyl)mercury and bis(diphenylphosphanyl)amine. These reactions normally provide a “one-pot” route to numerous organo, organoamido and aryloxo complexes of the lanthanoids[9–10] and appeared attractive for bis(diphenylphosphanyl)amide complexes as a complementary synthesis to the existing metathesis and protolysis routes.[1b,8]

Results and Discussion

Synthesis

The preparation of lanthanoid (Ln) complexes with chelating phosphanylamide ligands was attempted using redox

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transmetallation/ligand exchange with bis(pentafluorophenyl)mercury and bis(diphenylphosphanyl)amine [Equation (1); Ln = Nd].

$$\mathrm{Ln} + 1.5[\mathrm{Hg(C_6F_5)_2}] + 3(\mathrm{Ph_2P})_2\mathrm{NH} \rightarrow [\mathrm{Ln}\{(\mathrm{Ph_2P})_2\mathrm{N}\}_3] + 1.5\,\mathrm{Hg} + 3\,\mathrm{C_6F_5H} \quad (1)$$

Treatment of neodymium metal [Equation (1); Ln = Nd) with the reactants in the non-coordinating solvent toluene, did not yield the target $[\mathrm{Nd}\{(\mathrm{Ph_2P})_2\mathrm{N}\}_3]$ but rather an orange crystalline product that was identified as a subvalent mercury complex, $[\mathrm{Hg_3}\{\mu_2\text{-}(\mathrm{Ph_2P})_2\mathrm{N}\}_4]\cdot 3\,\mathrm{C_7H_8}$ (**1**$\cdot 3\,\mathrm{C_7H_8}$), by an X-ray structure determination (Figure 1 and i in Scheme 1). Compound **1**$\cdot 3\,\mathrm{C_7H_8}$ was also characterised by $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR, $^1\mathrm{H}$ NMR and infrared spectroscopy (below). Despite repeated attempts, $[\mathrm{Nd}\{(\mathrm{Ph_2P})_2\mathrm{N}\}_3]$ could not be isolated. A similar attempt with erbium metal [Equation (1); Ln = Er] also gave no isolable lanthanoid complex. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra of the reaction mixture indicated the presence of the same trinuclear complex **1**. Single crystals isolated from the Er reaction mixture were also identified by X-ray crystallography as **1**$\cdot 3\,\mathrm{C_7H_8}$ (see Experimental Section: Method 2). Attempts to effect reaction (1) were accompanied by formation of insoluble precipitates containing Ln and F.

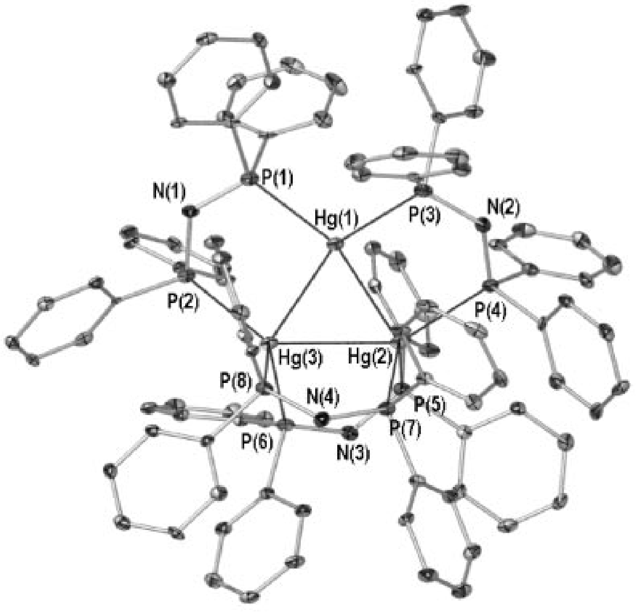


Figure 1. The molecular structure of $[\mathrm{Hg_3}\{\mu\text{-}(\mathrm{Ph_2P})_2\mathrm{N}\}_4]\cdot 3\,\mathrm{C_7H_8}$ (**1**$\cdot 3\mathrm{C_7H_8}$). POV-Ray graphic (www.povray.org), 40% thermal ellipsoids. All solvent molecules are removed for clarity.

As mercury metal is a sufficient reductant to give the subvalent $[\mathrm{Hg_3}(\mu\text{-dmpm})_4][\mathrm{O_3SCF_3}]_4$ [dmpm = bis(dimethylphosphanyl)methane] complex,[11] the reaction of $\mathrm{Hg(C_6F_5)_2}$ with $(\mathrm{Ph_2P})_2\mathrm{NH}$ was attempted in the presenceof mercury metal (and no lanthanoid) [see i in Scheme 1 and Equation (2)] and compound **1**$\cdot 3\,\mathrm{C_7H_8}$ was isolated in excellent yield.

$$2[\mathrm{Hg(C_6F_5)_2}] + 4(\mathrm{Ph_2P})_2\mathrm{NH} + \mathrm{Hg^0} \rightarrow [\mathrm{Hg_3}\{\mu_2\text{-}(\mathrm{Ph_2P})_2\mathrm{N}\}_4] + 4\,\mathrm{C_6F_5H} \quad (2)$$

Since the first step in redox transmetallation/ligand exchange reactions with Nd or Er can be formulated as in Equation (3), the mercury metal produced may well be the reductant in reactions with lanthanoid metals.

$$2\,\mathrm{Ln} + 3[\mathrm{Hg(C_6F_5)_2}] \rightarrow 2[\mathrm{Ln(C_6F_5)_3}] + 3\,\mathrm{Hg^0} \quad (3)$$

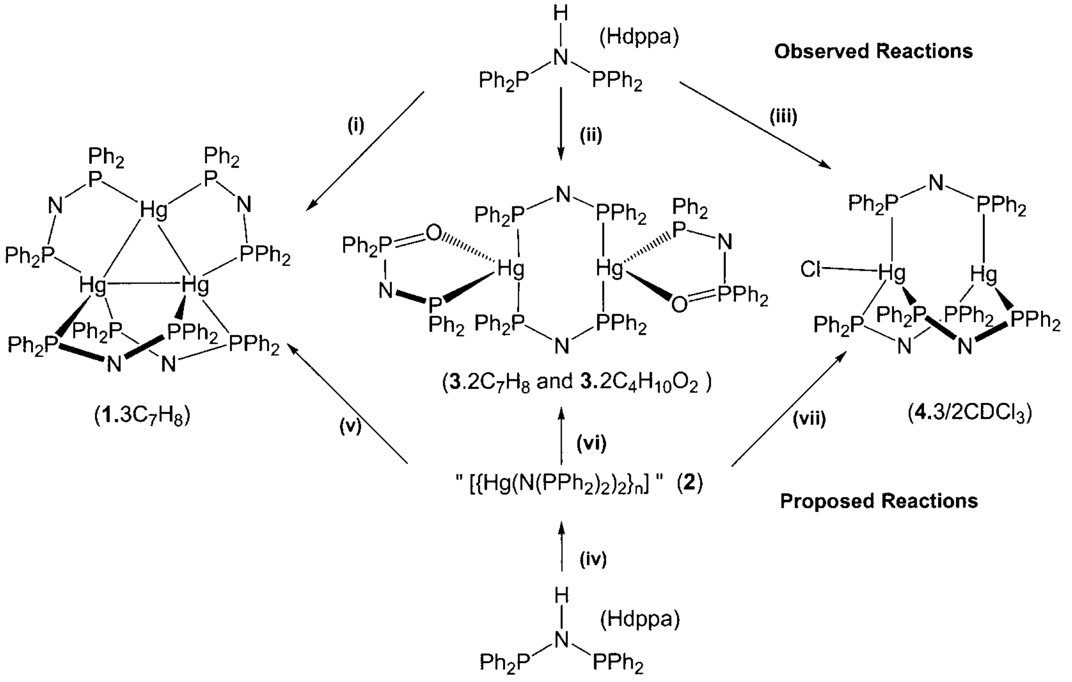
Independent attempts to prepare $[\mathrm{Ln(C_6F_5)_3}]$ by Equation (3) resulted in decomposition to $\mathrm{LnF_3}$,[9,12] by contrast with isolation of $[\mathrm{Ln(C_6F_5)_2(THF)}_n]$ (Ln = Eu, n = 5; Ln = Yb, n = 4),[13] and decomposition of such species accounts for the formation of intractable Ln/F containing precipitates in attempted reaction (1).

Although no direct reaction could be induced between Nd metal and $(\mathrm{Ph_2P})_2\mathrm{NH}$ in toluene, it was evident that the amine reacts with $\mathrm{Hg(C_6F_5)_2}$ at room temperature since an immediate orange colour developed. When this reaction was carried out on a 2:1 mole ratio, pentafluorobenzene was formed, indicative of ligand exchange. However, the expected exchange product $[\mathrm{Hg}\{(\mathrm{Ph_2P})_2\mathrm{N}\}_2]$ **2** (see iv in Scheme 1) was not isolated but instead a partly oxidised species, $[\mathrm{Hg_2}\{\mu_2\text{-}(\mathrm{Ph_2P})_2\mathrm{N}\}_2\{(\mathrm{Ph_2P})(\mathrm{OPPh_2})\mathrm{N}\}_2]\cdot 2\,\mathrm{C_7H_8}$ (**3**$\cdot 2\,\mathrm{C_7H_8}$), (Figure 2 and ii in Scheme 1), which was initially identified by X-ray crystallography.

$$2[\mathrm{Hg(C_6F_5)_2}] + 4(\mathrm{Ph_2P})_2\mathrm{NH} \xrightarrow{\mathrm{O_2}} [\mathrm{Hg_2}\{\mu_2\text{-}(\mathrm{Ph_2P})_2\mathrm{N}\}_2\{(\mathrm{Ph_2P})(\mathrm{OPPh_2})\mathrm{N}\}_2] + 4\,\mathrm{C_6F_5H} \quad (4)$$

Multiple preparations of **2** were attempted under dry anaerobic conditions but all resulted in the isolation solely of **3**$\cdot 2\,\mathrm{C_7H_8}$, which was additionally characterised by $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR, $^1\mathrm{H}$ NMR and IR spectroscopy (below). Since four phosphane sites are unaffected by oxidation, the amount of oxygen present must have been extremely small. This compound was also isolated as a DME solvate in low yield from DME washings of a similar reaction mixture involving Nd metal, and was identified by X-ray crystallography as $[\mathrm{Hg_2}\{\mu_2\text{-}(\mathrm{Ph_2P})_2\mathrm{N}\}_2\{(\mathrm{Ph_2P})(\mathrm{OPPh_2})\mathrm{N}\}_2]\cdot 2\,\mathrm{C_4H_{10}O_2}$ (**3**$\cdot 2\,\mathrm{C_4H_{10}O_2}$).

Protolysis (see iv in Scheme 1) implies that the phosphanylamine ligand is more acidic than pentafluorobenzene (pK_a = 25.6, in THF),[9,14] but this reaction is highly unexpected given that bis(pentafluorophenyl)mercury is very resistant to electrophilic attack, as evidenced by successful recrystallisation from concentrated sulphuric acid and the very slow reaction with bromine.[15] By contrast bis(pentafluorophenyl)mercury is prone to nucleophilic attack, being readily cleaved by nucleophiles, for example by $\mathrm{I^-}$ to give $[\mathrm{HgI_4}]^{2-}$ and pentafluorobenzene,[16] (see also recent isolation of a $[\mathrm{Hg(C_6F_5)_2I}]^-$ intermediate).[17] This may suggest that coordination of the neutral $(\mathrm{Ph_2P})_2\mathrm{NH}$ ligand through phosphorus provides nucleophilic assistance for



Scheme 1. (i) $Hg(C_6F_5)_2$, Er, Nd, Hg metal, toluene, 20 °C (ii) $Hg(C_6F_5)_2$, toluene, trace of O_2, 20 °C or DME extraction after (i), (iii) $Hg(C_6F_5)_2$, toluene, 20 °C, and crystallisation from $CDCl_3$ (iv) $Hg(C_6F_5)_2$ (v) Hg (vi) trace of O_2 (vii) $CHCl_3/CDCl_3$, $-(Ph_2P)_2NH$.

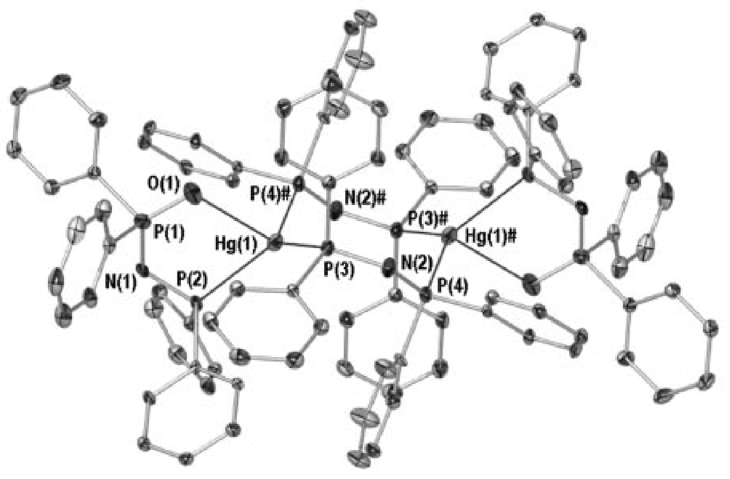


Figure 2. The crystal structure of $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_2\{(Ph_2P)(OPPh_2)N\}_2]\cdot 2C_4H_{10}O_2$ ($3\cdot 2C_4H_{10}O_2$), (POV-Ray, 40% thermal ellipsoids). All solvent molecules are removed for clarity.

protolysis by generation of partial carbanion character in the C_6F_5 group. Complexation of $Hg(C_6F_5)_2$ by phosphanes is known though the coordination is weak.[15,18] In previous studies of redox transmetallation/ligand exchange, blank reactions between $Hg(C_6F_5)_2$ and the protic ligand have failed, but no soft donor has been present to support X–H scission.[19]

In an attempt to stem the oxidation of **2** that yields **3** (see vi in Scheme 1) the preparation of **2** was attempted under even more strenuously anaerobic conditions (see Experimental Section) and spectroscopic characterisation of the initially deposited material was undertaken rapidly. Attempts to dissolve this material in C_4D_8O or C_7D_8 gave poor data, due to sparing solubility. Thus deuteriochloroform was employed, and gave NMR spectra suggesting a species with two separate ligand environments of equal resonance intensity, see below, as well as $(PPh_2)_2NH$ and the still persistent **3**. Slow evaporation of the NMR solution rendered a deep orange crystalline material suitable for X-ray structure analysis. This indicated the formation of a non-oxidised mercury(II) phosphanylamide chloride complex; $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_3Cl]\cdot 3/2CDCl_3$, $\mathbf{4}\cdot 3/2CDCl_3$ (Figure 3, iii in Scheme 1). Further crystallization from the reaction mixture filtrate gave $\mathbf{3}\cdot 2C_7H_8$.

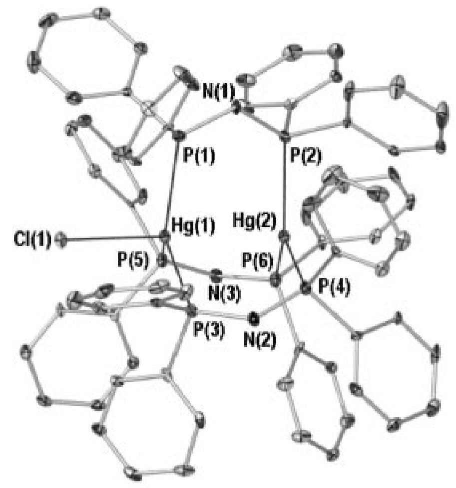


Figure 3. The crystal structure of [$Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_3Cl]\cdot 3/2CDCl_3$ (**4**·3/2$CDCl_3$), (POV-Ray 40% thermal ellipsoids). All solvent molecules removed for clarity.

X-ray Crystal Structures and Characterisation

Compound **1**·3C_7H_8 crystallises in the triclinic space group $P\bar{1}$ with three Hg metal ions and four deprotonated ligands in the asymmetric unit (Figure 1, Table1 and Table 2). The structure is a neutral homoleptic trinuclear complex with mercury atoms in a triangular array and considered to be linked by metal–metal bonds (below). This core is supported by four bridging phosphanylamide ligands. Hg(1) is coordinated by two phosphorus atoms [P(1,3)] from two ligands, while Hg(2) and Hg(3) are coordinated to three phosphorus atoms [P(2,5,7) and P(4,6,8)], respectively, from three different ligands. Including Hg–Hg bonds, Hg(2) and Hg(3) are five-coordinate and Hg(1) is four-coordinate. Different bond lengths are observed for all Hg–P contacts; these range from 2.526(2)–2.630(2) Å. Mercury to phosphorus interactions associated with Hg(2) and Hg(3) have an average length of 2.560 Å. Counterintuitively, this is smaller than to the analogous bonds of lower coordinate Hg(1) (mean 2.598 Å), as lower coordination numbers are usually associated with shorter bond lengths.[20] A similar dmpm based compound,[11] [$Hg_3(\mu\text{-dmpm})_4][O_3SCF_3]_4$, with a triangular Hg_3 cation and similar connectivity to the neutral compound **1**·3C_7H_8 has a mean Hg–P bond length of 2.539 Å. Neutrality and the increased steric bulk at phosphorus of **1**·3C_7H_8 results in lengthening of the Hg–P interactions overall. In [$Hg_3(\mu_2\text{-}(Ph_2P)_2NH)_3][O_3SCF_3]_4$,[21] a decrease in the number of ligands and the cationic nature offset lack of deprotonation leading to shorter Hg–P bond lengths (2.506–2.536 Å) than in **1**·3C_7H_8.

Overall charge neutrality indicates that the formal oxidation state of Hg in **1**·3C_7H_8 is +4/3. The Hg–Hg bond

Table 1. Selected (i) bond lengths [Å] and (ii) angles [°] for [$Hg_3\{\mu\text{-}(Ph_2P)_2N\}_4]\cdot 3C_7H_8$ (**1**·3C_7H_8).

(i)

Atoms	Bond lengths	Atoms	Bond lengths
Hg(1)–Hg(2)	2.7785(10)	Hg(1)–Hg(3)	2.8986(10)
Hg(2)–Hg(3)	3.0721(8)	Hg(1)–P(1)	2.566(2)
Hg(1)–P(3)	2.630(2)	Hg(2)–P(4)	2.571(2)
Hg(2)–P(5)	2.526(2)	Hg(2)–P(7)	2.562(2)
Hg(3)–P(2)	2.572(2)	Hg(3)–P(3)	2.573(2)
Hg(3)–P(8)	2.559(2)	P(1)–N(1)	1.606(7)
P(2)–N(1)	1.647(6)	P(3)–N(2)	1.627(7)
P(4)–N(2)	1.617(6)	P(5)–N(3)	1.620(6)
P(6)–N(3)	1.609(7)	P(7)–N(4)	1.614(7)
P(8)–N(4)	1.618(7)		

(ii)

Atoms	Angles	Atoms	Angles
Hg(2)–Hg(1)–Hg(3)	65.48(2)	Hg(1)–Hg(2)–Hg(3)	59.14(3)
Hg(1)–Hg(3)–Hg(2)	55.37(3)	P(1)–Hg(1)–Hg(2)	152.49(5)
P(3)–Hg(1)–Hg(2)	91.88(5)	P(3)–Hg(1)–Hg(3)	154.77(5)
P(1)–Hg(1)–P(3)	114.03(7)	P(4)–Hg(2)–Hg(1)	89.26(5)
P(5)–Hg(2)–Hg(1)	120.38(5)	P(7)–Hg(2)–Hg(1)	108.85(6)
P(4)–Hg(2)–Hg(3)	148.36(5)	P(5)–Hg(2)–Hg(3)	85.68(6)
P(7)–Hg(2)–Hg(3)	88.20(6)	P(4)–Hg(2)–P(5)	112.04(8)
P(4)–Hg(2)–P(7)	105.01(8)	P(5)–Hg(2)–P(7)	116.97(7)
P(2)–Hg(3)–Hg(1)	88.67(5)	P(6)–Hg(3)–Hg(1)	133.06(5)
P(8)–Hg(3)–Hg(1)	96.78(6)	P(2)–Hg(3)–Hg(2)	140.52(5)
P(6)–Hg(3)–Hg(2)	85.70(6)	P(8)–Hg(3)–Hg(2)	86.74(6)
P(2)–Hg(3)–P(6)	114.40(7)	P(2)–Hg(3)–P(8)	116.10(8)
P(6)–Hg(3)–P(8)	106.98(7)	N(1)–P(1)–Hg(1)	115.3(2)
N(1)–P(2)–Hg(3)	115.0(2)	N(2)–P(3)–Hg(1)	112.4(2)
N(2)–P(4)–Hg(2)	116.9(3)	N(3)–P(5)–Hg(2)	113.8(2)
N(3)–P(6)–Hg(3)	116.4(2)	N(4)–P(7)–Hg(2)	116.4(2)
N(4)–P(8)–Hg(3)	116.5(3)	P(1)–N(1)–P(2)	123.1(4)
P(3)–N(2)–P(4)	126.3(4)	P(5)–N(3)–P(6)	125.4(4)
P(7)–N(4)–P(8)	127.8(4)		

Table 2. Crystallographic data for compounds **1**·3 C_7H_8, **3**·2 C_7H_8,**3**·2 $C_4H_{10}O_2$ and **4**·3/2 $CDCl_3$.

	1·3 C_7H_8	**3**·2 C_7H_8	**3**·2 $C_4H_{10}O_2$	**4**·3/2 $CDCl_3$
Empirical formula	$C_{117}H_{104}Hg_3N_4P_8$	$C_{55}H_{48}Hg_1N_2O_1P_4$	$C_{52}H_{50}Hg_1N_2O_3P_4$	$C_{73.5}H_{60}Cl_{5.5}D_{1.5}Hg_2N_3P_6$
Mol. mass	2415.57	1077.42	1075.41	1770.33
Temperature (K)	123(2)	123(2)	123(2)	123(2)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	13.178(3)	12.177(2)	12.304(3)	11.653(2)
b [Å]	18.779(4)	12.605(3)	12.640(3)	13.129(3)
c [Å]	21.029(4)	16.196(3)	16.019(3)	24.457(5)
α [°]	88.38(3)	101.52(3)	101.31(3)	93.09(3)
β [°]	84.61(3)	96.07(3)	93.95(3)	98.91(3)
γ [°]	77.52(3)	101.52(3)	103.08(3)	109.27(3)
V [Å^3]	5058.5(18)	2369.6(8)	2362.8(8)	3467.1(12)
Z	2	2	2	2
$D_{calcd.}$ (g·cm^{-3})	1.586	1.510	1.512	1.694
μ (mm^{-1})	4.720	3.425	3.437	4.819
Reflections collected	24316	33655	40868	36967
Unique reflections	12336	11542	10186	16268
Parameters varied	1218	569	552	829
R(int.)	0.1257	0.0546	0.0768	0.1249
R_1	0.0618	0.0968	0.0361	0.0741
wR_2	0.0983	0.2130	0.0643	0.1267

lengths vary within the complex, the shortest being 2.7785(10) Å [Hg(1)–Hg(3)] and the longest 3.0721(8) Å [Hg(2)–Hg(3)]. The upper value is larger than the Hg–Hg bond lengths in [Hg_3(μ-dmpm)$_4$][O_3SCF_3]$_4$ (2.767(1) to 2.955(1) Å],[11] owing to the uncharged nature of **1** and greater crowding. The van der Waals radius of Hg (1.73 Å)[22] gives an upper limit of 3.46 Å for a dimercury bonding contact. Reported Hg^I–Hg^I bonds range from 2.48 to 2.60 Å,[23] while the closed shell configuration of Hg^{2+} does not favour participation in Hg^{II}–Hg^{II} bonds. Thus, the Hg–Hg bond lengths of **1**·3C_7H_8, are indicative of subvalent mercury between Hg^I and Hg^{II} oxidation states. With a $Hg^{4/3+}$ oxidation state there are two electrons in excess of the d^{10} Hg^{II} configuration. These electrons bind the trinuclear core of **1**·3 C_7H_8, and presumably occupy a molecular orbital within the triangle. For the $Hg_3{}^{4+}$ ion of [Hg_3(dppm)$_3$(SO_4)$_2$],[24a] the bonding electrons are considered to occupy a molecular orbital from overlap of the 6s orbitals of the mercury atoms.[24b,24c] The Hg–Hg distances suggest the bonding electrons are more associated with Hg(1) than Hg(2,3), and greater Hg^I character might explain the longer Hg–P bonds to Hg(1). The triangular planes described by the triphosphorus donor ensembles [P(2,6,8) and P(4,5,7)] lie roughly perpendicular [76.24(5) and 85.97(5)°, respectively] to the plane of the trinuclear core. Hg(2) resides 0.7659(14) Å out of its triphosphorus plane [P(4,5,7)] and Hg(3) 0.7168(14) Å out of the analogous plane [P(2,6,8)]. The neutral homoleptic compound **1**·3 C_7H_8 is the first crystallographically characterised triangular mercury complex of a phosphanylamide ligand. The P–N distance (1.606–1.647 Å) shows values between P–N single and double bond range as in phosphazines, (range of 1.60–1.65 Å).[25]

Examination of **1**·3 C_7H_8 by $^{31}P\{^1H\}$ NMR spectroscopy indicates three very broad signals at 130.4, 95.6 and 81.9 ppm, which are characteristic of [Hg_3(μ-dmpm)$_4$]-[O_3SCF_3]$_4$[11] but at much higher chemical shifts than observed for [Hg_3{(μ-Ph_2P)$_2$NH}$_3$][O_3SCF_3]$_4$.[21] The highest frequency resonance is attributed to the phosphorus atoms [P(1,3)] from two different ligands bound to the mercury of lowest coordination number. The next is assigned to the other two phosphorus atoms P(2,4) of these ligands, and the lowest frequency signal to P(5–8) of the two equivalent ligands linking Hg(2,3). These assignments are supported by intensities. Low solubility precluded low temperature measurements and resulted in very broad resonances, hence ^{199}Hg satellites could not be detected. The ^{1}H NMR spectrum of **1**·3 C_7H_8 shows three broad peaks situated at δ = 7.42, 6.91 and 6.81 ppm resulting from aromatic resonances associated with the ligands, as well as toluene resonances from lattice solvent. The IR spectrum of **1**·3 C_7H_8 is devoid of an N–H stretching band at 3300–3400 cm^{-1}, thus eliminating the possibility of remnant starting material or protonation of any of the coordinated ligands. Distinct bands at 1147 and 1229 cm^{-1} can be assigned as PNP stretching, which are typically found in the range of 1100 to 1300 cm^{-1}.[26] This is consistent with deprotonation of (Ph_2P)$_2$NH, resulting in delocalisation of the anionic charge across the PNP backbone. Characterisation of **1**·3 C_7H_8 by ^{199}Hg NMR spectroscopy proved unsuccessful due to insufficient solubility of this compound in suitable solvents.

Discussion of the structures of **3**·2 C_7H_8 and **3**·2 $C_4H_{10}O_2$ is centred on the latter, as it gave a more precise refinement than compound **3**·2 C_7H_8. Both contain the same complex and differ only in solvation. The crystallographic data are in Table 2 and selected bonds lengths and angles for **3**·2 $C_4H_{10}O_2$ in Table 3, whilst geometric values for **3**·2 C_7H_8 have been deposited.

Compound **3**·2 $C_4H_{10}O_2$ crystallises as a centrosymmetric dimer (triclinic, space group $P\bar{1}$) and consists of two mercury atoms bridged by two unoxidised phosphanylamide ligands. The metal coordination is completed by two terminal [(Ph_2P)($OPPh_2$)N]$^-$ ligands which are *transoid* across the centre of symmetry (Figure 2). The Hg atom resides

Table 3. Selected (i) bond lengths [Å] and (ii) angles [°] for $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_2\{(Ph_2P)(OPPh_2)N\}_2]\cdot 2C_4H_{10}O_2$ (**3**·$2C_4H_{10}O_2$).

(i)

Atoms	Bond lengths	Atoms	Bond lengths
Hg(1)–P(2)	2.5242(12)	Hg(1)–P(3)	2.4953(12)
Hg(1)–P(4#)	2.5123(12)	Hg(1)–O(1)	2.624(3)
P(1)–N(1)	1.513(3)	P(1)–O(1)	1.513(3)
P(2)–N(1)	1.618(3)	P(3)–N(2)	1.598(3)
P(4#)–P(2)	1.609(3)		

(ii)

Atoms	Angles	Atoms	Angles
P(2)–Hg(1)–P(3)	126.10(4)	P(2)–Hg(1)–P(4#)	109.37(4)
P(3)–Hg(1)–P(4#)	124.14(3)	P(2)–Hg(1)–O(1)	76.55(6)
P(3)–Hg(1)–O(1)	94.04(6)	P(4#)–Hg(1)–O(1)	105.34(7)
P(1)–N(1)–P(2)	121.55(19)	P(3)–N(2)–P(4)	133.1(2)
N(1)–P(2)–Hg(1)	108.91(12)	N(2)–P(3)–Hg(1)	118.52(12)
N(2#)–P(4#)–Hg(1)	117.41(12)	P(1)–O(1)–Hg(1)	111.96(13)
O(1)–P(1)–N(1)	118.10(15)		

Symmetry transformation used to generate # atoms $-x + 1$, $-y + 1$, $-z + 1$.

0.0893(15) Å out of the plane defined by the three associated P atoms with the O atom in an apical position completing four coordination. Thus, the geometry of mercury is best described as a distorted triangular-based pyramid [P(3)–Hg(1)–P(4*) 124.14(3)°, P(3)–Hg(1)–P(2) 126.10(4)°, P(4*)–Hg(1)–P(2) 109.37(4)°]. Unlike **1**·$3C_7H_8$, the Hg···Hg distance in **3**·$2C_4H_{10}O_2$ of 4.487(2) Å is well outside the sum of the van der Waals radii (3.46 Å).[22]

Comparison with the structure of $[Hg\{(OPPh_2)NPPh_2\}_2]$, which has two chelating diphenylphosphanyl(diphenylphosphoryl)amide ligands, shows this has much shorter Hg–P distances, 2.4042(7) Å, but longer Hg–O lengths, 2.7135(15) Å.[27] This arises from the different stereochemistry (square planar) which is skewed towards two short and two long bonds in accordance with the preference of mercury for digonal two coordination.[23,28] Similarly Hg–P distances in the dinuclear phosphanylamine complex $[Hg_2\{\mu\text{-}(Ph_2P)_2NH\}_2(O_3SCF_3)_4]$ are short [2.421(1)–2.426(1) Å] with longer Hg–O bond lengths [2.679(4)–2.893(5) Å],[27] again owing to the tendency of mercury to have two short colinear bonds. This factor is not in evidence in **3**·$2C_7H_8$ and **3**·$2C_4H_{10}O_2$ with the three soft P and one hard O donors giving rise to the trigonal pyramidal geometry.

The $^{31}P\{^1H\}$ NMR spectrum of bulk **3**·$2C_7H_8$ exhibits three broad resonances at δ = 60.1, 28.3 and 12.4 ppm with intensities in approximately a 2:4:2 ratio, corresponding to the three types of phosphorus atoms in the structure. The oxidised phosphorus P(1) should resonate at the highest chemical shift, since P^V centres are more deshielded than P^{III} centres. The ^{31}P resonance of the P=O group in the free (protonated) ligand, $(Ph_2P)(OPPh_2)NH$ occurs at δ = 21.4 ppm,[29] and the large shift of P(1) (60.1 ppm) can be attributed to chelation as observed for other phosphorus based systems that have five membered chelate rings.[30] The larger intensity indicates the middle resonance should be assigned to the four bridging phosphorus atoms [P(3,4,3#,4#)]. This leaves the remaining resonance to be assigned to P(2) (δ =12.4 ppm). The ^1H NMR spectrum of **3**·$2C_7H_8$ is unremarkable, while the IR spectrum exhibits a band at 1128 cm^{-1} characteristic of an *O*-coordinated phosphoryl group.[31] Other characteristic features include bands at 1228 and 1148 cm^{-1} attributed to P=N stretching.[26]

The structure of **4**·3/2 $CDCl_3$ (Figure 3) consists of two mercury atoms bridged by three phosphanylamide ligands with a chloride coordinated to Hg(1). Each mercury is coordinated by three phosphorus atoms, Hg(1) being four coordinate and Hg(2) three coordinate. The latter has an average Hg–P bond length of 2.482 Å and four coordinate Hg(1) has an average Hg–P bond length of 2.593 Å (Table 4). This is consistent with the higher coordination of Hg(1). The Hg(1)–Cl(1) terminal bond length in **4**·3/2 $CDCl_3$, 2.624(2) Å, is considerably extended relative to those in $[HgCl_4]^{2-}$ complexes, which possess an average Hg–Cl bond length of 2.472 Å,[32] but well inside the sum (3.58 Å) of the van der Waals radii of Hg and Cl. In $[Hg_2(\mu\text{-}dppm)_2(\mu\text{-}Cl)Cl_2][Cl]\cdot H_2O$[33] which has a somewhat similar structural core to **4**·3/2 $CDCl_3$, the mean terminal Hg–Cl bond length is 2.587 Å, similar to that of **4**·3/2 $CDCl_3$.

The HgP_3 geometry of Hg(1) and Hg(2) can be considered equilateral triangular with all P–Hg–P angles close to 120° (Table 4). Hg(1) is 0.3280 (14) Å out of the P(1,3,5) plane, *exo* to the Hg···Hg vector. The chloride ligand lies perpendicular to this plane. Overall the stereochemistry for Hg(1) is trigonal pyramidal. Hg(2) is 0.1260(13) Å out of the analogous P(2,4,6) plane being *endo* to the Hg···Hg vector and has triangular geometry. The two triphosphorus donor P(1,3,5) and P(2,4,6) ensembles are very close to coplanar with an interplanar angle of 0.68(3)°. Although the Hg···Hg distance [3.0042(7) Å] is well within two van der Waals radii (3.46 Å),[22] this does not indicate the presence of a mercury–mercury bond as there are no valence electrons available for bonding, unless some electron density is transmitted from the *trans* Hg–Cl bond. A closer non-bonding Hg···Hg contact has been reported in $[Hg_2(1,8\text{-}C_{10}H_6)_2]$ [2.797(1) Å],[34] whilst Hg···Hg [3.2805(7) Å] of $[Hg_2\{\mu\text{-}(Ph_2P)_2NH\}_2(O_3SCF_3)_4]$ is not considered bonding.[27] It has been claimed on the basis of a low frequency

Table 4. Selected (i) bond lengths [Å] and (ii) angles [°] for $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_3Cl]\cdot 3/2\,CDCl_3$ (**4**·3/2 $CDCl_3$).

(i)

Atoms	Bond lengths	Atoms	Bond lengths
Hg(1)–Hg(2)	3.0042(7)	Hg(1)–Cl(1)	2.624(2)
Hg(1)–P(1)	2.599(3)	Hg(1)–P(3)	2.583(3)
Hg(1)–P(5)	2.599(2)	Hg(2)–P(2)	2.483(3)
Hg(2)–P(4)	2.464(3)	Hg(2)–P(6)	2.468(3)
P(1)–N(1)	1.635(7)	P(2)–N(1)	1.618(7)
P(3)–N(2)	1.607(7)	P(4)–N(2)	1.605(7)
P(5)–N(3)	1.624(7)	P(6)–N(3)	1.612(8)

(ii)

Atoms	Angles	Atoms	Angles
P(1)–Hg(1)–Hg(2)	84.67(6)	P(3)–Hg(1)–Hg(2)	81.55(6)
P(5)–Hg(1)–Hg(2)	82.01(6)	Cl(1)–Hg(1)–Hg(2)	177.86(6)
P(1)–Hg(1)–Cl(1)	96.85(8)	P(3)–Hg(1)–Cl(1)	96.38(8)
P(5)–Hg(1)–Cl(1)	98.59(8)	P(1)–Hg(1)–P(3)	119.44(8)
P(1)–Hg(1)–P(5)	117.24(9)	P(3)–Hg(1)–P(5)	118.59(9)
P(2)–Hg(2)–Hg(1)	90.49(6)	P(4)–Hg(2)–Hg(1)	94.30(6)
P(6)–Hg(2)–Hg(1)	93.87(6)	P(2)–Hg(2)–P(4)	121.33(9)
P(2)–Hg(2)–P(6)	115.63(9)	P(4)–Hg(2)–P(6)	122.27(10)
N(1)–P(1)–Hg(1)	119.3(3)	N(1)–P(2)–Hg(2)	116.7(3)
N(2)–P(3)–Hg(1)	120.7(3)	N(2)–P(4)–Hg(2)	111.5(3)
N(3)–P(5)–Hg(1)	122.0(3)	N(3)–P(6)–Hg(2)	114.1(3)

Raman absorption (46 to 48 cm^{-1}) assigned to ν(Hg–Hg) that there is a weak mercury–mercury bond in $[Hg_2(\mu\text{-}dppm)_2(\mu\text{-}Cl)Cl_2][Cl]\cdot H_2O$, where the separation is 3.343(3) Å.[33] We find this difficult to sustain for an $Hg^{II}\cdots Hg^{II}$ interaction, unless electron density is transmitted from Hg–Cl bonds.

The crude product from which crystals of **4**·3/2 $CDCl_3$ were obtained was characterised by $^{31}P\{^1H\}$ NMR and ^1H NMR spectroscopy. Two equal intensity and very broadened resonances in the $^{31}P\{^1H\}$ NMR spectrum at δ = 71.0 and 37.2 ppm, can be assigned to P(2,4,6) on the lower coordinate mercury and P(1,3,5) of **4** respectively. There is also a resonance at δ = 45.8 ppm attributable to (protonated) $(Ph_2P)_2NH$,[5] in the appropriate ratio to **4** consistent with the formation of **4**·3/2 $CDCl_3$ by protolysis/deuterolysis (see vii in Scheme 1). The ^1H NMR spectrum of the crude product displays solely the expected protons from phenyl groups (7.8 to 6.9 ppm) and a resonance attributable to the amine proton of $(Ph_2P)_2NH$ (δ = 3.1 ppm).

Conclusions

The attempted synthesis of homoleptic lanthanoid chelating phosphanylamide complexes by redox transmetallation/ligand exchange, gave instead the unusual subvalent mercury compound **1**·3 C_7H_8, attributable to formation of intermediate $[Hg\{(Ph_2P)_2N\}_2]$ **2** followed by reduction by mercury metal. Consistent with this, reaction of $Hg(C_6F_5)_2$ with $(Ph_2P)_2NH$ in the presence of mercury metal provided a higher yielding route to **1**·3 C_7H_8. Attempted preparation of **2** yielded **3**·2 C_7H_8 and **3**·2 $C_4H_{10}O_2$ containing hemi-oxidised phosphanylamide as well as the unoxidised phosphanylamide ligands.

Experimental Section

Mercury complexes, lanthanoid metal filings and the phosphanylamine ligand were handled and stored under purified nitrogen (activated BASF R3/11 copper oxide "catalyst" and 4-Å molecular sieves). Toluene, tetrahydrofuran, 1,2-dimethoxyethane and hexane were pre-dried with sodium wire and then distilled from sodium benzophenone under purified nitrogen. The reagents $Hg(C_6F_5)_2$ and $(Ph_2P)_2NH$ were prepared as reported.[35] The former was recrystallised from hot methanol/water, followed by drying under reduced pressure for several hours. The latter was shown free of P=O species by ^{31}P NMR spectroscopy. $^{31}P\{^1H\}$, ^{19}F and ^1H nuclear magnetic resonance (NMR) spectra were recorded with a Bruker AC 300 spectrometer. ^{199}Hg NMR could not be recorded due to the low solubility of the mercury compounds. Deuterated solvents (C_6D_6 and C_4D_8O) were dried with calcium hydride (powdered) for 24 h. Deuterated $CDCl_3$ was dried with 4-Å molecular sieves. All dried deuterated solvents were degassed by three cycles of freezing, evacuating, and backfilling with nitrogen and thawing and were then vacuum transferred and stored under nitrogen. Infrared spectra (4000–650 cm^{-1}) of Nujol mulls (prepared in a drybox) were recorded with a Perkin–Elmer 1600 Fourier transform infrared spectrometer. Melting points were determined in sealed glass capillaries under nitrogen. Elemental analyses were by the Campbell Microanalytical Laboratory, University of Otago, New Zealand. The complicated isolation/preparation and solvation of **4**·3/2 $CDCl_3$ frustrated all attempts to obtain satisfactory elemental analyses.

$[Hg_3\{\mu_2\text{-}(Ph_2P)_2N\}_4]\cdot 3\,C_7H_8$(1·3 C_7H_8).Method1: Bis(diphenylphosphanyl)amine (1.01 g, 2.56 mmol) and $Hg(C_6F_5)_2$ (0.68 g, 1.28 mmol) were dissolved in toluene (40 mL). Nd metal (1.23 g, 8.5 mmol) was added and the mixture was stirred at 80 °C for 96 h. The resulting suspension was filtered through a cannula and a light green/blue precipitate remained. This was subsequently washed with 2 × 10 mL of toluene. The orange-coloured solution was then evaporated under reduced pressure to yield a bright orange solid. Dissolution in a mixture of toluene (15 mL) and hexane (5 mL) and concentration to 5 mL gave single rectangular orange crystals. These were filtered off, washed with hexane (5 mL) and dried in vacuo giving $[Hg_3\{\mu_2\text{-}(Ph_2P)_2N\}_4]\cdot 3C_7H_8$ (**1**$\cdot 3C_7H_8$). Yield 0.70 g (26%), and the crystals were used for the structure determination. EDAX analysis of the green/blue precipitate detected C, F, O, Nd, P and no Hg.

Method 2: A suspension of bis(diphenylphosphanyl)amine (0.10 g, 0.25 mmol), $Hg(C_6F_5)_2$ (0.07 g, 0.13 mmol) and Er metal (0.14 g, 0.85 mmol) in toluene (30 mL) was stirred for 15 d at room temperature. The resulting suspension was filtered through a cannula and a yellow/blue precipitate remained. The orange filtrate was evaporated under reduced pressure to yield a bright orange solid. Crystallisation from toluene/hexane gave a few orange crystals which were identified by X-ray crystallography as $[Hg_3\{\mu_2\text{-}(Ph_2P)_2N\}_4]\cdot 3C_7H_8$ (**1**$\cdot 3C_7H_8$). Yield 0.068g (22%), m.p. 253 °C. Unit cell data: a = 13.17, b = 18.79, c = 21.04 Å, α= 88.43, β= 84.61, γ= 77.52°. V = 5063.83 Å^3. $^{31}P\{^1H\}$ NMR (C_7H_8, 25 °C): δ = 80.5 (br. s, 4 P), 95.8 (br. s, 2 P), 130.1 (br. s, 2 P) ppm. The IR spectrum was in agreement with that of the analytically pure sample (Method 3).

Method 3: To bis(diphenylphosphanyl)amine (0.31 g, 0.80 mmol) dissolved in toluene (40 mL) was added $Hg(C_6F_5)_2$ (0.21 g, 0.40 mmol) and the solution turned yellow. Two drops of liquid mercury were added. The solution became bright orange, was left at room temperature overnight under nitrogen and filtered. The solvent was evaporated to 20 mL and left to crystallise, yielding **1**$\cdot 3C_7H_8$ (0.69 g, 80%). M.p. 250–252 °C. Unit cell data: a = 13.15, b = 18.76, c = 21.06 Å, α= 88.40, β= 84.61, γ= 77.53°. V = 5064.53 Å^3. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 2.11 (s, 9 H, *Me*Ph), 6.83–6.89 (m, 15 H, *Ph*Me), 6.81 [br. m, 16 H, *p*-H (PhP)], 6.91 [br. m, 32 H, *m*-H (PhP)], 7.42 [br. m, 32 H, *o*-H (PhP)] ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ = 81.9 (br. s, 4 P, P5,6,7,8), 95.6 (br. s, 2 P, P2,4), 130.4 (br. s, 2 P, P1,3) ppm. IR (Nujol): $\tilde{\nu}$ = 3020 m, 1229 s, 1147 s, 1098 m, 1025 w, 950 w, 755 m, 697 s cm^{-1}. $C_{117}H_{104}Hg_3N_4P_8$ (2415.57): calcd. C 58.17, H 4.34, N 2.32; found C 57.95, H 4.86, N 2.95.

$[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_2\{(Ph_2P)(OPPh_2)N\}_2]\cdot 2C_7H_8$ (3$\cdot 2C_7H_8$): To bis(diphenylphosphanyl)amine (0.31 g, 0.80 mmol) dissolved in toluene (50 mL) was added $Hg(C_6F_5)_2$ (0.21 g, 0.40 mmol) and the solution turned yellow. After 1 h the yellow solution became bright orange and was left at room temperature overnight under nitrogen. Yellow crystals formed and were filtered from the mother liquor and characterised by X-ray crystallography as $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_2\{(Ph_2P)(OPPh_2)N\}_2]\cdot 2C_7H_8$ (**3**$\cdot 2C_7H_8$). Yield 0.60 g (77%). M.p. 242–245 °C. ^1H NMR (300 MHz, C_4D_8O, 25 °C): δ = 2.04 (s, 6 H, *Me*Ph), 6.8–8.2 (m , 90 H, PhP and *Ph*Me) ppm. $^{31}P\{^1H\}$ NMR (C_4D_8O, 25 °C): δ = 12.4 (s, 2 P, Hg–P chelating) 28.3 (s, 4 P, Hg–P bridging) 60.1 (s, 2 P, PO) ppm. IR (Nujol): $\tilde{\nu}$ = 3055 w, 1228 br. s, 1178 w, 1149 m, 1128 m, 1101 m, 1080 m, 1063 m, 1026 m, 998 m, 793 s, 731 m, 694 vs cm^{-1}. $C_{110}H_{96}Hg_2N_4O_2P_8$ (2154.9): calcd. C 61.31, H 4.49, N 2.60; found C 60.60, H 4.65, N 2.84. The presence of C_6F_5H in the filtrate was established by ^{19}F NMR spectroscopy.[36]

$[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_2\{(Ph_2P)(OPPh_2)N\}_2]\cdot 2C_4H_{10}O_2$ (3$\cdot 2C_4H_{10}O_2$): Bis(diphenylphosphanyl)amine (0.10 g, 0.26 mmol) and $Hg(C_6F_5)_2$ (68 mg, 0.13 mmol) were dissolved in toluene (30 mL). Nd metal (12 mg, 0.09 mmol) was added and the mixture sonicated for 4 d. The resulting suspension was filtered through a cannula and a light green/blue precipitate remained. Evaporation of the filtrate yielded a bright orange solid, which on crystallisation from toluene/hexane gave single crystals, which were unsatisfactory for X-ray diffraction. The precipitate was washed with 1,2-dimethoxyethane (20 mL) which on partial evaporation deposited single crystals of $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_2\{(Ph_2P)(OPPh_2)N\}_2]\cdot 2C_4H_{10}O_2$ (**3**$\cdot 2C_4H_{10}O_2$). Yield 0.04 g (16%). IR (Nujol): $\tilde{\nu}$ = 1230 s, 1149 m, 1128 m, 1101 m, 1080 m, 983 w, 939 m, 830 w, 780 w-m, 754 m-s, 698 s, 668 s, 648 w cm^{-1}.

$[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_3Cl]\cdot 3/2CDCl_3$ (4$\cdot 3/2CDCl_3$): Solid bis(diphenylphosphanyl)amine (0.39 g, 1.0 mmol) and $Hg(C_6F_5)_2$ (0.27 g, 0.50 mmol) were mixed in the dry box (O_2 < 0.1 ppm) whereupon onset of reaction was indicated by a developing yellow colour. After connection to a vacuum/N_2 line with a recently regenerated purification train, addition of toluene (50 mL) gave a yellow solution which intensified to orange in 10 min. After 24 h an orange solid deposited, m.p. 205–208 °C. IR (Nujol): $\tilde{\nu}$ = 3034 w, 1495 m, 1164 s, 1097 m, 1025 s, 998 s, 769 s, 727 s, 692 s, 525 w cm^{-1}. This material when dissolved in $CDCl_3$ was shown to be a mixture of **3**, **4** and $(Ph_2P)_2NH$ by $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 15.7 (s, 2 P, Hg–P chelating of 3), 26.7 (s, 4 P, Hg–P bridging of 3), 37.2 (br. m, 3 P, P1,3,5 of **4**) 45.8 [s, $(Ph_2P)_2NH$], 64.0 (m, 2 P, PO of **3**), 71.03 (br. m, 3 P, P2,4,6 of **4**), together with further minor impurity signals. Single crystals formed in the $CDCl_3$ solution and were identified by X-ray crystallography as **4**$\cdot 3/2CDCl_3$. The mother liquor was evaporated to 5 mL. The resulting orange precipitate was dissolved on gentle heating and slow cooling deposited crystals of **3**$\cdot 2C_7H_8$ (unit cell data a = 12.19, b = 12.61, c = 16.19 Å, α= 101.53, β= 96.07, γ= 101.52°, V = 2370.3 Å^3).

X-ray Crystallography: Crystalline samples of compounds $[Hg_3\{\mu\text{-}(Ph_2P)_2N\}_4]\cdot 3C_7H_8$ (**1**$\cdot 3C_7H_8$), $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_2\{(Ph_2P)(OPPh_2)N\}_2]\cdot 2C_7H_8$ (**3**$\cdot 2C_7H_8$), $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_2\{(Ph_2P)(OPPh_2)N\}_2]\cdot 2C_4H_{10}O_2$ (**3**$\cdot 2C_4H_{10}O_2$), and $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_3Cl]\cdot 3/2CDCl_3$ (**4**$\cdot 3/2CDCl_3$) were mounted on glass fibres, in viscous hydrocarbon oil. Crystal data were obtained using an Enraf–NoniusKappa CCD at –150 °C (123 K). X-ray data were processed using the DENZO program.[37] Structural solution and refinement was carried out using the SHELX suite of programs[38,39] with the graphical interface X-Seed.[40] All hydrogen atoms were placed in calculated positions using the riding model.

CCDC-241398 (for **1**$\cdot 3C_7H_8$), CCDC-241399 (for **3**$\cdot 2C_4H_{10}O_2$), CCDC-241400 (for **3**$\cdot 2C_7H_8$) and CCDC-241401 (for **4**$\cdot 3/2CDCl_3$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound $[Hg_3\{\mu\text{-}(Ph_2P)_2N\}_4]\cdot 3C_7H_8$ (1$\cdot 3C_7H_8$): For compound $[Hg_3\{\mu\text{-}(Ph_2P)_2N\}_4]\cdot 3C_7H_8$ (**1**$\cdot 3C_7H_8$), one toluene molecule of solvation was disordered "tip-to-toe" over two sites of partial occupancy. These were satisfactorily modelled with half occupancy. No hydrogen atoms were appended to this disordered molecule and an ISOR 0.01 refinement was used to obtain satisfactory thermal parameters for atoms C(112), C(114), C(118) and C(120).

Compound $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_2\{(Ph_2P)(OPPh_2)N\}_2]\cdot 2C_7H_8$ (3$\cdot 2C_7H_8$): For compound $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_2\{(Ph_2P)(OPPh_2)N\}_2]\cdot 2C_7H_8$ (**3**$\cdot 2C_7H_8$), the poor R_1 value (see Table 2) can be attributed to a peak of residual electron density (20.086) located 0.829 Å from Hg(1). Incorporation of this density led to extension of the Hg(1)–O(1) and Hg(1)–P(2) bonds (lesser occupancy relative to greater Hg(1) occupancy) of greater than 0.16 and 0.80 Å, respectively. Accordingly, the disorder was not modelled.

Compound $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_2\{(Ph_2P)(OPPh_2)N\}_2]\cdot 2C_4H_{10}O_2$ (3$\cdot 2C_4H_{10}O_2$): For compound $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_2\{(Ph_2P)(OPPh_2)N\}_2]\cdot 2C_4H_{10}O_2$ (**3**$\cdot 2C_4H_{10}O_2$), a peak of residual electron density (3.97) is located 0.882 Å from Hg(1). Modelling of this electron density as a partial Hg occupancy led to extension of the original

Hg(1)–O(1) and Hg(1)–P(2) bonds, new occupancy less relative to Hg(1) of greater than 0.12 and 0.8 Å, respectively. Accordingly, the disorder was not modelled.

Compound $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_3Cl]\cdot 3/2\,CDCl_3$ ($\mathbf{4}\cdot 3/2\,CDCl_3$): For compound $[Hg_2\{\mu_2\text{-}(Ph_2P)_2N\}_3Cl]\cdot 3/2\,CDCl_3$ ($\mathbf{4}\cdot 3/2\,CDCl_3$), ISOR 0.01 refinement was required for atoms C(25), C(55) and N(1) in order to obtain satisfactory thermal parameters. Due to computational constraints the deuterium atoms of the lattice solvent were refined as hydrogen.

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