

## NEW MERCURY(II) COMPLEXES OF POLYDENTATE LIGANDS

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**ABSTRACT.** The mercury(II) complexes  $[\text{Hg}(\text{SCN})_2\{\text{PPh}[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\}_2]$  (**1**) and  $[\text{2,6-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{Se}][\text{HgCl}_3]$  (**3**) were prepared and structurally characterized in solution by multinuclear NMR and ESI mass spectrometry. The reactions performed to obtain the complex  $[\text{2,6-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{SeHgCl}]$  (**2**) failed and we could isolate only a mixture of **3** and  $[(\text{HgCl}_2)_3\{\text{2,6-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}]$  (**4**). Compounds **1** and **4** were characterized by single-crystal X-ray diffraction.

**Keywords:** mercury(II) complexes, triarylphosphane, organoselenium ligand; intramolecular coordination; solution behavior, solid state structure.

### INTRODUCTION

The necessity to obtain metal complexes with a better thermal and hydrolytic stability and significantly improved specific activity for catalytic or biological applications determined a permanently increased interest for new ligands, capable to stabilize both main group and transition metals. Various organic groups capable to act as *C,N*-chelating moieties towards phosphorus or chalcogens were used in order to design new ligands bearing both *hard* (N) and *soft* (P or chalcogen) donor atoms in their molecules, thus providing the appropriate conditions for *P,N*- or *E,N*-coordination (E = S, Se, Te) to metal centers [1,2]. Such species include bulky phosphanes, e.g.  $\text{PPh}_x[\text{C}_6\text{H}_4(\text{CH}(\text{R})\text{NR}'_2)_2]_{3-x}$  (R = H, Me, R' = Me, x = 0 – 2 [3-7], R = H, R' = Et [8]),  $\text{PPh}_x[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}]_{3-x}$  (x = 0, 2) [9] or diphosphanes, e.g.  $\text{2,6-(PR}_2\text{CH}_2)_2\text{py}$  (R = <sup>t</sup>Bu, Ph, py = pyridine) [10] and diorganochalcogenides, e.g.  $[\text{2-(R}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{E}$  (E = Se, Te) [11],  $[\text{2-(Me}_2\text{NCH}_2)\text{C}_6\text{H}_4][\text{Me}_2\text{C}(\text{OH})\text{CH}_2]\text{E}$  (E = S, Se, Te) [12].

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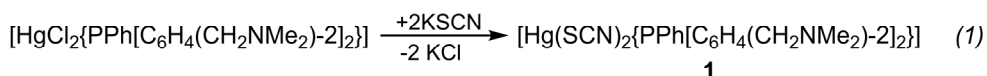
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During the last years we reported several group 12 metal complexes stabilized by *P,N*-chelating ligands, e.g.  $[\text{MCl}_2(\text{PPh}_x\text{R}_{3-x})]$  [ $\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$ ,  $\text{R} = 2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$ ,  $x = 0 - 3$ ] [13], organoselenolato groups, e.g.  $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\text{Se}]_2\text{M}$  ( $\text{M} = \text{Zn}, \text{Cd}$ ) [14] or by ligands of type  $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4][\text{Me}_2\text{C}(\text{OH})\text{CH}_2]\text{E}$  ( $\text{E} = \text{S}, \text{Se}$ ) [15]. As a continuation of our work, we report here about the new mercury(II) complexes  $[\text{Hg}(\text{SCN})_2\{\text{PPh}[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\}_2]$  (**1**) and  $[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{Se}][\text{HgCl}_3]$  (**3**). Our attempts to synthesize the complex  $[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{SeHgCl}]$  (**2**), as well as the crystal and molecular structure of the serendipitously obtained  $[(\text{HgCl}_2)_3\{2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}]$  (**4**) are also discussed.

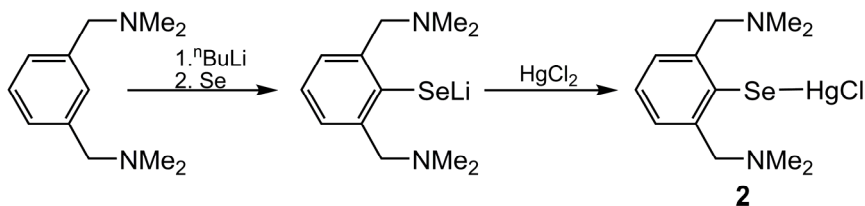
## RESULTS AND DISCUSSION

### Synthesis and solution behavior

The complex  $[\text{Hg}(\text{SCN})_2\{\text{PPh}[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\}_2]$  (**1**) was obtained by reacting  $[\text{HgCl}_2\{\text{PPh}[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\}_2]$  and KSCN in a 1:2 molar ratio, using a mixture of solvents ( $\text{CH}_2\text{Cl}_2$  and methanol), as depicted in equation 1.



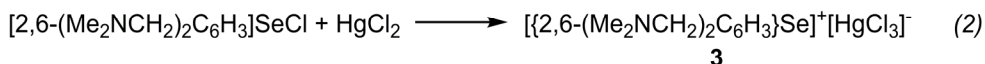
For the synthesis of the complex  $[\text{HgCl}\{\text{SeC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}\}]$  (**2**) we employed a multistep procedure based on the lithiation of 1,3- $(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_4$ , insertion of selenium into the newly formed C–Li bond and subsequent reaction of the lithium organoselenolate with  $\text{HgCl}_2$  in a 1:1 molar ratio, as displayed in Scheme 1.



Scheme 1

Instead of the desired product **2**, we obtained a yellowish solid which is only poorly soluble in chlorinated organic solvents. The multinuclear NMR spectra of this solid, recorded in  $\text{DMSO}-d_6$ , revealed a mixture containing  $[\{2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{Se}][\text{HgCl}_3]$  (**3**) and  $[(\text{HgCl}_2)_3\{2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}]$  (**4**). Recrystallization of the obtained solid resulted in a mixture of crystals

and we could separate only mechanically crystals of the two species. We succeeded to prepare compound **3** by reacting [2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Se]Cl with HgCl<sub>2</sub> in a 1:1 molar ratio (eq. 2).



The isolated compound **1** and compound **3** obtained in eq. 2, as well as the mixture of **3** and **4**, isolated as a product obtained after performing the reactions in Scheme 1, were characterized in solution by multinuclear NMR. The <sup>1</sup>H NMR spectrum of compound **1** shows in the aliphatic region a broad singlet and an AB spin system, which were assigned to the N(CH<sub>3</sub>)<sub>2</sub> and the CH<sub>2</sub>N protons, respectively, thus suggesting an intramolecular coordination, either N→P or N→Hg. Anyway, the <sup>1</sup>H NMR spectrum shows that the two aryl groups with pendant arms are equivalent in solution, at room temperature. In the aromatic region were observed multiplet resonances for the expected non-equivalent protons in the phenyl and the C<sub>6</sub>H<sub>4</sub> groups, with multiplicity determined by <sup>1</sup>H-<sup>1</sup>H and <sup>31</sup>P-<sup>1</sup>H couplings. The <sup>31</sup>P and the <sup>199</sup>Hg NMR spectra of **1** are consistent with the coordination of phosphorus to Hg(II). They appear as a singlet accompanied by <sup>199</sup>Hg satellites and a doublet, respectively, with very close values of the observed <sup>31</sup>P-<sup>199</sup>Hg coupling constants (6200 and 6211 Hz, respectively).

The <sup>1</sup>H NMR spectrum of compound **3** shows two singlet resonances in the aliphatic region for the N(CH<sub>3</sub>)<sub>2</sub> and the CH<sub>2</sub>N protons, respectively, thus suggesting the equivalence of the two pendant arms of the 2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> group. The aliphatic region suggests either no N→Se or N→Hg intramolecular coordination or a dynamic behaviour based on decoordination, inversion at nitrogen and re-coordination, too fast to be observed at room temperature [16]. In the aromatic region of the spectrum are displayed multiplet resonances for the three non-equivalent protons in the C<sub>6</sub>H<sub>3</sub> group. The <sup>77</sup>Se and the <sup>199</sup>Hg NMR spectra of **3** show singlet resonances at 1185 ppm and at -1353 ppm, respectively. These values are consistent with an ionic structure in solution, containing [{2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Se}]<sup>+</sup> cations and [HgCl<sub>3</sub>]<sup>-</sup> anions. The ESI+ and the ESI- mass spectra of this species contain peaks of high intensity at *m/z* 271.07133 (100%) and at 306.87647 (100%), with a characteristic pattern for the [{2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Se}]<sup>+</sup> cation and the [HgCl<sub>3</sub>]<sup>-</sup> anion, respectively, thus suggesting the formation of the ionic species **3**.

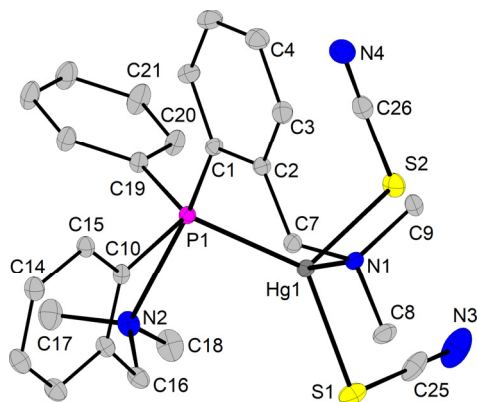
The formation of compound **4** is supported by mass spectrometry. The ESI+ spectrum of the mixture obtained as depicted in Scheme 1 shows,

besides the peaks at  $m/z$  271.07133 (77%) and at 306.87647 (92%), another one at  $m/z$  193.17054 (36%), corresponding to the cation  $[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3 + \text{H}]^+$ .

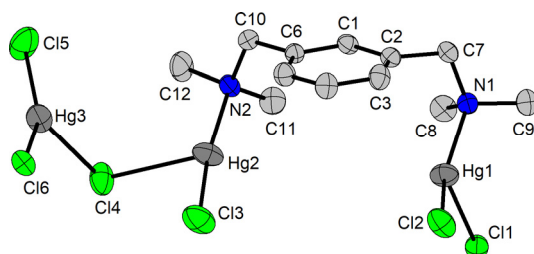
We suppose that the formation of these species, instead of the desired product **2**, was determined by incomplete lithiation of 2,6-( $\text{Me}_2\text{NCH}_2$ ) $_2\text{C}_6\text{H}_4$ , followed by secondary reactions between the species present in solution. Unfortunately, at this moment we don't have a certain reaction mechanism for the whole process which lead to the mixture of **3** and **4**. We can only have a certain explanation for the formation of **4** in the reaction between not lithiated 2,6-( $\text{Me}_2\text{NCH}_2$ ) $_2\text{C}_6\text{H}_4$  and  $\text{HgCl}_2$  in a 1:3 molar ratio.

### Single-crystal X-ray diffraction studies

The ORTEP-like diagram of **1** and **4** with the atom numbering schemes are depicted in Figure 1 and Figure 2, respectively, while selected interatomic distances and angles for the two compounds are given in Table 1.



**Figure 1.** Thermal ellipsoids representation at 30% probability and atom numbering scheme of  $\text{C}_{20}\text{H}_{28}\text{N}_3\text{P}\text{Hg}$ -**1**. Hydrogen atoms are omitted for clarity.



**Figure 2.** Thermal ellipsoids representation at 30% probability and atom numbering scheme of **4**. Hydrogen atoms are omitted for clarity.

**Table 1.** Selected interatomic distances [Å] and angles [°] in **1** and **4**

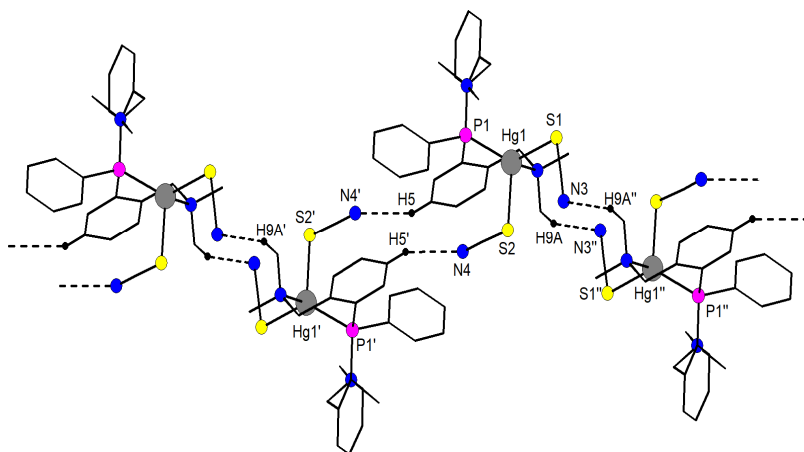
<b>1</b>			
Hg1–P1	2.4602(4)	N1–Hg1–S1	99.78(3)
Hg1–S1	2.5012(5)	N1–Hg1–S2	102.34(3)
Hg1–S2	2.5459(4)	S1–Hg1–S2	101.26(1)
N1…Hg1	2.457(1)	N1–Hg1–P1	91.08(3)
N2…P1	2.96	S1–Hg1–P1	117.43(1)
		S2–Hg1–P1	136.48(2)
<b>4</b>			
		N1–Hg1–Cl1	95.4(3)
		N1–Hg1–Cl2	150.6(3)
N1…Hg1	2.237(10)	N1–Hg1–Cl1'	101.7(3)
N2…Hg2	2.162(7)	Cl1–Hg1–Cl2	105.8(3)
Hg1–Cl1	2.636(5)	Cl1–Hg1–Cl1'	87.61(17)
Hg1–Cl2	2.354(4)	Cl2–Hg1–Cl1'	99.3(3)
Hg1…Cl1'	2.763(6)	Hg1–Cl1–Hg1'	92.39(17)
		Hg1–Cl2–Hg3'''	95.78(5)
		N2–Hg2–Cl3	166.2(2)
Hg2–Cl3	2.280(3)	N2–Hg2–Cl4	101.5(2)
Hg2–Cl4	2.888(3)	Cl3–Hg2–Cl4	90.97(11)
		Cl5–Hg3–Cl6	149.71(16)
		Cl5–Hg3–Cl4	103.62(14)
Hg3–Cl5	2.370(3)	Cl6–Hg3–Cl4	106.67(13)
Hg3–Cl6	2.406(3)	Cl5–Hg3–Cl6''	98.32(15)
Hg3…Cl6''	2.988(3)	Cl6–Hg3–Cl6''	82.83(10)
Hg3…Cl4	2.546(3)	Cl4–Hg3–Cl6''	88.98(10)
		Hg3–Cl4–Hg2	103.92(9)
		Hg3–Cl6–Hg3''	97.17(10)

Symmetry equivalent positions 1-x,-y,1-z; -x,1-y,1-z; and 1+x,1/2-y,1/2+z are given by *prime*, *double prime* and *triple prime*, respectively.

In compound **1**, the triarylphosphane behaves as a *P,N*-chelating ligand, while the SCN groups act as thiocyanato ligands, thus resulting in a tetrahedral coordination geometry about Hg(II). The second 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub> group behaves as a *C,N*-chelating moiety towards phosphorus. In this way phosphorus became pentacoordinate, with a distorted trigonal bipyramidal coordination geometry (N2–P1–C1 174.35°) and with the phosphorus atom placed at 0.48 Å above the C10C19Hg1 trigonal plane. The two chelate rings, Hg1N1C7C2C1P1 and P1N2C16C11C10, formed by the N→Hg and N→P, respectively, intramolecular coordination are not planar. The six-membered ring Hg1N1C7C2C1P1 has a boat conformation, with P1 and C7 in apices, while the five-membered ring P1N2C16C11C10 is folded about the P1…C16

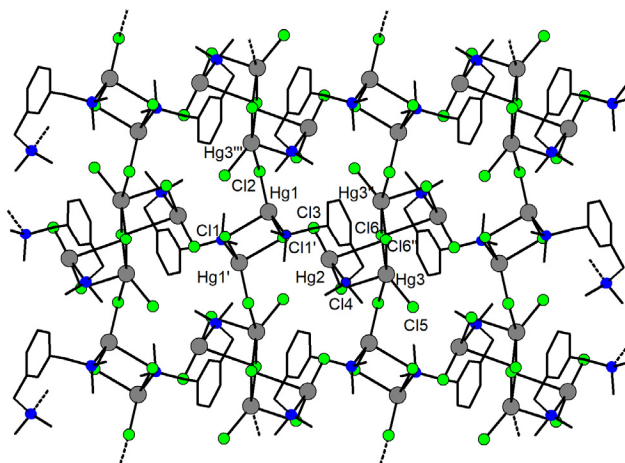
imaginary axis. As a result of the intramolecular coordination of the two pendant arms, one to Hg and the other to P, the crystal of compound **1** contains a racemic mixture of  $A_P\delta P\lambda_{Hg}$ ,  $C_P\delta P\lambda_{Hg}$ ,  $A_P\lambda P\lambda_{Hg}$  and  $A_P\lambda P\delta_{Hg}$  isomers, where  $\lambda$  and  $\delta$  refer to the chirality determined by the formation of the six- and five-membered rings about mercury and phosphorus, respectively, while  $A$  and  $C$  refer to the chirality determined by the phosphorus atom in a trigonal bipyramidal environment [17]. A similar behavior of the triarylphosphane ligand and a close magnitude of the  $P\rightarrow Hg$ ,  $N\rightarrow Hg$  and  $N\rightarrow P$  interactions were observed previously for the related  $[HgCl_2\{PPh[C_6H_4(CH_2NMe_2)-2\}_2]$  [13].

The nitrogen atoms of the two SCN ligands are involved in weak  $N\cdots H$  interactions ( $N4\cdots H5$  2.56 Å and  $N3\cdots H9A$  2.64 Å, vs.  $\Sigma r_{vdW}(N,H)$  2.86 Å [18]) with neighbor molecules, thus resulting in a ribbon-like polymeric structure, as depicted in Figure 3.



**Figure 3.** Ribbon-like association in the crystal of **1**. Hydrogen atoms, except those involved in intermolecular interactions are omitted for clarity.

The crystal of **4** contains three  $HgCl_2$  independent molecules which are connected in a 3D supramolecular network by a  $N,N$  bridging 2,6- $(Me_2NCH_2)_2C_6H_4$  ligand. The  $HgCl_2$  molecules based on Hg1 and Hg3 form parallel polymeric chains of  $Hg_2Cl_4$  dimers interconnected through chlorine bridges ( $Cl2\cdots Hg3$  3.08 Å). The 2,6- $(Me_2NCH_2)_2C_6H_4$  molecules act as  $N,N$  bridging, neutral ligands between Hg2 and Hg1 atoms ( $N1\rightarrow Hg1$  2.22 Å and  $N2\rightarrow Hg2$  2.15 Å, vs.  $\Sigma r_{vdW}(N,Hg)$  4.01 Å [18]), while the Hg3 atoms are not involved in any  $N\rightarrow Hg$  interaction. In this way the polymeric chains are connected in 2D layers (Figure 4).



**Figure 4.** A 2D layer in the crystal of **4**. Hydrogen atoms are omitted for clarity.

Such layers are further connected by weak Cl $\cdots$ Hg interactions (Cl5 $\cdots$ Hg2 3.24 Å, vs.  $\Sigma r_{vdW}$ (Cl,Hg) 4.27 Å [18]) in a 3D supramolecular network.

## EXPERIMENTAL SECTION

The starting materials [HgCl<sub>2</sub>{PPh[C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NMe<sub>2</sub>)-2]<sub>2</sub>}] [13] and 2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SeCl [19] were prepared as previously described. All the other reagents were commercially provided and used as received.

Solvents were dried and distilled under argon prior to use. Melting points were measured on an Electrothermal 9200 apparatus. <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H}, <sup>77</sup>Se{<sup>1</sup>H} and <sup>199</sup>Hg{<sup>1</sup>H} NMR spectra were recorded in CDCl<sub>3</sub> on a BRUKER Avance 400 instrument, operating at 400.1 (<sup>1</sup>H), 161.9 (<sup>31</sup>P), 76.3 (<sup>77</sup>Se) and 71.6 (<sup>199</sup>Hg) MHz. The chemical shifts are reported in  $\delta$  units (ppm) relative to TMS (<sup>1</sup>H, ref. CDCl<sub>3</sub> 7.26 ppm, DMSO-*d*<sub>6</sub> 2.50 ppm), H<sub>3</sub>PO<sub>4</sub> 85% (<sup>31</sup>P), Me<sub>2</sub>Se (<sup>77</sup>Se) and Me<sub>2</sub>Hg (<sup>199</sup>Hg), respectively. The NMR data were processed using the MestReNova software [20]. ESI mass spectra were recorded on a Thermo Scientific Orbitrap XL spectrometer equipped with a standard ESI/APCI source.

### **Synthesis of [Hg(SCN)<sub>2</sub>{PPh[C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NMe<sub>2</sub>)-2]<sub>2</sub>}] (1)**

A solution of KSCN (0.021 g, 0.22 mmol) in MeOH (15 mL) was added at room temperature to a solution of [HgCl<sub>2</sub>{PPh[C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NMe<sub>2</sub>)-2]<sub>2</sub>}] (0.07 g, 0.11 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL). The reaction mixture was stirred for 12 hours.

Subsequently, the solvents were removed under reduced pressure and the remained sticky product was washed with n-hexane (2 x 5 mL), when a colorless solid was formed. Hexane was removed by filtration and the solid was dried under reduced pressure. Yield: 0.07 g (51%). M.p. 156°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 2.10$  (s, br., 6H,  $\text{N}(\text{CH}_3)_2$ ), AB spin system with  $\delta_A$  3.28 and  $\delta_B$  4.00 (4H,  $\text{CH}_2\text{N}$ ,  $^2J_{\text{HH}} 12.9$  Hz), 7.02 (dd, 2H, P-C $_6$ H $_4$ ,  $^3J_{\text{HH}} = 7.3$ ,  $^3J_{\text{PH}} = 12.2$  Hz), 7.38 (t, 2H, P-C $_6$ H $_4$ ,  $^3J_{\text{HH}} 7.1$  Hz), 7.43 (t, 2H, P-C $_6$ H $_4$ ,  $^3J_{\text{HH}} 6.8$  Hz) 7.53-7.64 (m, 3H P-C $_6$ H $_5$ -meta+para + 2H P-C $_6$ H $_4$ ); 7.69 (br., 2H P-C $_6$ H $_5$ -ortho).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 19.4$  (s,  $^1J_{\text{HgP}} 6200$  Hz).  $^{199}\text{Hg}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -597.12$  (d,  $^1J_{\text{HgP}} 6211$  Hz).

### Synthesis of [2,6-(Me $_2$ NCH $_2$ ) $_2$ C $_6$ H $_3$ Se][HgCl $_3$ ] (3)

A suspension of HgCl $_2$  (0.136 g, 0.50 mmol) in methanol (15 mL) was added to a solution of 2,6-(Me $_2$ NCH $_2$ ) $_2$ C $_6$ H $_3$ SeCl (0.153 g, 0.50 mmol) in CH $_2$ Cl $_2$  (15 mL), under stirring, at room temperature. After 12 hours the solvents were removed in vacuum and the remained solid was washed with hexane (2x10 mL) and dried at reduced pressure, when the title compound resulted as a yellowish solid. Yield: 0.266 g (92%). M.p. 148-149 °C (dec.).  $^1\text{H}$  NMR (DMSO- $d_6$ ),  $\delta = 2.83$  [s, 12H,  $\text{N}(\text{CH}_3)_2$ ], 3,48 [s, 4H, (CH $_2$ N)], 7,24-7,31 (m, 3H, C $_6$ H $_3$ );  $^{77}\text{Se}$  NMR (DMSO- $d_6$ ),  $\delta = 1185$  (s);  $^{199}\text{Hg}$  NMR (DMSO- $d_6$ ),  $\delta = -1353$  (s). ESI+ MS (MeOH),  $m/z$  (%): 271.07133 (100) [2,6-(Me $_2$ NCH $_2$ ) $_2$ C $_6$ H $_3$ Se] $^+$ , ESI- MS (MeOH),  $m/z$  (%): 306.87647 (100) [HgCl $_3$ ] $^-$ .

### Formation of [2,6-(Me $_2$ NCH $_2$ ) $_2$ C $_6$ H $_3$ Se][HgCl $_3$ ] (3) and [(HgCl $_2$ ) $_3$ {2,6-(Me $_2$ NCH $_2$ ) $_2$ C $_6$ H $_3$ }] (4)

A solution of n-BuLi in n-hexane (1.6 M, 1.46 mL, 2.34 mmol) was added dropwise, under stirring, to a solution of 1,3-(Me $_2$ NCH $_2$ ) $_2$ C $_6$ H $_4$  (0.450 g, 2.34 mmol) in n-hexane (50 mL). Stirring continued over night, then n-hexane was removed under vacuum and the reaction mixture was dissolved in THF (50 mL). Selenium powder (0.185 g, 2.34 mmol) was added and stirring continued for other 4 hours. To the resulted red solution, HgCl $_2$  (0.635 g, 2.34 mmol) was added and stirring continued overnight. THF was removed under reduced pressure and the product was dissolved in CH $_2$ Cl $_2$  (50 mL). Then CH $_2$ Cl $_2$  was removed in vacuum and the product was washed with n-hexane and dried, when a yellowish solid was obtained. The NMR and the MS spectra suggested the formation of a mixture containing mainly [(2,6-(Me $_2$ NCH $_2$ ) $_2$ C $_6$ H $_3$ )Se][HgCl $_3$ ] (3) and [(HgCl $_2$ ) $_3$ {2,6-(Me $_2$ NCH $_2$ ) $_2$ C $_6$ H $_3$ }] (4). ESI+ MS (MeOH),  $m/z$  (%): 193.17054 (36) [RH+H] $^+$ , 271.07133 (77) [RSe] $^+$ , R = 2,6-(Me $_2$ NCH $_2$ ) $_2$ C $_6$ H $_3$ ; ESI- MS (MeOH),  $m/z$  (%): 306.87647 (92) [HgCl $_3$ ] $^-$ .



**X-ray structure determination**

The details of the crystal structure determination and refinement for compounds **1** and **4** are given in Table 2. Data were collected on a Bruker D8 VENTURE diffractometer at 100 K, by using a Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) from a  $1\mu\text{S}$  3.0 microfocus source with multilayer optics. The structure was refined with anisotropic thermal parameters for non-H atoms. Hydrogen atoms were placed in fixed, idealized positions and refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the Bruker APEX3 Software Package was used [21]. The drawings were created with the Diamond program [22].

**Table 2.** Crystallographic data for **1** and **4**

	<b>1</b>	<b>4</b>
Empirical formula	$\text{C}_{26}\text{H}_{29}\text{HgN}_4\text{PS}_2$	$\text{C}_{12}\text{H}_{20}\text{Cl}_6\text{Hg}_3\text{N}_2$
Formula weight	693.21	1006.77
Temperature (K)	100(2)	295(2)
Wavelength ( $\text{\AA}$ )	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	P21/n	P21/c
<i>a</i> ( $\text{\AA}$ )	9.0428(2)	11.3141(2)
<i>b</i> ( $\text{\AA}$ )	14.9881(4)	13.5832(2)
<i>c</i> ( $\text{\AA}$ )	20.2953(6)	14.4866(3)
$\alpha$ ( $^\circ$ )	90	90
$\beta$ ( $^\circ$ )	102.2860(10)	107.9830(10)
$\gamma$ ( $^\circ$ )	90	90
Volume, ( $\text{\AA}^3$ )	2687.71(12)	2117.56(7)
<i>Z</i>	4	4
Density (calculated) ( $\text{g/cm}^3$ )	1.713	3.158
Absorption coefficient ( $\text{mm}^{-1}$ )	5.963	22.452
<i>F</i> (000)	1360	1792
Crystal size, mm	0.23 x 0.12 x 0.097	0.140 x 0.110 x 0.090
$\theta$ range for data collections, $^\circ$	2.054 to 28.288	1.892 to 28.282
Reflections collected	22055	58817
Independent reflections	6477, [R(int) = 0.0163]	5258 [R(int) = 0.0412]
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	6477 / 0 / 314	5258 / 0 / 747
Goodness-of-fit on $F^2$	1.031	1.036
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	R1 = 0.0134, wR2 = 0.0301	R1 = 0.0276, wR2 = 0.0659
<i>R</i> indices (all data)	R1 = 0.0148, wR2 = 0.0306	R1 = 0.0372, wR2 = 0.0710
Largest diff. peak and hole, $\text{e}\text{\AA}^{-3}$	0.407 and -0.527	1.477 and -2.542

## CONCLUSIONS

The new metal complexes  $[\text{Hg}(\text{SCN})_2\{\text{PPh}[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)-2]_2\}]$  (**1**) and  $[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{Se}][\text{HgCl}_3]$  (**3**) were isolated as pure species, with good yields, by replacing  $\text{Cl}^-$  with  $\text{SCN}^-$  in  $[\text{HgCl}_2\{\text{PPh}[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)-2]_2\}]$  and by extracting  $\text{Cl}^-$  from  $2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{SeCl}$  by  $\text{HgCl}_2$ , respectively. Unfortunately, we could not obtain the complex  $[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{SeHgCl}]$  (**2**) by a succession of reactions based on the lithiation of  $2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_4$ , but we could prove by multinuclear NMR and ESI mass spectrometry the formation of a mixture of **3** and  $[(\text{HgCl}_2)_3\{2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}]$  (**4**), as a result of incomplete lithiation and subsequent insertion of selenium. The room temperature  $^1\text{H}$  NMR spectra gave no clear evidence for  $\text{N}\rightarrow\text{Hg}$ ,  $\text{N}\rightarrow\text{P}$  or  $\text{N}\rightarrow\text{Se}$  intramolecular interactions in compounds **1** and **3**, respectively. The X-ray diffraction studies revealed that both aryl groups with pendant arms act as *C,N*-chelating groups in **1**, one of them coordinated to mercury and the other to phosphorus, while in the crystal of **4** the  $2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_4$  molecules act as *N,N* bridging, neutral ligands.

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## SUPPLEMENTARY DATA

CCDC 2107690 and 2107691 contain the supplementary crystallographic data for compounds **1** and **4**. 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](mailto:deposit@ccdc.cam.ac.uk).

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