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2-(2-{Diphenylarsino}ethyl)-1,3-dioxane ($\mathbf{L}^1$) and 2-(diphenylarsinomethyl)tetrahydrofuran ($\mathbf{L}^2$) and their palladium(II), platinum(II) and mercury(II) complexes: synthesis and crystal structures of $[\mathrm{PdBr_2(\mathbf{L}^1)_2}]$ and $[\mathrm{HgBr_2(\mathbf{L}^2)}]_2$

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Abstract

Novel and potentially hemilabile ligands of (As, O) type, 2-(2-{diphenylarsino}ethyl)-1,3-dioxane ($\mathbf{L}^1$) and 2-(diphenylarsinomethyl)tetrahydrofuran ($\mathbf{L}^2$), are synthesised by reacting Ph_2AsLi generated in situ under a nitrogen atmosphere with an appropriate organic halide. The complexes of $\mathbf{L}^1$ and $\mathbf{L}^2$ with Pd(II), Pt(II) and Hg(II) having composition $[\mathrm{M(\mathbf{L}^1/\mathbf{L}^2)_2X_2}]$ (M = Pd or Pt; X = Cl or Br) or $[\mathrm{M(\mathbf{L}^1)Br_2}]_2$ (M = Hg) have been synthesised and characterised by elemental analyses, IR, ^{1}H- and ^{13}C{^{1}H}-NMR spectra and molecular weight and conductivity measurements. The crystal structures of $[\mathrm{PdBr_2(\mathbf{L}^1)_2}]$ and $[\mathrm{HgBr_2(\mathbf{L}^2)}]_2$ are solved. The potentially bidentate ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ coordinate with Pd/ Hg through As only. The CH_2O signals observed in ^{1}H- and ^{13}C{^{1}H}-NMR spectra of the present complexes do not show any shift with respect to those of $\mathbf{L}^1$ and $\mathbf{L}^2$. The Pd–As and Hg–As bond lengths are 2.414(1) and 2.504(3) Å, respectively The Hg complex has bromo-bridges (2.792(3)–2.884(4) Å) that are asymmetric. The geometry of Hg is a distorted tetrahedral and that of Pd square planar. The As has tetrahedral geometry as three C atoms and Hg or Pd surround it. The $[\mathrm{HgBr_2(\mathbf{L}^2)}]_2$ is the first example of a mercury(II)–arsine complex containing $\mathrm{Hg(\mu\text{-}Br)_2Hg}$ unit. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Arsenic ligand; 2-(Diphenylarsinomethyl)tetrahydrofuran; 2-(2-{Diphenylarsino}ethyl)-1,3-dioxane; Palladium; Platinum; Mercury complex; Crystal structure

1. Introduction

The complexation of a substrate by organotranstion metal compounds represents an important step in the course of a catalytically operating process [1]. This generally occurs by elimination of solvent molecules like ethers or ketones. The hemilabile ligands [2] can tune the catalytic activity of metal centre as well as play the role of these solvent molecules, by protecting temporarily the coordination site of metal ion before it is replaced by a substrate in the course of a catalytic reaction at the metal centre. The (P_x, O_y) type of ligands [3,4] are such species, as the oxygen present in the pendent arm coordinates weakly with the metal until the substrate reaches it, similar to that of solvent. The metal–oxygen bond is cleaved reversibly and, owing to an opening and closing mechanism [5], empty coordination sites are made available when needed in the course of catalytic cycles without separation of the oxygen donors from the complex fragment. Thus (P_x, O_y) type of ligands have been used to design several catalytically active species [3] found promising for oligomerization of olefins, carbonylation of methanol hydrogenation and ring opening metathesis polymerisation. Relatively very little attention has been paid to hemilabile ligands of the type (As_x, O_y). One interesting ligand of this type reported, is $i\text{-}Pr_2AsCH_2CH_2OMe$ [6]. Comparatively there are more reports on (As_x, S/P_y) type of donors, diarsine and triarsine ligands [7–11]. It was therefore thought worthwhile to design $\mathbf{L}^1$ and $\mathbf{L}^2$, the novel (As, O) type of donors which are potentially hemilabile.

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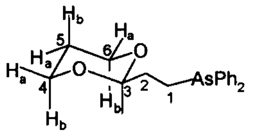
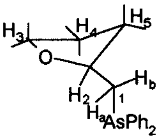


L^1



L^2

However, in the present paper their synthesis and complexation with palladium(II), platinum(II) and mercury(II) are reported. The [PdBr$_2$(**L^1**)$_2$] and [HgBr$_2$(**L^2**)]$_2$ are characterised structurally. These ligands may be useful for designing catalytically active species.

2. Experimental

The C and H analyses were carried out with a Perkin–Elmer elemental analyser 240 C. The ^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.1316507 and 75.4748884 MHz, respectively. IR spectra in the range 4000–250 cm^{-1} were recorded on a Nicolet Protége 460 FTIR spectrometer as KBr/CsI pellets. Molecular weights were determined in chloroform using a Knauer vapour pressure osmometer model A028 at a concentration $\sim$1 mM. The conductance measurements were made using an Orion conductivity meter model 162. The melting points determined in open capillary are reported as such. Triphenylarsine, 2-(2-bromoethyl)-1,3-dioxane and tetrahydrofurfural chloride were obtained from Aldrich, and used as received. The published method [12] was used to generate a deep red solution of Ph$_2$AsLi (10 mmol) in dry THF (50 ml). It was concentrated to 15 ml under reduced pressure and filtered through G-4 crucible before further use. A large fraction of the lithium chloride formed was removed.

2.1. Synthesis of *L^1*

The Ph$_2$AsLi (10 mmol) was prepared in situ in 15 ml of dry THF under a nitrogen atmosphere, as described above. 2-(2-Bromoethyl)-1,3-dioxane (1.95 g, 10 mmol) dissolved in THF (10 ml) was added to it dropwise under a nitrogen atmosphere. After completion of addition, the reaction mixture became colourless. It was further stirred for 30 min at room temperature. The THF from the reaction mixture was removed by a rotary evaporator under reduced pressure. The residue was treated with benzene (25–30 ml) and filtered through a G-4 sintered glass crucible. The filtrate was concentrated (5–7 ml) on a rotary evaporator under reduced pressure and mixed with hexane (10–15 ml). The resulting microcrystalline **L^1** was filtered and dried in vacuo. Yield 75%, m.p. 170°C. Anal. Calc. for $C_{18}H_{21}O_2As$: C, 62.79; H, 6.11. Found: C, 62.48; H, 6.33%. ^{1}H-NMR (CDCl$_3$, 25°C): δ (vs TMS) 1.27–1.32 (d, 1H, H_{5b}), 1.75–1.82 (m, 2H, H_2), 1.95–2.11 (m, 3H, $H_1 + H_{5a}$) 3.64–3.72 (t, 2H, $H_{4b} + H_{6b}$), 4.03–4.08 (2d, 2H, $H_{4a} + H_{6a}$), 4.49–4.53 (t, 1H, H_3), 7.29–7.33 (bm, 6H, ArH *o* + *p* to As), 7.41–7.44 (m, 4H, ArH *o* to As). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ (vs TMS) 21.6 (C_5), 25.7 (C_2), 32.0 (C_1), 66.8 ($C_4 + C_6$), 102.4 (C_3), 128.2 (C *m* to As), 128.5 (C *p* to As), 132.9 (C *o* to As), 140.4 (C–As).

2.2. Synthesis of *L^2*

The deep red solution of Ph$_2$AsLi (10 mmol) was prepared under a dry nitrogen atmosphere as described under the synthesis of **L^1**. Tetrahydrofurfuryl chloride (1.21 g, 10 mmol) dissolved in 10 ml of THF was added to it dropwise. After complete addition the reaction mixture became colourless. It was stirred further for 30 min and THF was removed under reduced pressure on a rotary evaporator. The residue was treated with 50 ml of benzene and filtered through a G-4 sintered crucible. The filtrate was concentrated to 5–7 ml and mixed with 10–15 ml of hexane, resulting in the microcrystalline **L^2**. It was washed with hexane recrystallized from the mixture (1:1) of dichloromethane–petroleum ether (40–60°C) and dried in vacuo. Yield 40%. Anal. Calc. for $C_{17}H_{19}OAs \cdot CH_2Cl_2$: C, 54.15; H, 5.26. Found C, 53.33; H, 4.83%. ^{1}H-NMR (CDCl$_3$, 25°C): δ (vs TMS) ^{1}H-NMR (CDCl$_3$, 25°C): δ (vs TMS) 1.50–2.03 (m, 4H, $H_4 + H_5$), 2.56 (bs, 2H, H_1), 3.52–3.54 (q, 1H, H_{3b}), 3.73–3.75 (q, 1H, H_{3a}) 4.12 (bm, 1H, H_2), 5.29 (CH_2Cl_2), 7.14–7.44 (m, 6H ArH, *m* + *p* to As), 7.58–7.63 (d, 4H, ArH *o* to As).

2.3. Synthesis of *[PdBr$_2$(L^1)$_2$] (1)*

The **L^1** ($\sim$1 mmol) was generated in situ in THF as described above. The THF was removed completely on a rotary evaporator. The residue was dissolved in CH$_2$Cl$_2$ (10 ml) and stirred for 30 min with a solution of Na$_2$PdCl$_4$ (0.147 g, 0.5 mmol) made in methanol (15 ml). The solvents from the reaction mixture were removed under reduced pressure. The orange crystals of complex **1**, suitable for X-ray diffraction, were grown from the solution of this residue made in 20 ml mixture (1:1) of dichloromethane–petroleum ether (40–60°C). The LiBr released in the synthesis of **L^1** was the source of Br for the complex **1**. Yield 74%, m.p. 198°C. Anal. Calc. for $C_{36}H_{42}O_4As_2PdBr_2$: C, 45.23; H, 4.39. Found: C, 46.19; H, 4.79%. Mol. wt.: 1102 (Calc. 955). ^{1}H-NMR (CDCl$_3$, 25°C): δ (vs TMS) 1.24–1.28 (d, 1H, H_{5b}), 1.85–1.94 (m, 2H, H_2), 1.97–2.07 (m, 1H, H_{5a}), 2.55–2.73 (m, 2H, H_1), 3.63–3.71 (t, 2H, $H_{4b} + H_{6b}$), 4.00–4.05 (2d, 2H, $H_{4a} + H_{6a}$), 4.52–4.55 (t, 1H, H_3), 7.37–7.39 (bs, 6H, ArH *m* + *p* to As), 7.87–7.69 (bm, 4H, ArH *o* to As). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ (vs TMS) 19.3 (C_5), 25.7 (C_2), 30.6 (C_1), 66.8 ($C_4 + C_6$), 101.8

(C_3), 128.6 (C *m* to As), 130.0 (C *p* to As), 133.7 (C *o* to As).

2.4. Synthesis of [$PtBr_2(\mathbf{L^1})_2$] (**2**)

The $\mathbf{L^1}$ (~ 1 mmol) was generated in situ in THF as described above. The THF was removed completely under reduced pressure. The residue was dissolved in CH_2Cl_2 (10 ml) and stirred for 30 min with a solution of K_2PtCl_4 (0. 208 g, 0.5 mmol) prepared in methanol (15 ml). The solvent was removed on a rotary evaporator. The residue was extracted with 25 ml of CH_2Cl_2. The extract was concentrated to 5–10 ml and mixed with 10 ml of petroleum ether (40–60°C). The resulting pale yellow compound **2** was filtered and recrystallized from dichloromethane–petroleum ether (40–60°C) mixture (1:1) and dried in vacuo. The LiBr released in the synthesis of $\mathbf{L^1}$ was also the source of Br for the complex **2**. Yield 78%, m.p. 188°C. Anal. Calc. for $C_{36}H_{42}O_4As_2PtBr_2$: C, 41.41; H, 4.02. Found: C, 41.89; H, 3.98%. Mol. wt.: 842 (Calc. 1043). ^{1}H-NMR ($CDCl_3$, 25°C): δ (vs TMS) 1.25–1.29 (d, 1H, H_{5b}), 1.75–1.82 (m, 2H, H_2), 1.87–2.07 (m, 1H, H_{5a}), 2.43–2. 48 (m, 2H, H_1), 3.62–3.70 (t, 2H, $H_{4b} + H_{6b}$), 3.95–4.05 (2d, 2H, $H_{4a} + H_{6a}$), 4.42–4.46 (t, 1H, H_3), 7.14–7.24 (m, 4H, ArH *m* to As), 7.30–7.55 (m, 6H, ArH $o + p$ to As). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ (vs TMS) 22.8 (C_5), 25.7 (C_2), 30.5 (C_1), 66.8 ($C_4 + C_6$), 101.5 (C_3), 128.7 (C *m* to As), 130.5 (C *p* to As), 132.9 (C *o* to As).

2.5. Synthesis of [$PdCl_2(\mathbf{L^2})]_2$ (**3**)

The $\mathbf{L^2}$ (1 mmol) was generated in dry THF as mentioned earlier in its synthesis. The THF was removed under reduced pressure and the residue dissolved in 15 ml of CH_2Cl_2. It was added to a solution of Na_2PdCl_4 (0.294 g, 1 mmol) prepared in 20 ml of methanol. The mixture was stirred for 30 min and the solvent was removed on a rotary evaporator. The yellowish orange residue was recrystallized from a 1:2 mixture of CH_2Cl_2–petroleum ether (40–60°C) and dried in vacuo. Yield 80%, m.p. 160°C. Anal. Calc. for $[C_{17}H_{19}OAsPdCl_2]_2$: C, 41.52; H, 3.87. Found: C, 40.34; H, 3.73%. Mol. wt.: 997 (Calc. 982). ^{1}H-NMR ($CDCl_3$, 25°C): δ (vs TMS) 1.56–2.10 (m, 4H, $H_4 + H_5$), 2.64–2.79 (m, 2H, H_1), 3.67–3.74 (q, 1H, H_{3b}), 3.83–3.90 (q, 1H, H_{3a}), 4.27 (bm, 1H, H_2), 7.37–7.54 (m, 6H ArH, $m + p$ to As), 7.66–7.79 (d, 4H, ArH *o* to As). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ (vs TMS) 25.8 (C_4), 33.1 (C_5), 33.9 (C_1), 68.04 (C_3), 74.9 (C_2), 128.8 and 129 (C *m* to As), 131.0 and 131.1 (C *p* to As), 133.4 (C *o* to As).

2.6. Synthesis of [$HgBr_2\mathbf{L^2}]_2$(**4**)

The $\mathbf{L^2}$ (2 mmol) was generated in dry THF as mentioned earlier in its synthesis. The THF was removed under reduced pressure and the residue dissolved in 10 ml of benzene. It was added to a solution of $HgBr_2$ (0.77 g, 2 mmol), prepared in 10 ml of acetone. The mixture was stirred for 30 min and the solvent was removed under reduced pressure. The residue was dissolved in 5 ml of DMSO and layered with 15 ml of acetone to grow the single crystals of **4**. Yield 82%, m.p. 120°C. Anal. Calc. for $[C_{17}H_{19}OAsHgBr_2]_2$: C, 30.25; H, 2.82. Found: C, 29.58; H, 2.98%. ^{1}H-NMR ($CDCl_3$, 25°C): δ (vs TMS) 1.47–1.99 (m, 4H, $H_4 + H_5$), 2.78–2.92 (m, 2H, H_1), 3.38–3.51 (q, 1H, H_{3b}), 3.66–3.73 (q, 1H, H_{3a}), 3.99–4.03 (quintet, 1H, H_2), 7.47 (bs, 6H ArH, $m + p$ to As), 7.64–7.68 (d, 4H, ArH *o* to As). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ (vs TMS) 25.8 (C_4), 33.1 (C_5), 33.9 (C_1), 68.04 (C_3), 74.9 (C_2), 128.8 and 129 (C *m* to As), 131.0 and 131.1 (C *p* to As), 133.4 (C *o* to As).

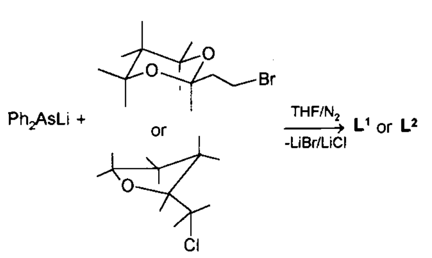
2.7. X-ray diffraction analysis

The single crystal structures of compounds **1** and **4** were determined. The crystal parameters are given in Table 1. Data for both the structures were collected on a Rigaku AFC6S diffractometer at 23 ± 1°C using graphite monochromated Mo–K_α radiation, $\lambda = 0.71069$ Å and ω–2θ scan technique. The intensities of three representative reflections were measured after every 150 reflections. The structure was solved by heavy atom Patterson method [13] and expanded using Fourier techniques [14]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement [15] on F^2 was carried out. The standard deviation of unit weight [16] was determined. The weighing scheme was based on the counting statistics and included a factor (p) to down weight the intense reflections. Neutral atom scattering factors were taken from Cromer and Waber [17]. Anomalous dispersion effects of all non-hydrogen atoms were included in Fcalc. [18]. The values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [19]. The values for the mass attenuation coefficients are those of Creagh and Hubbell [20]. All calculations were performed using the teXsan [21] crystallographic software package of the Molecular Structure Corporation except for refinement, which was performed using SHELXL-93 [22].

3. Results and discussion

The reactions given in Eqs. (1) and (2) have resulted in $\mathbf{L^1}$ and $\mathbf{L^2}$ which are soluble in common organic solvents.

$$Ph_3As \xrightarrow[\text{2. } t\text{-BuCl/THF/N}_2]{\text{1. Li/THF/N}_2} Ph_2AsLi + C_6H_6 + LiCl + (CH_3)_2\text{-}C{=}CH_2 \qquad (1)$$



(2)

Elemental analyses and molecular weights have authenticated the **L**^{1} and **L**^{2} and their metal complexes. All of them are non-ionic in acetonitrile, as the value of Λ_M is between 1.4 and 1.9 ohm^{-1} cm^2 mol^{-1}. The metal complexes of **L**^{1} and **L**^{2} can be prepared in good yield by reacting the in situ generated ligands with the metallic species as was performed for complexes **1** to **4**. The formation of a chloro-complex, i.e. [Pt/PdCl$_2$(**L**^{1})$_2$] with **1** and **2** is possible. The ionic character of LiBr, 'softer' donor character of Br in comparison to Cl and lower solubility of the bromo complex in comparison to that of the chloro, have probably made possible the isolation of [Pt/PdBr$_2$(**L**^{1})$_2$] in a reasonably pure form. The sample of [PdBr$_2$(**L**^{1})$_2$] has also been synthesised by reacting Na$_2$PdCl$_4$ with the isolated pure ligand **L**^{1} and NaBr (2–3 × mols of Pd) but unfortunately its single crystals suitable for X-ray diffraction could not be grown. However, its melting point is similar to that of **1**. The samples of **1**, **2** and **4** do not show any positive test (qualitative) for chloride and their purity is further supported by TLC (in dichloromethane–petroleum ether–methanol). However, due to the presence of chloride during synthesis of **1**, **2** and **4** the formation of chloro-complex is not ruled out completely. In the IR spectra of **L**^{1} and **L**^{2} the band around 478 cm^{-1} has been assigned to ν(As–C) [23]. It has been observed to undergo a red shift (~5 to 6 cm^{-1}) on complex formation. The signal of H$_1$ in the ^{1}H-NMR spectra of **1** and **2** appears downfield (0.37–0.66 ppm) with respect to that of **L**^{1}. Similarly aromatic protons of **L**^{1} shift downfield (0.2 ppm) on the formation of **1** and **2**. The signals of protons attached to carbon atoms next to oxygen atoms of **L**^{1} do not show any significant shift on its complexation with palladium(II) or platinum(II). In the ^{13}C{^{1}H}-NMR spectra of **1** and **2** the aliphatic carbon signals do not exhibit significant downfield shift in comparison to that of free **L**^{1}. However, the aromatic carbon signals, particularly of C *para* to As, appear marginally deshielded (~2 ppm). These observations favour the inference that **L**^{1} coordinates only through arsenic in the present palladium(II) and platinum(II) complexes. The single crystal structure of **1** has corroborated this inference. The signal of H$_1$ protons of **L**^{2} has been found deshielded (0.1–0.2 ppm) on the formation of complexes **3** and **4**. The signals due to the aromatic protons of **L**^{2} also exhibit a trend of low field shifting on complexation with Hg(II) and Pd(II). The H$_4$ and H$_5$ proton signals in the ^{1}H-NMR spectra of **3** and **4** do not exhibit any significant shift with respect to those of free **L**^{2}. Therefore, the **L**^{2} appears to be present in **3** and **4** in a monodentate mode. The single crystal structure of **4** has corroborated this inference. The geometries of Pd/Pt(II) and of Hg are the usual square planar and tetrahedral one, respectively as supported by crystal structure of **1** and **4**.

Table 1
Crystallographic data measurements and refinements of [PdBr$_2$(**L**^{1})$_2$] (**1**) and [HgBr$_2$(**L**^{2})]$_2$ (**4**)

	Compound **1**	Compound **4**
Empirical formula	$C_{18}H_{21}AsPd_{0.5}O_2Br$	$C_{17}H_{19}OAsHgBr_2$
Formula weight	477.39	674.66
Colour, habit	Orange prism	Clear prism
Crystal size (mm^3)	0.40 × 0.20 × 0.50	0.30 × 0.20 × 0.40
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
Unit cell dimensions		
a (Å)	10.200(5)	10.423(8)
b (Å)	10.661(4)	11.068(5)
c (Å)	9.883(4)	10.195(7)
α (°)	112.13(3)	91.71(6)
β (°)	115.52(9)	113.92(6)
γ (°)	70.56(7)	63.34(4)
V (Å^3)	879.4(6)	944.0(1)
Z	2	2
D_{calc} (g cm^{-3})	1.80	2.373
μ (cm^{-1})	47.1	141.6
F(000)	472	624
$2\theta_{max}$ (°)	55	55
Scan rate (per min in ω)	4.0 (up to four scans)	4.0 (up to four scans)
Scan width (°)	(1.47 + 0.34 tan θ)	(1.68 + 0.34 tan θ)
Reflections collected	4267	4586
Unique reflections	4093	4345
Corrections	Lorentz–polarization absorption	Lorentz–polarization absorption
Transmission factor	0.6460–1.0000	0.3259–1.0000
p-Factor	0.0175	0.0117
No. of observations [$I > 3.00\sigma(I)$]	2220	1706
No. of variables	206	200
Reflection/parameter ratio	10.78	8.53
R_1 [a]	0.057	0.054
wR_2 [b]	0.188	0.208
Goodness-of-fit	1.09	0.99
Max. shift/error in final cycle	1.28	0.04
Final difference map, peak and hole (e Å^{-3})	1.73 and −1.02	1.60 and −2.11

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$.

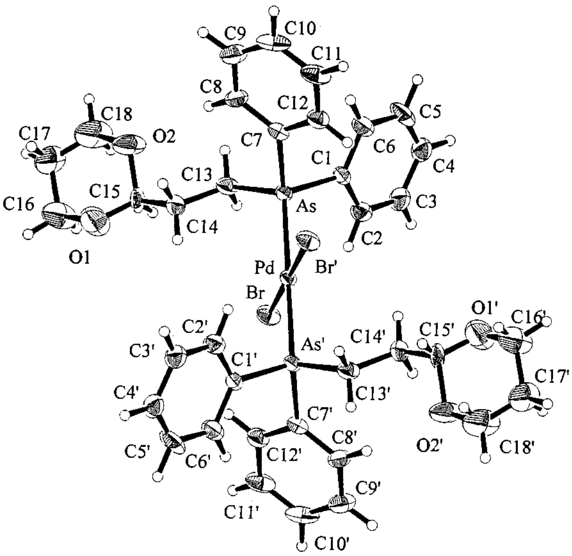


Fig. 1. Molecular structure of **1**.

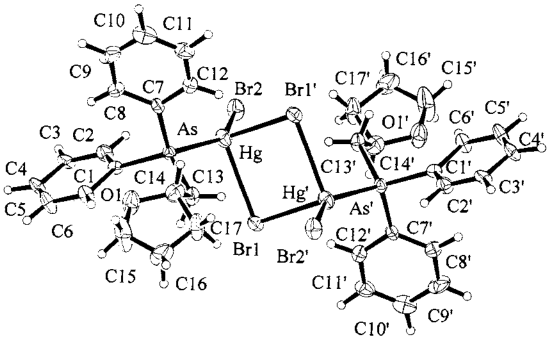


Fig. 2. Molecular structure of **4**.

3.1. Crystal structures of [PdBr$_2$(L^1)$_2$] (1) and [HgBr$_2$(L^2)]$_2$ (4)

The crystal structures of **1** and **4** are solved. The molecular structures are shown in Figs. 1 and 2. The selected bond lengths and bond angles are given in Table 2. All bond lengths, atomic coordinates and thermal parameters are deposited at the Cambridge Crystallographic Database. The geometry of palladium in complex **1** is square planar. The Pd–As bond length, 2.432(1) Å observed in this complex is a little longer than the value 2.406(3) Å reported by Vicente et al. [24] for [Pd(2,4,6-trinitrophenyl)Cl(AsPh$_3$)$_2$] but similar to the value 2.436(1) Å given by Doyle et al. [25] for Pd(II) complex of 1-(dimethylarsino)-2-(methylphenylphosphino)benzene. The organic groups linked to As and co-ligands of Pd are expected to be responsible for such small variations. The As–C bond lengths and Pd–As–C bond angles of **1** are consistent with the literature reports of 1.926(9)–1.970(2) Å [24,26,27] and 113.6(6)–116.2(6)° [24], respectively. The average bond angle C–As–C in the case of **1** is 102° and normal [26,27] and three carbon atoms with Pd make the geometry of the As nearly tetrahedral. The Pd–Br bond lengths of **1** (2.414(1) Å) are some what shorter than those where Br is *trans* to a strong σ-donor tellurium (2.480(1) Å) [28]. The bond lengths and angles of the phenyl group, 1,3-dioxanyl group and other aliphatic C–C bond lengths and associated bond angles are normal. The 1,3-dioxanyl group adopts the expected chair conformation. The greater difference (0.174 Å) between C(15)–O(1) and C(15)–O(2) is due to packing forces as these oxygen atoms are involved in the intermolecular interactions of O···H–C type (2.652–2.763 Å) with the molecules of nearby unit cell.

There are very few reports on the structural characterisation of mercury–arsine complexes and to the best of our knowledge there is none which has the Hg(μ-Br)$_2$Hg unit. Therefore, structural characterisation of complex **4** is of significance in the context of arsine ligand chemistry. The **4** has a dimeric structure with bromo-bridges (Fig. 2). The Hg–As bond lengths of **4** (2.504(3) Å) are comparable with the values 2.557(1), 2.476(3)/2.482(3) and 2.815(5)/2.595(5) Å reported for trigonal planar [Hg(SCN)$_2$As(Ph)$_2$] [29], dimeric [Hg(As(mesityl)$_3$)(NO$_3$)$_2$]$_2$ [30] and tetrahedral [HgBr$_2$(tris(*o*-diphenylarsino)phenylarsine)]·CH$_2$Cl$_2$ [27], respectively. The geometry of Hg in **4** is a distorted tetrahedral. The geometry of As is close to a tetrahedral as Hg–As–C and C–As–C bond angles are in the range 105.0(9)–113.8(9)°. The As–C(1) and As–C(13) bond lengths are consistent with the literature values 1.926(9)–1.970(2) Å [24,26,27]. However, As–C(7) (1.880(1) Å) is somewhat shorter, probably due to crystal packing factors. The Hg–Br(bridging) bond lengths, 2.792(3) and 2.884(4) Å, of **6** are consistent with the earlier reports 2.710(1) and 2.755(1) Å [31]. The bond lengths and angles of phenyl and tetrahydrofurfuryl group are normal. Further investigations to demonstrate **L^1** and **L^2**, as hemilabile ligands capable of protecting the coordination site of metal temporarily like solvents, are in progress.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre; CCDC Nos. 133005 and 133006 for the compounds **1** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-123-336033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 2
Selected bond lengths (Å) and angles (°) of **1** and **4** with estimated S.D. values in parentheses

Bond lengths		Bond angles			
Complex **1**					
Pd–Br	2.414(1)	Br–Pd–Br′	180.0	C(1)–As–C(7)	101.61(3)
Pd–As	2.432(1)	As–Pd–As′	180.0	C(1)–As–C(13)	100.51(3)
As–C(1)	1.9379(6)	Br′–Pd–As	92.15(1)	C(7)–As–C(13)	103.99(3)
As–C(7)	1.9323(7)	Br–Pd–As	87.85(1)	C(13)–C(14)–C(15)	105.33(3)
As–C(13)	1.9376(6)	Br′–Pd–As′	87.85(1)	C(14)–C(15)–O(1)	105.48(3)
C(13)–C(14)	1.4961(5)	Br–Pd–As′	92.15(1)	C(14)–C(15)–O(2)	98.26(3)
C(14)–C(15)	1.6322(2)	C(13)–As–Pd	113.66(3)	As–C(13)–C(14)	115.94(3)
C(15)–O(1)	1.2728(5)	C(1)–As–Pd	114.91(3)	C(15)–O(2)–C(18)	104.50(3)
C(15)–O(2)	1.4467(6)	C(7)–As–Pd	119.69(2)	C(15)–O(1)–C(16)	106.28(3)
Complex **4**					
Hg–As	2.504(3)	Br(1)–Hg–As	96.1(1)	As–C(13)–C(14)	113(2)
Hg–Br(1)	2.884(4)	Br(2)–Hg–As	145.5(1)	C(13)–C(14)–O(1)	110(2)
Hg–Br(2)	2.467(4)	Br(1)′–Hg–As	100.9(1)	C(14)–O(1)–C(15)	109(3)
Hg–Br(1)′	2.792(3)	Br(1)′–Hg–Br(2)	106.9(1)	C(7)–As–C(13)	105.8(7)
As–C(1)	1.91(2)	Br(1)–Hg–Br(2)	103.5(1)	C(7)–As–C(1)	105.0(9)
As–C(7)	1.88(1)	Br(1)′–Hg–Br(1)	90.6(1)	C(1)–As–C(13)	113.8(9)
As–C(13)	1.96(2)	Hg–As–C(13)	108.5(8)		
C(13)–C(14)	1.51(4)	Hg–As–C(1)	110.6(6)		
C(14)–O(1)	1.41(5)	Hg–As–C(7)	113.2(7)		

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[16] Standard deviation of an observation of unit weight: $[\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$, N_o = number of observations; N_v = number of variables.

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