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Tetraphosphinitoresorcinarene complexes: a new structural form for diphosphine mercury(II) halide complexes

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Mercury(II) halide derivatives of tetrakis(diphenylphosphinite) ligands derived from a resorcinarene have been characterized, in both the solid and solution states. The complexes have the general formula [Resorcinarene-$(O_2CR)_4(OPPh_2HgX_2)_4$], with Resorcinarene = $(PhCH_2CH_2CHC_6H_2)_4$; R = OCH_2Ph, C_6H_{11}, 4-C_6H_4Me, OCH_2CCH; X = Cl, Br, I, and each contains two $Hg_2X_2(\mu\text{-}X)_2(PP)$ units, in which PP represents a bis(diphenylphosphinite) group of the ligand. This is a new structural form for the much-studied mercury(II) halide complexes with phosphine ligands and it arises since the resorcinarene-derived ligands act as if they contain two separate diphosphinite bidentate ligands, each having a long bite distance that can span the $Hg_2(\mu\text{-}X)_2$ unit. In particular, this work provides the first structural characterization of mercury(II) halide diphosphine complexes with 1 : 1 Hg : P stoichiometry, and the first examples of complexes $[Hg_2X_2(\mu\text{-}X)_2L_2]$ with the *syn* arrangement of the phosphorus donor ligands L.

Introduction

Mercury(II) halide phosphine complexes have been known for many years and have been well characterized by solution NMR studies as well as X-ray structural determinations.[1–7] The majority of the known complexes have empirical formulae HgX_2L_2 or HgX_2L, where L = phosphine and X = Cl, Br, I.[1–7] When L is a monodentate tertiary phosphine ligand, the complexes HgX_2L_2 have tetrahedral structures (**A**, Chart 1), but the complexes HgX_2L can have any of the structures **B**–**E** (Chart 1), with a tendency to form dimers or polymers except with very bulky phosphine ligands.[2–5] Structures of the type **B** (Chart 1), with the *anti* arrangement of the terminal halides and the phosphine ligands, are common but no examples with the corresponding *syn* stereochemistry are known.[2,3] Most reported examples of mercury(II) halide complexes of diphosphine ligands have the general formula $HgX_2(PP)$ but they can exist as the monomer **F**, as the polymer **G**, or as the cationic binuclear form **H** (Chart 1).[6]

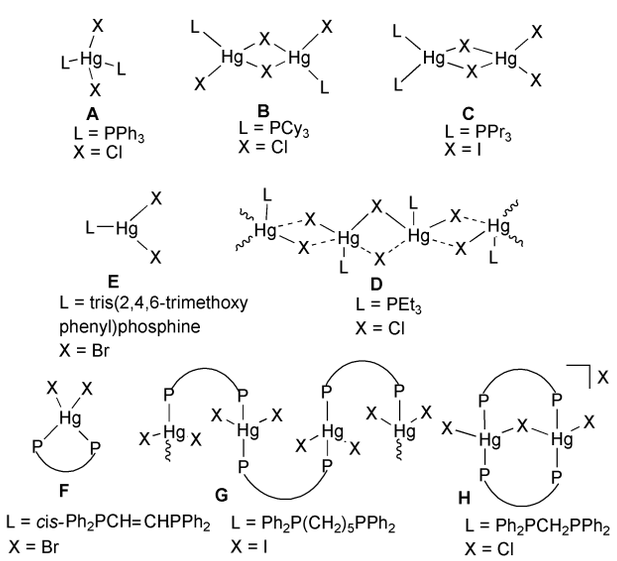

Chart 1

The resorcinarene skeleton provides a versatile platform for developing unusual coordination chemistry,[8] and resorcinarenes with phosphorus donors incorporated at the rim have proved to be particularly interesting.[9] The tetrakis(diphenylphosphinite) resorcinarene compounds, **1**–**4** (Chart 2), tend to adopt a boat conformation and the phosphinite groups can be present in either the flat or upright position.[10] In either conformation, the bite distance is not well suited to form any of the known diphosphine structures **F**–**H** (Chart 1) with mercury(II) halides, and so unusual coordination chemistry was expected to occur.

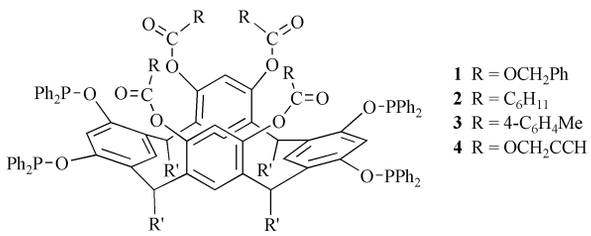

Chart 2

Results and discussion

Synthesis of the complexes

The mercury(II) halide complexes were synthesized by reaction of HgX_2 (X = Cl, Br, I) with the tetrakis(diphenylphosphinite) resorcinarene compounds **1**–**4** as outlined in Scheme 1. Pure complexes were obtained only when the ligand : HgX_2 ratio was 1 : 4; attempts to prepare complexes with ligand : HgX_2 ratios of 1 : 2 resulted in complex mixtures of products that could not be separated. Complexes **5a**–**8c** were characterized by ^1H and ^{31}P NMR spectroscopy, by elemental analysis and, in several cases, by X-ray structure determinations. The air-stable complexes **5a**–**8c** were soluble in chloroform, dichloromethane and THF but sparingly soluble in other common organic solvents.

Conformations of the complexes in the solid state

The structures of the complexes **5b**, **6a**–**c** and **7c** were determined crystallographically and are illustrated in Figs. 1–3, with selected bond distances and angles listed in Table 1 and conformational parameters for the resorcinarene skeletons in Table 2. Since the structures are related, only one will be described in detail.

The structure of the tetra(benzyl carbonato)tetrakis-(diphenylphosphinito)resorcinarene mercury(II) bromide complex **5b** is shown in Fig. 1. The resorcinarene skeleton adopts a boat conformation [10] in which the acylated rings are upright and the phosphinite derivatized rings are flattened. The angle between the planes of the upright acylated rings (fold angle Θ1,

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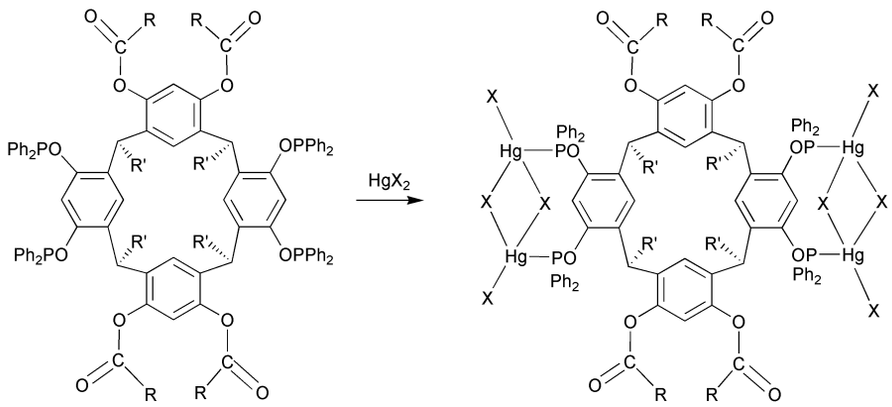


1, R = OCH_2Ph
2, R = C_6H_{11}
3, R = 4-C_6H_4Me
4, R = OCH_2CCH

R = OCH_2Ph; **5**a, X = Cl; **5**b, X = Br; **5**c, X = I
R = C_6H_{11}; **6**a, X = Cl; **6**b, X = Br; **6**c, X = I
R = 4-C_6H_4Me; **7**a, X = Cl; **7**b, X = Br; **7**c, X = I
R = OCH_2CCH; **8**a, X = Cl; **8**b, X = Br; **8**c, X = I

Scheme 1

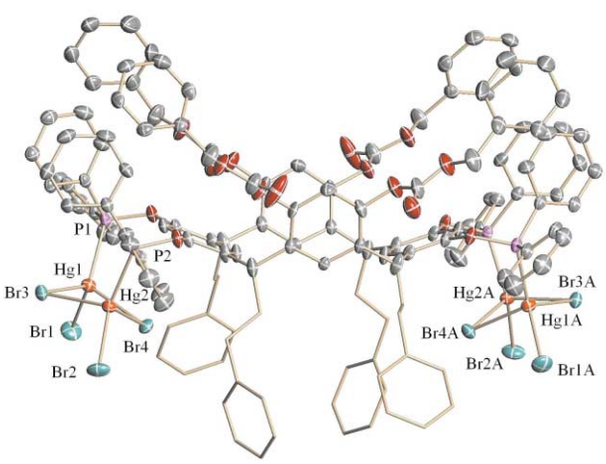


Fig. 1 Thermal ellipsoid diagram for complex **5b**. Oxygen atoms are shown in red. Hydrogen atoms have been removed for clarity.

Table 2) is 25°, while the fold angle $\Theta 2$ between the flattened phosphinite derivatized rings is 140°. There is little twisting distortion of the resorcinarene skeleton, as seen by the dihedral angles between opposite arene rings (upright rings, $\Phi 1$ = 3°; flattened rings, $\Phi 2$ = 5°). The molecule has crystallographically imposed C_2 symmetry.

The mercury(II) centers in **5b** are present as $Hg_2Br_2(\mu\text{-}Br)_2P_2$ units, where P represents a phosphorus donor of the resorcinarene ligand. This is a common structural motif in complexes of mercury(II) halides,[1–3] but all structurally characterized examples have the phosphine ligands, P, in the *anti* stereochemistry (Chart 1) rather than the *syn* stereochemistry found for **5b** (Fig. 1). The *syn* stereochemistry has been considered as a possible structure in the past, with some support on the basis of IR and Raman spectroscopy, but has never been firmly established.[6j] For complex **5b**, the common *anti* stereochemistry is impossible, because of the geometrical constraints of the ligand. The mercury(II) centers have highly distorted tetrahedral stereochemistry, with bond angles at mercury ranging from 91.69(3) to 125.48(5)° (Table 1).[1–7] The mean distances and angles are similar to those in *anti*-$[Hg_2Br_2(\mu\text{-}Br)_2(PPr_3)_2]$,[3] but there is higher symmetry of the bridging bromides and so less distorted tetrahedral geometry in **5b**. For example, in *anti*-$[Hg_2Br_2(\mu\text{-}Br)_2(PPr_3)_2]$,[3] the distances Hg–μ-Br = 2.667(2) and 3.051(2) Å are significantly different and lie well outside the range (Hg–μ-Br = 2.7057(9)–2.7520(9) Å) found for **5b**, while the terminal distance Hg–Br = 2.507(2) Å is shorter than in **5b** (Hg–Br = 2.515(1)–2.519(1) Å, Table 1). Hence the association between pairs of $PHgBr_2$ units is clearly weaker in *anti*-$[Hg_2Br_2(\mu\text{-}Br)_2(PPr_3)_2]$ than in **5b**. The structural data suggest that there is no electronic reason for the dominance of the *anti* geometry in these compounds, and that steric effects between bulky phosphine ligands disfavour the *syn* geometry for monodentate phosphine complexes.

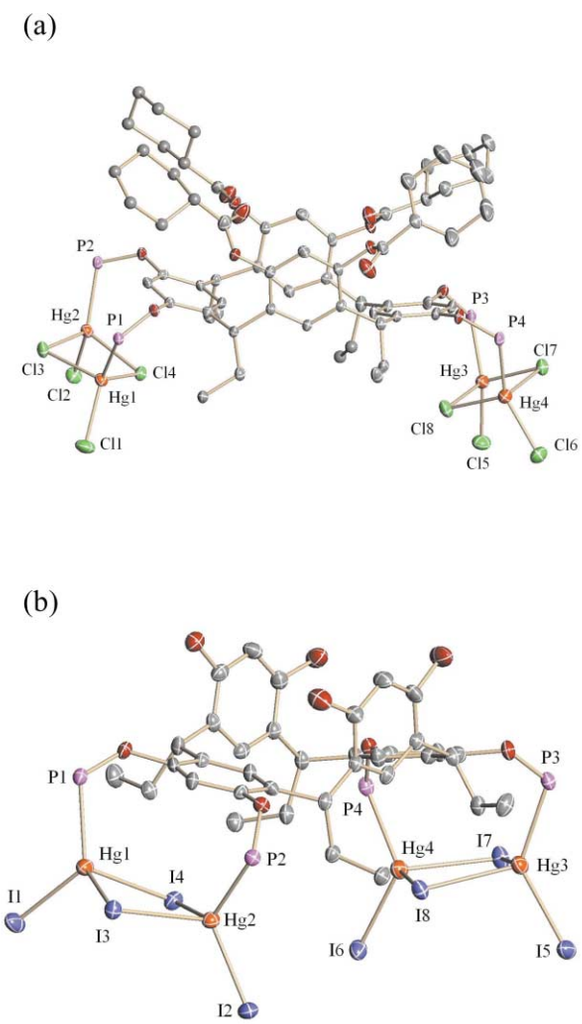


Fig. 2 Thermal ellipsoid diagram for complexes (a) **6a** and (b) **6c**. Phenyl rings of the phenethyl and diphenylphosphinite groups, all hydrogen atoms, and the cyclohexyl carbonyl groups (**6c**) have been removed for clarity . Oxygen atoms are shown in red.

The structures of the tetra(cyclohexylcarboxylato)tetrakis-(diphenylphosphinito)resorcinarene complexes **6a** and **6c** are

Table 1 Selected bond distances (Å) and angles (°) for complexes **5b**, **6a**–**c** and **7c**

	5b (X = Br)	**6a** (X = Cl)	**6b** (X = Br)	**6c** (X = I)	**7c** (X = I)
Hg1–X1	2.515(1)	2.392(2)	2.5096(8)	2.6904(7)	2.6862(7)
Hg2–X2	2.519(1)	2.380(2)	2.5125(8)	2.6925(6)	2.6639(7)
Hg3–X5		2.385(2)	2.5161(8)	2.7012(7)	
Hg4–X6		2.390(2)	2.5035(8)	2.6847(7)	
Hg1–X3	2.7264(9)	2.650(2)	2.7427(8)	2.8348(6)	2.9279(7)
Hg1–X4	2.7057(9)	2.595(1)	2.7601(7)	2.9472(6)	2.8355(6)
Hg2–X3	2.7096(9)	2.627(1)	2.7445(8)	2.9855(6)	2.8988(7)
Hg2–X4	2.7520(9)	2.660(1)	2.6982(7)	2.8157(6)	2.8889(6)
Hg3–X7		2.611(1)	2.7895(7)	2.9112(7)	
Hg3–X8		2.674(2)	2.6561(8)	2.8914(6)	
Hg4–X7		2.681(2)	2.7181(7)	2.8936(7)	
Hg4–X8		2.554(2)	2.7999(7)	2.8685(6)	
P1–Hg1–X1	117.52(6)	128.79(6)	134.70(4)	122.71(5)	118.79(5)
P1–Hg1–X3	115.34(5)	109.88(5)	104.16(4)	113.14(5)	98.36(5)
X3–Hg1–X4	92.33(3)	87.02(4)	89.45(2)	93.38(2)	94.52(2)
P2–Hg2–X2	125.48(5)	136.36(5)	126.85(4)	120.58(5)	118.83(5)
P2–Hg2–X3	112.10(5)	106.29(5)	107.79(4)	95.86(5)	105.34(5)
X3–Hg2–X4	91.69(3)	86.17(4)	90.71(2)	92.95(2)	94.01(2)
P3–Hg3–X5		132.48(6)	127.64(5)	127.00(5)	
P3–Hg3–X7		97.85(5)	98.77(4)	102.43(5)	
X7–Hg3–X8		89.04(5)	94.23(2)	93.84(2)	
P4–Hg4–X6		131.68(6)	131.40(4)	120.29(5)	
P4–Hg4–X7		99.46(5)	96.02(4)	100.93(5)	
X7–Hg4–X8		90.09(5)	92.65(2)	94.71(2)	

Table 2 Fold and twist angles (°) and non-bonded distances (Å) for complexes **5b**, **6a**–**c** and **7c**[a]

	Θ1	Θ2	Φ1	Φ2	*d*(HgHg)	*d*(PP)
5b	25	140	3	5	3.64	5.36
6a	10	155	13	17	3.80, 3.73	5.75, 5.89
6b	11	155	14	18	3.84, 3.76	5.80, 5.92
6c	7	161	20	22	3.92, 3.92	5.79, 5.93
7c	1	157	16	18	3.91	5.96

[a] Θ1 and Θ2 are the fold angles between upright and flattened arene rings, respectively, and Φ1 and Φ2 are the corresponding twist (dihedral) angles.

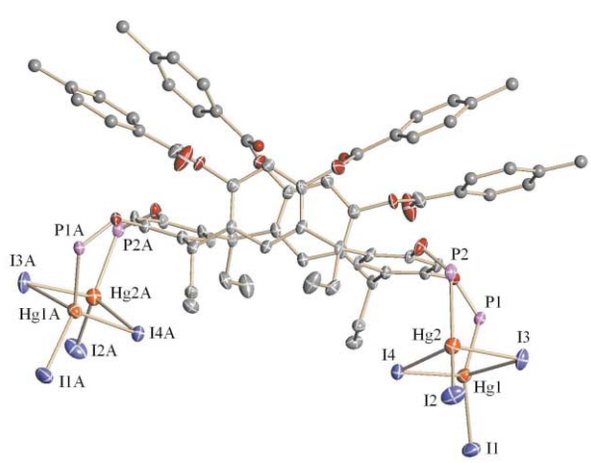


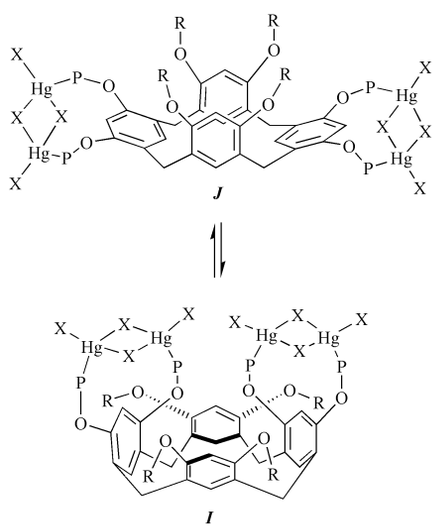
Fig. 3 Thermal ellipsoid diagram for complex **7c**. Phenyl rings of the phenethyl and diphenylphosphinite groups, and all hydrogen atoms have been removed for clarity. Oxygen atoms are shown in red.

shown in Fig. 2. Complexes **6a** and **6b** are isomorphous and exhibit very similar features (Tables 1 and 2), so the structure of **6b** is not shown. In each case, the resorcinarene skeleton is less folded than was observed in complex **5b**, but considerably more twisted (Table 2). The bite distance of each diphosphine, and also the mercury–mercury separation, varies only slightly for the different halide derivatives **6a**–**c**, despite the large differences in halogen size. The "tetrahedral" angles at mercury(II) differ significantly along the series **6a**–**c** to allow the above non-bonded distances to remain roughly constant (Table 1), and so it seems that the geometry of the Hg_2X_4 unit adapts to the preferred bite distance of the ligand rather than *vice versa*.

The structures of the iodide derivatives **6c** (Fig. 2(b)) and the corresponding tetra(4-methylbenzoato)tetrakis(diphenylphosphinito)resorcinarene complex **7c** (Fig. 3) are similar, as illustrated by the geometrical parameters in Tables 1 and 2, though complex **7c** has crystallographically imposed C_2 symmetry whereas **6c** does not. The resorcinarene skeletons of the iodide derivatives **6c** and **7c** are more twisted and have more flattened boat structures compared to the chloride or bromide derivatives **5b**, **6a** and **6b** (Table 2).

Conformations of the complexes in solution

The conformations of the complexes in solution in dichloromethane were investigated by variable-temperature NMR methods.[10] The ^{1}H NMR spectra of complexes **5a** and **5b** were broad and unresolved at room temperature due to fluxionality (eqn. (1)).



(1)

However, at lower temperatures (**5a**, 0 °C; **5b**, −20 °C) the spectra resolved, showing the presence of two conformers, assigned as **I** and **J** (eqn. (1), P = PPh_2HgX_2, R = acyl; **I** and **J** have phos-

phinite-derivatized rings upright and flat respectively). For each conformer, one resonance was observed for the bridging methine protons as well as one AB quartet for the diastereotopic OC(O)OCH_2Ph protons in the ^{1}H NMR, and a single resonance in the ^{31}P NMR spectrum, indicating that each conformer has effective C_{2v} symmetry. The structures of the conformers were assigned from the arene resonances CH^h and CH^d in the ^{1}H NMR spectrum (Chart 3), since CH^h in the flattened ring is more shielded.[10,11] In turn, the CH^h and CH^d resonances were assigned from the ^{1}H, ^{13}C, gHSQC and gHMBC correlated NMR spectra, as described elsewhere.[10] In each case, the major conformer present was **J**, while the minor conformer was **I** (eqn. (1)). Thus both possible boat conformations of **5a** and **5b** are present in solution, and the major conformer is **J** (**5a**, K_{eq} = 0.29(4) at −40 °C; **5b**, K_{eq} = 0.17(3) at −40 °C; K_{eq} = [**I**]/[**J**]), which is the conformer present in the solid state for **5b** (Fig. 1).

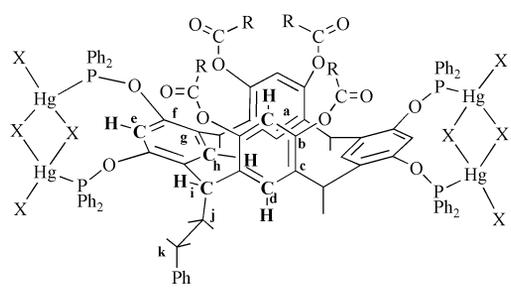


Chart 3

At −80 °C, the AB quartet in the ^{1}H NMR spectrum for the OC(O)OCH_2Ph resonances for conformer **I** of complex **5a** further split to give two AB quartets, and the ^{31}P NMR resonance split to give two equal intensity resonances (Fig. 4). Complex **5b** gave similar spectra. These data indicate that conformer **I** has C_2 symmetry, but is fluxional according to Scheme 2, and so has apparent C_{2v} symmetry at higher temperatures. For both complexes **5a** and **5b**, conformer **J** retains effective C_{2v} symmetry down to −80 °C. The activation energy for the fluxionality between C_2 conformers of **I** was determined from the coalescence temperature (T_c) of the phosphorus resonances (**5a**, ΔG^* = 42(1) kJ mol^{-1}, T_c = 223 K; **5b**, ΔG^* = 43(1) kJ mol^{-1}, T_c = 233 K).

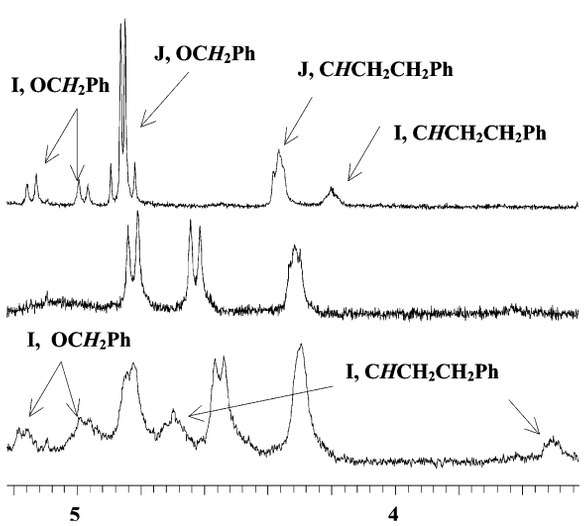
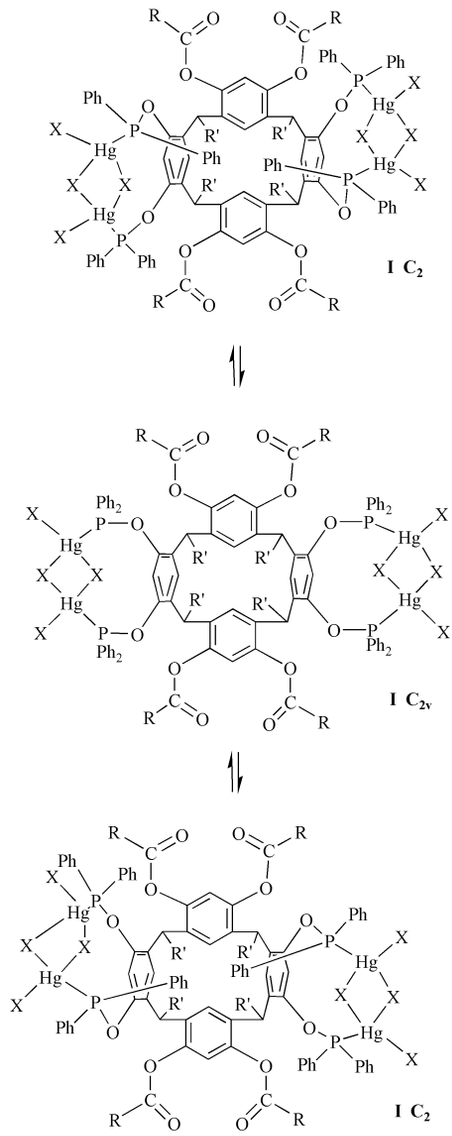


Fig. 4 VT ^{1}H NMR spectra of complex **5a**. Temperatures: top 253 K, middle 223 K, bottom 193 K.

The thermodynamic data for the equilibrium between **I** and **J** are given in Table 3. The enthalpy term clearly favors conformer **J** while the entropy term favors conformer **I**. Table 3 also shows



Scheme 2

that conformer **J** is favored for the bromo derivative **5b** compared to the chloro derivative **5a**. For complex **5c**, conformer **I** was not detected. This series indicates that, as the halogens increase in size, the conformer **J**, in which the Hg_2X_4 units are pseudo-equatorial, is progressively favored over conformer **I**, in which they are pseudo-axial.

The ^{1}H and ^{31}P NMR spectra of complexes **6a**–**c** were similar to complexes **5a** and **5b**, showing the presence of both conformers **I** and **J** in solution, with **J** being preferred (Table 3). The activation energies for the C_2–C_2 interconversion (Scheme 2) of conformer **I** of complexes **6a** and **6b** are ΔG^* = 47(1) and 50(1) kJ mol^{-1}, respectively. For the remaining complexes (**7a**–**8b**) the room temperature ^{1}H and ^{31}P NMR spectra were consistent with the presence of a single conformer with effective C_{2v} symmetry. For the iodomercury(II) complex **7c**, the NMR spectra clearly showed that the conformer present in solution was **J**, in accordance with the solid state structure.

The ^{31}P NMR data for the major conformer **J** of complexes **5a**–**8b** are listed in Table 4. The coupling constants ^1J(HgP) were resolved in the low temperature NMR spectra but not at room temperature. The low abundance of conformer **I** made it difficult to observe the ^1J(HgP) coupling constants and data are reported only for complex **5a**. For each ligand, the magnitudes of the coupling constants ^1J(HgP) followed the sequence Cl > Br > I (Table 4).[7] For complex **5a**, the coupling constants ^1J(HgP) for conformers **I** and **J** were 8024 and 7432 Hz, respectively.

Table 3 Equilibrium and thermodynamic data for complexes **5a** and **5b**

	Complex	$^{a}K_{eq}$ (T/K)	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	ΔG/kJ mol^{-1}
	5a	0.49(5) (273)			
		0.29(4) (233)			
		0.15(4) (193)	6.5(5)	17.6(2)	1.3
	5b	0.25(5) (253)			
		0.17(3) (233)			
		0.08(3) (193)	7.3(5)	16.9(3)	2.3

^{a} K_{eq} = [**I**]/[**J**]. ^{b} K_{eq} (273) **6a** = 0.13(4). ^{c} K_{eq} (273) **6b** = 0.10(4).

Table 4 ^{31}P NMR data for conformer **J** of complexes **5a**–**8c**

Complex	T/K	δ/ppm	$^{1}J_{HgP}$/Hz
5a ^{a}	273	121.51	7432
5b	253	114.35	6203
5c	253	91.87	4005
6a	193	122.54	7675
6b	233	115.89	6233
6c	233	92.95	3927
7a	293	124.89	7293
7b	273	117.11	6054
7c	193	92.81	4217
8a	193	113.81	6451
8b	213	93.18	4309

^{a} **5a**: **I**, T = 273, δ = 122.10 ppm, $^{1}J_{HgP}$ = 8024 Hz.

Conclusions

The resorcinarene tetraphosphinite ligands **1**–**4** are shown to give mercury(II) halide derivatives that have a new structural form, in which each arene diphosphinite unit binds to a $Hg_2X_2(\mu\text{-}X)_2$ unit with the phosphine donors mutually *syn*. The resorcinarene units adopt the boat conformation in these complexes, for which two major conformers are possible. In the solid state, the conformer with the phosphinite groups (and hence the Hg_2X_4 units) in the flat (equatorial) position is found in all cases studied. However, in solution, an equilibrium between the two boat conformers was present. The larger halides give a stronger preference for the conformer with equatorial phosphinite groups. The resorcinarene platform is shown to give a new structural form for the much studied mercury(II) halide complexes with phosphorus-donor ligands.

Experimental

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were freshly distilled, dried and degassed prior to use. NMR spectra were recorded using a Varian Inova 400 NMR spectrometer. Elemental analyses were carried out by Guelph Chemical. The tetraphosphinite resorcinarene compounds used in this work were prepared as described previously.[10] In the formulae below the resorcinarene skeleton $(C_6H_2CH\{CH_2CH_2Ph\})_4$ is represented as Resorcinarene. The proton and carbon resonances of the resorcinarene skeleton are identified according to the labeling scheme shown in Chart 3.

[Resorcinarene(OC(O)OCH$_2$Ph)$_4$(OPPh$_2${HgCl$_2$})$_4$], 5a

A mixture of **1** (0.075 g, 0.034 mmol) and $HgCl_2$ (0.0369 g, 0.136 mmol) in CH_2Cl_2 (10 mL) was stirred for 1 h. The solution was filtered through Celite and a white solid was precipitated with pentane. The solid was collected and washed with diethyl ether (10 mL). Yield 0.090 g, 81%. NMR (CD_2Cl_2, 0 °C): δ(^{1}H) (**I**, **J**) 1.76–2.28 [m, H^j, H^k]; 6.72–7.88 [m, Ar-H, Ph]. (**I**) 4.20 [m, 4H, H^i]; 5.06 [m, 8H, $^2J_{HH}$ = 12 Hz, OCH_2Ph]; 6.45 [s, 2H, H^d]; 6.87 [s, 2H, H^e]; 7.17 [s, 2H, H^a]; 7.49 [s, 2H, H^h]. (**J**) 4.36 [m, 4H, H^i]; 4.85 [m, 8H, $^2J_{HH}$ = 12 Hz, OCH_2Ph]; 6.41 [s, 2H, H^h]; 6.66 [s, 2H, H^e]; 6.86 [s, 2H, H^a]; 7.52 [s, 2H, H^d]. δ(^{13}C) (**I**, **J**) 124.95–134.96 [Ar-C, Ph]. (**J**) 33.78 [C^k]; 36.58 [C^i]; 37.68 [C^j]; 70.73 [OC(O)OCH$_2$Ph]; 108.71 [m, C^e]; 117.14 [C^a]; 124.95 [C^d]; 129.80 [C^h]; 131.52 [C^d]; 134.21 [C^g]; 140.68 [*ipso*-C, CH_2CH_2Ph]; 148.19 [C^c]; 149.73 [d, $^1J_{PC}$ = 5 Hz, C^f]; 152.66 [OC(O)OCH$_2$Ph]. δ(^{31}P) (**I**) 122.10 [s, $^1J_{HgP}$ = 8024 Hz]. (**J**) 121.51 [s, $^1J_{HgP}$ = 7432 Hz]. Anal. Calc. for $C_{140}H_{116}Cl_8Hg_4O_{16}P_4$: C, 51.51; H, 3.58. Found: C, 51.49; H, 3.70%.

[Resorcinarene(OC(O)OCH$_2$Ph)$_4$(OPPh$_2${HgBr$_2$})$_4$], 5b

This was prepared similarly from **1** (0.075 g, 0.034 mmol) and $HgBr_2$ (0.0492 g, 0.137 mmol). White solid. Yield 0.096 g, 78%. NMR (CD_2Cl_2, −20 °C): δ(^{1}H) (**I**, **J**) 1.90–2.23 [m, H^j, H^k]; 6.85–7.88 [m, Ar-H, Ph]. (**I**) 4.20 [br, 4H, H^i]; 5.16 [m, 8H, $^2J_{HH}$ = 12 Hz, OCH_2Ph]; 6.53 [s, 2H, Ar-H]. (**J**) 4.33 [t, 4H, $^3J_{HH}$ = 8 Hz, H^i]; 4.88 [m, 8H, $^2J_{HH}$ = 12 Hz, OCH_2Ph]; 6.36, 6.73 [s, 4H, Ar-H]. δ(^{31}P) (**I**) 115.91 [s]. (**J**) 114.35 [s, $^1J_{HgP}$ = 6203 Hz]. Anal. Calc. for $C_{140}H_{116}Br_8Hg_4O_{16}P_4$: C, 46.45; H, 3.23. Found: C, 46.03; H, 3.52%.

[Resorcinarene(OC(O)OCH$_2$Ph)$_4$(OPPh$_2${HgI$_2$})$_4$], 5c

This was prepared similarly from **1** (0.075 g, 0.034 mmol) and HgI_2 (0.0619 g, 0.136 mmol). White solid. Yield 0.118 g, 87%. NMR (CD_2Cl_2, −20 °C): δ(^{1}H) 1.84–2.22 [m, 16H, H^j, H^k]; 4.29 [t, 4H, $^3J_{HH}$ = 7 Hz, H^i]; 4.90 [m, 8H, $^2J_{HH}$ = 12 Hz, OCH_2Ph]; 6.35 [s, 2H, Ar-H]; 6.72–7.92 [m, 86H, Ar-H, Ph]. δ(^{31}P) 91.87 [s, $^1J_{HgP}$ = 4005 Hz]. Anal. Calc. for $C_{140}H_{116}Hg_4I_8O_{16}P_4$: C, 42.08; H, 3.23. Found: C, 42.23; H, 2.99%.

[Resorcinarene(OC(O)C$_6$H$_{11}$)$_4$(OPPh$_2${HgCl$_2$})$_4$], 6a

This was prepared similarly from **2** (0.075 g, 0.036 mmol) and $HgCl_2$ (0.0391 g, 0.144 mmol). White solid. Yield 0.062 g, 54%. NMR (CD_2Cl_2, 20 °C): δ(^{1}H) (**I**, **J**) 1.14–2.81 [m, H^j, H^k, C_6H_{11}]; 6.72–8.00 [m, Ar-H, Ph]. (**I**) = 4.57 [m, 4H, H^i]; 6.24, 6.41, 6.63 [s, 6H, Ar-H]. (**J**) 4.23 [m, 4H, H^i]; 6.26, 6.59 [s, 4H, Ar-H]. δ(^{31}P) (**I**) 117.10 [s]. (**J**) 123.99 [s]. NMR (CD_2Cl_2, −80 °C): δ(^{1}H) (**J**) 0.80–2.22 [m, 60H, H^j, H^k, C_6H_{11}]; 4.12 [m, 4H, H^i]; 6.18, 6.36 [s, 4H, Ar-H]; 6.60–7.86 [m, 64H, Ar-H, Ph]. δ(^{31}P) (**J**) 122.54 [s, $^1J_{HgP}$ = 7675 Hz]. Anal. Calc. for **6a**·$C_2H_4Cl_2$ ($C_{138}H_{136}Cl_{10}Hg_4O_{12}P_4$): C, 50.73; H, 4.20. Found: C, 50.61; H, 4.23%.

[Resorcinarene(OC(O)C$_6$H$_{11}$)$_4$(OPPh$_2${HgBr$_2$})$_4$], 6b

This was prepared similarly from **2** (0.075 g, 0.036 mmol) and $HgBr_2$ (0.0519 g, 0.144 mmol). White solid. Yield 0.094 g, 74%. NMR (CD_2Cl_2, 20 °C): δ(^{1}H) (**I**, **J**) 1.05–2.83 [m, H^j, H^k, C_6H_{11}]; 6.68–8.05 [m, Ar-H, Ph]. (**I**) 4.57 [m, 4H, H^i]; 6.17, 6.60 [s, 4H, Ar-H]. (**J**) 4.24 [m, 4H, H^i]; 6.29, 6.61 [s, 4H, Ar-H]. δ(^{31}P) (**I**) 111.39 [s]. (**J**) 117.29 [s]. NMR (CD_2Cl_2, −40 °C): δ(^{1}H) (**J**) 1.04–2.78 [m, 60H, H^j, H^k, C_6H_{11}]; 4.16 [m, 4H, H^i]; 6.19, 6.52, 6.81 [s, 6H, Ar-H]; 6.71–7.84 [m, 62H, Ar-H, Ph]. δ(^{31}P) (**J**) 115.89 [s, $^1J_{HgP}$ = 6233 Hz]. Anal. Calc. for $C_{136}H_{132}Br_8Hg_4O_{12}P_4$: C, 46.35; H, 3.78. Found: C, 45.99; H, 4.14%.

[Resorcinarene(OC(O)C_6H_{11})$_4$(OPPh$_2${HgI_2})$_4$], 6c

This was prepared similarly from **2** (0.075 g, 0.036 mmol) and HgI_2 (0.0655 g, 0.144 mmol). White solid. Yield 0.108 g, 77%. NMR (CD_2Cl_2, 0 °C): δ(^{1}H) (**I**, **J**) 1.12–2.83 [m, H^j, H^k, C_6H_{11}]; 6.66–8.10 [m, Ar-H, Ph]. (**I**) 4.55 [m, 4H, H^i]; 6.12, 6.53 [s, 4H, Ar-H]. (**J**) 4.19 [m, 4H, H^i]; 6.26, 6.60 [s, 4H, Ar-H]. δ(^{31}P) (**I**, **J**) 92.66 [s, br]. NMR (CD_2Cl_2, −40 °C): δ(^{1}H) (**J**) 1.04–2.90 [m, 60H, H^j, H^k, C_6H_{11}]; 4.14 [m, 4H, H^i]; 6.19, 6.55 [s, 4H, Ar-H]; 6.62–7.84 [m, 64H, Ar-H, Ph]. δ(^{31}P) (**J**) 92.95 [s, $^1J_{HgP}$ = 3927 Hz]. Anal. Calc. for $C_{136}H_{132}Hg_4I_8O_{12}P_4$: C, 41.88; H, 3.41. Found: C, 41.39; H, 3.90%.

[Resorcinarene(OC(O)$C_6H_4CH_3$)$_4$(OPPh$_2${$HgCl_2$})$_4$], 7a

This was prepared similarly from **3** (0.075 g, 0.036 mmol) and $HgCl_2$ (0.0385 g, 0.142 mmol). White solid. Yield 0.095 g, 84%. NMR (CD_2Cl_2, 20 °C): δ(^{1}H) 1.97, 2.28 [m, 16H, H^j, H^k]; 2.51 [s, 12H, $C_6H_4CH_3$]; 4.38 [m, 4H, H^i]; 6.43, 6.53 [s, 4H, Ar-H]. 6.79–7.97 [m, 80H, Ar-H, Ph, $C_6H_4CH_3$]. δ(^{31}P) 124.89 [s, $^1J_{HgP}$ = 7293 Hz]. Anal. Calc. for $C_{140}H_{116}Cl_8Hg_4O_{12}P_4$: C, 52.54; H, 3.65. Found: C, 52.61; H, 4.05%.

[Resorcinarene(OC(O)$C_6H_4CH_3$)$_4$(OPPh$_2${$HgBr_2$})$_4$], 7b

This was prepared similarly from **3** (0.075 g, 0.036 mmol) and $HgBr_2$ (0.0512 g, 0.142 mmol). White solid. Yield 0.104 g, 84%. NMR (CD_2Cl_2, 0 °C): δ(^{1}H) 1.92, 2.21 [m, 8H, H^j]; 1.79, 2.29 [m, 8H, H^k]; 2.51 [s, 12H, $C_6H_4CH_3$]; 4.34 [m, 4H, H^i]; 6.43, 6.46 [s, 4H, Ar-H]; 6.74–7.98 [m, 80H, Ar-H, Ph, $C_6H_4CH_3$]. δ(^{31}P) 117.11 [s, $^1J_{HgP}$ = 6054 Hz]. Anal. Calc. for $C_{140}H_{116}Br_8Hg_4O_{12}P_4$: C, 47.29; H, 3.29. Found: C, 46.98; H, 3.55%.

[Resorcinarene(OC(O)$C_6H_4CH_3$)$_4$(OPPh$_2${HgI_2 })$_4$], 7c

This was prepared similarly from **3** (0.075 g, 0.036 mmol) and HgI_2 (0.0645 g, 0.142 mmol). White solid. Yield 0.114 g, 82%. NMR (CD_2Cl_2, 20 °C): δ(^{1}H) 2.28, 2.42 [m, 8H, H^j]; 2.02, 2.56 [m, 8H, H^k]; 2.57 [s, 12H, $C_6H_4CH_3$]; 4.38 [m, 4H, H^i]; 6.51 [s, 2H, H^h]; 6.71[s, 2H, H^e]; 6.86 [s, 2H, H^a]; 7.57 [s, 2H, H^d]; 6.70–8.02 [m, 76H, Ar-H, Ph, $C_6H_4CH_3$]. δ(^{13}C) 22.29 [$C_6H_4CH_3$]; 34.01 [C^k]; 36.48 [C^j]; 38.13 [C^i]; 112.38 [m, C^e]; 118.52 [C^a]; 126.30–133.69 [Ar-C, Ph]; 127.02 [C^d]; 130.18 [C^h]; 131.15 [C^c]; 136.11 [C^g]; 140.24 [*ipso*-C, $CHCH_2CH_2Ph$]; 145.27 [*ipso*-C, $C_6H_4CH_3$]; 149.30 [C^b]; 149.96 [C^g]; 164.27 [C=O]. δ(^{31}P) 92.21 [s]. NMR (CD_2Cl_2, −80 °C): δ(^{31}P) 92.81 [s, $^1J_{HgP}$ = 4217 Hz]. Anal. Calc. for $C_{140}H_{116}Hg_4I_8O_{12}P_4$: C, 42.77; H, 2.97. Found: C, 42.39; H, 2.79%.

[Resorcinarene(OC(O)$OCH_2C{\equiv}CH$)$_4$(OPPh$_2${$HgBr_2$})$_4$], 8b

This was prepared similarly from **4** (0.075 g, 0.038 mmol) and $HgBr_2$ (0.0549 g, 0.152 mmol). White solid. Yield 0.122 g, 94%. NMR (CD_2Cl_2, −80 °C): δ(^{1}H) 1.89–2.28 [m, 16H, H^j, H^k]; 2.57 [s, br, 4H, $OCH_2C{\equiv}CH$]; 4.24 [m, 4H, H^i]; 4.44 [m, 8H, $^2J_{HH}$ = 15 Hz, $OCH_2C{\equiv}CH$]; 6.36, 6.66 [s, 4H, Ar-H]; 6.92–7.83 [m, 64H, Ar-H, Ph]. δ(^{31}P) 113.81 [s, $^1J_{HgP}$ = 6451 Hz]. Anal. Calc. for $C_{124}H_{100}Br_8Hg_4O_{16}P_4$: C, 43.66; H, 2.95. Found: C, 43.30; H, 3.22%.

[Resorcinarene(OC(O)$OCH_2C{\equiv}CH$)$_4$(OPPh$_2${HgI_2})$_4$], 8c

This was prepared similarly from **4** (0.075 g, 0.038 mmol) and HgI_2 (0.0692 g, 0.152 mmol). White solid. Yield 0.130 g, 90%. NMR (CD_2Cl_2, −60 °C): δ(^{1}H) 1.68–2.12 [m, 16H, H^j, H^k]; 2.60 [s, br, 4H, $OCH_2C{\equiv}CH$]; 4.13 [m, 4H, H^i]; 4.52 [m, 8H, $^2J_{HH}$ = 15 Hz, $OCH_2C{\equiv}CH$]; 6.21 [s, 2H, Ar-H]; 6.75–7.96 [m, 66H, Ar-H, Ph]. δ(^{31}P) 93.18 [s, $^1J_{HgP}$ = 4309 Hz]. Anal. Calc. for $C_{124}H_{100}Hg_4I_8O_{16}P_4$: C, 39.32; H, 2.66. Found: C, 39.08; H, 2.78%.

X-Ray structure determinations

Crystals suitable for X-ray analysis were mounted on glass fibres. Data were collected using a Nonius-Kappa CCD diffractometer using COLLECT (Nonius, B.V. 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction was carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, B.V. 1998). The SHELX-TL V5.1 and SHELX-TL V6.1 (G. M. Sheldrick) program packages were used to solve and refine the structures. The structures were solved by direct methods for complexes **6b** and **6c** while the remaining structures were solved using the automated Patterson routine of the SHELX-TL software package.[12] For complexes **5b** and **7c** the space group could not be unambiguously assigned from the systematic absences. In each case, the centrosymmetric space group *C*2/*c* was chosen based on E statistics, and resulted in successful refinement of the data. Except as mentioned, all non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. Crystal data are summarized in Table 5. All thermal ellipsoid diagrams are shown at 30% probability.

CCDC reference numbers 212238–212242.

See http://www.rsc.org/suppdata/dt/b3/b306408p/ for crystallographic data in CIF or other electronic format.

[Resorcinarene(OC(O)OCH_2Ph)$_4$(OPPh$_2${$HgBr_2$})$_4$], 5b

Crystals of [$C_{140}H_{116}Br_8Hg_4O_{16}P_4$]·($4CH_2Cl_2$)·($H_2O$) were grown by diffusion of hexane into a dichloromethane solution. There was some disorder in the compound. The phenethyl groups were each modeled as a 60 : 40 isotropic mixture. The carbon–carbon single bonds in these disordered groups were fixed at 1.54 Å. The carbon–chlorine bond lengths of the solvent molecules were fixed at 1.75 Å. One of the dichloromethane molecules was disordered over a two-fold axis and was modeled anisotropically as a 50 : 50 mixture. The molecule of adventitious water was modeled as an isotropic oxygen atom. The center of the molecule is situated on a two-fold axis.

[Resorcinarene(OC(O)C_6H_{11})$_4$(OPPh$_2${$HgCl_2$})$_4$], 6a

Crystals of [$C_{136}H_{132}Cl_8Hg_4O_{12}P_4$]·$8C_2H_4Cl_2$ were grown by diffusion of hexane into a dichloroethane solution. There was some disorder in the compound. One of the phenethyl groups was modeled as a 25 : 35 : 40 isotropic mixture. The carbon–carbon single bonds in this disordered group were restrained to be equal and allowed to refine. Two of the cyclohexyl groups were modeled as 60 : 40 isotropic mixtures with the carbon–carbon bonds restrained to be equal and allowed to refine. The carbon–carbon bonds of the solvents of crystallization were restrained to be equal and allowed to refine; the carbon–chlorine bonds were treated similarly. Two of the solvent molecules had disordered carbon atoms, which were modeled in one case as an isotropic 50 : 50 mixture, and in the second case as an isotropic 65 : 35 mixture.

[Resorcinarene(OC(O)C_6H_{11})$_4$(OPPh$_2${$HgBr_2$})$_4$], 6b

Crystals of [$C_{136}H_{132}Br_8Hg_4O_{12}P_4$]·$8C_2H_4Cl_2$ were grown by diffusion of hexane into a dichloroethane solution. There was disorder of the carbon atoms in four of the solvent molecules, which in each case was modeled as a 60 : 40 isotropic mixture. The carbon–carbon and the carbon–chlorine bond lengths of the solvent molecules were fixed to reasonable distances.

[Resorcinarene(OC(O)C_6H_{11})$_4$(OPPh$_2${HgI_2})$_4$], 6c

Crystals of [$C_{136}H_{132}O_{12}P_4Hg_4I_8$]·$7.5CH_2Cl_2$ were grown by diffusion of hexane into a dichloromethane solution. One of the cyclohexyl moieties was disordered and was modeled as a 60 : 40 isotropic mixture, with the C–C bond distances fixed at 1.54 Å. A second cyclohexyl group showed evidence of disorder, however no suitable model for this disorder could be refined, and the group was refined isotropically with all C–C bond

Table 5 Crystallographic data for complexes **5b**, **6a**–**c** and **7c**

	5b	**6a**	**6b**	**6c**	**7c**
Formula	$C_{144}H_{124}Br_8Cl_8Hg_4O_{17}P_4$	$C_{152}H_{164}Cl_{24}Hg_4O_{12}P_4$	$C_{152}H_{164}Br_8Cl_{16}Hg_4O_{12}P_4$	$C_{143.5}H_{147}Cl_{15}Hg_4I_8O_{12}P_4$	$C_{146}H_{124}Cl_6Hg_4I_8O_{12}P_4$
M_w	3975.55	3959.87	4315.55	4536.80	4224.59
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/n$	$P2_1/n$	$P2_1/c$	*C*2/*c*
a/Å	41.3843(3)	26.6994(2)	26.9092(2)	26.0428(1)	42.3855(4)
b/Å	14.4061(1)	16.0482(1)	16.0172(1)	19.2768(1)	13.3920(1)
c/Å	28.1428(2)	38.9034(2)	39.1752(3)	32.8951(2)	30.5744(3)
β/°	108.864(1)	104.395(1)	104.377(7)	91.007(1)	118.131(1)
V/Å^3	15877.2(2)	16145.9(2)	16356.1(2)	16511.5(2)	15304.7(2)
Z	4	4	4	4	4
μ/mm^{-1}	6.101	4.285	6.053	5.538	5.815
Data collected	100408	187054	116497	204349	71662
Unique data (R_{int})	18194 (0.075)	36959 (0.106)	37085 (0.082)	37863 (0.094)	17502 (0.073)
*R*1, *wR*2 [$I > 2\sigma(I)$]	0.0565, 0.1409	0.0468, 0.0962	0.0524, 0.1143	0.0534, 0.1438	0.0530, 0.1299
R indices (all data)	0.0866, 0.1520	0.1045, 0.1113	0.1029, 0.1315	0.0896, 0.1551	0.1109, 0.1477

distances fixed at 1.54 Å. One of the carbonyl groups was modeled as a 70 : 30 isotropic mixture, with the carbon–oxygen bond distance fixed. The carbon–chlorine bond lengths of the solvents of crystallization were restrained to be equal and allowed to refine; the half occupancy solvent molecule also had the Cl(C)Cl distance fixed at 2.85 Å. There was a solvent molecule that was severely disordered around a symmetry element, and all attempts to model the disorder were unsuccessful. Thus the SQUEEZE procedure of the PLATON suite of programs[13] was used to account for the solvent electron density. A total of 102 e$^-$ were removed in a volume of 689 Å^3 (4.2% of the unit cell), which corresponds to approximately 2.5 molecules of dichloromethane.

[Resorcinarene(OC(O)$C_6H_4CH_3$)$_4$(OPPh$_2${HgI$_2$})$_4$], 7c

Crystals of $[C_{140}H_{116}Hg_4I_8O_{12}P_4]\cdot 3C_2H_4Cl_2$ were grown by diffusion of hexane into a dichloroethane solution. Both of the tolyl groups were modeled as 60 : 40 isotropic mixtures. There was evidence for disorder of one of the phenyl rings of a diphenylphosphinite group (C1F–C6F), but no suitable disorder model could be refined. The carbon–carbon and the carbon–chlorine bond lengths of the dichloroethane molecules were fixed at 1.54 and 1.75 Å, respectively. One of the dichloroethane molecules was disordered over a symmetry element and was modeled as a 50 : 50 mixture without hydrogen atoms. For the two half occupancy solvent molecules, only the chlorine atoms were refined anisotropically. The center of the molecule is situated on a two-fold axis. The largest residual electron density peak (1.120 e Å^{-3}) was associated with one of the chlorine atoms (Cl20).

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