Mercury complexes of an *N*-heterocyclic carbene derived from a calixarene/azolium cyclophane hybrid[†]

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Abstract

Reaction of mercuric acetate with an imidazolium-linked cyclophane incorporating 2,6-phenolic moieties results in formation of an interesting new *N*-heterocyclic carbene (NHC) complex of mercury. The new complex is cationic and binuclear, incorporating two mercury centres and two bis(NHC) ligands, each mercury atom being bound by two NHC moieties and two phenol/phenoxy moieties. Forms of the complex having coordinating ($HgBr_4^{2-}$) and non-coordinating (PF_6^-) counterions have been structurally characterised.

Dedicated to Jack Harrowfield and Jacques Vicens: 'Nil illegitimae abradum!'

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Introduction

N-Heterocyclic carbene (NHC) ligands have been a focal point in organometallic chemistry over the last two decades, in part because of their ability to form stable complexes with many metals. Some NHC complexes in which the NHC components are part of a cyclophane skeleton have proved to be particularly robust, and have exhibited interesting catalytic and biological activities. There has also been much interest in metal complexes of NHCs that have pendant groups that can serve as ancillary hemilabile donors. For example, metal complexes of NHCs having pendant thiolate [1], thioether [2, 3], ether [4, 5], alkoxide [6, 7], phenol [8] and phenoxide [9-13] moieties have been reported, and in some of those studies their catalytic activities have been explored.

In a previous report [14], we explored the nature of compounds **1**.4PF$_6$ - **4** formed between mercury(II) and bis(NHC) ligands derived from imidazolium-linked cyclophanes **5**.2Br - **8**.2Br (Scheme 1). In the macrocycles, the groups linking the imidazolium/NHC components contained *o*-phenylene (e.g., **1**.4PF$_6$, **5**.2Br), *m*-phenylene (e.g., **2**.2PF$_6$, **6**.2Br), mesityl (e.g., **3**.2PF$_6$, **7**.2Br) or 2,6-pyridinediyl moieties (e.g., **4**, **8**.2Br). Among the complexes, **2**$^{2+}$ and **3**$^{2+}$ were mononuclear species, while **1**$^{4+}$ and **4** were binuclear; the macrocycle in **1**.4PF$_6$ and **5**.2Br is fourteen-membered, and sixteen-membered in **2**.2PF$_6$ - **4** and **6**.2Br - **8**.2Br. In **2**$^{2+}$ and **3**$^{2+}$, the mercury atom is quasi-linearly coordinated by a pair of carbene-carbon atoms, the heterocyclic rings of the NHC units being essentially coplanar. Despite the mercury atoms in **2**$^{2+}$ and **3**$^{2+}$ having additional long pi-interactions with the bridging aromatic groups to either side, we find one or two distant approaches in the remaining fifth (and sixth) coordination positions by anionic (hexafluorophosphate) fluorine atoms. In **1**$^{4+}$ and **4**, the still quasi-linearly coordinating carbenoid carbon atoms are drawn from different macrocycles, the mercury atom coordination environments now being augmented by (still rather distant) solvent DMSO O-donors (rather than PF$_6^-$ counterions) in **1**$^{4+}$, and, in **4**, by pairs of bromide ions (rather than the accompanying DMSO solvent).

In the preceding contribution [15], we explored a further macrocycle 9^{2+} (Scheme 1) in which the azolium cyclophane form was combined with the calix[4]arene form (which has certain similarities). Here, the imidazolium rings are now coupled with 2,6-phenolic linkages, the latter functionalized and potential donors (cf. the pyridine cyclophane 8^{2+}, and its NHC derivative in **4**, wherein any potential interaction of the potential pyridine donor with mercury was obviated by the presence of the coordinated bromide); in 9^{2+}, the macrocycle is the same size as in the pyridine-linked 8^{2+}. Arguably, however, the coordination propensity of the phenolic oxygen atom may be increased by virtue of its pendant nature, assisted by its enhanced its proximity to any receptor metal atom. In this paper, we explore this possibility via the synthesis and structural characterisation of two salts of a mercury(II) complex of the bis(NHC) ligand derived from 9^{2+}.

Results and discussion

Synthesis and NMR studies

Treatment of the cyclophane salt **9**.2PF$_6$ with an equimolar amount of mercuric acetate in acetonitrile at reflux resulted in formation of the binuclear Hg-NHC complex 10^{2+} (Scheme 2). The complex was obtained as colourless needles of the hexafluorophosphate salt **10**.2PF$_6$, which was easily purified by recrystallisation from acetonitrile. Unequivocal identification of the structure of the complex 10^{2+} required an X-ray study (see below). Nevertheless, formation of an Hg-NHC complex was confirmed by ^{1}H NMR spectroscopy, by loss of the signal due to the imidazolium H2 protons of 9^{2+} (~8.6 ppm, Fig. 1a), as well as loss of the broad singlet due to the benzylic protons in 9^{2+} and the appearance of two sharp doublet signals corresponding to benzylic protons in chemically distinct *exo* and *endo* environments in the complex 1^{2+} (~4.9 and 6.0 ppm, Fig. 1b). No signal due to the phenolic protons in 10^{2+} was detected, perhaps because of rapid exchange of the phenolic protons between sites on phenolic oxygen atoms in 10^{2+} and sites in adventitious water,=

or hydrogen-bound to solvent (d_6-DMSO) molecules. Consistent with this suggestion, the signal for adventitious water (~3.3 ppm, Fig. 1b) is somewhat broadened. In the ^{13}C NMR spectrum, the signal due to the Hg-C carbon atoms appears near 174 ppm.

Complex 10^{2+} was also formed when 9.2Br or the binuclear salt 11.2Br [15] (Scheme 3) were heated with mercuric acetate in DMF or acetonitrile respectively. From one such experiment, the complex crystallised from DMF as 10.HgBr$_4$, an adduct with tetrabromidomercurate (see below). The ^1H NMR spectra of solutions containing 10.HgBr$_4$ or 10.2PF$_6$ were essentially identical, suggesting little if any interaction between 10^{2+} and the counteranions in solution.

We conducted a few experiments aimed at synthesizing complexes of other metals with NHC ligands derived from 9^{2+}. When 9.2Br was treated with titanium(IV) tetra(isopropoxide) in THF at reflux, no reaction occurred. When 9.2Br was treated with silver(I) oxide in DMF or copper(I) oxide in CH$_2$Cl$_2$, 9^{2+} was partially deprotonated, to form the dimeric cation 11^{2+} [15], which was identified by ^1H NMR spectroscopy, but no evidence for metal complexes was seen. We also explored the possibility of preparing metal complexes from NHC ligands derived from the hexafluorophosphate salt of the mono-phenol imidazolium cyclophane 12^{2+} (Scheme 3). When 12.2PF$_6$ was treated with mercuric acetate in acetonitrile at reflux, there was no significant reaction. When 12.2PF$_6$ was treated with silver oxide in acetonitrile at reflux, or when 12.2Br was treated with palladium acetate in DMF at 90 °C overnight or at room temperature for 3 days, intractable mixtures were obtained. Examination of the product mixtures by ^1H NMR spectroscopy provided no evidence for formation of discrete complexes, and the presence of very broad signals suggested that polymeric products may have been formed.

Structural Studies

Two crystalline compounds were obtained from solutions of 10.2PF$_6$ and 10.HgBr$_4$ in acetonitrile and DMF respectively. The results of the 'low'-temperature single crystal X-ray studies (Tables 1 - 3

and Fig. 2) are consistent with the descriptions of the compounds and their structures as solvated salts of the same cation, the latter being binuclear and of putative mmm 2/m (C_{2h}) symmetry, modelled as **10**.2PF$_6$·5MeCN and **10**.HgBr$_4$·8DMF; a single one of these formulations, differing in the associated cation symmetry, comprises the asymmetric unit of structure in each case. The presence of core protonation is presumed from the chemistry in each case, none of the hydroxylic hydrogen atom locations being secured from the structure determinations, either from difference syntheses, or from associated phenolic C-O distances which are closely similar; Hg-O (distances) and Hg-O-C (angles) ranges (the latter very tight) (Table 2) are similarly unhelpful (but see below). In the PF$_6^-$ salt, one of the PF$_6$ groups (#2) was modelled as rotationally disordered over two sets of sites about one of its local F-P-F axes, occupancies 0.73(2) and complement. In the HgBr$_4^{2-}$ salt, two of the ligand t-Bu groups (#13, 23) were modelled as rotationally disordered over two sets of sites, occupancies set at 0.692(13), 0.5 and complements after trial refinement; two DMF groups (one closely approaching a cation mercury atom, ('coordinated'), one not), were modelled as disordered over pairs of sites in concert with the t-Bu groups.

In each case, the form of the cation comprises a pair of ligands, each grossly in a 'cone' conformation, approaching each other in 'eclipsed' confrontation about a common axis, so that their carbenoid carbon atoms confront pairwise, each pair linearly coordinating a mercury atom at ca. 2.0 Å (Table 2), so that a binuclear array is formed. The C-Hg-C linearity is not exact, bowing of the C-Hg-C lines being associated with mutual approaches of the pair of mercury atoms to ca. 4.8 Å, the C$_2$Hg$_2$C$_2$ array being quasi-planar (Fig. 2). The coordination environments of the mercury atoms are further augmented by interactions with two phenolic oxygen atoms from the same ligand; each ligand thus contributes a coordination triad of (C)(O)$_2$ to one mercury atom, with the other carbenoid carbon to the other. To either side of the C$_2$Hg$_2$C$_2$ plane, pairs of oxygen atoms, one pair from each of the ligands, approach at a distance ca. 2.5 Å, appropriate to the support of a pair of appropriately protonating putative hydrogen atoms between the pairs, consistent with a 2+ cationic

charge overall, counterbalancing the PF_6^- or $HgBr_4^{2-}$ anion array (Fig. 2). One possible protonic hydrogen disposition is shown in Fig. 2b; others, symmetrical or not, are also possible.

In respect of the anions and solvent molecules in the PF_6^- salt, there appear to be no close approaches (coordinative) to the mercury atom, or interactions with ligand aromatic rings within or without the ligand cones. There are two centrosymmetric arrays (e.g., Fig. 2a), one-half of each contributing to the asymmetric unit of the structure, so that, with a pair of PF_6^- anions and five acetonitrile molecules, one such formula unit comprises the contents of the unit cell, the arrays being essentially 'naked', cf. (e.g.) those of the compounds **1**.$4PF_6$ and **4** [14].

The array of the $HgBr_4^{2-}$ salt is a different matter. Here the two mercury atoms within the single binuclear cation of the asymmetric unit are crystallographically distinct, and, despite the presence of similar bowings of the C-Hg-C lines to those found in the PF_6^- salt, there are pairs of approaches, from the oxygen atoms of two of the solvating DMF molecules to Hg(2), and two of the bromine atoms of an $HgBr_4^{2-}$ anion to Hg(1) (at 3.129(8), 3.121(11); 3.5448(12), 3.5208(14) Å respectively) to putative distant fifth and sixth *pseudo*-octahedral coordination sites about these atoms (Fig. 2 b). It is interesting to compare the mercury environments of **1**.$2PF_6$ and **4** with those in **10**.$HgBr_4$·8DMF. In both **1**.$2PF_6$ and **4** the mercury centres are four-coordinate, the ancillary ligands being purely *O*-bound solvent (DMSO) in **1**.$2PF_6$ and bromide (in the presence of DMSO) in **4** [14]. In **10**.$HgBr_4$·8DMF, we find, in the six-coordinate environments of the pair of independent mercury atoms, that the enhancement above the $C_2Hg(O$-phenol$)_2$ arrays in one case comprises a pair of *cis*-bromide donors, in the other, a pair of *cis*-O-DMF. Hg-C,O distances in the case of the bromide coordinated mercury atom are slightly elongated cf. their counterparts in the case of the other (Table 2); Hg-O(solvent), Br in **10**.$HgBr_4$·8DMF are considerably longer than their counterparts in compounds **1**.$4PF_6$ and **4** [14].

For the cations in both **10**.$2PF_6$·5MeCN and **10**.$HgBr_4$·8DMF, 'platform' least-squares planes may be calculated through their mercury and carbene carbon atoms, deviations of the latter

being not greater than 0.03 Å. Dihedral angles between these planes and associated C_6 aromatic ring planes are 37.8, 39.4(3)° (PF_6^- salt) and 34.3, 37.6(2)° ($HgBr_4^{2-}$ salt); deviations of the mercury atoms from the C_6 and C_3N_2 ring planes are given in Table 3. The descriptors within Tables 2 and 3 are similar for all of the cations and suggest that the impacts of the coordinating anion and solvent on either of the interacting species in the $HgBr_4^{2-}$ salt are quite limited; the only seriously deviant parameter is perhaps one of the O-Hg-C angles in the $HgBr_4^{2-}$ salt, while, in the PF_6^- salt, one of the Hg…Hg' distances might be considered somewhat short.

The organizing effect of the introduction of the mercury atoms into the ligand pair is evident in the dihedral angle comparisons which may be made in Table 3. It is seen that those of the present cations are similar between **10**.2PF$_6$·5MeCN and **10**.HgBr$_4$·8DMF. For the imidazolium cyclophane salt **11**.2Br, the structure of which comprises a symmetry related pair maintained by the hydrogen-bonds alone (without the mercury atoms), the interplanar angle between the pairs of aromatic planes is similar to that of the mercury complexes, whereas the angle between the pair of imidazole planes (which have the perception of random orientation in the free ligand, the more so given the observation of the other isomer [16] wherein they are opposed), is quite different. The hydrogen-bonded O…O distances, assisting the anchoring of the aromatic rings in both ligand and complexes, are similar.

Conclusion

When mercuric acetate is allowed to react with the calixarene/azolium cyclophane hybrid **9**$^{2+}$, an interesting new binuclear complex **10**$^{2+}$ is formed, the calixarene/azolium cyclophane having been deprotonated at both imidazolium C2 positions and one of the phenolic positions. When the cyclophane is used as its hexafluorophosphate salt **9**.2PF$_6$, the mercury complex is isolated as **10**.2PF$_6$, and each mercury centre is four-coordinate. When the cyclophane is used as its bromide

salt **9**.2Br, the tetrabromidomercurate ion is formed under the reaction conditions. The binuclear complex **10**$^{2+}$ crystallises from DMF as a solvate of the tetrabromidomercurate adduct **10**.HgBr$_4$, each mercury centre in the cation being six-coordinate, one by virtue of coordination with the HgBr$_4$$^{2-}$ ion, the other by interactions with O atoms of two DMF molecules. The binding between **10**$^{2+}$ and HgBr$_4$$^{2-}$ does not persist in d$_6$-DMSO solution.

Experimental Section

General procedures and the synthesis of **9**.2Br were as described previously [15].

Bis(phenol) cyclophane salt **9**.2PF$_6$

A filtered solution of potassium hexafluorophosphate (277 mg, 1.51 mmol) in water (ca. 3 mL) was added to a solution of **9**.2Br [15] (302 mg, 0.47 mmol) in water (ca. 25 mL) and the resulting mixture was stirred at room temperature for 30 min. The precipitate was collected and dried in a desiccator under vacuum for 2 d to afford a colourless powder (223 mg, 61%). ^{1}H NMR (500.13 MHz d$_6$-DMSO): δ 1.26 (s, 18H, 6 x CH$_3$), 5.37 (br s, W$_{H/2}$ = 16Hz, 8H, 4 x CH$_2$), 7.59 (s, 4H, 4 x ArH), 7.68 (apparent d, splitting = 2 Hz, 4H, 2 x H4 and 2 x H5), 8.63 (br s, W$_{h/2}$ = 19 Hz, 2H, 2 x H2), 9.63 (br s, W$_{H/2}$ = 13 Hz, 2H, 2 x OH).

Phenol/ortho-cyclophane **12**.2PF$_6$

A solution of potassium hexafluorophosphate (131 mg, 0.71 mmol) in water (ca. 2 mL) was added to a stirred, filtered solution of **12**.2Br (101 mg, 0.18 mmol) in water (ca. 5 mL) and the resulting mixture was stirred at room temperature for 20 min. The precipitate was collected, washed with water and dried in a vacuum desiccator for 2 d to afford a white powder (96 mg, 77%). ^{1}H NMR

(500.13 MHz, d_6-DMSO): δ 1.34 (s, 9H, 3 x CH_3), 5.17 (d, $^2J_{HH}$ = 14 Hz, 2H, 2 x Hb), 5.34 (br d, splitting = 14 Hz, 2H, 2 x Ha), 5.54 (d, $^2J_{HH}$ = 14 Hz, 2H, 2 x Hb), 5.66 (d, $^2J_{HH}$ = 14 Hz, 2H, 2 x Ha), 7.60 (AA' part of AA'XX' pattern, 2H, 2 x H3a), 7.62 (s, 2H, 2 x H5), 7.81 (s, 2H, 2 x H4), 7.81 (s, 2H, 2 x H3b), 7.92 (XX' part of AA'XX' pattern, 2H, 2 x H2a), 8.40 (br s, $W_{H/2}$ = 12 Hz, 2H, 2 x H2), 9.23 (br s, $W_{H/2}$ = 25 Hz, 1H, OH). Anal. calcd. for $C_{26}H_{30}N_4OBr_2P_2F_{12}$: C, 44.33; H, 4.29; N, 7.95. Found: C, 44.33; H, 4.59; N, 7.86.

Mercury complex **10**.2PF$_6$

A solution of **9**.2PF$_6$ (63 mg, 81 μmol) and mercuric acetate (26 mg, 82 μmol) in anhydrous acetonitrile (40 mL) was heated at reflux for 24 h. The solution was cooled and the solvent was removed under vacuum. The residue was washed with water to afford a white powder that was collected and recrystallised from hot acetonitrile to afford **10**.2PF$_6$ as colourless needles (20 mg, 34%). ^{1}H NMR (500.13 MHz, d_6-DMSO) δ: 1.26 (s, 18H, 6 x CH_3), 4.92 (d, $^2J_{H,H}$ = 14 Hz, 4H, 4 x C*H*H), 6.00 (d, $^2J_{H,H}$ = 14 Hz, 4H, 4 x CH*H*), 7.09 (s, 4H, 2 x H4 and 2 x H5), 7.49 (s, 4H, 4 x ArH), phenol OH not detected. ^{13}C NMR (125.77 MHz, d_6-DMSO): δ 31.40 (CH_3), 33.55 (*C*$(CH_3)_3$), 51.97 (CH_2), 122.58 (C4 and C5), 124.56 (Ar *C*CH$_2$), 129.12 (Ar CH), 138.40 (Ar *C*-^{t}Bu), 157.26 (Ar C-O), 174.44 (C2). Anal. calcd. for $C_{60}H_{70}N_8O_4Hg_2(PF_6)_2$: C, 43.46; H, 4.25; N, 6.76. Found: C, 43.50; H, 4.52; N, 6.81.

Mercury complex **10**.HgBr$_4$

A solution of **11**.2Br (32 mg, 28.3 μmol) and mercuric acetate (21 mg, 65.9 μmol) in acetonitrile (4 mL) was heated at reflux for 18 h. The resulting precipitate was collected and dried under vacuum to afford a white powder (31 mg, 57%). ^{1}H NMR (500.13 MHz, d_6-DMSO): δ 1.26 (s, 36H, 12 x

CH_3), 4.89 (d, $^2J_{HH}$ = 14 Hz, 8H, 8 x CHH), 6.04 (d, $^2J_{HH}$ = 14 Hz, 8H, 8 x CHH), 7.04 (s, 8H, 4 x H4 and 4 x H5), 7.45 (s, 8H, 8 x ArH). ^{13}C NMR (125.76 MHz, d_6-DMSO): δ 33.49 (CH_3), 33.48 ($C(CH_3)_3$), 51.94 (CH_2), 122.37 (C4 and C5), 124.58 (Ar CCH$_2$), 128.79 (Ar CH), 138 (Ar C-^{t}Bu), 158 (Ar CO), 175.46 (C2). HRMS (FAB) m/z: 163.4703 ($C_{60}H_{68}N_4O_4$$^{199}Hg$$^{200}Hg$ [M-HgBr$_4$-H] requires 1363.4730), 1364.4781 ($C_{60}H_{68}N_4O_4$$^{199}Hg$$^{201}Hg$ [M-HgBr$_4$-H] requires 1364.4749), 1365.4791 ($C_{60}H_{68}N_4O_2$$^{199}Hg$$^{202}Hg$ [M-HgBr$_4$-H] requires 1365.4753). Anal. calcd. for $C_{60}H_{70}N_8O_4Hg_3Br_4$: C, 38.16; H, 3.74; N, 5.93. Found: C, 38.04; H, 4.19; N, 5.17.

Structure determinations

The general procedure is described in a preceding paper [15], but with the following minor variations. In **10**.HgBr$_4$.8DMF, two t-butyl groups, one coordinated DMF and one solvent DMF were modelled as disordered over two sets of sites. In **10**.2PF$_6$.5MeCN, two t-butyl groups were modelled as disordered, as also was one of the PF$_6^-$ anions. Phenolic hydrogen atoms could not be sensibly located, there being no outstanding differences in C-O parameters or environments, and they were omitted from the refinement. Pertinent results are given in the Tables, text and Fig. 2, the latter showing non-hydrogen atom displacement envelopes at the 50% probability amplitude level. Full .cif depositions for both structures reside with the Cambridge Structural Database, CCDC 1038211, 1038212.

Conflict of Interest: The authors declare that they have no conflict of interest.

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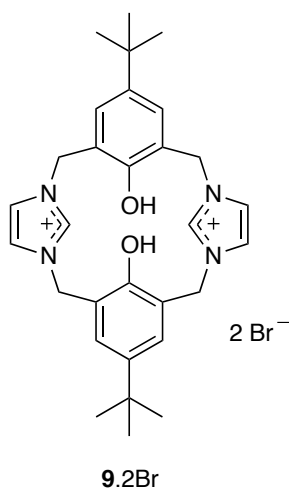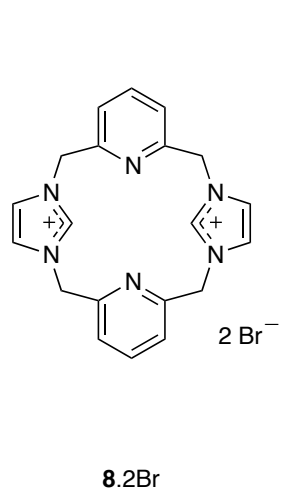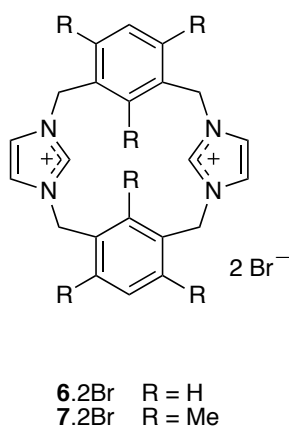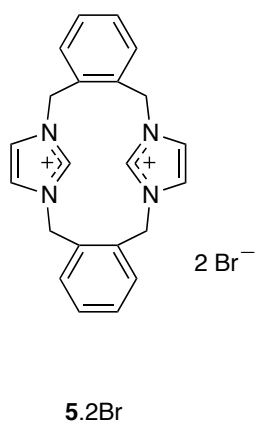**Figure and Scheme captions**
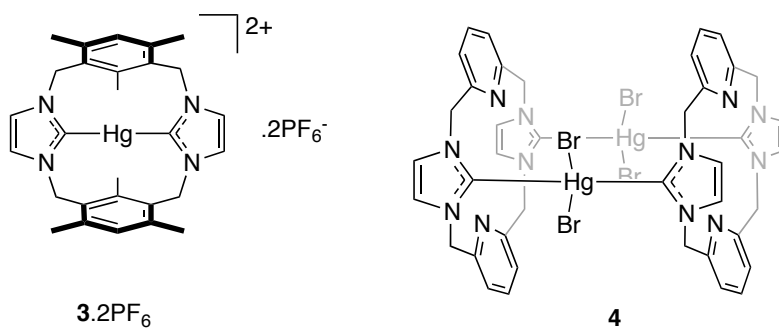
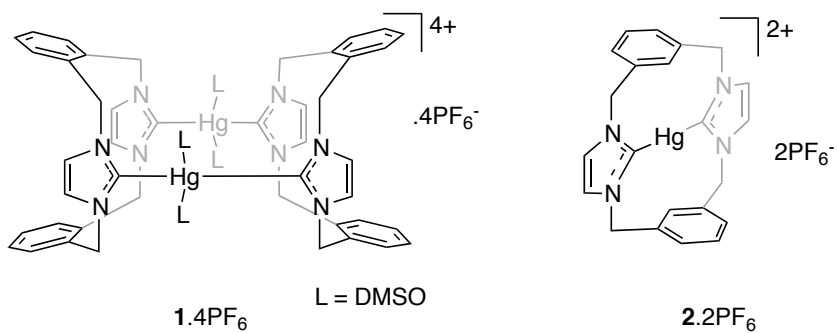**Scheme 1** Compounds **1**.4PF$_6$ - **9**.2Br

Scheme 2 Synthesis of the binuclear Hg-NHC complex **10**

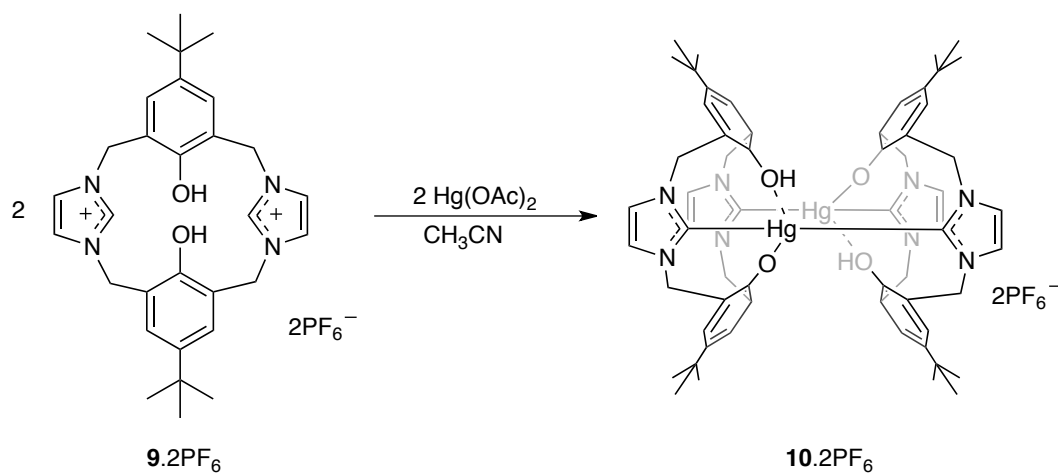**Scheme 3** The salts **11**.2Br and **12**.2PF$_6$
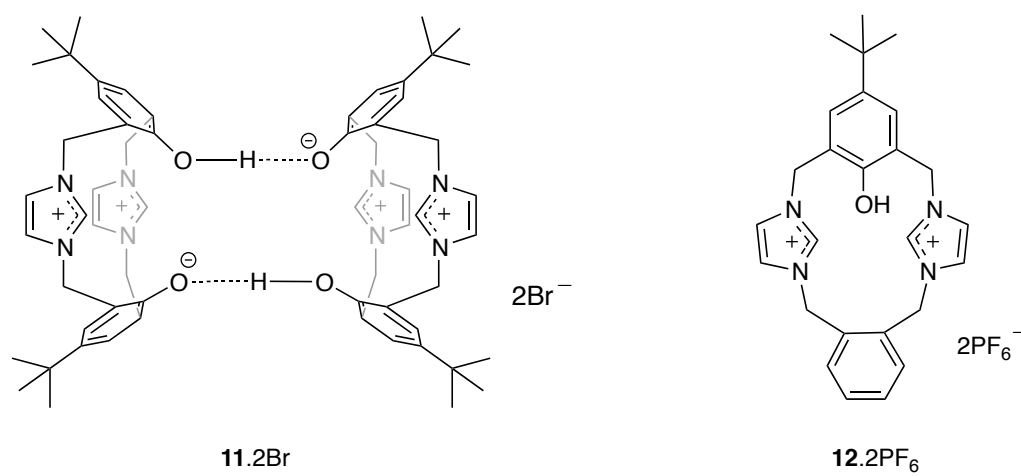
Fig. 1 ^{1}H NMR spectra (500 MHz, ambient temperature) for: **a**, a solution of **9**.2PF$_6$ in DMSO-d$_6$, and **b**, a solution of the Hg-NHC complex **10**.2PF$_6$ in DMSO-d$_6$. The signal marked with an asterisk (*) is due to traces of solvent impurity (CH$_3$CN, reaction solvent). Signals at 2.5 and ~ 3.3 ppm are due to residual solvent protons (DMSO-d$_5$) and adventitious moisture respectively. Signals marked with a tilde (~) have been cropped for clarity.

Fig. 2 a Projection of the binuclear cation 1 of **10**.2PF$_6$·5MeCN
Fig. 2 b Projection of the binuclear cation of **10**.HgBr$_4$·8DMF, together with the approaches of the anion and the 'coordinating' pair of DMF solvent molecules. One of the possible dispositions of the phenolic protonating hydrogen atoms is shown.

Scheme 1 Compounds **1**.4PF$_6$ - **9**.2Br

1.4PF$_6$ L = DMSO

2.2PF$_6$

3.2PF$_6$

4

5.2Br

6.2Br   R = H
7.2Br   R = Me

8.2Br

**9**.2Br

Scheme 2 Synthesis of the binuclear Hg-NHC complex **10**

2     $\xrightarrow[\text{CH}_3\text{CN}]{2\ \text{Hg(OAc)}_2}$

9.2PF$_6$ **10**.2PF$_6$

Scheme 3 The salts **11**.2Br and **12**.2PF$_6$
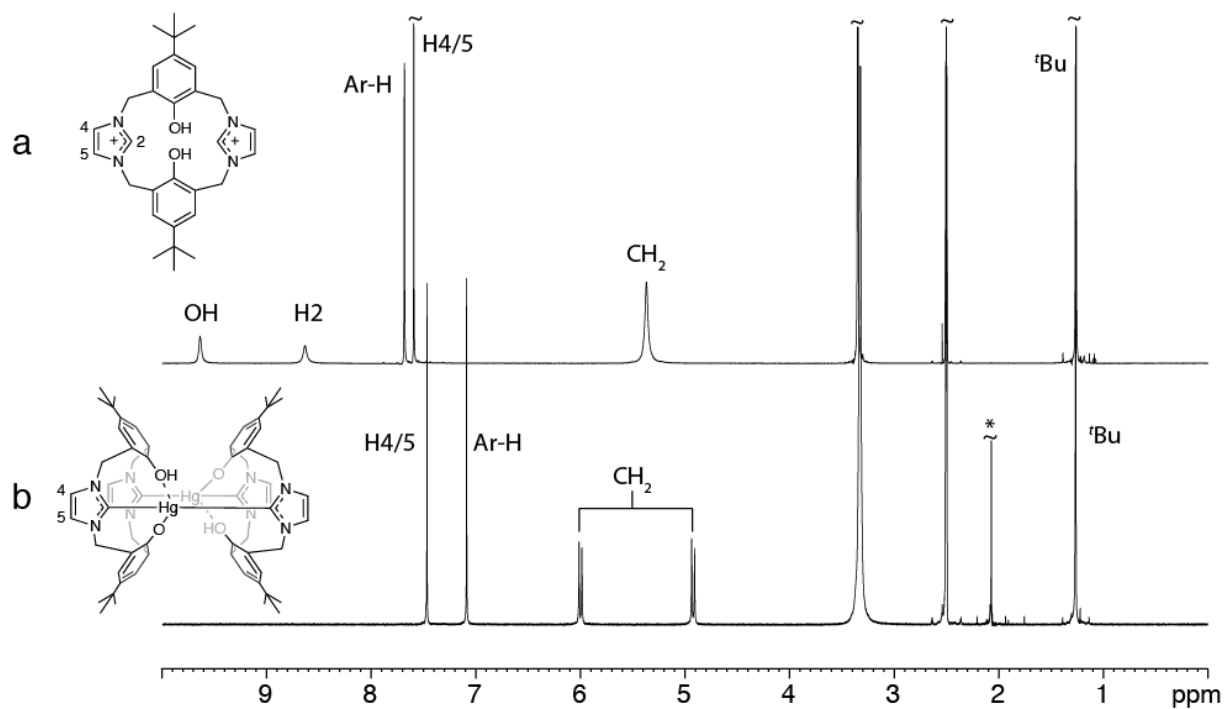

11.2Br   **12**.2PF$_6$

Fig. 1 ^{1}H NMR spectra (500 MHz, ambient temperature) for: **a**, a solution of **9**.2PF$_6$ in DMSO-d$_6$, and **b**, a solution of the Hg-NHC complex **10**.2PF$_6$ in DMSO-d$_6$. The signal marked with as asterisk (*) is due to traces of solvent impurity (CH$_3$CN, reaction solvent). Signals at 2.5 and ~ 3.3 ppm are due to residual solvent protons (DMSO-d$_5$) and adventitious moisture respectively. Signals marked with a tilde (~) have been cropped for clarity.

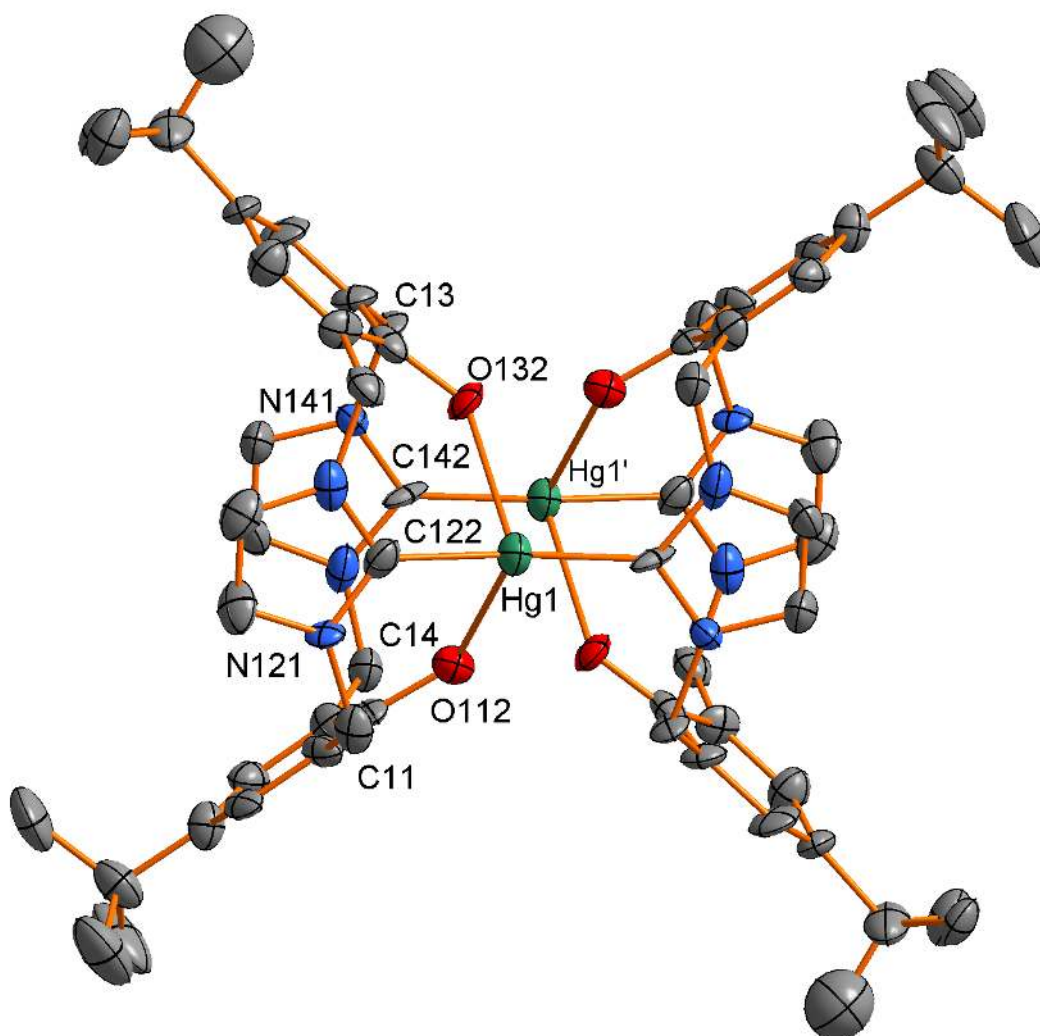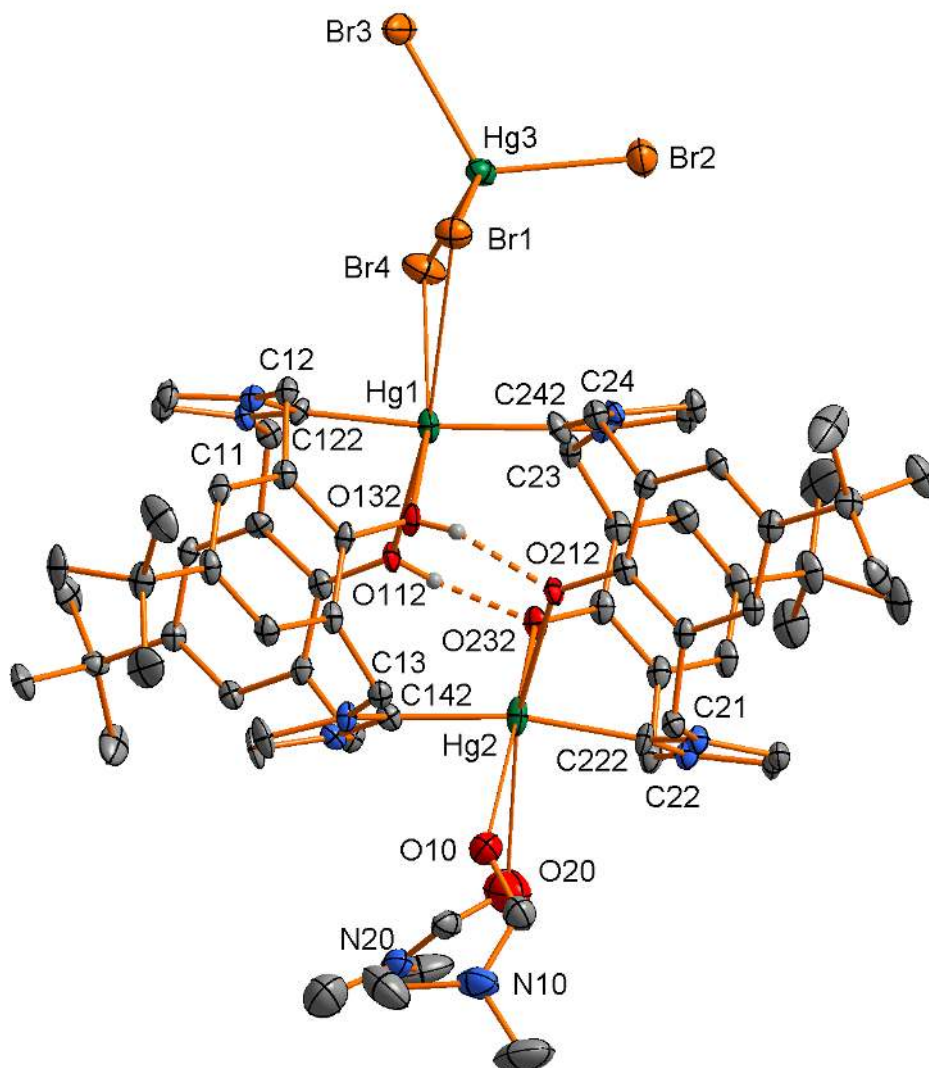**Fig. 2 a** Projection of binuclear cation 1 of **10**.2PF$_6$·5MeCN

Fig. 2 b Projection of the binuclear cation of **10**.HgBr$_4$·8DMF, together with the approaches of the anion and the 'coordinating' pair of DMF solvent molecules.

Table 1 Crystal/refinement data

	$10 \cdot 2PF_6 \cdot 5MeCN$	$10 \cdot HgBr_4 \cdot 8DMF$
Formula	$C_{70}H_{85}F_{12}Hg_2N_{13}O_4P_2$	$C_{84}H_{126}Br_4Hg_3N_{16}O_{12}$
M_r	1863.6 daltons	2473.4 daltons
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (C_i^1, No. 2)	$P2_1/n$ (C_{2h}^5, No. 14)
Unit cell	$a = 13.438(1)$ Å	$a = 14.308(3)$ Å
	$b = 14.306(1)$ Å	$b = 25.731(5)$ Å
	$c = 21.398(1)$ Å	$c = 26.257(5)$ Å
	$\alpha = 88.364(7)°$	$\alpha = 90°$
	$\beta = 72.578(7)°$	$\beta = 91.597(3)°$
	$\gamma = 89.442(8)°$	$\gamma = 90°$
V	$3923.3(5)$ Å^3	$9666(3)$ Å^3
Density (Z)	1.578 Mg.m^{-3} (2 f.u.)	1.700 Mg.m^{-3} (4 f.u.)
μ_{Mo} ('$T_{min/max}$)	4.0 mm^{-1} (0.87)	6.5 mm^{-1} (0.51)
Specimen	0.142x0.048x0.042 mm^3	0.52x0.12x0.10 mm^3
$2\theta_{max}$ (N_t)	50° (33774)	58° (89112)
N (R_{int})	13710 (0.092)	23917 (0.069)
N_o ($I > 2\sigma(I)$)	5414	15921
R_1 (S)	0.048 (0.70)	0.061 (1.08)
wR_2 (a(,b))	0.074 (0.013, -)	0.162 (0.063, 67)
$|\Delta\rho|_{max}$	1.32 eÅ^{-3}	4.5 eÅ^{-3}

Table 2 Selected mercury atom environments in **10**.2PF$_6$·5MeCN and **10**.HgBr$_4$·8DMF

	10.2PF$_6$·5MeCN		**10**.HgBr$_4$·8DMF	
	Cation 1	Cation 2	Hg(1)	Hg(2)
Distances (Å)				
Hg-C	2.034(9)	2.027(9)	2.050(7)	2.074(8)
Hg-C'	1.997(9)	2.028(8)	2.075(9)	2.035(8)
Hg-O	2.578(5)	2.625(6)	2.673(5)	2.633(5)
Hg-O'	2.632(5)	2.633(5)	2.732(5)	2.649(5)
Hg…Hg'	4.7208(6)	4.8082(6)	4.8127(12)	
O…O'	2.502(8)	2.486(8)	2.499(8)	2.532(8)
Angles (degrees)				
C-Hg-C'	167.4(3)	171.8(3)	174.5(3)	169.3(3)
O-Hg-O	94.4(2)	92.5(2)	93.7(2)	94.3(2)
O-Hg-C	87.1(3)	88.2(3)	84.1(2)	76.8(3)
O-Hg-C'	100.4(3)	98.4(3)	99.1(3)	99.7(3)
O-Hg-C	87.1(3)	85.7(3)	85.5(2)	89.1(3)
O-Hg-C'	102.3(3)	98.8(2)	98.8(2)	100.7(3)

In the PF$_6^-$ salt, in each binuclear cation there are two centrosymmetrically related mercury atoms; primed atoms belong to the other ligand/other half of the cation. About Hg(3) in the HgBr$_4^{2-}$ anion, Hg-Br range between 2.5940(11)-2.6076(13) Å, and Br-Hg-Br 106.23(4)-103.96(4)°; Hg(3)…Hg(1) is 4.1364(10) Å, and Hg(1)…Br(1,4) 3.5448(12), 3.5208(14) Å. Hg(2)…O(dmf(1,2)) are 3.129(8), 3.121(11) Å. In the PF$_6^-$ salt, Hg-O-C range between 132.7(5)-134.4(5)°, and in the HgBr$_4^{2-}$ salt 132.0(5)-134.8(4)°.

Table 3 Ligand plane parameters

Ring	10.2PF$_6$·5MeCN		10.HgBr$_4$·8DMF	
(a) Mercury atom out-of-plane distances (Å)				
	Hg(1)	Hg(2)	Hg(1)	Hg(2)
C$_3$N$_2$ (12)	0.16(2), -	- , -	0.066(14)	-
(14)	- , *0.24(2)*	- , -	-	0.394(15)
(22)	- , -	0.29(2), -	-	0.051(15)
(24)	- , -	- , *0.25(2)*	0.29(2)	-
C$_6$ (11)	0.86(2), *0.73(2)*	0.65(2), *0.78(2)*	0.82(2)	0.80(2)
(13)	0.67(2), *0.74(2)*	0.65(2), *0.61(2)*	0.95(2)	1.16(2)
(21)	- , -	- , -	0.75(2)	0.75(2)
(23)	- , -	- , -	10.2(2)	0.96(2)
(b) Interplanar dihedral angles (degrees)				
(i) C$_3$N$_2$ imidazole planes				
	ligand (1)	ligand (2)	ligand (1)	ligand (2)
n2/n4	14.2(4)	7.2(4)	16.2(4)	16.3(4)
(ii) C$_6$ aromatic planes				
	ligand (1)	ligand (2)	ligand (1)	ligand (2)
n1/n3	77.1(4)	80.7(3)	71.8(3)	73.2(3)

For the PF$_6^-$ salt, italicized values are symmetry related; in the monoprotonated cyclophane system **11**.2Br.4MeCN [15], devoid of mercury atoms, but with similar confronting pairs of ligands with oxygen atoms linked by hydrogen bonds, (O(-H)…O' 2.445(2) Å)), the im/im and Ar/Ar interplanar dihedral angles are 69.21(8), 78.84(6)º.