

Methyl substituted benzene adducts of trimeric perfluoro-*ortho*-phenylene mercury

Mason R. Haneline, Julie B. King and François P. Gabbaï*

Chemistry TAMU 3255, Texas A&M University, College Station, Texas 77843-3255, USA.

E-mail: francois@tamu.edu

Received 10th April 2003, Accepted 24th May 2003

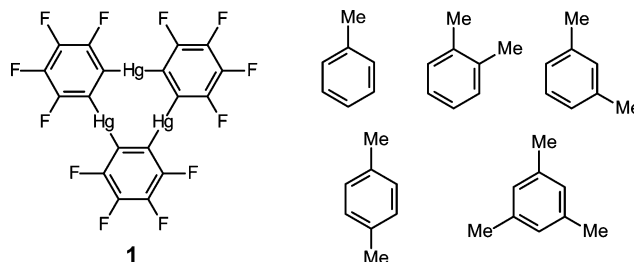
First published as an Advance Article on the web 9th June 2003

Trimeric perfluoro-*ortho*-phenylene mercury (**1**) dissolves in substituted benzenes including toluene, *ortho*-xylene, *meta*-xylene, *para*-xylene and is sparingly soluble in mesitylene. The ^{199}Hg NMR resonance of **1** in toluene, *ortho*-xylene, *meta*-xylene, and *para*-xylene appears at δ –1051.8, –1053.5, –1051.4 and –1059.1 ppm, respectively. These resonances are slightly upfield from the resonance observed for **1** in CH_2Cl_2 (δ –1045.2 ppm) and possibly indicates the solvation of the mercury centres by molecules of arenes. Slow evaporation of solutions of **1** in toluene, *ortho*-xylene, *meta*-xylene, *para*-xylene and mesitylene affords **1**·toluene (**2**), **1**·*ortho*-xylene (**3**), **1**·*meta*-xylene (**4**), **1**·*para*-xylene (**5**) and **1**·mesitylene (**6**), respectively, as crystalline complexes. These adducts have been characterized by elemental analysis and X-ray crystallography. Thermogravimetric analyses indicate that **2–5** begin to lose the coordinated arene at a temperature below 50 °C; however, in the case of **6** loss begins around 91 °C. The structures of **2**, **4** and **5** reveals the existence of binary stacks in which the aromatic core of the benzenes approaches the mercury centres of **1**. In the case of **3** and **6**, the aromatic molecule appears preferentially bound to one of the two proximal molecules of **1**. Hence, **3** and **6** are best described as discrete 1 : 1 complexes. In **2–6**, the resulting $\text{Hg} \cdots \text{C}_{\text{aromatic}}$ distances are in the range 3.2–3.5 Å and are within the sum of the van der Waals radii. They reflect the presence of secondary polyhapto π -interactions occurring between the electron-rich aromatic molecules and the acidic mercury centres.

Introduction

The complexation of arenes to mercury(II) cations constitutes a well established phenomenon.^{1–5} While original efforts focused on the spectroscopic characterization of the resulting arene-mercury complexes, structural studies have also been performed and indicate that the arene ligand shows a propensity for both η^1/η^2 -coordination to the mercury centres as shown by the work of the groups of Olah,¹ Dean,² Kochi,³ and Barron.⁴ The formation of such complexes results in the activation of the arene substrates toward electrophilic mercuriation reactions. Further support for electrophilic aromatic substitution reaction has been provided by Barron and co-workers who showed that arene mercury(II) cationic complexes catalyze H/D exchange reactions of C_6D_6 with arenes.⁶ While such reactivity is apparently limited to the case of arene complexes of mercury(II) salts, the mercury centres of organomercurials can also bind arenes in a π -fashion.⁷ Typically, however, the π -coordination of arenes observed in organomercurials is relatively weak and results in $\text{Hg} \cdots \text{C}_{\text{aromatic}}$ distances in the range 3–3.4 Å. While in most cases, arene coordination occurs intramolecularly,⁸ a growing number of investigations indicate that intermolecular π -arene complexation constitutes a viable motif.^{9–11} Nevertheless, the observation of such complexes necessitates the use of organomercurials in which the Lewis acidity of the mercury centre is enhanced through the use of fluorinated and therefore electron withdrawing ligands.^{9–11} We first observed such a phenomenon in the isolation of π -complexes involving *ortho*-bis(chloromercurio)tetrafluorophenylene and benzene.⁹ Taking advantage of favorable cooperative effects, we turned our attention to the case of trimeric perfluoro-*ortho*-phenylene mercury¹² (**1**), a tridentate Lewis acid¹³ which readily complexes neutral^{14–17} and anionic substrates.¹⁸ Compound **1** crystallizes from benzene solutions to afford the complex [**1**·benzene].¹⁰ The resulting complex [**1**·benzene] adopts a stacked structure in which the benzene molecules are sandwiched between nearly parallel, yet staggered molecules of **1**. As a result of this arrangement, the benzene molecule interacts with the six mercury centres of the two juxtaposed molecules of

1 in a $\mu_6\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2$ fashion. Formation of binary stacks is also observed with larger arenes such as biphenyl, naphthalene and triphenylene.¹¹ In an effort to determine how steric effects might affect complex formation, we have now turned our attention to the case of methylated benzenes and wish to report on the complexation of toluene, *ortho*-xylene, *meta*-xylene, *para*-xylene and mesitylene by **1**.



Results and discussion

Synthesis and thermal stability

Compound **1** is only sparingly soluble in benzene (<0.2 mg ml^{-1}) and mesitylene (0.34 mg ml^{-1}), but dissolves in toluene (6.5 mg ml^{-1}), *ortho*-xylene (4.5 mg ml^{-1}), *meta*-xylene (2.5 mg ml^{-1}), and *para*-xylene (4.0 mg ml^{-1}). The ^{199}Hg NMR resonance of **1** in toluene, *ortho*-xylene, *meta*-xylene, and *para*-xylene appears at δ –1051.8, –1053.5, –1051.4 and –1059.1 ppm, respectively. Despite extended acquisition time, the ^{199}Hg NMR resonance of **1** in benzene or mesitylene could not be obtained due to the poor solubility of **1** in those solvents. We also note that the detection of the ^{199}Hg NMR resonance of **1** is complicated by its high multiplicity which results from Hg–F coupling.¹⁶ Slow evaporation of solutions of **1** in toluene, *ortho*-xylene, *meta*-xylene and mesitylene affords [**1**·toluene] (**2**), [**1**·*ortho*-xylene] (**3**), [**1**·*meta*-xylene] (**4**), [**1**·*para*-xylene] (**5**) and [**1**·mesitylene] (**6**), respectively, as crystalline complexes. These colourless complexes are stable for months at room temperature. Upon elevation of the temperature,

Table 1 Crystal data, data collection, and structure refinement for 2–6

	2	3	4	5	6
<i>Crystal data</i>					
Formula	C ₂₅ H ₈ F ₁₂ Hg ₃	C ₂₆ H ₁₀ F ₁₂ Hg ₃	C ₂₆ H ₁₀ F ₁₂ Hg ₃	C ₂₆ H ₁₀ F ₁₂ Hg ₃	C ₂₇ H ₁₂ F ₁₂ Hg ₃
<i>M_r</i>	1138.08	1152.11	1152.11	1152.11	1166.14
Crystal size/mm	0.44 × 0.21 × 0.16	0.33 × 0.17 × 0.14	0.54 × 0.06 × 0.06	0.30 × 0.15 × 0.13	0.25 × 0.24 × 0.40
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/n</i>	<i>Pna2₁</i>	<i>Pna2₁</i>	<i>P2₁/c</i>
<i>a</i> /Å	9.514(2)	20.050(4)	15.923(3)	16.854(3)	16.453(3)
<i>b</i> /Å	7.4205(19)	6.8569(14)	21.678(4)	20.891(4)	7.3780(15)
<i>c</i> /Å	35.267(9)	20.158(4)	7.2192(14)	7.1384(14)	22.030(4)
β /°	93.550(4)	115.23(3)			96.43(3)
<i>V</i> /Å ³	2485.1(11)	2507.0(9)	2491.9(9)	2513.4(9)	2657.4(9)
<i>Z</i>	4	4	4	4	4
<i>D_c</i> /g cm ⁻³	3.042	3.052	3.071	3.045	2.915
μ (Mo-K α)/mm ⁻¹	18.592	18.432	18.544	18.385	17.391
<i>F</i> (000)/e	2024	2056	2056	2056	2088
<i>Data collection</i>					
<i>T</i> /K	110(2)	110(2)	200(2)	293(2)	293(2)
Scan mode	ω	ω	ω	ω	ω
<i>hkl</i> Range	–10 to 10, –8 to 8, –40 to 40	–23 to 21, –8 to 6, –23 to 23	–17 to 17, –24 to 23, –8 to 8	–19 to 18, –23 to 23, –7 to 8	–22 to 19, –9 to 9, –29 to 29
Measured refl.	21172	16191	19871	15314	29640
Unique refl. (<i>R_{int}</i>)	3906 (0.1125)	4385 (0.0440)	3573 (0.0368)	3779 (0.0452)	6307 (0.0508)
Refl. used for refinement	3906	4385	3573	3779	6307
Absorption correction	Empirical	SADABS	SADABS	SADABS	SADABS
<i>T_{min}</i> / <i>T_{max}</i>	0.2620/0.9655	0.4031	0.326298	0.624366	0.252773
<i>Refinement</i>					
Refined parameters	361	370	370	370	379
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0433, 0.1046	0.0439, 0.1033	0.0217, 0.0498	0.0504, 0.1174	0.0420, 0.1035
$\Delta\rho$ (max., min.)/e Å ⁻³	1.681, –2.237	4.019, –2.832	1.249, –0.562	4.524, –1.364	3.708, –1.449
Flack parameter	–	–	–0.001(9)	–0.06(2)	–

^a $R1 = \Sigma(F_o - F_c)/\Sigma F_o$, ^b $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2 / [\Sigma w(F_o^2)^3]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0747$ (2), 0.0700 (3), 0.0690 (4), 0.0272 (5), 0.0800 (6); $b = 0$ (2), 0 (3), 70 (4), 0 (5), 40 (6).

Table 2 Metrical parameters for the respective orientation of the molecular component in 2–6 (Fig. 3)

Complex	2	3	4	5	6
Interplanar angle/°	3.5	1.9	5.0	7.1	2.3
Intercentroid distances/Å	3.63, 3.81	3.28, 3.99	3.40, 3.89	3.61, 3.60	3.39, 4.54
Interplanar separations/Å	3.28, 3.26	3.23, 3.21	3.41, 3.33	3.34, 3.33	3.39, 3.39
Intercomponent offset/Å	1.61, 2.04	0.59, 2.39	0.90, 1.95	1.38, 1.38	0.10, 3.02
Tilt/°	29.3		23.2	21.0	

however, loss of the arene is readily observed. These adducts have been characterized by elemental analysis and thermogravimetric analysis. Compounds 2–5 feature a similar behaviour with loss of arene occurring in the temperature range of 35–125 °C. For compound 6, however, higher temperatures (90–160 °C) are required. In all cases, heating to temperatures higher than 160 °C leads to further weight loss which results from the sublimation of the trimercury derivative 1.

The ¹⁹⁹Hg NMR resonance of 1 in toluene, *ortho*-xylene, *meta*-xylene and *para*-xylene resonance is slightly upfield from the resonance observed for 1 in CH₂Cl₂ (δ –1045.2 ppm). This phenomenon possibly reflects the solvation of the mercury centres by molecules of arenes. The facile crystallization of these binary solids and their thermal stability at ambient temperature points to the affinity of 1 for aromatic substrates. These results are in agreement with previous studies dealing with the complexation of benzene,¹⁰ biphenyl, naphthalene and triphenylene by 1.¹¹

Structural studies

The crystal structures of compound 2–6 have been determined and the pertinent crystallographic data have been assembled in Tables 1–3 and in the captions of Figs. 1, 4 and 5. In all cases, there is one molecule of 1·arene in the asymmetric unit. The

structures of 2, 4 and 5 reveal the existence of binary stacks. The dihedral angles formed between the planar trinuclear core of 1 and the aromatic ring (3.5, 5.0 and 7.1° for 2, 4 and 5, respectively) indicate that the alternating molecules are almost parallel to one another. The distances separating the centroid of the substituted benzene ring from the centroid of the two proximal molecules of 1 (3.63 and 3.81 Å for 2, 3.40 and 3.89 Å, for 4, 3.60 and 3.61 Å for 5) are relatively close; hence the stacks are regular and do not feature any discontinuity. In each stack, the successive molecules of 1 adopt an eclipsed rather than a staggered arrangement. It is also worth noting that the stacks are tilted with respect to the normal of the plane containing the three mercury centres of 1 (Fig. 2). This tilt (29.3, 23.2 and 21.0° for 2, 4 and 5, respectively) results from a moderate slippage of the sandwiched aromatic with respect to the centroid of the Hg₃ core of two closest molecules of 1. Despite this slippage which is best measured by the offset distances defined in Fig. 3 (1.61 and 2.04 Å for 2, 0.90 and 1.95 Å, for 4, 1.38 and 1.38 Å for 5) we note that the aromatic ring of the substituted benzene remains situated above and below the core of the trinuclear complexes. In each case, the substituted benzene derivatives exhibit Hg...C_{aromatic} interactions with distances ranging from 3.189(15) to 3.506(8) Å with the mercury centres of the neighbouring molecules of 1. While in 2, 4 and 5, the arene is almost equidistant from the two neighbouring molecules of 1,

Table 3 Selected intramolecular distances (Å) and angles (°)

	2	3	4	5	6	Atom numbering scheme
Hg(1)–C(8)	2.063(13)	2.065(10)	2.051(9)	2.086(18)	2.074(8)	
Hg(1)–C(1)	2.069(14)	2.072(10)	2.054(8)	2.102(18)	2.071(8)	
Hg(2)–C(7)	2.046(13)	2.070(11)	2.076(8)	2.028(18)	2.078(9)	
Hg(2)–C(14)	2.067(13)	2.062(10)	2.076(9)	2.07(2)	2.065(8)	
Hg(3)–C(2)	2.049(13)	2.086(10)	2.075(9)	2.07(2)	2.053(8)	
Hg(3)–C(13)	2.084(13)	2.075(10)	2.066(8)	2.110(19)	2.066(8)	
C(8)–Hg(1)–C(1)	174.6(5)	176.6(4)	174.7(4)	177.4(8)	176.4(3)	
C(7)–Hg(2)–C(14)	173.5(6)	175.1(4)	173.6(3)	174.8(8)	174.6(3)	
C(2)–Hg(3)–C(13)	173.2(5)	174.6(4)	175.9(4)	177.0(9)	176.3(3)	

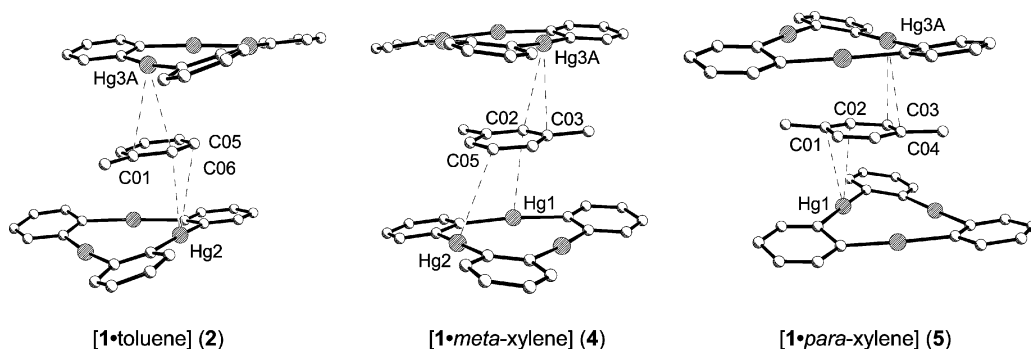


Fig. 1 Molecular structures of compounds **2**, **4** and **5**. Intermolecular bond distances (Å) for each compound. Compound **2**: Hg(3)–C(06) 3.189(15), Hg(3)–C(01) 3.323(15), Hg(2A)–C(05) 3.403(15), Hg(2A)–C(06) 3.387(15). Compound **4**: Hg(1)–C(02) 3.359(9), Hg(2)–C(05) 3.462(11), Hg(3A)–C(02) 3.383(11), Hg(3A)–C(03) 3.243(11). Compound **5**: Hg(1)–C(02) 3.19(2), Hg(1)–C(01) 3.42(2), Hg(3A)–C(03) 3.48(3), Hg(3A)–C(04) 3.31(3).

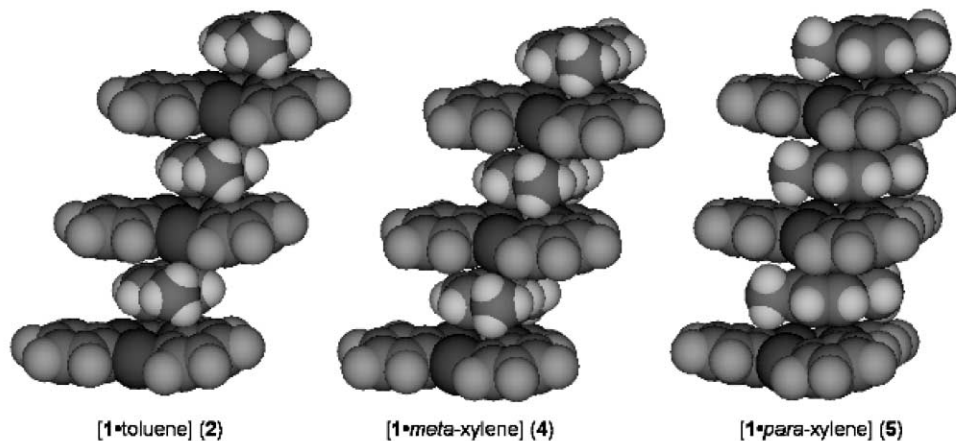


Fig. 2 Space-filling diagrams of compounds **2**, **4** and **5**.

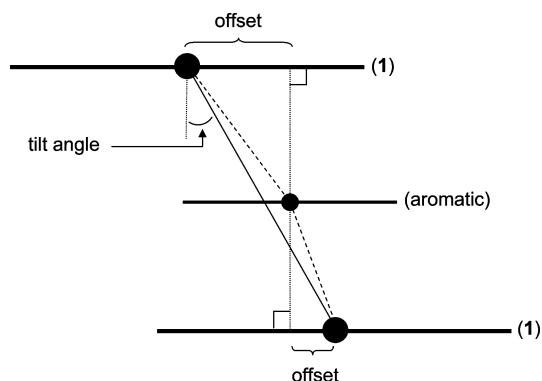


Fig. 3 Diagram defining the tilt angle and the offsets.

the molecule of *ortho*-xylene in **3** appears preferentially bound to one of the two proximal molecules of **1** with which it forms four short Hg \cdots C_{aromatic} contacts with distances ranging from

3.265(11) to 3.474(11) Å (Fig. 4). By contrast, the *ortho*-xylene molecule forms a single dihapto contact between the C(01)–C(06) atom pair and the Hg(2) centre of the most distant neighbouring molecule of **1** ((Hg(2)–C(01) 3.324(12), Hg(2)–C(06) 3.217(12)). The disparity found in the distances formed between the centroid of the substituted benzene ring and those of the closest two molecules of **1** (3.28 and 4.00 Å) corroborate this general observation. This situation is even more acute in **6** which features very disparate inter-centroid distances of 3.41 and 4.52 Å. As a result, **6** can be described as a 1 : 1 complex (Fig. 5). In this 1 : 1 complex, the mesitylene molecule is located directly above of the trinuclear core of **1** and interacts with the mercury centres *via* three contacts of 3.506(8), 3.445(8) and 3.443(8) Å which involve the non-substituted carbon atoms of the aromatic ring. Inspection of the cell packing diagram indicate that the 1 : 1 complexes interact with one another *via* an additional Hg \cdots C_{aromatic} interaction with a distance of 3.443(8) Å involving C(02) and the Hg(1) centre of a neighbouring molecule.

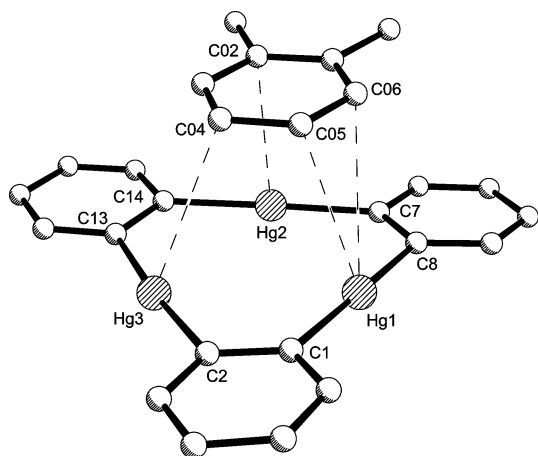


Fig. 4 Molecular structure of compound **3** showing the *ortho*-xylene derivative and the closest neighboring molecule of **1**. Intermolecular bond distances (Å): Hg(1)–C(05) 3.321(12), Hg(1)–C(06) 3.451(11), Hg(2)–C(02) 3.265(11), Hg(3)–C(04) 3.474(11).

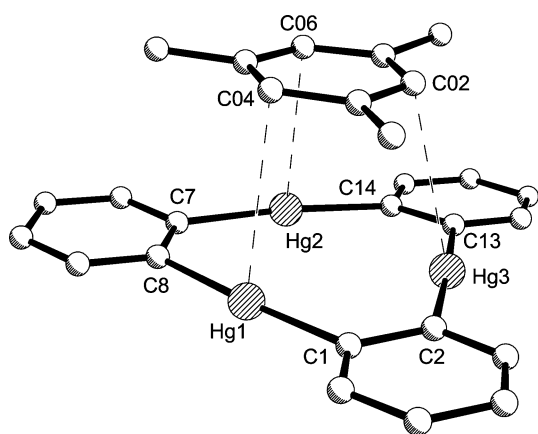


Fig. 5 Molecular structure of compound **6**. Intermolecular bond distances (Å): Hg(1)–C(04) 3.506(8), Hg(2)–C(06) 3.445(8), Hg(3)–C(02) 3.443(8).

Although electrostatic forces likely contribute to the stability of these assemblies, it is important to note that in all cases, there are short contacts between the mercury centres of **1** and the substituted benzene molecules. These distances are in the 3.2–3.5 Å range and exceed the Hg–C bonds observed in arene mercury(II) cation complexes by approximately 0.8 Å. Nevertheless, they remain within the sum of the van der Waals radius of mercury ($r_{\text{vdw}}(\text{Hg}) = 1.73\text{--}2.00$ Å)^{19,20} and that of carbon in aromatic systems ($r_{\text{vdw}}(\text{C}_{\text{aromatic}}) = 1.7$ Å).²¹ They are similar to those observed in [1·benzene], [1·biphenyl], [1·naphthalene] and [1·triphenylene] (3.25–3.55 Å)^{10,11} and indicate the presence of weak secondary π interactions. Similar contacts are present in the structure of [1·4-phenylpyridine].¹⁴ While 1·benzene features stacks whose propagation direction is perpendicular to the plane of **1**, the stacks observed in **2**, **4** and **5** are tilted with respect to the normal of the plane containing the three mercury centres of **1**. This structural difference likely arises from the increased steric requirements of the substituted benzene derivatives which apparently interfere with the regularity of the stacking motif. Further increase of the steric bulk as in **6**, prevents efficient stacking and leads to the formation of 1 : 1 complexes. In a final note, although arene–fluoroarene interactions are not evident in **2–6**, these supramolecules are reminiscent of those involving methyl substituted benzenes and electron deficient molecules.^{22,23}

Conclusion

The results presented herein further document the affinity of **1** for aromatic derivatives. While previous studies focused on

unsubstituted arenes,^{10,11} the present findings indicate that **1** tolerates increased steric bulk and readily complexes methyl substituted benzenes. In compounds **2–6** the supramolecular stacks are held by the presence of secondary π -interactions between the mercury centres of **1** and the aromatic molecule. We have previously proposed that the formation of such species results from donor interactions involving the filled π orbitals of the aromatic substrate and the empty 6p orbitals of the mercury centres. While such interactions are likely to be at play in the structure of **2–6**, we note that in several cases, the aromatic molecule appears randomly oriented above and below the trinuclear core of **1**. This feature might be taken as an evidence for the weakness of the donor interactions and probably reflects the participation of less directional electrostatic and dispersion forces. DFT calculations undertaken on **1** show a positively charged electrostatic potential surface in the centre of the complex.²⁴ With a negatively charged electrostatic potential surface at their locus,²⁵ the observed arrangement of the aromatic molecules might also result from favourable electrostatic interactions. Finally, we note that dispersion forces between the soft mercury atoms of **1** and the polarizable aromatic derivatives may also be present.²⁶

Experimental

General

Due to the toxicity of the mercury compounds discussed in these studies extra care was taken at all times to avoid contact with solid, solution, and air-borne particulate mercury compounds. The studies herein were carried out in a well-aerated fume hood. Atlantic Microlab, Inc., Norcross, GA, performed the elemental analyses. All commercially available starting materials and solvents were purchased from Aldrich Chemical and were used as provided. Compound **1** was prepared according to the published procedure outlined by Sartori and Golloch.¹² All NMR measurements were acquired at ambient temperature on an INOVA 400 MHz spectrometer.

General synthetic procedure

Compound **1** was dissolved by boiling in the selected solvents: toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene. Upon cooling, followed by slow evaporation of the solvent in a well-aerated fume hood, crystallization occurs to afford quantitative yields of [1·toluene] (**2**), [1·*ortho*-xylene] (**3**), [1·*meta*-xylene] (**4**), [1·*para*-xylene] (**5**) and [1·mesitylene] (**6**). Compound **2**. Found: C, 26.42; H, 0.76. $\text{C}_{25}\text{H}_8\text{F}_{12}\text{Hg}_3$ requires C, 26.38; H, 0.71. Compound **3**. Found C, 27.55; H, 0.86. $\text{C}_{26}\text{H}_{10}\text{F}_{12}\text{Hg}_3$ requires C, 27.10; H, 0.88. Compound **4**. Found: C, 27.11; H, 0.84. $\text{C}_{26}\text{H}_{10}\text{F}_{12}\text{Hg}_3$ requires C, 27.10; H, 0.88. Compound **5**. Found: C, 27.40; H, 0.93. $\text{C}_{26}\text{H}_{10}\text{F}_{12}\text{Hg}_3$ requires C, 27.10; H, 0.88. Compound **6**. Found: C, 27.71; H, 1.01. $\text{C}_{27}\text{H}_{12}\text{F}_{12}\text{Hg}_3$ requires C, 27.81; H, 1.04%.

Single-crystal X-ray analysis

X-Ray data for **2**, **3**, **4**, **5** and **6** were collected on a Bruker Smart-CCD diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Specimens of suitable size and quality were selected and mounted onto a glass fibre with either Apiezon grease (for low-temperature data collections) or epoxy (for room-temperature data collections). The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 6.1) allowed location of the remaining non-hydrogen atoms.

CCDC reference numbers 208162–208166.

See <http://www.rsc.org/suppdata/dt/b3/b304023b/> for crystallographic data in CIF or other electronic format.

Solubility measurements

A weighed vial and stir bar were charged with a known amount of **1** (approximately 20 mg for toluene, *o*-xylene, *m*-xylene, and *p*-xylene and approximately 2 mg for benzene and mesitylene). The solvent was then added incrementally to the vial while stirring until the presence of solid **1** was no longer observed. The vial was then reweighed to determine the amount of solvent added.

Thermal gravimetric analyses

These analyses were carried out on a TA Instruments TGA Q500 using an argon flow (rate 60 ml min⁻¹), a heating rate of 2 °C min⁻¹ and a sample size between 6 and 45 mg. The temperature range in which the weight loss occurs is given for each compound, along with the calculated and observed weight loss (WL_{calc} and WL_{obs}, respectively). **2**, 37 °C –114 °C (WL_{calc}, 8.10%; WL_{obs}, 8.09%); **3**, 47 °C –115 °C (WL_{calc}, 9.22%; WL_{obs}, 8.65%); **4**, 42 °C –124 °C (WL_{calc}, 9.22%; WL_{obs}, 8.97%); **5**, 43 °C –117 °C (WL_{calc}, 9.22%; WL_{obs}, 9.52%); **6**, 91 °C –154 °C (WL_{calc}, 10.31%; WL_{obs}, 10.56%).

Acknowledgements

We would like to thank Charles Peñaloza for his participation to this work as well as Dr. Joy Heising and Professor Abraham Clearfield for their help with the TGA measurements. Acknowledgment is made to the donors of the American Chemical Society Petroleum Research Fund for support of this research (Grant ACS PRF#38143-AC 3). The purchase of the X-ray diffractometers was made possible by two grants from the National Science Foundation (CHE-9807975 and CHE-0079822).

References

- 1 G. A. Olah, S. H. Yu and D. G. Parker, *J. Org. Chem.*, 1976, **41**, 1983–1986.
- 2 L. C. Damude and P. A. W. Dean, *J. Organomet. Chem.*, 1979, **181**, 1–15; L. C. Damude, P. A. W. Dean, M. D. Sefcik and J. Schaefer, *J. Organomet. Chem.*, 1982, **226**, 105–114.
- 3 W. Lau, J. C. Huffman and J. K. Kochi, *J. Am. Chem. Soc.*, 1982, **104**, 5515–5517.
- 4 A. S. Borovik, S. G. Bott and A. R. Barron, *Angew. Chem., Int. Ed.*, 2000, **39**, 4117–4118; A. S. Borovik, S. G. Bott and A. R. Barron, *J. Am. Chem. Soc.*, 2001, **123**, 11219–11228.
- 5 For arene complexes of Hg₂²⁺, see, for example: W. Frank and B. Dincher, *Z. Naturforsch., B: Chem. Sci.*, 1987, **42**, 828–834; S. Ulvenlund, J. Rosdahl, A. Fischer, P. Schwerdtfeger and L. Kloo, *Eur. J. Inorg. Chem.*, 1999, 633–642.
- 6 C. S. Branch and A. R. Barron, *J. Am. Chem. Soc.*, 2002, **124**, 14156–14161; A. S. Borovik and A. R. Barron, *J. Am. Chem. Soc.*, 2002, **124**, 3743–3748.
- 7 L. G. Kuz'mina and Yu. T. Struchkov, *Croat. Chem. Acta*, 1984, **57**, 701–724 and references therein.
- 8 N. W. Alcock, P. A. Lampe and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1978, 1324–1328; P. A. Lampe and P. Moore, *Inorg. Chim. Acta*, 1979, **36**, 27–30; A. J. Cathy, N. Chaichit and B. M. Gatehouse, *Acta Crystallogr., Sect. B*, 1980, **36**, 786–789; N. G. Furmanova, Yu. T. Struchkov, V. N. Kalinin, B. Ya. Finkel'shtein and L. I. Zakharkin, *Zh. Strukt. Khim.*, 1980, **21**, 96–100; X. Delaigue, M. W. Hosseini, N. Kyriatsakas, A. De Cian and Jean Fischer, *J. Chem. Soc., Chem. Commun.*, 1995, 609–610; M. Tschinkl, R. E. Bachman and F. P. Gabbai, *J. Organomet. Chem.*, 1999, **582**, 40–44.
- 9 J. R. Gardinier and F. P. Gabbai, *J. Chem. Soc., Dalton Trans.*, 2000, 2861–2865.
- 10 M. Tsunoda and F. P. Gabbai, *J. Am. Chem. Soc.*, 2000, **122**, 8335–8336.
- 11 M. R. Haneline, M. Tsunoda and F. P. Gabbai, *J. Am. Chem. Soc.*, 2002, **124**, 3737–3742.
- 12 P. Sartori and A. Golloch, *Chem. Ber.*, 1968, **101**, 2004–2009.
- 13 For a series of general reviews on this topic, see: J. D. Wuest, *Acc. Chem. Res.*, 1999, **32**, 81–89; J. Vaugeois, M. Simard and J. D. Wuest, *Coord. Chem. Rev.*, 1995, **145**, 55–73; M. F. Hawthorne and Z. Zheng, *Acc. Chem. Res.*, 1997, **30**, 267–276; M. F. Hawthorne, *Pure Appl. Chem.*, 1994, **66**, 245–254; F. P. Schmidtchen and M. Berger, *Chem. Rev.*, 1997, **97**, 1609–1646; W. E. Piers, G. J. Irvine and V. C. Williams, *Eur. J. Inorg. Chem.*, 2000, 2131–2142.
- 14 M. C. Ball, D. S. Brown, A. G. Massey and D. A. Wickens, *J. Organomet. Chem.*, 1981, **206**, 265–277.
- 15 J. Baldamus, G. B. Deacon, E. Hey-Hawkins, P. C. Junk and C. Martin, *Aust. J. Chem.*, 2002, **55**, 195–198.
- 16 I. A. Tikhonova, F. M. Dolgushin, K. I. Tugashov, P. V. Petrovskii, G. G. Furin and V. B. Shur, *J. Organomet. Chem.*, 2002, **654**, 123–131; I. A. Tikhonova, F. M. Dolgushin, K. I. Tugashov, G. G. Furin, P. V. Petrovskii and V. B. Shur, *Russ. Chem. Bull.*, 2001, **50**, 1673–1678; I. A. Tikhonova, F. M. Dolgushin, A. I. Yanovsky, Z. A. Starikova, P. V. Petrovskii, G. G. Furin and V. B. Shur, *J. Organomet. Chem.*, 2000, **613**, 60–67.
- 17 J. B. King, M. Tsunoda and F. P. Gabbai, *Organometallics*, 2002, **21**, 4201–4205; J. B. King, M. R. Haneline, M. Tsunoda and F. P. Gabbai, *J. Am. Chem. Soc.*, 2002, **124**, 9350–9351.
- 18 E. S. Shubina, I. A. Tikhonova, E. V. Bakhmutova, F. M. Dolgushin, M. Y. Antipin, V. I. Bakhmutov, I. B. Sivaev, L. N. Teplitskaya, I. T. Chizhevsky, I. V. Pisareva, V. I. Bregadze, L. M. Epstein and V. B. Shur, *Chem. Eur. J.*, 2001, **7**, 3783–3790; A. L. Chistyakov, I. V. Stankevich, N. P. Gambaryan, Yu. T. Struchkov, A. I. Yanovsky, I. A. Tikhonova and V. B. Shur, *J. Organomet. Chem.*, 1997, **536**, 413–424; V. B. Shur, I. A. Tikhonova, F. M. Dolgushin, A. I. Yanovsky, Yu. T. Struchkov, A. Yu. Volkonsky, E. V. Solodova, S. Yu. Panov, P. V. Petrovskii and M. E. Vol'pin, *J. Organomet. Chem.*, 1993, **443**, C19–C21; V. B. Shur, I. A. Tikhonova, A. I. Yanovskii, Yu. T. Struchkov, P. V. Petrovskii, S. Yu. Panov, G. G. Furin and M. E. Vol'pin, *J. Organomet. Chem.*, 1991, **418**, C29–C32.
- 19 A. J. Canty and G. B. Deacon, *Inorg. Chim. Acta*, 1980, **45**, L225–L227.
- 20 P. Pyykko and M. Straka, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2489–2493.
- 21 J. Caillet and P. Claverie, *Acta Crystallogr., Sect. A*, 1975, **31**, 448–461.
- 22 T. Dahl, *Acta Chem. Scand.*, 1998, **52**, 1006–1009; T. Dahl, *Acta Chem. Scand.*, 1994, **48**, 95–106; T. Dahl, *Acta Chem. Scand. Ser. A*, 1975, **A29**, 170–174; T. Dahl, *Acta Chem. Scand., Ser. A*, 1971, **25**, 1031–1039; D. Britton, *J. Chem. Crystallogr.*, 1997, **27**, 405–412; J. A. Swift, A. M. Reynolds and M. D. Ward, *Chem. Mater.*, 1998, **10**, 4159–4168.
- 23 For general references on arene–fluoroarene interactions, see: M. Weck, A. R. Dunn, K. Matsumoto, G. W. Coates and E. B. Lobkovsky and R. H. Grubbs, *Angew. Chem., Int. Ed.*, 1999, **38**, 2741–2745; G. P. Bartholomew, X. Bu and G. C. Bazan, *Chem. Mater.*, 2000, **12**, 2311–2318; J. C. Collings, K. P. Roscoe, R. L. Thomas, A. S. Batsanov, L. M. Stimson, J. A. K. Howard and T. B. Marder, *New J. Chem.*, 2001, **25**, 1410–1417.
- 24 A. Burini, J. P. Jr. Fackler, R. Galassi, T. A. Grant, M. A. Omary, M. A. Rawashdeh-Omary, B. R. Pietroni and R. J. Staples, *J. Am. Chem. Soc.*, 2000, **122**, 11264–11265.
- 25 J. C. Ma and D. A. Dougherty, *Chem. Rev.*, 1997, **97**, 1303–1324.
- 26 T. Weber, E. Riedle, H. J. Neusser and E. W. Schlag, *Chem. Phys. Lett.*, 1991, **183**, 77–83.