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Interaction of benzene and 1,2-bis(chloromercurio)tetrafluorobenzene. Supramolecular frameworks based on Hg · · · Cl, Hg · · · F, Hg · · · π and π–π interactions

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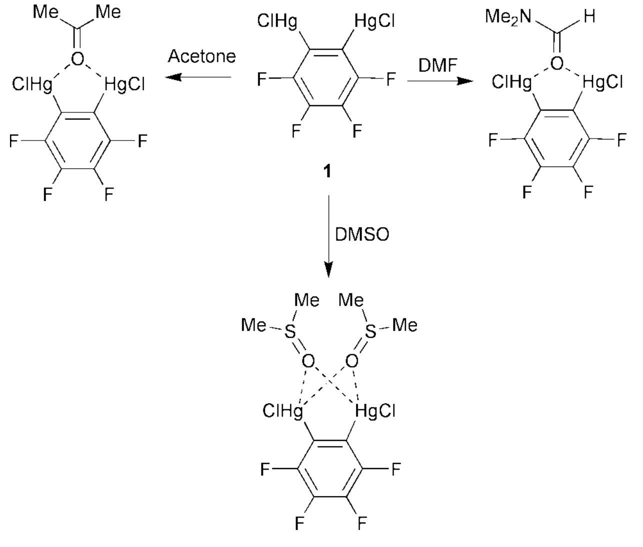
The crystallization of 1,2-bis(chloromercurio)tetrafluorobenzene (**1**) from a mixture of THF and benzene yields **1**·THF·0.5C_6H_6 (**2**), which contains the Lewis base–Lewis acid adduct **1**·μ-THF associated to benzene. When **1** is crystallized from a mixture of propylene oxide and benzene, a compound of composition **1**·1.5C_6H_6 (**3**) is obtained. Both **2** and **3** have been analyzed by solid-state ^{13}C CP/MAS NMR spectroscopy and their structures have been investigated by X-ray crystallography. The solid state structure of **2** is that of a framework wherein layers of **1**·μ-THF are linked by pillars of sandwiched benzene molecules. The cohesion of this framework results from the presence of intermolecular Hg · · · Cl interactions as well as arene-1,2-bis(chloromercurio)tetrafluorobenzene π–π stacking interactions. The crystal structure of **3** reveals the existence of parallel polymeric chains of **1** embedded in a benzene matrix in which the benzene molecules adopt an edge-to-face arrangement. The polymeric chains of **1** are formed by Hg · · · Cl and Hg · · · F interactions that link the monomers. Finally, part of the benzene molecules in **3** interacts with molecules of **1** by Hg · · · π rather than π–π stacking interactions.

Introduction

Organometallic compounds that contain two or more metal centers have received increased attention because of their unique reactivity towards Lewis bases. These polyfunctional Lewis acids exhibit potential in catalysis,[1–6] as well as in molecular[7–12] and anion[13–21] recognition. Our laboratory has been interested in the coordination chemistry of 1,2-bis(chloromercurio)tetrafluorobenzene (**1**),[22] a bidentate Lewis acid that readily interacts with a variety of Lewis basic organic molecules. In particular, we have found that in solution, **1** forms complexes with a variety of molecules such as DMSO,[23] DMF,[12] and acetone.[12] A series of solid state X-ray structural studies of the complexes reveals that **1** behaves as a bidentate Lewis acid that chelates the oxygen donor atom of the bound substrate (Scheme 1).[12,23] The unusual ligative behavior of **1** toward Lewis bases is a result of the synergy exercised by the juxtaposed metallic centers as well as of the electron-withdrawing ability of the perfluorophenylene backbone. In the crystal, these complexes associate *via* intermolecular Hg · · · Cl and fluoroarene–fluoroarene π–π interactions to yield supramolecular networks. While layered compounds are often formed, it has been observed that the assembly of **1** can lead to the formation of a microporous solid when DMSO is used as a templating agent.[23]



Scheme 1

Perfluoroarenes show an unusual chemical affinity for arenes. In particular, a 1 : 1 mixture of hexafluorobenzene and benzene forms a complex that contains alternating face to face stacks of benzene and hexafluorobenzene molecules in the solid state.[24,25] Theoretical treatments on this system have shown that the individual molecules associate *via* interactions that are mostly electrostatic in nature and are the result of marked, yet opposite, quadrupole moments of the two components.[25] Theoretical investigations have also provided an estimation of the energy of this stacking interaction that was calculated to be 3.7 kcal mol^{-1}.[26] Since the discovery of the benzene–hexafluorobenzene interaction, a series of elegant contributions have been made which document the use of similar electrostatic forces for the construction and organization of various arene–perfluoroarene supramolecular edifices.[27–30] Recent work indicates that the interactions between arenes and perfluoroarenes may not be strictly limited to organic compounds; rather, organometallic compounds bearing perfluorinated aromatic ligands may be able to associate with arenes, in a manner very similar to their organic cousins.[31] Although ring substitution can greatly influence the electrostatic potential surface of aromatic molecules,[32] we have embarked on an investigation into the ability of **1** to engage in interactions with the simplest of arenes, benzene.

Results and discussion

Preparation and physical properties

Colorless needle-like crystals that had the composition **1**·μ-THF·0.5C_6H_6 (**2**), as determined by elemental analysis, were formed by allowing a THF solution of **1** and benzene to evaporate (Scheme 2). The solid-state ^{13}C CP/MAS NMR spectrum had resonances consistent with those expected for

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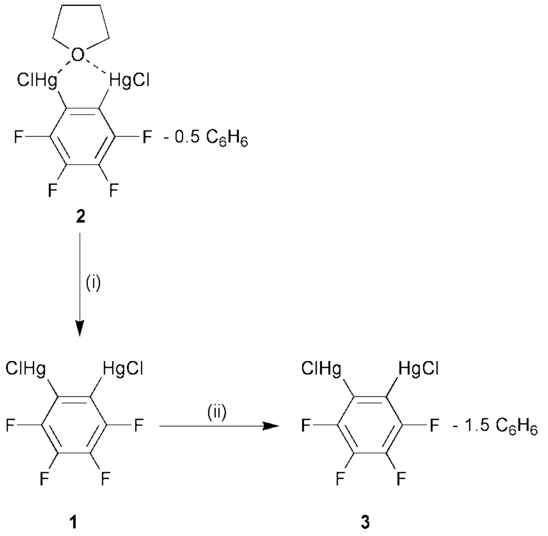
Table 1 Crystal data, data collection, and structure refinement for **2** and **3**

Crystal data	**2**	**3**
Formula	$C_{13}H_{11}Cl_2F_4Hg_2O$	$C_{15}H_9Cl_2F_4Hg_2$
M_r	731.30	737.30
Crystal size/mm	0.60 × 0.14 × 0.05	0.70 × 0.10 × 0.07
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*P*2(1)/*c*
a/Å	29.042(2)	7.9488(7)
b/Å	7.1266(6)	32.206(3)
c/Å	20.5464(17)	6.6881(6)
β/°	124.922(1)	99.195(2)
V/Å^3	3486.7(5)	1690.2(3)
ρ_{calc}/g cm^{-3}	2.786	2.898
Z	8	4
F(000) (e)	2616	1316
μ(Mo-Kα)/cm^{-1}	179.3	184.9
Data collection		
T/°C	22	−183
Scan mode	ω	ω
hkl range	−33→34, −7→8, −24→21	−8→9, −38→33, −7→7
Measured refl.	8596	8768
Unique refl., [R_{int}]	3022, [R_{int} = 0.0651]	2961, [R_{int} = 0.0867]
Refl. used for refinement	3022	2961
Absorption correction	SADABS[46]	psi-scans
T_{min}/T_{max}	0.13/0.83	0.16/0.90
Refinement		
Refined parameters	199	208
Final R values [$I > 2\sigma(I)$]		
$R1^a$ (%)	0.0546	0.0455
$WR2^b$ (%)	0.1312	0.1071
ρ_{fin} (max/min)/e Å^{-3}	3.497/−3.139, at Hg atoms	6.269/−1.591, at Hg atoms

[a] $R1 = (F_o - F_c)/F_o$. [b] $wR2 = \{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.01013$ (**2**), 0.0644 (**3**); $b = 0.0000$ (**2**), 0.0000 (**3**).



Scheme 2 (i) THF/benzene; (ii) propylene oxide/benzene.

both THF and benzene. The resonances for the $(HgCl)_2C_6F_4$ moiety were detected as a broad series of signals. Compound **2** is soluble in THF but insoluble in either benzene or aliphatic solvents. Compound **2** exhibits only a moderate stability. Crystals of **2** become opaque either when stored under ambient conditions for one day or when heated to *ca.* 60 °C in sealed glass capillaries.

Interestingly, when **1** and benzene were mixed with propylene oxide rather than THF, a compound of composition **1**·$1.5C_6H_6$ (**3**) was obtained after slow evaporation of the solvent (Scheme 2). The solid-state ^{13}C CP/MAS NMR spectrum of **3** confirmed the absence of propylene oxide and allowed the detection of a resonance corresponding to benzene at 129.52 ppm. When heated to *ca.* 50 °C in a sealed glass capillary or when stored under ambient conditions for one day, crystals of **3** become rapidly opaque. Elemental analysis of the opaque solid indicated partial loss of the benzene component. It is interesting to note that since compound **1** is insoluble in benzene, propylene oxide was necessary for the preparation of **3**.

Solid-state studies

The crystal structure of **2** has been determined by X-ray diffraction analysis and the pertinent crystallographic data are assembled in Table 1. Compound **2** crystallizes in the monoclinic space group *C*2/*c* with one molecule of **1**·THF and one-half of a benzene molecule in the asymmetric unit. The structure of two adjacent asymmetric units is given in Fig. 1. In **2**, a THF molecule is chelated by the bidentate Lewis acid, **1**, and the resulting Hg–O bonds are approximately perpendicular to the respective C–Hg–Cl sequences. The oxygen center has a distorted tetrahedral coordination geometry with an acute Hg(1)–O–Hg(2) angle of 83.5°. The Hg–O bond distances (av. 2.80(2) Å) are shorter than the sum of the van der Waals radii of oxygen (1.54 Å)[33] and mercury (1.73–2.00 Å), [34] are slightly longer than those measured in **1**·(μ-acetone) (av. 2.73 Å),[12] **1**·(μ-DMF) (av. 2.70 Å),[12] and **1**·$(\mu\text{-DMSO})_2$ (av. 2.70 Å).[23] Wuest and Zacharie observed the chelation of THF in a macrocycle containing two 1,2-bismercury-benzene subunits bound by perfluoroglutarate linkers.[35] In this system, the coordination of the THF molecule is similar to that found in **2** and the corresponding Hg–O bond distances (2.85(4) Å) are identical within experimental error to that encountered in **2**. Interestingly, 12-mercuracarborand-4 $(C_2B_{10}H_{10}Hg)_4$ forms a tetrakis

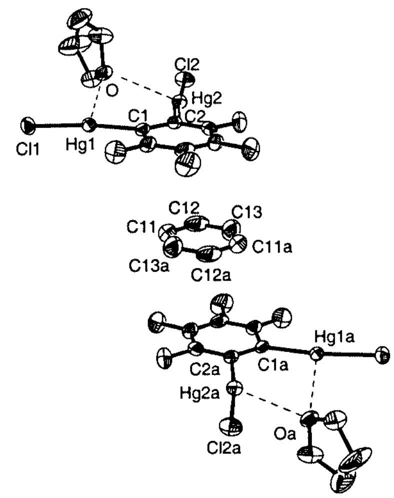


Fig. 1 ORTEP[45] drawing of **2** with 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Hg(1)–C(1) 2.033(11), Hg(1)–Cl(1) 2.306(3), Hg(2)–C(2) 2.074(11), Hg(2)–Cl(2) 2.312(3); C(1)–Hg(1)–Cl(1) 173.6(3), C(2)–Hg(2)–Cl(2) 173.5(3).

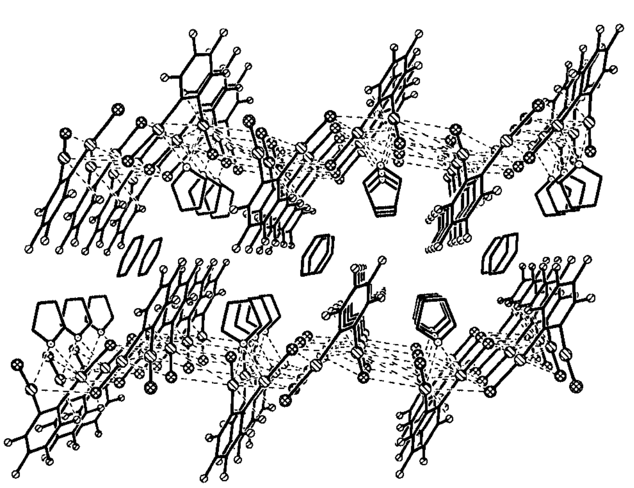


Fig. 2 View of the crystal packing in **2**. The layered structure is evident from this view.

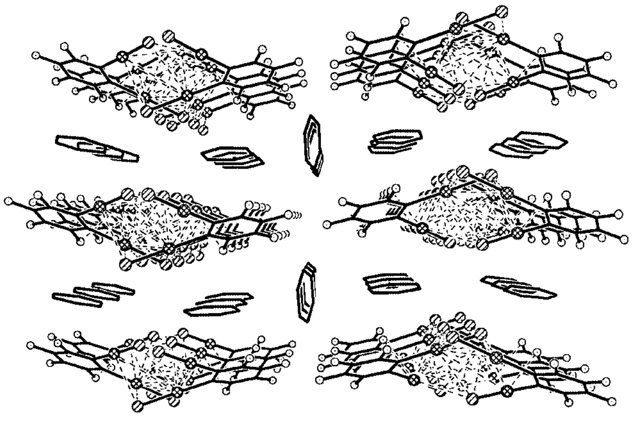


Fig. 3 View of the crystal packing in **3** showing polymeric chains of **1** surrounded by benzene molecules.

THF adduct in which the THF molecules act as terminal ligands with a short Hg–O distance of 2.65 Å.[36]

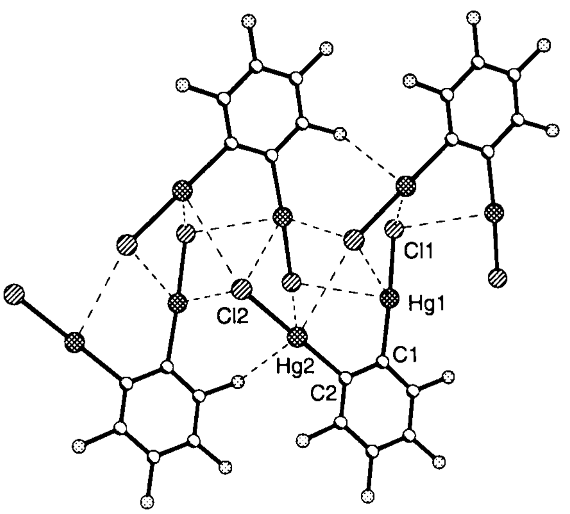


Fig. 4 Portion of a polymeric chain in the structure of **3**. The Hg···Cl and Hg···F intermolecular contact are listed in Table 3. Selected intramolecular bond lengths (Å) and angles (°): Hg(1)–C(1) 2.059(10), Hg(2)–C(2) 2.063(10), Hg(1)–Cl(1) 2.319(3), Hg(2)–Cl(2) 2.325(3), C(1)–Hg(1)–Cl(1) 177.2(3), C(2)–Hg(2)–Cl(2) 177.9(3).

Table 2 Intermolecular Hg···Cl distances (Å) in the structure of **2**

Hg(1)–Cl(1)[a]	3.314(5)	Hg(2)–Cl(1)[a]	3.332(5)
Hg(1)–Cl(2)[b]	3.274(5)	Hg(2)–Cl(2)[c]	3.366(5)

[a] $-x + 0.5, y + 0.5, -z + 0.5$. [b] $x, y - 1, z$. [c] $-x + 0.5, -y + 1.5, z$.

Table 3 Intermolecular Hg···Cl and Hg···F distances (Å) in the structure of **3**

Hg(1)–Cl(1)[a]	3.249(5)	Hg(2)–Cl(1)[a]	3.100(5)
Hg(1)–Cl(2)[b]	3.314(5)	Hg(2)–Cl(2)[c]	3.437(5)
Hg(1)–Cl(2′)[c]	3.455(5)	Hg(2)–F(6)[d]	3.09(2)

[a] $x, -y + 0.5, z + 0.5$. [b] $x, y, z - 1$. [c] $x, -y + 0.5, z - 0.5$. [d] $x, y, z + 1$.

In the structure of **2** (Fig. 2), pairs of molecules of **1** are assembled into a a triple-decker aggregate whose midlevel position is occupied by benzene molecule. The distance between the centroids of the benzene and tetrafluorobenzene motifs in **2** of 3.72(2) Å is close to that observed for the benzene–hexafluorobenzene system (3.77 Å) and fall within the range of 3.7–3.8 Å that has been observed for other systems with arene–perfluoroarene interactions.[27–30] The benzene and tetrafluorobenzene planes in **2** are nearly parallel (dihedral angle of 2°) and the shortest inter-ring carbon–carbon atom distances occur between C(5) and C(13a) (3.52(2) Å) and C(3) and C(12) (3.57(2) Å). Altogether, these structural features suggest the presence of an arene-1,2-bis(chloromercurio)tetrafluorobenzene interaction in the structure of **2**.

An examination of the cell-packing diagram (Fig. 3) reveals the presence of additional intramolecular interactions. Aside from arene–perfluoroarene interactions, the structure of **2** contains intermolecular Hg···Cl contacts that link the individual monomers into an intricate network. These Hg···Cl contacts are in the range of 3.32–3.33 Å which is comparable to the sum of the van der Waals radii of the respective elements (r_{vdw}(Cl) = 1.58–1.78 Å,[33] r_{vdw}(Hg) = 1.73–2.00 Å)[34] and is within the range found for other organomercury halides (Table 2).[37–39] The overall structure of **2** is that of a framework wherein layers of **1**·THF are linked by pillars of sandwiched benzene molecules (Fig. 2).

The determination of the structure of **3** by single crystal X-ray analysis was complicated by the fragility and anistropic morphology of the crystals. A specimen, however, was selected and successfully mounted. A summary of the crystallographic data is given in Table 1. Examination of the packing diagram of **3** reveals the existence of parallel polymeric chains of **1** embedded in a benzene matrix (Fig. 3). The polymeric chains are formed by the presence of Hg···Cl and Hg···F interactions that link the individual molecules of **1** (Fig. 4, Table 3). These distances fall within the sum of the van der Waals radii of the elements (r_{vdw}(F) = 1.30–1.38 Å,[33] r_{vdw}(Cl) = 1.58–1.78 Å,[33] r_{vdw}(Hg) = 1.73–2.00 Å)[34] and are comparable to those

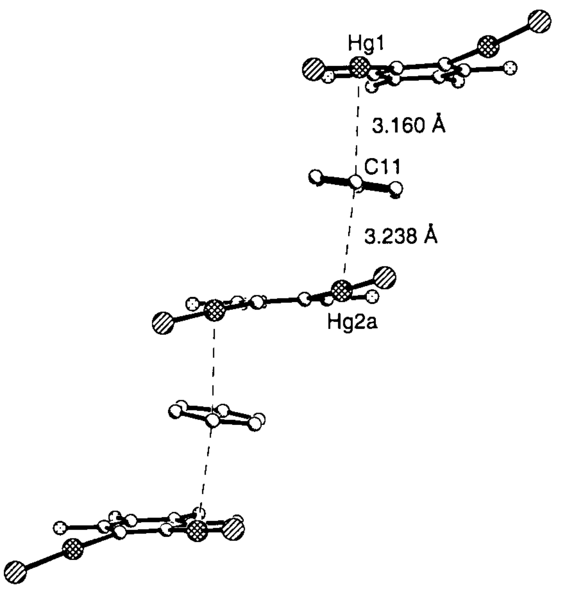


Fig. 5 View emphasizing the mercury–benzene interaction in **3**.

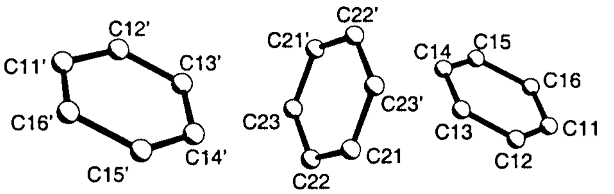


Fig. 6 Stacking arrangement of the benzene triad in the structure of **3**.

found in the structures of other organomercury halides.[12] It is noteworthy that the association of molecules of **1** within a chain is dense and is such that each molecule interacts with three neighbors. The secondary coordination spheres of the mercury atoms Hg(1) and Hg(2) also involve a carbon atom C(11) belonging to a benzene molecule that occupies a bridging position (Fig. 5). The resulting mercury–benzene carbon distances Hg(1)–C(11) (3.16 Å) and Hg(2a)–C(11) (3.24 Å) are relatively short and indicate the presence of π-interactions. These distances are similar to those found in several organomercurials that feature intramolecular Hg · · · π-interactions[40,41] but remain much longer than those found in π-complexes of mercury cations.[42] In **3**, all other mercury–benzene carbon distances are longer than Hg(1)–C(11) and Hg(2a)–C(11) and exceed 3.5 Å. As a result, the benzene molecule at C(11) is best described as η^1-μ-bonded. With centroid–centroid distances of 3.98(2) and 4.01(2) Å between the benzene molecule and the neighboring tetrafluorophenylene units, there appears to be little involvement of arene–perfluorarene interactions in the structure of **3**. In that respect, the structure of **3** differs from that of **2**. Unlike in **2**, the molecules of benzene are in close proximity and form triads in which the three successive molecules adopt an edge-to-face-to-edge arrangement (Fig. 6). This edge-to-face-to-edge stacking arrangement is similar to that observed in solid state structure of benzene.[43,44] In fact, the shortest intermolecular carbon–carbon distances within the benzene triads in **3** (C(14)–C(21′) 3.85(2) Å; C(13)–C(21) 4.07(2) Å) can be compared to the corresponding distances of 3.7 Å and 4.2 Å observed in the structure of benzene at −55 °C.[44]

Conclusions

Our previous investigations had established that **1** readily interacts with substrates containing terminal oxo groups such as carbonyl or sulfoxide functionalities. The isolation of compound **2** indicates that **1** is also able to chelate the oxygen atom of the cyclic ether THF. More importantly, the structure of **2** shows that the substituted tetrafluorophenylene backbone of **1** is able to engage in π–π interactions with arenes such as benzene. The observed supramolecular structure suggests that these interactions are similar to those found in purely organic substrates. It should however be kept in mind that **1** cannot be compared to hexafluorobenzene and that the substitution of two fluorine atoms by mercury chloride moieties should greatly affect the electrostatic potential surface. In fact, the structure of **3** reveals the presence of a different type of interaction between **1** and benzene. In this case, a benzene molecule interacts concomitantly with the mercury centers of two neighboring molecules of **1** to form two Hg · · · π contacts.

Experimental

General

The solid-state ^{13}C CP/MAS NMR spectra were recorded on a Bruker MSL 300 spectrometer operating at a field strength of 7.05 T. ^{1}H–^{13}C Cross-polarization and high-power proton decoupling with magic angle spinning were applied with a 90° pulse width of 4 μs, a contact time of 1 ms, and a recycle delay of 5 s. Alternatively, direct excitation with a 45° pulse and high-power proton decoupling with magic angle spinning were applied with a recycle delay of 60 s. ^{13}C NMR chemical shifts are referenced to an external sample of adamantane, with the methylene signal set to 38.3 ppm. Approximately 50 milligrams of sample were packed into a 7 mm ZrO_2 Bruker rotor with Kel-F inserts and cap. The rotor spinning speed was 4.8 kHz. Atlantic Microlab (Norcross, Georgia) performed the elemental analyses. All melting points were measured by using a Mel-Temp II instrument on samples contained in flame sealed capillaries and are uncorrected. All solvents were distilled before use and stored over molecular sieves. 1,2-$(HgCl)_2C_6F_4$ was prepared by following the published procedure.[22]

Synthesis of 1,2-bis(chloromercurio)tetrafluorobenzene·THF·0.5C_6H_6 (2)

Compound **1** (78 mg, 0.13 mmol) placed in a preweighed vial was dissolved in 3 ml of THF and 3 mL of C_6H_6. Slow evaporation of the solvents from the loosely-capped vial resulted in the formation of colorless needle-like crystals of **2** which were washed with 1 mL of benzene. The benzene was removed by pipette and the crystals were dried with a paper towel (Kimwipes). Yield 80% (74 mg). mp 65–67 °C (the crystals become opaque). Found: C, 21.53; H, 1.25. $C_{13}H_{11}Cl_2F_4Hg_2O$ requires C, 21.35; H, 1.52%. ^{13}C CP/MAS-NMR: δ 127.29 (C_6H_6), 68.85 (OCH_2), 25.70 (CH_2).

Synthesis of 1,2-bis(chloromercurio)tetrafluorobenzene·1.5C_6H_6 (3)

Compound **1** (63 mg, 0.10 mmol) placed in a preweighed vial was dissolved in 2 mL of propylene oxide and 2 mL of C_6H_6. Slow evaporation of the solvents from the loosely-capped vial resulted in the formation of colorless needle like crystals of **3** which were washed with a minimal amount of benzene (*ca.* 0.5 mL) and were dried with a paper towel (Kimwipes). Yield 85% (64 mg). mp 50–55 °C (the crystals become opaque). Due to facile loss of the solvent, a correct elemental analysis could not be obtained. Found: C, 17.76; H, 0.57. $C_{15}H_9Cl_2F_4Hg_2$ requires C, 24.44; H, 1.23%. This corresponds to the loss of 0.85 equivalents of benzene from **3** which contains 1.5 benzene. ^{13}C CP/MAS-NMR: δ 129.52 (C_6H_6).

Single crystal X-ray analysis for 2 and 3

X-Ray data were collected on a Bruker SMART-CCD diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Lorentz polarization correction was applied using the data reduction program SAINT (Program for

SMART 1000-CCD, data reduction, Bruker AXS, Madison, Wisconsin). For **2**, the data were corrected for absorption using the SADABS sub-routine.[46] For **3** the data were corrected for absorption using the Psi-scan method. The remaining important crystallographic data are collected in Table 1. The structure was solved by direct methods and refined on F^2 using the SHELXTL/PC package (ver. 5.1).[47] All non-hydrogen atoms in the structure were refined anisotropically and the hydrogen atoms were included in calculated positions using a standard riding model. There is a relatively large residual electron density in the structure of **3**. This electron density is located at 0.02 Å from Hg(1) and arises from the strong absorption effects that could not be totally accounted in the absorption correction. This situation was complicated by the extreme fragility of the crystals, which did not allow the preparation of a sample with ideal metrical proportions.

CCDC reference number 186/2055.

See http://www.rsc.org/suppdata/dt/b0/b001420f/ for crystallographic files in .cif format.

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References

1 H. Hanawa, N. Maekawara and K. Maruoka, *Tetrahedron Lett.*, 1999, **40**, 8379.

2 N. Asao, S. Kii, H. Hanawa and K. Maruoka, *Tetrahedron Lett.*, 1998, **39**, 3729.

3 T. Ooi, E. Tayama, M. Takahashi and K. Maruoka, *Tetrahedron Lett.*, 1997, **38**, 7403.

4 J. Vaugeois and J. D. Wuest, *J. Am. Chem. Soc.*, 1998, **120**, 13016.

5 J. D. Wuest and B. Zacharie, *J. Am. Chem. Soc.*, 1985, **107**, 6121.

6 H. Lee, M. Diaz and M. F. Hawthorne, *Tetrahedron Lett.*, 1999, **40**, 7651.

7 H. E. Katz, *J. Org. Chem.*, 1989, **54**, 2179.

8 K. Nozaki, T. Tsutsumi and H. Takaya, *J. Org. Chem.*, 1995, **60**, 6668.

9 J. D. Wuest, *Acc. Chem. Res.*, 1999, **32**, 81.

10 J. Vaugeois, M. Simard and J. D. Wuest, *Coord. Chem. Rev.*, 1995, **145**, 55.

11 F. P. Gabbaï, A. Schier, J. Riede and M. J. Hynes, *Chem. Commun.*, 1998, 897.

12 M. Tschinkl, A. Schier, J. Riede and F. P. Gabbaï, *Organometallics*, 1999, **18**, 1747.

13 J. D. Wuest and B. Zacharie, *Organometallics*, 1985, **4**, 410.

14 H. E. Katz, *J. Org. Chem.*, 1985, **50**, 5027.

15 R. Altmann, K. Jurkschat, M. Schuermann, D. Dakternieks and A. Duthie, *Organometallics*, 1998, **17**, 5858.

16 R. Altmann, M. Fontani, O. Gausset, K. Jurkschat, M. Schurmann and P. Zanello, *Phosphorus Sulfur Silicon Relat. Elem.*, 1999, **150–151**, 299.

17 W. Uhl, F. Hannemann, W. Saak and R. Wartchow, *Eur. J. Inorg. Chem.*, 1998, 921.

18 M. F. Hawthorne and Z. Zheng, *Acc. Chem. Res.*, 1997, **30**, 267.

19 M. F. Hawthorne, X. Yang and Z. Zheng, *Pure Appl. Chem.*, 1994, **66**, 245.

20 W. Uhl and F. Hannemann, *J. Organomet. Chem.*, 1999, **579**, 18.

21 M. Tschinkl, A. Schier, J. Riede and F. P. Gabbaï, *Inorg. Chem.*, 1997, **36**, 5706.

22 A. G. Massey, N. A. A. Al-Jabar, R. E. Humphries and G. B. Deacon, *J. Organomet. Chem.*, 1986, **316**, 25.

23 M. Tschinkl, A. Schier, J. Riede and F. P. Gabbaï, *Angew. Chem., Int. Ed.*, 1999, **38**, 3547.

24 J. H. Williams, J. K. Cockcroft and A. N. Fitch, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1655.

25 J. H. Williams, *Acc. Chem. Res.*, 1993, **26**, 593.

26 A. P. West, Jr., S. Mecozzi and D. A. Dougherty, *J. Phys. Org. Chem.*, 1997, **10**, 347.

27 G. W. Coates, A. R. Dunn, L. M. Henling, D. A. Dougherty and R. H. Grubbs, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 248.

28 G. W. Coates, A. R. Dunn, L. M. Henling, J. W. Ziller, E. B. Lobkovsky and R. H. Grubbs, *J. Am. Chem. Soc.*, 1998, **120**, 3641.

29 M. Weck, A. R. Dunn, K. Matsumoto, G. W. Coates, E. B. Lobkovsky and R. H. Grubbs, *Angew. Chem., Int. Ed.*, 1999, **38**, 2741.

30 C. Dai, P. Nguyen, T. B. Marder, A. J. Scott, W. Clegg and C. Viney, *Chem. Commun.*, 1999, 2493.

31 D. J. Parks, W. E. Piers, M. Parvez, R. Atencio and M. J. Zaworotko, *Organometallics*, 1998, **17**, 1369.

32 J. C. Ma and D. A. Dougherty, *Chem. Rev.*, 1997, **97**, 1303.

33 S. C. Nyburg and C. H. Faerman, *Acta Crystallogr., Sect. B*, 1985, **41**, 274.

34 A. J. Canty and G. B. Deacon, *Inorg. Chim. Acta*, 1980, **45**, L225.

35 J. D. Wuest and B. Zacharie, *J. Am. Chem. Soc.*, 1987, **109**, 4714.

36 X. Yang, S. E. Johnson, S. I. Khan and M. F. Hawthorne, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 893.

37 M. Tschinkl, R. E. Bachman and F. P. Gabbaï, *J. Organomet. Chem.*, 1999, **582**, 40.

38 M. Tschinkl, A. Schier, J. Riede and F. P. Gabbaï, *Organometallics*, 1999, **18**, 2040.

39 M. Tschinkl, A. Schier, J. Riede, G. Mehltretter and F. P. Gabbaï, *Organometallics*, 1998, **17**, 2921.

40 X. Delaigue, M. W. Hosseini, N. Kyritsakas, A. De Cian and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1995, 609.

41 L. G. Kuz'mina and Y. T. Struchkov, *Croat. Chem. Acta*, 1984, **57**, 701.

42 W. Lau, J. C. Huffman and J. K. Kochi, *J. Am. Chem. Soc.*, 1982, **104**, 5515.

43 G. E. Cox, D. W. J. Cruickshank and J. A. S. Smith, *Proc. R. Soc. London, Ser. A*, 1958, **247**, 1.

44 G. E. Bacon, N. A. Curry and S. A. Wilson, *Proc. R. Soc. London, Ser. A*, 1964, **279**, 98.

45 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

46 G. M. Sheldrick, SADABS, Program for Siemens area detector absorption correction, Institut für Anorganische Chemie, Universität Göttingen, 1996.

47 G. M. Sheldrick, SHELXTL/PC, version 5.1, Siemens Analytical X-Ray Instruments, Madison, WI, 1998.