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μ_6-η^2:η^2:η^2:η^2:η^2:η^2 As a New Bonding Mode for Benzene

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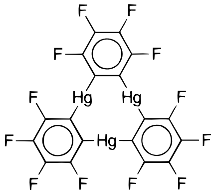
With the advent of polyfunctional Lewis acids, the multiple coordination of electron-rich species has flourished into an area of relevance to both molecular recognition[1−5] and catalysis.[6−8] Examination of the factors that govern these chemistries has led to the discovery of electrophilic complexes that feature electron-rich species in unusual coordination environments and geometries.[3−5] In particular, both molecular and supramolecular anionic complexes that contain tetra-, penta-, and hexa-coordinated halide and pseudohalide anions bound to mercury polydentate Lewis acids have been reported.[3,4,9−11] Such phenomena are not limited to the case of anions and also include neutral electron-rich molecules that undergo multiple coordination to the binding sites of polydentate Lewis acids. While organic substrates such as nitriles,[3] ketones,[12] formamides,[5,12] and sulfoxide[13] have been involved in such complexes, the interaction of arenes with main group polydentate Lewis acids has never been studied.

In an effort to model the sorption of benzene on metal surfaces,[14] the synthesis of molecular complexes that feature multiply bridging benzene molecules has been investigated. These studies led to the isolation of a series of compounds in which benzene interacts in a μ_3-η^2:η^2:η^2 fashion with three transition metal centers.[15,16] However, higher coordination of benzene has never been achieved. It occurred to us that complexes in which benzene is coordinated to more than three metals might be prepared if two adequately chosen polydentate Lewis acid molecules interact concomitantly with a unique benzene molecule. The affinity of mercury for aromatic compounds is well documented. While electrophilic mercuration reactions[17] and π-complex formations[18] substantiate the high affinity of Hg^{2+} cations for arenes, weaker but measurable interactions also occur between arenes and organomercurials.[19] In this contribution, we report that the reaction of benzene with trimeric *o*-tetrafluorophenylene mercury (**1**)[20] leads to the formation of a supramolecule that contains sandwiched μ_6-η^2:η^2:η^2:η^2:η^2:η^2-benzene.



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Compound **1** dissolves in boiling benzene. Upon cooling, followed by slow evaporation of the solvent, crystallization occurs to afford a quantitative yield of **1**·C_6H_6 (**2**). Initial information on the composition of **2** was gained from elemental analysis[21] and thermogravimetric analysis which revealed that, between 70 and 110 °C, benzene loss occurred (6.5% of original weight). As indicated by MAS ^{13}C NMR spectroscopy, the benzene resonance of **2** (133.3 ppm) is slightly deshielded when compared to free benzene (128.0 ppm). Also, this resonance is sharp and suggests that benzene in **2** exists in a very symmetrical environment. The infrared spectrum of **2** was dominated by absorption bands of **1**. While the C═C stretching bands of benzene in **2** could not be observed due to interference with those of **1**, the spectrum permitted the detection of an intense out-of-plane (oop) C−H deformation band (mode ν_4) at 716 cm^{-1} (525 cm^{-1} for **1**·C_6D_6; $\nu_H/\nu_D = 1.36$). When compared to that of free benzene, this oop deformation is shifted to higher energy by $\delta\nu_{oop}$ 42 cm^{-1}. It is interesting to note that this shift is stronger than that observed when benzene is adsorbed on metal surfaces such as Pd(111) ($\delta\nu_{oop}$ 21 cm^{-1}).[22]

The result of a single-crystal X-ray analysis[23] of **2** revealed extended stacks that run parallel to one another. Each stack consists of nearly parallel, yet staggered molecules of **1** that sandwich benzene molecules (Figure 1). These stacks are rather

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(21) Anal. Calcd (found) for $C_{24}H_6F_{12}Hg_3$: 25.64 (25.63); H, 0. 53 (0.51).

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(23) Crystal data for **2**: $C_{24}H_6F_{12}Hg_3$, *M* 1124.06, rhombohedral, space group $R\bar{3}c$, $a = 10.9331(13)$ Å, $\alpha = 105.383(17)°$, $V = 1133.0(2)$ Å^3, $Z = 2$, $\rho_{calc} = 3.295$ g cm^{-3}. Siemens SMART-CCD area detector diffractometer, Mo Kα radiation ($\lambda = 0.71069$ Å), $T = -163$ °C. Crystal size 0.14 × 0.12 × 0.03 mm^3, ω-scan mode, measurement range $2.34 \leq \theta \leq 24.97°$, 651 unique reflections, 587 reflections with $I > 2\sigma(I)$, $\mu = 20.389$ mm^{-1}. The structure was solved by direct methods and refined by full-matrix least squares against F^2 using the SHELXTL/PC (version 5.10) package, 60 parameters, $R1 = 0.0365$, $wR2 = 0.0865$ (all data).

10.1021/ja0016598 CCC: $19.00

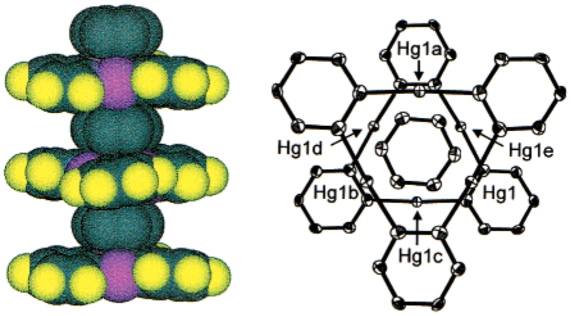

Figure 1. Left: Side view of a portion of a stack in the structure of **2**. Color code: fluorine, green; carbon, gray; and mercury, purple. H atoms omitted for clarity. Right: ORTEP view (50% ellipsoids) showing the sandwiched benzene molecule. F and H atoms are omitted for clarity.

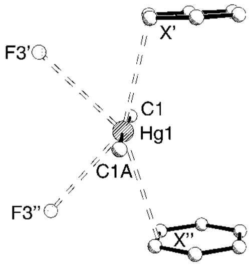

Figure 2. View of the mercury primary and secondary coordination sphere. Selected bond length (Å) and angles (deg): Hg(1)−C(1) 2.058(8) and C(1)−Hg(1)−C(1A), 175.9(5).

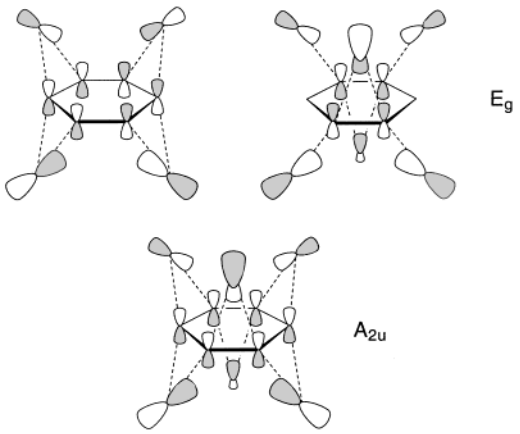

Figure 3. Schematic interaction diagram depicting the bonding molecular orbitals between benzene and two molecules of **1**. A D_{3d} symmetry is assumed.

compact and exhibit a short centroid distance of 3.24 Å.[24] With a dihedral angle of 8.1° formed between the phenylene ring and the plane containing the three mercury atoms, the molecules of **1** deviate slightly from planarity and adopt a propeller conformation. This distortion is only minute and the stacks approach a D_{3d} symmetry reminiscent of that recently described by Hawthorne et al. in an octahedral iodide electrophilic sandwich complex.[11] The mercury atom is linearly coordinated to the two carbon atoms of the bound tetrafluorophenylene rings. The secondary coordination sphere of the mercury center contains two benzene molecules and two fluorine atoms, the latter belonging to molecules of **1** in neighboring stacks (Figure 2). The Hg⋯F distance (3.273 Å) falls within the sum of the van der Waals radii ($r_{\mathrm{vdw}}(\mathrm{F}) = 1.30-1.38$ Å,[25] $r_{\mathrm{vdw}}(\mathrm{Hg}) = 1.73-2.00$ Å).[26] The distance between the C−C bond centroid (X) and the mercury center (3.36 Å) is comparable to those distances found in organomercurial−aromatic complexes that feature intramolecular mercury−π secondary interactions.[19] Further inspection of the secondary coordination sphere of the mercury center reveals a nearly right F′⋯Hg⋯F″ angle (92.8°) and an obtuse X′−Hg−X″ angle (149.7°).

It is interesting to note that each of the six C−C bonds of the benzene molecule interacts with one of the six mercury centers of the two juxtaposed molecules of **1**. Assuming a D_{3d} symmetry, we propose that these interactions result in the formation of a molecular orbital of A_{2u} symmetry and two degenerate molecular orbitals of E_g symmetry as shown in Figure 3. These molecular orbitals result from π−electron donation of the benzene into sets of available 6p orbitals of mercury. As suggested by the location of the fluorine secondary ligands, these mercury 6p orbitals do not point directly toward the center of each C−C bond but are orientated inward at approximately 30° from the vector defined by the mercury atom and the C−C bond centroid. While Kekulé-type distortions have been observed in transition-metal complexes that feature μ_3-η^2:η^2:η^2 benzene ligands,[15,16] all benzene C−C bond lengths in **2** are equivalent and no lengthening could be established within the error of the X-ray measurement. This situation reflects the symmetry of the interactions that affect each C−C bond equally. It also substantiates the modest character of the interactions that occur between organomercurials and arenes.[19,27]

In conclusion, we report the formation of a supramolecule that features sandwiched μ_6-η^2:η^2:η^2:η^2:η^2:η^2-benzene in a double face-capping mode. We are presently investigating the interaction of **1** with acetylene.

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Note added in proof: We have been informed by Prof. John P. Fackler, Jr., that his group has observed the formation of stacked structure involving **1** and trinuclear cyclic gold complexes such as [Au(μ-C^2,N^3-bzim)]$_3$ (C^2,N^3-bzim = 1-benzylimidazolate). An account of this work should soon appear in the literature.

Supporting Information Available: X-ray crystal analysis data for **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[24] Distance between centroid of benzene and the centroid of the three mercury atoms of **1**.

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