Complexation of Aldehydes and Ketones by Trimeric Perfluoro-*ortho*-phenylene Mercury, a Tridentate Lewis Acid

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A series of adducts formed by the interaction of trimeric perfluoro-*ortho*-phenylene mercury (**2**) with various organic carbonyls including acetaldehyde, acetone, acetophenone, and benzophenone have been characterized. The crystal structures of [**2**·μ_3-acetaldehyde] (**3**) and [**2**·μ_3-benzophenone] (**7**), respectively, reveal the formation of 1:1 complexes in which one molecule of the organic carbonyl is concomitantly coordinated to the three mercury centers of **2** via the oxygen atom. In the benzophenone adduct **7**, one of the phenyl rings of the coordinated benzophenone molecule engages in an intramolecular arene−fluoroarene interaction with a tetrafluorophenylene ring of **2** (intercentroid distance: 3.687 Å). When **2** is combined with acetone and acetophenone, adducts [**2**·(acetone)(μ_3-acetone)$_2$] (**4**) and [**2**·(μ_3-acetophenone)$_2$] (**6**) are obtained. In both cases, two molecules of the ketone are positioned on each side of the planar trifunctional Lewis acid and are complexed via their respective oxygen atom to the three mercury centers of **2**. In **4**, a third molecule of acetone acts as a terminal ligand and forms a relatively long bond with one of the mercury atoms. In **3**, **4**, **6**, and **7** the Hg−O bonds formed by the triply bridging carbonyl substrate range from 2.813(6) to 3.056(14) and are within the sum of the van der Waals radii of oxygen and mercury. In all cases, the carbonyl stretching vibration of the carbonyl substrate is shifted to a lower wavenumber, which suggests a weakening of the C═O bond.

Introduction

The multiple activation of organic carbonyls by polydentate Lewis acids is an emerging paradigm in organic catalysis. Indeed, a series of investigations have shown that polyfunctional Lewis acids are valuable catalysts for reactions involving organic carbonyls such as aldehydes and ketones.[1−3] It has been proposed that the high catalytic activity observed in these reactions results from the ability of the polydentate Lewis acid to chelate the carbonyl oxygen atom. On a few occasions, related phenomena have been discovered in reactions involving thioketones and thionoesters as substrates.[4−6] Although kinetic studies suggest the multiple activation of ketones and aldehydes, structural data supporting this phenomenon are extremely scarce. As shown by Wuest,[7,8] the multiple coordination of formamides by polyfunctional organomercurials is readily observed and is apparently facilitated by the relatively high basicity of these carbonyl substrates.[9] Ketones and aldehydes, however, are much less basic and,[9] as a result, less prone to multiple coordination.[10] In fact, while NMR studies have suggested the chelation of ketones,[11] only on one occasion has a bimolecular complex featuring a chelated ketone been isolated and characterized by X-ray diffraction methods.[12,15] This complex, [**1**·μ_2-acetone], involves the bidentate Lewis acid 1,2-bis(chloromercurio)tetrafluorobenzene (**1**), whose acceptor properties are enhanced by the presence of an electron-withdrawing backbone. Interestingly, attempts to isolate such complexes with aldehydes have led only to the isolation of adducts in which the carbonyl substrate adopts a terminal rather than bridging position.[16] In this paper, we report on the multiple coordination of

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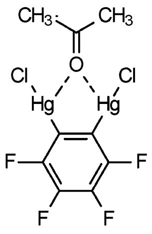
Table 1. Crystal Data, Data Collection, and Structure Refinement for 3, 4, 6, and 7

	3	**4**	**6**	**7**
		Crystal Data		
formula	$C_{20}H_4F_{12}Hg_3O$	$C_{27}H_{18}F_{12}Hg_3O_3$	$C_{34}H_{16}F_{12}Hg_3O_2$	$C_{31}H_{10}F_{12}Hg_3O$
M_r	1090.00	1220.18	1286.24	1228.16
cryst size (mm^3)	0.46 × 0.27 × 0.17	0.26 × 0.26 × 0.17	0.21 × 0.04 × 0.04	0.39 × 0.15 × 0.14
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/m$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	6.9082(17)	9.3365(19)	11.098(2)	9.9401(7)
b (Å)	15.665(4)	10.684(2)	17.058(3)	19.6770(15)
c (Å)	9.727(2)	15.466(3)	17.319(4)	14.3063(10)
	90	79.47(3)		90
β (deg)	100.265(7)	83.04(3)	92.30(3)	91.4750(10)
	90	84.57(3)		90
V (Å^3)	1035.7(4)	1501.4(5)	3276.2(11)	2797.3(4)
Z	2	2	4	4
ρ_{calc} (gcm^{-3})	3.495	2.699	2.608	2.916
μ(Mo Kα) (mm^{-1})	22.300	15.404	14.124	16.532
F(000) (e)	960	1104	2336	2208
		Data Collection		
T (K)	110(0)	110(0)	110(0)	110(0)
scan mode	ω	ω	ω	ω
hkl range	$-3\rightarrow6, -18\rightarrow15, -11\rightarrow7$	$-10\rightarrow10, -12\rightarrow12, -17\rightarrow17$	$-10\rightarrow13, -19\rightarrow20, -20\rightarrow20$	$-11\rightarrow11, -20\rightarrow21, -12\rightarrow15$
no. of reflns measd	4949	13 508	16 891	12 280
no. of unique reflns, [R_{int}]	1506 [0.0469]	4714 [0.0276]	5747 [0.0587]	3987 [0.0576]
no. of reflns used for refinement	1506	4714	5747	3987
abs corr	empirical	SADABS	SADABS	empirical
T_{min}/T_{max}	0.2716/0.7389	0.4164/1	0.4031/1	0.4233/0.9417
		Refinement		
no. of params refined	169	406	460	424
R1, wR2 [$I > 2\sigma(I)$]	0.0417, 0.1070	0.0353, 0.0955	0.0705, 0.1500	0.0292, 0.0738
ρ_{fin} (max/min) (e Å^{-3})	4.354, −2.673	3.183, −1.999	2.645, −3.122	1.738, −1.275

[a] $R1 = \sum(F_o - F_c)/\sum F_o$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0838$ (**3**), 0.0732 (**4**), 0.0289 (**6**); 0.0508 (**7**); $b = 11.2989$ (**3**), 2.93 (**4**), 200 (**6**), 0.4977 (**7**).

acetaldehyde, acetone, acetophenone, and benzophenone by trimeric perfluoro-*ortho*-phenylene mercury (**2**).[17,18]


1-μ_2-acetone

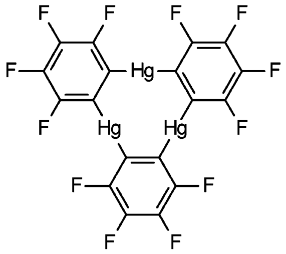

2

Table 2. Hg−O Distances (Å) in the Structure of 3, 4, 6, and 7

Compound **3**	
Hg(1)−O(1) = 2.912(13)	Hg(2)−O(1) = 2.965(8)
Compound **4**	
Hg(1)−O(1) = 2.978(6)	Hg(1)−O(3) = 2.905(6)
Hg(2)−O(1) = 2.813(6)	Hg(2)−O(3) = 2.858(6)
Hg(3)−O(1) = 2.899(6)	Hg(3)−O(3) = 2.814(6)
Hg(1)−O(2) = 3.088(8)	
Compound **6**	
Hg(1)−O(1) = 2.910(14)	Hg(1)−O(2) = 2.841(13)
Hg(2)−O(1) = 2.873(16)	Hg(2)−O(2) = 3.056(14)
Hg(3)−O(1) = 2.883(14)	Hg(3)−O(2) = 2.956(15)
Compound **7**	
Hg(1)−O(1) = 2.953(5)	Hg(3)−O(1) = 3.047(5)
Hg(2)−O(1) = 2.888(5)	

Results

Interaction of 2 with Acetaldehyde. Compound **2** dissolves spontaneously in excess acetaldehyde. Slow concentration of the resulting solution yields large crystals of [**2**·μ_3-acetaldehyde] (**3**), whose elemental analysis corresponds to that expected for a 1:1 complex. Compound **3** crystallizes in the monoclinic space group $P2_1/m$ with two molecules in the unit cell (Table 1). Examination of the atomic connectivity confirms the simultaneous coordination of the carbonyl oxygen atom to the mercury centers of **2**. The resulting Hg−O distances fall within the narrow range 2.912(13)−2.965(8) Å (Table 2, Figure 1). As a result, the oxygen atom is essentially equidistant from the three Lewis acidic sites and sits 2.086 Å from the plane defined by the three mercury atoms. The linear carbonyl functionality is not perpendicular to the plane of the trinuclear complex with which it forms an angle of 66.4°. The carbonyl stretching frequency of the coordinated acetaldehyde ($\nu_{CO} = 1706$ cm^{-1}) is substantially shifted to a lower wavenumber when compared to that of the pure acetaldehyde ($\nu_{CO} = 1726$ cm^{-1}). Crystals of **3** are stable for several weeks at room temperature. Thermal gravimetric analysis (TGA) shows that acetaldehyde loss occurs in one step at 120 °C, which further substantiates the stability of this 1:1 adduct. Altogether, these results contrast with the previous observation that acetaldehyde does not coordinate to bifunctional **1**.[16]

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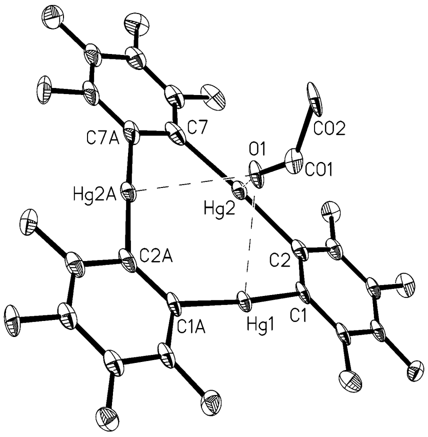

Figure 1. Structure of **3** in the crystal. ORTEP drawing (50%). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: O(1)−C(01) 1.19(2); C(1)−Hg(1)−O(1) 88.5(3), C(2)−Hg(2)−O(1) 87.5(4), C(7)−Hg(2)−O(1) 91.6(4), C(01)−O(1)−Hg(1) 112.0(13), C(01)−O(1)−Hg(2) 142.75(19), Hg(1)−O(1)−Hg(2) 76.2(2), O(1)−C(01)−C(02) 129(2).

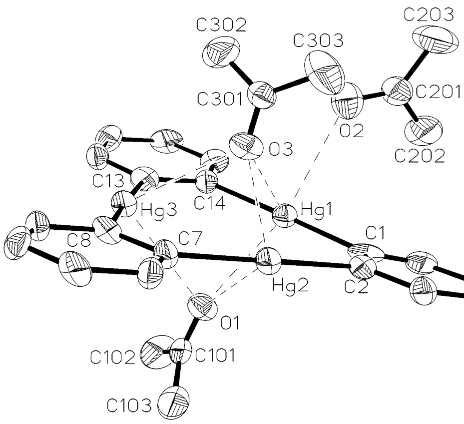

Figure 2. Solid-state structure of **4**. ORTEP drawing (40%). Hydrogen and fluorine atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: O(1)−C(101) 1.212(10), O(2)−C(201) 1.193(12), O(3)−C(301) 1.201(10); O(3)−Hg(1)−O(1) 85.46(17), O(3)−Hg(1)−O(2) 67.59(18), O(1)−Hg(1)−O(2) 152.98(19), O(1)−Hg(2)−O(3) 89.50(17), O(3)−Hg(3)−O(1) 88.64(17), C(101)−O(1)−Hg(2) 138.8(6), C(101)−O(1)-Hg(3) 126.0(5), Hg(2)−O(1)−Hg(3) 77.77(15), C(101)−O(1)−Hg(1) 137.1(6), Hg(2)−O(1)−Hg(1) 76.78(14), Hg(3)−O(1)−Hg(1) 75.04(14), C(201)−O(2)−Hg(1) 125.9(7), C(301)−O(3)−Hg(3) 133.5(6), C(301)−O(3)−Hg(2) 142.1(6), Hg(3)−O(3)−Hg(2) 78.44(15), C(301)−O(3)−Hg(1) 123.3(6), Hg(3)−O(3)−Hg(1) 77.48(15), Hg(2)−O(3)−Hg(1) 77.26(15), O(1)−C(101)−C(103) 121.7(9), O(1)−C(101)−C(102) 118.4(9), O(2)−C(201)−C(202) 119.9(10), O(2)−C(201)−C(203) 123.8(11), O(3)−C(301)−C(302) 120.4(9), O(3)−C(301)−C(303) 122.8(10).

Interaction of 2 with Acetone. The interaction of **2** with acetone has been previously studied, although no details are available on the structure and stoichiometry of the resulting complex.[19] We have found that slow concentration of an acetone solution of **2** yields [**2**·(acetone)(μ_3-acetone)$_2$] (**4**), in which three molecules of acetone are bound to the trifunctional Lewis acid. Compound **4** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. One of the acetone molecules of the adduct is terminally ligated to Hg(1) via a relatively long contact of 3.088(8) Å (Figure 2). The other two acetone molecules are located above and below the plane of the trinuclear complex and interact simultaneously with the three mercury atoms via formation of Hg−O interactions that range from 2.813(6) to 2.978(6) Å (Table 2) as observed in the structure of **3**. This situation is reminiscent of that recently encountered by Shur in a bis-acetonitrile complex of **2**.[20] The linear carbonyl functionalities of the triply bridging acetone molecules are oriented almost perpendicularly to the plane of the trinuclear complex with which they form angles of 81.8° and 79.5°. Crystals of **4** become quickly opaque and brittle through partial loss of acetone when removed from the mother liquor. Elemental analysis carried out on the resulting material indicates the loss of exactly 2 equiv of acetone. This observation suggests the formation of a stable 1:1 adduct **2**·acetone (**5**). While the structure of this adduct is unknown, infrared studies show a shift of the carbonyl stretching frequency to 1683 cm^{-1} (compared to ν_{CO} = 1716 cm^{-1} for neat acetone). These results suggest that the remaining molecule of acetone is multiply coordinated to the mercury centers of **2**. In support of this view, we note that a shift of 1693 cm^{-1} was observed in [**1**·μ_2-acetone].[12]

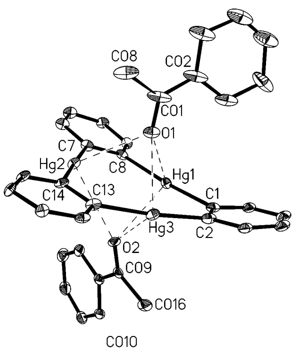

Figure 3. Solid-state structure of **6**. ORTEP drawing (50%). Hydrogen and fluorine atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: O(2)−C(09) 1.23(2), O(1)−C(01) 1.24(2); O(2)−Hg(1)-O(1) 91.9(4), O(1)−Hg(2)−O(2) 88.3(4), O(1)−Hg(3)−O(2) 90.1(4), C(09)−O(2)−Hg(1) 115.1(12), C(09)−O(2)−Hg(3) 128.6(14), Hg(1)−O(2)−Hg(3) 75.9(4), C(09)−O(2)−Hg(2) 157.0(15), Hg(1)−O(2)−Hg(2) 74.5(3), Hg(3)−O(2)−Hg(2) 73.0(3), C(01)−O(1)−Hg(2) 126.1(18), C(01)−O(1)−Hg(3) 136.4(13), Hg(2)−O(1)−Hg(3) 76.8(4), C(01)−O(1)−Hg(1) 139.9(15), Hg(2)−O(1)−Hg(1) 76.4(3), Hg(3)−O(1)−Hg(1) 76.0(3), O(1)−C(01)−C(02) 123(3), O(1)−C(01)−C(08) 118(3), O(2)−C(09)−C(010) 122(2), O(2)−C(09)−C(016) 120(2).

Interaction of 2 with Acetophenone. A crystalline acetophenone adduct, [**2**·(μ_3-acetophenone)$_2$] (**6**), can be obtained upon slow concentration of a solution of **2** in this ketone. As in the case of the acetone complex, crystals of **6** become brittle when exposed to a dry atmosphere. A low-temperature single-crystal X-ray diffraction study of **6** indicates that this adduct crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. Its structure is that of a 2:1 complex in which two molecules of acetophenone are

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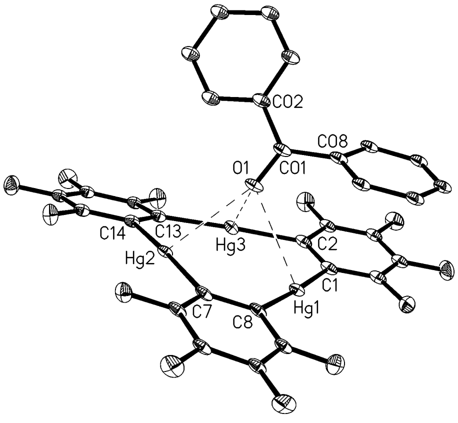

Figure 4. Solid-state structure of **7**. ORTEP drawing (50%). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: O(1)−C(01) 1.217(8); C(1)−Hg(1)−C(8) 176.6(3), C(1)−Hg(1)−O(1) 88.4(2), C(8)−Hg(1)−O(1) 88.6(2), C(7)−Hg(2)−O(1) 88.9(2), C(14)−Hg(2)−O(1) 92.7(2), C(2)−Hg(3)−O(1) 85.8(2), C(13)−Hg(3)−O(1) 91.4(2), C(01)−O(1)−Hg(2) 164.9(5), C(01)−O(1)−Hg(1) 118.3(5), Hg(2)−O(1)−Hg(1) 75.88(11), C(01)−O(1)−Hg(3) 102.9(4), Hg(2)−O(1)−Hg(3) 75.19(11), Hg(1)−O(1)−Hg(3) 73.23(11), O(1)−C(01)−C(08) 118.2(7), O(1)−C(01)−C(02) 121.0(7).

triply coordinated to the mercury centers of **2**. With two triply bridging ketones on both sides of the planar trifunctional Lewis acid, its structure resembles that of the acetone adduct **4**. The Hg−O contacts fall within the range 2.873−3.056 Å (Table 2), and the carbonyl functionalities are oriented at 81.1° and 63.1° from the plane containing the three mercury atoms. Elemental analysis carried out on a sample stored at room temperature for 24 h reveals a 30% loss of the acetophenone component. After 72 h, the loss corresponds exactly to 1 equiv of acetophenone, thus suggesting the formation of a 1:1 adduct. IR spectroscopy carried out on a freshly prepared sample reveals that the carbonyl stretching vibration is only barely shifted when compared to that of the neat ketone (1680 vs 1686 cm^{-1} for neat acetophenone).

Interaction of 2 with Benzophenone. The crystalline 1:1 complex [**2**·μ_3-benzophenone] (**7**) is readily obtained upon cooling of a CH_2Cl_2 solution containing a mixture of **2** and the ketone. This adduct crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. The carbonyl oxygen is triply coordinated to the mercury atoms of **2**. The resulting Hg−O distances range from 2.888(5) to 3.047(5) Å (Table 2) and are comparable to those observed in the structures of **3**, **4**, and **6**. The linear carbonyl functionality is tilted with respect to the plane containing the three mercury atoms that it approaches at an angle of 53.6°. This situation contrasts with those encountered in **3**, **4**, and **6**, where the orientation of the triply coordinated carbonyl functionalities with respect to the plane containing **2** is closer to 90°. This situation possibly results from the presence of an intramolecular arene−fluoroarene interaction that involves a tetrafluorophenylene ring of **2** and one of the phenyl rings of the coordinated molecule of benzophenone. The centroids of tetrafluorophenylene and phenyl rings are separated by 3.687 Å. Examination of the cell-packing diagram indicates that this phenyl ring also engages in short contacts with the mercury centers of the neighboring monomer. These Hg−C contacts range from 3.517 to 3.626 Å (Table 3). Infrared studies show only a moderate shift of the carbonyl stretching frequency when compared to that of pure benzophenone (1647 vs 1650 cm^{-1} for the pure ketone).

Table 3. Mercury Carbon Distances (Å) for the Polyhapto−π Interactions in the Structure of 7

Hg(2)−C(09) = 3.626[a]
Hg(2)−C(010) = 3.518[a]
Hg(2)−C(011) = 3.571[a]

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

Discussion

The structures of **3**, **4**, **6**, and **7** show that triple coordination of the carbonyl oxygen atom of both aldehydes and ketones is a readily observable phenomenon. The Hg−O bond distances in **3**, **4**, **6**, and **7** are within the sum of the van der Waals radii for oxygen (r_{vdw} = 1.54 Å)[21] and mercury (r_{vdw} = 1.73−2.00 Å)[22,23] (Table 2). They are also comparable to the value of 2.91 Å observed by Wuest in a complex featuring a diethylformamide quadruply coordinated to a cyclic tetradentate mercury Lewis acid.[24] These Hg−O distances are however longer than those measured in [**1**·μ_2-acetone] (av 2.73 Å), which features a carbonyl functionality coordinated to only two mercury centers.[12] Whereas the precision of the crystallographic measurement does not confirm a lengthening of the C═O bond in **3**, **5**, **6**, and **7**, the carbonyl stretching vibration is shifted to lower wavenumber, which suggests a weakening of the C═O bond. Interestingly, this effect is much more acute in the case of the 1:1 acetaldehyde and acetone adducts **3** and **5** than in **6** and **7**, which both contain aromatic ketones.

With an intercentroid distance of 3.687 Å, the arene−fluoroarene contact observed in the structure of **7** falls within the range typically observed for such interactions.[25,26] These interactions, which result at least in part from electrostatic forces, have often been observed in organic arene−fluoroarene assemblies[27−30] as well as in organometallic complexes.[31,32] Finally, the intermolecular Hg−C interactions that occur between the

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phenyl ring of the benzophenone molecule and the mercury center of the neighboring monomer are within the sum of the van der Waals radius of mercury ($r_{\mathrm{vdw}}(\mathrm{Hg}) = 1.73-2.00$ Å)[22,23] and that of carbon in aromatic systems ($r_{\mathrm{vdw}}(\mathrm{C}_{\mathrm{aromatic}}) = 1.7$ Å)).[29] They reflect the presence of secondary polyhapto-π interactions occurring between the electron-rich aromatic molecules and the acidic mercury centers. Similar distances have been previously observed in adducts involving **2** and aromatic substrates such as benzene, naphthalene, biphenyl, and triphenylene.[34,35]

Conclusions

The results presented herein demonstrate that trimeric perfluoro-*ortho*-phenylene mercury behaves as a tridentate Lewis acid toward both aldehydes and ketones. The resulting adducts constitute the first examples of bimolecular complexes featuring triply bridging aldehydes or ketones. Earlier investigations showed that bidentate Lewis acids such as **1** readily chelate acetone but not acetaldehyde or benzaldehyde.[12,16] In this regard, the isolation of **3** is especially noteworthy and shows that weakly basic carbonyl substrates undergo multiple coordination with the appropriate polydentate Lewis acid. The structures of the adducts as well as the IR stretching vibration of the carbonyl functionality confirm the presence of a bonding interaction between the mercury centers of **2** and the oxygen atom of the carbonyl substrate. DFT calculations undertaken on **2** show a positively charged electrostatic potential surface in the center of the macrocycle.[36] Hence, in addition to covalent forces, it is likely that electrostatic forces also contribute to the stability of these adducts.

Experimental Section

General Considerations. All experiments were carried out in a fume hood. Atlantic Microlab (Norcross, GA) performed the elemental analyses. Infrared spectra were recorded as KBr pellets on a Mattson Genesis Series FTIR. Acetaldehyde, acetone, acetophenone, and benzophenone were purchased from Aldrich Chemical and used as provided. Compound **2** was prepared by the published procedure.[17] Thermal gravimetric analyses were carried out on an Instrument Specialists Incorporated TGA 1000 analyzer.

Single-Crystal X-ray Analysis. X-ray data for **3**, **4**, **6**, and **7** were collected on a Bruker Smart-CCD diffractometer using graphite-monochromated Mo Kα radiation (=0.71073 Å). Specimens of suitable size and quality were selected and mounted onto a glass fiber with Apiezon grease. The structure was solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms. Further crystallographic details can be found in Table 1 and in the Supporting Information.

Synthesis of [2·μ_3-Acetaldehyde] (3). Slow evaporation of a solution of **2** (50 mg, 0.048 mmol) in acetaldehyde (2 mL) afforded a quantitative yield of **3** (52 mg, 100% yield). The crystals were stable for weeks at room temperature. Anal. Calcd for $C_{20}H_4O_1F_{12}H_3$: C, 22.04; H, 0.36. Found: C, 22.08; H, 0.30. IR: 1706, 1653, 1616, 1468, 1418,1354, 1321, 1304, 1248, 1080, 1004, 815, 770 cm^{-1}.

Synthesis of [2·(Acetone)(μ_3-acetone)$_2$] (4) and [2·Acetone] (5). Compound **2** (50 mg, 0.048 mmol) was dissolved in pure acetone (1 mL). After partial evaporation of the solvent, crystals of **4** were collected and analyzed. These crystals are not stable and rapidly lose two molecules of acetone, yielding a 1:1 adduct of **2**·acetone (**5**) (32 mg, 60% yield). Anal. Calcd for $C_{21}H_6O_1F_{12}Hg_3$: C, 22.85; H, 0.58. Found: C, 23.06; H, 0.52. IR: 2170, 1684, 1683, 1653, 1636, 1617, 1576, 1559, 1540, 1507, 1472, 1457, 1419, 1395, 1386, 1322, 1287, 1251, 1238, 1079, 1088, 1004, 1004, 835, 772 cm^{-1}.

Synthesis of [2·(μ_3-Acetophenone)$_2$] (6). Slow evaporation of a solution of **2** (50 mg, 0.048 mmol) in pure acetophenone (1.5 mL) affords crystals of **6** (60 mg, 100% yield). At room temperature, crystals of **6** become opaque and brittle over a period of 8 h. Elemental analysis of a sample stored at room temperature for a period of 24 h reveals a 30% loss of the acetophenone component. Anal. Calcd for $C_{34}H_{16}F_{12}Hg_3O_2$: C, 31.1; H, 1.10. Found: C, 28.8; H, 0.95. IR: 1680, 1599, 1583, 1470, 1417, 1362, 1272, 1248, 1181, 1003, 959, 812, 760, 689, 590 cm^{-1}. After 72 h, the elemental analysis indicates a 50% loss of acetophenone and suggests the formation of [**2**·acetophenone]. Anal. Calcd for $C_{26}H_8F_{12}Hg_3O$: C, 26.8; H, 0.69. Found C, 26.94; H, 0.66.

Synthesis of [2·(μ_3-Benzophenone)] (7). In a vial, compound **2** (50 mg, 0.048 mmol) was added to benzophenone (25 mg, 0.14 mmol) in CH_2Cl_2. Upon refrigeration of the solution, crystals of **7** formed (32 mg, 54% yield based on **2**). Anal. Calcd for $C_{31}H_{10}F_{12}Hg_3O$: C, 30.30; H, 0.80; F, 18.56. Found: C, 30.54; H, 0.83; F, 18.52. IR: 1653, 1616, 1594, 1576, 1558, 1540, 1472, 1418, 1353, 1322, 1307, 1286, 1251, 1126, 1083, 1076, 1006, 943, 919, 815, 768, 710, 698, 636 cm^{-1}.

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Note Added in Proof: While the manuscript was being processed, the synthesis and crystal structure of [**2**·(μ_3-DMF)$_2$] was reported by two independent research groups.[37,38] We have also been able to isolate the adduct [**2**·μ_3-acetone], whose composition is identical to that of **5**.[39]

Supporting Information Available: Tables of structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for complexes **3**, **4**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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