Interaction of the Bifunctional Lewis Acid 1,2-Bis(chloromercurio)tetrafluorobenzene with Aldehydes, Nitriles, and Epoxides

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The formation of adducts involving the bidentate Lewis acid 1,2-bis(chloromercurio)-tetrafluorobenzene (**1**) and small electron rich organic molecules has been investigated. Compound **1** does not form stable adducts with aliphatic aldehydes and can be crystallized in base-free form from acetaldehyde. The X-ray crystal structure of **1** reveals the existence of a highly cross-linked supramolecular structure in which the individual molecules are associated by Hg···Cl and Hg···F interactions. By contrast, **1** forms an adduct (**2**) with benzaldehyde. In this adduct, the benzaldehyde molecule acts as a terminal ligand and coordinates one of the mercury centers through the formation of a long Hg–O bond of 2.68(1) Å. The supramolecular structure of **2** is that of a layered compound in which the monomers are held by numerous intermolecular Hg···Cl and Hg···F contacts. Arene–fluoroarene interactions are also present and involve the aromatic ring of benzaldehyde, which stacks with neighboring tetrafluorophenylene units (centroid distances = 3.58 and 3.77 Å). Interestingly, compound **1** forms chelate complexes with acetonitrile (**3**) and propylene oxide (**4**). As shown by X-ray single-crystal analyses of **3** and **4**, the electron rich organic derivatives interact simultaneously with the two mercury centers via formation of long coordination bonds (Hg–N = 2.82(1) and 2.93(1) Å in **3**; Hg–O =2.71(2) and Hg(2)–O = 2.77(2) Å in **4**). As observed in the structure of **2**, compound **3** and **4** form layered solids in which the monomers interact by Hg···Cl and Hg···F contacts. Finally, compound **1** readily catalyzes the polymerization of propylene sulfide.

Introduction

Owing to distinct cooperative effects, the use of polyfunctional Lewis acids as catalysts for small molecule transformation is gaining an increasing interest. Among a variety of systems that contain several Lewis acidic metal centers,[1–7] those able to chelate electron rich organic substrates have attracted particular attention. Especially noteworthy contributions have dealt with the use of bifunctional aluminum,[3,4] titanium,[5] or lithium[6] phenoxides for the activation of ketones and aldehydes toward nucleophilic addition.[7] Although the potency of these catalysts has been clearly demon-

strated, the nature of the interaction that occurs between the catalysts and the substrates remains poorly explored. For this reason and in order to explain the activity of these catalysts, structural studies of adducts involving polyfunctional Lewis acids and electron rich organic substrates have become desirable. Examination of the literature indicates that only a limited number of such studies are available,[8–10] the majority of which deal with the coordination of formamides to derivatives featuring the 1,2-bis(mercury)benzene motif.[11] As part of this effort, we have recently studied the coordination chemistry of the fluorinated bifunctional Lewis acid 1,2-bis(chloromercurio)tetrafluorobenzene (**1**).[12–16] Com-

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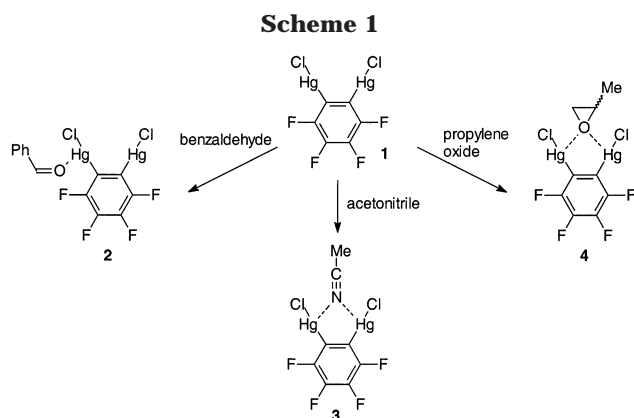(13) Tschinkl, M.; Schier, A.; Riede, J.; Gabbaï, F. P. *Organometallics* **1999,** *18,* 1747–1753.
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Table 1. Crystal Data, Data Collection, and Structure Refinement for 1, 2, 3, and 4

	1	2	3	4
formula	$C_6Cl_2F_4Hg_2$	$C_{13}H_6Cl_2F_4Hg_2O$	$C_8H_3Cl_2F_4Hg_2N$	$C_9H_6Cl_2F_4Hg_2O$
M_r	620.14	726.26	661.19	678.22
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2(1)/n$	$P2(1)$	$P2(1)/n$	$C2/c$
a (Å)	14.855(3)	7.1795(14)	18.8319(9)	20.354(5)
b (Å)	6.7905(14)	7.0079(14)	7.6827(8)	6.5325(16)
c (Å)	19.281(4)	15.109(3)	18.4683(19)	21.358(5)
α (deg)	90	90	90	90
β (deg)	96.19(3)	99.55(3)	102.440(2)	108.031(5)
γ (deg)	90	9090	90	90
V (Å^3)	1933.6(7)	749.6(3)	1223.7(2)	2700.3(12)
ρ_{calc} (g cm^{-3})	4.260	3.217	3.589	3.337
Z	8	2	4	8
$F(000)$ (e)	2128	644	1152	2384
μ(Mo K) (cm^{-1})	322.8	208.5	255.2	231.4
		Data Collection		
cryst size	$0.2 \times 0.04 \times 0.02$ mm^3	$0.2 \times 0.1 \times 0.9$ mm^3	$0.2 \times 0.2 \times 0.3$ mm^3	$0.2 \times 0.1 \times 0.1$ mm^3
T (K)	110(2)	110(2)	173(2)	110(2)
scan mode	ω	ω	ω	ω
hkl range	$-16\rightarrow16, -7\rightarrow7, -20\rightarrow20$	$-8\rightarrow7, -7\rightarrow8, -17\rightarrow17$	$-11\rightarrow11, -10\rightarrow10, -23\rightarrow24$	$-20\rightarrow24, -7\rightarrow7, -25\rightarrow21$
measured reflns	11422	3889	14011	6732
no. of unique reflns, [R_{int}]	3016, [$R_{int} = 0.0685$]	2418, [$R_{int} = 0.0271$]	3004, [$R_{int} = 0.0364$]	2363, [$R_{int} = 0.1120$]
no. of reflns used for refinement	3016	2418	3016	2363
abs corr	empirical	SADABS	SADABS	Psi-scan
T_{min}/T_{max}	0.01/0.30	0.42	0.43/0.93	0.20/0.92
		Refinement		
no. of refined params	253	194	156	163
final R values [$I>2\sigma(I)$]				
R1^a (%)	0.0473	0.0276	0.0247	0.0556
wR2^b (%)	0.1073	0.0649	0.0540	0.1311
ρ_{fin} (max/min) (e Å^{-3})	4.391/-2.264, at Hg	2.198 and -1.814, at Hg	1.708/-1.441, at Hg	4.256/-1.923, at Hg

^{a} R1 = $(F_o - F_c)/F_o$. ^{b} wR2 = $\{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0349$ (**1**), 0.0642 (**2**); 0.0840 (**3**), 0.0276 (**4**), $b = 0.00$ (**1**), 0.00 (**2**), 0.00 (**3**), 0.00 (**4**).

Scheme 1

Table 2. Intermolecular Hg···Cl and Hg···F Distances (Å) in the Supramolecular Structure of 1

Hg(1)−Cl(1)^a = 3.449	Hg(1)−Cl(3)^b = 3.655
Hg(1)−Cl(4)^c = 3.221	Hg(1)−F(3)^c = 3.10
Hg(2)−Cl(1)^d = 3.298	Hg(2)−Cl(4)^c = 3.235
Hg(2)−Cl(4)^e = 3.239	Hg(3)−Cl(1)^d = 3.350
Hg(3)−F(6)^a = 2.864	Hg(3)−F(9)^c = 3.009
Hg(4)−Cl(1)^d = 3.367	Hg(4)−Cl(3)^d = 3.315
Hg(4)−F(10)^f = 3.537	

^{a} $-x+1.5$, $y-0.5$, $-z+0.5$. ^{b} $-x+1.5$, $y+0.5$, $-z+0.5$. ^{c} x, $y+1$, z. ^{d} x, $y-1$, z. ^{e} $-x+2$, $-y+1$, $-z+1$. ^{f} $1.5+x$, $-0.5-y$, $-0.5+z$.

pound **1** forms chelate complexes with a variety of substrates containing terminal oxo functionalities including ketones,[13] formamides,[13] sulfoxides,[14] and phosphonate diesters.[15] To provide a more complete understanding of its coordination chemistry, we have set out to prepare and structurally characterize adducts involving **1** and small electron rich organic molecules that constitute elementary building blocks for higher organic molecules and polymers. The present report is concerned with a study on the interaction of **1** with aldehydes, nitriles, and epoxides (Scheme 1).

Results and Discussions

Interaction of 1 with Aldehydes. Compound **1** dissolves spontaneously in small amounts of acetalde-

hyde. Upon slow evaporation, pure **1** spontaneously crystallizes. It is interesting to note that analogous experiments involving ketones, formamides, sulfoxides, and phosphonate diesters as solvent always led to the formation of adducts. In the present case, however, **1** is obtained as the base-free acid as confirmed by NMR, IR, and X-ray analysis. This finding substantiates the weak donicity of the aldehydic carbonyl functionality. Crystals of **1** obtained from acetaldehyde were suitable for an X-ray analysis. Compound **1** crystallizes in the monoclinic space group $P2(1)/n$ (Table 1) with two molecules in the asymmetric unit. Examination of the cell-packing diagram reveals the existence of an intricate supramolecular structure. The formation of chains along the *y*-axis can first be recognized. In those chains, the neighboring molecules interact by Hg···Cl and Hg···F intermolecular contacts (Table 2, Figure 1), whose lengths fall within the limit of the sum of the van der Waals radii ($r_{vdw}(F) = 1.30-1.38$ Å,[17] $r_{vdw}(Cl)$

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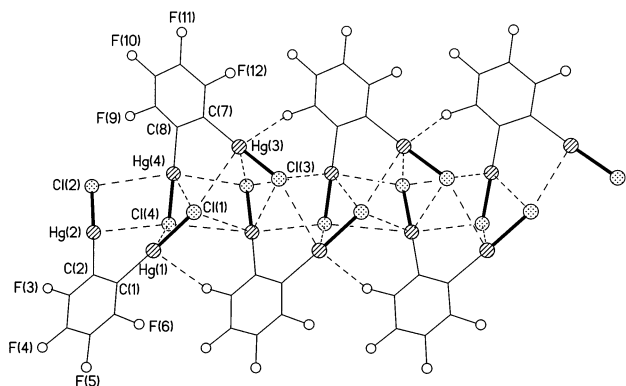
Figure 1. View of a chain formed in the structure of **1**. Selected bond lengths [Å] and angles [deg]: Hg(1)−C(1) 2.07(2), Hg(1)−Cl(1) 2.336(5), Hg(2)−C(2) 2.07(2), Hg(2)−Cl(2) 2.314(5) Hg(3)−C(7) 2.08(2), Hg(3)−Cl(3) 2.325(5), Hg(4)−C(8) 2.10(2); Hg(4)−Cl(4) 2.315(5), C(1)−Hg(1)−Cl(1) 178.2(6), C(7)−Hg(3)−Cl(3) 173.7(6), C(2)−Hg(2)−Cl(2) 176.9(5), C(8)−Hg(4)−Cl(4) 178.5(6).
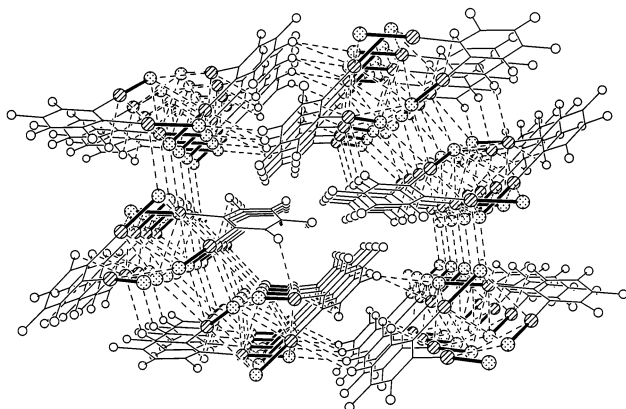

Figure 2. View of the intricate framework formed in the structure of **1**.

= 1.58−1.78 Å,[17] r_{vdw}(Hg) = 1.73−2.00 Å).[18] These chains run parallel to one another and interact by additional Hg···Cl and Hg···F contacts to yield a highly cross-linked tridimensional structure (Table 2, Figure 2).

The isolation of adducts involving **1** and propionaldehyde and pivaldehyde was also unsuccessful and yielded pure **1**. This lack of interaction suggested that aliphatic aldehydes could serve as innocent solvents capable of dissolving **1** without forming any stable adducts. It was therefore decided to use acetaldehyde as a solvent to study the interaction of **1** with other potential donors. Upon slow evaporation of the solvent, the adduct **1**·benzaldehyde (**2**) crystallizes from an acetaldehyde solution containing **1** and benzaldehyde in a 1:12 ratio. The crystals belong to the monoclinic space group *P*2(1) with two molecules in the unit cell (Table 1). In this adduct, benzaldehyde acts as a terminal ligand and coordinates to only one mercury center (Figure 3). In **2**, the Hg(1)−O bond (2.68(1) Å) is shorter than the sum of the van der Waals radii of oxygen (1.54 Å)[17] and mercury (1.73−2.00 Å)[18] and comparable to the Hg−O distances observed in the structure of related compounds such as **1**·μ_2-acetone[13] and **1**·μ_2-DMF.[13] The resulting Hg(1)−O−C(17) angle

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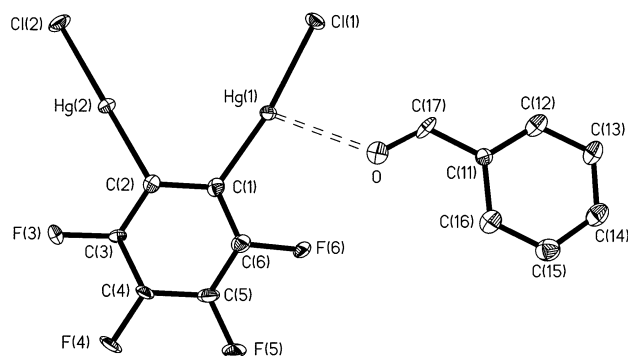
Figure 3. Structure of **2** in the crystal. ORTEP drawing (50%). Selected bond lengths [Å] and angles [deg]: Hg(1)−C(1) 2.03(1), Hg(1)−Cl(1) 2.331(3), Hg(2)−C(2) 2.06(1), Hg(2)−Cl(2) 2.317(2), O−C(17) 1.20(1), C(1)−Hg(1)−Cl(1) 171.9(3), C(2)−Hg(2)−Cl(2) 175.1(3).

Table 3. Intermolecular Hg···Cl and Hg···F Distances (Å) in the Supramolecular Structure of 2

Hg(1)−Cl(1)[a] = 3.245	Hg(2)−Cl(1)[d] = 3.210
Hg(1)−Cl(2)[b] = 3.247	Hg(2)−Cl(2)[a] = 3.222
Hg(1)−F(3)[c] = 3.060	Hg(2)−Cl(2)[b] = 3.531

[a] −*x*−1, *y*−0.5, −*z*. [b] -*x*−2, *y*+0.5, −*z*. [c] *x*, *y*+1, *z*. [d] *x*, *y*−1, *z*.
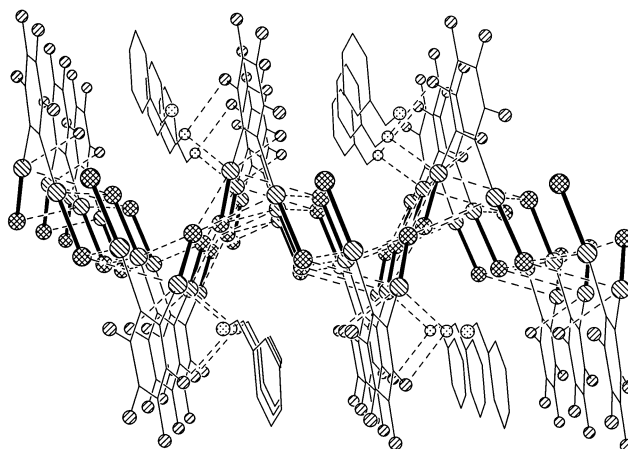

Figure 4. Side view of a layer formed in the structure of **2**.

(127.7°) suggests the formation of a long dative bond involving one of the oxygen lone pairs. Although no lengthening of the C=O bond could be confirmed within the experimental error of the X-ray measurement, insight into the magnitude of the Hg−O interaction was provided by IR spectroscopy, which revealed a slightly weakened carbonyl stretching frequency at 1684 cm^{-1} (v_{CO} = 1701 cm^{-1} in pure benzaldehyde). Interestingly, the ^{13}C NMR CP/MAS spectrum of **2** exhibits a slightly shielded carbonyl resonance at δ = 186.7 ppm (vs δ = 192.0 ppm for free benzaldehyde). The origin of this shielding remains unclear and contrasts with the downfield shift of the carbonyl carbon resonance observed upon complexation of ketones and formamides.

The supramolecular structure of **2** is that of a layered compound (Table 3, Figure 4). In the layers, the monomers are held by numerous intermolecular Hg···Cl and Hg···F contacts that are shorter than the sum of the van der Waals radii (r_{vdw}(F) = 1.30−1.38 Å,[17] r_{vdw}(Cl) = 1.58−1.78 Å,[17] r_{vdw}(Hg) = 1.73−2.00 Å).[18] It is interesting to note that the aromatic ring of benzalde-
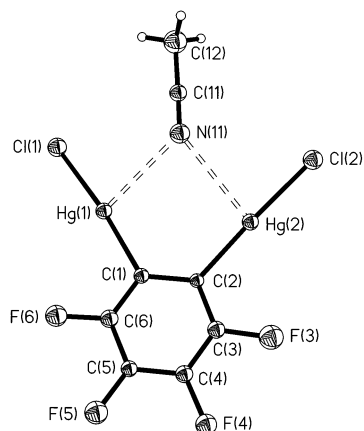
Figure 5. Structure of **3** in the crystal. ORTEP drawing (50%). Selected bond lengths [Å] and angles [deg]: Hg(1)−C(1) 2.061(6), Hg(1)−Cl(1) 2.3076(16), Hg(2)−C(2) 2.056-(6) Hg(2)−Cl(2) 2.3049(16), N(11)−C(11) 1.134(8), C(1)−Hg(1)−Cl(1) 174.17, C(2)−Hg(2)−Cl(2) 175.95(17).

hyde stacks with neighboring tetrafluorophenylene units (centroid distances = 3.58 and 3.77 Å). This type of interaction constitutes a well-documented phenomenon.[19] Theoretical investigations have shown that these interactions are mostly electrostatic and result from the marked, yet opposite, quadrupole moments of the two interacting components.[19] In fact, such interactions have been observed in structures involving **1** and benzene.[16] They have also been observed in the structure of $(C_6F_5)_3B \cdot$benzaldehyde.[20] It is important to note that the energy associated with these interactions is nonnegligible[21] and might explain why the observed structure is favored over one in which the benzaldehyde would act as an oxygen-bound bridging ligand between the metal centers. The existence of these interactions might also be at the origin of the difference observed between benzaldehyde and aliphatic aldehydes that do form isolable adducts with **1**.

Interaction of 1 with Nitriles. Colorless crystals of $1 \cdot \mu_2$-MeCN (**3**) were obtained by slow evaporation of the solvent from an acetonitrile solution. These crystals were found unstable under normal conditions and decomposed by loss of MeCN. As shown by infrared spectroscopy carried out on a freshly prepared sample, the coordination of the acetonitrile molecule is weak and does not result in any noticeable spectroscopic changes (ν_{CN} = 2255 cm^{-1} in **3** vs ν_{CN} = 2254 cm^{-1} in free MeCN). Suitable crystals for single-crystal X-ray diffraction analysis could be transferred from a solution onto the diffractometer (Table 1). In the structure of **3**, the acetonitrile molecule occupies a bridging position between the two mercury centers (Hg(1)−N(11)−Hg(2) 83.1°) (Figure 5). The Hg(1)−N(11) (2.82(1) Å) and Hg-(2)−N(11) (2.93(1) Å) are shorter than the sum of the van der Waals radii for nitrogen (1.60 Å)[17] and mercury (1.73−2.00 Å),[18] which indicates the presence of an interaction similar to that described for adducts involving acetonitrile and mercuracarborands[22] or trimeric

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Table 4. Intermolecular Hg⋯Cl and Hg⋯F Distances (Å) in the Supramolecular Structure of 3

Hg(1)−Cl(1)^a = 3.577	Hg(2)−Cl(1)^a = 3.170
Hg(1)−Cl(2)^b = 3.246	Hg(2)−Cl(2)^c = 3.757
	Hg(2)−F(6)^d = 3.362

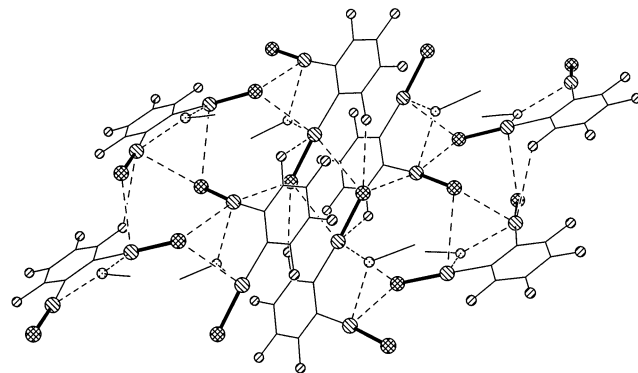^{a} −x+1.5, y−0.5, −z+0.5. ^{b} x, y+1, z. ^{c} −x+1, −y+2, −z. ^{d} x, y−1, z.

Figure 6. Top view of a layer formed in the structure of **3**.

ortho-tetrafluorophenylene mercury.[23] In **3**, the NHgC-CHg five-membered ring adopts a folded envelope conformation (dihedral angle between the planes defined by Hg(1)−N(11)−Hg(2) and Hg(1)−C(1)−C(2)−Hg(2) = 18.6°). The departure of the C−Hg−Cl bond angles from an ideal linearity reflects the presence of secondary Hg⋯Cl and Hg⋯F interactions which link the monomers into layers (Table 4, Figure 6).

Interaction of 1 with Oxiranes. Compound **1** dissolves in small amounts of propylene oxide (PO). Due to the low boiling point of PO, the resulting compound (**3**) can be isolated by slow evaporation of excess PO at room temperature. Compound **3** is a crystalline derivative that contains an equimolar amount of **1** and PO. While it is stable for months at −25 °C, storage at room temperature results in the progressive loss of PO. The ^{13}C CP/MAS NMR spectrum of freshly prepared **4** confirmed the presence of complexed propylene oxide, as evidenced by the observation of three broad resonances at 17, 50, and 52 ppm. The results of a single-crystal X-ray analysis revealed that **4** is in fact a racemic mixture that contains both $1 \cdot \mu_2$-(R)-PO and $1 \cdot \mu_2$-(S)-PO (Table 1). In these adducts, the oxygen atom of the propylene oxide is chelated by bifunctional **1** (Figure 7). We note that the double coordination of epoxides by diprotic molecules has been recently suggested to explain the unusual activity of bifunctional Brønsted acid catalysts.[24,25] While theoretical calculations have helped confirm this hypothesis,[26] the isolation of a bimolecular complex in which the oxygen of an oxirane interacts simultaneously with two Lewis or Brønsted acids had never been achieved. In **4**, the oxygen atom forms two long coordination bonds with the mercury centers at Hg(1) and Hg(2). These bonds are approximately per-

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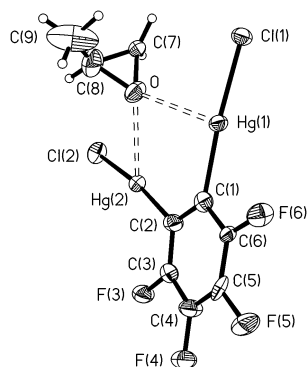
Figure 7. Structure of **4** in the crystal. ORTEP drawing (50%). Selected bond lengths [Å] and angles [deg]: Hg(1)–C(1) 2.071(16), Hg(1)–Cl(1) 2.313(4), Hg(2)–C(2) 2.055(17), Hg(2)–Cl(2) 2.307(4), O–C(8) 1.44(2), O–C(7) 1.50(2), C(7)–C(8) 1.39(3); C(1)–Hg(1)–Cl(1) 174.1(4), C(2)–Hg(2)–Cl(2) 172.3(4), C(8)–O–C(7) 56.4(13), C(8)–C(7)–O 59.6(13), C(7)–C(8)–O 64.0(14).

Table 5. Intermolecular Hg⋯Cl and Hg⋯F Distances (Å) in the Supramolecular Structure of 4

Hg(1)–Cl(1)^a = 3.423	Hg(2)–Cl(1)^a = 3.235
Hg(1)–Cl(1)^b = 3.475	Hg(2)–Cl(2)^d = 3.403
Hg(1)–Cl(2)^c = 3.318	Hg(2)–F(6)^e = 3.352

^{a} $-x+0.5$, $-y+1.5$, $-z$. ^{b} $-x+0.5$, $-y+2.5$, $-z$. ^{c} x, $y+1$, z. ^{d} $-x$, $-y+1$, $-z$. ^{e} x, $y-1$, z.

pendicular to the respective C–Hg–Cl sequences. The Hg–O bond distances (Hg(1)–O = 2.71(2) and Hg(2)–O = 2.77(2) Å) are shorter than the sum of the van der Waals radii of oxygen (1.54 Å)[17] and mercury (1.73–2.00 Å)[18] and are comparable to those measured in **1**·(μ_2-THF) (av 2.80 Å)[16] and slightly longer than those measured in **1**·(μ_2-acetone) (av 2.73 Å),[12] **1**·(μ_2-DMF) (av 2.70 Å),[12] and **1**·(μ_2-DMSO)$_2$ (av 2.70 Å).[14] The oxygen center has a distorted tetrahedral coordination geometry with an acute Hg(1)–O–Hg(2) angle of 84.5°. While it is tempting to suggest that the propylene oxide is coordinated to **1** via two Hg–O dative bonds, we note that the Hg(1)–O–Hg(2) angle is small, 84.5°, and that the three-membered oxirane ring forms a dihedral angle of 112.6° with the average plane defined by the phenylene ring and the two mercury atoms. The standard deviations of the oxirane C–O distances are large and do not demonstrate conclusively a lengthening of the bonds. It can, however, be noted that the C(7)–O–C(8) (56.4°) angle appears smaller than that observed in free oxiranes (~60°).[27] We note that the structural characterization of compounds that contain coordinated oxiranes remains extremely scarce.[28] In all cases, the oxirane is a terminal ligand unlike in **4**, where it bridges two metal centers. As observed in the structure of **1**, **2**, and **3**, the supramolecular structure of **4** is that of a layered compound in which the molecules interact via

(27) See for example: (a) O'Hagan, D.; Zaidi, N. A.; Lamont, R. B. *Tetrahedron: Asymmetry* **1993**, *4*, 1703–8. (b) Langer, V.; Becker, H.-D. *Z. Kristallogr.* **1993**, *207* (1), 153–155. (c) Coxon, J. M.; Simpson, G. W.; Steel, P. J.; Trenerry, V. C. *Tetrahedron Lett.* **1983**, *24*, 1427–1428. (d) Williams, D. J.; Crotti, P.; Macchia, B.; Macchia, F. *Tetrahedron* **1975**, *31*, 993–996.
(28) (a) Dias, H. V. R.; Wang, Z. *Inorg. Chem.* **2000**, *39*, 3724–3727. (b) Darensbourg, D. J.; Holtcamp, M. W.; Khandelwal, B.; Klausmeyer, K. K.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 538–539. (c) Harder, S.; Boersma, J.; Brandsma, L.; Kanters, J. A.; Duisenberg, A. J. M.; Van Lenthe, J. H. *Organometallics* **1990**, *9*, 511–516. (d) Groves, J. T.; Han, Y.; Van Engen, D. *J. Chem. Soc., Chem. Commun.* **1990**, 436–437.
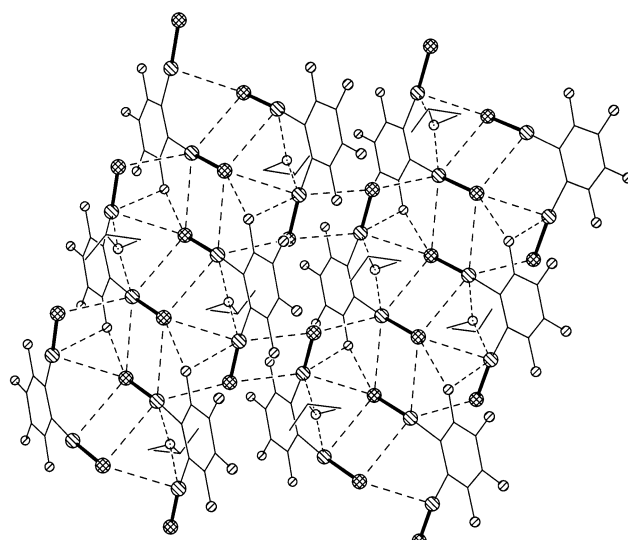

Figure 8. Top view of a layer formed in the structure of **4**.

intermolecular Hg⋯Cl and Hg⋯F bridges (Table 5, Figure 8). In an effort to isolate the sulfur analogue of compound **4**, neat propylene sulfide was added to solid **1**. Interestingly, however, attempts to isolate the adduct failed due to rapid formation of polypropylene sulfide as shown by ^{1}H and ^{13}C NMR.[29]

Conclusion

The results reported herein complete a series of earlier accounts on the formation of adducts involving **1** and a variety of donors including THF, acetone, DMF, DMSO, and dimethylmethylphosphonate (DMMP).[13–16] While both 1:1 (**1**·(μ_2-THF),[16] **1**·(μ_2-acetone),[13] and **1**·(μ_2-DMF))[13] and 1:2 complexes (**1**·(μ_2-DMSO)$_2$[14] and **1**·(μ_2-DMMP)$_2$)[15] have been previously isolated, structural investigation showed a marked preference for the double coordination of the donor molecule to the two mercury center of **1**. Complexes **3** (**1**·(μ_2-MeCN)) and **4** (**1**·(μ_2-PO)) fall in this category as, in both cases, the donor molecule is chelated by bifunctional **1**. While the formation of long dative interactions certainly occurs between the electron rich terminus of the organic substrates and the metal centers, we suggest that dipole–dipole interactions also contribute to the stability of the chelate complexes. Interestingly and by contrast to other substrates so far tested, aldehydes do not interact strongly with the mercury centers of **1**. In particular, no adduct is formed when **1** is mixed with aliphatic aldehydes, and only a terminal complex is isolated in the case of benzaldehyde.

Multiply coordinated nitrile complexes have been previously characterized,[22,23] and the isolation of compound **3** complements those original reports. Nevertheless, we document the first example of a complex in which propylene oxide is chelated by a bidentate Lewis acids. In light of the s-character of the lone-pairs and associated low donicity of the oxygen atom in oxiranes, the isolation of **4** is noteworthy and might provide insights into new Lewis acid catalysts for reactions involving these strained heterocycles.

(29) Nicol, E. Bonnans-Plaisance, C.; Levesque, G. *Macromolecules* **1999**, *32*, 4485–4487.

Experimental Section

General Considerations. The solid-state $^{13}C\{^1H\}$ CP/MAS NMR spectra were recorded on a Bruker MSL 300 spectrometer operating at a field strength of 7.05 T. Cross-polarization and high-power proton decoupling were applied with a 90 pulse time of 5 μs, a contact time of 5 ms, and a recycle delay of 8 s. ^{13}C NMR shifts are referenced to an external sample of adamantane, with the signal at low frequency being set to 29.472 ppm relative to TMS. Approximately 50 mg of sample was packed into a 7 mm ZrO_2 Bruker rotor with Kel-F inserts and cap. The rotor spinning speed was 7 kHz. All NMR measurements were acquired at ambient temperature. Atlantic Microlab (Norcross, GA) performed the elemental analyses. The infrared spectra were recorded as KBr pellets on a Mattson Genesis Series FTIR. All melting points were measured on samples in sealed capillaries and are uncorrected. All solvents were distilled before use and stored over molecular sieves. Compound **1** was prepared by following the published procedure.[12] Acetaldehyde, benzaldehyde, and propylene oxide were purchased from Aldrich and used as provided.

Single-Crystal X-ray Analysis. X-ray data for **1**, **2**, **3**, and **4** were collected on a Bruker SMART-CCD diffractometer using graphite-monochromated Mo Kα radiation (=0.710 73 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 (1·Benzaldehyde). Inside a glovebox, **1** (50 mg, 0.08 mmol) was mixed with benzaldehyde (0.1 g, 0.94 mmol) and acetaldehyde (2 mL) in a vial. The aperture of the vial was left slightly open, and the solvent was allowed to evaporate slowly. The residue was washed with benzene, affording a quantitative yield of **2**. ^{13}C CP/MAS NMR: δ 186.7 ppm (CO). Anal. Calcd for $C_{13}H_6Cl_2F_4Hg_2O$: C, 21.50; H, 0.83. Found: C, 21.63; H, 0.73. IR: 1685, 1653, 1558,1540, 1507, 1484, 1457, 1311, 1290, 1208, 1093, 1008, 822, 772, 745, 686, 668 cm^{-1}.

Synthesis of 3 (1·μ_2-Acetonitrile). Compound **1** (62 mg, 0.1 mmol) was dissolved in acetonitrile (2 mL). The solvent was allowed to evaporate in a well-aerated fume hood at room temperature, giving a quantitative yield of crystalline **3** (66 mg). In the absence of solvent, **3** loses acetonitrile, which precluded satisfactory elemental analysis. Solid-state CP/MAS ^1H and ^{13}C NMR were run on freshly prepared samples. ^{13}C CP/MAS NMR: ^1H, δ 1.99 ppm (CH_3); ^{13}C, δ 1.4 ppm(CH_3), the signal from CN was not detected. IR: 3514, 2937, 2291, 2255, 1617, 1482, 1419, 1314, 1290, 1094, 1038, 1009, 922, 824, 768 cm^{-1}.

Synthesis of 4 (1·μ_2-Propylene Oxide). Compound **1** (310 mg, 0.5 mmol) was dissolved in propylene oxide (3 mL) in an open vial. The excess propylene oxide was allowed to evaporate at 25 °C in a ventilated hood. After 12 h, compound **4** was obtained as a dry crystalline residue (367 mg, 100% yield). At room temperature, crystals of **4** slowly become brittle. Elemental analysis of a sample stored at room temperature for 3 days reveals a 68% depletion in propylene oxide. Anal. Calcd for $C_9H_6Cl_2F_4Hg_2O$: C, 15.93; H, 0.96. Found: C, 13.35; H, 0.31. ^{13}C CP/MAS NMR: δ 17 (CH_3), 50 (CH), 52 (CH_2).

Reaction of 1 with Propylene Sulfide. Propylene sulfide (120 mg, 1.6 mmol) was added to a vial containing solid **1** (10 mg, 16 μmol). Compound **1** spontaneously dissolved upon stirring, and an exothermic reaction rapidly took place. After a few minutes, the solution became highly viscous. The reaction was quenched after 30 min by removing the unreacted propylene sulfide under vacuum. The residue (84 mg, 60% yield) was analyzed by NMR in CDCl$_3$. The proton spectrum was found identical to that reported for polypropylene sulfide in ref 29.

Supporting Information Available: Spectral data: Tables of structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for complexes **1**–**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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