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Binding of Dienophiles by Macrocyclic Multidentate Lewis Acids. Synthesis and X-ray Crystal Structure Determination of Unusual Complexes of Cyclic Trimeric Perfluoro-*o*-phenylenemercury with *p*-Benzoquinone and Maleic Anhydride

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Unusual host−guest complexes with dienophiles have been synthesized by the interaction of cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ (**3**) with *p*-benzoquinone (BQ) and maleic anhydride (MA). In the case of BQ, the resulting complex $\{[(o\text{-}C_6F_4Hg)_3]_2(BQ)\}$ (**4**) contains one molecule of a dienophile per two molecules of the macrocycle. According to X-ray diffraction data, it has a sandwich structure wherein a dienophilic guest is located between the mutually parallel planes of two macrocyclic hosts and is bonded to each of these through a symmetrical coordination of its carbonyl oxygen atoms by all Hg centers of the neighboring macrocycle. The reaction of **3** with MA results in the formation of a sandwich complex, $\{[(o\text{-}C_6F_4Hg)_3]_2(MA)_2\}$ (**5**), containing two dienophilic species per two macrocycles. In this unique sandwich, both molecules of the dienophile are arranged between the mutually parallel planes of the macrocycles and are coordinated to their Hg centers by the oxygen atoms of the carbonyl groups. Each molecule of MA in complex **5** is bound by three Hg−O bonds with one of the macrocyclic hosts and by only one Hg−O bond with the other molecule of **3**.

Introduction

Diels−Alder reactions between 1,3-dienes and olefins containing a conjugated carbonyl or thiocarbonyl group are known to be accelerated by Lewis acids.[1−5] It is assumed that a key step of these catalytic reactions is a complexation of the C═O or C═S functionality with the Lewis acidic center of the catalyst, which leads to activation of the C═C bond of a dienophile for its subsequent interaction with a 1,3-diene. The use of recently emerged macrocyclic multidentate Lewis acids (for reviews, see, e.g., refs 6−10) in the catalysis of Diels−Alder reactions could result in a further increase in the rate of the process owing to cooperative effect of several Lewis acidic centers.

The first examples of the successful application of macrocyclic multidentate Lewis acids as catalysts for Diels−Alder reactions were described by Hawthorne et al., who reported that *o*-carboranylmercury macrocycles $(9,12\text{-}Me_2\text{-}o\text{-}C_2B_{10}H_8Hg)_4$ (**1**) and $(9,12\text{-}Me_2\text{-}o\text{-}C_2B_{10}H_8\text{-}Hg)_3$ (**2**) are able to accelerate strongly the reaction of an unsaturated thionoester *trans*-MeCH═CHC(S)OMe with cyclopentadiene in CH_2Cl_2 at 0 °C.[11] In the case of **1**, its capacity to coordinate the thionoester was proved by ^{199}Hg NMR studies. In the case of **2**, no complexation with the dienophile was observed in a CH_2Cl_2 solution by the NMR method because of, apparently, very low concentration of the postulated complex. The replacement of **1** or **2** by their monomer analogue $(9,12\text{-}Me_2\text{-}o\text{-}C_2B_{10}H_9)_2Hg$ led to a considerable decrease in the rate of the reaction between the thionoester and cyclopentadiene, thus showing the essential contribution of the cooperative effect of several Hg centers in **1** and **2** to the catalytic acceleration of the process. In contrast to the thionoester, methyl crotonate did not form Diels−

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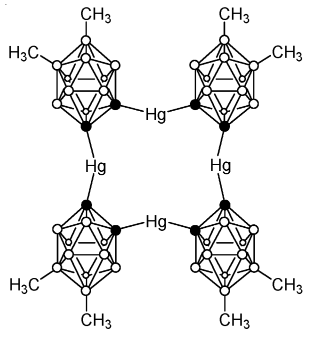
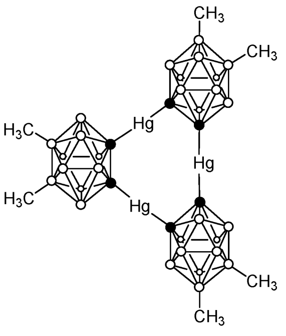
Alder adducts with cyclopentadiene in the presence of **1** or **2**, which was explained by its inability to coordinate with the mercury atoms, as evidenced by ^{199}Hg NMR spectra.



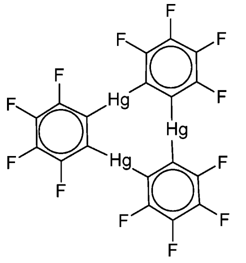
(**1**)



(**2**)

○ BH ● C

In our continuing research into coordination and catalytic chemistry of macrocyclic multidentate Lewis acids,[6,8] cyclic trimeric perfluoro-*o*-phenylenemercury (*o*-$C_6F_4Hg)_3$ (**3**),[12,13] containing three Hg atoms in a planar nine-membered cycle, is successfully used as a multidentate Lewis acidic host. A study of binding properties of **3** demonstrated that it readily reacts with various anions and neutral Lewis bases to give complexes wherein the Lewis basic species is cooperatively coordinated by all Lewis acidic centers of the cycle.[6,8,9,14,15] This intriguing feature of macrocycle **3** makes it potentially useful for the activation of dienophiles and catalysis of Diels−Alder reactions.



(**3**)

In the present article, the remarkable ability of **3** to coordinate *p*-benzoquinone (BQ) and maleic anhydride (MA) is reported. As a result of the reactions, quite stable and isolable complexes {[(*o*-$C_6F_4Hg)_3]_2$(BQ)} (**4**) and {[(*o*-$C_6F_4Hg)_3]_2(MA)_2$} (**5**), respectively, are produced. According to the X-ray diffraction data, both carbonyl oxygen atoms of the dienophile in **4** and **5** are involved in the bonding to the Hg centers. The synthesized compounds are the first structurally characterized complexes of a macrocyclic multidentate Lewis acid with dienophiles.

Results and Discussion

Complex **4** was prepared by the reaction of BQ with a 2-fold excess of **3** in CH_2Cl_2 at room temperature. The complex precipitates from the solution immediately after the mixing of **3** with BQ. The use of an equimolar ratio of the reagents in this reaction results in the formation of the same compound **4**. The isolated **4** is a bright yellow crystalline solid readily soluble in THF and acetone and practically insoluble in CH_2Cl_2. According to elemental analysis, the complex can be formulated as {[(*o*-$C_6F_4Hg)_3]_2$(BQ)}, i.e., contains one molecule of a dienophile per two macrocycle molecules. The IR spectrum of **4** (in Nujol mull) shows the ν_{as}(CO) band at 1640 (s) cm^{-1} shifted by 14 cm^{-1} to a low-frequency region relative to the corresponding ν_{as}(CO) band of noncoordinated BQ. The ν_{as}(C=C) band in the IR spectrum of **4** (at 1596 (w) cm^{-1}) is shifted by 4 cm^{-1} to a high-frequency region in comparison to the ν_{as}(C=C) band of free BQ. The ^{199}Hg NMR spectrum of **4** at 20 °C in THF ($[\mathbf{4}]_0 = 8 \times 10^{-2}$ M) differs only insignificantly from the corresponding spectrum of **3**.

Complex **5** was obtained by the interaction of MA with an equimolar amount of **3** at 20 °C in ether. The isolated compound is a colorless crystalline solid readily soluble in ether, THF, and acetone and moderately soluble in CH_2Cl_2. The complex has the composition {[(*o*-C_6F_4-$Hg)_3]_2(MA)_2$}, i.e., contains two molecules of a dienophile per two molecules of the macrocycle. The IR spectrum of **5** in Nujol mull exhibits the ν_{as}(CO) bands at 1758 (s) and 1770 (s) cm^{-1} as well as the ν_s(CO) band at 1847 (m) cm^{-1}, which are shifted by 24, 12, and 9 cm^{-1}, respectively, to lower wavenumbers as compared to the corresponding bands for neat MA (ν_{as}(CO) = 1782 (vs) cm^{-1}, ν_s(CO) = 1856 (m) cm^{-1}). The ν(C=C) band was not detected in the IR spectra due, apparently, to its overlapping with the bands of the C_6F_4 groups. The IR spectrum of **5** in CH_2Cl_2, in addition to the ν(CO) bands of free MA (at 1782 (s) and 1851 (m) cm^{-1}), displays the weak ν(CO) bands of undissociated **5** at 1757, 1768, and 1844 cm^{-1}. The room-temperature ^{199}Hg NMR spectrum of **5** ($[\mathbf{5}]_0 = 3.33 \times 10^{-3}$ M) in CH_2Cl_2 shows only negligible differences from the spectrum of **3**. Complex **5** was also synthesized by the reaction of **3** with a 5-fold excess of MA in CH_2Cl_2. The crystals of thus prepared **5** were used for its X-ray diffraction study.

Figure 1 shows the structure of **4**. Selected bond lengths and angles are listed in Table 1. The complex occupies in the crystal a special position on an inversion center and has an unusual sandwich structure wherein a dienophilic guest is located between the mutually parallel planes of two macrocyclic hosts and is bonded to each of these through a symmetrical coordination of its carbonyl oxygen atoms by all Hg centers of the neighboring molecule of **3**. The Hg−O distances in **4** are equal to 2.922(9), 2.972(9), and 2.944(9) Å (av 2.95 Å). All these distances are considerably shorter than the sum of the van der Waals radii of mercury (1.73−2.00,[16,17] 2.1 Å[18]) and oxygen (1.5,[18] 1.54 Å[19]) atoms. The plane of the coordinated molecule of BQ in **4** is practically perpendicular to the mean planes of the central nine-membered rings of the macrocycles (the dihedral angle is 89.1°). However, the C(19)−O(1) and C(19A)−O(1A) bond vectors deviate from the normal to these

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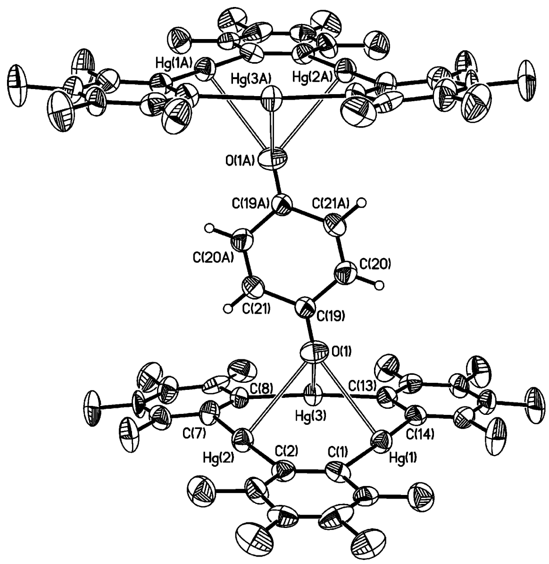

Figure 1. ORTEP representation of the molecular structure of complex **4** with thermal ellipsoids drawn at the 40% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in Complex 4

Bond Lengths			
Hg(1)−O(1)	2.922(9)	Hg(3)−C(8)	2.041(13)
Hg(2)−O(1)	2.972(9)	Hg(3)−C(13)	2.054(13)
Hg(3)−O(1)	2.944(9)	C(19)−O(1)	1.226(15)
Hg(1)−C(1)	2.083(13)	C(19)−C(20)	1.488(18)
Hg(1)−C(14)	2.069(13)	C(19)−C(21)	1.470(19)
Hg(2)−C(2)	2.052(13)	C(20)−C(21A)[a]	1.295(18)
Hg(2)−C(7)	2.094(12)		
Bond Angles			
C(1)−Hg(1)−C(14)	174.3(5)	O(1)−C(19)−C(21)	120.5(12)
C(2)−Hg(2)−C(7)	174.5(5)	C(20)−C(19)−C(21)	118.1(12)
C(8)−Hg(3)−C(13)	174.7(5)	C(19)−C(20)−C(21A)[a]	120.2(13)
O(1)−C(19)−C(20)	121.2(12)	C(19)−C(21)−C(20A)[a]	121.7(12)

[a] Symmetry transformation −x+2, −y, −z was used to generate equivalent atoms.

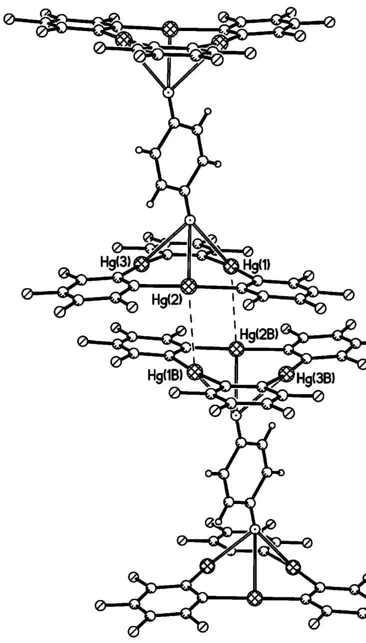

Figure 2. View of a fragment of the crystal structure of complex **4**, showing the shortest intermolecular Hg⋯Hg contacts between neighboring molecules of **4**. The shortest intermolecular Hg⋯C contacts are omitted for clarity

mean planes by 13.8°. As a result, the projections of the centroids of the macrocycles onto the plane parallel to these cycles are shifted relative to each other by 1.13 Å. The mutual orientation of the macrocycles in **4** is close to a staggered conformation.

In the crystal, complex **4** forms extended stacks (Figure 2) due to shortened (as compared to the sum of the van der Vaals radii) intermolecular Hg⋯Hg and Hg⋯C contacts between the adjacent molecules of **4** (Hg(1)⋯Hg(2B)$_{1-x,-y,1-z}$ 3.447(1) Å, Hg⋯C 3.44−3.56 Å; $r_{\mathrm{vdw}}(\mathrm{C_{arom}}) = 1.7$ Å[18]). The stacks are disposed along the [101] crystallographic direction and are linked with one another through shortened intermolecular Hg⋯F contacts (Hg(3)⋯F(9)$_{1-x,-y,-z}$ 3.22(1) Å, Hg(2)⋯F(16)$_{-x,1-y,-z}$ 3.36(1) Å; $r_{\mathrm{vdw}}(\mathrm{F}) = 1.4$ Å[18]), thereby leading to the highly networked crystal structure of **4**. The distance between the mean planes of the central nine-membered rings of the neighboring macrocycles in the stack is 3.36 Å, and the projections of their centroids onto the plane parallel to these rings are shifted with respect to each other by 2.40 Å. The mutual orientation of these juxtaposed rings is close to a staggered conformation as well. The formation of similar extended stacks with shortened Hg⋯Hg (3.39−3.91 Å) and Hg⋯C (3.38−3.78 Å) contacts was earlier observed in crystals of the sandwich complexes of **3** with *closo*-$[\mathrm{B_{10}H_{10}}]^{2-}$, *closo*-$[\mathrm{B_{12}H_{12}}]^{2-}$, *closo*-$[\mathrm{B_{12}H_{11}SCN}]^{2-}$, $[\mathrm{Fe(CN)_6}]^{3-}$, and $\mathrm{Fe[(CN)_5NO]}^{2-}$ anions[20−22] as well as with ferrocene[14,15] and nickelocene.[14] However, shortened intermolecular Hg⋯F contacts between the adjacent stacks in the crystal packing of these complexes are absent. The pyramidal 1:1 complexes of **3** with *n*-butyronitrile[23] and acetone[24] form cofacial dimers in the crystals. In these dimers, the shortest Hg⋯Hg intermolecular contacts are 3.372 and 3.512 Å, respectively, while the shortest intermolecular Hg⋯C distances are 3.58, 3.59 and 3.40, 3.48 Å.

The structure of complex **5** is presented in Figure 3. Selected bond lengths and angles are given in Table 2. Like **4**, complex **5** occupies in the crystal a special position on an inversion center and also has a sandwich structure. A unique feature of **5** is that here two molecules of the dienophile are disposed between the mutually parallel planes of the macrocycles and are coordinated to their Hg centers by the oxygen atoms of the carbonyl groups. Each molecule of MA in the complex is bound by three Hg−O bonds with one of the macrocyclic units and by only one Hg−O bond with the other molecule of **3**. The Hg−O distances in **5** vary within the range 2.919(6)−3.122(6) Å (av 2.99 Å) and again are significantly shorter than the corresponding

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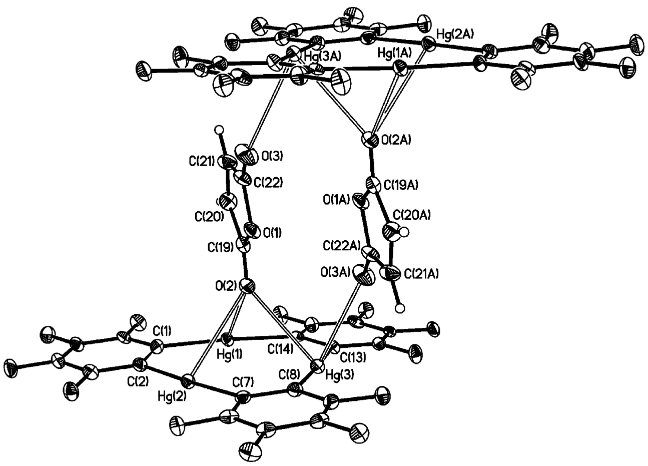

Figure 3. ORTEP representation of the molecular structure of complex **5** with thermal ellipsoids drawn at the 40% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in Complex 5

Bond Lengths

Hg(1)−O(2)	2.950(6)	Hg(3)−C(13)	2.068(7)
Hg(2)−O(2)	3.122(6)	C(19)−O(2)	1.190(9)
Hg(3)−O(2)	2.919(6)	C(22)−O(3)	1.189(10)
Hg(3)−O(3A)[a]	2.981(6)	C(19)−O(1)	1.388(9)
Hg(1)−C(1)	2.064(8)	C(22)−O(1)	1.407(10)
Hg(1)−C(14)	2.063(7)	C(19)−C(20)	1.480(11)
Hg(2)−C(2)	2.075(8)	C(20)−C(21)	1.332(12)
Hg(2)−C(7)	2.066(8)	C(21)−C(22)	1.473(12)
Hg(3)−C(8)	2.066(8)		

Bond Angles

C(1)−Hg(1)−C(14)	175.0(3)	O(1)−C(19)−C(20)	108.7(7)
C(2)−Hg(2)−C(7)	176.1(3)	C(19)−C(20)−C(21)	108.4(8)
C(8)−Hg(3)−C(13)	175.3(3)	C(20)−C(21)−C(22)	107.3(8)
C(19)−O(1)−C(22)	106.3(6)	O(1)−C(22)−O(3)	119.9(8)
O(1)−C(19)−O(2)	121.3(7)	O(3)−C(22)−C(21)	130.9(9)
O(2)−C(19)−C(20)	129.9(7)	O(1)−C(22)−C(21)	109.2(7)

[a] Symmetry transformation $-x+2$, $-y+1$, $-z+1$ was used to generate equivalent atoms.

van der Waals distance. The planes of the five-membered cycles of the MA molecules are parallel to each other and are almost perpendicular to the mean planes of the central nine-membered rings of the macrocycles (the dihedral angle is 83.9°). The C(19)−O(2) and C(19A)−O(2A) carbonyl groups are also located nearly perpendicularly toward the mean planes of the nine-membered mercuracarbon rings (deviation from the perpendicular is 4.8°). The C(22)−O(3) and C(22A)−O(3A) bond vectors deviate from the normal to the plane of the nearest Hg_3C_6 cycle by 47.2°. The projections of the centroids of the macrocycles onto the plane parallel to these cycles in **5** are shifted relative to each other by 4.42 Å. The mutual orientation of the macrocycles corresponds again to a staggered conformation.

Because of the large relative shift of the projections of the centroids of the macrocycles in the molecule of **5** (4.42 Å, see above), the crystal packing of **5** differs significantly from that of **4** and can be described as consisting of extended ladder-like chains (Figure 4) with shortened intermolecular Hg···F and Hg···C contacts between the neighboring molecules of **5** (Hg(2)···F(16B)$_{1-x,-y,-z}$ 3.32(1) Å, Hg···C 3.42−3.63 Å). The chains are arranged along the [111] crystallographic direction and are linked with each other also through shortened intermolecular Hg···F contacts (3.22−3.48 Å).

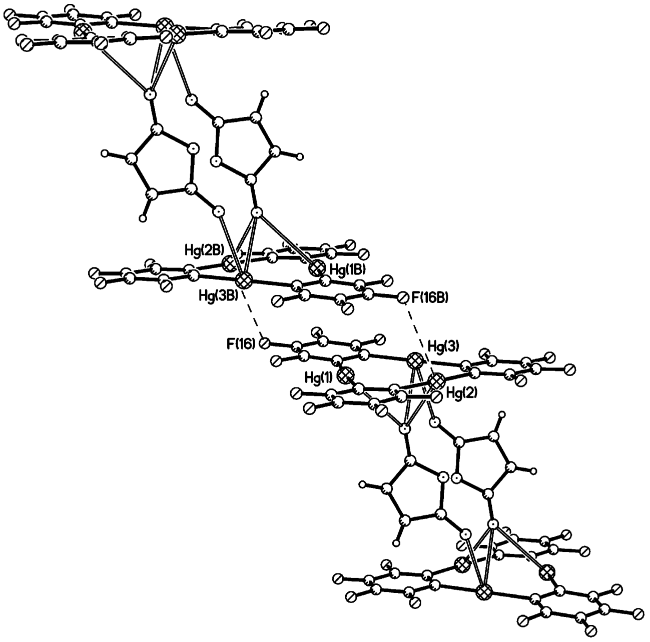

Figure 4. View of a fragment of the crystal structure of complex **5**, showing the shortest intermolecular Hg···F contacts between neighboring molecules of **5**. The shortest intermolecular Hg···C contacts are omitted for clarity.

The projections of the centroids of two adjacent macrocycles in the chain onto the plane parallel to these cycles are shifted with respect to one another by 5.00 Å, and the distance between the mean planes of the central Hg_3C_6 rings of these macrocycles is 3.35 Å. In contrast to **4**, the crystal packing of **5** does not contain any shortened intermolecular Hg···Hg contacts (the shortest intermolecular Hg···Hg distance in **5** is 4.326(1) Å). As in **4**, the neighboring macrocycles in the crystal structure of **5** adopt a staggered mutual orientation.

The complexation of **3** with BQ and MA does not affect essentially the geometry of the dienophiles and the macrocycle. The Hg−C bond lengths in **4** and **5** (2.04−2.09 Å) are unexceptional. The Hg−C−Hg bond angles span the range from 174.3(5)° to 176.1(3)°, thus suggesting the insignificant perturbation of the sp hybridization of the Hg atoms, if any. The C=O and C=C bond lengths in the BQ and MA ligands are close to the corresponding distances in the noncoordinated BQ and MA.[25,26] The molecules of the dienophiles retain their planarity in the complexes.

As our preliminary experiments have shown, macrocycle **3** is able to noticeably accelerate the Diels−Alder reaction between BQ and cyclopentadiene in THF at 20 °C to form the corresponding 1:1 *endo*-adduct. Thus, on carrying out this reaction in the presence of **3** at the **3**:CpH:BQ molar ratio of 2.4:2.5:1 ([**3**]$_0$ = 0.12 M), the time of the half-transformation ($\tau_{1/2}$) of BQ amounts to 12.5 min, while in the absence of **3** the value of $\tau_{1/2}$ is 20 min under the same conditions. A similar accelerating effect is observed on introducing complex **4** in the reaction with cyclopentadiene. The results of this study will be described in greater detail in a subsequent publication.

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Conclusion

The ability of **3** to bind monocarbonyl Lewis bases such as aldehydes,[27] ketones,[24,27] esters,[28] and amides of carboxylic acids[23,28,29] is now well established. The reactions lead to complexes containing one, two, or three Lewis basic species per one molecule of **3**. The bonding of the carbonyl compound to the Hg atoms of the macrocycle in these adducts is accomplished through the carbonyl oxygen atom. In all the complexes, there is at least one fragment wherein a basic oxygen atom of the Lewis base is simultaneously coordinated to all Lewis acidic sites of **3**, which results in realization of unusual pyramidal or bipyramidal structures.

A different situation is observed when macrocycle **3** reacts with BQ and MA, which contain two carbonyl groups. Here, double-decker sandwich complexes **4** and **5** are obtained. In these sandwiches, the dienophile molecule behaves as a bidentate Lewis base and is bonded to the Hg centers of the macrocycles by both its C═O groups. Particularly interesting is complex **5**, wherein two molecules of a Lewis base are disposed between the planes of the macrocycles. This type of double-decker sandwiches has not been known earlier. In complex **4**, each carbonyl group of BQ is cooperatively coordinated by all Hg atoms of the adjacent molecule of **3**. In complex **5**, one carbonyl group of each MA guest is bound by three Hg centers of the neighboring macrocyclic host, whereas another C═O group interacts with a single Hg atom of the other macrocycle molecule. The synthesized **5** is the first example of a structurally characterized complex wherein a molecule of MA is coordinated through the carbonyl oxygen atoms with metal centers. In all presently known complexes of MA, its C═C bond is involved in the bonding to a metal.

Experimental Section

The starting macrocycle **3** was prepared according to the published procedure.[12] Commercial BQ was additionally purified by sublimation at 95 °C in vacuo (14 mmHg) with subsequent recrystallization from CH_2Cl_2. Commercial MA was sublimated at 87 °C in vacuo (14 mmHg). Solvents were purified by conventional methods and were distilled prior to use. The IR spectra were recorded on a Nicolet Magna 750 Series II Fourier spectrometer. The ^{199}Hg NMR spectra were registrated on a Bruker AMX-400 spectrometer using a solution of Ph_2Hg in pyridine as an external standard.

Synthesis of {[(*o*-C_6F_4Hg)$_3$]$_2$(BQ)} (4). To a solution of **3** (0.209 g, 0.2 mmol) in CH_2Cl_2 (30 mL) was added at room temperature a solution of BQ (0.011 g, 0.1 mmol) in CH_2Cl_2 (2 mL). Immediately, a light yellow powder of complex **4** began to precipitate. After 3−5 min, the complex was filtered, washed with a small amount of CH_2Cl_2, and dried at 20 °C in vacuo. Yield: 0.17 g (77%). Anal. Calcd for $C_{42}H_4F_{24}O_2Hg_6$: C, 22.93; H, 0.18; F, 20.73. Found: C, 23.12; H, 0.34; F, 20.61. IR (Nujol mull, cm^{-1}): 1640 (s), 1596 (w). Single crystals of **4** for the X−ray diffraction study were grown by slow vapor diffusion of diethyl ether into a THF solution of **4**.

Table 3. Crystal Data, Data Collection, and Structure Refinement Parameters for Complexes 4 and 5

	4	**5**
formula	$C_{42}H_4F_{24}O_2Hg_6$	$C_{44}H_4F_{24}O_6Hg_6$
molecular wt	2199.99	2288.01
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.4166(8)	9.4235(5)
b (Å)	10.885(1)	10.1101(5)
c (Å)	11.673(1)	13.3638(7)
α (deg)	87.828(2)	104.821(1)
β (deg)	76.033(2)	108.918(1)
γ (deg)	65.899(2)	92.554(1)
V (Å^3)	1057.5(2)	1153.0(1)
Z	1	1
D_{calcd} (g cm^{-3})	3.455	3.295
T (K)	295(2)	110(2)
θ_{max} (deg)	30.0	30.0
μ(Mo Kα, λ = 0.71073 Å) (cm^{-1})	218.44	200.47
transmn factors, min./max.	0.033/0.123	0.020/0.068
no. of unique reflns (R_{int})	6128 (0.0523)	6684 (0.0421)
no. of obsd reflns ($I > 2\sigma(I)$)	3363	5480
no. of params	334	361
R_1 (on F for obsd reflns)^a	0.0574	0.0406
wR_2 (on F^2 for all reflns)^b	0.1378	0.1007

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Synthesis of {[(*o*-C_6F_4Hg)$_3$]$_2$(MA)$_2$} (5). To a solution of **3** (0.1046 g, 0.1 mmol) in ether (30 mL) was added at 20 °C a solution of MA (0.010 g, 0.1 mmol) in ether (2 mL), and the resulting mixture was allowed to slowly evaporate at room temperature. After 2 days, the fine colorless crystals of complex **5** were washed with a mixture of 10 mL of *n*-pentane and two drops of ether and dried at 20 °C in vacuo for 1 h. Yield: 0.05 g (44%). Anal. Calcd for $C_{44}H_4F_{24}O_6Hg_6$: C, 23.09; H, 0.18; F, 19.93. Found: C, 23.10; H, 0.17; F, 19.98. IR (Nujol mull, cm^{-1}): 1758 (s), 1770 (s), 1847 (m). For obtaining crystals of **5** suitable for the X-ray analysis, a solution of MA (0.049 g, 0.5 mmol) in CH_2Cl_2 (2 mL) was added at room temperature to a solution of **3** (0.1046 g, 0.1 mmol) in CH_2Cl_2 (30 mL), and after slow evaporation of the resulting mixture at 20 °C for 2 days to dryness, the large colorless crystals of **5** were manually separated from the excess of the white fine crystalline MA. The IR spectrum of thus prepared **5** in the ν_{as}(CO) and ν_s(CO) region was totally identical (1758 (s), 1770 (s), 1847 (m) cm^{-1}) to that of **5** synthesized in ether at the equimolar ratio of the reagents (see above). For carrying out the X-ray diffraction study, the crystals of **5** were not dried in vacuo.

X-ray Diffraction Study. Details of the crystal data, data collection, and structure refinement parameters for complexes **4** and **5** are given in Table 3. Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD area detector (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å, ω-scans with a 0.3° step in ω, and 10 s per frame exposure). The semiempirical method SADABS[30] was applied for absorption correction. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with anisotropic temperature parameters for all non-hydrogen atoms. The hydrogen atoms were placed geometrically and included in the structure factor calculation in the riding motion approximation. Data reduction and further calculations were performed using the SAINT[31] and SHELXTL-97[32] program packages.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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