logues[30] where inversion of configuration of the main-group element effects site exchange. Barriers to site exchange in these cases ($\Delta G^{\ddagger}$, 14.3–17.8 kcal mol^{-1}) are comparble to the lowest energy barriers measured for inversion of configuration of phosphane phosphorus nuclei with two organic and one transition-metal complex substituent. Gladysz et al.[31] have shown that barriers to inversion at phosphide phosphorus bound to Ru lie in the range 11–14 kcal. The exchange process to be invoked above would therefore necessarily require an unprecedented low barrier to inversion in order that such a process be the source of the observed spectral patterns and their temperature independence. Although we cannot rule out such a facile exchange process, we think, in view of the barriers noted above, that rapid exchange is unlikely.

Conclusions

Although the (trifluoromethyl)diphosphetene ligands described herein are weak bases because of the presence of electron-withdrawing CF_3 substituents on phosphorus, they are sufficiently basic to displace a weakly bound ligand (N_2) from Ir^I. The coordination complexes so formed are stable only at reduced temperatures and only if the backbone substituents on carbon are not too bulky. The η^1 coordination complexes are intermediate for the formation of metallacycles by means of an oxidative addition of the P–P bond to Ir^I. The resultant Ir^{III} metallacycles appear to be stable only if the backbone carries a substituent with some electron-withdrawing character (e.g., CF_3 or phenyl) perhaps because electron delocalization into the metallacyclic framework is necessary to stabilize the structure.

Acknowledgment. We thank the NSERC (Ottawa) for financial support.

Registry No. **1**, 114297-14-2; **9**, 114198-79-7; **10**, 114198-80-0; **11**, 114220-87-0; **11b**, 114198-81-1; **12**, 114198-75-3; **13**, 114198-76-4; **14**, 114198-77-5; **16**, 114198-78-6; **17**, 114220-86-9; $[(CF_3)P]_4$, 393-02-2; $[(CF_3)P]_5$, 745-23-3; $Me_3SiC{\equiv}CSiMe_3$, 14630-40-1; $PhC{\equiv}CPh$, 501-65-5; $MeC{\equiv}CSiMe_3$, 6224-91-5; $[IrCl(N_2)(PPh_3)_2]$, 15695-36-0.

Supplementary Material Available: Anisotropic thermal parameters (Table X), derived positional and thermal parameters for hydrogen atoms (Table XI), RMS amplitudes of thermal vibration (Table XII), all bond angles (Table XIII), and torsional angles (Table XIV) (4 pages); calculated and observed structure factors (Table XV) (10 pages). Ordering information is given on any current masthead page.

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(29) Kopf, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 134.
(30) Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947.
(31) Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1985**, *24*, 3507.
(32) J. S. Martin, University of Alberta, and K. Worvill, University of East Anglia; personal communication from J.S.M.

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Metallamacrocycles Built from Mercury(II) and Bis((diphenylphosphino)methyl)phenylarsine

Alan L. Balch,* Marilyn M. Olmstead, and Steven P. Rowley

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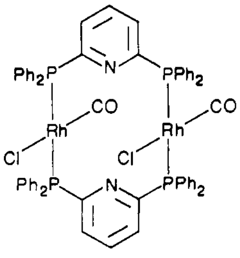
Addition of bis((diphenylphosphino)methyl)phenylarsine (dpma) to $[Hg\{(CH_3)_2SO\}_6][O_3SCF_3]_2$ in methanol followed by the addition of ammonium hexafluorophosphate yields $[Hg_2(\mu\text{-dpma})_2(O_3SCF_3)_2(CH_3OH)_3][PF_6]_2{\cdot}CH_3OH$ (**3**). Colorless parallelepipeds of this crystallize in the in the triclinic space group $P\bar{1}$ (No. 2) with a = 12.273 (4) Å, b = 16.941 (5) Å, c = 20.468 (5) Å, α = 93.77 (2)°, β = 91.70 (2)°, and γ = 105.47 (2)° at 130 K. Least-squares refinement of 600 parameters using 8139 reflections yielded R = 0.069, R_w = 0.074. The structure consists of a $Hg_2(dpma)_2$ metallamacrocycle with nearly linear P–Hg–P coordination. One trifluoromethanesulfonate bridges the two mercury ions. One mercury is loosely coordinated by two methanol molecules, while the other is bound to one methanol and one monodentate trifluoromethanesulfonate. Treatment of **3** with tin(II) chloride yields $[Hg_2(\mu\text{-dpma})_2(\mu\text{-Cl})_2][PF_6]_2$ (**4**). Colorless parallelepipeds of **4** belong to the triclinic space group $P\bar{1}$ (No. 2) with a = 10.351 (3) Å, b = 13.514 (5) Å, c = 14.297 (5) Å, α = 62.95 (2)°, β = 77.78 (2)°, and γ = 70.73 (2)° at 130 K. Least-squares refinement of 207 parameters using 5275 reflections yielded R = 0.037, R_w = 0.042. The structure of the centrosymmetric dication involves a $Hg_2(dpma)_2$ metallamacrocycle with two bridging chloride ligands. Each mercury has grossly distorted tetrahedral geometry. Comparison of the structures of **3** and **4** indicates the $Hg_2(dpma)_2{}^{4+}$ metallacycle must fragment into $Hg_2(dpma)^{4+}$ and dpma units or into two $Hg(dpma)^{2+}$ units during the conversion of **3** into **4**.

Introduction

The metallamacrocycles **1** and **2**, which involve two planar, d^8 metal ions, have been shown to bind a variety of cations, anions, and neutral molecules.[1-11] The combination of traditional Lewis base binding sites (N or As) and the amphoteric d^8 metal ions gives these macrocycles a unique ability to interact with substrates. In order to expand the range of such metallamacrocycles, we have undertaken the preparation of new examples involving different



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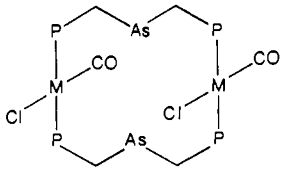

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* Address correspondence to this author.

(1) Balch, A. L. *Pure Appl. Chem.* **1988**, *60*, 555.
(2) Wood, F. E.; Hvoslef, J.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 6986.
(3) Wood, F. E.; Hvoslef, J.; Hope, H.; Balch, A. L. *Inorg. Chem.* **1984**, *23*, 4309.
(4) Balch, A. L.; Hope, H.; Wood, F. E. *J. Am. Chem. Soc.* **1985**, *107*, 6936.
(5) Balch, A. L.; Fossett, L. A.; Olmstead, M. M.; Oram, D. E.; Reedy, P. E., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 5272.
(6) Balch, A. L.; Fossett, L. A.; Guimerans, R. R.; Olmstead, M. M.; Reedy, P. E., Jr. *Inorg. Chem.* **1986**, *25*, 1397.
(7) Balch, A. L.; Fossett, L. A.; Olmstead, M. M.; Reedy, P. E., Jr. *Organometallics* **1986**, *5*, 1929.
(8) Balch, A. L.; Ghedini, M.; Oram, D. E.; Reedy, P. E., Jr. *Inorg. Chem.* **1987**, *26*, 1223.
(9) Balch, A. L.; Oram, D. E.; Reedy, P. E., Jr. *Inorg. Chem.* **1987**, *26*, 1836.
(10) Balch, A. L.; Nagle, J. K.; Olmstead, M. M.; Reedy, P. E., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 4123.
(11) Bailey, D. A.; Balch, A. L.; Fossett, L. A.; Olmstead, M. M.; Reedy, P. E., Jr. *Inorg. Chem.* **1987**, *26*, 2413.

0020-1669/88/1327-2275$01.50/0

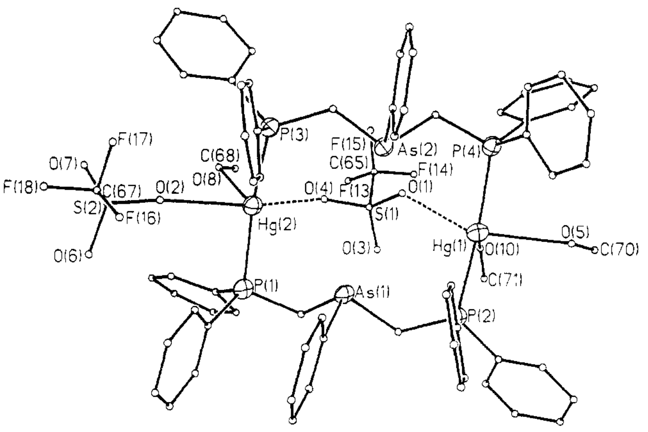

Figure 1. Perspective view of $[Hg_2(\mu\text{-dpma})_2(O_3SCF_3)_2(CH_3OH)]_3]^{2+}$ showing 50% thermal contours for Hg, P, and As atoms and arbitrarily sized circles for all other atoms.

metal ions in place of the Rh(I) and Ir(I) found in **1** and **2**. For this metal ions that prefer low coordination and linear P–M–P units are preferable, since they will leave the center of the macrocycle relatively uncrowded and present vacant coordination sites (at M) that are available for substrate binding.

Here we describe two metallamacrocycles derived from bis((diphenylphosphino)methyl)phenylarsine (dpma) and mercury(II). Typically, mercury(II) complexes prefer two-coordinate linear geometry, so the choice to involve mercury in these metallamacrocycles was obvious. Our studies are related to those on Lewis acidic ligands (particularly those involving mercury) that recently have gained attention.[12]

Results

Treatment of $[Hg\{(CH_3)_2SO\}_6][O_3SCF_3]_2$[13] with dpma in methanol followed by the addition of ammonium hexafluorophosphate yields white crystals of $[Hg_2(\mu\text{-dpma})_2(O_3SCF_3)_2(CH_3OH)_3][PF_6]$ in 76% yield. The product is soluble in methanol, dichloromethane, and acetone and insoluble in ethyl ether and chloroform. The ^{31}P NMR spectrum in dichloromethane shows a singlet at 48.5 ppm with ^{199}Hg (spin $^1/_2$, 16.8% natural abundance) satellites, $^1J(^{31}P,^{199}Hg) = 5294$ Hz. No change was seen upon cooling to −80 °C. Consequently, the asymmetry seen in the solid state (vide infra) is not maintained in solution. Apparently, the loosely bound methanol and trifluoromethanesulfonate ligands are able to move about the mercury ions on the NMR time scale.

In an attempt to bind tin(II) to this metallamacrocycle, it was treated with tin(II) chloride in methanol. A white crystalline product of very limited solubility precipitated from solution. The product, $[Hg_2(\mu\text{-dpma})_2(\mu\text{-Cl})_2][PF_6]_2$, was too insoluble to obtain an NMR spectrum.

Crystal Structure of $[Hg_2(\mu\text{-dpma})_2(O_3SCF_3)_2(CH_3OH)_3][PF_6]_2\cdot CH_3OH$. The asymmetric unit consists of the dication, two hexafluorophosphate ions with entirely regular geometry, and a molecule of methanol, which is not bound to the cation (closest Hg···O contact 8.029 (5) Å). A perspective view of the entire cation is shown in Figure 1. Figure 2 shows two other views of the inner core of the macrocycle, with the top portion showing thermal ellipsoids for all atoms in the core and the lower part emphasizing the orientation of the bridging trifluoromethanesulfonate. Atomic positional parameters are given in Table I. Selected interatomic distances and angles are presented in Table II.

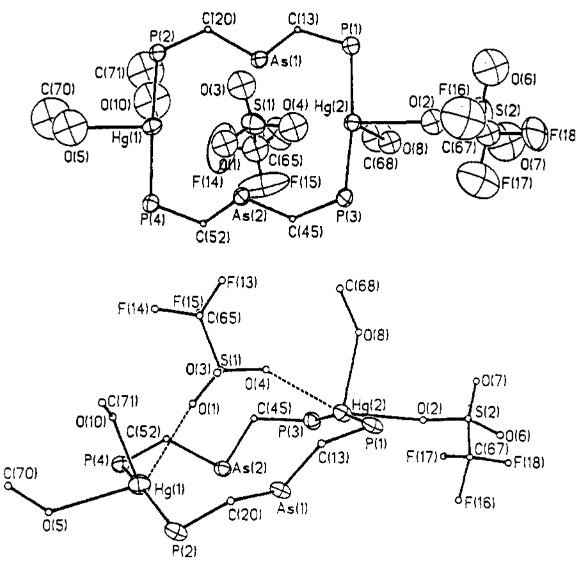

Figure 2. Views of the inner core of $[Hg_2(\mu\text{-dpma})_2(O_3SCF_3)_2(CH_3OH)_3]^{2+}$: top, 50% thermal contours for all but the methylene carbons; bottom, the bridging trifluoromethanesulfonate.

Table I. Selected Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[Hg_2(\mu\text{-dpma})_2(O_3SCF_3)_2(CH_3OH)_3][PF_6]_2\cdot CH_3OH$[a]

	x	*y*	*z*	*U*
Hg(1)	4337 (1)	4337 (1)	2101 (1)	36[b]
Hg(2)	2533 (1)	484 (1)	2247 (1)	31[b]
As(1)	4961 (1)	2200 (1)	2621 (1)	28[b]
As(2)	1832 (1)	2786 (1)	2705 (1)	28[b]
S(1)	3367 (4)	2246 (3)	991 (3)	57[b]
S(2)	1647 (6)	−1728 (4)	3040 (4)	94
P(1)	4438 (3)	343 (2)	2180 (2)	30[b]
P(2)	6066 (3)	4107 (2)	2540 (2)	31[b]
P(3)	816 (3)	826 (2)	2554 (2)	31[b]
P(4)	2436 (3)	4500 (3)	2075 (2)	30[b]
P(5)	8357 (4)	2358 (3)	959 (2)	33[b]
P(6)	−3259 (4)	−2854 (3)	3914 (2)	47[b]
O(1)	3158 (13)	2899 (10)	1370 (7)	77 (4)
O(2)	1864 (11)	−915 (8)	2819 (7)	61 (4)
O(3)	4479 (15)	2396 (11)	853 (8)	94 (5)
O(4)	2896 (15)	1477 (11)	1236 (8)	95 (5)
O(5)	5101 (20)	5942 (15)	1970 (12)	135 (8)
O(6)	2676 (19)	−1961 (14)	3208 (11)	126 (7)
O(7)	699 (21)	−2283 (15)	2690 (12)	148 (9)
O(8)	1551 (11)	−427 (8)	1301 (7)	58 (3)
O(9)	10781 (13)	7964 (10)	1371 (8)	79 (4)
O(10)	4983 (24)	4284 (16)	948 (13)	158 (9)
F(1)	7236 (8)	2666 (6)	961 (4)	48[b]
F(2)	8383 (9)	2395 (6)	192 (4)	50[b]
F(3)	9494 (8)	2068 (6)	969 (5)	46[b]
F(4)	8327 (9)	2329 (7)	1742 (4)	57[b]
F(5)	7619 (9)	1432 (6)	883 (5)	55[b]
F(6)	9114 (8)	3302 (6)	1066 (5)	50[b]
F(7)	−3189 (11)	−2807 (7)	3128 (5)	68[b]
F(8)	−4034 (9)	−3769 (7)	3792 (6)	64[b]
F(9)	−3357 (11)	−2898 (8)	4685 (5)	71[b]
F(10)	−2503 (11)	−1919 (7)	4012 (6)	75[b]
F(11)	−2172 (10)	−3182 (8)	3931 (6)	71[b]
F(12)	−4375 (9)	−2530 (6)	3878 (5)	57[b]
F(13)	2753 (14)	1598 (10)	−145 (7)	108[b]
F(14)	2955 (22)	2858 (12)	−57 (9)	185[b]
F(15)	1560 (14)	2080 (18)	331 (10)	180[b]
F(16)	1899 (17)	−1030 (13)	4207 (8)	138[b]
F(17)	304 (16)	−1325 (12)	3804 (7)	124[b]
F(18)	903 (14)	−2317 (10)	4070 (9)	127[b]

[a] Positions of carbon atoms are given in the supplementary material. [b] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The dication has the desired macrocyclic structure with slightly bent P–Hg–P units. The P–Hg–P angles are 158.9 (1) and 166.2 (1)° at Hg(1) and Hg(2), respectively. The Hg–P bond distances are all close to 2.42 Å and fall in the normal range (2.39–2.51 Å).[14] In addition to the two phosphine ligands, each mercury

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[12] For examples see: (a) Beauchamp, A. L.; Olivier, M. J.; Wuest, J. D.; Zacharie, B. *Organometallics* **1987**, *6*, 153. (b) Beauchamp, A. L.; Olivier, M. J.; Wuest, J. D.; Zacharie, B. *J. Am. Chem. Soc.* **1986**, *108*, 73. (c) Karol, T. J.; Hutchinson, J. P.; Hyde, J. R.; Kuivila, H. G.; Zubieta, J. A. *Organometallics* **1983**, *2*, 106.

[13] Beringer, P. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1501.

Table II. Structural Parameters for $[Hg_2(\mu\text{-dpma})_2(O_3SCF_3)_2(CH_3OH)_3][PF_6]_2\cdot CH_3OH$ (**3**)

Selected Interatomic Distances, Å			
Hg(1)–P(2)	2.416 (4)	Hg(1)–O(1)	2.79 (1)
Hg(1)–P(4)	2.420 (4)	Hg(1)–O(5)	2.66 (3)
Hg(2)–P(1)	2.421 (4)	Hg(1)–O(10)	2.52 (3)
Hg(2)–P(3)	2.420 (5)	Hg(2)–O(2)	2.65 (1)
Hg(1)···Hg(2)	6.339 (4)	Hg(2)–O(4)	2.73 (1)
As(1)···As(2)	4.221 (3)	Hg(2)–O(8)	2.46 (1)
S(1)–O(1)	1.39 (2)	S(2)–O(2)	1.44 (2)
S(1)–O(3)	1.36 (2)	S(2)–O(6)	1.46 (3)
S(1)–O(4)	1.41 (2)	S(2)–O(7)	1.43 (2)
S(1)–C(65)	1.72 (3)	S(2)–C(67)	1.50 (2)

Selected Interatomic Angles, deg			
P(2)–Hg(1)–P(4)	158.9 (1)	P(1)–Hg(2)–P(3)	166.2 (1)
P(2)–Hg(1)–O(1)	107.2 (4)	P(1)–Hg(2)–O(2)	91.6 (4)
P(2)–Hg(1)–O(5)	98.3 (6)	P(1)–Hg(2)–O(4)	89.6 (6)
P(2)–Hg(1)–O(10)	91.8 (7)	P(1)–Hg(2)–O(8)	89.6 (6)
P(4)–Hg(1)–O(1)	79.1 (4)	P(3)–Hg(2)–O(2)	89.7 (4)
P(4)–Hg(1)–O(5)	88.3 (6)	P(3)–Hg(2)–O(4)	94.6 (6)
P(4)–Hg(1)–O(10)	109.1 (7)	P(3)–Hg(2)–O(8)	92.1 (4)
O(1)–Hg(1)–O(5)	139.7 (9)	O(2)–Hg(2)–O(4)	156.7 (0)
O(1)–Hg(1)–O(10)	80.8 (12)	O(2)–Hg(2)–O(8)	80.4 (7)
O(5)–Hg(1)–O(10)	68.0 (8)	O(4)–Hg(2)–O(8)	76.6 (9)
Hg(1)–O(5)–C(70)	126.8 (8)	Hg(2)–O(8)–C(68)	129.8 (8)
Hg(1)–O(10)–C(71)	144.9 (9)		

Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[Hg_2(\mu\text{-dpma})_2(\mu\text{-Cl})_2][PF_6]_2$ (**4**)[a]

	x	y	z	U
Hg(1)	4783 (1)	3553 (1)	1109 (1)	20[b]
As(1)	6539 (1)	5398 (1)	1707 (1)	19[b]
Cl(1)	3281 (2)	5723 (1)	473 (1)	23[b]
P(1)	4317 (2)	2442 (1)	341 (1)	19[b]
P(2)	5249 (2)	3354 (1)	2791 (1)	19[b]
P(3)	2207 (2)	−2176 (2)	3000 (2)	37[b]
F(1)	2310 (5)	−3147 (4)	2628 (4)	47 (1)
F(2)	1623 (5)	−2921 (4)	4155 (4)	58 (1)
F(3)	3744 (6)	−2798 (4)	3350 (4)	58 (1)
F(4)	2793 (5)	−1429 (4)	1864 (4)	55 (1)
F(5)	681 (5)	−1569 (4)	2646 (4)	57 (1)
F(6)	2121 (6)	−1201 (5)	3374 (4)	63 (1)

[a] Positions of carbon atoms are given in the supplementary material. [b] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

is loosely coordinated by three oxygen donors that lie near a plane that is roughly perpendicular to the P–Hg–P units. One of these oxygen donors come from a trifluoromethanesulfonate ligand that loosely bridges the two mercury ions. The Hg–O distances, 2.79 (1) and 2.73 (1) Å, are very long. Coordination about Hg(1) is completed by two methanol molecules (Hg–O distances 2.66 (3) and 2.52 (3) Å), while at Hg(2) it involves a methanol molecule and a trifluoromethanesulfonate (Hg–O distances 2.46 (1) and 2.65 (1) Å, respectively). While the range of Hg–O distances is large, and all of these distances are longer than the Hg–P distances, there nevertheless appears to be weak bonding between each mercury and these adjacent oxygens. Notice that these Hg–O distances are all substantially shorter than those seen in the crown ether complexes of $Hg(CN)_2$ and $Hg(CF_3)_2$ (range 2.73–3.00 Å).[15] However, the size of the thermal ellipsoids associated with the oxygen donors, which are seen in the top part of Figure 2, suggests that these donors are only loosely bonded to mercury.

Crystal Structure of $[Hg_2(\mu\text{-dpma})_2(\mu\text{-Cl})_2][PF_6]_2$. The asymmetric unit consists of one-half of a dication and one normal hexafluorophosphate ion. A drawing of the entire cation is shown in Figure 3. Atomic positional parameters are given in Table III. Selected interatomic distances and angles are given in Table IV.

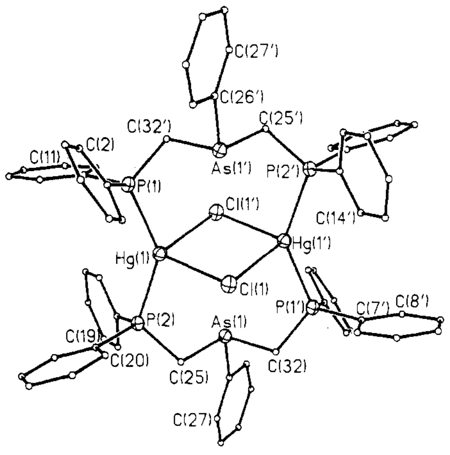


Figure 3. Perspective view of $[Hg_2(\mu\text{-dpma})_2(\mu\text{-Cl})_2]^{2+}$ showing 50% thermal contours for Hg, P, As, and Cl atoms and arbitrarily sized circles for carbon atoms.

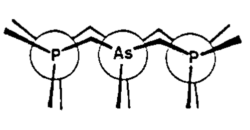
Table IV. Structural Parameters for $[Hg_2(\mu\text{-dpma})_2(\mu\text{-Cl})_2][PF_6]_2$ (**4**)

Selected Interatomic Distances, Å			
Hg(1)–P(1)	2.427 (2)	Hg(1)–P(2)	2.431 (2)
Hg(1)–Cl(1)	2.674 (1)	Hg(1)–Cl(1')	2.729 (1)
Hg(1)···Hg(1')	3.85 (2)	As(1)···As(1')	6.983 (2)

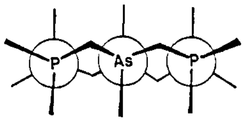
Selected Interatomic Angles, deg			
P(1)–Hg(1)–P(2)	140.2 (3)	Cl(1)–Hg(1)–Cl(1')	88.5 (4)
P(1)–Hg(1)–Cl(1)	115.3 (3)	P(1)–Hg(1)–Cl(1')	92.5 (3)
P(2)–Hg(1)–Cl(1)	96.11 (3)	P(2)–Hg(1)–Cl(1')	113.3 (3)
Hg(1)–Cl(1)–Hg(1')	91.5 (4)		

The dication, which is centrosymmetric, consists of a $Hg_2(dpma)_2$ metallamacrocycle with two additional chloride bridges. The coordination about each mercury is a grossly distorted tetrahedron with a very wide P–Hg–P angle, 140.2 (3)°, and a very narrow Cl–Hg–Cl angle, 88.5 (4)°. The Hg–P distances are similar to those in $[Hg_2(\mu\text{-dpma})_2(O_3SCF_3)_2(CH_3OH)_3]^{2+}$ and other mercury phosphine complexes.[14] The Hg–Cl distances are also normal.[14]

Comparison of the structures of $[Hg_2(\mu\text{-dpma})_2(O_3SCF_3)_2(CH_3OH)_3]^{2+}$ and $[Hg_2(\mu\text{-dpma})_2(\mu\text{-Cl})_2]^{2+}$ leads to the conclusion that phosphorus–mercury bond breaking must accompany the transformation of **3** into **4**. Idealized Newman projections down the P–Hg–P bonds in **3** are shown in A and compared to that for **4** in B. These two forms are not interconvertable through simple bond rotations. Either bond rupture, with the Hg–P bonds as the weakest links in the metallamacrocycle, or pyramidal inversion at arsenic, generally a high-energy process,[16] is necessary to allow for conversion of A to B (or **3** to **4**). The most reasonable path involves breaking of two Hg–P bonds. This can be accomplished by dissociation of the metallamacrocycles into dpma and $Hg_2(dpma)^{4+}$ fragments or dissociation into $Hg(dpma)^{2+}$ units. Dissociation into Hg^{2+} and $Hg(dpma)_2^{2+}$ fragments will not allow for the requisite interconversion. The implication of these observations is clear. The $Hg_2(dpma)_2^{4+}$ metallamacrocycle does not have the stability to remain intact through the mild conditions used to transform **3** into **4**. This contrasts sharply with the rhodium and iridium metallamacrocycles **2**, which do retain their structural integrity in binding a variety of cations. Consequently, while it may be possible to bind other substrates within these



A



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(14) Allen, D. W.; Bell, N. A.; Fong, S. T.; March, L. A.; Nowell, I. W. *Inorg. Chim. Acta* **1985**, *99*, 157. Bell, N. A.; Goldstein, M.; March, L. a.; Nowell, I. W. *J. Chem. Soc., Dalton Trans.* **1984**, 1621.

(15) Rebeck, J., Jr.; Costello, T.; Marshall, L.; Wattley, R.; Gadwood, R. C.; Onan, K. *J. Am. Chem. Soc.* **1985**, *107*, 7481.

(16) Senkler, G. H.; Mislow, K. *J. Am. Chem. Soc.* **1972**, *94*, 291.

Table V. Crystal Data and Data Collection Parameters[a] for $[Hg_2(\mu\text{-dpma})_2(O_3SCF_3)_2(CH_3OH)_3][PF_6]_2 \cdot CH_3OH$ (**3**) and $[Hg_2(\mu\text{-dpma})_2(\mu\text{-Cl})_2][PF_6]_2$ (**4**)

	3	**4**
formula	$Hg_2As_2S_2F_{18}O_{10}C_{70}H_{62}$	$Hg_2As_2O_6F_{12}C_{64}H_{58}$
fw	2205.5	1791.9
cryst system	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	12.273 (4)	10.351 (3)
b, Å	16.941 (5)	13.514 (5)
c, Å	20.468 (5)	14.297 (5)
α, deg	93.77 (2)	62.95 (2)
β, deg	91.78 (2)	77.78 (2)
γ, deg	105.47 (2)	70.73 (2)
V, Å^3	4087 (2)	1677.0 (9)
Z	2	1
d_{calcd}(130 K), g/cm^3	1.79	1.77
cryst dimens, mm	0.30 × 0.20 × 0.55	0.225 × 0.125 × 0.50
μ(Mo Kα), cm^{-1}	48.74	58.41
temp, K	130	130
range of transm factors	0.237–0.444	0.288–0.540
2θ max, deg	50	50
scan type	ω	ω
scan speed, deg/min	20	15
scan range, deg	1.8	0.9
w bgd offset, deg	1.2	0.9
octants collected	$+h,\pm k,\pm l$	$+h,\pm k,\pm l$
no. of unique data	14410	5275
no. of unique data used	8139 ($I_o > 3\sigma(I_o)$)	5275 ($I_o > 2\sigma(I_o)$)
no. of params refined	600	207
R^b	0.070	0.037
$R_w{}^c$	0.074	0.042
GoF^d	1.158	0.98

[a] Diffractometer Syntex $P2_1$; radiation Mo Kα (0.71069 Å). [b] $R = \sum||F_o| - |F_c||/|F_o|$. [c] $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o w^{1/2}|$; $w = [\sigma^2|F_o|]^{-1}$. [d] Goodness of fit $= [\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$, where n is the number of observations and m is the number of variables.

mercury-containing macrocycles, the integrity of macrocycle during reaction cannot be ensured.

Experimental Section

Preparation of Compounds. Samples of dpma[5] and $[Hg\{(CH_3)_2SO\}_6][O_3SCF_3]_2$[13] were prepared as previously described.

$[Hg_2(\mu\text{-dpma})_2(O_3SCF_3)_2(CH_3OH)_3][PF_6]_2$. Solid dpma (200 mg, 0.364 mmol) was added in one portion to a stirred solution of 356 mg (0.364 mmol) of $[Hg\{(CH_3)_2SO\}_6][O_3SCF_3]_2$ in 8 mL of methanol. After 1 h of stirring, all of the dpma had dissolved to give a colorless solution. Solid ammonium hexafluorophosphate (200 mg, 1.2 mmol) was added to the solution, and the mixture was then filtered. Diethyl ether was added dropwise to the filtrate to precipitate a white, crystalline solid. The product was collected by filtration and washed with ethyl ether. Purification was achieved by dissolving the product in a minimum of methanol, filtering the solution, and adding diethyl ether to the filtrate to precipitate the product; yield 306 mg (76.4%).

$[Hg_2(\mu\text{-dpma})_2(\mu\text{-Cl})_2][PF_6]_2$. A solution of 8.6 mg (0.453 mmol) of tin(II) chloride dihydrate in 1 mL of methanol was added dropwise to a solution of 100 mg (0.453 mmol) of $[Hg_2(\mu\text{-dpma})_2(O_3SCF_3)_2(CH_3OH)_3][PF_6]_2$ in 4 mL of methanol. A white crystalline solid began to form immediately. The product was washed with methanol and vacuum-dried; yield 64.7 mg (79.7%).

X-ray Data Collection. $[Hg_2(\mu\text{-dpma})_2(O_3SCF_3)_2(CH_3OH)_3][PF_6]_2 \cdot CH_3OH$ (3). Clear parallelepipeds were formed by slow diffusion of diethyl ether into a methanol solution of $Hg_2(\mu\text{-dpma})_2(O_3SCF_3)_2(CH_3OH)_3][PF_6]_2 \cdot CH_3OH$. On removal of the crystals from the diffusion tube, a light hydrocarbon oil was placed over them to reduce the loss of solvent from the crystals. The crystal was mounted on a glass fiber in the cold stream of a Syntex $P2_1$ diffractometer equipped with a modified LT-1 low-temperature apparatus. Unit cell parameters were obtained by a least-squares refinement of 10 reflections with $15 \leq 2\theta \leq 25$. No decay in intensities of the two check reflections occurred. Crystal data and data collection parameters are given in Table V.

The usual corrections for Lorentz and polarization effects were applied to the data. Crystllographic programs used were those of SHELXTL, version 5, installed on a Data General Eclipse computer. Scattering factors for neutral atoms[17a] and corrections for anomalous dispersion[17b] were from a standard source.

$[Hg_2(\mu\text{-dpma})_2(\mu\text{-Cl})_2][PF_6]_2$ (4). Clear parallelepipeds were formed by diffusion of a solution of tin(II) chloride in methanol into a solution of **3** in methanol. Determination of unit cell parameters and all other aspects of the data collection were the same as in **3**.

Solution and Refinement of Structures. $[Hg_2(\mu\text{-dpma})_2(O_3SCF_3)_2(CH_3OH)_3][PF_6]_2 \cdot CH_3OH$. All structure determinations were done on a Data General Eclipse MV/10000 computer equipped with the SHELXTL version 5 software package. Positions of the two mercury and arsenic atoms were determined by using FMAP8, the Patterson solving routine for SHELXTL. All other non-hydrogen atoms were located by successive difference Fourier maps. Anisotropic thermal parameters were assigned to all mercury, arsenic, phosphorus, fluorine, and sulfur atoms. Isotropic thermal parameters were assigned to all other atoms. All hydrogens were fixed by using a riding model in which the C–H vector is fixed at 0.96 Å, and isotropic thermal parameters are 20% greater than those of the carbons to which they were bonded. Final stages of refinement included an absorption correction.[18] A value of 2.6 e/Å^3 was found as the largest feature on the final difference Fourier map. This peak was 1.12 Å from Hg(2). Thermal parameters for the sulfur and oxygen atoms in the two triflates were high due to some large thermal motion or disorder, but no attempt was made to model this.

$[Hg_2(\mu\text{-dpma})_2(\mu\text{-Cl})_2][PF_6]_2$. The positions of the mercury and the arsenic atoms were generated by FMAP8, and all other atoms were located by difference Fourier maps. Anisotropic thermal parameters were assigned to the mercury, arsenic, phosphorus, and chlorine atoms, and isotropic thermal parameters were used for the remaining atoms. Hydrogen atoms were included as in **3**. An absorption correction was also made as in **3**. The largest peak in the final difference map was 1.2 e/Å^3 and was 0.95 Å away from Hg(1).

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Registry No. 3, 114059-34-6; 4, 114059-36-8; $[Hg\{(CH_3)_2SO\}_6][O_3SCF_3]_2$, 76703-09-8.

Supplementary Material Available: Listings of atom positions, isotropic and anisotropic thermal parameters, and additional bond lengths and bond angles for **3** and **4** (17 pages); listings of observed and calculated structure factors (78 pages). Ordering information is given on any current masthead page.

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[17] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 14: (a) p 149–150; (b) p 99–101.

[18] XABS produces an absorption tensor from an expression relating F_o and F_c: Hope, H.; Moezzi, B., Department of Chemistry, University of California, Davis, unpublished results.