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Structural Studies of Steric Effects in Phosphine Complexes. 5.[1] Synthesis and Crystal and Molecular Structures of the Dimers Bis(acetato)(tricyclohexylphosphine)mercury(II) and Bis(acetato)(tri-*o*-tolylphosphine)mercury(II)

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X-ray crystallographic studies have been carried out on two new mercury compounds containing bulky phosphine ligands $[HgPCy_3(OAc)_2]_2$ (I) and $[HgP(o\text{-tol})_3(OAc)_2]_2$ (II). Crystals of I and II are monoclinic, with two dimeric molecules in each unit cell. Cell data for I are a = 9.714 (1) Å, b = 15.163 (3) Å, c = 16.686 (2) Å, β = 93.91 (1)°, and space group $P2_1/c$; for II the cell data are a = 10.485 (8) Å, b = 21.64 (2) Å, c = 10.762 (8) Å, β = 97.47 (5)°, and space group $P2_1/n$. For both compounds, three-dimensional intensity data were collected by four-circle diffractometer measurements and refinement was by full-matrix least-squares calculations. At convergence $R_F = 0.040$ and $R_{wF} = 0.044$ for 3181 observed reflections for I; for II the corresponding values are $R_F = 0.085$ and $R_{wF} = 0.074$ for 1398 observed reflections. The dimeric molecules are isostructural with $[HgPCy_3(NO_3)_2]_2$; a hitherto unknown acetato bridging mode with only one oxygen atom from each of two acetato groups linking pairs of mercury atoms is found. In both molecules, the predominant feature of the mercury coordination is the presence of three nearly coplanar strong bonds: Hg–P = 2.378 (1), Hg–O = 2.194 (5) and 2.292 (4) Å in I; Hg–P = 2.41 (1), Hg–O = 2.36 (4) and 2.20 (4) Å in II. A fourth weaker bond (Hg–O = 2.523 (4) Å in I and 2.73 (4) Å in II) forms the bridge to the other centrosymmetrically related mercury atom; sixfold coordination about mercury is achieved in each case by weaker intramolecular interactions with acetato oxygens (Hg–O = 2.63–2.92 Å). Both compounds exist as monomers in dichloroethane solution. Cone angle calculations are made for PCy_3 (θ = 179°) and $P(o\text{-tol})_3$ (θ = 191°) and ligand profiles are given for the bulky phosphines in I and II.

Introduction

In an attempt to relate steric and electronic properties of the ligand to molecular stereochemistry, a systematic investigation of the bulky tertiary phosphine derivatives of mercury(II) is in progress in our laboratories. We have already reported the crystal structures of $[HgPCy_3(SCN)_2]_n$,[2] $[HgPCy_3(NO_3)_2]_2$,[3] and $HgP(t\text{-Bu})_3(OAc)_2$[4] and have developed the concept of a ligand profile[5] which provides cone angle[6] data and rationalizes the effects of steric properties of bulky phosphine ligands such as PCy_3, $P(t\text{-Bu})_3$, $P(o\text{-tolyl})_3$, and $P(mesityl)_3$.[7] To provide data for cone angle and ligand profile calculations of PCy_3 and $P(o\text{-tolyl})_3$ ligands, we prepared complexes of these ligands with $Hg(OAc)_2$. Molecular weight determinations (see Experimental Section) indicated that these structures are monomeric in solution. However, our X-ray analyses show unequivocally that the solid-state structures are dimeric, $[HgPCy_3(OAc)_2]_2$ (I) and $[Hg(P(o\text{-tolyl})_3)(OAc)_2]_2$ (II), with a unique mode of acetate bridging, and are essentially isostructural with $[HgPCy_3(NO_3)_2]_2$.[3]

Experimental Section

$[HgPCy_3(OAc)_2]_2$ (I) was prepared by adding a solution of PCy_3 in dichloromethane to a suspension of $Hg(OAc)_2$ in dichloromethane in a 1:1 molar ratio. After stirring for 2 h, the resulting clear, colorless solution was concentrated on a rotary evaporator. The product so obtained was washed with ether and recrystallized from dichloromethane/hexane as white crystals; yield 98%, mp 149–150 °C dec. Anal. Calcd for $C_{22}H_{39}O_4PHg$: C, 44.11; H, 6.51. Found: C, 43.93; H, 6.56. X-ray analysis was done on a sample recrystallized from ethanol/hexane. I has molar conductance in dry nitromethane (10^{-3} M solution) of 22 Ω^{-1} cm^2. The molecular weight by osmometry in dichloroethane (ca. 10^{-3} M solution) is 627 (calcd 599). The ^{1}H NMR spectrum of I in deuteriochloroform showed a broad unresolved multiplet between δ 0.92 and 2.83 ppm, downfield from 0.63 and 2.33 ppm in free PCy_3, and a sharp singlet (due to acetato methyl protons) at δ 2.01 ppm. The ^{31}P NMR spectrum of I in dichloromethane solution at ambient temperature shows a signal at 60.5 ppm (δ, downfield from external 85% H_3PO_4 as reference) with satellite peaks due to mercury-199; $^1J(^{199}Hg–^{31}P)$ = 7461 Hz. Acetato infrared spectral bands (in cm^{-1}) occur at 1605 (vs), 1592 (vs), 1578 (vs), and 1370 (s, br) in the solid state (halocarbon mull/CsI plates) and at 1608 (m, sh), 1575 (vs, br), 1402 (s, br), and 1340 (w) in dichloromethane solution. The synthesis and characterization of II and a number of other $Hg(PR_3)_n(OAc)_2$ (n = 1, 2) complexes have been reported elsewhere.[8] II is also a nonconductor in nitromethane and a monomer in dichloroethane.

Crystallographic Measurements. Initial film examination of $[HgPCy_3(OAc)_2]_2$ (I) and $[HgP(o\text{-tol})_3(OAc)_2]_2$ (II) crystals provided approximate cell dimensions. The space group for I was determined to be $P2_1/c$ (C_{2h}^5, No. 14) from the systematic absences ($h0l$ if $l = 2n + 1$, $0k0$ if $k = 2n + 1$); for II space group $P2_1/n$ (an alternate setting of $P2_1/c$ with equivalent positions x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $^1/_2 + x, ^1/_2 - y, ^1/_2 + z$; $^1/_2 - x, ^1/_2 + y, ^1/_2 - z$) was determined by the systematic absences ($h0l$ if $h + l = 2n + 1$, $0k0$ if $k = 2n + 1$). In each case accurate cell parameters (Table I) and the crystal orientation matrix were determined by a least-squares treatment of the diffractometer setting angles of 12 reflections which were widely separated in the reciprocal space. Three-dimensional intensity data were collected in our usual way[3] by using a computer-controlled Hilger and Watts Y290 four-circle diffractometer with monochromated Mo Kα (λ = 0.710 69 Å) radiation; details are given in Table I. The crystals of both compounds turned black during data collection and the intensities of three standard reflections monitored every 100 reflections decreased by 35% for I and 15% for II. This was allowed for by appropriate scaling.[9] Intensity data for I and II were corrected for Lorentz, polarization,[10] and absorption factors;[11] only data with $I > 3\sigma(I)$ were used in structure solution and refinement.

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Table I. Crystallographic Data for $[HgPCy_3(OAc)_2]_2$ and $[HgP(o\text{-tol})_3(OAc)_2]_2$

compd	$[HgPCy_3(OAc)_2]_2$	$[HgP(o\text{-tol})_3(OAc)_2]_2$
formula	$C_{44}H_{78}Hg_2O_8P_2$	$C_{50}H_{54}Hg_2O_8P_2$
a, Å	9.714 (1)	10.485 (8)
b, Å	15.163 (3)	21.64 (2)
c, Å	16.686 (2)	10.762 (8)
β, deg	93.91 (1)	97.47 (5)
V, Å^3	2451.9	2421.1
space group	$P2_1/c$ (C_{2h}^5, No. 14)	$P2_1/n$ (C_{2h}^5, No. 14) alternate setting
Z	2	2
density, g cm^{-3}	1.621 (calcd) 1.62 ± 0.01 (exptl)	1.709 (calcd) 1.71 ± 0.01 (exptl)
μ, cm^{-1}	61.1	61.9
crystal dimens, mm^3	0.12 × 0.15 × 0.41	0.09 × 0.12 × 0.25
transmission coeff	0.19–0.25	0.70–0.77
reflctns measd	with indices hkl, $\bar{h}kl$ (θ = 2–25°)	with indices hkl, $\bar{h}kl$ (θ = 2–20°)
total no. of reflcts scanned	5007	2515
final no. of variables in least-square calcn	256	136
unique data $\|F_o^2\| > 3\sigma(\|F_o\|^2)$	3181	1398

Structure Solution and Refinement. For both structures, the position of the mercury atom was determined from a sharpened three-dimensional Patterson synthesis; the positions of remaining nonhydrogen atoms were determined via the heavy-atom phases and difference Fourier syntheses. The structures were refined by full-matrix least-squares calculations using the SHELX program.[12] The analytical scattering factors for the nonhydrogen atoms were taken from ref 13 and for hydrogen from ref 14. Both real and imaginary components of anomalous dispersion[15] were included for all nonhydrogen atoms. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$; in the initial stages of refinement unit weights were used and in the final stages weights were derived from the counting statistics.

For I, three cycles of full-matrix least-squares refinement of the positional and thermal parameters of the nonhydrogen atoms (all anisotropic) converged at $R_F = \sum||F_o| - |F_c||/\sum|F_o| = 0.057$. A difference Fourier synthesis then showed electron-density maxima in most of the plausible hydrogen atom locations. Thereafter, all hydrogen atoms were included (in idealized positions with C–H = 0.95 Å, and H–C–H 109.5°, but not refined) in subsequent cycles of refinement and overall isotropic thermal parameters for three different kinds of hydrogens (details are in Supplementary Data) were refined. In three further cycles of refinement, convergence was achieved with $R_F = 0.040$ and $R_{wF} = (\sum w\Delta^2/\sum wF_o^2)^{1/2} = 0.044$. In the final cycle of refinement the largest shift/error ratio was 0.80 for the U_{13} coordinate of C(25). The final atomic coordinates are listed in Table II and interatomic distances and angles are in Table III.

For II, because of the paucity of the data, only the mercury and phosphorus atoms were allowed to vibrate anisotropically and all carbon and oxygen atoms were constrained to isotropic thermal motion. After two cycles of full-matrix least-squares refinement, a difference synthesis showed maxima in positions consistent with some of the phenyl hydrogen atoms but no indication of methyl hydrogens could be found. Allowance was made for the phenyl hydrogen atoms (with C–H 1.08 Å[5] and U_{iso} = 0.10 Å^2) in subsequent rounds of calculations but they were not refined. Convergence was achieved in two more cycles with $R_F = 0.085$ and $R_{wF} = 0.074$. In the final cycle of refinement the largest shift/error ratio was 0.20 for the thermal parameter of C(3). The final difference map had no features of chemical significance. The final atomic coordinates are in Table IV and interatomic distances and angles in Table V.

Results and Discussion

The X-ray analyses of I and II show that in each case the crystal structure consists of discrete centrosymmetric dimeric molecules separated by normal van der Waals contacts (Figures 1 and 2, Tables III and V). Views of the individual dimers with our atomic numbering schemes are in Figure 3, where it can be seen that both I and II are essentially isostructural with $[HgPCy_3(NO_3)_2]_2$[3] (III).

Table II. Final Positional Parameters (Hg, ×10^5; P, O, and C, ×10^4) for $[HgPCy_3(OAc)_2]_2$[a]

	x	y	z
Hg	−947 (3)	−1137 (2)	11351 (2)
P	873 (2)	789 (1)	2195 (1)
O(1)	−1904 (8)	−944 (5)	829 (4)
O(2)	−1778 (10)	−1125 (8)	2112 (5)
O(3)	1029 (6)	−709 (4)	99 (3)
O(4)	2750 (8)	−700 (6)	1039 (4)
C(1)	−3763 (10)	−1694 (8)	1388 (7)
C(2)	−2398 (11)	−1219 (6)	1458 (7)
C(3)	3234 (12)	−1094 (10)	−285 (7)
C(4)	2285 (10)	−816 (6)	345 (6)
C(11)	2214 (8)	130 (5)	2759 (5)
C(12)	2997 (10)	617 (6)	3453 (6)
C(13)	4090 (11)	48 (6)	3860 (7)
C(14)	3525 (11)	−814 (7)	4146 (6)
C(15)	2785 (11)	−1299 (6)	3462 (7)
C(16)	1661 (11)	−743 (6)	3025 (7)
C(21)	−446 (8)	1088 (5)	2878 (5)
C(22)	−1900 (9)	1154 (8)	2493 (6)
C(23)	−2978 (11)	1280 (9)	3089 (9)
C(24)	−2625 (13)	2043 (9)	3647 (8)
C(25)	−1221 (12)	1974 (9)	4034 (7)
C(26)	−129 (10)	1879 (7)	3422 (6)
C(31)	1678 (8)	1782 (5)	1813 (4)
C(32)	611 (10)	2331 (6)	1287 (6)
C(33)	1312 (11)	3158 (6)	975 (6)
C(34)	2547 (11)	2955 (7)	539 (7)
C(35)	3615 (10)	2405 (8)	1054 (7)
C(36)	2920 (10)	1579 (6)	1353 (6)

[a] Estimated standard deviations are in parentheses. The calculated hydrogen coordinates have been deposited in the supplementary material.

Table III. Interatomic Distances (Å) and Angles (deg) for $[HgPCy_3(OAc)_2]_2$[a]

(a) Intramolecular Distances

Hg–P	2.378 (1)	C(2)–O(2)	1.218 (9)
Hg–O(1)	2.194 (5)	C(3)–C(4)	1.505 (10)
Hg–O(2)	2.836 (6)	C(4)–O(3)	1.270 (7)
Hg–O(3)	2.292 (4)	C(4)–O(4)	1.228 (8)
Hg–O(3^I)	2.523 (4)	P–C(11)	1.848 (6)
Hg–O(4)	2.918 (5)	P–C(21)	1.829 (6)
C(1)–C(2)	1.507 (10)	P–C(31)	1.831 (5)
C(2)–O(1)	1.255 (9)	C–C[b]	1.514 (9)

(b) Angles

P–Hg–O(1)	140.6 (1)	Hg–O(3)–Hg^I	104.9 (3)
P–Hg–O(2)	95.6 (1)	Hg^I–O(3)–C(4)	127.7 (3)
P–Hg–O(3)	127.1 (1)	O(1)–C(2)–C(1)	118.6 (7)
P–Hg–O(3^I)	115.1 (1)	O(1)–C(2)–O(2)	121.1 (7)
P–Hg–O(4)	83.6 (1)	O(2)–C(2)–C(1)	120.3 (8)
O(1)–Hg–O(2)	48.7 (2)	O(3)–C(4)–C(3)	115.6 (6)
O(1)–Hg–O(3)	90.8 (2)	O(3)–C(4)–O(4)	124.7 (7)
O(1)–Hg–O(3^I)	81.7 (2)	O(4)–C(4)–C(3)	119.7 (6)
O(1)–Hg–O(4)	124.0 (2)	P–C(11)–C(12)	114.9 (4)
O(2)–Hg–O(3)	122.9 (2)	P–C(11)–C(16)	111.8 (4)
O(2)–Hg–O(3^I)	123.1 (2)	P–C(21)–C(22)	115.2 (4)
O(2)–Hg–O(4)	116.9 (2)	P–C(21)–C(26)	116.4 (4)
O(3)–Hg–O(3^I)	75.1 (2)	P–C(31)–C(32)	110.6 (4)
O(3)–Hg–O(4)	48.5 (1)	P–C(31)–C(36)	112.7 (4)
O(3^I)–Hg–O(4)	113.3 (2)	C(11)–P–C(21)	108.4 (3)
Hg–O(1)–C(2)	110.0 (4)	C(11)–P–C(31)	108.6 (2)
Hg–O(2)–C(2)	79.5 (5)	C(21)–P–C(31)	110.3 (3)
Hg–O(3)–C(4)	107.7 (4)		
Hg–O(4)–C(4)	78.8 (4)	C–C–C[b]	111.5 (6)

[a] The superscript I refers to the atom at equivalent position $-x, -y, -z$. [b] Mean ring value.

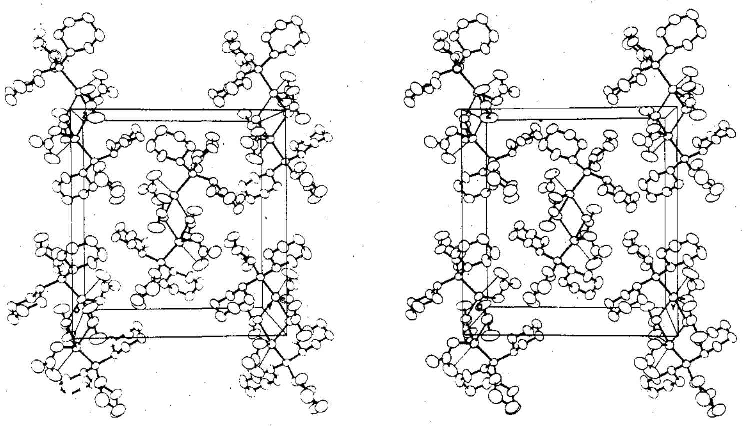

Figure 1. Stereoview of the crystal structure of $[HgPCy_3(OAc)_2]_2$. In this diagram the cell shown runs from $(-^1/_2, -^1/_2, -^1/_2)$ to $(^1/_2, ^1/_2, ^1/_2)$; the points labeled "O", "*X*", "*Y*", and "*Z*" have crystal coordinates $(-^1/_2, -^1/_2, -^1/_2)$, $(^1/_2, -^1/_2, -^1/_2)$, $(-^1/_2, ^1/_2, -^1/_2)$, and $(-^1/_2, -^1/_2, ^1/_2)$, respectively.

Table IV. Final Fractional Coordinates (× 10^4 for Hg, ×10^3 for Others) for $[HgP(o\text{-tol})_3(OAc)_2]_2$[a]

atom	*x*	*y*	*z*
Hg	5349 (2)	4281 (1)	6157 (2)
P	402 (1)	345 (1)	676 (1)
O(1)	607 (3)	506 (1)	762 (3)
O(2)	747 (3)	431 (2)	775 (2)
O(3)	623 (3)	476 (1)	469 (3)
O(4)	636 (3)	379 (2)	411 (3)
C(1)	796 (5)	516 (2)	915 (5)
C(2)	718 (4)	485 (2)	810 (4)
C(3)	730 (4)	456 (2)	290 (4)
C(4)	655 (4)	436 (2)	392 (4)
C(11)	229 (4)	365 (2)	625 (4)
C(12)	156 (4)	367 (2)	726 (4)
C(13)	21 (5)	387 (2)	692 (5)
C(14)	−7 (5)	406 (2)	563 (5)
C(15)	62 (5)	407 (2)	470 (5)
C(16)	196 (4)	382 (2)	504 (4)
C(17)	274 (4)	381 (2)	392 (4)
C(21)	430 (4)	334 (2)	844 (4)
C(22)	462 (5)	389 (2)	916 (4)
C(23)	490 (5)	384 (3)	1049 (5)
C(24)	485 (4)	329 (2)	1105 (5)
C(25)	451 (4)	276 (2)	1040 (5)
C(26)	417 (4)	279 (2)	908 (4)
C(27)	349 (5)	224 (3)	842 (5)
C(31)	439 (4)	274 (2)	613 (4)
C(32)	333 (4)	240 (2)	540 (4)
C(33)	360 (5)	180 (2)	495 (4)
C(34)	491 (5)	156 (2)	514 (4)
C(35)	572 (4)	192 (2)	575 (4)
C(36)	561 (4)	249 (2)	623 (4)
C(37)	680 (4)	281 (2)	693 (4)

[a] Estimated standard deviations are in parentheses. The calculated hydrogen coordinates have been deposited in the supplementary material.

In I the mercury atom takes part in three strong bonds (Hg–P = 2.378 (1), Hg–O(1) = 2.194 (5), Hg–O(3) = 2.292 (4) Å); a fourth weaker bond (Hg–$O(3^I)$ = 2.523 (4) Å) produces the dimer structure. The remaining oxygen atoms O(2) and O(4) of the two acetate ligands lie at distances (2.836 (6) and 2.918 (5) Å) from mercury which are comparable with the sum of the relevant van der Waals radii (2.90 Å) and at best represent weak interactions. The three strong bonds to mercury define a distorted trigonal-planar coordination (sum of relevant bond angles 358°) with the mercury atoms displaced 0.15 Å from the P–O(1)–O(3) plane toward $O(3^I)$. We previously described[3] the mercury coordination in III as a distorted square pyramid because the Hg–O bridge bond lengths were comparable (2.48 and 2.50 Å) and another oxygen atom was clearly within bonding distance (2.73 Å).

Table V. Interatomic Distances (Å) and Angles (deg) for $[HgP(o\text{-tol})_3(OAc)_2]_2$[a]

(a) Interatomic Distances			
Hg–P	2.41 (1)	C(3)–C(4)	1.50 (8)
Hg–O(1)	2.36 (4)	C(4)–O(3)	1.27 (7)
Hg–O(2)	2.63 (4)	C(4)–O(4)	1.26 (8)
Hg–O(3)	2.20 (4)	P–C(11)	1.87 (6)
Hg–$O(3^I)$	2.73 (4)	P–C(21)	1.81 (6)
Hg–O(4)	2.77 (4)	P–C(31)	1.75 (6)
C(1)–C(2)	1.47 (9)	C–C[b]	1.41 (9)
C(2)–O(1)	1.29 (7)	CH_3–$C(sp^2)$[c]	1.53 (9)
C(2)–O(2)	1.28 (7)		
(b) Angles			
P–Hg–O(1)	120 (1)	Hg–P–C(21)	110 (3)
P–Hg–O(2)	108 (1)	Hg–P–C(31)	113 (3)
P–Hg–O(3)	149 (1)	Hg–O(1)–C(2)	102 (4)
P–Hg–$O(3^I)$	108 (1)	Hg–O(2)–C(2)	90 (4)
P–Hg–O(4)	103 (1)	Hg–O(3)–Hg^I	108 (4)
O(1)–Hg–O(2)	51 (2)	Hg–O(3)–C(4)	108 (4)
O(1)–Hg–O(3)	91 (2)	Hg^I–O(3)–C(4)	120 (4)
O(1)–Hg–$O(3^I)$	79 (2)	Hg–O(4)–C(4)	81 (4)
O(1)–Hg–O(4)	133 (2)	O(1)–C(2)–O(2)	116 (7)
O(2)–Hg–O(3)	94 (2)	O(1)–C(2)–C(1)	122 (7)
O(2)–Hg–$O(3^I)$	129 (2)	O(2)–C(2)–C(1)	120 (7)
O(2)–Hg–O(4)	99 (2)	O(3)–C(4)–O(4)	120 (7)
O(3)–Hg–$O(3^I)$	72 (2)	O(3)–C(4)–C(3)	119 (7)
O(3)–Hg–O(4)	51 (2)	O(4)–C(4)–C(3)	121 (7)
$O(3^I)$–Hg–O(4)	108 (2)	C–P–C[c]	108 (3)
Hg–P–C(11)	109 (3)	P–C–C[c]	120 (5)
		C–C–C[d]	120

[a] The superscript I refers to the atom at equivalent position $1 - x, 1 - y, 1 - z$. [b] Mean aromatic value. [c] Mean value. [d] Mean phenyl value.

With the benefit of hindsight and our analysis of other mercury structures[5] it is now clear that a predominant feature of mercury geometry in I, II, and III, as well as in $[HgP(mesityl)_3(NO_3)_2]_2$,[16] involves three strong bonds (one Hg–P and two Hg–O) to mercury which are close to planar. The difference in lengths (and presumably strengths) of the Hg–O(3) and Hg–$O(3^I)$ bond lengths (0.23 Å) probably accounts for the predominance of the monomer form of I in dichloroethane solution.

An exactly analogous situation is found for the mercury coordination in II. Thus, there are three strong bonds (Hg–P = 2.41 (1), Hg–O(1) = 2.36 (4), Hg–O(3) = 2.20 (4) Å) which are coplanar to within the limited accuracy of the data (the sum of the bond angles is 360°), and a fourth weaker bond (Hg–$O(3^I)$ = 2.73 (4) Å) leads to the dimeric structure. The remaining two oxygen atoms O(2) and O(4) lie slightly closer to Hg (2.63 and 2.77 (4) Å, respectively) than was found in I as a direct consequence of the different steric requirements

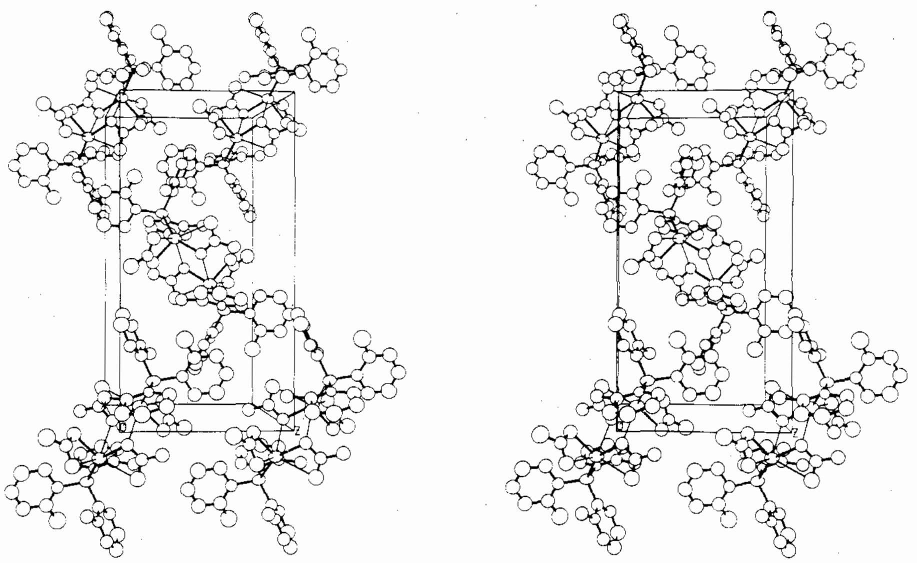

Figure 2. Stereoview of the crystal structure of $[HgP(o\text{-tol})_3(OAc)_2]_2$.

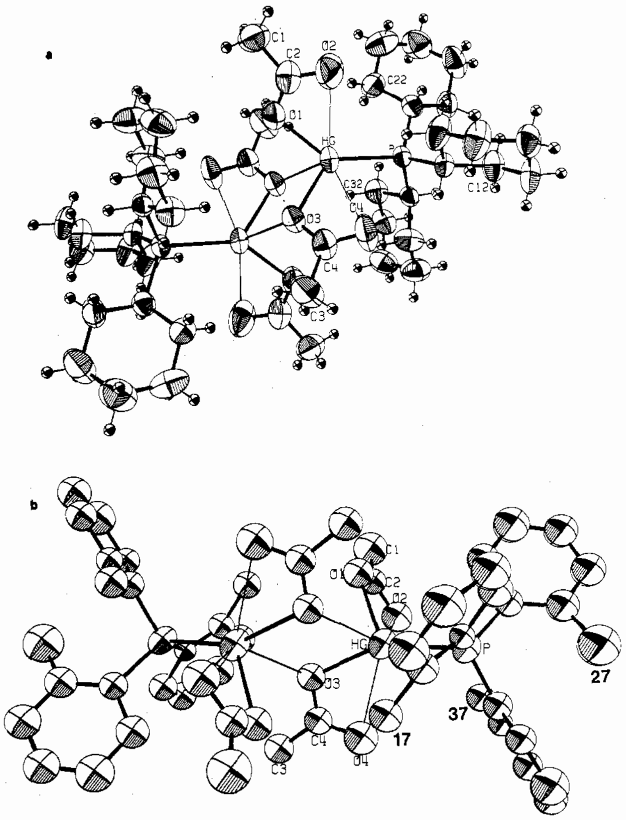

Figure 3. Views of the centrosymmetric dimeric structures (a) $[HgPCy_3(OAc)_2]_2$ and (b) $[HgP(o\text{-tol})_3(OAc)_2]_2$. The unique mode of acetato bridging is shown with our numbering schemes.

of the notionally bulkier $P(o\text{-tol})_3$ ligand (see below).

The mode of acetato bridging in I and II, in which dimers are formed involving only *one* bridging acetato oxygen, has not been found previously; bridging via acetato groups has always been considered to involve both oxygen atoms.[17] Although the infrared acetato bands of I (see Experimental Section) are suggestive of the presence of at least two kinds of acetato groups, infrared spectroscopic studies of II and related $HgPR_3(OAc)_2$ complexes[8] did not allow differentation between any bridging type and the unsymmetrical bidentate modes found, for example, in $HgP(t\text{-Bu})_3(OAc)_2$, which is shown by X-ray studies[4] to be monomeric with asymmetric Hg–O bonds (2.25, 2.66 and 2.27, 2.58 (1) Å).

In both I and II the coordination at the bridging oxygen atom O(3) (Figure 3) is approximately tetrahedral (Tables III and V), whereas in the essentially isostructural $[HgPCy_3(NO_3)_2]_2$[3] the bridging nitrato oxygen had *nearly* trigonal-planar coordination with the atoms of the $(HgONO_2)_2$ moiety close to coplanar.

In I the C–O bond lengths in the acetato group are inversely related to the relevant Hg–O distances, the shorter Hg–O distances being associated with longer C–O bonds and vice versa, as expected. The lower accuracy for dimensions of II precludes any such comparison in its case.

The coordination about phosphorus is essentially tetrahedral with angles at phosphorus in the ranges 107–112° in I and 104–113° in II; in $P(o\text{-tol})_3$,[19] the C–P–C angles are in the range 101.6–103.4 (1)°. The Hg–P bond lengths 2.378 (1) Å (I) and 2.41 (1) Å (II) are comparable with those found in $HgP(t\text{-Bu})_3(OAc)_2$ (2.371 (4) Å),[4] in $HgPPh_3NO_3$ (2.395 (3) Å),[20] in $HgPCy_3(SCN)_2$[2] (2.411 (3) Å), and in III (2.395 (2) Å).[3] The mean P–C bond lengths of 1.836 (6) Å in I and 1.81 (6) Å in II are in accord with expected values as are the dimensions (Tables III and V) of the cyclohexyl and *o*-tolyl rings.

The ligand profiles[5] of PCy_3 in I and $P(o\text{-tol})_3$ in II are shown in Figure 4. For the PCy_3 group the ligand profile is a typical representative of a relatively uncrowded system and compares well with the ligand profile of, for example, PCy_3 in $[HgPCy_3(NO_3)_2]_2$. The cyclohexyl rings adopt chair conformations similar to those found in $[HgPCy_3(NO_3)_2]_2$. The torsion angles (Hg–P–C–H) which describe the conformation of the cyclohexyl rings are given in the ligand profile diagram and these values (86, 63, and 177°) can be compared with the values (95, 65, and 172°) reported for $[HgPCy_3(NO_3)_2]_2$.[5] The semicone angles ($\theta/2$) for I are 84.5, 95.1, and 88.9° which yield a cone angle (θ) of 179°, as compared to $\theta/2$ angles of 90.5, 89.9, and 90.9° and a cone angle (θ) of 181° for PCy_3 in $[HgPCy_3(NO_3)_2]$.

For the $P(o\text{-tol})_3$ group (Figure 4b) the ligand profile shows that the *o*-tolyl rings do not adopt a regular propeller conformation as was found in $[HgP(o\text{-tol})_3Cl{\cdot}ClO_4]_2$[5,18] and in the uncomplexed phosphine $P(o\text{-tol})_3$;[19] the Hg–P–C–C(*i*1) torsion angles for II (32, −125, and −121°) reflect this when compared with the 127–128° values found in $[HgP(o\text{-tol})_3Cl{\cdot}ClO_4]_2$. Semicone angles $\theta/2$ for II are 86.6, 99.7, and 99.8°, leading to a mean cone angle, θ, of 191° for the $P(o\text{-tol})_3$ ligand; this value is slightly smaller than was found in the relatively uncrowded $[HgP(o\text{-tol})_3Cl{\cdot}ClO_4]_2$ (198°) but larger than the value 183°[5] found in more crowded environments.

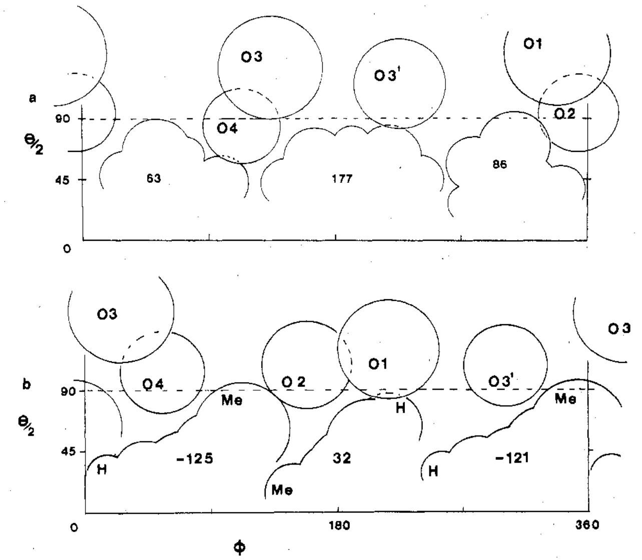

Figure 4. Ligand profiles for (a) PCy_3 in $[HgPCy_3(OAc)_2]_2$ and (b) $P(o\text{-tol})_3$ in $[HgP(o\text{-tol})_3(OAc)_2]_2$. The ordinate is the maximum semicone angle $\theta/2$; the abscissa is the angle ϕ through which a cone generating vector Hg→X is rotated about the Hg–P bond. For full details see ref 5. Also included in the profile diagrams are the outlines of the encroaching acetato oxygen atoms. The numbers under the profile curves are values of the torsion angles (a) Hg–P–C–H and (b) Hg–P–C–C(H).

The encroaching acetato atoms are also shown in the ligand profiles for I and II, and it can be seen that in spite of the larger overall cone angle for the $P(o\text{-tol})_3$ group the gaps between the *o*-tolyl moieties are large enough to allow the acetato oxygen to get close enough to the mercury to form the dimer; such was not the case in $HgP(t\text{-Bu})_3(OAc)_2$ where dimer formation is not allowed because there are no large gaps between the *tert*-butyl moieties to accommodate a potentially bridging oxygen.[4]

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Registry No. I (dimer), 70644-13-2; I (monomer), 66119-64-0; II (dimer), 70644-14-3; II (monomer), 66119-59-3.

Supplementary Material Available: Listings of structure factor amplitudes, calculated hydrogen coordinates, thermal parameters, and bond lengths and angles involving the cyclohexyl and *o*-tolyl rings (37 pages). Ordering information is given on any current masthead page.

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(9) Crystals of II decomposed fairly rapidly in the X-ray beam and an initial data collection using the same scan times as for I was abandoned because of severe decomposition. Data collected by more rapid scans (Table I) were less affected by decomposition but are not as accurate.
(10) Calculations were performed on the University of Guelph IBM 370/155 computer using our own data reduction programs.
(11) Numerical absorption corrections were applied by using a locally modified version of DABS (R. F. Dellaca, University of Canterbury, Christchruch, New Zealand).
(12) Fourier and least-squares calculations were performed by using the SHELX program system written by G. M. Sheldrick, University Chemical Laboratory, Cambridge CB2 1EW, England.
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