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**Structural Studies of Steric Effects in Phosphine Complexes. Part XII<sup>1</sup>. Synthesis, Characterisation, and Crystal and Molecular Structure of Bis(trifluoroacetato)(trimesitylphosphine)mercury(II) Dimer, [Hg(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>P(mesityl)<sub>3</sub>]<sub>2</sub>\***

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The synthesis and crystal and molecular structure of the bis(trifluoroacetato)(trimesitylphosphine)mercury(II) dimer are reported. Crystals are triclinic, space group  $P\bar{1}$  with one centrosymmetric dimer in a unit cell of dimensions  $a = 12.854(3)$ ,  $b = 12.877(4)$ ,  $c = 12.405(2)$  Å,  $\alpha = 107.34(2)$ ,  $\beta = 118.55(2)$ ,  $\gamma = 63.65(2)^\circ$ . The structure was solved by the heavy atom method and refined by full-matrix least-squares calculation,  $R = 0.051$  for 1656 observed reflections measured by diffractometer. The mercury coordination is characterized by three strong nearly coplanar bonds (Hg-P 2.415(5), Hg-O(12) 2.29(2), Hg-O 2.18(2) Å) and two weaker bonds (Hg-O(22) 2.95(2) and Hg-O(11) 2.66(2) Å). The Pmes<sub>3</sub> ligand has a regular propeller conformation (Hg-P-C-C torsion angles 45—49°), enlarged C-P-C angles (mean 112.6(9)°), decreased Hg-P-C angles (mean 106.2(6)°), and a maximum cone angle of 208°. Bridging in the solid state utilizes both oxygens of the CF<sub>3</sub>CO<sub>2</sub> moiety; the complex becomes monomeric in dichloroethane solution. Infrared, <sup>1</sup>H, and <sup>31</sup>P NMR data are discussed.

## INTRODUCTION

Our study of metal complexes of tertiary phosphines containing bulky substituents has recently focused on the bulkiest known phosphine, trimesitylphosphine.<sup>1-5</sup> Facile metallation of trimesitylphosphine and its arsine analogue readily occurs with palladium(II) and platinum(II).<sup>4,5</sup> Application of the concept of a 'ligand profile'<sup>6</sup> has provided maximum cone angle data and has allowed precise comparison of the conformation of the mesityl groups from the X-ray analysis of the complexes [HgEmes<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (where E = As<sup>1</sup> and P<sup>3</sup>, and mes = C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>, and [Ag(Pmes<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub>.<sup>2</sup>

In continuing our structural studies of bulky phosphine complexes we report herein the preparation, characterization, and crystal and molecular structure determination of [HgPmes<sub>3</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>]<sub>2</sub>. Particular interest focuses not only on the bulkiness of trimesitylphosphine but on the mercury coordination geometry<sup>7</sup> and the bonding mode of the trifluoroacetato group.<sup>8</sup>

\* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

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## EXPERIMENTAL

Spectroscopic and other physical measurements were obtained as described previously.<sup>9</sup> Trimesitylphosphine was prepared by the literature method.<sup>10</sup>

*Preparation of the Bis(trifluoroacetato)(trimesitylphosphine)mercury(II) Dimer, [HgPmes<sub>3</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>]<sub>2</sub>.*

A solution of Pmes<sub>3</sub> (0.535 g, 1.38 mmol) in absolute ethanol (100 mL) was added to a solution of Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> (0.585 g, 1.37 mmol) in dry cooled ethanol (10 mL). The clear solution was refluxed under dinitrogen for 1 h before removal of the solvent on a rotary evaporator. The residue was washed with ether and recrystallized from dichloromethane/ether as colourless crystals; m. p. 204–205 (dec.) Anal. Calcd for [HgPmes<sub>3</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>]<sub>2</sub> C, 45.68; H, 4.08. Found: C, 45.44; H, 4.10.

Crystal data for [HgPmes<sub>3</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, C<sub>62</sub>H<sub>66</sub>F<sub>12</sub>Hg<sub>2</sub>O<sub>8</sub>P<sub>2</sub>,  $M_r = 1630.1$ ,  $a = 12.854(3)$ ,  $b = 12.877(4)$ ,  $c = 12.405(2)$  Å,  $\alpha = 107.34(2)$ ,  $\beta = 118.55(2)$ ,  $\gamma = 63.65(2)^\circ$ ,  $V = 1606.6$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 1.68$  g cm<sup>-3</sup>,  $F(000) = 800$ , Mo K $\alpha$  radiation  $\lambda = 0.71069$  Å  $\mu$  (Mo K $\alpha$ ) = 47 cm<sup>-1</sup>. Space group  $P1$  or  $P\bar{1}$ ,  $P\bar{1}$  assumed and confirmed by the analysis. The dimeric molecule has crystallographic inversion symmetry.

Preliminary photographic work with Weissenberg and precession cameras showed that the crystals did not diffract strongly at high  $\theta$  values, and established triclinic crystal symmetry. Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 21 reflections (with  $\theta$  in the range 10–15°) measured on a CAD-4 diffractometer. Intensity data were collected using the  $\omega - 2\theta$  scan technique and monochromated Mo K $\alpha$  radiation to a maximum  $\theta$  (Mo K $\alpha$ ) of 18°, with a small (0.1 × 0.3 × 0.3 mm) crystal. The intensities of three well separated reflections were monitored at regular intervals and over the course of the data collection their intensities decreased by 19%. Data were corrected for decay by appropriate scaling and for florentz, polarization and absorption factors. The data with  $I > 3\sigma(I)$  (1656) were retained, labelled observed, and used in structure solution and refinement.

## STRUCTURE SOLUTION AND REFINEMENT

The coordinates of the Hg atom were obtained from an analysis of a three-dimensional Patterson function and the remaining non-hydrogen atoms were located in a heavy-atom-phased Fourier summation. Refinement with unit weights was by full-matrix least-squares<sup>11</sup> calculations initially with isotropic vibration parameters. In the penultimate round of calculations the atoms, except the mesityl carbons, were allowed anisotropic motion. The CF<sub>3</sub> moieties had large vibration parameters and in the final round of calculations they were treated in rigid groups with C—F 1.32 Å and C—C 1.54 Å. A difference map at the conclusion of the refinement showed some diffuse maxima around the CF<sub>3</sub> groups and in positions near to those expected for some hydrogen atoms. In view of the fact that the crystal did not diffract well and decayed in the X-ray beam, no allowance for hydrogen was made. At convergence,  $R$  and  $R_w (= \sum \omega \Delta^2 / \sum \omega F_o^2)^{1/2}$  were 0.051. Scattering factors used in the structure factor calculations were taken from references<sup>12,13</sup> and allowance was made for anomalous dispersion.<sup>14</sup> The final coordinates are given in Table I and molecular dimensions are summarized in Table II. Table III gives the thermal parameters. A listing of observed and calculated structure amplitudes is available. A stereoview of the centrosymmetric dimer with the numbering scheme is shown in Figure 1. Figure 2 (in which the mesityl rings have been omitted for clarity) shows the thermal ellipsoids.

TABLE I  
*Final Fractional Coordinates (x 10<sup>4</sup>)*

Atom	x	y	z
Hg	4777(1)	1823(1)	4369(1)
P	3055(6)	2876(5)	2651(5)
O(11)	4806(17)	433(17)	6357(15)
O(12)	4479(19)	2196(15)	6142(17)
C(11)	4645(17)	1465(17)	6726(11)
C(12)	4645	1962	8020
F(11)	3516	2753	7912
F(12)	5512	2447	8656
F(13)	4904	1111	8600
O(21)	6825(15)	1121(18)	5428(18)
O(22)	6880(19)	2592(18)	5056(20)
C(21)	7383(12)	1709(19)	5504(18)
C(22)	8806	1272	6349
F(21)	9367	1841	6214
F(22)	9322	145	6050
F(23)	8949	1456	7509
C(111)	1926(19)	4054(16)	3208(17)
C(112)	2440(19)	4714(17)	4338(18)
C(113)	1602(22)	5625(18)	4817(19)
C(114)	301(23)	5859(19)	4250(21)
C(115)	-187(21)	5239(19)	3155(20)
C(116)	592(21)	4343(17)	2623(13)
C(117)	3850(20)	4587(17)	5022(18)
C(118)	-577(26)	6890(23)	4842(22)
C(119)	-89(23)	3752(20)	1359(22)
C(121)	3803(19)	3379(19)	2091(17)
C(122)	4905(22)	2593(18)	1966(19)
C(123)	5712(23)	2964(20)	1774(21)
C(124)	5285(22)	4174(19)	1689(19)
C(125)	4179(21)	4946(17)	1744(18)
C(126)	3388(21)	4597(17)	1920(18)
C(127)	5396(21)	1264(19)	1953(20)
C(128)	6229(25)	4575(22)	1589(23)
C(129)	2119(22)	5527(19)	1909(20)
C(131)	2380(19)	1797(17)	1520(18)
C(132)	2196(19)	1047(17)	1989(18)
C(133)	1872(21)	98(18)	1207(20)
C(134)	1735(22)	-67(19)	-1(21)
C(135)	1834(23)	660(21)	-505(22)
C(136)	2152(21)	1659(19)	250(20)
C(137)	2221(20)	1227(18)	3261(19)
C(138)	1399(26)	-1172(23)	-849(25)
C(139)	2138(24)	2499(21)	-381(22)

TABLE II  
Molecular Dimensions

(a) Bond distances (Å)		C(111) — P — C(121)	113.1(9)
Hg — P	2.415(5)	C(111) — P — C(131)	112.5(9)
Hg — O(12)	2.29(2)	C(121) — P — C(131)	112.2(9)
Hg — O(21)	2.18(2)	O(11) — C(11) — O(12)	126(1)
Hg — O(22)	2.95(2)	O(11) — C(11) — C(12)	121(1)
Hg — O(11)'	2.66(2)	O(12) — C(11) — C(12)	114(1)
P — C(111)	1.81(2)	O(21) — C(21) — O(22)	124(2)
P — C(121)	1.81(2)	O(21) — C(21) — C(22)	114(1)
P — C(131)	1.84(2)	O(22) — C(21) — C(22)	122(1)
O(11) — C(11)	1.23(2)	P — C(111) — C(112)	116(2)
O(12) — C(11)	1.24(2)	P — C(111) — C(116)	125(2)
O(21) — C(21)	1.21(2)	C(112) — C(111) — C(116)	119(2)
O(22) — C(21)	1.18(2)	C(111) — C(112) — C(113)	118(2)
C(111) — C(112)	1.42(3)	C(111) — C(112) — C(117)	125(2)
C(111) — C(116)	1.42(3)	C(113) — C(112) — C(117)	117(2)
C(112) — C(113)	1.40(3)	C(112) — C(113) — C(114)	122(2)
C(112) — C(117)	1.54(3)	C(113) — C(114) — C(115)	119(2)
C(113) — C(114)	1.39(3)	C(113) — C(114) — C(118)	119(2)
C(114) — C(115)	1.36(3)	C(115) — C(114) — C(118)	122(2)
C(114) — C(118)	1.57(3)	C(114) — C(115) — C(116)	121(2)
C(115) — C(116)	1.39(3)	C(111) — C(116) — C(115)	120(2)
C(116) — C(119)	1.54(3)	C(111) — C(116) — C(119)	124(2)
C(121) — C(122)	1.38(3)	C(115) — C(116) — C(119)	116(2)
C(121) — C(126)	1.46(3)	P — C(121) — C(122)	118(2)
C(122) — C(123)	1.45(3)	P — C(121) — C(126)	123(2)
C(122) — C(127)	1.54(3)	C(122) — C(121) — C(126)	119(2)
C(123) — C(124)	1.42(3)	C(121) — C(122) — C(123)	122(2)
C(124) — C(125)	1.35(3)	C(121) — C(122) — C(127)	126(2)
C(124) — C(128)	1.58(3)	C(123) — C(122) — C(127)	113(2)
C(125) — C(126)	1.40(3)	C(122) — C(123) — C(124)	116(2)
C(126) — C(129)	1.53(3)	C(123) — C(124) — C(125)	123(2)
C(131) — C(132)	1.41(3)	C(123) — C(124) — C(128)	116(2)
C(131) — C(136)	1.43(3)	C(125) — C(124) — C(128)	122(2)
C(132) — C(133)	1.40(3)	C(124) — C(125) — C(126)	121(2)
C(132) — C(137)	1.51(3)	C(121) — C(126) — C(125)	119(2)
C(133) — C(134)	1.38(3)	C(121) — C(126) — C(129)	124(2)
C(134) — C(135)	1.35(3)	C(125) — C(126) — C(129)	117(2)
C(134) — C(138)	1.59(3)	P — C(131) — C(132)	117(2)
C(135) — C(136)	1.44(3)	P — C(131) — C(136)	122(2)
C(136) — C(139)	1.50(3)	C(132) — C(131) — C(136)	121(2)
(b) Bond angles (°)		C(131) — C(132) — C(133)	119(2)
P — Hg — O(11)'	107.4(5)	C(131) — C(132) — C(137)	125(2)
P — Hg — O(12)	117.4(5)	C(133) — C(132) — C(137)	116(2)
P — Hg — O(21)	146.9(5)	C(132) — C(133) — C(134)	119(2)
P — Hg — O(22)	105.2(5)	C(133) — C(134) — C(135)	124(2)
O(11) — Hg — O(12)	105.9(7)	C(133) — C(134) — C(138)	117(2)
O(11)' — Hg — O(21)	80.7(7)	C(135) — C(134) — C(138)	119(2)
O(11)' — Hg — O(22)	116.5(7)	C(134) — C(135) — C(136)	120(2)
O(12) — Hg — O(21)	89.5(7)	C(131) — C(136) — C(135)	117(2)
O(12) — Hg — O(22)	104.9(7)	C(131) — C(136) — C(139)	126(2)
O(21) — Hg — O(22)	45.8(7)	C(135) — C(136) — C(139)	117(2)
Hg — P — C(111)	108.3(6)	Hg — O(12) — C(11)	127(1)
Hg — P — C(121)	104.7(6)	Hg — O(21) — C(21)	114(1)
Hg — P — C(131)	105.5(6)	Hg — O(22) — C(21)	76(1)
		Hg — O(11)' — C(11)	178(1)

The coordinates of the primed atom are obtained by the symmetry operation  $1 - x, -y, 1 - z$ .

TABLE III  
 Thermal Parameters ( $\text{\AA}^2 \times 10^3$ )
(a) Anisotropic values $\ddagger$ 

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Hg	56(1)	56(1)	53(1)	-20(1)	6(1)	25(1)
P	50(5)	52(4)	36(4)	-20(3)	7(3)	15(3)
O(11)	95(15)	85(14)	76(12)	-32(12)	25(11)	11(11)
O(12)	152(19)	59(13)	106(15)	-54(13)	45(13)	18(11)
C(11)	55(20)	27(19)	114(27)	-7(16)	21(17)	-5(18)
C(12)	179(45)	53(24)	137(33)	-9(26)	127(32)	-13(23)
F(11)	108(14)	99(12)	130(13)	-14(11)	78(12)	7(10)
F(12)	218(26)	155(20)	133(18)	-86(18)	25(16)	-6(14)
F(13)	246(23)	92(13)	119(14)	-45(14)	106(15)	21(11)
O(21)	25(12)	124(17)	167(19)	-24(11)	2(11)	104(15)
O(22)	100(17)	98(16)	172(20)	-55(14)	-12(14)	79(15)
C(21)	102(35)	72(24)	115(24)	-58(26)	34(24)	29(20)
C(22)	28(31)	174(46)	216(47)	34(27)	10(30)	130(41)
F(21)	83(17)	214(24)	432(43)	-35(15)	43(20)	206(27)
F(22)	60(14)	101(14)	384(37)	8(12)	60(18)	60(19)
F(23)	133(22)	342(39)	246(30)	-109(24)	-93(22)	172(30)

 $\ddagger$  Coefficients in the temperature factor expression:

$$\exp [-2\pi^2 (U_{11} h^2 a^{*2} + U_{22} k^2 b^{*2} + U_{33} l^2 c^{*2} + 2U_{12} hka^* b^* + 2U_{13} hla^* c^* + 2U_{23} klb^* c^*)]$$

(b) Isotropic values

Atom	$U_{iso}$	Atom	$U_{iso}$
C(111)	43(6)	C(125)	48(6)
C(112)	44(6)	C(126)	53(6)
C(113)	55(6)	C(127)	65(7)
C(114)	63(7)	C(128)	87(8)
C(115)	60(7)	C(129)	67(7)
C(116)	51(6)	C(131)	47(6)
C(117)	51(6)	C(132)	51(6)
C(118)	95(9)	C(133)	60(7)
C(119)	78(8)	C(134)	67(7)
C(121)	41(6)	C(135)	78(8)
C(122)	55(6)	C(136)	60(7)
C(123)	70(7)	C(137)	58(7)
C(124)	61(7)	C(138)	99(9)
		C(139)	83(8)

## DISCUSSION

The title compound involving the bulkiest known phosphine ligand was prepared to allow a direct comparison with the previously characterized complex  $[\text{HgPmes}_3(\text{NO}_3)_2]_2$ .<sup>3</sup> We wished to ascertain not only maximum cone angle data for the phosphine from the 'ligand profile' data derived from the X-ray analysis but also to determine if the trifluoroacetato moiety bonded in a bridging fashion *via* one oxygen from each  $\text{CF}_3\text{CO}_2$  ligand as found for the bridging acetato groups in  $[\text{HgPCy}_3(\text{CH}_3\text{CO}_2)_2]_2$ .<sup>15</sup> Earlier structural determinations also revealed this unique bonding mode for the nitrate group in 1:1 mercury-phosphine complexes.<sup>3,16</sup>

The complex  $[\text{HgPmes}_3(\text{O}_2\text{CCF}_3)_2]_2$ , which is a non-electrolyte in nitromethane ( $\Lambda$  7 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>,  $10^{-3}$  mol · dm<sup>-3</sup>), has a molar mass by osmometry

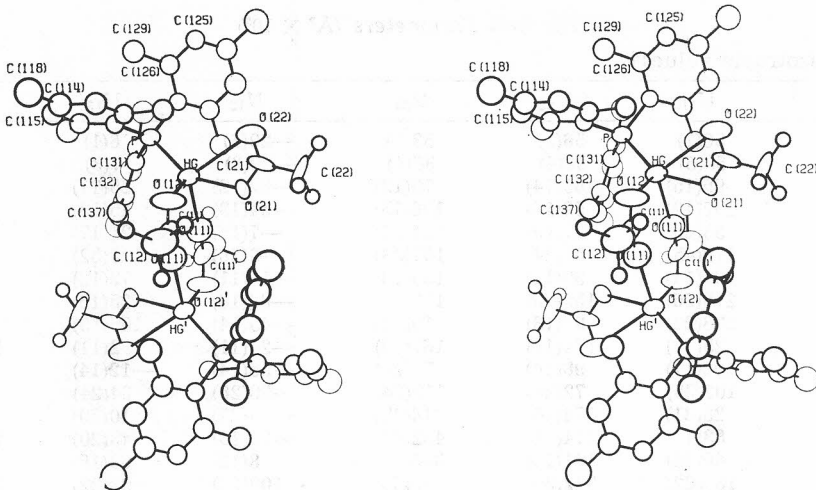


Figure 1. A stereoview of  $[\text{Hg}(\text{Pmes}_3)(\text{CF}_3\text{CO}_2)_2]_2$  showing the crystallographic numbering scheme. Atoms marked with a prime are related to those in Table I by the operation  $1-x, -y, 1-z$ .

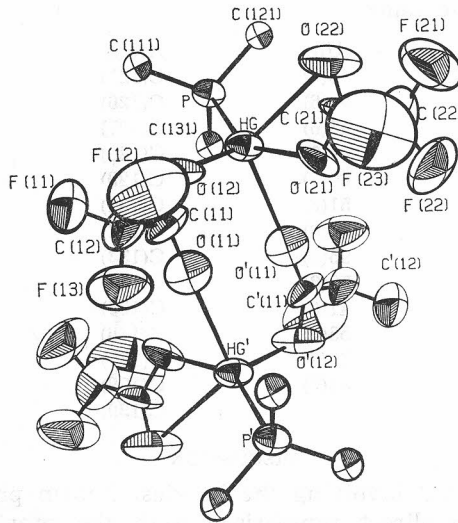


Figure 2. A view  $[\text{Hg}(\text{Pmes}_3)(\text{CF}_3\text{CO}_2)_2]_2$  showing the thermal motion ellipsoids (50% probability level). All the mesityl carbon atoms are omitted for clarity except those bonded to phosphorus.

in dichloroethane (ca.  $10^{-3}$  mol · dm<sup>-3</sup> solution) of 840 (theory; monomer 815). This monomeric value is expected since analogous dimeric 1:1 adducts exhibited facile dissociation if nitrate and acetato bridges.<sup>3,15</sup> The <sup>1</sup>H NMR spectrum of the complex for a CDCl<sub>3</sub> solution at ambient temperature showed a multiplet centred at  $\delta$  2.35 ppm due to the methyl groups and a doublet at  $\delta$  7.02 ppm

( $^4J(^1\text{H} - ^{31}\text{P}) = 5.0$  Hz) assignable to the aromatic protons. The presence of a multiplet signifies inequivalent methyl groups due to restricted rotation about the P—C bonds.<sup>3</sup> The  $^{31}\text{P}$  NMR of the complex in  $\text{CH}_2\text{Cl}_2$  at ambient temperatures shows a chemical shift at +2.41 ppm ( $\delta$ , downfield from  $\text{H}_3\text{PO}_4$  as external reference), giving a coordination chemical shift of 41.4 ppm. The coupling constant  $^1J(^{199}\text{Hg} - ^{31}\text{P})$  of 9453 Hz is large, as expected<sup>17</sup> for a complex containing the electronegative trifluoroacetato groups. In contrast, the complex  $\text{HgPPh}_3(\text{O}_2\text{CCF}_3)_2$  of unknown<sup>18</sup> but probably similar structure has a coupling constant of 9111 Hz. The measurement of  $^1J(^{199}\text{Hg} - ^{31}\text{P})$  at ambient temperature attests to the non-lability of the phosphines in both of these complexes; triphenyl-phosphine and other smaller phosphine complexes of mercury(II) halides, acetates and pseudohalides display fast phosphine exchange at room temperature.<sup>9,17,18</sup>

The  $\text{CO}_2$  stretching frequencies for  $[\text{HgPmes}_3(\text{O}_2\text{CCF}_3)_2]_2$  are assigned at  $1668\text{ cm}^{-1}$  and  $1442\text{ cm}^{-1}$ , both for the solid state (halocarbon mull) and in solution ( $\text{CH}_2\text{Cl}_2$ ). The difference in frequency of  $226\text{ cm}^{-1}$  is suggestive of chelating bidentate trifluoroacetato groups rather than monodentate carboxylate groups<sup>8,18</sup> but does not rule out the possibility of bridging modes. This X-ray investigation provides (vide infra) another example of the inability of vibrational spectroscopy to identify the presence of bridging carboxylate groups (in contrast to asymmetrically bidentate ones).<sup>9,15</sup>

In the solid, centrosymmetric dimers are formed (Figure 1) by utilizing both acetate oxygens in each bridging  $\text{CF}_3\text{CO}_2$  moiety in contrast to what was found in the corresponding *o*-tolyl complex  $[\text{HgP}(\text{o-tolyl})_3(\text{CH}_3\text{CO}_2)_2]_2$  where only one oxygen was used in each bridging acetate.<sup>15</sup>

The mercury coordination is essentially trigonal planar with three strong bonds (Hg—P 2.415(2) Å, Hg—O(12) 2.29(2) Å and Hg—O(21) 2.18(2) Å). Centrosymmetric dimer formation involves O(11)' of the bridging  $\text{CF}_3\text{CO}_2$  moiety (at 2.66(2) Å); the remaining oxygen (O(22)) of the non-bridging ligand is only weakly bonded (2.95 Å) to Hg. In the  $[\text{Hg}(\text{Pmes}_3)(\text{NO}_3)_2]_2$  and  $[\text{Hg}(\text{P}(\text{o-tol})_3)(\text{CH}_3\text{CO}_2)_2]_2$  dimers, similar strong three-fold coordination was found around mercury but there were three additional longer Hg—O interactions giving a (3 + 3) coordination in contrast to the (3 + 2) coordination found here, and in  $\text{HgP}(\text{t-Bu})_3(\text{CH}_3\text{CO}_2)_2$ .<sup>19</sup> Presumably the additional steric bulk of the  $\text{CF}_3\text{CO}_2$  moiety over  $\text{NO}_3$  is a significant factor in changing the mode of bridging from mono-dentate in  $[\text{Hg}(\text{Pmes}_3)(\text{NO}_3)_2]_2$  to bidentate in the present molecule.

The phosphorus coordination in the  $\text{Pmes}_3$  ligand is distorted tetrahedral with the Hg—P—C angles averaging  $106.2(6)^\circ$  and the C—P—C angles  $112.6(9)^\circ$  as was found in  $[\text{Hg}(\text{Pmes}_3)(\text{NO}_3)_2]_2$  where the mean Hg—P—C and C—P—C angles are  $105.4(4)$  and  $113.2(5)^\circ$ ; in the free  $\text{Pmes}_3$  ligand<sup>20</sup> the C—P—C angles are  $109.7^\circ$ . The Hg—P bond length (2.415(5) Å) is characteristic of distances found in overcrowded phosphines, e. g. 2.415(4) Å in  $[\text{HgP}(\text{o-tolyl})_3(\text{CH}_3\text{CO}_2)_2]_2$ . The mean P—C (1.82(2) Å), aromatic C—C (1.40(3) Å), and  $\text{CH}_3\text{—C}(\text{sp}^2)$  (1.54(3) Å) are in agreement with those found in other  $\text{Pmes}_3$  structures.<sup>2,3</sup>

As in other  $\text{P}(\text{mesityl})_3$  moieties, steric crowding is relieved by out-of-plane bending of phosphorus and methyl groups and by increases in (P)C—C—CH<sub>3</sub> angles. Thus, the phosphorus atoms are displaced by 0.07 to 0.37 Å from the mesityl ring planes and *o*-methyl groups 0.10 to 0.18 Å. At the *o*-methyl groups

the mean  $\text{CH}_3\text{—C—C(P)}$  angle is  $125^\circ$  with a concomitant decrease in the  $\text{CH}_3\text{—C—C(C)}$  angle ( $116^\circ$ ). In each case, the *o*-methyl groups are displaced on the same side of the ring plane and the phosphorus atom to the other side.

To gauge the steric bulk of the P(mesityl)<sub>3</sub> ligands we have prepared ligand profile diagrams and computed maximum semi-cone angles  $\Theta/2$  as described previously,<sup>1,6</sup> maximum  $\Theta/2$  values are 105.1, 103.6 and  $103.9^\circ$  with a mean value of  $104.1^\circ$  leading to a maximum cone angle  $\Theta$  of  $208^\circ$ , identical to that found in  $[\text{Hg}(\text{Pmes}_3)(\text{NO}_3)_2]_2$ ,<sup>3</sup> and in reasonable agreement with the value  $212^\circ$  predicted by Tolman from molecular models. The P(mesityl)<sub>3</sub> ligand adopts a regular propeller conformation with dihedral angles between the appropriate  $\text{Hg—P—C}$  and mesityl plane in the range  $45\text{—}49(1)^\circ$ , the same values as were found in  $[\text{Hg}(\text{Pmes}_3)(\text{NO}_3)_2]_2$ ,<sup>3</sup> in the free ligand a value of  $44^\circ$  was reported.<sup>20</sup>

It therefore appears that attempting to replace the  $\text{NO}_3$  moieties by bulkier  $\text{CF}_3\text{CO}_2$  ligands causes no change at all in the Pmes<sub>3</sub> conformation. Instead the molecule accommodates the bulkier  $\text{CF}_3\text{CO}_2$  ligand by changing the mode of bridging from a bridge involving one oxygen to one involving both  $\text{CF}_3\text{CO}_2$  oxygen atoms.

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## SAŽETAK

Strukturno proučavanje steričkih efekata u fosfinskim kompleksima. Dio XII.<sup>1</sup>  
Sinteza, karakterizacija, te kristalna i molekularna struktura bis(trifluoroacetato)-  
(trimezitifosfin)živa(II)-dimera,  $[\text{Hg}(\text{CF}_3\text{CO}_2)_2\text{P}(\text{mezitil})_3]_2$

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Opisane su sinteza, te kristalna i molekulska struktura bis(trifluoroacetato)(trimezitifosfin)živa(II)-dimera. Kristali su triklinski, prostorne grupe  $\overline{P1}$ , s jednim centrosimetričnim dimerom u jediničnoj ćeliji:  $a = 12,854(3)$ ,  $b = 12,877(4)$ ,  $c = 12,405(2)$  Å,  $\alpha = 107,34(2)$ ,  $\beta = 118,55(2)$ ,  $\gamma = 63,65(2)^\circ$ . Struktura je riješena metodom teškog atoma i utočnjena metodom najmanjih kvadrata uz upotrebu kompletne matrice;  $R = 0,051$  za 1656 opaženih refleksa, izmjerenih pomoću difraktometra. Koordinaciju žive karakteriziraju tri jake, gotovo koplanarne veze ( $\text{Hg}-\text{P}$  2,415(5),  $\text{Hg}-\text{O}(12)$  2,29(2),  $\text{Hg}-\text{O}(21)$  2,18(2) Å) i dvije slabije veze ( $\text{Hg}-\text{O}(22)$  2,95(2) i  $\text{Hg}-\text{O}(11)$  2,66(2) Å). Ligand  $\text{Pmez}_3$  ima pravilnu konformaciju propelera (torzijski kutevi  $\text{Hg}-\text{P}-\text{C}-\text{C}$  45–49°), povećane kuteve  $\text{C}-\text{P}-\text{C}$  (prosjeak 112,6(9)°), smanjene kuteve  $\text{Hg}-\text{P}-\text{C}$  (prosjeak 106.2(6)°) i maksimalni kut stošca od 208°. U čvrstom stanju iskorištena su oba kisika iz  $\text{CF}_3\text{CO}_2$  za premoštenje, a u dikloroetanskoj otopini kompleks postaje monomernan. Diskutirani su infracrveni, te  $^1\text{H}$  i  $^{31}\text{P}$  NMR podaci.