Structural Studies of Steric Effects in Phosphine Complexes. Part 3.[1] The Synthesis, Characterization, and Molecular Structure of Diacetato-[tris(t-butyl)phosphine]mercury(II)

By **Paul J. Roberts, George Ferguson,* Ram G. Goel,* William O. Ogini,** and **Roderic J. Restivo,** Guelph–Waterloo Centre for Graduate Work in Chemistry, The University of Guelph, Guelph, Ontario, Canada N1G 2Wl

The title complex has been synthesized and found to crystallize in the monoclinic space group $P2_1/c$ with a = 12.326(5), b = 10.938(3), c = 16.005(3) Å, and β = 111.16(1)°. The structure has been solved from diffractometer data using Patterson and Fourier techniques and refined by least-squares methods to a final R of 0.049 for 1 478 independent observed reflections. The geometry at the mercury atom is distorted trigonal bipyramidal with three strong bonds forming a trigonal plane [Hg–P 2.371(4), Hg–O(2) 2.25(1), and Hg–O(4) 2.27(1) Å] and the remaining oxygens of the asymmetrically bidentate acetate groups above and below this plane [Hg–O(1) 2.66(2) and Hg–O(3) 2.58(1) Å]. Other mean dimensions include P–C 1.90(2) Å, Hg–P–C 106.8(5)°, and C–P–C 112.0(7)°. A ligand profile for PBu^t_3 is given and the maximum cone angle for the ligand is 187(2)°.

THE stereochemistry and reactivity of metal complexes of tertiary phosphines depend to a considerable degree on the bulk of the substituents bonded to phosphorus and this has prompted estimations[2,3] of the steric requirements of bulky phosphine ligands in terms of a maximum cone angle, θ. Whereas a number of physical properties show correlation with cone angles, it is abundantly clear that bulky phosphines are better described as irregular conic cogs rather than as solid cones. The concept of a 'ligand profile' has been developed to show not only how the cone angle depends critically on the conformations of the groups bonded to phosphorus, but also to provide quantitative data about the gaps between these moieties. We have been using 'ligand profiles' to evaluate the steric requirements of a number of phosphine ligands, particularly in complexes of d^{10} metals where other ligand effects are largely absent. As part of this systematic study,[1,4] we report herein the preparation, characterization, and crystal and molecular structure determination of $[Hg(O_2CMe)_2(PBu^t_3)]$, the first phosphine complex of mercury(II) acetate to be characterized structurally.

EXPERIMENTAL

General Procedures.—Microanalyses were performed by M.H.W. Laboratories, Garden City, Michigan. The molecular weight of the complex was determined on a Hitachi–Perkin-Elmer 115 osmometer. Conductance, and ^{1}H n.m.r., i.r., and Raman spectral, measurements were made as reported previously.[5] Tris(t-butyl)phosphine[5] was handled either in a glove-box under an oxygen-free dry nitrogen atmosphere, or in a conventional vacuum system.

Preparation and Characterization of Diacetato[tris(t-butyl)-phosphine]mercury(II).—Mercury(II) acetate (1.00 mmol) and tris(t-butyl)phosphine (2.20 mmol) were mixed in 1,2-dichloroethane (25 cm^3). The mixture was stirred for 6 h to give a clear solution which was concentrated *in vacuo* and from which $[Hg(O_2CMe)_2(PBu^t_3)]$ was precipitated by the subsequent addition of light petroleum (b.p. 30—60 °C). The product was recrystallized from 1,2-dichloroethane to give colourless crystals in 87% yield (Found: C, 36.5; H, 6.30. Calc. for $C_{16}H_{33}HgO_4P$: C, 36.9; H, 6.35%).

The ^{1}H n.m.r. spectrum of the complex showed a doublet [δ 1.62 p.p.m., ^3J(P–H) 15.5 Hz] due to the co-ordinated phosphine and a singlet (δ 1.92 p.p.m.) due to the acetyl protons. The i.r. spectrum of the complex in the solid state shows strong bands at 1 575 and 1 403 cm^{-1}. Since there are no i.r. bands due to PBu^t_3 in this region,[6] these bands can be assigned to the CO_2 stretching frequencies[7,8] of the $MeCO_2$ groups and indicate the non-equivalence of the oxygen atoms. That the acetate groups are not present as anions is clear from conductance measurements in nitromethane (10^{-3} mol dm^{-3} solution) which showed the complex to be a non-electrolyte (Λ 0.92 S cm^2 mol^{-1}). The CO_2 frequencies for the complex were unaltered when the i.r. spectrum was recorded in dichloromethane. The additional evidence that the molecular weight of the complex in 1,2-dichloroethane is 512, showing its monomeric constitution in solution, implies that both the acetate groups act as bidentate ligands and that the complex has a five-co-ordinate molecular structure in solution as well as in the solid state. The band at 128 cm^{-1} in the Raman spectrum can be assigned as the Hg–P stretching frequency

---

[1] Part 2, E. C. Alyea, S. A. Dias, G. Ferguson, and R. J. Restivo, *Inorg. Chem.*, 1977, **16**, 2329.

[2] C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313; *J. Amer. Chem. Soc.*, 1970, **92**, 2956.

[3] W. C. Trogler and L. G. Marzilli, *Inorg. Chem.*, 1975, **14**, 2942; H. C. Clark, 1st Chemical Congr. North American Continent, 1975, Inorg. Abstract No. 013.

[4] E. C. Alyea, G. Ferguson, and R. J. Restivo, *J.C.S. Dalton*, 1977, 1845.

[5] E. C. Alyea, G. T. Fey, and R. G. Goel, *J. Co-ordination Chem.*, 1975, **5**, 143.

[6] H. Schumann and L. Rosh, *Chem. Ber.*, 1974, 854.

[7] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' 2nd edn., Wiley–Interscience, New York, 1970, p.223.

[8] 'Spectroscopic Properties of Inorganic and Organometallic Compounds,' 1969, vol. 2, p. 334 and refs. therein.

Table 1

Final co-ordinates (fractional, × 10^5 for Hg, × 10^4 for P, × 10^3 for others) with standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*
Hg	24 782(6)	13 734(6)	23 460(4)
P	2 531(3)	3 541(4)	2 368(2)
C(1)	403(1)	399(1)	322(1)
C(2)	132(1)	407(2)	273(1)
C(3)	234(1)	406(1)	120(1)
C(11)	404(2)	372(2)	416(1)
C(12)	433(2)	528(1)	313(1)
C(13)	496(2)	310(2)	310(1)
C(21)	126(2)	329(2)	350(1)
C(22)	141(2)	543(2)	298(1)
C(23)	13(2)	390(2)	195(1)
C(31)	135(2)	332(2)	51(1)
C(32)	345(2)	369(2)	101(1)
C(33)	210(2)	543(2)	105(1)
C(4)	327(2)	−34(2)	371(1)
C(5)	372(2)	−135(2)	434(1)
C(6)	181(2)	−30(1)	94(1)
C(7)	129(2)	−134(2)	29(1)
O(1)	263(1)	29(1)	90(1)
O(2)	132(1)	−9(1)	150(1)
O(3)	242(1)	25(1)	374(1)
O(4)	374(1)	−6(1)	317(1)
H(5A)	350(7)	−227(2)	398(3)
H(5B)	469(3)	−137(6)	462(5)
H(5C)	342(8)	−139(7)	489(4)
H(7A)	117(8)	−213(3)	65(2)
H(7B)	187(5)	−158(6)	−6(4)
H(7C)	46(4)	−107(5)	−19(4)
H(11A)	350(2)	429(2)	441(1)
H(11B)	495(2)	390(2)	454(1)
H(11C)	386(2)	277(2)	423(1)
H(12A)	430(2)	556(1)	247(1)
H(12B)	519(2)	543(1)	361(1)
H(12C)	370(2)	581(1)	331(1)
H(13A)	501(2)	307(2)	245(1)
H(13B)	472(2)	221(2)	327(1)
H(13C)	579(2)	336(2)	359(1)
H(21A)	193(2)	349(2)	414(1)
H(21B)	130(2)	234(2)	334(1)
H(21C)	42(2)	348(2)	354(1)
H(22A)	202(2)	584(2)	358(1)
H(22B)	55(2)	544(2)	301(1)
H(22C)	141(2)	594(2)	240(1)
H(23A)	−3(2)	300(2)	165(1)
H(23B)	4(2)	458(2)	143(1)
H(23C)	−48(2)	409(2)	227(1)
H(31A)	47(2)	327(2)	50(1)
H(31B)	177(2)	245(2)	69(1)
H(31C)	133(2)	358(2)	−15(1)
H(32A)	424(2)	418(2)	138(1)
H(32B)	317(2)	396(2)	31(1)
H(32C)	361(2)	272(2)	107(1)
H(33A)	272(2)	604(2)	151(1)
H(33B)	125(2)	558(2)	109(1)
H(33C)	206(2)	560(2)	38(1)

Table 2

Bond lengths (Å) and angles (°) with standard deviations in parentheses

(*a*) Bond lengths

Hg–P	2.371(4)
O(1)–Hg	2.66(1)
O(2)–Hg	2.25(1)
O(3)–Hg	2.58(1)
O(4)–Hg	2.27(1)
O(1)–C(6)	1.23(3)
O(2)–C(6)	1.27(3)
O(3)–C(4)	1.24(3)
O(4)–C(4)	1.24(3)
P–C(1)	1.93(1)
P–C(2)	1.88(2)
P–C(3)	1.89(1)
C(1)–C(11)	1.53(2)
C(1)–C(12)	1.48(2)
C(1)–C(13)	1.56(3)
C(2)–C(21)	1.53(3)
C(2)–C(22)	1.53(3)
C(2)–C(23)	1.55(2)
C(3)–C(31)	1.55(2)
C(3)–C(32)	1.55(3)
C(3)–C(33)	1.53(2)
C(4)–C(5)	1.45(3)
C(6)–C(7)	1.51(2)

(*b*) Bond angles

O(1)–Hg–O(2)	52.4(5)
O(1)–Hg–O(3)	125.0(4)
O(2)–Hg–O(3)	88.3(4)
O(1)–Hg–O(4)	87.2(5)
O(2)–Hg–O(4)	90.7(4)
O(3)–Hg–O(4)	52.4(5)
O(1)–Hg–P	116.5(3)
O(2)–Hg–P	136.9(3)
O(3)–Hg–P	118.3(3)
O(4)–Hg–P	132.3(3)
Hg–P–C(1)	106.3(5)
Hg–P–C(2)	107.1(6)
Hg–P–C(3)	107.0(5)
C(1)–P–C(2)	111.8(7)
C(1)–P–C(3)	111.7(7)
C(2)–P–C(3)	112.6(7)
C(6)–O(1)–Hg	82.7(11)
C(6)–O(2)–Hg	101.1(11)
C(4)–O(3)–Hg	85.7(12)
C(4)–O(4)–Hg	100.5(12)
O(3)–C(4)–O(4)	120.9(17)
O(3)–C(4)–C(5)	118.5(20)
O(4)–C(4)–C(5)	120.6(20)
O(1)–C(6)–O(2)	123.5(15)
O(1)–C(6)–C(7)	121.0(20)
O(2)–C(6)–C(7)	115.5(18)
P–C(1)–C(11)	108.2(13)
P–C(1)–C(12)	112.1(10)
P–C(1)–C(13)	108.2(10)
C(11)–C(1)–C(12)	112.0(15)
C(11)–C(1)–C(13)	104.7(14)
C(12)–C(1)–C(13)	111.4(17)
P–C(2)–C(21)	110.5(13)
P–C(2)–C(22)	112.7(14)
P–C(2)–C(23)	109.9(14)
C(21)–C(2)–C(22)	110.6(16)
C(21)–C(2)–C(23)	106.0(16)
C(22)–C(2)–C(23)	106.8(15)
P–C(3)–C(31)	109.7(12)
P–C(3)–C(32)	108.5(10)
P–C(3)–C(33)	113.1(11)
C(31)–C(3)–C(32)	104.4(14)
C(31)–C(3)–C(33)	109.8(12)
C(32)–C(3)–C(33)	111.0(16)

by comparison with the spectra of the complexes [$HgX_2(PBu^t_3)$] in which the corresponding frequencies occur in the range 123—110 cm^{-1}.[9]

Crystal Data.—$C_{16}H_{33}HgO_4P$, $M = 521$, Monoclinic, $a = 12.326(5)$, $b = 10.938(3)$, $c = 16.005(3)$ Å, $\beta = 111.16(1)°$, $U = 2\,012.1$ Å^3, $Z = 4$, $D_m = 1.72$ g cm^{-3}, $F(000) = 1\,024$. Space group $P2_1/c$ (C^5_{2h}, no. 14) from systematic absences

---

[9] E. C. Alyea, S. A. Dias, R. G. Goel, and W. O. Ogini, *Canad. J. Chem.*, in the press.

($h0l$ when $l = 2n + 1$, $0k0$ when $k = 2n + 1$). Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 74.43$ cm^{-1}.

Preliminary Weissenberg and precession photographs provided unit-cell dimensions and determined the space group. Accurate lattice parameters were obtained by least-squares treatment of the diffractometer co-ordinates of 12 reflections for which θ(Mo-K_α) was between 10 and 20°. Three-dimensional intensity data for all the reflections having $\theta \leqslant 20°$ were collected on a computer-controlled Hilger and Watts four-circle diffractometer using graphite-monochromated Mo-K_α radiation and the θ–ω step-scan technique. For each reflection, 36 steps of 0.02° (θ) and 1-s duration were taken through the diffracting position and backgrounds of 9 s were measured at each end of the scan. Standard deviations in intensity were calculated using $\sigma^2(I) = S + 4B + (0.05S)^2$, where S is the scan count, B is the sum of the two backgrounds, and $I = S - 2B$. The crystal turned black during irradiation and the counts from standard reflections measured after every 100 reflections decreased by 17% during the course of the data collection. This was allowed for by appropriate scaling, and Lorentz and polarization corrections were applied. Since a small needle of uniform cross-section was used for the data collection, no corrections for absorption were made. A total of 1 478 independent reflections had $I > 3\sigma(I)$ and were retained as the observed data.

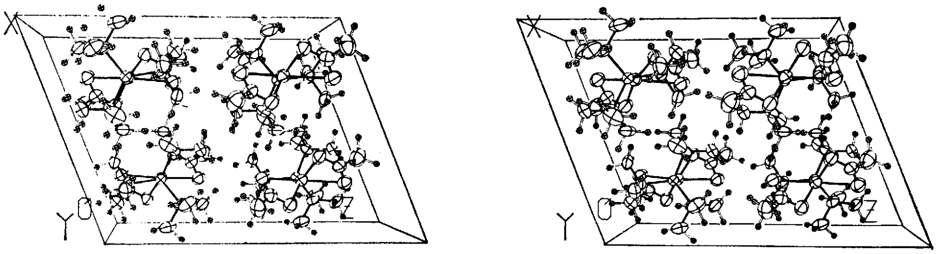

FIGURE 1 A stereoscopic view of the crystal structure of the complex projected down b

The structure was solved by Patterson and Fourier methods and refined by blocked full-matrix techniques * using weights derived from counting statistics. The methyl hydrogen atoms were located from a difference synthesis at R 0.054, but rather than refine them independently we chose to treat them as ideal rigid groups with C–H 1.08 Å, H–C–H 109.5°, and a single isotropic thermal parameter U which subsequently refined to the value 0.11(1) Å^2. The scattering factors of ref. 10 were used for the hydrogen atoms, while the non-hydrogen atoms were refined with anisotropic temperature factors using the scattering factors of ref. 11. Final values of R and R' † were 0.049 and 0.057 respectively. Atomic co-ordinates and their standard deviations are given in Table 1. Table 2 contains bond lengths and valency angles and their standard deviations calculated using the co-variance matrix. A list of calculated and observed structure factors, thermal parameters, and an analysis of variance calculated after the final refinement cycle have been deposited as Supplementary Publication No. 22161 (13 pp.).‡

DISCUSSION

The crystal structure (Figure 1) consists of discrete molecules with intermolecular contacts of normal van der Waals distances (Table 3). The co-ordination geometry of the mercury atom (Figure 2) can be described as distorted trigonal bipyramidal, with the equatorial plane having a root-mean-square deviation of only 0.019 Å. The acetate groups are characterized by mean C–O and C–C distances of 1.25(1) and 1.48(3) Å respectively, and are asymmetrically bidentate, with one oxygen atom tightly bound in the equatorial plane of the mercury atom [mean Hg–O 2.26(1) Å] and the other more loosely bonded in an approximately axial position [mean Hg–O 2.62(4) Å]. The O_{ax}–Hg–O_{eq} chelate angle is 52.4(5)° in both ligands, while the O–Hg–O angle between the two equatorial oxygen atoms is 90.7(4)°. The third equatorial position is occupied by the phosphorus atom situated 2.371(4) Å from the mercury and making P–Hg–O_{eq} angles of 136.9(3) and 132.3(3)° with O(2) and O(4) and P–Hg–O_{ax} angles of 116.5(3) and 118.3(3)° with O(1) and O(3) respectively. The geometry around the phosphorus atom is distorted tetrahedral, with Hg–P–C angles [mean 106.8(2)°] less than, and C–P–C angles [mean 112.0(3)°] greater than, the tetrahedral value. The mean P–C bond length [1.90(2) Å] is within the range of previously reported values.[12]

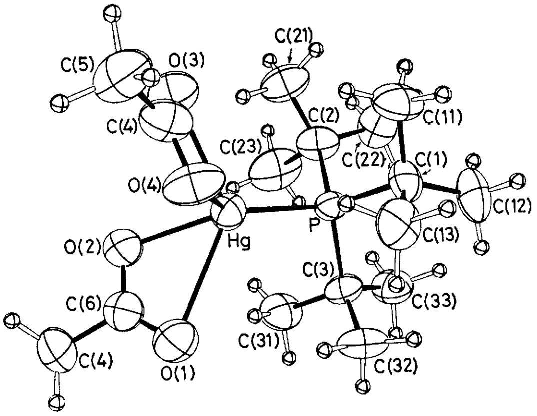

FIGURE 2 The molecular structure of the complex

---

* Fourier and least-squares calculations were performed using the SHELX program system written by G. M. Sheldrick, University Chemical Laboratory, Cambridge CB2 1EW.

† $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$.

‡ For details see Notices to Authors No. 7. *J.C.S. Dalton*, 1977, Index issue.

[10] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[11] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[12] E. C. Alyea, A. Costin, G. Ferguson, G. T. Fey, R. G. Goel, and R. J. Restivo, *J.C.S. Dalton*, 1975, 1294.

In order to give a quantitative estimate of the bulk of the phosphine ligands and of the size of the gaps between the hydrocarbon groups of such species, we have developed the concept of a 'ligand profile.' This graphical representation of the steric requirements of a ligand is constructed by plotting the maximum semi-cone angle $\theta/2$ (Figure 3) subtended at the mercury atom by the vectors Hg–P and Hg–X as a function of the rotation angle ϕ as Hg–X precesses around Hg–P, just making contact with the van der Waals spheres of the ligand atoms. Such a construction for the PBu^t_3 ligand is shown in Figure 4 and serves to emphasize the irregular cog-like nature of the ligand. The CMe_3 groups of the ligand each have one hydrogen which makes a large semi-cone angle, $\theta/2$. The maximum $\theta/2$ values for each CMe_3 moiety are 95.1, 93.9, and 91.9°, leading to a mean cone angle θ of 187(2)°, in excellent agreement with the value of 182° predicted from models.[2] Simple integration of the area under the ligand profile shows that the PBu^t_3 ligand occupies *ca.* 88% of the area below $\theta/2 = 90°$, leaving only 12% 'free' space. The corresponding 'free' areas in complexes of $P(C_6H_{11})_3$ are much larger and vary between 20% in $[\{Hg(NO_3)_2[P(C_6H_{11})_3]\}_2]$[1] and 24% in $[Pt\{P(C_6H_{11})_3\}_3]$.* This allows easy rationalization of the existence of complexes with more than two tricyclohexylphosphine moieties by meshing of the cog-like ligands. We find it difficult, however, to envisage a metal complex containing more than two PBu^t_3 moieties bonded to the central atom.

TABLE 3

Selected intermolecular distances (Å)
(H · · · H <2.6, O · · · H <2.8, C · · · H,O <3.4 Å)

$H(5B^{I}) \cdots H(11C)$	2.55
$H(5B^{II}) \cdots H(32A)$	2.50
$H(5C^{III}) \cdots H(33C)$	2.26
$H(7A^{IV}) \cdots H(31A)$	2.52
$H(7B^{V}) \cdots H(22A)$	2.40
$O(1^{II}) \cdots H(12B)$	2.52
$O(1^{II}) \cdots H(13C)$	2.78
$O(2^{VI}) \cdots H(7C)$	2.73
$O(2^{IV}) \cdots H(21C)$	2.63
$O(2^{VI}) \cdots H(22B)$	2.75
$O(2^{VI}) \cdots H(23C)$	2.68
$O(3^{VI}) \cdots H(23C)$	2.68
$O(3^{III}) \cdots H(32B)$	2.49
$O(4^{II}) \cdots H(32A)$	2.48
$C(4^{VI}) \cdots H(23C)$	3.29
$C(4^{II}) \cdots H(32A)$	3.17
$C(4^{III}) \cdots H(32B)$	3.01
$C(6^{IV}) \cdots H(7C)$	3.01
$C(6^{II}) \cdots H(13C)$	3.14
$C(23^{VII}) \cdots O(3)$	3.28

Symmetry operators are:

I $1 - x, -y, 1 - z$;
II $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$;
III $x, \frac{1}{2} - y, -\frac{1}{2} + z$;
IV $-x, -y, -z$;
V $x, \frac{1}{2} - y, \frac{1}{2} + z$;
VI $-x, \frac{1}{2} + y, \frac{1}{2} - z$;
VII $-x, -\frac{1}{2} + y, \frac{1}{2} - z$

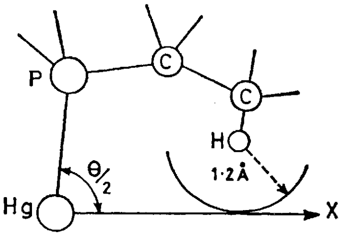

FIGURE 3 Geometrical definition of the semi-cone angle $\theta/2$. The vector Hg–X precesses around the vector Hg–P just grazing the van der Waals spheres of the ligand atoms

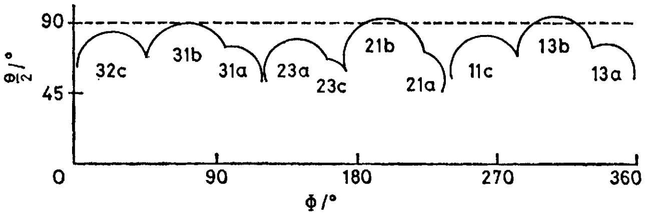

FIGURE 4 Ligand profile for PBu^t_3 in $[Hg(O_2CMe)_2(PBu^t_3)]$. The ordinate is the maximum semi-cone angle $\theta/2$. The abscissa is the angle ϕ through which the vector Hg–X (Figure 3) has been rotated about the Hg–P bond; the origin of ϕ was arbitrarily chosen. The numbers under the curve denote the hydrogen atoms (Figure 2) whose van der Waals spheres define the ligand profile

We thank the National Research Council of Canada for the award of Operating Grants (to G. F. and R. G. G.).

[7/1169 *Received, 4th July,* 1977]

---

* We thank Dr. A. Immirzi for details of the co-ordinates of $[Pt\{P(C_6H_{11})_3\}_3]$ prior to their publication.