X-Ray Crystal and Molecular Structure of Phenyl(triphenylphosphine)-mercury(II) Nitrate†

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Reaction of phenylmercury(II) nitrate with triphenylphosphine in dry ethanol gives the adduct $[HgPh(PPh_3)]NO_3$ whose structure has been determined by *X*-ray crystallography. The complex crystallizes in the monoclinic space group $P2_1/n$ with unit-cell parameters a = 13.119(5), b = 10.529(2), c = 16.233(4) Å, and β = 102.79(1)°. The geometry about mercury(II) is nearly T-shaped with P–Hg–C(Ph) 167.5(2)°. The Hg–P distance of 2.431 (2) Å indicates strong interaction and there is weak interaction between mercury and the nitrate oxygen atoms. This complex represents the first structurally characterized organomercury(II) complex with a tertiary phosphine.

The co-ordination chemistry of phenylmercury(II) has been poorly studied unlike that of methylmercury(II).[1,2] Most studies on organomercury(II) have dealt with nitrogen-containing ligands.[1] Among tertiary phosphine ligands, only one complex, *viz.* $[HgPh(PEt_3)]NO_3$, is known, but its structure is unknown. An attempt by Coates and Lauder[3] to prepare $[HgPh(PPh_3)]NO_3$ led to the disproportionation reaction $2HgPh(PPh_3)(NO_3) \rightleftharpoons Hg(PPh_3)_2(NO_3)_2 + HgPh_2$.

In the present paper we report the stabilization of $[HgPh(PPh_3)]NO_3$ complex and its *X*-ray study. This complex is the first structurally characterized complex of organomercury(II) with phosphorus-containing ligands.

Experimental

Growth of Crystals.—The complex $[HgPh(PPh_3)]NO_3$ was prepared by the addition of a solution of PPh_3(77 mg, 0.29 mmol) in ethanol (10 cm^3) to $HgPh(NO_3)$ (100 mg, 0.29 mmol) in the same solvent (30 cm^3). The mixture was stirred with a magnetic stirrer for 4 h and then filtered. The filtrate was allowed to evaporate slowly (≈5—10 °C) for 4 d when fine transparent crystals were formed. These were separated and dried, m.p. 119—120 °C (Found: C, 48.0; H, 3.4; Hg, 33.3. Calc. for $C_{24}H_{20}HgNO_3P$: C, 47.9; H, 3.3; Hg, 33.9%).

X-*Ray Structure Determination.*—*Crystal data.* $C_{24}H_{20}HgNO_3P$, M = 601.99, monoclinic, a = 13.119(5), b = 10.529(2), c = 16.233(4) Å, β = 102.79(1)°, U = 2 186.5 $Å^3$ (by least-squares refinement of 25 automatically centred reflections, λ = 0.710 69 Å), space group $P2_1/n$, Z = 4, D_c = 1.829 g cm^{-3}, colourless prisms, approximate dimensions 0.4 × 0.4 × 0.5 mm, $F(000)$ = 1 160, μ(Mo-K_α) = 71.3 cm^{-1}.

Data collection and processing. Enraf-Nonius CAD 4 diffractometer; ω—2θ mode with ω scan width = 0.75 + 0.35 tan θ, ω scan speed 3.33° min^{-1}, graphite-monochromated Mo-K_α radiation. 4 729 Reflections ($hk \pm l$; $1 \leqslant \theta \leqslant 25°$) yielding 3 327 unique reflections with $I \geqslant 3\sigma(I)$.

Structure analysis and refinement. The structure was solved by the heavy-atom method. Full-matrix isotropic refinement of all non-hydrogen atoms, with hydrogens in calculated positions, until convergence at R = 0.091 followed by application of a DIFABS[4] absorption correction. Full-matrix anisotropic refinement of all non-hydrogen atoms, hydrogens fixed as before, converted at R = 0.029, R' = 0.035. The weighting scheme $w = 1/[\sigma(I)^2 + (0.06I)^2]^{\frac{1}{2}}$ where I = raw net intensity, gave satisfactory agreement analysis. All calculations were performed on a DEC PDP 11/73 computer using scattering factor data from ref. 5.

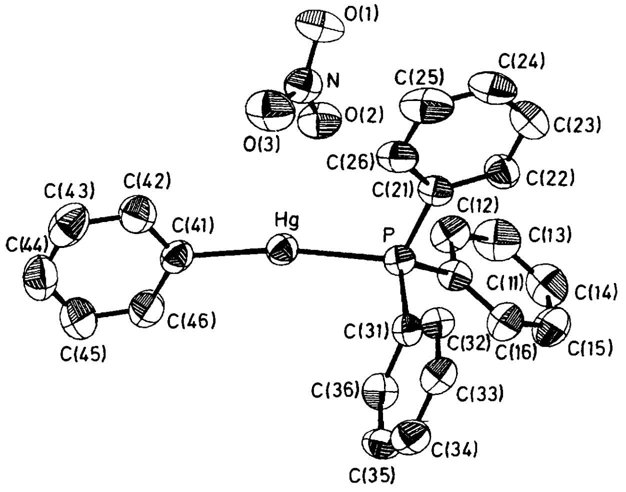

Figure. The molecular structure of $[HgPh(PPh_3)]NO_3$ showing the atom numbering scheme

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Table 1 contains the atomic positional parameters, Table 2 the bond distances and angles. The Figure shows the molecular structure of $[HgPh(PPh_3)]NO_3$. The space group, though non-standard, provides satisfactory Hg–P, Hg–C(41) bond distances and C(41)–Hg–P bond angle.

The mercury–phenyl ring distance [Hg–C(41) 2.090(5) Å] is slightly shorter than the sum of the covalent radii [1.48(Hg) + 0.68(C) = 2.18 Å],[6] but is similar to that found in [HgPh(CN)(phen)] (phen = 1,10-phenanthroline) [2.067(12) Å],[7]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Fractional atomic co-ordinates with estimated standard deviations in parentheses for $[HgPh(PPh_3)]NO_3$

Atom	*x*	*y*	*z*
Hg	0.151 48(2)	0.056 94(2)	0.193 61(1)
C(41)	0.160 7(4)	0.040 6(5)	0.067 1(3)
C(42)	0.106 1(5)	0.122 7(6)	0.007 5(4)
C(43)	0.103 8(6)	0.100 6(7)	−0.077 4(4)
C(44)	0.153 4(6)	−0.001 6(8)	−0.102 0(4)
C(45)	0.207 3(7)	−0.079 1(7)	−0.042 9(4)
C(46)	0.212 8(6)	−0.059 4(6)	0.041 4(4)
O(1)	0.143 3(4)	0.487 3(4)	0.233 8(3)
O(2)	0.223 6(3)	0.305 5(4)	0.251 3(3)
O(3)	0.076 4(4)	0.323 5(4)	0.161 6(3)
N	0.147 4(3)	0.372 5(5)	0.215 3(3)
P	0.105 2(1)	0.038 5(1)	0.330 10(8)
C(11)	0.211 6(4)	0.010 5(5)	0.419 1(3)
C(12)	0.298 5(5)	0.090 3(6)	0.429 7(4)
C(13)	0.376 8(5)	0.079 7(7)	0.502 4(5)
C(14)	0.370 2(5)	−0.006 6(7)	0.563 6(4)
C(15)	0.285 4(5)	−0.086 1(6)	0.553 2(4)
C(16)	0.206 1(5)	−0.077 2(6)	0.481 1(4)
C(21)	0.035 3(4)	0.173 6(5)	0.359 1(3)
C(22)	0.049 4(5)	0.211 7(5)	0.443 1(3)
C(23)	−0.008 0(5)	0.310 8(6)	0.464 4(4)
C(24)	−0.079 9(5)	0.372 3(6)	0.404 6(4)
C(25)	−0.093 4(5)	0.336 1(6)	0.321 2(5)
C(26)	−0.036 5(5)	0.237 9(5)	0.297 8(4)
C(31)	0.015 3(4)	−0.095 2(5)	0.323 8(3)
C(32)	−0.082 8(4)	−0.081 3(5)	0.341 3(3)
C(33)	−0.150 7(4)	−0.816(6)	0.330 7(3)
C(34)	−0.122 5(5)	−0.298 4(6)	0.303 1(3)
C(35)	−0.025 0(5)	−0.311 8(5)	0.286 4(4)
C(36)	0.043 7(4)	−0.212 6(6)	0.296 9(3)

Table 2. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Hg–P	2.431(2)	P–Hg–C(41)	167.5(2)
Hg–C(41)	2.090(5)	C(11)–P–C(21)	105.5(2)
Hg–O(1)	2.787(3)	C(11)–P–C(31)	107.2(2)
Hg–O(2)	2.868(3)	C(21)–P–C(31)	105.2(2)
Hg–O(3)	2.981(3)	P–C(11)–C(12)	117.9(4)
Hg–N	3.343(4)	P–C(11)–C(16)	122.7(4)
Hg–C(11)	3.604(5)	P–C(21)–C(22)	121.1(4)
Hg–C(21)	3.568(5)	P–C(21)–C(26)	120.0(4)
Hg–C(31)	3.449(5)	P–C(31)–C(32)	121.7(4)
P–C(11)	1.797(5)	P–C(31)–C(36)	119.3(4)
P–C(21)	1.810(5)	O(1)–N–O(2)	120.2(5)
P–C(31)	1.825(5)	O(1)–N–O(3)	120.5(5)
O(1)–N	1.249(6)	O(2)–N–O(3)	119.3(5)
O(2)–N	1.257(5)		
O(3)–N	1.238(6)		

$HgPh_2$ [2.085(7) Å],[8] and $Hg(C_6F_5)_2$ [2.090(10) Å].[9] The Hg–P bond distance [2.431(2) Å] is considerably shorter than the sum of the covalent radii [1.48(Hg) + 1.10(P) = 2.58 or 1.50(Hg) + 1.10(P) = 2.60 Å],[6,10] but similar to that found in $Hg(CN)_2(PPh_3)_2$[Hg–P(1), 2.434(5) and Hg–P(2), 2.589(5) Å] and $Hg(PPh_3)_2(NO_3)_2$ [Hg–P 2.451(1) Å].[11] All the bond distances in the phenyl ring bonded to mercury atom are satisfactory.

The nitrate ion occupies two symmetry-related positions about Hg and allows two oxygen atoms, O(2) and O(3), in the *xyz* position as listed, to be 2.87 and 2.98 Å from mercury, while O(1) in the position ($\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$) lies 2.79 Å away. The Hg–O distances close to the sum of the van der Waals radii [1.50(Hg) + 1.40(O) = 2.90 or 1.73(Hg) + 1.40(O) = 3.13 Å][6,11] indicate weak interaction of nitrate oxygens similar to that [2.94(2) Å] observed[12] in $[HgPh(C_4H_7N_3O)]NO_3 \cdot H_2O$ [$C_4H_7N_3O$ is creatinine $\overline{NC(NH_2)NMeCH_2CO}$]. The Hg–O single bond distance[11] is of the order of 2.14 Å [1.48(Hg) + 0.66(O) Å].

As expected, three rings of the PPh_3 ligand lie in different planes. The dihedral angles between planes (1) and (2), (1) and (3), (1) and (4), (2) and (3), (3) and (4), and (2) and (4) are 86.4, 81.2, 94.3, 79.9, 87.9, and 167.5° respectively. The angle between the planes (2) and (4) shows that C(41)–Hg–P is not linear but is bent at 167.5(2)°, a phenomenon often observed in organomercury(II) complexes[1] in which the angle about mercury tends not to be 180°. Thus in the complex $[HgPh(PPh_3)]NO_3$ the geometry about mercury can be regarded as nearly T-shaped with the third axis lying in the plane containing N–O(1) and bisecting O(2) ⋯ O(3) of the NO_3 group.

The CPC angles of 105.5(2), 107.2(2), and 105.2(2)° are in agreement with those reported for $[Hg(PPh_3)_2I_2]$[13] (105.5°) and $[Hg(PPh_3)_2(SCN)_2]$ (107.2°).[14] They are larger in the metal complexes than in free PPh_3 (103°)[15] but smaller than the ideal tetrahedral angle of 109.5°. The mean P–C bond lengths (1.797–1.825 Å) and aromatic C–C bond lengths (1.38—1.39 Å) are in agreement with the values found for the free phosphine.[15]

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