Inorganica Chimica Acta, 141 (1988) 155–156

Mercury(II) Halide Complexes of Tertiary Phosphines.
Part 11*. Crystal Structure of α-HgI_2PPr_3; the Adoption of an Unsymmetrical $I_2Hg(\mu\text{-}I)_2Hg(PPr_3)_2$ Arrangement

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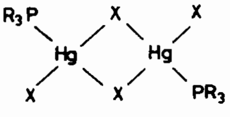
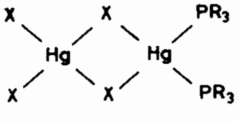
(Received June 26, 1987)

X-ray analysis of the α-form of HgI_2PPr_3 shows the 1:1 complex adopts the unsymmetric dimeric arrangement $I_2Hg(\mu\text{-}I)_2Hg(PPr_3)_2$ in the solid state. Although both metal atoms are four coordinate, coordination about the mercury to which both phosphine ligands are attached is considerably distorted. In particular the P–Hg–P angle is found to be 149.1(5)° and is attributed to the strong σ-donating ability of the PPr_3 ligands.

Tertiary phosphines give rise to a wide range of complexes with mercury(II) halides of which the 1:1 and 1:2 complexes $HgX_2(PR_3)_n$ (n = 1 or 2) have been most widely studied. Although the $HgX_2(PR_3)_2$ complexes exist as discrete monomers (albeit with differing degrees of tetrahedral distortion [1–4]), the 1:1 complexes formed with mercury(II) chloride have been shown to adopt a remarkable variety of structural types in the solid state, *viz.* (i) polymeric arrangements containing five coordinate mercury (R = Me, Et, or CH_2CH_2CN), (ii) a discrete tetrameric arrangement in α-$HgCl_2(PBu_3)$, (iii) centrosymmetric dimers [R = Ph, Cy, TPP†, or Bu (β-form)]. These structural types can all be considered to be based on the centrosymmetric dimer (I) present either as the discrete entity itself or associated to give polymeric arrangements [5–11].



I



II

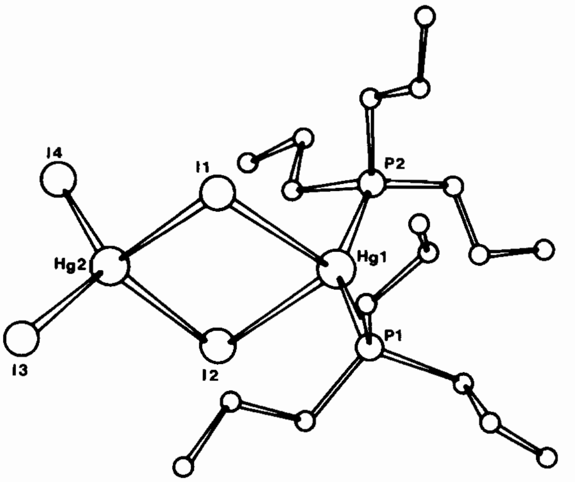


Fig. 1. Molecular structure of α-HgI_2PPr_3. Selected bond distances and angles: P1–Hg1–P2 149.1(5)°; Hg1–P 2.421(15), 2.457(14); Hg1–I_b 3.027(4), 3.050(5); Hg2–μ(I) 2.921(4), 2.937(5); Hg2–I_t 2.685(5), 2.694(4) A (b = bridging; t = terminal).

^{31}P NMR studies [11–13] have shown that for the bromo and iodo complexes $HgX_2(PBu_3)$ (X = Br or I) the unsymmetrical dimer (II) is also present in solution as a minor component. We herein report the molecular structure‡ of α-$HgI_2(PPr_3)$, the first evidence for the existence of the unsymmetrical isomer (II) in the solid state. Although both mercury atoms are four coordinate (Fig. 1) a highly distorted tetrahedral arrangement is adopted about Hg1 and this may be attributed to the strong σ-donating ability of the PPr_3 ligands. The P–Hg–P angle of 149.1(5)° is comparable to that found [2, 4] in 1:2 complexes $HgX_2(PR_3)_2$ formed by strong σ-donating phosphines [X = Cl, R = Et 158.5(5)°; X = Br, R = CH_2CH_2CN 151.3(1)°]. In contrast the P–Hg–P angle in $HgI_2(PPh_3)_2$, 108.95(9)°, lies [15] close to a regular tetrahedral value and reflects the poorer σ-donating ability of triphenylphosphine compared to the trialkyl phosphines. The molecular structure in fact closely resembles that adopted [16] by the mixed-metal complex $I_2Cd(\mu\text{-}I)_2Hg(PPr_3)_2$ [P–Hg–P 152.8(1)°; Hg–P 2.410, 2.424(4) Å; Hg–μ(I) 3.056, 3.077(1) Å].

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*For Part 10, see ref. 1.

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†TPP = 1,2,5-(triphenyl)phosphole.

‡Crystal data: $C_{18}H_{42}P_2Hg_2I_4$, M = 1229.3, monoclinic, space group $P2_1/c$, a = 10.707(3), b = 13.766(5), c = 22.399(8) A, β = 96.5(1)°, U = 3280.3 A^3, Z = 4, D_c = 2.49 g cm^{-3}, $F(000)$ = 2208 electrons, graphite monochromated Mo Kα X-radiation, λ = 0.71069 A, μ(Mo Kα) 126.3 cm^{-1}; R = 0.103, R' = 0.103 for 1638 independent reflections having $I/\sigma(I) \geq 3.0$ collected as a Stöe Stadi 2 two-circle diffractometer. The structure was solved by Patterson and Fourier methods and refined by least-squares calculations using SHELX [14]. See also 'Supplementary Material'.

0020-1693/88/$3.50

Supplementary Material

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Labotory. Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Acknowledgement

We thank the S.E.R.C. for an equipment grant.

References

1 D. W. Allen, N. A. Bell, S. T. Fong, L. A. March and I. W. Nowell, *Inorg. Chim. Acta, 99,* 157 (1985).
2 N. A. Bell, T. D. Dee, P. L. Goggin, M. Goldstein, R. J. Goodfellow, T. Jones, K. Kessler, D. M. McEwan and I. W. Nowell, *J. Chem. Res., S,* 2; *M,* 201 (1981).
3 N. A. Bell, T. D. Dee, M. Goldstein, P. J. McKenna and I. W. Nowell, *Inorg. Chim. Acta, 71,* 135 (1983).
4 N. A. Bell, M. Goldstein, L. A. March and I. W. Nowell, *J. Chem. Soc., Dalton Trans.,* 1621 (1984).
5 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta, 43,* 87 (1980).
6 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta, 48,* 185 (1981).
7 N. A. Bell, M. Goldstein, T. Jones, L. A. March and I. W. Nowell, *Inorg. Chim. Acta, 61,* 83 (1982).
8 N. A. Bell, T. D. Dee, M. Goldstein and I. W. Nowell, *Inorg. Chim. Acta, 70,* 215 (1983).
9 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta, 69,* 155 (1983).
10 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta, 75,* 21 (1983).
11 S. O. Grim, P. J. Lui and R. L. Keiter, *Inorg. Chem., 13,* 342 (1974).
12 P. L. Goggin, R. J. Goodfellow, D. M. McEwan and K. Kessler, *Inorg. Chim. Acta, 44,* L111 (1980).
13 R. Colton and D. Dakternieks, *Aust. J. Chem., 33,* 955 (1980).
14 G. M. Sheldrick, 'SHELX', a programme for crystal structure analysis, University of Cambridge, U.K., 1976.
15 L. Falth, *Chem. Scripta, 9,* 71 (1976).
16 N. A. Bell, M. Goldstein, L. A. March and I. W. Nowell, *Inorg. Chim. Acta, 83,* 75 (1984).