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trans-Di-μ-iodo-diiodobis(triphenylphosphoniumcyclopentadienylide)dimercury(II)

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Abstract. $[(C_6H_5)_3PC_5H_4HgI_2]_2$, triclinic, yellow crystals, $P\bar{1}$, $a = 10.786$ (2), $b = 11.412$ (2), $c = 11.016$ (2) Å, $\alpha = 116.01$ (2), $\beta = 104.93$ (2), $\gamma = 93.60$ (2)°, $Z = 1$, $D_m = 2.27$ [determined by flotation in a 1,2-dibromoethane/dibromomethane mixture (3:1)], $D_x = 2.25$ g cm^{-3}; prepared by reacting HgI_2 with triphenylphosphoniumcyclopentadienylide in tetrahydrofuran. The compound is an iodine-bridged dimer [Hg–I(bridge), 2.982 (1), 2.937 (1) Å; Hg–I(external), 2.681 (1) Å] with a Hg–C σ bond at C(3) of the cyclopentadienylide. The P–C distance [1.748 (7) Å] is longer than that in the unsubstituted ylide [1.718 (3) Å].

Introduction. The crystal structure was investigated because NMR solution data did not unequivocally differentiate between a σ and π type of complex. The solution NMR data could best be interpreted as a fluxional σ-type complex with the Hg–C bond having roughly equal probability of being at C(2) or C(3) (Holy, Baenziger, Flynn & Swenson, 1976). 8532 reflections were measured (sin $\theta/\lambda_{max} \leq 0.481$ Å^{-1}) using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) with an automated FACS-I diffractometer, yielding the 4052 independent reflections (3571 > 3σ) which were used in the least-squares refinement. A stepped θ–2θ scan data-collection method was used (Baenziger, Foster, Howells, Howells, Vander Valk & Burton, 1977) with a step size varying from 0.08° to 0.12° (2θ) and background measured at ±1.2° (2θ) offset. The data were corrected for absorption (Templeton & Templeton, 1973) since $\mu = 88.73$ cm^{-1} and the crystal dimensions are approximately $0.24 \times 0.24 \times 0.36$ mm. The maximum and minimum correction factors were 4.50 and 2.59 (average = 3.23). The structure was found from Patterson and electron density maps. Full-matrix least-squares refinement of a model with 154 parameters (Hg, I, P and C atoms of the cyclopentadiene ring with anisotropic thermal parameters, individual isotropic temperature factors for C atoms of the phenyl rings) gave $R_1 = \sum ||F_o| - |F_c||/\sum F_o = 0.060$, $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.052$. Atom scattering factors used for Hg, I, P, and C were from *International Tables for X-ray Crystallog-*

Table 1. *Atom parameters for the title compound*
($\times 10^5$ *for* Hg, I, P; $\times 10^4$ *for* C; $\times 10^3$ *for* H)

	x	y	z
Hg	2313 (4)*	13362 (4)	20388 (4)
I(1)	86016 (5)	9853 (6)	92211 (6)
I(2)	87254 (6)	8698 (6)	34355 (6)
P	35100 (18)	45210 (19)	67461 (20)
C(1)	2594 (7)	4175 (7)	5025 (7)
C(2)	2690 (7)	3186 (8)	3782 (8)
C(3)	1708 (8)	3185 (9)	2629 (8)
C(4)	1024 (8)	4221 (9)	3224 (9)
C(5)	1518 (7)	4815 (8)	4676 (8)
C(11)	4641 (7)	3416 (7)	6619 (8)
C(12)	5681 (8)	3602 (9)	6208 (9)
C(13)	6560 (8)	2744 (9)	6056 (9)
C(14)	6365 (9)	1693 (10)	6359 (10)
C(15)	5350 (9)	1520 (10)	6810 (10)
C(16)	4449 (8)	2344 (9)	6925 (9)
C(21)	2467 (8)	4330 (8)	7698 (8)
C(22)	1478 (7)	3171 (8)	7032 (8)
C(23)	736 (9)	2961 (10)	7744 (10)
C(24)	902 (8)	3880 (9)	9179 (9)
C(25)	1845 (8)	5026 (9)	9843 (9)
C(26)	2615 (7)	5256 (8)	9094 (8)
C(31)	5502 (7)	3819 (9)	2247 (7)
C(32)	4473 (8)	3557 (9)	1052 (9)
C(33)	3738 (8)	2254 (9)	214 (9)
C(34)	4026 (9)	1280 (9)	605 (9)
C(35)	5041 (8)	1565 (9)	1762 (9)
C(36)	5838 (8)	2818 (8)	2567 (8)
H(2)	330	261	370
H(3)	211	332	199
H(4)	34	446	269
H(5)	122	551	534
H(12)	582	433	602
H(13)	728	287	575
H(14)	695	109	625
H(15)	525	82	705
H(16)	371	220	721
H(22)	134	254	607
H(23)	8	217	727
H(24)	38	371	968
H(25)	197	566	81
H(26)	325	606	955
H(32)	427	424	80
H(33)	304	204	938
H(34)	350	41	5
H(35)	520	90	204
H(36)	661	298	332

* Values in parentheses are the estimated standard deviations in the last given place.

Table 2. Bond distances (Å) and angles (°)

Hg–I(1)	2·982 (1)	I(1)–Hg–I(1)'	93·76 (2)
Hg–I(1)'	2·937 (1)	I(1)–Hg–I(2)	110·99 (2)
Hg–I(2)	2·681 (1)	I(1)–Hg–C(3)	97·0 (2)
Hg–C(3)	2·292 (8)	I(1)'–Hg–C(3)	107·2 (2)
C(1)–C(2)	1·375 (10)	I(1)'–Hg–I(2)	109·40 (2)
C(2)–C(3)	1·429 (10)	I(2)–Hg–C(3)	131·5 (2)
C(3)–C(4)	1·432 (12)	Hg–I(1)–Hg'	86·23 (2)
C(4)–C(5)	1·367 (11)		
C(5)–C(1)	1·467 (10)	C(5)–C(1)–C(2)	109·0 (6)
C(1)–P	1·748 (7)	P–C(1)–C(2)	125·5 (6)
P–C(11)	1·796 (8)	P–C(1)–C(5)	125·2 (6)
P–C(21)	1·786 (8)		
P–C(31)	1·803 (7)	Sum	359·7
		C(1)–C(2)–C(3)	107·3 (7)
C(11)–C(12)	1·351 (11)	C(2)–C(3)–C(4)	107·7 (7)
C(11)–C(16)	1·420 (11)	C(2)–C(3)–Hg	98·7 (7)
C(12)–C(13)	1·392 (12)	C(4)–C(3)–Hg	101·2 (7)
C(16)–C(15)	1·385 (13)		
C(13)–C(14)	1·397 (12)	C(3)–C(4)–C(5)	109·1 (7)
C(14)–C(15)	1·350 (13)	C(4)–C(5)–C(1)	106·8 (7)
	1·382 [27]*		
C(21)–C(22)	1·412 (11)	C(1)–P–C(11)	108·6 (3)
C(21)–C(26)	1·390 (11)	C(1)–P–C(21)	110·9 (3)
C(22)–C(23)	1·334 (12)	C(1)–P–C(31)	112·2 (3)
C(26)–C(25)	1·390 (11)	C(11)–P–C(21)	110·4 (3)
C(23)–C(24)	1·416 (12)	C(11)–P–C(31)	105·9 (3)
C(25)–C(24)	1·375 (12)	C(21)–P–C(31)	108·7 (3)
	1·386 [30]*		
C(31)–C(36)	1·379 (10)		
C(31)–C(32)	1·383 (10)	Average C–C–C bond angles	
C(32)–C(33)	1·401 (11)	in phenyl rings	
C(36)–C(35)	1·383 (11)	Ring 1	120·0
C(33)–C(34)	1·384 (11)	Ring 2	119·7
C(35)–C(34)	1·342 (11)	Ring 3	119·9
	1·379 [23]*		

Equations of planes:† $uX + vY + wZ = d$

	u	v	w	d
C(1), C(2), C(3), C(4), C(5)	0·6479	0·7613	–0·0276	2·2573

[Hg–C(3)]–(plane normal): 13·3°

Deviations of atoms from plane (Å)

C(1), 0·01; C(2), 0·00; C(3), –0·01; C(4), –0·01; C(5), –0·01; P, –0·09

Dihedral angle

Cp ring/(Hg–I)₂ square: 8·1°

* Values in square brackets are: $\left[\dfrac{\Sigma(X - m)^2}{n - 1}\right]^{1/2}$, where X is the bond distance and m the estimate of the mean bond distance.

† The unit vectors are chosen with i ∥ a; k ∥ a × b.

raphy (1962) and that for H from Stewart, Davidson & Simpson (1965). Atomic positions are given in Table 1. Bond lengths and angles are given in Table 2.* H atoms were placed at 0·95 Å from the C atoms and were not

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33439 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
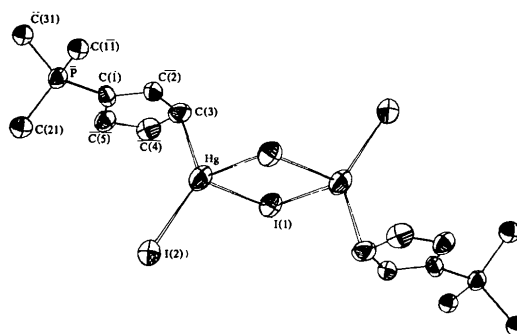

Fig. 1. An ORTEP plot (Johnson, 1965) of the title compound. Thermal ellipsoids represent the 50% probability level. Only the C atoms attached to P are shown for the phenyl groups.

refined. They were assigned the thermal parameters of the atoms to which they are attached. Weights in the least-squares refinement were $1/S_F^2$, where S_F is the estimate of the standard deviation of F_{ave}. The standard deviation of F_{ave} was estimated both from counting statistics and from the agreement among equivalent reflections. The largest estimate was taken as S_F. An ORTEP plot of the molecule is shown in Fig. 1.

Discussion. In the solid state, the σ bond is localized at C(3). The C(3) atom has tetrahedral coordination with the Hg–C(3) distance 2·292 (8) Å. The ylide carbon atom, C(1), has triangular-planar coordination, and the P–C(1) bond, 1·748 (7) Å, is 0·030 Å longer than that observed in the unsubstituted ylide (Ammon, Wheeler & Watts, 1973). The cyclopentadiene C–C distances imply double bonds located at C(1)–C(2) and C(4)–C(5), and they appear to be shorter (but not significantly so) than the double-bond distances in the unsubstituted ylide [1·375 (10) and 1·367 (11) Å vs 1·392 (4) and 1·376 (4) Å respectively]. Although the presence of the heavy scatterers prevents very precise location of the C atoms, it does appear that substitution of the ylide reduces the double-bond character of the ylide P–C bond and changes the location of the double bond from C(2)–C(3) to C(1)–C(2).

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