

The angle O(1)–Rh–O(2) = 89.5 (4)° for molecule *A* [90.0 (4)° for molecule *B*] and the Rh angle formed with the centres of the double bonds C(8)=C(9) and C(12)=C(13) is 88.1 (6)° for molecule *A* [88.5 (5)° for molecule *B*] – close to 90° (*cf.* Ibers & Snyder, 1962). This indicates that the prevailing orbitals that participate in the hybridization of the Rh orbitals are 4*p_x*, 4*p_y* and 4*d* of suitable symmetry. The angle between the double bond C(8)=C(9) and the normal to the chelate ring is 3°. The corresponding double bond in molecule *B* shows an angle of 2°. The angle between the chelate ring of molecule *A* and the double bond C(12)=C(13) is 12°; similarly in molecule *B* we found 8°. The bonds C(6)–C(7) and C(10)–C(11) are not coplanar but are crossed with respect to each other, forming an angle of 27.4° in molecule *A* and 23.2° in molecule *B*. The half-normal probability plot (De Camp, 1973; Hamilton & Abrahams, 1972) applied to the intramolecular distances of all the nonhydrogen atoms is significantly nonlinear; in particular, this is due to the longer non-valence distances between the chelate ring and the cyclooctadiene ring. This indicates differences between both independent molecules. Thermal-motion analysis (Schomaker & Trueblood, 1968) gives negative eigenvalues for the L tensors. This can be interpreted as non-rigid behaviour of the

molecules. No intermolecular contacts involving non-hydrogen atoms shorter than 3.4 Å were found.

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Cyclooctynebis(triphenylphosphine)platinum(0)–0.5 Benzene

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Abstract. C₄₄H₄₂P₂Pt.½C₆H₆, [Pt(C₈H₁₂)(C₁₈H₁₅-P)₂].½C₆H₆, *M_r* = 866.9, triclinic, *P*1̄, *a* = 11.334 (5), *b* = 15.931 (6), *c* = 12.021 (6) Å, *α* = 97.77 (5), *β* = 113.66 (4), *γ* = 90.80 (3)°, *V* = 1964 (2) Å³, *Z* = 2, *D_c* = 1.466 Mg m⁻³. Cu *Kα*, *λ* = 1.5418 Å, *μ* = 7.8 mm⁻¹. The structure is based on 2579 diffractometric intensities refined to *R* 0.093. Two P and two acetylenic C atoms define a plane about the zero-valent Pt atom. The conformation of the cyclooctyne ring is such that the C–C–C≡C–C–C unit is planar to within ±0.06 Å; the remaining two ring C atoms are displaced from this plane in the same direction by 0.85 (5) and 1.14 (5) Å.

Introduction. Haase & Krebs (1971) have shown that gaseous cyclooctyne adopts a conformation in which the C–C–C≡C–C–C unit is planar and the remaining

two C atoms lie 0.571 Å from this plane in opposite directions. We have examined the title compound by X-ray diffraction to see whether this conformation persists when cyclooctyne is complexed to [Pt(PPh₃)₂]. An X-ray study of [Pt(C₈H₁₂)(Ph₃P)₂] has been mentioned by Robertson & Whimp (1975) but no details were given.

A sample of the title compound was kindly provided by Professor C. W. Rees (Gilchrist, Graveling & Rees, 1968). A suitable crystal was obtained from benzene solution only after many recrystallizations. It was a white plate 0.2 × 0.2 × 0.1 mm. Preliminary Weissenberg and precession photographs indicated triclinic symmetry. Final cell dimensions and the intensities of all independent reflexions with *θ*(Cu *Kα*) ≤ 57° were measured with Ni-filtered Cu radiation on a Hilger & Watts Y290 diffractometer. Integrated intensities were

obtained from symmetrical $\theta/2\theta$ scans of 0.70° in θ (Cu $K\alpha$), 1 s counts being taken at intervals of 0.01° . Stationary-crystal-stationary-counter backgrounds were measured for 10 s at each end of the scan. The intensities of two strong reflexions, periodically remeasured, decreased steadily and were finally *ca* 60% of their initial values.

The integrated intensities were corrected for the variation in intensity of the standard reflexions, for absorption (transmission factors on F^2 were 0.37–0.56), and for Lp effects. The analysis was carried out with 2579 reflexions for which $I \geq 3\sigma(I)$.

A satisfactory structural model was found in the space group $P\bar{1}$. The positions of the non-hydrogen atoms were determined by Patterson and difference Fourier methods. The final atomic positional (Table 1) and vibrational* parameters were obtained by least-squares minimization of $\sum (|F_o| - |F_c|)^2 / \sigma^2(F_o)$. Refinement was terminated at $R = 0.093$ and $R_w = 0.12$. Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). Calculations were performed on the Numac IBM 370 Computer with the XRAY system (Stewart, 1972).

Discussion. The crystals contain well separated molecules of $[\text{Pt}(\text{C}_8\text{H}_{12})(\text{Ph}_3\text{P})_2]$ and of benzene, the latter displaying $\bar{1}$ symmetry.

The poor quality of the crystal and its decomposition in the X-ray beam have adversely affected the

* Anisotropic only for Pt and P atoms. Lists of final vibrational parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34620 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^3$)

	x	y	z
Pt	141.7 (1)	279.6 (1)	364.8 (1)
P(1)	222.5 (7)	247.4 (4)	225.0 (8)
P(2)	-71.6 (7)	298.1 (4)	273.6 (8)
C(1)	206 (3)	296 (2)	550 (3)
C(2)	298 (3)	278 (2)	528 (3)
C(3)	443 (4)	267 (2)	568 (4)
C(4)	501 (5)	278 (3)	720 (5)
C(5)	470 (5)	232 (3)	789 (5)
C(6)	343 (5)	228 (3)	788 (5)
C(7)	271 (4)	308 (3)	778 (4)
C(8)	160 (3)	305 (2)	651 (4)
C(11)	325 (3)	158 (2)	262 (3)
C(12)	455 (3)	165 (2)	290 (4)
C(13)	528 (4)	94 (3)	334 (4)
C(14)	466 (4)	23 (3)	349 (5)
C(15)	341 (3)	13 (2)	321 (4)
C(16)	266 (4)	84 (2)	277 (4)
C(21)	337 (2)	328 (2)	223 (3)
C(22)	382 (3)	327 (2)	134 (3)
C(23)	472 (3)	388 (2)	137 (4)
C(24)	514 (3)	456 (2)	236 (4)
C(25)	470 (4)	463 (2)	319 (4)
C(26)	377 (3)	399 (2)	321 (3)
C(31)	128 (3)	217 (2)	58 (3)
C(32)	32 (3)	267 (2)	2 (3)
C(33)	-43 (4)	247 (2)	-135 (4)
C(34)	-15 (4)	176 (2)	-199 (4)
C(35)	76 (5)	124 (3)	-144 (5)
C(36)	150 (3)	143 (2)	-8 (4)
C(41)	-114 (3)	380 (2)	176 (3)
C(42)	-27 (3)	450 (2)	202 (3)
C(43)	-53 (4)	514 (2)	129 (4)
C(44)	-168 (4)	510 (2)	26 (4)
C(45)	-253 (4)	441 (3)	1 (4)
C(46)	-230 (3)	376 (2)	71 (3)
C(51)	-143 (3)	333 (2)	384 (3)
C(52)	-175 (3)	280 (2)	438 (4)
C(53)	-221 (3)	301 (2)	537 (4)
C(54)	-234 (4)	391 (2)	553 (4)
C(55)	-204 (4)	446 (3)	504 (4)
C(56)	-158 (3)	421 (2)	414 (3)
C(61)	-183 (3)	209 (2)	173 (3)
C(62)	-134 (3)	151 (2)	112 (3)
C(63)	-223 (4)	82 (2)	21 (4)
C(64)	-344 (4)	75 (2)	10 (4)
C(65)	-396 (3)	130 (2)	74 (4)
C(66)	-312 (3)	201 (2)	159 (3)
C(100)	101 (4)	-28 (3)	597 (5)
C(101)	119 (5)	32 (3)	538 (5)
C(102)	22 (5)	61 (3)	440 (5)

Table 2. Selected bond lengths (\AA)

Pt—C(1)	2.02 (3)	Pt—P(1)	2.22 (1)
Pt—C(2)	2.05 (3)	Pt—P(2)	2.26 (1)
C(1)—C(2)	1.20 (4)	P(1)—C(11)	1.84 (3)
C(2)—C(3)	1.54 (5)	P(1)—C(21)	1.82 (3)
C(3)—C(4)	1.66 (7)	P(1)—C(31)	1.85 (3)
C(4)—C(5)	1.32 (7)	P(2)—C(41)	1.81 (3)
C(5)—C(6)	1.44 (7)	P(2)—C(51)	1.84 (3)
C(6)—C(7)	1.52 (7)	P(2)—C(61)	1.83 (3)
C(7)—C(8)	1.53 (6)	Mean P—C	1.83 (1)
C(8)—C(1)	1.49 (5)		

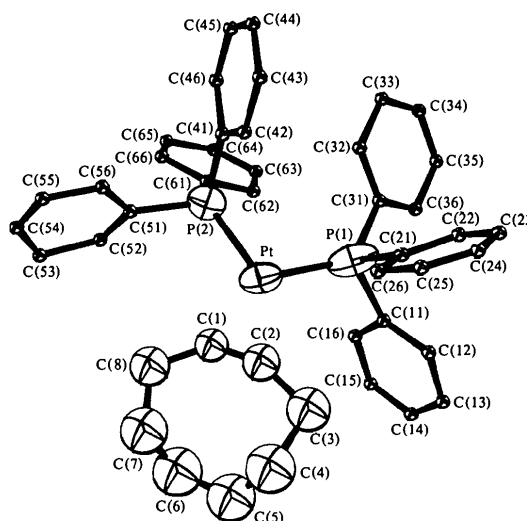


Fig. 1. A perspective view of the molecule. H atoms are omitted and phenyl C atoms are represented by spheres of arbitrary size. For other atoms 50% probability ellipsoids are shown.

Table 3. *Selected bond angles* (°)

P(1)—Pt—P(2)	110.7 (3)	C(8)—C(1)—C(2)	142 (3)
P(1)—Pt—C(2)	103 (1)	C(1)—C(2)—C(3)	152 (4)
P(2)—Pt—C(1)	112 (1)	C(2)—C(3)—C(4)	104 (3)
C(1)—Pt—C(2)	34 (1)	C(3)—C(4)—C(5)	129 (4)
Pt—C(1)—C(2)	74 (2)	C(4)—C(5)—C(6)	122 (5)
Pt—C(2)—C(1)	71 (2)	C(5)—C(6)—C(7)	119 (4)
Pt—C(1)—C(8)	142 (2)	C(6)—C(7)—C(8)	112 (4)
Pt—C(2)—C(3)	136 (3)	C(7)—C(8)—C(1)	112 (3)

accuracy of the analysis. Nevertheless, the geometries of the triphenylphosphine ligands (Tables 2 and 3) are as expected and the Pt coordination is similar to that found in the cyclohexyne and cycloheptyne complexes of Pt(PPh₃)₂ for which more accurate structural details are available (Robertson & Whimp, 1975). Here Pt, P(1), P(2), C(1), and C(2) (Fig. 1) lie within 0.03 (3) Å of their common plane.

The cyclooctyne atoms C(1)—C(4) and also C(7) and C(8) are coplanar ($\chi^2 = 5.8$ on three degrees of

freedom), while C(5) and C(6) are displaced from this plane in the same direction by 0.85 (5) and 1.14 (5) Å respectively. Thus the conformation of the cyclooctyne ligand is different from that displayed by gaseous cyclooctyne (Haase & Krebs, 1971). A further difference lies in the C—C≡C angles, 142 (3) and 152 (4)° in the complex, and 159 (1)° in gaseous cyclooctyne.

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