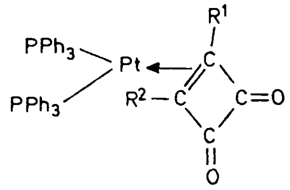
# Crystal and Molecular Structure of (1-Methyl-2-phenylcyclobutenedione)bis(triphenylphosphine)platinum(0)

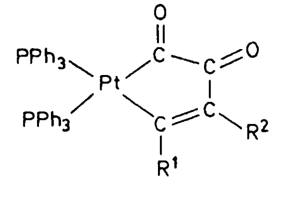
By **David R. Russell** * and **Paul A. Tucker**, Department of Chemistry, University of Leicester, Leicester LE1 7RH

Crystals of the title compound are triclinic, space group $P\bar{1}$, with $a$ = 20.967(10), $b$ = 12.478(6), $c$ = 9.358(6) Å, $\alpha$ = 109.7(4), $\beta$ = 107.1(4), $\gamma$ = 103.5(5)°, $Z$ = 2. The structure has been refined by least-squares analysis of intensities to $R$ 0.089 for 4 413 reflexions. The cyclobutenedione is co-ordinated *via* its olefinic bond. Important bond lengths are Pt-C(olefinic) 2.00(2) and 2.12(2), and Pt–P 2.271(4) and 2.309(4) Å. The geometry of the co-ordinated cyclobutenedione is discussed and the distorted co-ordination geometry attributed to steric crowding in the molecule.

1,2-DISUBSTITUTED cyclobutenediones react with *trans*-(stilbene)bis(triphenylphosphine)platinum(0) to form olefinic complexes (I) which, in most instances, are not isolated but are intermediate to the ring-opened complexes (II).[1] In the case of the title compound (I; $R^1$ = Me, $R^2$ = Ph), ring opening apparently does not occur in solution even over long periods and we undertook the crystal structure determination to confirm its assignment as an olefin complex and to compare its geometry with those of other olefin complexes of platinum(0).†



(I)



(II)

## EXPERIMENTAL

Pale yellow crystals of the title compound from chloroform–light petroleum (b.p. 40—60 °C) were plates on {$\bar{1}$10}, with the faces {110}, {011}, and {11$\bar{1}$} commonly developed. Unit-cell dimensions were derived from precession photographs recorded with Mo-$K_\alpha$ radiation, and are more precise than those originally reported.†

*Crystal Data*.—$C_{47}H_{38}O_2P_2Pt$, $M$ = 891.9, Triclinic, $a$ = 20.967(10), $b$ = 12.478(6), $c$ = 9.358(6) Å, $\alpha$ = 109.7(4), $\beta$ = 107.1(4), $\gamma$ = 103.5(5)°, $U$ = 2 050.4 Å$^3$, $D_c$ = 1.45 g cm$^{-3}$, $Z$ = 2, $D_m$ = 1.44 g cm$^{-3}$, $F(000)$ = 888. $\lambda$(Mo-$K_\alpha$) = 0.710 69 Å, $\mu$(Mo-$K_\alpha$) = 35.1 cm$^{-1}$. Space group $P\bar{1}$ (from structure analysis).

Intensities for a crystal of dimensions *ca*. 0.08 × 0.16 × 0.39 mm were measured for the layers $hk0$—9 on a Stoe Weissenberg diffractometer by use of monochromatic Mo-$K_\alpha$ radiation and an $\omega$-scan technique.

The 4 456 reflexions with significant intensity $I > 3\sigma(I)$ and 0.1 Å$^{-1}$ < sin $\theta/\lambda$ < 0.7 Å$^{-1}$ were corrected for Lorentz, polarisation, and absorption effects.[2,3]

Scattering factors for the atoms were taken from ref. 4, and the structure solved by conventional heavy-atom methods. Full-matrix least-squares refinement of positional and thermal parameters (using a local modification of ORFLS) for the non-hydrogen atoms reduced $R$ to 0.090 for 4 456 reflexions. Anisotropic temperature factors for platinum and phosphorus atoms were refined. The methyl hydrogen atoms could not be located from a difference Fourier synthesis but phenyl hydrogen atom positions were calculated from the molecular geometry assuming C–H 1.00 Å. Further cycles of block-diagonal least-squares refinement, including the phenyl hydrogen atoms in the structure-factor calculations each with a temperature factor of $B$ 5.0 Å$^2$ and including an anomalous dispersion correction [5] for platinum, produced only small shifts and the final $R$ was 0.089. In the final cycles 43 reflexions with small $|F_o|$ and poor agreement between $|F_o|$ and $|F_c|$ were excluded from the refinement. The function minimised throughout was $\Sigma w(|F_o| - |F_c|)^2$ where $w$ = 1 for the initial cycles and $w = (0.202 - 0.078|F_o| + 0.015|F_o|^2)^{-1}$ in later cycles. The maximum shift in the final cycle was 0.5$\sigma$, a difference-Fourier synthesis showed no significant features, and an analysis of the weighting scheme over $|F_o|$ and sin $\theta/\lambda$ was satisfactory.

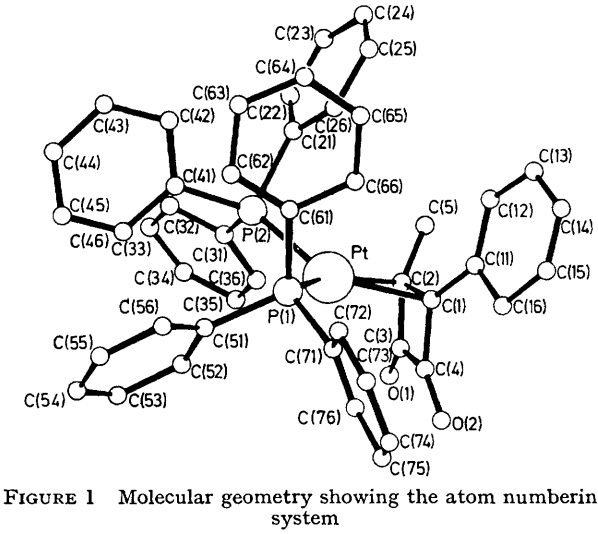


FIGURE 1 Molecular geometry showing the atom numbering system

Final non-hydrogen atomic parameters are listed in Table 1. The atom numbering is shown in Figure 1. Anisotropic thermal parameters gave a satisfactory tensor analysis. Observed and calculated structure factors and hydrogen atom co-ordinates have been deposited as

---

† A report of this work was given at the 10th Internat. Congress Crystallography, Amsterdam, August 1975 (*Acta Cryst.*, 1975, **A31**, S139).

[1] E. R. Hamner, R. D. W. Kemmitt, and M. A. R. Smith, *J.C.S. Chem. Comm.*, 1974, 841.

[2] J. de Meulenaer and H. Tompa, *Acta Cryst.*, 1965, **19**, 1014.

[3] N. W. Alcock, *Acta Cryst.*, 1969, **A25**, 518.

[4] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[5] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

Supplementary Publication No. SUP 21810 (24 pp., 1 microfiche).*

TABLE 1

Final atomic co-ordinates and thermal parameters, with estimated standard deviations in parentheses

| | $x/a$ | $y/b$ | $z/c$ | $B$/Å$^2$ |
|---|---|---|---|---|
| Pt | 0.265 96(3) | 0.421 20(6) | 0.128 83(9) | * |
| P(1) | 0.157 8(2) | 0.438 2(4) | 0.030 9(5) | * |
| P(2) | 0.336 7(2) | 0.609 3(4) | 0.351 3(6) | * |
| O(1) | 0.394 2(9) | 0.325 1(16) | −0.030 7(22) | 5.8(4) |
| O(2) | 0.227 6(10) | 0.152 4(16) | −0.260 7(23) | 5.8(3) |
| C(1) | 0.249 6(10) | 0.232 4(18) | 0.044 6(25) | 3.9(4) |
| C(2) | 0.327 7(10) | 0.321 0(17) | 0.143 3(25) | 3.4(3) |
| C(3) | 0.341 7(11) | 0.296 2(19) | −0.002 3(27) | 4.1(4) |
| C(4) | 0.262 8(11) | 0.214 5(19) | −0.114 0(27) | 4.1(4) |
| C(5) | 0.383 5(11) | 0.325 2(18) | 0.307 2(27) | 3.9(4) |
| C(11) | 0.199 6(10) | 0.152 5(18) | 0.077 3(26) | 3.8(3) |
| C(12) | 0.208 6(12) | 0.159 7(21) | 0.228 5(30) | 4.7(4) |
| C(13) | 0.155 6(15) | 0.083 7(26) | 0.244 0(37) | 6.2(6) |
| C(14) | 0.090 8(20) | −0.003 4(35) | 0.106 7(48) | 8.3(8) |
| C(15) | 0.086 8(15) | −0.006 7(25) | −0.030 9(36) | 6.2(6) |
| C(16) | 0.132 5(13) | 0.066 1(22) | −0.064 5(31) | 5.0(4) |
| C(21) | 0.351 9(9) | 0.580 3(15) | 0.536 6(23) | 3.1(3) |
| C(22) | 0.418 2(11) | 0.629 9(19) | 0.670 4(27) | 4.2(4) |
| C(23) | 0.422 6(19) | 0.594 0(33) | 0.807 3(46) | 8.1(8) |
| C(24) | 0.367 8(16) | 0.518 2(26) | 0.790 7(38) | 6.6(6) |
| C(25) | 0.303 3(17) | 0.472 1(29) | 0.671 4(40) | 7.0(6) |
| C(26) | 0.295 5(11) | 0.496 9(18) | 0.536 9(27) | 4.0(4) |
| C(31) | 0.426 5(8) | 0.685 0(14) | 0.364 9(21) | 2.5(3) |
| C(32) | 0.450 9(10) | 0.618 7(18) | 0.265 9(26) | 3.8(4) |
| C(33) | 0.519 5(13) | 0.674 9(22) | 0.270 9(31) | 4.9(4) |
| C(34) | 0.557 7(15) | 0.795 3(26) | 0.382 5(36) | 6.0(6) |
| C(35) | 0.534 3(14) | 0.864 8(25) | 0.473 8(34) | 5.7(5) |
| C(36) | 0.467 0(11) | 0.805 8(19) | 0.472 6(27) | 4.1(4) |
| C(41) | 0.304 1(9) | 0.735 1(15) | 0.401 9(23) | 3.0(3) |
| C(42) | 0.304 6(11) | 0.803 2(19) | 0.308 7(27) | 4.1(4) |
| C(43) | 0.277 4(13) | 0.897 9(21) | 0.338 2(30) | 4.9(4) |
| C(44) | 0.255 9(13) | 0.926 0(22) | 0.471 1(31) | 5.1(5) |
| C(45) | 0.264 5(13) | 0.868 9(25) | 0.569 5(34) | 5.5(5) |
| C(46) | 0.285 3(13) | 0.769 1(23) | 0.534 4(32) | 5.1(5) |
| C(51) | 0.158 5(8) | 0.560 2(14) | −0.033 3(21) | 2.5(3) |
| C(52) | 0.213 3(12) | 0.606 3(21) | −0.071 1(30) | 4.7(4) |
| C(53) | 0.212 5(13) | 0.698 3(21) | −0.130 2(30) | 4.7(4) |
| C(54) | 0.162 7(15) | 0.749 5(25) | −0.140 5(36) | 5.8(5) |
| C(55) | 0.105 3(12) | 0.694 0(21) | −0.111 0(30) | 4.8(4) |
| C(56) | 0.102 8(10) | 0.604 3(16) | −0.054 7(23) | 3.3(3) |
| C(61) | 0.122 9(9) | 0.455 6(15) | 0.189 0(21) | 2.7(3) |
| C(62) | 0.120 6(10) | 0.566 9(18) | 0.276 4(25) | 3.8(4) |
| C(63) | 0.095 1(13) | 0.571 7(23) | 0.414 2(32) | 5.0(5) |
| C(64) | 0.082 4(14) | 0.467 5(24) | 0.445 9(33) | 5.6(5) |
| C(65) | 0.083 1(13) | 0.366 6(23) | 0.351 2(32) | 5.3(5) |
| C(66) | 0.102 3(10) | 0.353 0(17) | 0.223 0(24) | 3.5(3) |
| C(71) | 0.081 4(9) | 0.310 0(15) | −0.158 3(22) | 2.9(3) |
| C(72) | 0.013 2(11) | 0.278 1(19) | −0.172 3(27) | 4.1(4) |
| C(73) | −0.046 4(16) | 0.187 3(27) | −0.326 3(38) | 6.1(6) |
| C(74) | −0.025 2(14) | 0.140 4(24) | −0.453 9(34) | 5.7(5) |
| C(75) | 0.037 9(13) | 0.166 9(23) | −0.444 9(32) | 5.2(5) |
| C(76) | 0.097 0(12) | 0.254 9(20) | −0.286 2(28) | 4.4(4) |

* Temperature factors in the form: $\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$, with parameters

| | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{23}$ | $B_{13}$ | $B_{12}$ |
|---|---|---|---|---|---|---|
| Pt | 2.48(3) | 2.53(3) | 2.71(3) | 1.09(2) | 1.66(2) | 1.12(2) |
| P(1) | 2.76(16) | 2.94(18) | 1.86(17) | 0.93(14) | 1.53(13) | 1.26(14) |
| P(2) | 2.68(17) | 3.28(19) | 2.20(19) | 1.28(15) | 1.76(14) | 1.07(14) |

## DISCUSSION

The complex (I; $R^1$ = Me, $R^2$ = Ph) is the expected olefin complex of platinum(0) with the olefinic bond approximately in the plane of the platinum and phosphorus atoms. The difference in Pt–P bond lengths (Table 2) is significant and surprising because the longer bond is ' opposite ' the longer Pt–C bond;[1] however, both bond lengths are within the range found in other bis(triphenylphosphine)olefin complexes of platinum(0).

TABLE 2

Bond lengths (Å), with estimated standard deviations in parentheses; mean C–C(Ph) bond length 1.38(6) Å

| | | | |
|---|---|---|---|
| Pt–C(1) | 2.12(2) | C(1)–C(2) | 1.53(3) |
| Pt–C(2) | 2.00(2) | C(1)–C(4) | 1.54(3) |
| | | C(2)–C(3) | 1.43(3) |
| Pt–P(1) | 2.271(4) | C(3)–C(4) | 1.54(3) |
| Pt–P(2) | 2.309(4) | | |
| | | C(2)–C(5) | 1.61(3) |
| P(1)–C(51) | 1.814(17) | | |
| P(1)–C(61) | 1.807(18) | C(1)–C(11) | 1.45(3) |
| P(1)–C(71) | 1.872(17) | | |
| P(2)–C(21) | 1.842(19) | C(3)–O(1) | 1.21(3) |
| P(2)–C(31) | 1.847(16) | C(4)–O(2) | 1.21(3) |
| P(2)–C(41) | 1.828(17) | | |
| Mean | 1.835(23) | | |

Phenylcyclobutenedione itself has an olefinic bond length[6] of 1.36 Å and the phenyl group is coplanar with the cyclobutenedione ring. On co-ordination there is a significant lengthening of the olefinic bond, due to back-donation from the metal into the olefinic antibonding orbitals, otherwise the bond lengths do not differ significantly on co-ordination. There is no obvious explanation for the difference in C(1)–C(4) and C(2)–C(3) bond lengths in the title compound, which borders on significance. Bonding interactions with the metal cause a rehybridisation[7] of the olefinic carbon atoms (see Figure 2) such that the phenyl and cyclobutenedione rings are no longer coplanar. In addition, the overlap between $p$ orbitals on C(1) and C(11) is further reduced by a twist of the phenyl group about the C(1)–C(11) bond such that the dihedral angle between the ring plane and the plane defined by C(1), C(2), C(5), and C(11) is 23.8° (Table 3). However the short † contact of 2.81 Å

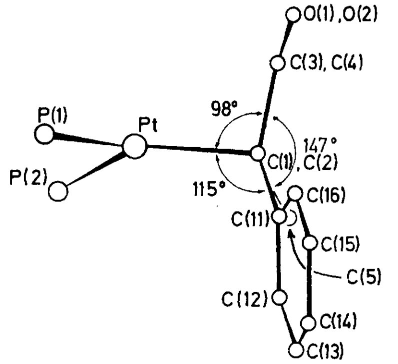


FIGURE 2 A view of the co-ordinated cyclobutenedione along the olefinic C(1)–C(2) bond. Angles (°) shown lie in the plane of projection

---

* For details, see Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

† Defined as shorter than the sum of van der Waals radii, estimated as 1.2 Å for H, and 2.0 Å for Me, with the half-thickness of an aromatic ring as 1.7 Å.[8]

[6] C. H. Wong, R. E. Marsh, and V. Shomaker, *Acta Cryst.*, 1964, **17**, 131.

[7] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939; M. J. S. Dewar, *Bull. Soc. chim. France*, 1951, *C***79**, 18.

[8] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.

between C(5) and H(12) (Figure 3) suggests that this is a steric rather than electronic effect and that even in the unco-ordinated 1-methyl-2-phenylcyclobutenedione the phenyl and cyclobutene rings would not be coplanar.

The co-ordination of the cyclobutenedione is illustrated in Figure 3. The atoms C(1) and C(2) are respectively 0.72 and 0.26 Å from, and on the same side of, the Pt, P(1), P(2) plane. The dihedral angle between the planes Pt, P(1), P(2) and Pt, C(1), C(2) is 22.1°. These deviations are several times larger than those observed in platinum(0) complexes with co-ordinated symmetrically substituted ethylenes and it is tempting to postulate some (small) interaction of the orbitals on C(3) and C(4) with the metal. However the distances Pt · · · C(3) (2.73 Å) and Pt · · · C(4) (2.78 Å) are not much smaller than the non-bonded Pt · · · C distance (2.83 Å)[9] in 1,2-dimethylcyclopropenebis(triphenylphosphine)platinum(0) and so it would appear that steric crowding in the molecule is mainly responsible for the non-planarity of the co-ordination about platinum.

TABLE 3

Some mean planes of sets of atoms in one molecule, with deviations (Å) of relevant atoms from the planes

(i): C(11)—(16)
C(11) 0.01, C(12) 0.00, C(13) −0.01, C(14) −0.01, C(15) 0.03, C(16) −0.03, C(1) −0.05
(ii): C(21)—(26)
C(21) −0.01, C(22) 0.00, C(23) −0.01, C(24) 0.03, C(25) −0.05, C(26) 0.03, P(2) 0.07
(iii): C(31)—(36)
C(31) 0.00, C(32) −0.01, C(33) −0.01, C(34) 0.03, C(35) −0.04, C(36) 0.02, P(2) −0.03
(iv): C(41)—(46)
C(41) −0.04, C(42) 0.05, C(43) −0.01, C(44) −0.04, C(45) 0.05, C(46) −0.01, P(2) −0.03
(v): C(51)—(56)
C(51) 0.02, C(52) 0.00, C(53) −0.03, C(54) 0.05, C(55) −0.03, C(56) −0.00, P(1) −0.03
(vi): C(61)—(66)
C(61) 0.02, C(62) 0.01, C(63) −0.04, C(64) 0.04, C(65) −0.01, C(66) −0.02, P(1) 0.19
(vii) : C(71)—(76)
C(71) −0.02, C(72) 0.00, C(73) 0.02, C(74) −0.01, C(75) −0.01, C(76) 0.03, P(1) −0.23
(viii): C(1)—(4), O(1), O(2)
C(1) 0.06, C(2) −0.04, C(3) −0.01, C(4) −0.04, O(1) 0.03, O(2) 0.00
(ix): C(1), C(2), C(11), C(5)
C(1) 0.06, C(2) −0.06, C(5) 0.02, C(11) −0.03

Angles (°) between planes: (i)–(ix) 23.8, (viii)–(ix) 23.3.

The short[8] H(66) · · · C(11) and H(66) · · · C(12) contacts (2.88 and 2.90 Å) suggest that the Pt–C(1) is longer than the Pt–C(2) bond and that the P(1)–Pt–C(1) angle is larger than the P(2)–Pt–C(2) angle (Table 4) in order to avoid too close an approach of the phenyl substituent on the cyclobutenedione with those of the adjacent triphenylphosphine ligand. There is further evidence of steric crowding in the configuration of the triphenylphosphine ligands. Normally, the phenyl groups in triphenylphosphine ligands display a propellor conformation which minimises C(β) · · · C′(β) contacts. In *cis*-bis(triphenylphosphine)-complexes the two ligands frequently pack such that a ring from one ligand is approximately parallel to one from the other with an inter-ring separation of *ca.* 3.4 Å. In the title compound the ligand adjacent to the phenyl-substituted carbon does not have the propellor conformation, resulting in a short[8] H(56) · · · H(62) contact of 2.30 Å. Furthermore, the distances of P(1) from the mean planes defined by C(61)—(66) and C(71)—(76) are larger than usual (Table 3). The two triphenylphosphine ligands do not pack with a pair of phenyl groups parallel; the two shortest C · · · C contacts between ligands are C(62) · · · C(45) 3.33 and C(62) · · · C(41) 3.54 Å. The separation of the methyl-substituted olefinic carbon atom and the adjacent triphenylphosphine ligand is probably controlled by the short[8] C(5) · · · C(21) contact of 3.52 Å.

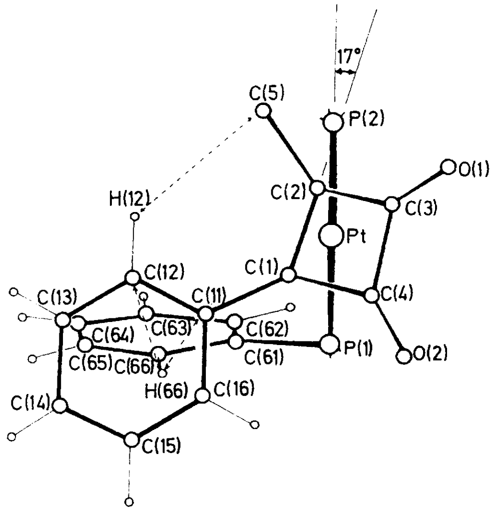


FIGURE 3 A view of the co-ordinated cyclobutenedione parallel to the Pt, P(1), P(2) plane

TABLE 4

Bond angles (°), with estimated standard deviations in parentheses; mean C–C–C(Ph) angle 120(3)°

| | | | |
|---|---|---|---|
| P(1)–Pt–C(1) | 108.2(5) | Pt–P(1)–C(51) | 115.2(5) |
| P(2)–Pt–C(2) | 103.6(5) | Pt–P(1)–C(61) | 107.8(5) |
| P(1)–Pt–P(2) | 103.9(2) | Pt–P(1)–C(71) | 120.9(6) |
| C(1)–Pt–C(2) | 43.5(7) | C(51)–P(1)–C(61) | 110.8(8) |
| | | C(51)–P(1)–C(71) | 98.8(8) |
| C(1)–C(4)–O(2) | 135(2) | C(61)–P(1)–C(71) | 102.6(8) |
| C(1)–C(4)–C(3) | 88(2) | | |
| C(3)–C(4)–O(2) | 136(2) | Pt–P(2)–C(21) | 105.2(6) |
| C(2)–C(3)–O(1) | 135(2) | Pt–P(2)–C(31) | 117.4(6) |
| C(2)–C(3)–C(4) | 91(2) | Pt–P(2)–C(41) | 121.8(6) |
| C(4)–C(3)–O(1) | 133(2) | C(21)–P(2)–C(31) | 106.1(8) |
| | | C(21)–P(2)–C(41) | 101.8(8) |
| C(4)–C(1)–C(2) | 87(2) | C(31)–P(2)–C(41) | 102.5(8) |
| C(4)–C(1)–C(11) | 131(2) | | |
| C(2)–C(1)–C(11) | 135(2) | C(1)–C(11)–C(12) | 124(2) |
| C(3)–C(2)–C(1) | 93(2) | C(1)–C(11)–C(16) | 116(2) |
| C(3)–C(2)–C(5) | 120(2) | | |
| C(1)–C(2)–C(5) | 125(2) | | |

These steric considerations indicate that the distortion

---

[9] J. P. Visser, A. J. Schipperijn, J. Lukas, D. Bright, and J. J. de Boer, *Chem. Comm.*, 1971, 1266.

from planar co-ordination of the platinum atom is not primarily due to electronic factors, and that, in solution, the lack of ring-opening in the case of the title compound may also be related to steric crowding. There are no exceptionally short intermolecular contacts.

We thank E. R. Hamner for supplying a sample of the title compound, the University of Leicester Computer Laboratory for facilities, and the S.R.C. for financial support.

[5/2191 *Received, 11th November, 1975*]