

= 3.2°. The nitro group is roughly perpendicular to the five-membered ring, with the dihedral angle between the least-squares planes* equal to 95°. Bond distances and angles appear to be within the normal range for similar compounds.

The crystal packing (Fig. 3) is of the familiar herringbone design. There are a number of short intermolecular contacts which may possibly be described as CH...O bonding interactions. In particular the contact C(2)H...O(1) with C...O 3.15 Å and H...O 2.36 Å is a reasonable candidate for this description. In this case the tertiary H is expected to be quite acidic in view of the electron-withdrawing effects of the nitro group.

In a future communication we will describe the molecular conformation of a 2-nitrocyclohexanone and at that time discuss more fully the relationship of the observed conformations of cyclic nitroketones and the observed NMR spectra of these compounds.

* Atoms defining the planes are C(1) through C(5), and C(2), N(1), O(1N) and O(2N).

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Acetylacetonato(1,*cis*-3,*trans*-tetraphenyl-4-ethoxybutadien-1-yl)- (dimethylphenylphosphine)palladium(II)

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Abstract. C₄₃H₄₃O₃PPd, *M_r* = 745.07, triclinic, *P1* or *P1̄* (latter confirmed); *a* = 11.54 (2), *b* = 15.68 (2), *c* = 23.29 (3) Å, α = 96.27 (1), β = 117.07 (1), γ = 91.47 (1)°; *V* = 3717 Å³; *D_c* (for *Z* = 4) = 1.33, *D_m* = 1.31 g cm⁻³; μ(Mo *Kα*) = 5.3 cm⁻¹. The structure, refined to a final residual of 0.059 from 9538 diffractometric intensity data, consists of two independent molecules of opposite chirality in each asymmetric unit. The tetraphenylbutadienyl moiety is one of four square-planar ligands about Pd (using a terminal *sp*² C atom), the other three ligands being P and the planar bidentate acetylacetonate group (itself coplanar with the Pd coordination plane).

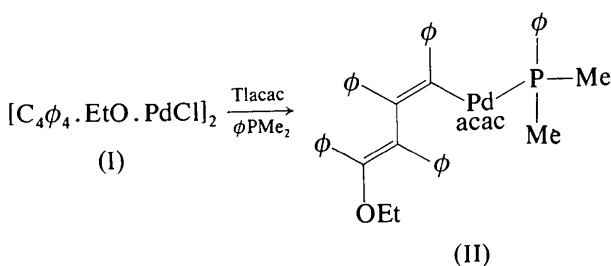
Introduction. Diphenylacetylene is dimerized by PdCl₂ in ethanol and forms an equilibrium mixture of tetraphenylbutadienyl and tetraphenylcyclobutadienyl complexes (I) with Pd. To understand the reaction mecha-

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nism it is of importance to know whether the ethoxy group is *cis* or *trans* to the central single bond. To this end, and to ensure that the cyclobutadiene ring was opened, (I) has been treated with thallium acetylacetonate (acac) and then with dimethylphenylphosphine to form the complex (II) (Cheng, Jack, May, Nyburg & Powell, 1975), whose crystal and molecular structure analysis is reported here.



Yellowish, well formed crystals of known elemental analysis were supplied by Professor J. Powell. The crystal used for data collection was a parallelepiped of dimensions *ca* 0.21 × 0.22 × 0.34 mm. It was mounted about the *x* axis, parallel to its longest dimension. The cell parameters and their standard deviations were obtained from diffractometer angular settings of 12 well centred reflexions. Intensities were collected on a computer-controlled Picker four-circle diffractometer with a pulse-height analyser and Zr-filtered Mo *K*α radiation. Scanning was in the θ - 2θ mode at 2° min⁻¹. Backgrounds were determined for 30 s at each end of

the scan range of 2°, adjusted for α splitting. The take-off angle was 3.0°. During the course of data collection there was a random deviation of <5% from the mean in the intensity of the standard reflexion, recorded every 50 reflexions. Counting statistics and an Abrahams factor (Abrahams & Bernstein, 1965) of 0.02 were used to calculate $\sigma(I)$. Of the 14 125 independent reflexions measured, 9538 were considered significant according to the criterion $|F_o| \geq 3\sigma(F_o)$. Absorption corrections were not applied.

The Patterson function showed only four strong independent peaks, indicative (four Pd atoms per cell) of

Table 1. Atomic fractional coordinates ($\times 10^4$, except $\times 10^5$ for Pd)

Molecule 1	<i>x</i>	<i>y</i>	<i>z</i>	Molecule 2	<i>x</i>	<i>y</i>	<i>z</i>
Pd	17224 (4)	21730 (3)	7997 (2)	Pd'	10901 (4)	16530 (3)	42797 (2)
P	-72 (2)	2611 (1)	829 (1)	P'	-996 (2)	1886 (1)	3690 (1)
O(1)	2450 (5)	2007 (3)	1790 (2)	O(1')	908 (5)	869 (3)	3433 (2)
O(2)	3377 (4)	1660 (3)	801 (2)	O(2')	3042 (4)	1410 (3)	4764 (2)
O(3)	4905 (5)	4263 (3)	639 (3)	O(3')	4595 (4)	3964 (3)	4937 (2)
Me(1)	351 (9)	3236 (6)	1632 (4)	Me(1')	-1205 (8)	2216 (5)	2917 (3)
Me(2)	-1166 (8)	3269 (5)	251 (4)	Me(2')	-1838 (8)	2662 (5)	3968 (4)
Me(3)	3968 (9)	1896 (8)	2873 (4)	Me(3')	1460 (10)	-105 (6)	2766 (4)
Me(4)	5449 (8)	1123 (6)	1174 (4)	Me(4')	5162 (8)	1074 (5)	4926 (5)
C(1)	3605 (7)	1807 (5)	2142 (3)	C(1')	1852 (7)	496 (4)	3397 (3)
C(2)	4504 (7)	1560 (5)	1944 (4)	C(2')	3156 (7)	554 (5)	3875 (3)
C(3)	4356 (6)	1477 (4)	1294 (3)	C(3')	3685 (6)	1027 (4)	4504 (3)
C(4)	1038 (6)	2353 (3)	-134 (3)	C(4')	1260 (6)	2342 (3)	5098 (3)
C(5)	1722 (6)	2922 (4)	-293 (3)	C(5')	2165 (6)	3020 (3)	5402 (3)
C(6)	2857 (6)	3510 (3)	224 (3)	C(6')	2823 (6)	3397 (3)	5041 (3)
C(7)	4014 (6)	3604 (4)	209 (3)	C(7')	4124 (6)	3499 (3)	5270 (3)
C(8)	6270 (8)	4120 (8)	973 (5)	C(8')	5431 (9)	3493 (5)	4714 (5)
C(9)	6557 (13)	3592 (9)	1481 (7)	C(9')	5753 (12)	4062 (6)	4321 (6)
C(A1)	-1088 (6)	1670 (4)	775 (3)	C(A1')	-2038 (6)	883 (4)	3452 (3)
C(A2)	-2083 (8)	1319 (5)	165 (4)	C(A2')	-2619 (8)	659 (6)	3820 (5)
C(A3)	-2792 (10)	551 (6)	96 (6)	C(A3')	-3450 (10)	-128 (6)	3614 (6)
C(A4)	-2481 (10)	140 (6)	633 (6)	C(A4')	-3607 (9)	-670 (6)	3092 (6)
C(A5)	-1517 (11)	472 (7)	1237 (6)	C(A5')	-2975 (10)	-462 (5)	2737 (5)
C(A6)	-787 (9)	1248 (6)	1312 (4)	C(A6')	-2218 (8)	325 (5)	2919 (4)
C(B1)	-134 (5)	1788 (3)	-625 (3)	C(B1')	440 (6)	2021 (4)	5386 (3)
C(B2)	-190 (7)	906 (4)	-567 (3)	C(B2')	303 (7)	1147 (4)	5433 (3)
C(B3)	-1312 (8)	357 (4)	-1023 (4)	C(B3')	-504 (8)	848 (5)	5691 (4)
C(B4)	-2295 (7)	1587 (5)	-1543 (3)	C(B4')	-1179 (8)	1402 (6)	5891 (4)
C(B5)	-2357 (8)	703 (5)	-1498 (3)	C(B5')	-1066 (7)	2301 (5)	5850 (4)
C(B6)	-1194 (6)	2109 (4)	-1117 (3)	C(B6')	-273 (6)	2591 (4)	5583 (3)
C(C1)	1407 (6)	3015 (4)	-987 (3)	C(C1')	2599 (6)	3422 (4)	6086 (3)
C(C2)	1181 (7)	2307 (5)	-1446 (3)	C(C2')	2775 (7)	2921 (5)	6574 (3)
C(C3)	881 (8)	2435 (6)	-2102 (4)	C(C3')	3229 (8)	3308 (6)	7221 (3)
C(C4)	776 (8)	3241 (7)	-2277 (4)	C(C4')	3470 (9)	4193 (6)	7376 (4)
C(C5)	971 (8)	3929 (6)	-1831 (4)	C(C5')	3331 (8)	4717 (5)	6892 (4)
C(C6)	1300 (7)	3837 (4)	-1182 (3)	C(C6')	2879 (7)	4311 (4)	6250 (3)
C(D1)	2664 (7)	4071 (4)	732 (3)	C(D1')	1915 (6)	3769 (4)	4433 (3)
C(D2)	3426 (8)	3974 (6)	1400 (4)	C(D2')	2072 (8)	3628 (6)	3863 (3)
C(D3)	3259 (11)	4580 (9)	1863 (4)	C(D3')	1224 (11)	4096 (7)	3330 (4)
C(D4)	2297 (13)	5219 (7)	1627 (7)	C(D4')	343 (11)	4632 (7)	3384 (5)
C(D5)	1581 (12)	5255 (6)	985 (6)	C(D5')	187 (10)	4727 (6)	3926 (5)
C(D6)	1742 (8)	4691 (4)	539 (4)	C(D6')	994 (7)	4288 (5)	4448 (4)
C(E1)	4385 (6)	3128 (4)	-265 (3)	C(E1')	5146 (6)	3259 (4)	5884 (3)
C(E2)	4197 (7)	2223 (4)	-380 (4)	C(E2')	6297 (7)	3807 (4)	6229 (3)
C(E3)	4532 (8)	1777 (5)	-832 (4)	C(E3')	7330 (7)	3594 (5)	6798 (4)
C(E4)	5057 (8)	2208 (6)	-1164 (4)	C(E4')	7223 (7)	2817 (5)	7030 (3)
C(E5)	5282 (8)	3132 (7)	-1022 (4)	C(E5')	6061 (7)	2272 (5)	6679 (3)
C(E6)	4914 (7)	3570 (5)	-578 (3)	C(E6')	5049 (7)	2487 (4)	6120 (3)

$P\bar{1}$ rather than $P1$ (six peaks expected). $P\bar{1}$ was confirmed by the complete structure analysis. Application of the heavy-atom method was routine. Refinement was by *XFLS-3* with $1/\sigma^2(F_o)$ as weights and Hartree–Fock scattering factors (Cromer & Mann, 1968); corrections for anomalous dispersion were applied for Pd, P and O. Three cycles of ‘isotropic’ refinement gave a conventional unweighted R of 0.104 for all significant reflexions. Another three cycles with anisotropic temperature factors, applied to all 96 non-hydrogen atoms, gave a final unweighted R of 0.059 and a value of 1.11 for the e.s.d. of a unit observation. H atomic positions could not be determined from the Fourier difference map and were not included in the F_c calculations.* The final difference map showed a few spurious peaks at ca $1.5 \text{ e } \text{\AA}^{-3}$ in the neighbourhood of the Pd atoms. Atomic coordinates are given in Table 1.

Discussion. The unit cell contains two pairs of centrosymmetrically related enantiomorphs: R_1, L_1 and R_2, L_2 . Molecules R_1 and R_2 are crystallographically independent but, apart from the torsional angles of substituents, are substantially identical. Molecules R_1 and L_2 (which are therefore approximate mirror images) lie adjacent in the cell and are illustrated in Fig. 1.

* Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32474 (48 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Bond lengths and angles are listed in Tables 2 and 3. The coordination of each Pd atom is square planar; in molecule 2 this plane is only slightly puckered (maximum deviation 0.06 Å), that of molecule 1 is slightly more so [O(2) out by 0.13 Å]. The bidentate acac ligand is practically planar with the best planes (maximum 0.03 Å for molecule 1; 0.06 Å for molecule 2) bending away from the coordination planes of Pd by 6.1 (6) and 4.6 (6)° respectively. The Pd–P distances [2.226 (3) and 2.227 (3) Å] are comparable to those found in similar complexes. The Pd–O(1) distances [average 2.121 (5) Å, *trans* to the sp^2 C(4)] are significantly longer than the Pd–O(2) distances [average 2.084 (5) Å, *trans* to P], but are far shorter than the ‘long’ Pd–O bond [2.158 (9) Å] observed in Pd(acac)-(C₁₈H₂₀) (Calvo, Hosokana, Reinheimer & Maitlis, 1972) which is *trans* to a Pd–C(sp^3) bond. The Pd–C bond lengths [average 2.007 (5) Å] compare well with other reported Pd–C(sp^2) σ bonds (Russel & Tucker, 1975). The butadienyl ligand is found to be monodentate, being attached to Pd by C(4) only [all other Pd...C distances >2.9 Å; Pd–C=C angles, 118.8 (5), 120.8 (5)°]. The butadienyl moiety is not conjugated, because the normals to the two vinyl planes subtend an average angle of 60.9 (6)°. While the –C(6)=C(7)– planes are only slightly puckered (maximum deviation 0.07 Å), those at –C(4)=C(5)– are more distorted (maximum deviation 0.26 Å) probably because of ring *D* (Fig. 1) which sits on top of the coordination plane, prying C(6) away from the vinyl plane. The torsional angles on C(4)=C(5) are 8 (1) and 14 (1)°. All the phenyl substituents have very good best planes, each tilted at an angle of 37–66° relative to a vinyl plane.

Table 2. Bond lengths (Å)

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Pd–P	2.226 (3)	2.227 (3)	C(2)–C(3)	1.43 (1)	1.41 (1)
Pd–O(1)	2.115 (5)	2.127 (5)	C(4)–C(5)	1.36 (1)	1.35 (1)
Pd–O(2)	2.090 (5)	2.078 (5)	C(5)–C(6)	1.51 (1)	1.52 (1)
Pd–C(4)	2.004 (5)	2.009 (5)	C(6)–C(7)	1.36 (1)	1.34 (1)
C(1)–O(1)	1.276 (10)	1.281 (10)	C(7)–O(3)	1.28 (1)	1.39 (1)
C(3)–O(2)	1.259 (8)	1.276 (9)	O(3)–C(8)	1.44 (1)	1.47 (1)
C(1)–C(2)	1.36 (1)	1.40 (1)	C(8)–C(9)	1.44 (2)	1.50 (2)

Table 3. Bond angles (°)

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
P–Pd–O(1)	87.7 (1)	86.5 (1)	C(1)–C(2)–C(3)	127.2 (8)	126.3 (7)
P–Pd–O(2)	174.9 (1)	175.7 (1)	O(2)–C(3)–C(2)	125.7 (7)	126.2 (7)
P–Pd–C(4)	92.0 (2)	94.3 (2)	Pd–C(4)–C(5)	118.8 (5)	120.8 (5)
O(1)–Pd–O(2)	89.4 (2)	89.5 (2)	C(4)–C(5)–C(6)	121.4 (6)	119.1 (5)
O(2)–Pd–C(4)	91.0 (2)	89.8 (2)	C(5)–C(6)–C(7)	121.8 (6)	123.7 (6)
Pd–O(1)–C(1)	123.7 (5)	123.9 (5)	C(6)–C(7)–O(3)	116.8 (6)	117.5 (6)
Pd–O(2)–C(3)	125.6 (4)	125.7 (4)	C(7)–O(3)–C(8)	119.7 (7)	114.1 (6)
O(1)–C(1)–C(2)	127.5 (7)	127.4 (7)	O(3)–C(8)–C(9)	112.7 (10)	106.5 (8)

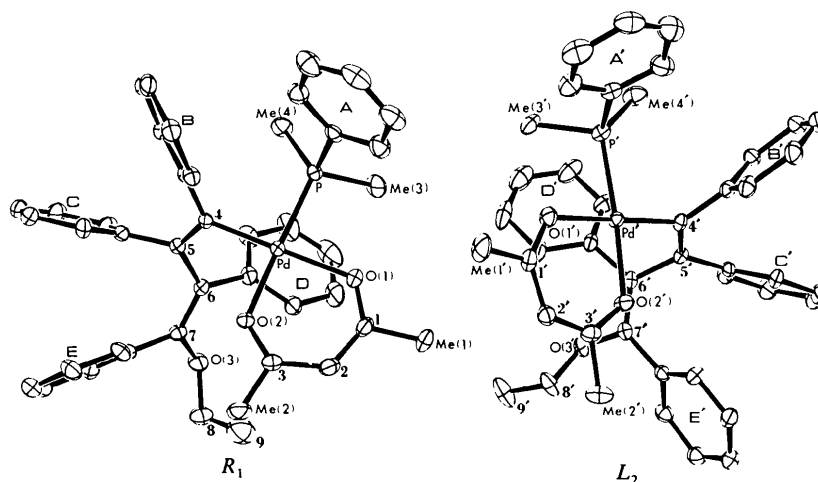


Fig. 1. Molecules R_1 and L_2 as located in the unit cell.

The ethyl group, being the most flexible moiety, has large thermal motion and hence less accurate bond lengths and angles.

This analysis shows that the ethoxy substituent of the butadienyl moiety [O(3)—C(8)—C(9)] is *trans* to the single bond C(5)—C(6).

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Neutron Diffraction of α -Calcium Formate at 100 and 296 K

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Abstract. α -Ca(HCOO)₂, orthorhombic, *Pcab*; $T = 100$ K: $a = 10.231(3)$, $b = 13.239(3)$, $c = 6.263(1)$ Å; $T = 296$ K: $a = 10.168(4)$, $b = 13.407(2)$, $c = 6.278(2)$ Å; $Z = 8$; $\mu(\lambda = 0.9106 \text{ Å}) = 0.74(6) \text{ cm}^{-1}$.

The Ca²⁺ ions are coordinated to eight O atoms and form chains parallel to *c* which are laterally bound through formate ions. The formate groups, strongly influenced by crystal-field effects, contract with increasing temperature.

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Introduction. Small colourless orthorhombic bipyramidal crystals were obtained by neutralizing a