group; the Pt–C(1)–C(2) angle of 132 (1)° gives a Pt···C(2) contact of 3·15 Å, while the C(1)–C(2)–C(3) angle of 124 (2)° gives a C(1)···C(3) distance of 2·50 Å. These angles may also be influenced by the interaction between Pt and C(3), which are separated by 3·58 Å, with a calculated Pt···H–C(3) contact of 2·99 Å.

We are grateful to Dr B. Sheldrick of the Biophysics Department, University of Leeds, for use of the diffractometer and to the Science Research Council for a studentship (to K.H.P.O'F.).

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1-Oxo-2-oxa-3,3-dimethylpent-4-ene-1,4-diylbis(triphenylphosphine)platinum(II)

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Abstract. [Pt(CO.OCMe$_2$C:CH$_2$)(PPh$_3$)$_2$], $C_{42}H_{38}O_2P_2Pt$, monoclinic, $P2_1/c$, $a=12{\cdot}298$ (2), $b=11{\cdot}038$ (3), $c=27{\cdot}207$ (3) Å, $\beta=102{\cdot}66$ (1)°, $D_m=1{\cdot}53$, $D_x=1{\cdot}533$ g cm^{-3}, $Z=4$, $V=3603$ Å^3. The compound, obtained by carbonylation of a hydroxyacetylene complex, is shown to have a 'platinalactone' structure with a five-membered chelate ring and exocyclic oxo and methylene groups adjacent to the metal.

Introduction. Measurements were made on a Nonius CAD-4 diffractometer using monochromatized Cu $K\alpha_1$ radiation ($\lambda=1{\cdot}54051$ Å). The cell dimensions and their e.s.d.'s were obtained by a least-squares fit of sin θ values for 25 reflexions centred using the program *SETANG*. Intensities were recorded in the θ–2θ scan mode using a scintillation counter and pulse-height discrimination. A control reflexion, monitored every 50 reflexions, had fallen in intensity by 16% at the end of data collection, and the measured reflexions were scaled accordingly. The structure determination used the 3732 independent reflexions with $\theta<70°$ and $I>3\sigma(I)$, where $I=P-2(B_1+B_2)$ and $\sigma^2(I)=P+4(B_1+B_2)+(0{\cdot}06I)^2$.

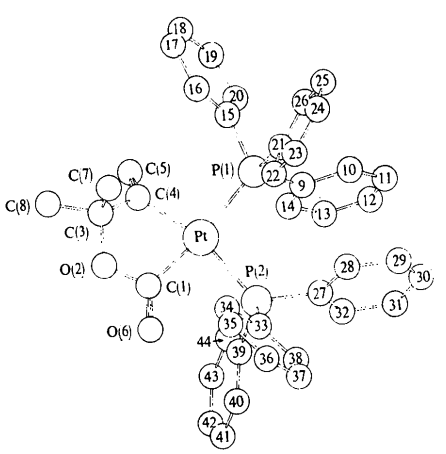


Fig. 1. Atom numbering.

The structure was solved by the heavy-atom method and refined by full-matrix least squares using the X-RAY programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Atomic coordinates, anisotropic temperature factors for Pt and P, and isotropic temperature factors for O and C were refined; the phenyl H atoms were included in calculated positions, assigned the temperature factors of the C atoms to which they are attached, but were not refined. Atomic scattering factors, including $\Delta f'$ and $\Delta f''$, were taken from *International Tables for X-ray Crystallography* (1974). Minimization of $w(F_o-|F_c|)^2$, with weights derived from the expression for $\sigma^2(I)$ given above, gave a final R of 6·21%. The atomic coordinates and vibration parameters with their e.s.d.'s are given in Table 1.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31679 (25 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional coordinates* ($\times 10^4$) *and vibration parameters* (Å$^2\times 10^3$) *and their e.s.d.'s*

The temperature factors are in the form $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{31}lhc^*a^*+2U_{12}hka^*b^*)]$ or $\exp[-2\pi^2U_{iso}(2\sin\theta/\lambda)^2]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
Pt	1286·4 (5)	3164·6 (5)	3553·1 (2)	41·6 (2)	36·2 (3)	41·6 (3)	8·0 (4)	17·3 (2)	10·9 (3)
P(1)	2718 (3)	3742 (3)	3163 (1)	45 (2)	38 (2)	41 (2)	3 (2)	18 (2)	6 (2)
P(2)	2343 (3)	2504 (3)	4330 (1)	44 (2)	40 (2)	46 (2)	7 (2)	19 (2)	10 (2)

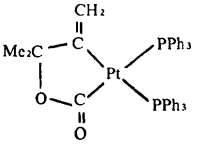
Table 1 (*cont.*)

	x	*y*	*z*	U_{iso}
C(1)	−94 (10)	2927 (11)	3828 (4)	37 (3)
O(2)	1068 (8)	3418 (9)	3557 (4)	57 (3)
C(3)	−974 (14)	3992 (18)	3086 (7)	72 (5)
C(4)	5 (13)	3453 (14)	2919 (6)	58 (4)
C(5)	−54 (15)	2940 (16)	2462 (7)	69 (5)
O(6)	−200 (8)	2466 (10)	4225 (4)	54 (3)
C(7)	−757 (17)	5298 (22)	3186 (8)	102 (7)
C(8)	−2115 (19)	3787 (22)	2724 (9)	108 (7)
C(9)	3853 (11)	2654 (13)	3209 (5)	43 (4)
C(10)	4985 (13)	2977 (15)	3315 (6)	61 (3)
C(11)	5806 (15)	2079 (16)	3310 (7)	71 (5)
C(12)	5478 (14)	941 (17)	3188 (6)	69 (5)
C(13)	4387 (14)	598 (16)	3074 (6)	65 (5)
C(14)	3558 (12)	1474 (14)	3087 (6)	54 (4)
C(15)	2339 (11)	4044 (13)	2489 (5)	43 (3)
C(16)	1673 (12)	5044 (14)	2333 (6)	57 (4)
C(17)	1302 (14)	5314 (16)	1826 (6)	70 (5)
C(18)	1589 (14)	4544 (16)	1471 (6)	66 (4)
C(19)	2246 (14)	3547 (16)	1611 (6)	68 (5)
C(20)	2631 (11)	3314 (13)	2134 (5)	50 (4)
C(21)	3340 (11)	5220 (13)	3385 (5)	45 (3)
C(22)	3051 (12)	5748 (15)	3799 (6)	58 (4)
C(23)	3515 (15)	6906 (18)	3951 (7)	77 (5)
C(24)	4183 (15)	7463 (19)	3695 (7)	78 (5)
C(25)	4455 (14)	6932 (17)	3281 (7)	71 (5)
C(26)	4019 (12)	5827 (14)	3134 (5)	52 (4)
C(27)	3857 (11)	2356 (14)	4443 (5)	47 (3)
C(28)	4509 (12)	3425 (13)	4547 (5)	53 (4)
C(29)	5687 (14)	3356 (16)	4648 (6)	66 (5)
C(30)	6215 (15)	2260 (17)	4637 (7)	71 (5)
C(31)	5591 (16)	1200 (19)	4547 (7)	82 (5)
C(32)	4373 (14)	1240 (16)	4442 (6)	63 (4)
C(33)	2236 (11)	3441 (12)	4873 (5)	46 (3)
C(34)	1519 (12)	4422 (14)	4817 (5)	52 (4)
C(35)	1481 (13)	5182 (15)	5215 (6)	61 (4)
C(36)	2158 (14)	4978 (16)	5684 (7)	72 (5)
C(37)	2895 (14)	2988 (16)	5756 (6)	68 (5)
C(38)	2939 (13)	3246 (15)	5352 (6)	61 (4)
C(39)	1867 (11)	963 (13)	4431 (5)	46 (3)
C(40)	1615 (12)	590 (14)	4889 (6)	52 (4)
C(41)	1233 (13)	−590 (16)	4923 (6)	65 (4)
C(42)	1066 (15)	−1323 (17)	4536 (7)	73 (5)
C(43)	1249 (14)	−998 (17)	4072 (7)	74 (5)
C(44)	1705 (12)	200 (14)	4035 (6)	57 (4)

Table 2. *Bond lengths* (Å) *and angles* (°) *with their e.s.d.'s*

Pt—P(1)	2·334 (4)	P(1)–Pt—P(2)	99·8 (1)
Pt—P(2)	2·341 (4)	P(1)–Pt—C(4)	95·2 (5)
Pt—C(1)	2·016 (14)	P(2)–Pt—C(1)	88·3 (3)
Pt—C(4)	2·091 (14)	C(1)–Pt—C(4)	77·4 (6)
C(1)–O(2)	1·37 (2)	Pt—C(1)–O(2)	117 (1)
C(1)–O(6)	1·23 (2)	Pt—C(1)–O(6)	130 (1)
O(2)–C(3)	1·46 (2)	O(2)–C(1)–O(6)	113 (1)
C(3)–C(4)	1·50 (3)	C(1)–O(2)–C(3)	115 (1)
C(4)–C(5)	1·35 (2)	O(2)–C(3)–C(4)	109 (1)
C(3)–C(7)	1·48 (3)	C(7)–C(3)–C(8)	111 (2)
C(3)–C(8)	1·54 (3)	C(3)–C(4)–Pt	109 (1)
P(1)–C(9)	1·83 (1)	C(3)–C(4)–C(5)	124 (1)
P(1)–C(15)	1·82 (1)	Pt—C(4)–C(5)	125 (1)
P(1)–C(21)	1·85 (1)	Pt—P(1)–C(9)	115·5 (5)
P(2)–C(27)	1·83 (1)	Pt—P(1)–C(15)	117·1 (5)
P(2)–C(33)	1·83 (1)	Pt—P(1)–C(21)	113·1 (5)
P(2)–C(39)	1·84 (1)	Pt—P(2)–C(27)	121·6 (5)
C–C (benzene ring)		Pt—P(2)–C(33)	115·4 (4)
= 1·30–1·46 (3), mean 1·38		Pt—P(2)–C(39)	107·0 (4)

Discussion. The molecular structure and atom numbering are shown in Fig. 1 and Table 2 gives bond lengths and angles with their e.s.d.'s. The compound was prepared by Empsall, Shaw & Stringer (1976) by carbonylation of the platinum(0) hydroxyacetylene complex [Pt(HC:CCMe$_2$OH) (PPh$_3$)$_2$], and is found to have the 'platinalactone' structure (I).



(I)

The chelate ring has an envelope conformation with the 'fold' along the Pt···C(3) line. The five atoms of the Pt–CO–O–C grouping are very nearly coplanar, the maximum deviation from the weighted mean plane being about two standard deviations. The planarity of this grouping is probably associated with conjugation in the O–C–O system, as evidenced by the C=O and C–O bond lengths of 1·23 and 1·37 (2) Å. The atoms of the C(5)=C(4)C(3)Pt olefin grouping are not accurately coplanar, a slight pyramidal distortion at C(4) taking that atom about 7σ from the weighted mean plane. The dihedral angle is 45·6° between these two planes. Details of the mean planes are given in Table 3.

Table 3. *Weighted mean planes*

(*a*) Equations referred to unit (Å) orthogonal axes parallel to a^*, b, c

(1) $0{\cdot}185X + 0{\cdot}872Y + 0{\cdot}453Z = 7{\cdot}553$
(2) $0{\cdot}382X + 0{\cdot}875Y - 0{\cdot}296Z = 0{\cdot}887$
(3) $-0{\cdot}018X + 0{\cdot}925Y + 0{\cdot}379Z = 6{\cdot}737$

(*b*) Atoms defining the planes, their displacements (Å), with the ratio (displacement/e s.d.) in parentheses

(1) Pt 0·000 (0·0), C(1) −0·028 (2·3), O(2) +0·011 (1·1), C(3) −0·011 (0·6), O(6) +0·006 (0·5)
(2) Pt 0·000 (0·0), C(3) −0·045 (2·3), C(4) +0·102 (6·8), C(5) −0·058 (3·2)
(3) Pt 0·000 (0·0), P(1) +0·010 (3·3), P(2) −0·005 (1·6), C(1) +0·212 (17·6), C(4) −0·199 (13·2)

The coordination of Pt departs significantly from planarity, a tetrahedral distortion giving C(1) and C(4) displacements of ±0·2 Å from the mean plane, with smaller displacements for the P atoms (see Table 3). The C–Pt–C angle in the chelate ring is only 77·4 (6)°, accompanied by an increase of the P–Pt–P angle to 99·8 (1)°. The inequality of the two *cis* C–Pt–P angles [95·2 (5) and 88·3 (3)°] is surprising, since it leads to close nonbonded contacts on one side of the chelate ring [P(2)···C(1) and P(2)···O(6) = 3·04 and 3·08 Å] while the corresponding distances on the other side of the ring are much longer [P(1)···C(4) and P(1)···C(5) = 3·27 and 3·63 Å]. These features sug-

gest some attractive contact between the carbonyl and phosphine groups, although the effect of the many repulsive interactions within and between the triphenylphosphine ligands is hard to assess.

We are grateful to Dr B. Sheldrick of the Biophysics Department, University of Leeds, for use of the diffractometer and to the Science Research Council for a studentship (to M.C.N.).

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Bis-(2,2,6,6-tetramethylheptane-5-thiolo-3-onato)palladium(II)

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Abstract. Pd($C_{11}H_{19}OS)_2$, monoclinic, $P2_1/c$, $a=11{\cdot}15$ (1), $b=21{\cdot}22$ (1), $c=12{\cdot}40$ (1) Å, $\beta=119{\cdot}3$ (1)°, $Z=4$. The two S and two O atoms occur in *cis* arrangement in a distorted square-planar configuration around Pd at distances of 2·232 (2) and 2·028 (6) Å respectively. The bond lengths in the chelate rings indicate partial double bonds and hence incomplete delocalization.

Introduction. Shkol'nikova, Yutal, Shugam & Knyazeva (1973) found a surprisingly short Pd–S bond (2·235 Å), which they ascribed to $d\pi$–$p\pi$ back donation in palladium monothiodibenzoylmethanate. The Pd–O bond (2·10 Å) was also considered short, and this was ascribed to the strong *trans* effect of S. Because both observations have significant implications, an independent investigation of these effects is desirable.

Table 1. *Final fractional positional* ($\times 10^4$) *and anisotropic thermal parameters* (Å$^2 \times 10^3$) *with e.s.d.'s in parentheses*

$T=\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ring I									
Pd	−493 (1)	1184 (0)	226 (1)	34 (0)	44 (0)	32 (0)	−6 (0)	18 (0)	−4 (0)
S	1547 (2)	1645 (1)	1371 (2)	37 (1)	59 (2)	44 (1)	−14 (1)	23 (1)	−8 (1)
O	−1394 (6)	1580 (3)	1142 (6)	40 (4)	54 (5)	45 (4)	−14 (3)	24 (3)	−5 (3)
C(1)	1502 (9)	2119 (4)	2461 (8)	37 (5)	41 (6)	38 (5)	−3 (4)	16 (4)	−3 (4)
C(2)	405 (9)	2233 (6)	2657 (9)	38 (5)	49 (6)	51 (6)	−10 (5)	25 (4)	−3 (4)
C(3)	−939(9)	1963 (5)	2032 (8)	41 (5)	41 (6)	42 (5)	−2 (5)	21 (4)	1 (5)
C(4)	2888 (10)	2430 (5)	3361 (10)	37 (5)	69 (8)	55 (6)	−21 (5)	24 (5)	−13 (5)
C(5)	−1984 (10)	2159 (5)	2446 (9)	42 (5)	51 (7)	51 (5)	−7 (5)	28 (4)	1 (5)
M(1)	4039 (12)	2345 (8)	3033 (13)	54 (6)	141 (12)	93 (8)	−53 (8)	45 (5)	−33 (7)
M(2)	2718 (15)	3140 (8)	3495 (21)	71 (11)	74 (10)	248 (28)	−67 (9)	66 (12)	−20 (8)
M(3)	3405 (17)	2078 (11)	4628 (14)	101 (13)	236 (20)	65 (9)	20 (11)	21 (11)	−64 (12)
M(4)	−3279 (11)	1743 (6)	1802 (12)	47 (5)	88 (8)	94 (7)	−39 (6)	46 (5)	−25 (5)
M(5)	−1324 (12)	2078 (7)	3871 (10)	68 (7)	108 (11)	47 (6)	2 (6)	39 (5)	5 (7)
M(6)	−2384 (12)	2865 (6)	2072 (12)	66 (7)	57 (7)	87 (8)	6 (6)	41 (6)	17 (5)
Ring II									
S	416 (2)	751 (1)	−849 (2)	40 (1)	59 (2)	41 (1)	−13 (1)	24 (1)	−8 (1)
O	−2362 (6)	776 (3)	−775 (6)	39 (3)	59 (5)	46 (4)	−13 (3)	25 (3)	−8 (3)
C(1)	−832 (9)	363 (4)	−2105 (8)	47 (5)	35 (5)	30 (4)	−2 (3)	21 (3)	1 (4)
C(2)	−2170 (10)	246 (5)	−2384 (8)	45 (5)	52 (6)	40 (4)	5 (4)	26 (4)	3 (4)
C(3)	−2848 (9)	433 (5)	−1724 (8)	34 (4)	50 (6)	38 (5)	−2 (4)	17 (4)	1 (4)
C(4)	−374 (10)	147 (5)	−3044 (8)	54 (5)	47 (6)	41 (4)	1 (4)	31 (4)	0 (4)
C(5)	−4318 (10)	224 (6)	−2161 (9)	38 (5)	70 (7)	49 (6)	18 (5)	20 (4)	8 (4)
M(1)	1211 (11)	34 (6)	−2424 (10)	54 (5)	83 (8)	63 (5)	14 (5)	40 (4)	−1 (5)
M(2)	−1110 (12)	−473 (6)	−3700 (10)	73 (6)	64 (7)	60 (5)	−26 (5)	41 (5)	−14 (5)
M(3)	−796 (13)	695 (6)	−4002 (10)	99 (7)	70 (8)	53 (5)	−12 (5)	51 (5)	−12 (6)
M(4)	−4836 (16)	−319 (10)	−3148 (19)	74 (6)	185 (11)	169 (11)	89 (9)	73 (7)	54 (7)
M(5)	−5212 (18)	778 (10)	−2714 (33)	65 (8)	115 (15)	487 (30)	1 (17)	106 (15)	−5 (9)
M(6)	−4527 (18)	15 (17)	−1128 (15)	93 (6)	499 (20)	67 (7)	25 (9)	36 (5)	123 (7)