Crystal and Molecular Structure of Di-μ-acetato-bis-[(2-methylallyl-3-norbornyl)palladium(II)]

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A three-dimensional structure analysis of the title compound has been carried out from diffractometer data by Patterson and Fourier methods. Crystals are orthorhombic, with $a = 11{\cdot}822$, $b = 12{\cdot}513$, $c = 17{\cdot}609$ Å, space group *Pbcn*, $Z = 8$. The structure was refined by least squares to a final R of 0·062 for 2215 observed reflections. The molecule is dimeric, symmetry C_2, with a Pd ··· Pd distance of 2·960(1) Å. The co-ordination geometry about each Pd ion is approximately square-pyramidal, with the vinyl end of the lateral chain of the hydrocarbon ligand being shifted from the ' normal ' position in related Pd and Pt complexes. The Pd–O distances show evidence of *trans*-influence by the co-ordinated carbon atom of the norbornyl moiety.

THE insertion reaction of norbornene into nickel–allyl and palladium–allyl bonds has recently been studied [1] since it can be considered as the first step in the polymerization of olefins by transition-metal catalysts. A preliminary communication on the structure of the title compound, formed on treatment with AcONa of the product of one of those reactions, has already appeared; [2] however, because of its interesting stereochemistry and the good quality of the X-ray intensity data, we felt that it was worthwhile to refine this crystal structure further.

EXPERIMENTAL

Crystals were regular parallelopipeds. The crystal used for the structural analysis was approximately cube-shaped, edge *ca.* 0·03 cm, and extinguished sharply under crossed polarizers. In order to prevent any possible decomposition, the crystal was sealed under vacuum in a very thin glass capillary before being mounted on a goniometer head.

Crystal Data.—$C_{13}H_{20}O_2Pd$, $M = 314{\cdot}4$, Orthorhombic, $a = 11{\cdot}822(2)$, $b = 12{\cdot}513(2)$, $c = 17{\cdot}609(3)$ Å, $U = 2604{\cdot}9$ Å^3, $Z = 8$, $D_c = 1{\cdot}60$ g cm^{-3}. Space group *Pbcn*. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 15·2 cm^{-1}.

The intensities were measured with a General Electric XRD 6 three-circle diffractometer (Zr-filtered Mo-K_α radiation) up to a sin θ/λ value of 0·70 Å^{-1}, by the ω—2θ scanning technique and by averaging two background counts for each reflection. During data collection the intensities of three standard reflections were monitored every hour. The intensity variations of the standard reflections were such that the relative standard deviations of the corresponding structure factors were $<2\%$.

Of the 3690 independent reflections measured, 2215 were considered observed, having $I \geqslant 2{\cdot}5\sigma(I)$.

Data were corrected for Lorentz and polarization factors, but not for absorption since the crystal was small and of regular shape.

Preliminary checks on various reflections, for which the azimuth of the corresponding planes could be varied, showed no intensity anomalies which could have been attributed to extinction or multiple diffraction. After a first refinement of the structure, the strong 002 reflection was suspected to be affected by extinction and was excluded from the final least-squares cycles.

In order to prevent even small effects of simultaneous diffraction altering systematically a particular class of reflections, the crystal was oriented on the diffractometer so that no rational direction was parallel to the Φ-circle axis.

Structure Determination.—The structure was solved by Patterson and Fourier methods. Refinement was carried out by a least-squares method, using the weighting scheme suggested by Cruickshank,[3] in three steps, as follows. (i) The palladium, carbon, and oxygen atomic positional and isotropic thermal parameters were refined in the block-diagonal approximation (3 cycles) by use of Moore [4] coefficients for atomic scattering factors down to R 0·099 ($R = \Sigma|K|F_o| - |F_c||/\Sigma|KF_o|$, where K is the scale factor) for the 2215 observed reflections.

(ii) In three further cycles, also in the block-diagonal approximation, in addition to the three positional parameters, six anisotropic thermal parameters for each atom were also refined. Dirac–Slater atomic scattering factors from ref. 5 for palladium and Hartree–Fock factors from ref. 6 for carbon, and oxygen were used. An anomalous scattering correction according to ref. 7 was applied for palladium. R was then 0·070.

(iii) The positional parameters of the hydrogen atoms were calculated by assuming sp^2 or sp^3 hybridization for their attached carbon atoms. A Fourier difference map, based on the structure factors calculated for non-hydrogen atoms, confirmed the calculated position except for hydrogen bonded to C(10) (see Figure 1), which was *ca.* 0·6 Å from the calculated position.

Three full-matrix cycles were then carried out, without varying the hydrogen atom positional and isotropic thermal parameters, but including them in the structure factor calculations. The atomic scattering factors used here were the same as for the previous step. R for the 2215 observed reflections converged at 0·062.

Three more cycles, carried out with Hartree–Fock scattering factors but without the anomalous scattering correction for palladium, resulted in the same final set of parameters except for the Pd anisotropic thermal parameters which were significantly lower than before. This result is in accordance with that reported by Stewart.[8]

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[2] M. Zocchi, G. Tieghi, and A. Albinati, *J. Organometallic Chem.*, 1971, **33**, C47.

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[8] R. F. Stewart, A.C.A. Winter Meeting, University of South Carolina, Jan 31, 1971.

A final difference-Fourier map showed no significant features except for a small peak of *ca.* 0·8 eÅ^{-3} at the Pd position, and a spherical shell of electron density about this position, averaging 0·8 eÅ^{3}, possibly indicating a series termination effect.

The refined atomic positional and thermal parameters and their estimated standard deviations are given in Table 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20618 (23 pp., 1 microfiche).*

DISCUSSION

A list of the bond lengths and angles, together with their estimated standard deviations, is given in Table 2.

As shown in Figure 1, two oxygen atoms belonging to two different acetate groups, one carbon atom of the norbornyl moiety and the vinyl end of the lateral chain of the hydrocarbon ligand form approximately a square about each Pd ion. The other Pd ion in the dimeric molecule (symmetry C_2) completes the co-ordination at a distance of 2·960(1) Å. This relatively short distance can be compared with that of 2·94 Å [9] in an acetato-π-allylpalladium dimer. Following the reasoning in ref. 9, one may speculate that a rather strong interaction must exist between the two Pd ions in this complex also. Since Pd(1) lies only 0·02 Å from the plane defined by O(1), O(2′), and C(2), the co-ordination geometry about each Pd ion can be described as a very distorted square pyramid, with the Pd(1) ··· Pd(1′) axis making an angle of 15·70° with the normal to the basal plane, already defined.

TABLE 1

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

	x/a	*y/b*	*z/c*	B_{11} *	$B_{22}(\sigma)$	$B_{33}(\sigma)$	B_{12}	B_{13}	B_{32}
Pd(1)	0·11611(5)	0·15379(5)	0·21853(4)	2·74(2)	3·21(2)	3·53(2)	−0·62(2)	−0·04(2)	−0·06(2)
O(1)	0·11758(52)	0·01392(55)	0·29396(38)	4·41(29)	3·93(28)	4·45(28)	0·97(22)	0·02(22)	0·73(22)
O(2)	−0·03171(46)	0·06194(44)	0·36413(33)	3·22(21)	3·44(22)	4·00(24)	−0·83(18)	−0·02(18)	−0·28(19)
C(1)	0·09152(97)	0·27592(85)	0·06758(61)	5·47(49)	4·72(45)	4·81(45)	−1·50(39)	−0·50(39)	1·04(37)
C(2)	0·11537(76)	0·28785(71)	0·15250(53)	4·30(38)	3·44(33)	4·00(36)	−0·71(28)	−0·56(29)	−0·04(29)
C(3)	0·23143(91)	0·34891(75)	0·15723(61)	5·28(48)	4·00(39)	5·09(45)	−1·96(35)	0·21(38)	−1·22(34)
C(4)	0·25557(114)	0·36746(110)	0·07096(72)	5·93(58)	6·87(63)	5·85(57)	−2·69(50)	0·86(49)	0·41(51)
C(5)	0·16721(144)	0·44783(108)	0·04080(86)	9·05(88)	5·47(59)	7·94(78)	−1·72(61)	0·23(70)	2·73(57)
C(6)	0·05675(114)	0·38300(108)	0·03672(87)	5·94(61)	6·03(59)	9·22(85)	−1·49(51)	−2·31(59)	3·66(60)
C(7)	0·21199(111)	0·26339(97)	0·03591(62)	6·53(60)	5·94(56)	4·71(46)	−1·67(48)	0·10(43)	−0·27(43)
C(8)	0·32234(84)	0·28197(94)	0·19640(66)	3·55(37)	5·92(53)	5·99(50)	−2·13(37)	−0·78(36)	0·51(43)
C(9)	0·27475(71)	0·21616(82)	0·26206(51)	3·14(33)	5·67(46)	3·79(34)	−1·83(32)	−0·79(27)	−0·16(33)
C(10)	0·18415(86)	0·25342(84)	0·30660(50)	4·71(42)	5·43(47)	3·11(32)	−0·92(37)	−0·19(30)	−0·93(32)
C(11)	0·34972(110)	0·12675(127)	0·29207(85)	4·05(46)	7·78(75)	8·45(82)	−0·95(51)	−0·87(50)	2·50(64)
C(12)	0·05494(62)	0·00749(56)	0·35136(42)	3·29(28)	2·51(25)	3·03(27)	0·72(22)	0·49(23)	0·37(21)
C(13)	0·08404(87)	−0·08081(82)	0·40891(61)	4·46(41)	4·51(42)	5·18(45)	1·02(35)	−0·24(36)	1·52(36)

* Temperature factor = $\exp -\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)$.

TABLE 2

Molecular geometry

(*a*) Bond distances (Å)

Pd(1)–Pd(1′)	2·960(1)	C(2)–C(3)	1·572(14)
Pd(1)–O(1)	2·198(7)	C(3)–C(4)	1·563(17)
Pd(1)–O(2′)	2·106(6)	C(3)–C(8)	1·528(15)
Pd(1)–C(2)	2·043(9)	C(4)–C(5)	1·540(20)
Pd(1)–C(9)	2·171(9)	C(4)–C(7)	1·527(18)
Pd(1)–C(10)	2·146(10)	C(5)–C(6)	1·536(21)
O(1)–C(12)	1·257(10)	C(8)–C(9)	1·527(15)
O(2)–C(12)	1·248(9)	C(9)–C(10)	1·405(13)
C(1)–C(2)	1·525(14)	C(9)–C(11)	1·524(18)
C(1)–C(6)	1·507(17)	C(12)–C(13)	1·540(19)
C(1)–C(7)	1·539(17)		

(*b*) Bond angles (°)

Pd(1)–O(1)–C(12)	122·1(5)	O(1)–C(12)–C(13)	116·2(4)
Pd(1′)–O(2)–C(12)	124·2(1)	O(2)–C(12)–C(13)	116·3(4)
Pd(1)–C(2)–C(1)	118·4(5)	C(1)–C(2)–C(3)	105·2(4)
Pd(1)–C(2)–C(3)	111·3(4)	C(1)–C(6)–C(5)	102·7(5)
Pd(1)–C(9)–C(8)	104·2(4)	C(1)–C(7)–C(4)	94·5(5)
Pd(1)–C(9)–C(11)	111·1(5)	C(2)–C(1)–C(6)	108·4(5)
Pd(1)–C(9)–C(10)	70·0(5)	C(2)–C(1)–C(7)	101·2(4)
Pd(1)–C(10)–C(9)	72·0(5)	C(2)–C(3)–C(4)	100·3(4)
O(1)–Pd(1)–O(2′)	89·3(1)	C(2)–C(3)–C(8)	111·9(4)
O(2′)–Pd(1)–C(2)	93·0(2)	C(3)–C(4)–C(5)	107·9(5)
O(1)–Pd(1)–C(9)	93·8(2)	C(3)–C(4)–C(7)	101·9(4)
O(1)–Pd(1)–C(10)	91·3(2)	C(3)–C(8)–C(9)	112·2(4)
O(1)–Pd(1)–C(2)	177·6(4)	C(4)–C(3)–C(8)	113·0(4)
O(2′)–Pd(1)–C(9)	148·2(4)	C(4)–C(5)–C(6)	104·4(5)
O(2′)–Pd(1)–C(10)	173·7(4)	C(5)–C(4)–C(7)	100·9(5)
C(2)–Pd(1)–C(9)	84·8(2)	C(6)–C(1)–C(7)	102·0(4)
C(2)–Pd(1)–C(10)	86·4(2)	C(8)–C(9)–C(10)	121·7(4)
C(9)–Pd(1)–C(10)	38·0(8)	C(8)–C(9)–C(11)	116·3(4)
O(1)–C(12)–O(2)	126·4(3)	C(10)–C(9)–C(11)	119·5(5)

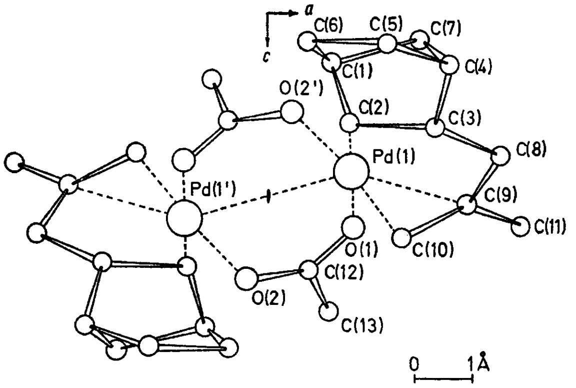

FIGURE 1 Projection of the dimeric molecule along *b*

This plane passes through the C:C vinyl bond much closer to atom C(10) than to atom C(9), the distance of the former from the plane being only 0·20 Å. The C:C

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Index Issue No. 20.

[9] M. R. Churchill and R. Mason, *Nature*, 1964, **204**, 777.

bond axis makes an angle of 12·66° with the normal to this plane, while the angle between this normal and the normal to the plane defined by Pd(1), C(9), and C(10) is 93·9°. This co-ordination geometry is presented in Figure 2.

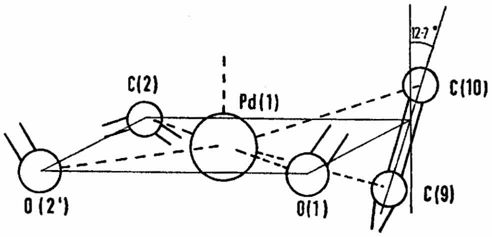

FIGURE 2 A view of the co-ordination geometry about the Pd ion

The shift of the C⁚C bond from its ' normal ' position, perpendicular to the basal plane and symmetrically located with respect to it, is not easily explained in terms of steric factors in view of the conformational freedom of rotation about the C(3)–C(8) and C(8)–C(9) single bonds and about the co-ordination bond Pd(1)–C(2). We feel that an explanation should rather be found in the asymmetry induced by the substituents of C(9) into the ligand π^* orbital. As a consequence of this asymmetry, if the C⁚C bond were in a ' normal ' position, the overlap of this π^* orbital with the filled metal d orbitals would decrease and a weakening of the μ-bond would derive. In this asymmetric situation the overlap can be improved only by causing a shift of the C⁚C bond in such a way that C(9) will be closer to the main axis of one of the lobes of a d_{xz} or d_{yz} orbital of the metal (our reference system is so oriented that the Z axis is coincident with the normal to the ' basal ' plane of the co-ordination pyramid). In fact the direction of the shift observed in the present structure is in agreement with the above interpretation.

The length of the C(9)–C(10) bond (1·41 Å) compares well with those for other co-ordinated olefinic bonds. Carbon atom C(9) shows a significant distortion from trigonal symmetry as indicated by the internal rotation angles Pd(1)–C(10)–C(9)–C(11) 76·5 and Pd(1)–C(10)–C(9)–C(8) 85·4°. The difference of 2σ between the distances Pd(1)–C(9) and Pd(1)–C(10) is probably not significant.

The Pd(1)–O(1) and Pd(1)–O(2′) distances are significantly different and the difference (10σ) may be attributed to the fact that the σ-bonded C(2) atom has a *trans*-influence larger than the one of the vinyl bond. This result is in accord with that for di-μ-chloro-bis-[(methoxydicyclopentadiene)platinum] [10] and for (acetylacetonato)cyclo-octenylnickel(II).[11]

The mean C–C distance in the norbornyl moiety is 1·539 Å and no single distance differs from this by $>2\sigma$. However, significant distortions are indicated by the values of the bond angles and especially by the angle C(1)–C(7)–C(4) which is smaller than the tetrahedral angle by $>30\sigma$. Similar distortions have already been found in other norbornane derivatives.[12]

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[2/1890 *Received, 9th August,* 1972]

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[10] W. A. Whitla, H. M. Powell, and L. M. Venanzi, *Chem. Comm.*, 1966, 310.

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[12] A. V. Fratini, K. Britts, and I. L. Karle, *J. Phys. Chem.*, 1967, **71**, 2482.