Crystal and Molecular Structures of the Isobutene Insertion Product of *endo*-Hexafluoroacetylacetonato(methoxytetraphenylbutadienyl)-palladium(II)

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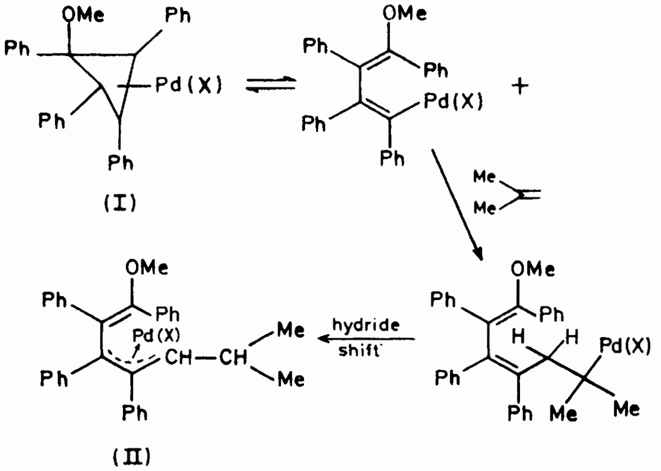
X-Ray analysis shows crystals of the title compound to be monoclinic, space group $P2_1/c$, with cell dimensions a = 19.680(7), b = 12.470(6), c = 17.532(7) Å, β = 118.9(1)°, Z = 4. The complex has the structure assigned to it (on the basis of several physical techniques) except for the stereochemistry of the PhC=CPhOMe group which is unexpectedly *cis*-diphenyl. The crystal contains one molecule of n-pentane of crystallization per two molecules of complex.

A VARIETY of physical techniques has been used to show that complexes of type (I), where X = acetylacetonate (acac) or 1,1,1,5,5,5-hexafluoroacetylacetonate (hfacac), exist in a state of equilibrium in solution. The 'ring-opened' forms can be obtained as stable products by forming suitable adducts.[1] The crystal structure of one such adduct with PMe_2Ph (X = acac) has been determined.[2]

The equilibrium mixture in solution undergoes insertion reactions with alkenes, 1,2-dienes, and 1,3-dienes. The mechanism for insertion of isobutene,[3] for example, is thought to be as shown in the Scheme.



SCHEME

We report here on the crystal structure of (II) (X = hfacac), which confirms the structure drawn except that the stereochemistry is *cis*-phenyl instead of *trans*. The crystal structure of a similar complex made from $[Pd\{\eta^3\text{-}C_4(O_2SC_6H_4Me\text{-}p)_4Ph\}(acac)]$ however shows *trans* stereochemistry at this bond.[4]

EXPERIMENTAL

Crystals of the complex, crystallized from n-pentane, were yellowish and had well developed faces. A specimen of dimensions 0.18 × 0.18 × 0.32 mm was used for *X*-ray analysis. Lattice constants were determined on a Picker four-circle diffractometer from the 2θ values of 11 centred reflections.

Crystal Data.—$C_{38}H_{32}F_6O_3Pd\cdot0.5(C_5H_{12})$. $M = 793.15$, Monoclinic, space group $P2_1/c$, $a = 19.680(7)$, $b = 12.470(6)$, $c = 17.532(7)$ Å, $\beta = 118.9(1)°$, $U = 3\,767.1$ Å^3, $D_m = 1.37$, $Z = 4$, $D_c = 1.398$ g cm^{-3}, $F(000) = 648$, $\mu(\text{Mo-}K_\alpha) = 5.57$ cm^{-1}, $\lambda = 0.710\,69$ Å.

Intensity data were collected using Zr-filtered Mo-K_α radiation in θ—2θ scan mode at 2° min^{-1} in the range $0 < \sin\theta < 0.5$. A standard recorded every 30 reflections showed the crystal to be stable. $\sigma(F_o)$ was taken as $[(\sigma(I)/Lp)^2 + 0.02F_o^4]^{\frac{1}{2}}/2F_o$ where Lp is the Lorentz-polarization factor. On the criterion $|F_o| > 2\sigma(F_o)$, 3 497 reflections out of a total of 6 221 were considered significant. No absorption corrections were applied.

Structure Determination.—The structure was solved by routine application of the heavy-atom method. Anisotropic full-matrix least-squares refinement using corrections for anomalous dispersion of Pd ($\Delta f' = -1.177$, $\Delta f'' = 1.007$) was uneventful. All the hydrogen atoms of the complex were found on the final difference map but the positions used for refinement were established by FINDH [5] with isotropic temperature factors $B = 6$ Å^2. Atomic co-ordinates for the complex are given in Table 1. Structure factor amplitudes, atomic co-ordinates of non-hydrogen atoms, and anisotropic parameters are deposited as Supplementary Publication No. SUP 23084 (24 pp.).*

The difference map also showed the presence of n-pentane solvent molecules at the symmetry centres ($\frac{1}{2}$,0,$\frac{1}{2}$) and ($\frac{1}{2}$,$\frac{1}{2}$,0) but not at the other six centres. Since n-pentane cannot be centric in any conformation these sites must represent two disordered solvent molecules with occupancy 0.5. Thus the ratio complex : solvent is 2 : 1. Because of disorder, the atomic co-ordinates could only be assigned approximately, Table 1(*b*).

The final conventional R factor was 0.095; R' = 0.100.

DISCUSSION

A general view of the complex is given in Figure 1. Bond lengths and angles are given in Table 2. The structure of the complex is that given as (II) above, except that the phenyl groups at the double bond C(14)–C(16) are *cis* not *trans*. The Pd atom is co-ordinated on one side to the bidentate hfacac system and on the other to the chain of three sp^2-hybridized carbon atoms C(9), C(10), and C(12) in the butadienyl system. Atoms O(1), C(2), C(3), C(4), and O(2) of the hfacac are closely co-

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

TABLE 1

Atomic co-ordinates ($\times 10^4$ for complex, $\times 10^3$ for solvent) for the non-hydrogen atoms of the complex $[Pd\{\eta^3\text{-}C_7H_5Me(OMe)Ph_4\}(hfacac)]\cdot0.5C_5H_{12}$, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
(*a*) Complex			
Pd	2 463(1)	363(1)	−1 348(1)
O(1)	3 211(6)	−544(7)	−1 653(6)
O(2)	1 742(5)	489(8)	−2 711(5)
O(3)	1 865(5)	2 671(6)	−2 132(5)
F(1)	4 039(8)	−2 179(10)	−1 727(9)
F(2)	4 343(7)	−835(9)	−2 250(8)
F(3)	3 505(9)	−2 040(12)	−3 119(9)
F(4)	1 182(7)	−364(10)	−4 821(6)
F(5)	904(6)	1 107(8)	−4 359(6)
F(6)	510(7)	−390(9)	−4 163(7)
C(1)	3 734(11)	−1 463(12)	−2 375(11)
C(2)	3 055(10)	−830(11)	−2 391(13)
C(3)	2 409(11)	−666(11)	−3 187(11)
C(4)	1 807(9)	−21(10)	−3 278(9)
C(5)	1 135(10)	69(11)	−4 169(10)
C(6)	3 687(11)	−303(15)	1 514(9)
C(7)	4 201(12)	−778(17)	509(12)
C(8)	3 492(10)	−537(11)	583(9)
C(9)	3 015(8)	370(11)	26(8)
C(10)	2 222(8)	471(10)	−307(7)
C(11A)	1 737(8)	−318(10)	−166(8)
C(11B)	1 423(11)	−93(11)	348(10)
C(11C)	979(12)	−801(14)	512(11)
C(11D)	793(11)	−1 791(12)	84(12)
C(11E)	1 074(10)	−2 053(11)	−456(10)
C(11F)	1 552(9)	−1 340(11)	−588(9)
C(12)	1 867(8)	1 399(9)	−885(8)
C(13A)	1 003(7)	1 453(10)	−1 413(7)
C(13B)	631(8)	2 349(11)	−1 287(9)
C(13C)	−168(10)	2 443(12)	−1 781(11)
C(13D)	−611(9)	1 634(17)	−2 384(12)
C(13E)	−224(11)	765(14)	−2 502(10)
C(13F)	586(8)	676(9)	−2 003(8)
C(14)	2 289(7)	2 469(8)	−661(7)
C(15A)	2 413(7)	4 254(9)	−1 247(7)
C(15B)	2 668(9)	4 657(11)	−1 781(9)
C(15C)	2 890(10)	5 745(12)	−1 736(11)
C(15D)	2 859(9)	6 407(10)	−1 125(11)
C(15E)	2 584(9)	6 029(12)	−617(10)
C(15F)	2 369(8)	4 950(10)	−669(8)
C(16)	2 187(7)	3 107(10)	−1 321(7)
C(17)	1 184(9)	3 202(11)	−2 832(8)
C(18A)	2 789(8)	2 734(9)	284(8)
C(18B)	3 532(9)	3 090(11)	590(10)
C(18C)	3 983(10)	3 358(13)	1 461(13)
C(18D)	3 677(14)	3 240(13)	2 022(12)
C(18E)	2 931(12)	2 907(11)	1 722(10)
C(18F)	2 497(8)	2 646(10)	847(8)
(*b*) Solvent			
C(A)	0.500	0.352	−0.110
C(B)	0.500	0.361	−0.023
C(C)	0.500	0.480	0.000
C(D)	0.500	0.489	0.087
C(E)	0.500	0.608	0.110

planar but Pd, C(1), and C(5) are −0.220, 0.212, and −0.113 from this plane respectively (Table 3). The C–F distances do not differ significantly, the range [1.31—1.36(2) Å] being much less than those determined in hfacac complexes of Cu^{II} (1.21—1.35 Å) and of Mg^{II} (1.21—1.40 Å), attributed to systematic errors.[6]

Pd–hfacac co-ordination resembles Pd–acac co-ordination [7] except that the Pd–O distances here [2.11—2.12(1) Å] are significantly longer than those in the Pd–acac complex [2.084, 2.007(5) Å]. The Pd co-ordination can be represented (Figure 2) as that of a somewhat distorted

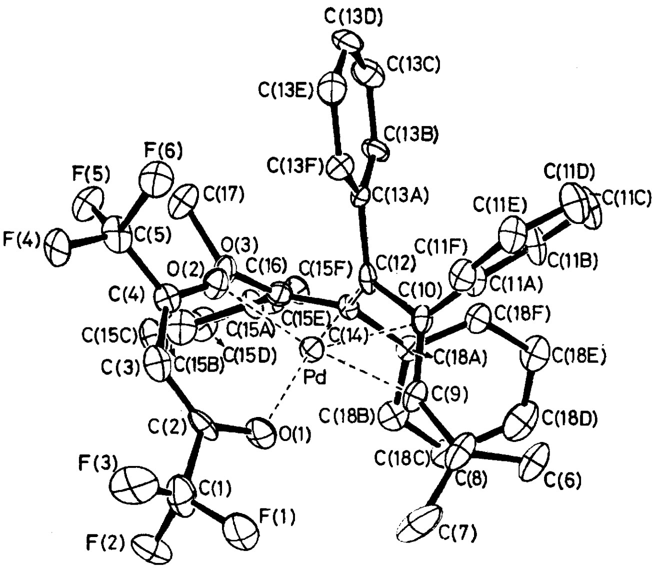

FIGURE 1 ORTEP plot of molecule of complex with 50% probability ellipsoids (hydrogen atoms not shown)

rectangle. The corners of the rectangle are almost coplanar (Table 3) and Pd lies 0.042 Å from the best least-squares plane.

The allyl part [C(9), C(10), C(12)] of the tetraphenylbutadienyl moiety is tilted 108.7° from the plane C(9)–Pd–C(12) but the Pd···C distances remain closely similar, 2.11, 2.10, and 2.15(1) Å. Similar geometries have been reported for allyl- [8] and methylallyl-palladium [9,10] complexes. In these, the Pd–C distances are also

TABLE 2

Bond distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances

Pd–O(1)	2.12(1)	C(5)–F(5)	1.36(2)
Pd–O(2)	2.11(1)	C(5)–F(6)	1.36(2)
Pd–C(9)	2.11(1)	C(7)–C(8)	1.49(3)
Pd–C(10)	2.10(1)	C(6)–C(8)	1.51(2)
Pd–C(12)	2.15(1)	C(8)–C(9)	1.49(2)
C(2)–O(1)	1.23(2)	C(9)–C(10)	1.38(2)
C(4)–O(2)	1.24(2)	C(10)–C(11A)	1.47(2)
C(2)–C(3)	1.36(3)	C(10)–C(12)	1.47(2)
C(3)–C(4)	1.38(3)	C(12)–C(13A)	1.49(2)
C(1)–C(2)	1.54(3)	C(12)–C(14)	1.52(2)
C(4)–C(5)	1.49(2)	C(14)–C(18A)	1.50(2)
C(1)–F(1)	1.34(2)	C(14)–C(16)	1.34(2)
C(1)–F(2)	1.36(3)	C(16)–O(3)	1.36(1)
C(1)–F(3)	1.36(2)	C(17)–O(3)	1.47(2)
C(5)–F(4)	1.31(2)	C(16)–C(15A)	1.49(2)

C–C (aromatic) mean 1.383(25)

(*b*) Angles

O(1)–Pd–O(2)	85.6(4)	C(7)–C(8)–C(9)	114(1)
Pd–O(1)–C(2)	125(1)	C(8)–C(9)–C(10)	125(1)
Pd–O(2)–C(4)	127(9)	C(9)–C(10)–C(12)	115(1)
O(1)–C(2)–C(3)	131(2)	C(9)–C(10)–C(11A)	124(1)
C(2)–C(3)–C(4)	122(2)	C(11A)–C(10)–C(12)	121(1)
C(3)–C(4)–C(2)	129(2)	C(10)–C(12)–C(13A)	119(1)
O(1)–C(2)–C(1)	111(2)	C(13A)–C(12)–C(14)	116(1)
C(3)–C(2)–C(1)	118(2)	C(12)–C(14)–C(16)	118(1)
C(3)–C(4)–C(5)	116(1)	C(12)–C(14)–C(18A)	118(1)
O(2)–C(4)–C(5)	115(1)	C(14)–C(16)–O(3)	118(1)
C(6)–C(8)–C(7)	112(1)	C(16)–O(3)–C(17)	118(1)
C(6)–C(8)–C(9)	108(1)	C(14)–C(16)–C(15A)	126(1)

closely similar: 2.12, 2.11, 2.12(1) Å (ref. 9); 2.20, 2.10, 2.14(4) Å (ref. 10); and 2.16, 2.07, 2.11(1) Å (ref. 11), respectively. One aspect of the allyl grouping, for which we have no explanation, is the surprising difference in lengths C(9)–C(10), 1.38(2), and C(10)–C(12), 1.47(2) Å. Admittedly, C(9) and C(12) are differently substituted but the large difference in lengths is unexpected. The tetraphenylbutadienyl moiety as a whole has C–C–C angles close to 120° indicative of sp^2 hybridization throughout. This backbone is not coplanar, however, as can be clearly seen in Figure 1.

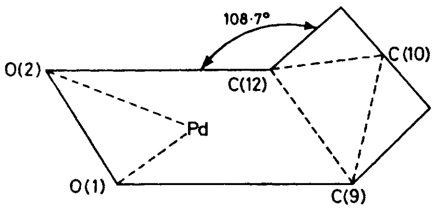

FIGURE 2 Co-ordination of the Pd atom in the complex

TABLE 3

Best least-squares planes $AX + BY + CZ = D$ where X,Y,Z are real orthogonal co-ordinates (Å) with X along x and Z along z^*. Deviations of atoms from the planes are given in square brackets

Plane (1): O(1), C(2), C(3), C(4), O(2)
$0.6023X + 0.7884Y - 0.1250Z = -4.4423$
[Pd −0.220, C(1) 0.212, C(5) − 0.113]

Plane (2): O(1), O(2), C(12), C(9)
$0.5801X + 0.8144Y - 0.0130Z = -3.9123$
[Pd −0.042]

Despite the bulky phenyl substituents, there is little sign of intramolecular overcrowding, the only possibly short contact being H(11B) · · · H(18F) at 2.30 Å. As can be seen in Figure 1 the phenyl groups are twisted to different extents with respect to the backbone to minimise intramolecular conflicts.

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