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A palladium(0) complex of dibenzylideneacetone and a chelating diphosphine

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Key indicators

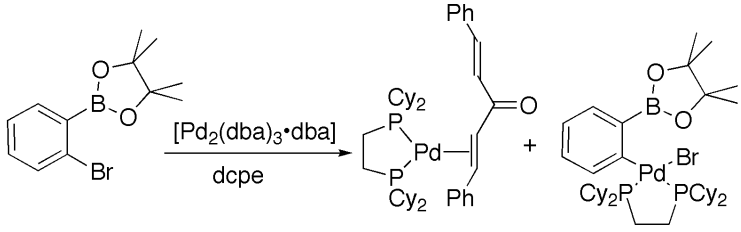
Single-crystal X-ray study
T = 200 K
Mean σ(C–C) = 0.004 Å
R factor = 0.040
wR factor = 0.049
Data-to-parameter ratio = 18.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the crystal structure of [Pd{η^2–PhCH=CHC(O)-CH=CHPh}{$(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$}] or [Pd($\eta^2$-dba)-(dcpe)], where dba is dibenzylideneacetone ($C_{17}H_{14}O$) and dcpe is 1,2-bis(dicyclohexylphosphino)ethane ($C_{26}H_{48}P_2$), the complex has a trigonal-planar coordination and only one double bond of the dba ligand is coordinated to the metal.

Comment

The palladium(0) complexes $[Pd_2(dba)_3]\cdot$dba and $[Pd_2(dba)_3]\cdot CHCl_3$, in which the two low-valent metal centres are bridged by three π-coordinated molecules of dibenzylideneacetone (dba) (Ukai *et al.*, 1974), have been extensively used as precursors to prepare a large variety of palladium complexes. The dba fragment is labile and can readily be exchanged for other ligands, while the palladium(0) centre can undergo oxidative addition. The title complex, (II), was obtained as the unexpected major product from the reaction of *o*-BrC_6H_4B(pinacol), (I), with $[Pd_2(dba)_3]\cdot$dba, in an attempt to prepare the aryl–palladium(II) species (III) (Bennett *et al.*, 2002). Complex (II) has already been prepared and used as a highly reactive reagent for oxidative additions (McGuinness *et al.*, 2001). The fluxionality of the dba ligand has also been studied, and the X-ray structure of the CH_2Cl_2 solvate of (II) has been reported (Reid *et al.*, 2000).



(I) (II) (major) (III) (minor)

The complex is trigonal planar, with only one double bond of the dba ligand coordinated to the metal in an η^2 fashion. The double bonds have the same s-*trans*,s-*trans* conformation observed in (II)$\cdot CH_2Cl_2$ (Reid *et al.*, 2000) and in other palladium(0)–dba complexes (Herrmann *et al.*, 1993). The C atoms of the coordinated double bond (C1 and C2) are almost coplanar with Pd1, P1 and P2 (the distances from the PdP_2 plane are only 0.0601 and 0.0983 Å, respectively). As expected, the C1=C2 bond [1.417 (3) Å] is elongated by the coordination, compared to C4=C5 [1.332 (3) Å]. The second double bond does not interact with the palladium centre or with neighbouring molecules. The keto group shows some very weak interaction with the dcpe ligand of an adjacent molecule, atoms C18 and C31 of the latter being located 3.371 (3) and

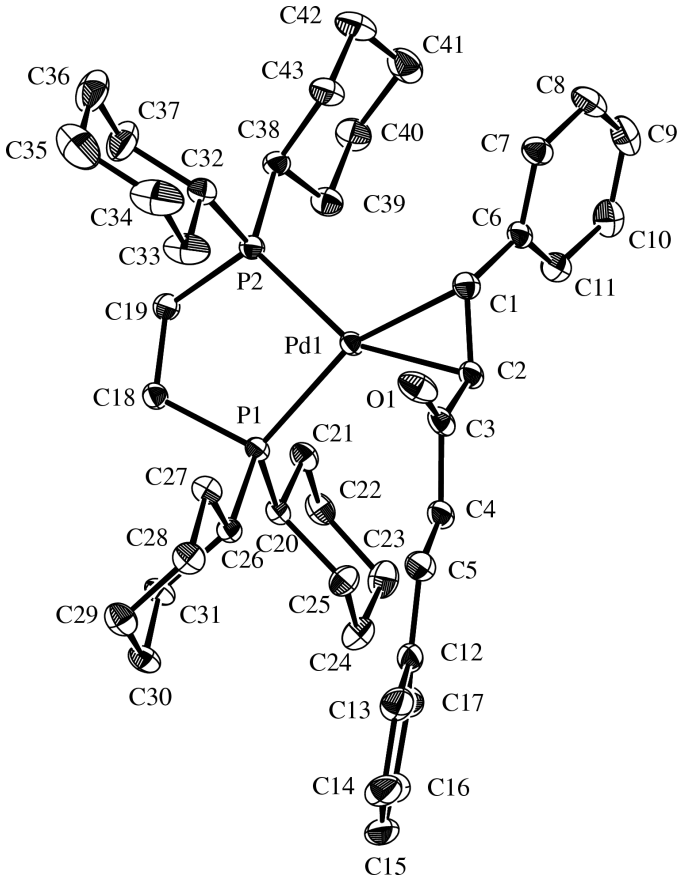


Figure 1
The molecular structure of (II), showing 30% probability displacement ellipsoids. For clarity, H atoms have been omitted.

3.547 (3) Å from atom O1. The Pd—P distances [2.3161 (6) and 2.2820 (6) Å] are similar to those reported for (II)·CH_2Cl_2 [2.307 (1) and 2.283 (1) Å], analogous [Pd(η^2-dba)(dippe)] [dippe is bis(diisopropylphosphino)ethane] (Reid *et al.*, 2000) and other [Pd(η^2-alkene)(dippe)] species (Goddard *et al.*, 1995). In the present case, however, dba is not coordinated symmetrically and Pd—C1 is longer than Pd—C2, whereas the corresponding distances in the solvated complex (II)·CH_2Cl_2 are identical; this is probably due to differences in the packing.

Experimental

$[Pd_2(dba)_3]$·dba (45 mg, 0.078 mmol), dcpe (35 mg, 0.083 mmol), *o*-BrC_6H_4B(pinacol), (I) (25 mg, 0.088 mmol), and THF (2 ml) were placed in a Schlenk tube under a nitrogen atmosphere and the mixture was stirred at room temperature for 16 h. Monitoring by ^{31}P NMR spectroscopy showed only traces of the desired product (III) and broad signals at δ_P 59.4 and 57.5 p.p.m. due to the title compound (II). The data for (II) were similar to those previously reported (McGuinness *et al.*, 2001; Reid *et al.*, 2000). Single crystals of complex (II) were obtained by layering hexane over the reaction mixture in THF.

Crystal data

$[Pd(C_{26}H_{48}P_2)(C_{17}H_{14}O)]$
M_r = 763.31
Monoclinic, $P2_1/a$
a = 21.0704 (2) Å
b = 8.6065 (1) Å
c = 23.6443 (3) Å
β = 112.4591 (6)°
V = 3962.50 (8) Å^3
Z = 4
D_x = 1.279 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 77106 reflections
θ = 2.9–27.5°
μ = 0.58 mm^{-1}
T = 200 K
Plate, orange
0.35 × 0.16 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: by integration *via* Gaussian method (Coppens, 1970) implemented in *maXus* (Mackay *et al.*, 2000)
T_{min} = 0.873, T_{max} = 0.941
77106 measured reflections
9057 independent reflections
7970 reflections with $I > 2\sigma(I)$
R_{int} = 0.053
θ_{max} = 27.5°
$h = -27 \rightarrow 27$
$k = -11 \rightarrow 11$
$l = -30 \rightarrow 30$

Refinement

Refinement on F
R = 0.040
wR = 0.049
S = 1.97
7970 reflections
430 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o) + 0.00022|F_o|^2]$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.95 e Å^{-3}
$\Delta\rho_{min}$ = −0.65 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—P1	2.3161 (6)	O1—C3	1.247 (3)
Pd1—P2	2.2820 (6)	C1—C2	1.417 (3)
Pd1—C1	2.169 (2)	C1—C6	1.482 (3)
Pd1—C2	2.124 (2)	C1—H1	0.86 (2)
P1—C18	1.856 (2)	C2—C3	1.447 (3)
P1—C20	1.853 (2)	C2—H2	0.96 (3)
P1—C26	1.847 (2)	C3—C4	1.487 (3)
P2—C19	1.852 (2)	C4—C5	1.332 (3)
P2—C32	1.851 (2)	C5—C12	1.467 (4)
P2—C38	1.847 (2)	C18—C19	1.522 (3)
P1—Pd1—P2	88.23 (2)	Pd1—C1—C2	69.0 (1)
P1—Pd1—C1	158.59 (7)	Pd1—C1—C6	119.3 (2)
P1—Pd1—C2	120.07 (7)	Pd1—C1—H1	104 (2)
P2—Pd1—C1	113.12 (7)	C2—C1—C6	123.1 (2)
P2—Pd1—C2	151.55 (7)	C2—C1—H1	114 (2)
C1—Pd1—C2	38.52 (9)	C6—C1—H1	117 (2)
Pd1—P1—C18	106.29 (8)	Pd1—C2—C1	72.4 (1)
Pd1—P1—C20	118.31 (7)	Pd1—C2—C3	98.2 (2)
Pd1—P1—C26	119.41 (7)	Pd1—C2—H2	105 (2)
Pd1—P2—C19	106.76 (8)	C1—C2—C3	122.3 (2)
Pd1—P2—C32	114.03 (9)	C1—C2—H2	119 (2)
Pd1—P2—C38	120.89 (8)	C3—C2—H2	119 (2)

H atoms were included in the refinement at idealized positions. The exceptions were H1 and H2, which were refined positionally.

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1992–1997); software used to prepare material for publication: *TEXSAN*.

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