metal-organic papers

The twinned crystal structure of diiodobis(triphenylphosphine)palladium(II) dichloromethane disolvate at 173 K

Thomas Theissmann[a] **and Michael Bolte**[b]*

[a]Institut für Organische Chemie, J. W. Goethe-Universität Frankfurt, Max-von-Laue-Strasse 7, 60438 Frankfurt/Main, Germany, and [b]Institut für Anorganische Chemie, J. W. Goethe-Universität Frankfurt, Max-von-Laue-Strasse 7, 60438 Frankfurt/Main, Germany

Correspondence e-mail: bolte@chemie.uni-frankfurt.de

The structure of the title compound, $[PdI_2(C_{18}H_{15}P)_2]\cdot 2CH_2Cl_2$, has previously been reported by Debaerdemaeker, Kutoglu, Schmid & Weber [*Acta Cryst.* (1973), B**29**, 1283–1288] at room temperature. We report the structure determination of this compound from a twinned crystal at 173 (2) K. The Pd atom is located on a centre of inversion and has square-planar coordination geometry.

Comment

While attempting to synthesize (*R*)-2,2′-bis(methoxymethoxy)-3,3′-diphenanthren-9-yl[1,1′]binaphthalenyl by a Suzuki coupling reaction (see scheme), we instead obtained crystals of the title compound, (I). The structure of (I) has previously been reported by Debaerdemaeker *et al.* (1973). The structure was determined using data collected from a yellow needle at room temperature, but the coordinates of the H atoms were not reported. We obtained dark-red block-shaped crystals of (I) which appeared to be twinned. However, after applying the appropriate twin law, satisfactory refinement was possible and our results are of higher precision than that previously reported.

expected product

Phenanthr.-B(OH)$_2$
Ba(OH)$_2$
Pd(PPh$_3$)$_4$

Dioxan/H$_2$O, 110^{0}C, 48h

Ph$_3$P—Pd—PPh$_3$ 2CH$_2$Cl$_2$

(I)

In the current determination, the standard uncertainties of the cell parameters are lower and the precision of the calcu-
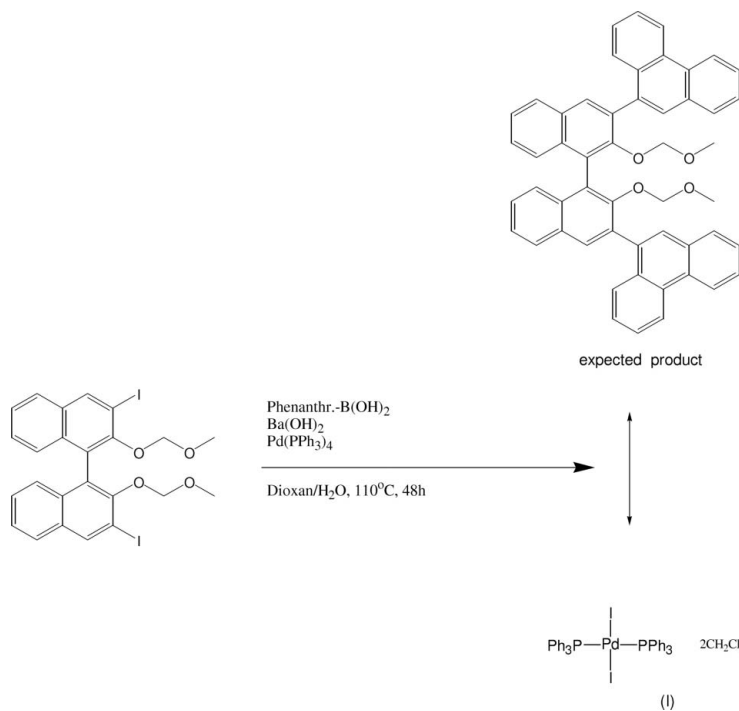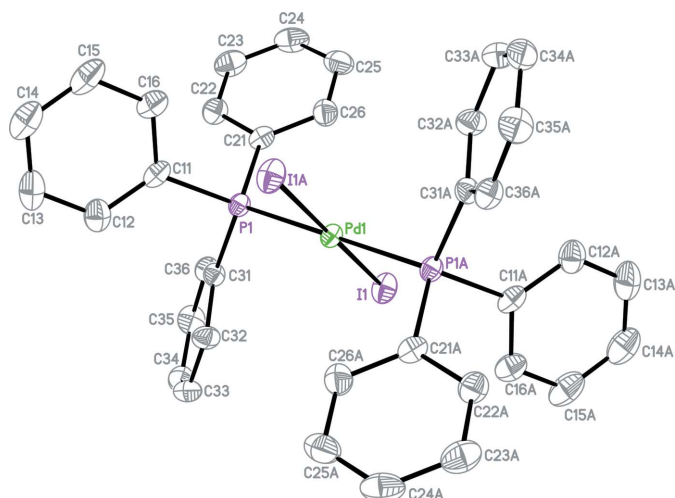
Figure 1
A perspective view of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The CH_2Cl_2 solvent molecule and all H atoms have been omitted for clarity. Atoms with the label suffix A are generated by the symmetry operator $(1 - x, 1 - y, 1 - z)$.

lated bond lengths and angles are higher overall. The final residual indices for the title compound are lower, with $R_1 = 0.047$ compared with 0.081 in the original determination.

The Pd atom is located on a centre of inversion. It is coordinated by two I and two P atoms in a square-planar fashion. The C—P—C angles are significantly smaller than the C—P—Pd angles. The crystal structure of (I) was discussed extensively by Debaerdemaeker *et al.* (1973) and those details agree with the title structure.

Experimental

A mixture of (*R*)-3,3'-diiodo-2,2'-bis(methoxmethoxy)-1,1'-binaphthalenyl (3.0 g, 5 mmol), $Ba(OH)_2 \cdot 8H_2O$ (7.90 g, 25 mmol, 5 equivalents) and 9-phenanthrenyl boronic acid (3.30 g, 15 mmol, 3 equivalents) was dissolved in dioxan–H_2O (3:1 *v*/*v*, 120 ml). The solution was degassed, followed by addition of $Pd(PPh_3)_4$ (0.55 g, 0.5 mmol, 10 mol%). The reaction mixture was heated to 383 K for 48 h. After cooling, the dioxan was evaporated and the residue was extracted with CH_2Cl_2 (3 × 70 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2) with hexane–ethyl acetate as eluent. For further purification, the isolated product was recrystallized from CH_2Cl_2–hexane (1:10) (yield 2.50 g, 72%), and crystals of $I_2Pd(PPh_3)_2$ were isolated as a by-product.

Crystal data

$[PdI_2(C_{18}H_{15}P)_2] \cdot 2CH_2Cl_2$
$M_r = 1054.59$
Monoclinic, $P2_1/c$
$a = 11.8422$ (6) Å
$b = 20.3802$ (7) Å
$c = 8.2420$ (4) Å
$\beta = 95.364$ (4)°
$V = 1980.47$ (15) Å^3

$Z = 2$
$D_x = 1.768$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.40$ mm^{-1}
$T = 173$ (2) K
Block, dark red
$0.32 \times 0.30 \times 0.28$ mm

Data collection

Stoe IPDS-II two-circle diffractometer
ω scans
Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)

$T_{min} = 0.513$, $T_{max} = 0.553$ (expected range = 0.474–0.510)
43265 measured reflections
4044 independent reflections
3868 reflections with $I > 2\sigma(I)$
$R_{int} = 0.074$
$\theta_{max} = 26.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.148$
$S = 1.37$
4044 reflections
215 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0112P)^2 + 25.7032P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.36$ e Å^{-3}
$\Delta\rho_{min} = -1.20$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—P1	2.340 (2)	P1—C21	1.826 (9)
Pd1—I1	2.6009 (6)	P1—C11	1.834 (9)
P1—C31	1.823 (9)		
P1^i—Pd1—I1	92.70 (5)	C21—P1—C11	102.1 (4)
P1—Pd1—I1	87.30 (5)	C31—P1—Pd1	111.5 (3)
C31—P1—C21	107.7 (4)	C21—P1—Pd1	112.5 (3)
C31—P1—C11	103.1 (4)	C11—P1—Pd1	118.9 (3)

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Having encountered problems during the determination of the unit-cell parameters of several crystals of (I), all of which looked of good quality, the unit cell was eventually determined using approximately two thirds of the inital reflections. The same cell in a different orientation was obtained for the remaining third of the reflections, indicating that the crystals were twinned. However, the structure could be solved, but anisotropic refinement converged with w$R_2 = 0.261$ and $R_1 = 0.125$ using all data. At this point, the anisotropic displacement parameters appeared strange and high residual peaks showed up in difference electron-density maps (highest peak 5.64 e Å^{-3} and deepest hole -3.17 e Å^{-3}). The twin law (1 0 0.268/ 0 $\overline{1}$ 0/0 0 $\overline{1}$) was obtained using the program *TWINLAW* (Bolte, 2004). The file containing the reflection data was then modified using the program *HKLF5* (Bolte, 2004), using a distance of 0.015 Å^{-1} as the maximum distance for overlap of two reflections of the different domains. This treatment provided ultimate success (R_1 dropped below 0.1) and all H atoms could now be located in a difference Fourier map. They were refined with fixed individual isotropic displacement parameters [$U_{iso}(H) = 1.2U_{eq}(C)$] using a riding model, with C—H(aromatic) = 0.95 Å or C—H(methylene) = 0.99 Å. The twin ratio refined to 0.316 (2)/0.684 (2). The highest peak in the final difference map is located 1.48 Å from atom C32 and the deepest hole 1.22 Å from C11.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bolte, M. (2004). *J. Appl. Cryst.* **37**, 162–165.
Debaerdemaeker, T., Kutoglu, A., Schmid, G. & Weber, L. (1973). *Acta Cryst.* B**29**, 1283–1288.

metal-organic papers

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Stoe & Cie (2001). *X-AREA*. Stoe & Cie, Darmstadt, Germany.