Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

μ-1,2-Bis(dicyclohexylphosphino)ethane-κ^2P:P'-bis{[1,2-bis(dicyclohexylphosphino)ethane-κ^2P,P']-palladium(0)}

Robert C. Boyle, Joel T. Mague* and Mark J. Fink

Department of Chemistry, Tulane University,
New Orleans, LA 70118, USA

Correspondence e-mail: joelt@tulane.edu

Received 31 March 2004
Accepted 15 April 2004
Online 24 April 2004

The title compound, $[Pd_2(C_{26}H_{48}P_2)_3]$, crystallizes in an 'extended' conformation with crystallographically imposed centrosymmetry. The crystal used was twinned *via* a 180° rotation about the reciprocal axis (0,0,1). The ratio of the two twin components is 54.16 (4):46.84 (4). The crystal packing involves significant interdigitation of the cyclohexyl groups with a considerable number of short H$\cdots$H contacts.

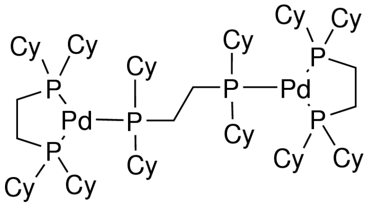
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
R factor = 0.041
wR factor = 0.089
Data-to-parameter ratio = 37.9

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

Comment

Zero-valent complexes of palladium which possess chelating bisphosphine ligands can be important catalytic intermediates in a number of organic transformations (Hegedus, 1994). One characteristic of these complexes is the facile redistribution of the phosphine ligands in solution, often affording complex equilibria involving mononuclear and dinuclear complexes (Reid & Fink, 2001; Pan *et al.*, 1993; Fryzuk *et al.*, 1996). The title complex, (I), is a very minor component in solutions containing $[(\mu\text{-dcpe})Pd]_2$ [dcpe is 1,2-bis(dicyclohexylphosphino)ethane].



(I)

Complex (I) crystallizes in an 'extended' conformation with crystallographically imposed centrosymmetry (Fig. 1). The coordination geometry about Pd is best described as a distorted trigonal plane [sum of angles = 359.82°], with a P1—Pd—P2 ring angle of 90.22 (3)° and external angles of 129.24 (3) (P2—Pd—P3) and 140.36 (3)° (P1—Pd—P3). The Pd—P1 bond distance [2.3037 (8) Å] is somewhat longer than the Pd—P2 bond distance [2.2857 (8) Å], which is a likely consequence of the Pd—P1 bond having a more '*trans*' orientation relative to the Pd—P3 bond. The backbone framework of (I) is nearly planar, with a least-squares plane containing atoms Pd, P1, P2, P3, C13, and C39 showing a maximum deviation of 0.039 (1) Å. The mean planes of the cyclohexyl rings are oriented nearly orthogonal to this plane (dihedral angles of ~73–88°). A packing diagram (Fig. 2) shows that the cyclohexyl groups of adjacent molecules are clearly interdigitated. A number of close H$\cdots$H contacts between these cyclohexyl groups (20 per molecule less than 2.40 Å) are evident.

Experimental

Complex (I) was obtained as a side-product from the reaction of [(μ-dcpe)Pd]$_2$ with di-*tert*-butylsilane. In this reaction, the silane (26 µl, 0.019 mg, 1.31 mmol) and [(μ-dcpe)Pd]$_2$ (14 mg, 0.13 mmol) were placed into a 5 mm NMR tube in a nitrogen-filled dry-box. Approximately 0.5 ml of C_6D_6 was vacuum-transferred into the tube which was then flame-sealed. In approximately 2 d, crystals were observed to be forming in the tube and after two weeks the tube was opened and a crystal selected for analysis; this proved to be (I).

Crystal data

$[Pd_2(C_{26}H_{48}P_2)_3]$
$M_r = 1480.55$
Triclinic, $P\overline{1}$
$a = 10.732$ (1) Å
$b = 12.442$ (1) Å
$c = 15.523$ (1) Å
$\alpha = 106.244$ (2)°
$\beta = 73.645$ (2)°
$\gamma = 102.621$ (2)°
$V = 1887.4$ (3) Å^3
$Z = 1$
$D_x = 1.303$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9913 reflections
$\theta = 2.3$–28.2°
$\mu = 0.65$ mm^{-1}
$T = 100$ (2) K
Plate, yellow
0.20 × 0.16 × 0.02 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 2002)
$T_{min} = 0.851$, $T_{max} = 0.987$
19 239 measured reflections
14 762 independent reflections
11 113 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 27.5°$
$h = -13 \rightarrow 13$
$k = -16 \rightarrow 15$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.089$
$S = 0.94$
14 762 reflections
389 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.56$ e Å^{-3}
$\Delta\rho_{min} = -0.68$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd—P2	2.2857 (8)	P3—C39	1.846 (3)
Pd—P3	2.2956 (8)	C39—C39^i	1.532 (5)
Pd—P1	2.3037 (8)		
P2—Pd—P3	129.24 (3)	C39—P3—Pd	119.64 (8)
P2—Pd—P1	90.22 (3)	C39^i—C39—P3	112.5 (2)
P3—Pd—P1	140.36 (3)		

Symmetry code: (i) $2 - x, -y, -z$.

The crystal used was twinned *via* a 180° rotation about the reciprocal axis (0,0,1). This was determined with the program *CELL_NOW* (Sheldrick, 2002). Integration of the raw intensity data for the two twin components was accomplished with *SAINT* as controlled by the two-component orientation matrix generated by *CELL_NOW* and the data were further corrected for absorption and decay effects with *TWINABS*. Solution of the structure was accomplished with rough intensities derived from the major twin component and final refinement (including refinement of the twin ratio) was performed with the full reflection file which included contributions from both twin components. Merging of equivalent reflections other than Friedel pairs could not be performed before refinement, because of the overlap of twin components.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

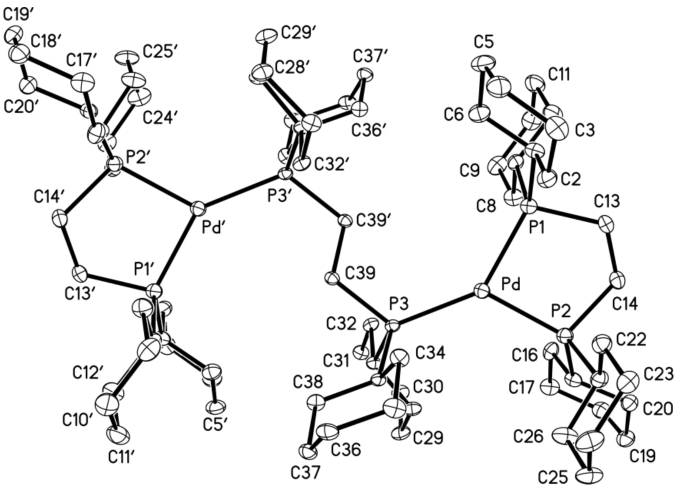


Figure 1
Perspective view of (I). Primed atoms are related to non-primed atoms by the crystallographic inversion center. C atoms are numbered sequentially around each cyclohexyl ring starting with the *ipso*-C atom. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

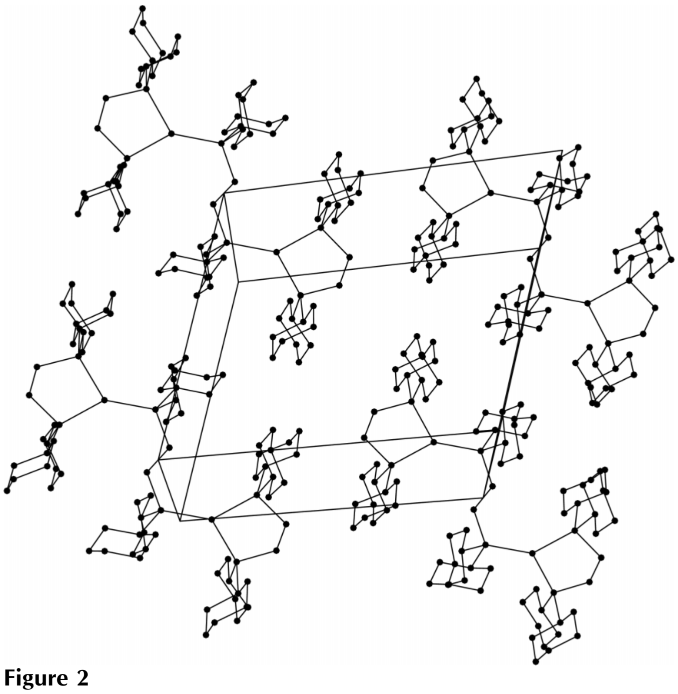


Figure 2
A view of the packing of (I), projected approximately down the crystallographic *a* axis.

We thank the Chemistry Department of Tulane University for support of the X-ray laboratory and the Louisiana Educational Quality Support Fund administered by the Louisiana Board of Regents for purchase of the CCD diffractometer under grant LEQSF (2002–03)-ENH-TR-67. MJF acknowledges support from DoE/EPSCoR (DE–FG-03ER46046) and NSF (CHE-0092001).

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