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Chloro{1-[(dimethylamino)methyl-κN]-1H-indolyl-κC^2}(triphenylphosphine-κP)-palladium(II) dichloromethane solvate

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Key indicators

Single-crystal X-ray study
T = 190 K
Mean σ(C–C) = 0.003 Å
R factor = 0.025
wR factor = 0.059
Data-to-parameter ratio = 19.7

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

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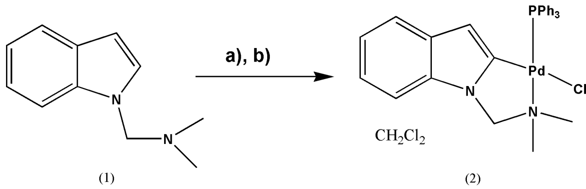
The title compound, $[Pd(C_{11}H_{13}N_2)Cl(C_{18}H_{15}P)]\cdot CH_2Cl_2$, crystallizes readily from a mixture of dichloromethane and light petroleum. The structure is one of few examples of palladacycles that incorporate the *N*-substituent in five-membered ring heterocycles [Nonoyama & Nakajima (1998). *Polyhedron* **18**, 533–543.].

Comment

Cyclometallation represents one of the most useful methods for the activation and *ortho*-functionalization of Csp^2—H bonds in aromatic compounds (Ryabov *et al.*, 1993). The presence of a tethered donor group allows the initial coordination of the ligand to the metal and favourable intramolecular cyclization. Whereas heteroatom-directed cyclometallation of benzenoid and heteroaromatic systems has been exhaustively investigated, the chemistry of the analogous indole derivatives has remained virtually unexplored (Valk *et al.*, 1994; Tollari *et al.*, 1997). Palladacycles are amongst the most active catalysts for C—C and C—heteroatom bond formation (Herrmann *et al.*, 1999; Albrecht & van Koten, 2001; Dupont *et al.*, 2001). In addition to their high activity, they permit easy synthesis, facile modification and comparative stability. We report here the synthesis and structure of a five-membered indole-fused *ortho*-palladacycle, (2), which incorporates *N*-isogramine, (1), as a *C,N*-bidentate ligand.



a) $PdCl_2$, LiCl, AcONa, EtOH
b) PPh_3, CH_2Cl_2

The coordination geometry of the Pd atom closely approximates planarity. The mean plane through the Pd/C/Cl/N/P atoms intersects that of the ring system of the *N*-isogramine ligand (atoms C1–C5/N6/C7–C10) at an angle of 26.69 (6)°. The structure of a related six-membered indole-fused *ortho*-palladacycle which incorporates an *N*-methyleneoxazoline as the *C,N*-bidentate ligand has also been reported (Cowley *et al.*, 2005).

Experimental

A suspension of $PdCl_2$ (0.135 g, 0.76 mmol) and LiCl (0.064 g, 1.52 mmol) in ethanol (5 ml) was heated under reflux condition for

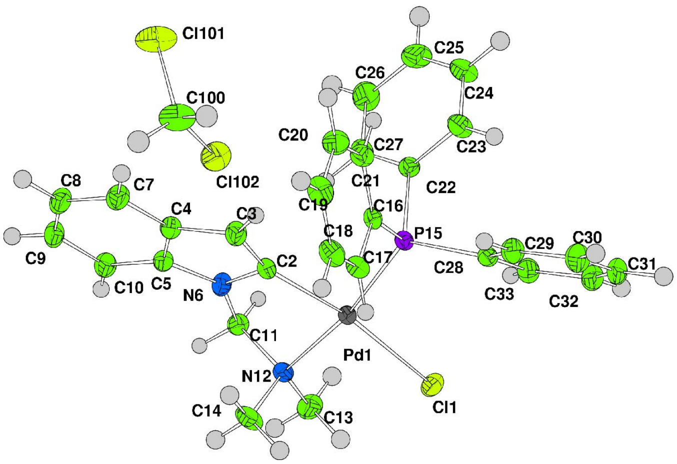


Figure 1
The molecular structure of (2), drawn with 50% probability ellipsoids for the anisotropically refined atoms.

2 h to give a dark red solution of $Li_2[PdCl_4]$. The solution was cooled to room temperature and *N*-isogramine (Swaminathan & Narasimhan, 1966) (0.11 g, 0.63 mmol) in ethanol (2 ml) and sodium acetate trihydrate (0.086 g, 0.63 mmol) were added. The resulting suspension was stirred at room temperature for 1.5 h. The insoluble brown solid was filtered off, washed with ethanol and dried *in vacuo*. Degassed CH_2Cl_2 (8 ml) and PPh_3 (0.413 g, 1.58 mmol) were then added to the solid and the mixture was stirred at room temperature for 1 h under an argon atmosphere. Addition of pentane to the solution resulted in precipitation of a yellow solid. Recrystallization of the crude product from dichloromethane–pentane gave the yellow product, (2) (m.p. 398–402 K); full spectroscopic and physical characterization will be reported elsewhere.

Crystal data

$[Pd(C_{11}H_{13}N_2)Cl(C_{18}H_{15}P)]\cdot CH_2Cl_2$
$M_r = 662.31$
Monoclinic, $P2_1/n$
$a = 11.0324$ (1) Å
$b = 23.9623$ (3) Å
$c = 11.2437$ (1) Å
$\beta = 102.9338$ (8)°
$V = 2896.99$ (5) Å^3
$Z = 4$

$D_x = 1.518$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6527 reflections
$\theta = 1–27°$
$\mu = 1.00$ mm^{-1}
$T = 190$ K
Block, yellow
$0.28 \times 0.20 \times 0.20$ mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: none
12861 measured reflections
6622 independent reflections
5789 reflections with $I > 2\sigma(I)$

$R_{int} = 0.012$
$\theta_{max} = 27.5°$
$h = -14 \rightarrow 14$
$k = -31 \rightarrow 31$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.059$
$S = 1.00$
6593 reflections
334 parameters

H-atom parameters not refined
$w = 1/[\sigma^2(F^2) + 0.02 + 2.41P]$
where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.81$ e Å^{-3}
$\Delta\rho_{min} = -0.64$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—C2	1.9974 (18)	Pd1—P15	2.2536 (5)
Pd1—N12	2.1867 (15)	Pd1—Cl1	2.3618 (5)
C2—Pd1—N12	80.76 (7)	N12—Pd1—Cl1	91.59 (4)
C2—Pd1—P15	91.69 (5)	P15—Pd1—Cl1	96.583 (17)
N12—Pd1—P15	169.10 (4)	Pd1—C2—C3	142.04 (14)
C2—Pd1—Cl1	170.75 (5)	Pd1—C2—N6	110.00 (12)

The 29 reflections below $[\sin(\theta)/\lambda]^2$ of 0.011 (= ~4.27°) were not used in the refinement. It was suspected that some of them may have been partially obscured by the beam stop. All H atoms were placed in geometrically calculated positions after each refinement cycle, with X—H = 1.0 Å; U_{iso}(H) values were set at $1.2U_{eq}$ of the connected atom.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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References

Albrecht, M. & Van Koten, G. (2001). *Angew. Chem. Int. Ed.* **40**, 3750–3753.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Cowley, A. R., Cooper, R. I., Capito, E., Brown, J. M., Ricci, A. (2005). *Acta Cryst.* E**61**, m582–m584.
Dupont, J., Pfeffer, M. & Spencer, J. (2001). *Eur. J. Inorg. Chem.* pp. 1917–1927.
Herrmann, W. A., Böhm, V. P. W. & Reisinger, C. P. (1999). *J. Organomet. Chem.* **576**, 23–41.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Nonoyama, M. & Nakajima, K. (1998). *Polyhedron* 18, 533–543.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
Ryabov, A. D., van Eldik, R., Le Borgue, G. & Pfeffer, M. (1993). *Organometallics*, **12**, 1386–1393.
Swaminathan, S. & Narasimhan, K. (1966). *Chem. Ber.* **99**, 889–894.
Tollari, S., Demartin, F., Cenini, S., Palmisano, G. & Raimondi, P. (1997). *J. Organomet. Chem.* **527**, 93–102.
Valk, J., Maassarani, F., van der Sluis, P., Spek, A. L., Boersma, J. & van Koten, G. (1994). *Organometallics*, **13**, 2320–2329.
Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.

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