

trans-[1,3-Bis(2,4-dimethylphenyl)-imidazolidin-2-ylidene]dichloro(tri-phenylphosphine- κP)palladium(II)

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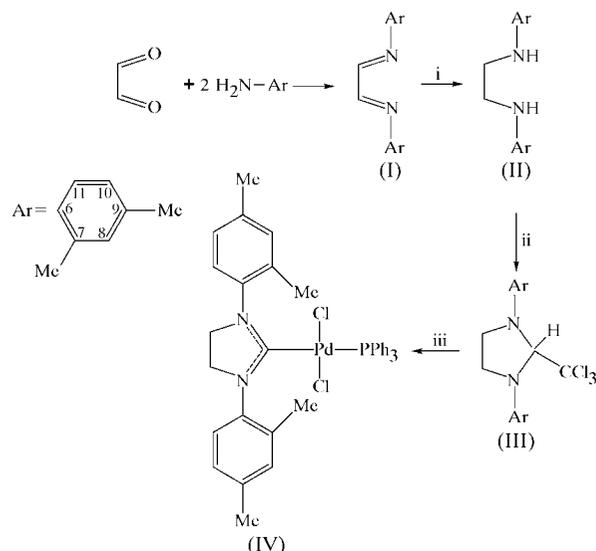
The title complex, [PdCl₂(C₁₉H₂₂N₂)(C₁₈H₁₅P)], shows slightly distorted square-planar coordination of the palladium(II) metal center. The Pd–C bond distance between the N-heterocyclic ligand and the metal atom is 2.008 (3) Å. The dihedral angle between the two dimethylphenyl ring planes is 33.17 (13)°.

Comment

Recently, increasing attention has been focused on using imidazole-based N-heterocyclic carbene (NHC) compounds as ancillary ligands for a number of transition-metal-mediated catalytic reactions (Bourissou *et al.*, 2000; Perry & Burgess, 2003; Herrmann, 2002). The donating properties of these ligands are superior to those of the most basic phosphanes. The ability of NHCs to coordinate metal centers makes them excellent candidates for the design of well defined catalysts. Increasing knowledge of the chemical properties of ligands and derived complexes has led to a growing demand for systems with more and more complex structures. In view of the growing importance of palladium complexes as C–C and C–heteroatom catalysts (Culkin & Hartwig, 2003), we have synthesized and structurally characterized the title compound, (IV).

A *trans* coordination of the carbene group and one phosphine group to the palladium(II) center is found in the crystal structure of (IV), as shown in Fig. 1. The coordination of the ligands is not exactly planar, the deviations of ligating atoms Cl1, Cl2, P1 and C1 from the plane through these atoms and the Pd atom being –0.054 (1), –0.057 (1), 0.052 (1) and 0.064 (1) Å, respectively. The Pd1/Cl1/Cl2/P1/C1 coordination plane that is formed by the slightly distorted square-planar coordination of the palladium(II) metal center is approximately perpendicular to the plane of the carbene ring

[89.35 (12)°], as reported for similar N-heterocyclic carbene complexes (Herrmann *et al.*, 1997, 2001). The bond angles at the Pd atom involving *trans* pairs of substituents deviate from



the expected value of 180°, being 176.23 (11)° for the Cl1–Pd1–P1 angle and 175.94 (4)° for the Cl1–Pd–Cl2 angle. The bonding within the NHC ring indicates a pattern of delocalization that extends from atom N1 to atom N2 through atom C1, the N1–C1 [1.326 (5) Å] and N2–C1 [1.334 (4) Å] distances being significantly shorter than the N2–C2 [1.473 (5) Å] and N1–C3 [1.479 (4) Å] distances, in accordance with a previous study (McGuinness *et al.*, 1998). The Cl2–Pd1–P1 and Cl1–Pd1–P1 bond angles are 93.57 (4) and 89.69 (3)°, respectively. The compression of the bond angles may be attributed to steric interaction between the Cl atoms and the aromatic rings. There is a significant difference between the two Pd–Cl bond lengths in the title complex

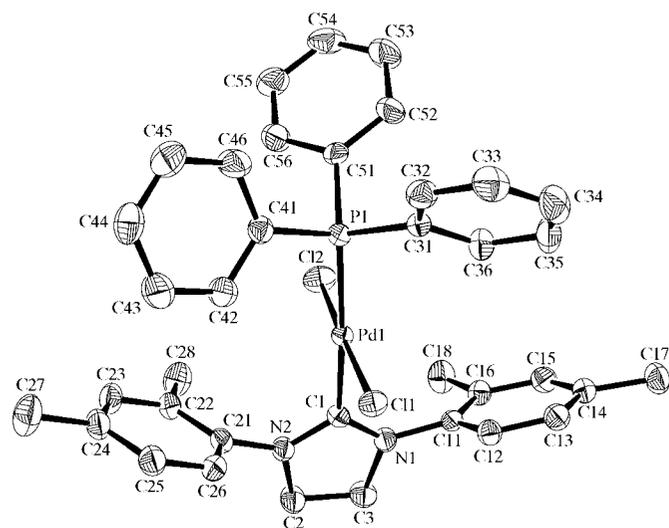


Figure 1

A view of the title compound, (IV), showing the labeling of the non-H atoms. Displacement ellipsoids are shown at the 30% probability level and H atoms have been omitted for clarity.

[Pd1—C12 = 2.2847 (10) Å and Pd1—C11 = 2.3242 (9) Å], probably because of the presence of intramolecular C—H···Cl interactions. There are two intramolecular C—H···Cl interactions with the following dimensions: C12···C11 = 3.538 (3) Å, H12···C11 = 2.81 Å and C12—H12···C11 = 136°; C42···C11 = 3.563 (5) Å, H42···C11 = 2.83 Å and C42—H42···C11 = 136°.

The C1—Pd1 bond distance between the NHC ligand and the metal atom is 2.008 (3) Å, comparable to that in other palladium(II)–NHC complexes (Liu *et al.*, 2003; Magill *et al.*, 2001). The Pd—P bond distance [2.3318 (9) Å] is also similar to those reported previously (Aupers *et al.*, 2000; McCrindle *et al.*, 2000). The dihedral angle between the two dimethylphenyl ring planes is 33.17 (13)°. Selected geometric parameters are given in Table 1.

Experimental

A 50 ml Schlenk tube was charged with (III) (0.198 g, 0.5 mmol), [PdCl₂(PPh₃)₂] (0.219 g, 0.25 mmol) and toluene (5 ml). The mixture was heated under reflux for 4 h, after which the solution was cooled to room temperature and hexane (10 ml) was added. The resulting orange precipitate was filtered off and recrystallized from CH₂Cl₂/Et₂O (yield 0.122 g, 65%; m.p. 546 K). Calculated for C₃₇H₃₈N₂Pd: C 61.81, H 5.33, N 3.90%; found: C 61.37, H 4.53, N 4.67%. ¹H NMR (400 MHz, CDCl₃): δ 7.88 (*d*, *J* = 1.9 Hz, 2H, Ar), 7.31–7.15 (*m*, 19H, Ar, PPh₃), 4.09 (*s*, 4H, NCH₂CH₂N), 2.46, 2.44 (12H, NCH₃); ¹³C{H} NMR (400 MHz, CDCl₃): δ 196.87 (*d*, ²*J*_{C–P} = 180.8 Hz, CPd), 137.58, 136.44, 135.30 (C₆, C₇, C₉), 134.41 (*d*, *J*_{C–P} = 11.30 Hz, *o*-PC₆H₅), 131.34, 129.99, 129.47, 126.63 (C₈, C₁₀, C₁₁, *p*-PC₆H₅), 129.80 (*d*, *J*_{C–P} = 42.4 Hz, *ipso*-C, PC₆H₅), 127.24 (*d*, *J*_{C–P} = 10.0 Hz, *m*-C, PC₆H₅), 51.95 (NCH₂CH₂N), 20.84, 18.04 (*o*-CH₃, *p*-CH₃); ³¹P{H} NMR (400 MHz, CDCl₃): δ 19.46.

Crystal data

[PdCl₂(C₁₉H₂₂N₂)(C₁₈H₁₅P)]
M_r = 717.96
 Monoclinic, *P*2₁/*n*
a = 13.9423 (6) Å
b = 14.7120 (8) Å
c = 17.2894 (7) Å
 β = 105.446 (3)°
V = 3418.3 (3) Å³
Z = 4

D_x = 1.395 Mg m^{−3}
 Mo *K*α radiation
 Cell parameters from 26 499 reflections
 θ = 1.9–29.2°
 μ = 0.77 mm^{−1}
T = 293 (2) K
 Plate, yellow
 0.40 × 0.21 × 0.09 mm

Data collection

Stoe IPDS-II diffractometer
 ω scans
 Absorption correction: by integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.823, *T_{max}* = 0.933
 34 434 measured reflections

9467 independent reflections
 5018 reflections with *I* > 2σ(*I*)
R_{int} = 0.125
 θ_{max} = 29.8°
h = −19 → 17
k = −20 → 20
l = −22 → 23

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.046
wR (*F*²) = 0.081
S = 0.83
 9467 reflections
 392 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0266P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.78 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -1.03 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

P1—C31	1.813 (4)	C28—C22	1.512 (6)
P1—C41	1.822 (4)	C16—C18	1.501 (5)
P1—C51	1.830 (4)	C14—C17	1.514 (5)
N1—C11	1.428 (4)	C3—C2	1.508 (6)
N2—C21	1.437 (5)	C24—C27	1.505 (6)
C1—Pd1—C12	84.80 (10)	C41—P1—Pd1	112.50 (12)
C1—Pd1—C11	92.09 (10)	C51—P1—Pd1	117.39 (12)
C31—P1—C41	108.08 (18)	N1—C1—N2	108.9 (3)
C31—P1—C51	103.16 (16)	N1—C1—Pd1	128.0 (3)
C41—P1—C51	103.09 (17)	N2—C1—Pd1	122.9 (3)
C31—P1—Pd1	111.71 (13)		

H atoms were treated as riding atoms, with C—H distances of 0.93 Å for aromatic H atoms, 0.96 Å for methyl H atoms and 0.97 Å for methylene H atoms.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1470). Services for accessing these data are described at the back of the journal.

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