

***trans*-[1,3-Bis(2,4,6-trimethylphenyl)-imidazolidin-2-ylidene]dichlorido-(triphenylphosphine- κ P)palladium(II)**Resul Sevinçek,^a Hayati Türkmen,^b Muhittin Aygün,^{a*}
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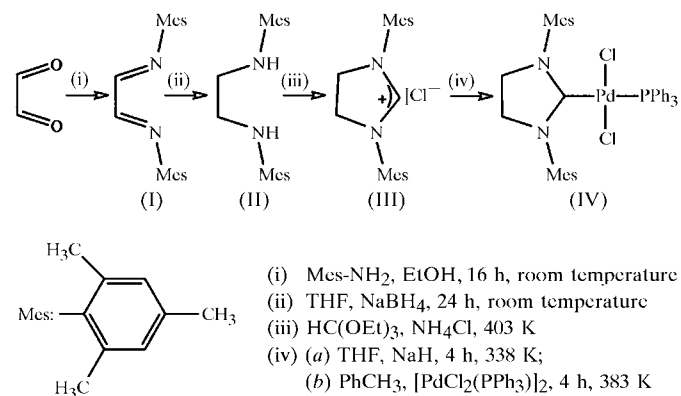
The title complex, [PdCl₂(C₂₁H₂₆N₂)(C₁₈H₁₅P)], shows slightly distorted square-planar coordination around the Pd^{II} metal centre. The Pd–C bond distance between the N-heterocyclic ligand and the metal atom is 2.028 (5) Å. The dihedral angle between the two trimethylphenyl ring planes is 36.9 (2)°.

Comment

There are relatively few homogeneous transition metal catalysts where both steric and electronic effects can be finely controlled by small changes of ligand structure within the series. N-Heterocyclic carbenes (NHCs), in conjunction with widely used phosphines, have broadened the scope for the screening of ligands for desired properties (Bourissou *et al.*, 2000; Türkmen *et al.*, 2006). NHC ligands in metal complexes are known to have electronic similarities with trialkylphosphines but appear to be stronger coordinating ligands which undergo little to no dissociation from the metal in solution (Lappert, 1975). In contrast with most metal–carbene complexes which have found extensive application in organic synthesis and which incorporate the carbene group into the organic product (Zaragoza Dörwald, 1998), NHCs act as non-participating ligands in catalytic processes and are not consumed (Bourissou *et al.*, 2000; Türkmen *et al.*, 2006). We describe here the preparation and characterization of the title palladium–NHC complex, (IV) (see scheme).

A *trans* coordination of the carbene group and one phosphine group to the Pd^{II} centre 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 0.074 (1), 0.079 (1), –0.070 (1) and –0.078 (2) Å, respectively. The dihedral angle between the Pd1/Cl1/Cl2/P1/C1 coordination plane, formed by the slightly distorted

square-planar coordination of the Pd^{II} metal centre, and the carbene ring is 74.90 (17)°, as reported for similar N-heterocyclic carbene complexes (Gökçe, Gülcemal *et al.*, 2006; Gökçe, Günay *et al.*, 2006). The Pd–C bond distance between the N-heterocyclic ligand and the metal atom is 2.028 (5) Å, comparable with that in other palladium(II)–NHC complexes (Gökçe *et al.*, 2004; Liu *et al.*, 2003; Magill *et al.*, 2001).



The bond angles at the Pd atom involving *trans* pairs of substituents deviate from the expected value of 180°, being 173.87 (15)° for the Cl1–Pd1–P1 angle and 175.71 (6)° for the Cl1–Pd–Cl2 angle, and this distortion of the bond angles at Pd may be attributed to steric interaction between the Cl atoms and the aromatic rings. There are two short intramolecular C–H...Cl contacts (Table 2), both of them involving methyl groups at the 2-position.

Although both C–N bonds in the NHC ring of (IV) are single bonds, their distances are different (Table 1), as observed in similar complexes (Karabıyık *et al.*, 2006; Karabıyık, Kılınçarslan, Aygün, Çetinkaya & Büyükgüngör, 2007; Karabıyık, Kılınçarslan, Aygün, Çetinkaya & García-Granda,

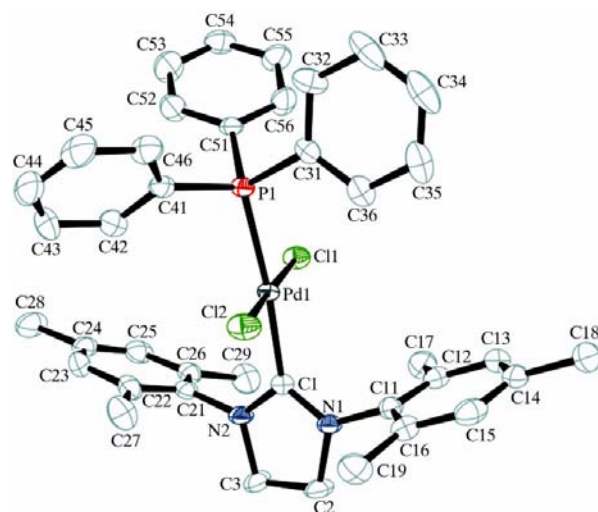


Figure 1
The molecular structure of (IV), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

2007; Gökçe *et al.*, 2004, 2006, 2007). The bond distances between the carbene C atom bonded to Pd and the N atoms in the NHC ring are shorter than the other C–N bond distances (Table 1). This is possibly indicative of a greater partial double-bond character due to partial electron donation by nitrogen to the carbene C-atom donor (Herrmann *et al.*, 2001; Fröhlich *et al.*, 1997). Theoretical study also indicates that the stability of these carbenes is due to electron donation from the nitrogen lone pairs into the formally vacant $p(\pi)$ orbital of the carbene C atom (Karabiyik *et al.*, 2005). The Pd–P bond distance is also similar to those reported previously (Aupers *et al.*, 2000; McCrindle *et al.*, 2000; Gökçe *et al.*, 2004).

Experimental

A suspension of salt (III) (0.17 g, 0.5 mmol), prepared as indicated in the scheme, and sodium hydride (0.17 g, 0.75 mmol) in tetrahydrofuran (10 ml) was heated under reflux for 4 h. The mixture was cooled to ambient temperature and the volatiles were removed. To the residue were added $[\text{PdCl}_2(\text{PPh}_3)]_2$ (0.22 g, 0.25 mmol) and then toluene (5 ml). The mixture was heated under reflux for 4 h, after which it was cooled to ambient temperature and hexane (10 ml) was added. The resulting cream precipitate was collected by filtration and recrystallized from $\text{CH}_2\text{Cl}_2\text{--Et}_2\text{O}$ (yield 0.28 g, 75%; m.p. 545–547 K). IR (KBr): $\nu(\text{NCN}) = 1457 \text{ cm}^{-1}$; analysis calculated for $\text{C}_{39}\text{H}_{41}\text{Cl}_2\text{N}_2\text{PPd}$: C 62.79, H 5.54, N 3.75%; found: C 61.63, H 5.55, N 3.75%; ^1H NMR (CDCl_3): δ 2.41 (*s*, 12H, *ortho*- CH_3), 2.53 (*s*, 6H, *para*- CH_3), 4.00 (*s*, 4H, Im- $\text{H}^{4,5}$), 7.30–7.16 (*m*, 19H, Ar, PPh_3); ^{13}C NMR (CDCl_3): δ 19.5 (*ortho*- CH_3), 21.4 (*para*- CH_3), 51.45 (Im- $\text{C}^{4,5}$), 127.7 (*d*, $J_{\text{C-P}} = 9.9 \text{ Hz}$, *m*-C PC_6H_5), 129.4 (Ar), 129.9 (*d*, $J_{\text{C-P}} = 2.3 \text{ Hz}$, *p*-C PC_6H_5), 130.7 (*d*, $J_{\text{C-P}} = 43.5 \text{ Hz}$, *ipso*-C PC_6H_5), 135.2 (*d*, $J_{\text{C-P}} = 10.7 \text{ Hz}$, *o*-C PC_6H_5), 135.6, 137.6, 138.0 (Ar), 197.2 (*d*, $2J_{\text{C-P}} = 185.3 \text{ Hz}$, C–Pd); ^{31}P (CDCl_3): δ 20.88.

Crystal data

$[\text{PdCl}_2(\text{C}_{21}\text{H}_{26}\text{N}_2)(\text{C}_{18}\text{H}_{15}\text{P})]$	$V = 3599.7 (16) \text{ \AA}^3$
$M_r = 746.01$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 17.418 (3) \text{ \AA}$	$\mu = 0.74 \text{ mm}^{-1}$
$b = 13.8020 (17) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 14.982 (6) \text{ \AA}$	$0.30 \times 0.20 \times 0.10 \text{ mm}$
$\beta = 91.90 (5)^\circ$	

Data collection

Enraf–Nonius CAD-4 diffractometer	7060 independent reflections
Absorption correction: analytical (Katayama, 1986)	5215 reflections with $I > 2\sigma(I)$
$T_{\text{min}} = 0.760$, $T_{\text{max}} = 0.782$	$R_{\text{int}} = 0.034$
7676 measured reflections	3 standard reflections
	frequency: 60 min
	intensity decay: 0.9%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$	410 parameters
$wR(F^2) = 0.161$	H-atom parameters constrained
$S = 1.10$	$\Delta\rho_{\text{max}} = 0.75 \text{ e \AA}^{-3}$
7060 reflections	$\Delta\rho_{\text{min}} = -0.93 \text{ e \AA}^{-3}$

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, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic and methylene H atoms, or $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms. CH_3 groups were allowed to rotate freely around their C–C bond.

Table 1

Selected geometric parameters (Å, °).

Pd1–Cl1	2.2915 (15)	N1–C1	1.333 (6)
Pd1–Cl2	2.3047 (15)	N1–C11	1.439 (7)
Pd1–P1	2.3185 (14)	N1–C2	1.478 (6)
P1–C31	1.814 (5)	N2–C1	1.331 (6)
P1–C41	1.827 (6)	N2–C21	1.440 (7)
P1–C51	1.831 (5)	N2–C3	1.471 (7)
C1–Pd1–Cl1	92.89 (15)	C31–P1–C51	103.1 (2)
C1–Pd1–Cl2	88.76 (15)	C41–P1–C51	102.4 (2)
C11–Pd1–Cl2	175.71 (6)	C31–P1–Pd1	110.69 (19)
C1–Pd1–P1	173.87 (15)	C41–P1–Pd1	109.08 (18)
C31–P1–C41	110.5 (3)	C51–P1–Pd1	120.58 (17)

Table 2

Hydrogen-bond geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
C17–H17C···Cl1	0.96	2.65	3.606 (7)	174
C27–H27B···Cl2	0.96	2.69	3.582 (8)	155

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CRYSDA* (Beurskens *et al.*, 1999); data reduction: *REFLEX* (García-Granda *et al.*, 1999; Lehman & Larsen, 1974; Grant & Gabe, 1978); 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: GD3106). Services for accessing these data are described at the back of the journal.

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