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Key indicators

Single-crystal X-ray study
T = 100 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.034
wR factor = 0.099
Data-to-parameter ratio = 43.2

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

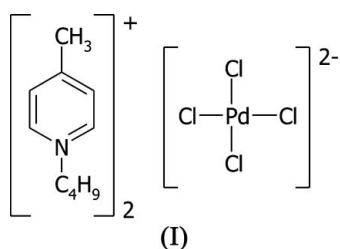
Bis(1-butyl-4-methylpyridinium) tetrachloropalladate(II)

The title compound, $(\text{C}_{10}\text{H}_{16}\text{N})_2[\text{PdCl}_4]$, has been crystallized from acetonitrile. The asymmetric unit contains two 1-butyl-4-methylpyridinium cations in general positions and two halves of tetrachloropalladate(II) anions, with the metal atoms lying on inversion centers. The Pd atoms are four-coordinated in a slightly distorted square-planar geometry. The crystal structure is stabilized by numerous weak C—H...Cl interactions.

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Comment

Palladium complexes with phosphine ligands are frequently used as catalyst precursors in carbon–carbon bond formation reactions. Recently, however, phosphine-free catalytic systems, economically profitable and environmentally friendly, have attracted increasing interest (Trzeciak & Ziólkowski, 2005). Ionic liquids, characterized by very low vapor pressure, have often been used as replacements for less environmentally friendly compounds (Dullius *et al.*, 1998). In this paper we report the synthesis and crystallization of such a palladium(II) complex obtained from an ionic liquid, 1-butyl-4-methylpyridinium chloride. We believe that this complex may be successfully employed as an efficient catalyst of carbonylation of aryl halides (Mizushima *et al.*, 2001; Wojtków *et al.*, 2004) and the Suzuki reaction (Singh *et al.*, 2005).



Pd atoms of the title compound, (I), are located at inversion centers. There are four Cl atoms in the coordination sphere of each of the central ions. The $[\text{PdCl}_4]^{2-}$ anions are planar, with the Cl—Pd—Cl angles between adjacent Cl atoms (Table 1) deviating only slightly from 90°. The Pd—Cl bond lengths fall within typical ranges (2.298–2.354 Å) reported for four-coordinate palladium(II) complexes (Orpen *et al.*, 1989). All other bond distances and angles (Table 1) are also typical. The angle between the planes of the pyridinium rings is 69.9 (1)°.

The structure is stabilized by a large number of weak C—H...Cl hydrogen bonds (Table 2). As a result, a three-dimensional network of such interactions is formed in the crystal structure. The shortest C—H...Cl distances observed in the title compound are similar to the values of the N—H...Cl hydrogen bonds identified for Cl bonded to a transi-

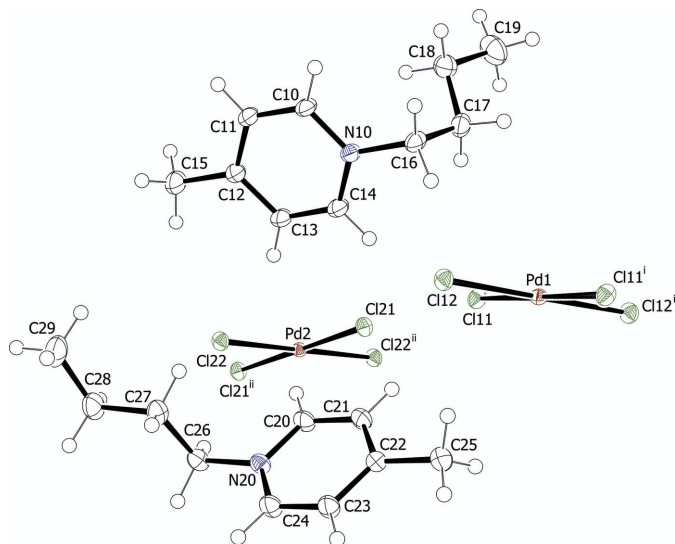


Figure 1
The molecular structure and atom-numbering scheme of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $1 - x, 1 - y, 1 - z$.]

tion metal (Desiraju & Steiner, 1999; Aullón *et al.*, 1998). However, in this structure there are numerous C—H...Cl interactions with longer H...Cl separations. Even though these distances may first appear to be somewhat large, the presence of C—H...Cl hydrogen bonds was confirmed spectroscopically for bis(tetramethylammonium) tetrachloropalladate(II) with H...Cl spacings of about 3 Å (Fábry *et al.*, 2004).

Experimental

1-Butyl-4-methylpyridinium chloride (0.072 g, 0.3 mmol) and PdCl₂(cod) (cod = cyclooctadiene) (0.042 g, 0.15 mmol) were dissolved in hot CH₃CN (4 ml) and stirred. After 15 min, the solvent was removed *in vacuo*. The red-brown product, bis(1-butyl-4-methylpyridinium) tetrachloropalladate(II), was recrystallized from CH₃CN and toluene (3:1). Analysis found: C 36.6, H 5.6, N 10.5%; calculated: C 36.5, H 5.7, N 10.6%. Spectroscopic analysis: ¹H NMR (CD₃CN): δ 8.74, 7.86 (*d*, 2H, Ph—H, *J*_{H—H} = 6.64 Hz), 4.55 (*t*, 2H, N—CH₂—, *J*_{H—H} = 7.47 Hz), 2.60 (*s*, 3H, N—CH₃), 1.93 (*qt*, 2H, —CH₂—, *J*_{H—H} = 7.68 Hz), 1.33 (*sx*, 2H, —CH₂—, *J*_{H—H} = 7.47 Hz), 0.92 (*t*, 3H, —CH₃). ¹³C NMR (CD₃CN): δ 160.5 (*s*, CH₃—C—CH), 144.5 (*d*, —N—CH=CH—, *J* = 83.4 Hz), 129.6 (*d*, —N—CH=CH—, *J* = 32.1 Hz), 61.5 (*s*, N—CH₂—), 33.8 (*s*, —C—CH₃), 22.3, 19.9 (*s*, —CH₂—), 13.8 (*s*, —CH₃). IR (KBr, cm⁻¹): 3137, 3104, 3072 ν(C—H), 2973, 2960, 2940, 1466, 1477, 873, 768, 628 ν(C—H), 1637 ν(C=C), 1564 ν(C=N).

Crystal data

(C₁₀H₁₆N)₂[PdCl₄]
*M*_r = 548.68
Triclinic, *P* $\bar{1}$
a = 8.710 (3) Å
b = 8.818 (3) Å
c = 16.354 (5) Å
 α = 95.54 (3)°
 β = 94.03 (3)°
 γ = 90.99 (3)°

V = 1246.7 (7) Å³
Z = 2
*D*_x = 1.462 Mg m⁻³
Mo *K*α radiation
 μ = 1.18 mm⁻¹
T = 100 (2) K
Block, red-brown
0.18 × 0.15 × 0.11 mm

Data collection

Kuma KM-4 CCD diffractometer
 φ and ω scans
Absorption correction: analytical
(*CrysAlis RED*; Oxford
Diffraction, 2003)
*T*_{min} = 0.819, *T*_{max} = 0.903

28914 measured reflections
10839 independent reflections
8173 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.035
 θ _{max} = 35.0°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.034
wR(*F*²) = 0.099
S = 1.06
10839 reflections
251 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.5036P]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} < 0.001
Δρ_{max} = 2.52 e Å⁻³
Δρ_{min} = -1.32 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Pd1—Cl11	2.2979 (8)	N10—C14	1.355 (3)
Pd1—Cl12	2.3158 (9)	N10—C16	1.486 (3)
Pd2—Cl21	2.3136 (8)	N20—C20	1.355 (3)
Pd2—Cl22	2.3095 (9)	N20—C24	1.345 (3)
N10—C10	1.358 (3)	N20—C26	1.484 (3)
Cl11—Pd1—Cl12	89.71 (3)	C14—N10—C16	119.3 (2)
Cl22—Pd2—Cl21	90.53 (3)	C20—N20—C24	120.6 (2)
C10—N10—C14	120.2 (2)	C20—N20—C26	119.1 (2)
C10—N10—C16	120.5 (2)	C24—N20—C26	119.9 (2)
N10—C16—C17—C18	62.5 (2)	N20—C26—C27—C28	-179.9 (2)
C16—C17—C18—C19	174.2 (2)	C26—C27—C28—C29	-172.8 (2)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C10—H10...Cl11 ⁱⁱⁱ	0.95	2.81	3.472 (3)	127
C10—H10...Cl12 ^{iv}	0.95	2.74	3.642 (3)	159
C11—H11...Cl11 ⁱⁱⁱ	0.95	2.89	3.507 (3)	124
C11—H11...Cl21 ⁱⁱⁱ	0.95	2.81	3.687 (3)	154
C13—H13...Cl21	0.95	2.86	3.478 (3)	124
C13—H13...Cl22	0.95	2.72	3.632 (3)	162
C14—H14...Cl11	0.95	2.69	3.586 (3)	158
C14—H14...Cl21	0.95	2.94	3.522 (3)	121
C16—H16A...Cl12	0.99	2.75	3.699 (3)	160
C16—H16B...Cl12 ^{iv}	0.99	2.86	3.768 (3)	153
C20—H20...Cl21	0.95	2.72	3.461 (3)	135
C20—H20...Cl22	0.95	2.86	3.727 (3)	153
C21—H21...Cl11	0.95	2.67	3.590 (3)	164
C23—H23...Cl11 ^v	0.95	2.89	3.399 (3)	115
C23—H23...Cl12 ^{vi}	0.95	2.85	3.751 (3)	158
C24—H24...Cl11 ^v	0.95	2.85	3.384 (3)	117
C24—H24...Cl21 ^v	0.95	2.82	3.697 (3)	155
C25—H25A...Cl12	0.98	2.80	3.746 (3)	165
C26—H26A...Cl21 ^v	0.99	2.84	3.656 (3)	141
C26—H26A...Cl22 ^{vii}	0.99	2.85	3.736 (3)	149
C26—H26B...Cl22	0.99	2.81	3.592 (3)	137

Symmetry codes: (iii) $x, y - 1, z$; (iv) $-x + 1, -y, -z$; (v) $x - 1, y, z$; (vi) $-x, -y + 1, -z$; (vii) $-x, -y + 1, -z + 1$.

All H atoms were positioned geometrically and refined using a riding model with C—H = 0.95–0.99 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C) or 1.5*U*_{eq}(C_{methyl}). The highest residual peak and the deepest hole in the final difference map are located 0.90 and 0.71 Å, respectively, from Pd2.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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