

Full Paper

Palladate Salts from Chiral Pyridinium Ionic Liquids: Synthesis and Crystal Structures

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Abstract: This paper reports the preparation, characterization and the crystal X-ray structures of metal-containing ionic liquid complexes based on chiral pyridinium cations and tetrachloropalladate (II) [PdCl₄]²⁻.

Keywords: Chiral Ionic Liquids, Pyridinium, Transition metal complexes, Palladium

Introduction

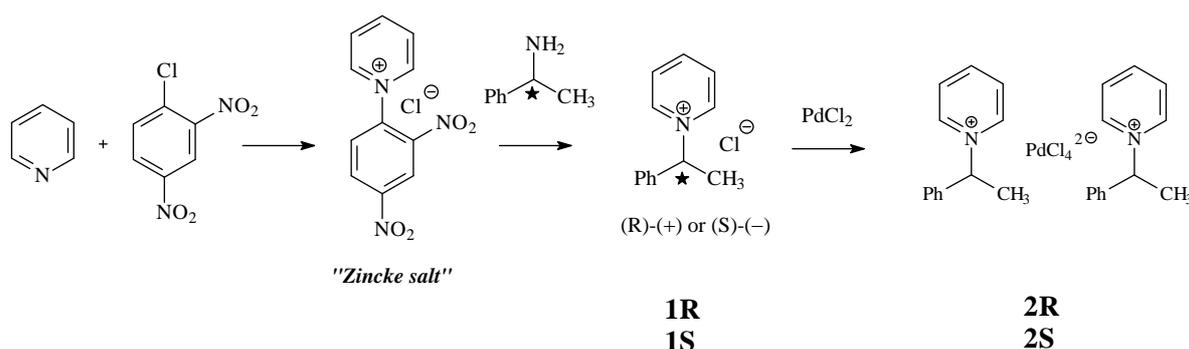
Ionic Liquids (ILs) are ionic compounds with relatively low melting points. They are characterized by very low vapor pressures and consequently, are considered as environmentally benign solvents. In addition ILs possess interesting properties such as tunable polarity, Lewis acidity, coordinating ability, hydrophilicity/lipophilicity and miscibility with various compounds [1-3]. These properties can be readily adjusted by a suitable choice of cation/anion. Therefore, the solubilities both of organic compounds and of metal salts in ILs are important with regard to chemical synthesis and catalytic processes [4]. The ammonium, phosphonium, pyridinium and imidazolium cations of ILs can coordinate to MX₄²⁻ (M=Co,Ni,Cu,Zn,Cd,Pd and X=Cl, Br) complex ions to form ionic liquid crystals

(ILCs) [5-18]. These ILCs contain a metal center, and so have been used as catalyst or catalyst precursors [5]. Moreover, they have a high degree of order, and so they are prime candidates for the synthesis of inorganic nanostructures [5]. Among them, imidazolium ILCs have been the most widely used [6-9]. Indeed for catalytical applications, imidazolium ILs can generate metal-carbene complexes in situ [10]. Other cores such as pyridinium, ammonium and phosphonium have been employed to a lesser extent [11]. In the case of transition metal-pyridinium salts (*N*-alkylpyridinium tetrahalo-metallates), most of the studies focused on their lyotropic and/or thermotropic liquid crystal behaviour [12-18]. To our knowledge, the synthesis of chiral pyridinium metal salts has not yet been described. This paper reports the preparation, characterization and the crystal X-ray structure of complexes metal-containing ILs based on chiral pyridinium cations and tetrachloropalladate (II) $[\text{PdCl}_4]^{2-}$.

Results and Discussion

The use of Marazano's route [19], based on the original work of Zincke [20], allowed access to unique chiral pyridinium salts. Reaction of Zincke's salt, readily obtained from pyridine and 1-chloro-2,4-dinitrobenzene, with chiral primary amines give the corresponding enantiopure alkyl pyridinium chlorides (*R*)- or (*S*)-1-phenylethylpyridinium chloride (**1R** and **1S**, Figure 1) [21]. Enantiopure (*R*)- and (*S*)-bis(1-phenylethylpyridinium) tetrachloropalladate complexes (**2R** and **2S**) were prepared in quantitative yields by reacting palladium chloride with a 2 molar excess of the corresponding stereoisomer **1R** and **1S** in acetonitrile during 24 hours under reflux. Procedures used for the synthesis of **2** were similar to those described in the literature for corresponding imidazolium salts [7,22].

Figure 1. Synthesis of chiral pyridinium ILs and of the corresponding metallates.



All the products have been fully characterized by means of C, H, N combustion analysis and IR, ^1H - and ^{13}C -NMR spectroscopies (see Experimental section for further details). Crystals suitable for X-ray crystallography were obtained by recrystallisation of **1R** and **2R** from acetonitrile solution at room temperature (respectively colorless and light brown crystals). The crystal structures of **1R** and **2R** (this one is the first example of metal-containing ILs based on pyridinium chiral salts) are given respectively in Figures 2 and 3 with 50 % thermal ellipsoids probability. Crystallographic data and parameters are given in Table 1. Compound **1R** is hygroscopic; consequently the asymmetric unit presents 0.25 molecule of water per molecule of **1R**. The water molecules and **1R** are involved in a hydrogen bonding network, as confirmed by FT-IR spectrum that shows a broad band at 3453 cm^{-1} .

Characteristics of these hydrogen bonds were summarized in Table 2. Moreover this asymmetric unit contains 5 anions and 4 cations due to the presence of anions Cl4 and Cl5 disordered over 2 positions with 50% occupancy factors. In **2R**, the metal-containing anion $[\text{PdCl}_4]^{2-}$, has a regular square-planar geometry around the Pd^{II} center, the average Cl-Pd-Cl angle being 90.0° (Table 3). The bond lengths and angles of the pyridinium cation in **2R** are similar to those found for **1R**. All the halogen of the anion are part of a three-dimensional hydrogen-bonding network and the shortest H...X contacts involve only the hydrogen atoms of the pyridine rings. The distances of these H...Cl H-bonding (Table 4) are in the range of 2.7 to 2.9 Å, and are within the sum of the van der Waals radii of H and Cl (2.95 Å). This was confirmed by FT-IR spectrum that shows bands between 3100 and 3400 cm^{-1} characteristic of hydrogen bonding. Moreover, the initial conformation of the asymmetric pyridinium was not modified during the salt formation as demonstrated by X-ray molecular structure.

Figure 2. Molecular structure and atom labelling scheme of **1R** with thermal ellipsoids drawn at the 50 % probability level (hydrogen atoms are not represented).

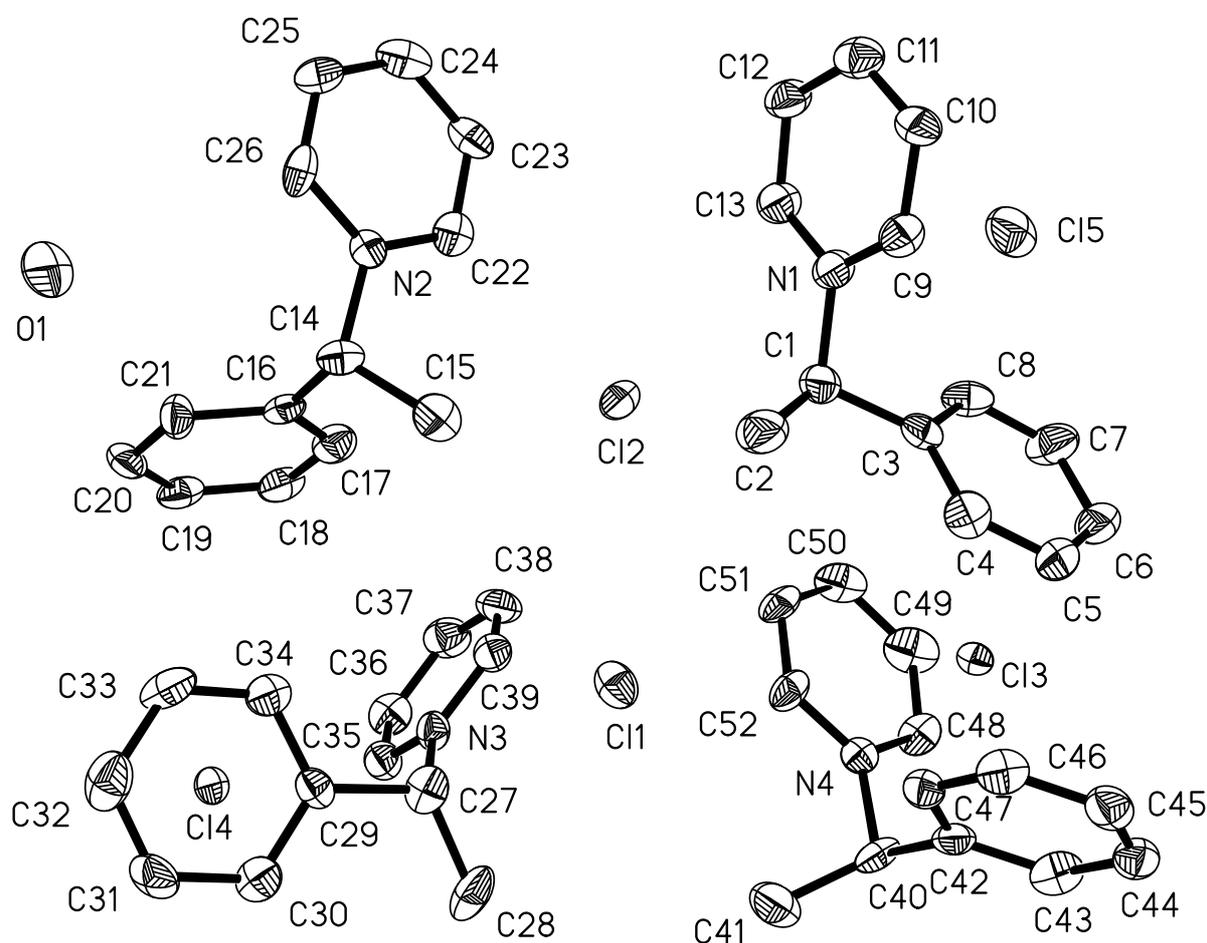
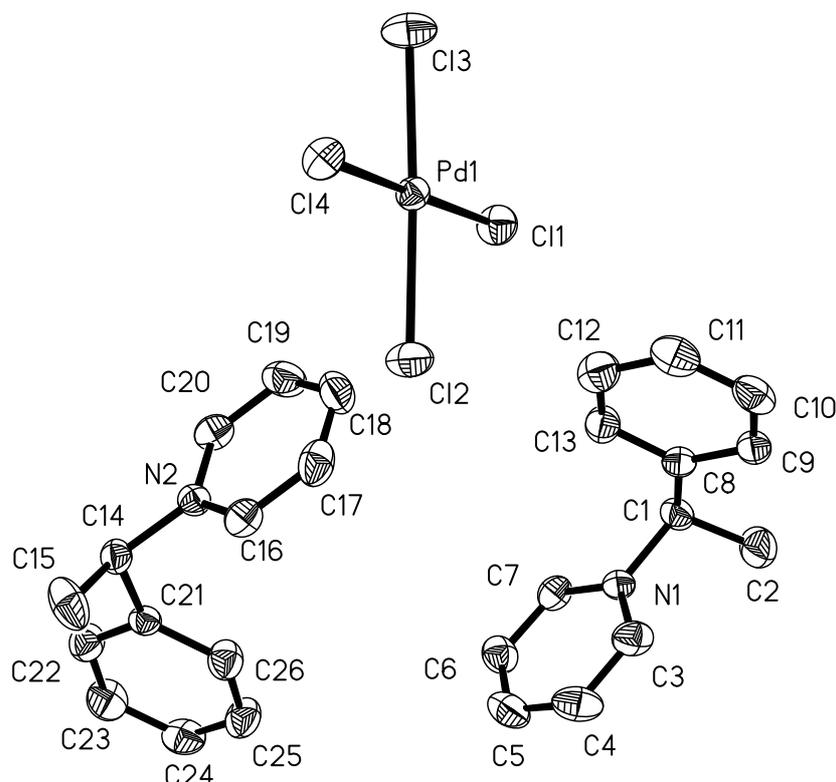


Figure 3. Molecular structure and atom labelling scheme of **2R** with thermal ellipsoids drawn at the 50 % probability level (hydrogen atoms are not represented).



The thermal behavior of compounds **1R** and **2R** was determined by optical microscopy and differential scanning calorimetry (DSC) and, as expected, is dependent on the nature of the counter anion. The melting point of (*R*)-1-phenylethylpyridinium chloride (**1R**) was found to be equal to 125°C. As described in a previous paper, the substitution of the chloride anion by a bis(trifluoromethanesulfonyl)imide anion (CF₃SO₂)₂N⁻ led to a room temperature ionic liquid (RTILs) (T_m = -30°C) [21]. Here, the substitution of Cl⁻ by [PdCl₄]²⁻ (leading to **2R**) slightly increased this temperature to 155 °C, and so ILCs **2R** could not be described as RTILs. Moreover, the upper limit of the liquidus range of these salts which is bounded by the thermal decomposition was also determined: 200°C for compound **1R** and 210°C for compounds **2R**. Further experiments are in progress to use the compound **2R** (and corresponding gold salts) as a precursor for the formation of nanoparticles [23,24] surrounded by a chiral shell.

Conclusions

New pyridinium chiral salts: (*S*) and (*R*)-1-phenylethylpyridinium chloride and (*S*) and (*R*)-bis(1-phenylethylpyridinium) tetrachloropalladate were synthesized. Crystallographic data of **1R** and **2R** were presented and showed that H-bonding interactions play an important role in the formation of both complexes. The catalytic activities of the palladium complexes and palladium nanoparticles are currently under investigation.

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Experimental.

General.

All chemicals were purchased from Aldrich Fine Chemicals and were used in this study as received. Solvents (HPLC grade) were from SDS. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ analysis were conducted with a Bruker Avance 500 MHz. Chemical shifts were reported as parts per million (ppm). Infrared measurements were performed on Perkin-Elmer IR FT 1600. Optical rotations measurements were realized at 20°C on a Perkin Elmer 241 polarimeter (Na lamp, $\lambda = 589$ nm) using solutions at 1% in MeOH. Micro-analysis were performed on a EAH10 apparatus from Carlo Erba and mass spectrometry measurements on an Applied Biosystem Q TRAP equipped with an electrospray source. The thermal properties of the samples were determined by polarised-light optical microscopy (Olympus microscope equipped with a Mettler FP82HT hot stage) and Differential Scanning Calorimetry (DSC) using a Perkin Elmer PYRIS 1 calorimeter. DSC calibration was done with indium and lead. DSC measurements were made at heating rates of 10, 20, 30, 40 °C/min and then extrapolated to 0 °C/min.

Synthesis of (*R*)- or (*S*)-1-phenylethylpyridinium chloride (**1R** and **1S**)

To a solution of Zincke salt (15.38 g, 70 mmol) in *n*-BuOH (200 mL) was added (+)-(*R*) or (-)-(*S*)-1-phenylethylamine (9.38 g, 77 mmol). The mixture was boiled under reflux for 24 h. The solvent was removed under vacuum. Distilled water was added to the residue. The solid that appeared was filtered off, and the filtrate was washed three times with dichloromethane. The aqueous solution was concentrated under reduced pressure. The residue was purified by HPLC (Waters Alliance 2695, column C18 Delta Park 300Å, 19x300mm, isocratic mode water-acetonitrile 80:20, flow rate 5mL/min.) to afford compounds **1R** or **1S** as colourless very hydroscopic salts (**1R**: 92 %; **1S**: 93%). $[\alpha]_{\text{D}}^{20}$ (**1R**-enantiomer) = $+44.9 \pm 0.5^\circ\text{mL/g/dm}$, $[\alpha]_{\text{D}}^{20}$ (**1S**-enantiomer) = $-45.2 \pm 0.5^\circ\text{mL/g/dm}$ (1% in methanol). $^1\text{H-NMR}$ (500 MHz, D_2O): $\delta = 1.97$ (d, $J = 7.0$ Hz, 3H, CH_3), 6.05 (q, $J = 7.0$ Hz, 1H, CH), 7.39 (m, 5H, Ph), 7.93 (t, $J = 6.8$ Hz, 2H, *p*-py), 8.41 (t, $J = 7.0$ Hz, 1H, *m*-py), 8.83 (d, $J = 5.5$ Hz, 2H, *o*-py) ppm; $^{13}\text{C-NMR}$ (125 MHz, D_2O): $\delta = 19.7$ (CH_3), 70.7 (CH), 127.4 (py C^3), 128.3 (Ph C^2), 129.4 (Ph C^4), 129.8 (Ph C^3), 136.7 (Ph C^1), 143.0 (py C^2), 145.9 (py C^4) ppm. MS (ESI) positive mode: $m/z = 184$ [py+]. FT-IR (KBr pellet): 3423, 3054 ($\nu_{\text{C-H}}$ aromatic); 2934 ($\nu_{\text{C-H}}$ aliphatic), 1630, 1478, 1141, 771, 738, 702 and 686 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{NCl}$: C, 71.07; H, 6.42; N, 6.37%; Found: C, 71.17; H, 6.52; N, 6.36% (Elemental analysis was obtained from crystals strictly maintained in dry atmosphere). Melting point: 125°C.

Synthesis of (*R*)- or (*S*)-bis(1-phenylethylpyridinium) tetrachloropalladate (**2R** and **2S**)

A mixture of 1-phenylethylpyridinium chloride (500 mg, 2.28 mmol) and palladium chloride (808 mg, 4.56 mmol) in acetonitrile (75 mL) was heated at reflux temperature for 24 h. The formed orange solution was concentrated to 3 mL under reduced pressure. Addition of toluene (25 mL) affords an yellow-orange solid that was recovered by filtration, washed with toluene (2 x 10 mL), and dried in vacuum. Crystals suitable for X-ray diffraction study were obtained by recrystallisation from acetonitrile solution at room temperature (1.2 g, 95% based on Pd). ¹H-NMR (500 MHz, D₂O): δ = 2.06 (d, *J* = 7.0 Hz, 3H, CH₃), 6.25 (q, *J* = 7.0 Hz, 1H, CH), 7.40 (m, 5H, Ph), 7.94 (t, *J* = 7 Hz, 2H, *p*-py), 8.43 (t, *J* = 8 Hz, 1H, *m*-py), 8.84 (d, *J* = 7 Hz, 2H, *o*-py) ppm; ¹³C-NMR (125 MHz, D₂O): δ = 19.7 (CH₃), 70.7 (CH), 127.5 (py C³), 128.3 (Ph C^{2'}), 129.4 (Ph C^{4'}), 129.8 (Ph C^{3'}), 136.7 (Ph C^{1'}), 143.1 (py C²), 145.9 (py C⁴) ppm. IR (KBr): 3434, 3040 (ν_{C-H} aromatic); 2972, 2929, 2870 (ν_{C-H} aliphatic); 1624, 1479, 1451, 1143, 698 cm⁻¹. MS (ESI): Positive mode: 184 [py⁺]; Negative mode: 581 [Py]₂[PdCl₄]⁻. Anal. Calcd for C₂₆H₂₈Cl₄N₂Pd: C, 50.63; H, 4.58; N, 4.54. Found: C, 50.73; H, 4.53; N, 4.87. Melting point: 155°C.

Crystal data for **1R** and **2R**

Crystallographic data and details of the structure determination of **1R** and **2R** are presented in Table 1. All data for all structures represented in this paper were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods (SHELXS-97, G. M. Sheldrick, *Acta Crystallogr.* 1990, *A46*, 467-473) and all non hydrogen atoms were refined anisotropically using the least-squares method on F^2 (SHELXL-97, Program for Crystal Structure Refinement, G. M. Sheldrick, University of Göttingen 1997). CCDC 647626 (**1R**) and CCDC 647627 (**2R**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Summary of Crystallographic Data and Parameters for [py*][Cl] and for [py*]₂[PdCl₄].

Identification code	[py*][Cl] (1R)	[py*] ₂ [PdCl ₄] (2R)
Empirical formula	C ₁₃ H _{14.50} ClNO _{0.25}	C ₂₆ H ₂₈ Cl ₄ N ₂ Pd
Formula weight	224.21	616.70
Temperature	193(2) K	173(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Tetragonal	Orthorhombic
Space group	P4 ₁	P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	a = 22.369(1) Å b = 22.369(1) Å c = 9.570(1) Å	a = 8.059(1) Å b = 12.211(1) Å c = 27.872(2) Å
Volume	4788.9(4) Å ³	2742.7(3) Å ³
Z	16	4
Density (calculated)	1.244 Mg/m ³	1.494 Mg/m ³

Table 1. Cont.

Absorption coefficient	0.29 mm ⁻¹	1.08 mm ⁻¹
F(000)	1896	1248
Crystal size	0.5 x 0.6 x 0.6 mm ³	0.1 x 0.1 x 0.5 mm ³
Theta range for data collection	5.1 to 23.3°.	1.5 to 26.4°.
Index ranges	-24<=h<=24 -23<=k<=24 -10<=l<=8	-10<=h<=9 -12<=k<=15 -30<=l<=34
Reflections collected	21441	16203
Independent reflections	6428 [R(int) = 0.0184]	5600 [R(int) = 0.0225]
Completeness to theta	(=23.3°) 98.5 %	(=26.4°) 99.8 %
Absorption correction	Semi-empirical	Semi-empirical
Ratio T _{min} /T _{max}	0.694	0.776
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	6428 / 1 / 569	5600 / 0 / 300
Goodness-of-fit on F ²	1.18	1.05
Final R indices [I>2sigma(I)]	R1 ^a = 0.070 wR2 ^b = 0.175	R1 = 0.021 wR2 = 0.046
R indices (all data)	R1 = 0.072 wR2 = 0.176	R1 = 0.024 wR2 = 0.047
Absolute structure parameter	0.00(10)	-0.019(19)
Largest diff. peak and hole	0.76 and -1.24 e.Å ⁻³	0.30 and -0.23 e.Å ⁻³

^aR1=Σ||F_o| - |F_c||/Σ|F_o|. ^bwR2=Σ|F_o|² - |F_c|²/Σ|w(F_o)²|^{1/2} (F_o: observed, F_c: calculated).

w = 1/[σ²(F_o)²+(aP)²+bP], where P=(F_o²+2F_c²)/3 and a = 0.0419, b = 18.7495 for **1R** and a = 0.0199, b = 0.7641 for **2R**.

Table 2. Hydrogen bonds for **1R** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2B)...Cl(1)	0.98	2.80	3.687(8)	151
C(12)-H(12)...Cl(1)#1	0.95	2.75	3.528(7)	139
C(23)-H(23)...Cl(1)#1	0.95	2.63	3.562(7)	166
C(27)-H(27)...Cl(1)	1.00	2.49	3.478(7)	168
C(41)-H(41C)...Cl(1)	0.98	2.98	3.944(9)	167
C(44)-H(44)...Cl(1)#2	0.95	2.90	3.823(7)	163
C(52)-H(52)...Cl(1)	0.95	2.51	3.419(7)	161
C(1)-H(1)...Cl(2)	1.00	2.54	3.499(6)	161
C(13)-H(13)...Cl(2)	0.95	2.99	3.811(7)	146
C(15)-H(15C)...Cl(2)	0.98	2.96	3.909(8)	162
C(17)-H(17)...Cl(2)	0.95	2.97	3.914(7)	173
C(22)-H(22)...Cl(2)	0.95	2.52	3.444(7)	165
C(28)-H(28B)...Cl(2)#3	0.98	2.75	3.665(8)	156
C(38)-H(38)...Cl(2)	0.95	2.80	3.578(7)	139
C(51)-H(51)...Cl(2)	0.95	2.65	3.540(7)	156
C(14)-H(14)...Cl(3)#4	1.00	2.80	3.710(7)	151
C(43)-H(43)...Cl(3)#5	0.95	2.80	3.691(7)	157
C(48)-H(48)...Cl(3)#5	0.95	2.66	3.595(7)	168

Table 2. Cont.

C(49)-H(49)...Cl(3)	0.95	2.74	3.559(8)	145
O(1)-H(1O)...Cl(3)#4	0.97(5)	2.32(6)	3.234(6)	157
O(1)-H(2O)...Cl(3)#6	1.02(5)	2.37(7)	3.226(6)	141
C(19)-H(19)...Cl(4)#7	0.95	2.90	3.662(7)	137
C(35)-H(35)...Cl(4)#4	0.95	2.99	3.593(7)	122
C(36)-H(36)...Cl(4)	0.95	2.85	3.766(8)	162
C(10)-H(10)...Cl(5)#6	0.95	2.82	3.737(8)	163
C(45)-H(45)...Cl(5)#8	0.95	2.86	3.608(8)	136
O(1)-H(2O)...Cl(3)#6	1.02(5)	2.37(7)	3.226(6)	141
O(1)-H(1O)...Cl(3)#4	0.97(5)	2.32(6)	3.234(6)	157
C(21)-H(21)...O(1)	0.95	2.47	3.395(9)	164
C(25)-H(25)...O(1)#9	0.95	2.88	3.506(9)	124
C(26)-H(26)...O(1)	0.95	2.75	3.672(9)	164
C(40)-H(40)...O(1)#10	1.00	2.57	3.396(9)	139

Symmetry transformations used to generate equivalent atoms:

#1 $x, y, z+1$ #2 $y, -x, z-1/4$ #3 $x, y, z-1$ #4 $y, -x+1, z-1/4$
 #5 $-x+1, -y, z-1/2$ #6 $-y, x, z+1/4$ #7 $-y+1, x, z+1/4$
 #8 $-x, -y, z-1/2$ #9 $-x, -y+1, z+1/2$ #10 $-y+1, x, z-3/4$

Table 3. Selected Bond Angles ($^{\circ}$) for salt **2R**.

2R	
Cl(1)-Pd(1)-Cl(2)	90.57(2)
Cl(1)-Pd(1)-Cl(3)	90.39(3)
Cl(2)-Pd(1)-Cl(4)	89.08(2)
Cl(3)-Pd(1)-Cl(4)	90.03(2)

Table 4. Hydrogen bonds for 2R [\AA and $^{\circ}$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
C(1)-H(1)...Cl(4)#1	1.00	2.69	3.641(2)	158
C(3)-H(3)...Cl(2)#2	0.95	2.55	3.463(3)	160
C(5)-H(5)...Cl(4)#3	0.95	3.00	3.614(3)	123
C(6)-H(6)...Cl(3)#3	0.95	2.72	3.504(3)	140
C(7)-H(7)...Cl(2)#1	0.95	2.70	3.486(3)	140
C(14)-H(14)...Cl(4)#4	1.00	2.88	3.744(3)	144
C(16)-H(16)...Cl(1)#5	0.95	2.72	3.580(2)	150
C(16)-H(16)...Cl(3)#5	0.95	2.73	3.374(3)	126
C(17)-H(17)...Cl(2)	0.95	2.84	3.559(3)	133
C(18)-H(18)...Cl(1)	0.95	2.77	3.668(3)	157
C(25)-H(25)...Cl(4)#3	0.95	3.00	3.648(3)	126

Symmetry transformations used to generate equivalent atoms:

#1 $x, y+1, z$ #2 $-x+1, y+1/2, -z+1/2$ #3 $x+1, y+1, z$
 #4 $x+1/2, -y+1/2, -z$ #5 $x+1, y, z$

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Sample Availability: Samples of compounds **1R**, **1S**, **2R**, **2S** are available from authors.