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A simple access to palladium complexes of functionalized heterocyclic carbenes

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Abstract

Methylation of 2-(1-imidazolyl)cyclohexanol (**1a**) and of the acylated derivative **1b** using CH_3I gives the corresponding imidazolium iodides **2a**,**b**. These are reacted with $Pd(OAc)_2$ to yield the carbene complexes *trans*-L_2PdI_2 (**3a**,**b**) bearing functionalized heterocyclic carbene ligands, which have been characterized spectroscopically and by X-ray structure analysis.

Keywords: Imidazoles; Carbene ligands; Transition metal complexes; Palladium

1. Introduction

Starting with the report on 1,3-diadamant-1-ylimidazol-2-ylidene, the first stable heterocyclic carbene, in 1991 by Arduengo et al. [1] something like a renaissance of transition metal carbene chemistry took place. Complexes of *N*,*N*-heterocyclic carbenes were first described independently by Wanzlick and Öfele, who succeeded in the preparation of a series of transition metal imidazolin-2-ylidene complexes [2–4]. In general, such complexes can either be achieved by reacting basic precursors with the corresponding azolium salts [2–4] or by generating the free carbene ligand in situ [1,5,6] and reacting it with an appropriate coordinatively unsaturated metal fragment [7].

It has been shown, that *N*,*N*-heterocyclic carbenes can be compared with electron rich phosphines in terms of their donor properties [7]. This feature has initiated tremendous efforts to apply such ligands in catalysis and resulted in a whole series of catalytic applications, which have been worked out during the last few years [8–18].

Similar to phosphine chemistry, increasing knowledge of the chemical properties of ligands and derived complexes led to a growing demand for systems with more and more complex chemical structures like biscarbenes or functionalized carbenes. In the present paper, we report a simple access to functionalized imidazoles, imidazolium salts and the derived imidazolin-2-ylidene palladium complexes, which we characterized spectroscopically and by X-ray structure analysis.

2. Results and discussion

For the past three years we have been interested in the synthesis of chiral *N*-donor ligands obtained by ring opening of epoxides with substituted pyrazoles and triazoles and the application of these systems in coordination chemistry and enantioselective catalysis [19–25]. In the present paper we have extended this methodology to the corresponding imidazole derivative **1a**. Owing to the enhanced nucleophilicity of imidazole compared to pyrazole [26] heating of epoxycyclohexane with an equimolar amount of imidazole under pressure by microwave irradiation gives the desired product **1a** in a rapid reaction with high yields and 100% *trans* selectivity (Scheme 1).

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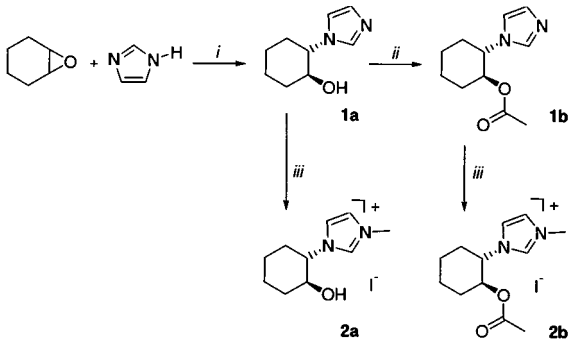
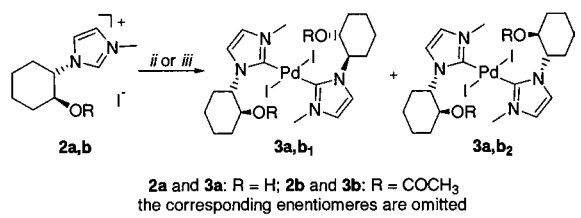


Scheme 1. Only one of the enantiomers is shown for **1a**,**b** and **2a**,**b**; (i) microwave heating, 3 min; (ii) lipase B (*C. antarctica*), isopropenyl acetate, 60°C, 24 h; (iii) CH_3I, CH_3CN, 80°C, 30 min.

Since we do not add any chiral agent, **1a** is obtained as a racemic mixture. In the case of the corresponding pyrazolyl derivative, the enantiomeres can be separated after a kinetic resolution catalyzed by lipase B of *Candida antarctica* (Fa. Novo Nordisk) with isopropenylacetate as the acylating agent [19,21,23]. Performing this reaction with **1a** as the substrate, the racemic ester **1b** is obtained in good yields (Scheme 1). At the moment we can only speculate about the reasons for this result: steric hindrance can be excluded since the enzyme accepts even bulky substituents at the corresponding pyrazole derivatives [21]. Maybe, the non alkylated nitrogen atom of the imidazole ring undergoes an unfavorable hydrogen bonding to the enzyme which allows the conversion of the substrate but prevents the stereoselection of the enantiomeres.

Alkylation of **1a**,**b** with CH_3I in CH_3CN under pressure gives the desired imidazolium iodides **2a**,**b** (Scheme 1). Performing the reaction in CH_3CN reduces the reaction times drastically compared to an alcoholic reaction medium [27].

In situ deprotonation of the azolium iodides **2a**,**b** using palladium(II) acetate leads to the *trans* configured iodo palladium(II) carbene complexes **3a**,**b**, which are obtained purely as yellow, air stable solids after recrystallization (Scheme 2). Since the precursor compounds **2a**,**b** are applied as racemates, **3a**,**b** are mixtures of diastereomers enclosing either two heterochiral (e.g. **3a**$_1$) or homochiral (e.g. **3a**$_2$) carbene ligands. This feature is confirmed by the ^{1}H- and ^{13}C-NMR spectra of the complexes, which show two sets of signals.



Scheme 2. Only one of the enantiomers is shown for **2a**,**b**, **3a**$_1$, **3a**$_2$, **3b**$_1$, and **3b**$_2$; (ii) for **3a**$_1$ and **3a**$_2$, THF, refl. 3h; (iii) for **3b**$_1$ and **3b**$_2$, DMSO, 150°C, 15 min.

The stretching frequency of the OH moiety shifts from 3107 (**1a**) to 3315 (**2a**) and 3470 cm^{-1} (**3a**), indicating a constant increase in the OH bond strength. We know from the X-ray structure analysis of pyrazolyl cyclohexanol ($\nu_{OH} = 3245$ cm^{-1}) that strong H-bonds are formed between the OH functionality and pyrazolyl moiety [19], which will also be the case for **1a**. Alkylation destroys the proton acceptability of the azole fragment, and forces the system to form weaker H-bonds to the counter ion I^-. The X-ray structure analysis of **3a** (discussed below) shows hydrogen interaction to an even weaker proton acceptor, an iodo ligand co-ordinated to palladium, which is confirmed by the high energy of the OH absorption.

The molecular structures of the complexes **3a**$_{1/2}$ and **3b**$_2$ are presented in Fig. 1 and Fig. 2, respectively, a selection of characteristic bond lengths and angles is given in Table 1.

In the case of **3a**, we took a crystal containing both the diastereomer **3a**$_1$ with heterochiral carbene ligands and the diastereomer **3a**$_2$ with homochiral carbene ligands disordered around a crystallographic center of symmetry located at the Pd atom. We call this arrangement **3a**$_{1/2}$. In the case of **3b**, the homochiral diastereomer **3b**$_2$ was investigated [28]. Therefore **3a**$_{1/2}$ shows centrosymmetric Pd-carbene units, the OH groups are statistically disordered. In **3b**$_2$, both carbene ligands are inequivalent in terms of symmetry. However, all characteristic intermolecular distances and angles can be regarded as identical (see Table 1) and are

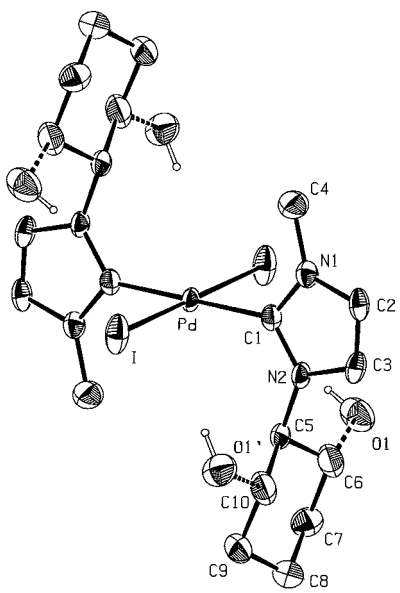


Fig. 1. PLATON plot of the solid state structure of **3a**$_{1/2}$. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity. The disorder of the OH groups is indicated by dashed lines.

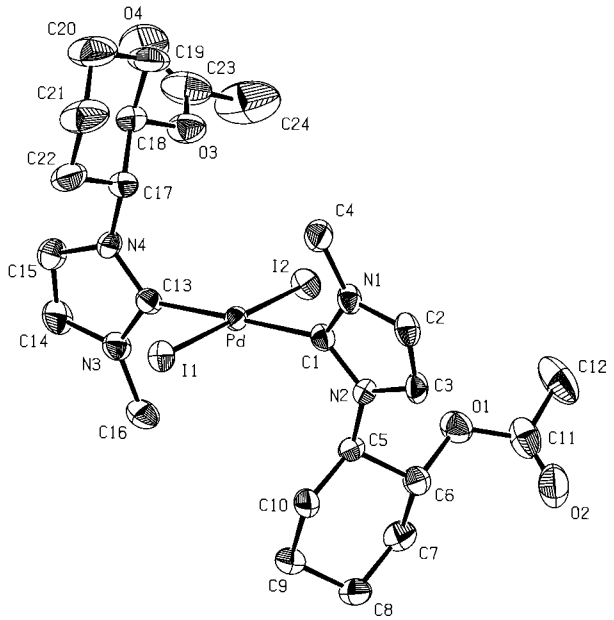


Fig. 2. PLATON plot of the solid state structure of **3b$_2$**. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity.

similar to those found in other Pd complexes bearing a square-planar $Pd(I)_2(carbene)_2$ core [9,29,30]. The contact distances I···O observed in the hydroxyl complex **3a$_{1/2}$** (mean 3.640 Å) are shortened compared to those observed in the acetyl derivative **3b$_2$**. (mean 4.002 Å). We assign this shortening to weak hydrogen bonding between the disordered OH groups and the iodo ligands (see discussion of IR spectra) [31].

Table 1
Bond lengths (Å) and angles (°) for **3a$_{1/2}$** and **3b$_2$** [a]

3a$_{1/2}$		**3b$_2$**	
Bond lengths			
Pd–I	2.5947(4)	Pd–I1	2.6138(4)
		Pd–I2	2.6073(4)
Pd–C1	2.030(4)	Pd–C1	2.033(4)
		Pd–C13	2.024(4)
I···O1′	3.578(8)	I2···O1	4.172(3)
I_a···O1	3.703(8)	I2···O3	3.832(3)
Bond angles			
I–Pd–I_a	180	I1–Pd–I2	177.11(1)
I–Pd–C1	90.87(11)	I1–Pd–C1	90.39(12)
I–Pd–C1_a	89.13(11)	I1–Pd–C13	88.89(11)
		I2–Pd–C1	91.86(12)
		I2–Pd–C13	88.85(11)
C1–Pd–C1_a	180	C1–Pd–C13	179.04(15)
Pd–C1–N1	127.6(3)	Pd–C1–N1	127.6(3)
Pd–C1–N2	127.4(3)	Pd–C1–N2	127.6(3)
		Pd–C13–N3	126.5(3)
		Pd–C13–N4	127.6(3)
Torsion angles			
I–Pd–C1–N1	96.9(4)	I1–Pd–C1–N1	−74.2(4)
		I2–Pd–C13–N3	84.7(4)
C3–N2–C5–C6	62.3(5)	C3–N2–C5–C6	−36.9(5)
		C15–N4–C17–C22	62.1(5)

[a] Translation of symmetry code to equivalent positions: _$a = 1-x$, $1-y$, $1-z$.

3. Conclusions

We have presented a new and simple access to palladium complexes of functionalized heterocyclic carbene ligands. The protocol described here is now going to be extended to enantiomerically pure chiral epoxides (e.g. epoxystyrene), which will be used as starting materials for the synthesis of enantiomerically pure complexes. The hydroxy function of the ligand will additionally allow the facile introduction of different functional groups.

4. Experimental

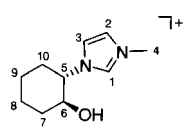
The synthesis of the palladium complexes was performed under a nitrogen atmosphere, solvents were dried and distilled before use. The NMR spectra of the compounds **1**–**3** are assigned according to Scheme 3.

4.1. trans-2-(1-Imidazolyl)cyclohexanol (*1a*)

Imidazole (1.0 g, 14.7 mmol) and epoxycyclohexane (1.5 g, 14.7 mmol) were heated in a pressure tube (Aldrich, Z18,108-0) for 3 min in a microwave oven (510 W). The resulting brown solid was recrystallized from hot ethylacetate. Colorless needles (1.54 g, 62%), m.p. 134°C. Anal. Calc. for $C_9H_{14}N_2O$ (166.23): C, 65.03; H, 8.49; N, 16.85. Found: C, 64.85; H, 8.60; N, 16.71%. IR (KBr, cm^{-1}): 3107 vs ν_{O-H}. ^{1}H-NMR (400 MHz, 25°C, $CDCl_3$): δ 7.20 (s, 1-H), 6.82, 6.72 (2 × s, $^3J_{2,3} < 1.5$ Hz, 2-H, 3-H), 5.91 (br, OH), 3.55 (m, 5-H, 6-H), 2.08–1.26 (m, 8H). ^{13}C{^{1}H}-NMR (100.25 MHz, 25°C, $CDCl_3$): δ 136.0 (C-1), 128.0 (C-3), 117.1 (C-2), 72.6 (C-6), 63.8 (C-5), 34.2, 32.2 (C-7, C-10), 25.0, 24.3 (C-8, C-9). MS (EI): m/z (%) = 166 (68) [M^+], 139 (12) [$M^+ - C_2H_3$], 109 (14) [$M^+ - C_4H_9$], 95 (61) [$C_5H_7N_2^+$], 82 (55) [$C_4H_6N_2^+$], 69 (100) [$C_4H_7N^+$], 55 (20) [$C_3H_5N^+$], 41 (45) [$C_2H_3N^+$].

4.2. trans-1-Acetoxy-2-(1-imidazolyl)cyclohexane (*1b*)

1a (1.5 g, 9.0 mmol), isopropenylacetate (6.0 ml, 54 mmol), molecular sieve 4 Å (1.0 g) and immobilized



Scheme 3.

lipase B of *Candida antarctica* (150 mg, Novo Nordisk) and 10 ml of $CHCl_3$ were slowly stirred at 60°C for 24 h. After quenching the reaction by filtration and extraction of the solid residue with Et_2O, **1b** was crystallized by slow evaporation of the solvents. Colorless crystals in a colorless oil (1.52 g, 81%), pure by GC/MS. Anal. Calc. for $C_{11}H_{16}N_2O_2$ (208.26): C, 63.44; H, 7.74; N, 15.45. Found: C, 64.06; H, 9.00; N, 16.38%. IR (KBr, cm^{-1}): 1734 vs $\nu_{C=O}$. MS (EI): m/z (%) = 208 (49) [M^+], 165 (9) [$M^+ - C_2H_3O$], 148 (100) [$M^+ - C_2H_4O_2$], 121 (14) [$M^+ - C_4H_7O_2$], 95 (59) [$C_5H_7N_2^+$], 81 (46) [$C_4H_5N_2^+$], 69 (100) [$C_4H_7N^+$].

4.3. 1-[(2-Hydroxy)cyclohex-1-yl]-3-methylimidazoliumiodide (2a)

1a (1.50 g, 9.02 mmoles) and CH_3I (1.41 g, 9.93 mmoles) were dissolved in 15 ml of CH_3CN and heated in a pressure tube for 30 min to 80°C. After removing the solvent, the resulting solid was recrystallized from isopropanol at 0°C. Colorless solid (2.39 g, 86%), m.p. 158°C. Anal. Calc. for $C_{10}H_{17}IN_2O$ (308.16): C, 38.98; H, 5.56; N, 9.09. Found: C, 38.77; H, 5.61; N, 9.08%. IR (KBr, cm^{-1}): 3315 vs ν_{O-H}. ^{1}H-NMR (400 MHz, 25°C, $CDCl_3$): δ 9.16 (s, 1-H), 7.84, 7.72 (2 × s, $^3J_{2,3}$ < 1.5 Hz, 2-H, 3-H), 5.91 (d, $^3J_{OH,6}$ = 5.0 Hz, OH), 3.99 (m, 6-H), 3.83 (s, 4-H), 3.59 (m, 5-H), 1.97–1.30 (m, 8H). ^{13}C{^{1}H}-NMR (100.25 MHz, 25°C, $CDCl_3$): δ 136.0 (C-1), 123.3, 120.9 (C-2, C-3), 70.9 (C-6), 65.2 (C-5), 35.7 (C-4), 34.3 (C-7), 30.8 (C-10), 24.2, 23.5 (C-8, C-9).

4.4. 1-[trans-(2-Acetoxy)cyclohex-1-yl]-3-methylimidazoliumiodide (2b)

Synthesized analogously to **2a** using **1b** instead of **1a**. Colorless solid, pure by NMR, yield 81%, m.p. 178°C. Anal. Calc. for $C_{12}H_{19}IN_2O_2$ (350.20): C, 41.16; H, 5.47; N, 8.00. Found: C, 39.01; H, 5.40; N, 8.98%. IR (KBr, cm^{-1}): 1724 vs $\nu_{C=O}$. ^{1}H-NMR (400.13 MHz, 25°C, $CDCl_3$): δ 9.90 (s, 1-H), 7.57 (s, $^3J_{2,3}$ < 1.5 Hz, 2-H, 3-H), 4.88 (m, 6-H), 4.42 (m, 5-H), 4.04 (s, 4-H), 2.24–1.42 (m, 8H), 1.87 (s, $COCH_3$). ^{13}C{^{1}H}-NMR (100.25 MHz, 25°C, $CDCl_3$): δ 169.6 ($COCH_3$), 136.1 (C-1), 123.5, 120.8 (C-2, C-3), 73.7 (C-6), 62.7 (C-5), 37.0 (C-4), 31.4, 30.7(C-7, C-10), 23.9, 23.1(C-8, C-9), 20.9 ($COCH_3$).

4.5. trans-Bis{1-[(trans-2-hydroxy)cyclohex-1-yl]-3-methylimidazolin-2-ylidene}diiodopalladium(II) (3a)

$Pd(OAc)_2$ (0.20 g, 0.89 mmol) and **2a** (0.55 g, 1.78 mmol) were dissolved in 25 ml of abs. THF and heated for 3 h under reflux conditions. A dark solid residue was filtered off and the solvent was evaporated. The oily orange–yellow residue was dissolved in 10 ml of CH_2Cl_2 and Et_2O was slowly condensed on the solution. After a few days yellow crystals and a red oil had formed. The oil was removed by washing with cold acetone yielding pure **3a** (0.42 g, 65%) as clear yellow crystals. Anal. Calc. for $C_{20}H_{32}I_2N_4O_2Pd$ (720.71): C, 33.33; H, 4.48; N, 7.77. Found: C, 33.19; H, 4.45; N, 7.69%. IR (KBr, cm^{-1}): 3470 vs ν_{O-H}. ^{1}H-NMR (400.13 MHz, 25°C, d_6-dmso): isomers **3a$_1$** and **3a$_2$** δ 6.95 (s, 2H, 2-H, 3-H), 4.91 (m, 6-H), 3.97 (m, 5-H), 3.94 (s, 4-H), 2.79–1.31 (m, 8H, CH_2). ^{13}C{^{1}H}-NMR (100.25 MHz, 25°C, d_6-dmso): isomer with heterochiral carbene ligands (**3a$_1$**) δ 165.3 (C-1), 122.9 (C-3), 118.8 (C-2), 70.6 (C-6), 65.4 (C-5), 37.5 (C-4), 35.0, 31.8 (C-7, C-10), 24.6, 23.5 (C-8, C-9); isomer with homochiral carbene ligands (**3a$_2$**) δ 165.3 (C-1), 122.8 (C-3), 118.9 (C-2), 70.5 (C-6), 65.3 (C-5), 37.4 (C-4), 34.9, 31.9 (C-7, C-10), 24.5, 23.6 (C-8, C-9).

4.6. trans-Bis{1-[(2-acetoxy)cyclohex-1-yl]-3-methylimidazolin-2-ylidene}diiodopalladium(II) (3b)

$Pd(OAc)_2$ (0.20 g, 0.89 mmol) and **2b** (0.62 g, 1.78 mmol) were dissolved in 4 ml of DMSO and heated under vacuum to 150°C. After 15 min, the solvent was removed in vacuum at the same temperature. The resulting brown oil was dissolved in 20 ml of CH_2Cl_2, 3.0 g silica were added and the solvent was removed again. The powdery residue was extracted with 50 ml of CH_2Cl_2, the volume of the resulting yellow solution was reduced to 10 ml and the product was crystallized by slow diffusion of Et_2O. Yellow crystals (0.51 g, 71%). Anal. Calc. for $C_{24}H_{36}I_2N_4O_4Pd$ (804.79): C, 35.82; H, 4.51; N, 6.96. Found: C, 35.73; H, 4.59; N, 6.87%. IR (KBr, cm^{-1}): 1720 vs $\nu_{C=O}$. ^{1}H-NMR (400.13 MHz, 25°C, $CDCl_3$): isomer with heterochiral carbene ligands (**3b$_1$**) δ 6.98 (s, 2-H, 3-H), 5.08 (m, H-5, H-6), 4.19 (s, H-4), 2.78–1.31 (m, 8H, CH_2), 1.37 (s, $COCH_3$); isomer with homochiral carbene ligands (**3b$_2$**) δ 7.00 (d, $^3J_{2,3}$ = 2.0 Hz, 3-H), 6.91 (d, 2-H), 5.08 (m, H-5, H-6), 4.23 (s, H-4), 2.78–1.31 (m, 8H, CH_2), 1.37 (s, $COCH_3$); isomer ratio **3b$_1$**:**3b$_2$** = 4.5:1. ^{13}C{^{1}H}-NMR (100.25 MHz, 25°C, $CDCl_3$): **3b$_1$** δ 169.5 (C=O), 165.5 (C-1), 123.9 (C-3), 118.4 (C-2), 72.8 (C-6), 62.5 (C-5), 40.4 (C-4), 33.8, 31.8 (C-7, C-10), 24.6, 24.0 (C-8, C-9), 20.6 ($COCH_3$); **3b$_2$** δ 169.5 (C=O), 165.5 (C-1), 123.7 (C-3), 117.9 (C-2), 72.1 (C-6), 65.8 (C-5), 40.4 (C-4), 32.5, 31.6 (C-7, C-10), 22.2, 20.6 (C-8, C-9), 15.2 ($COCH_3$).

4.7. Structure determination of 3a$_{1/2}$ and 3b$_2$

Crystals of the complexes suitable for a single crystal X-ray structure determination were grown by vapor diffusion of Et_2O into a saturated CH_2Cl_2 solution.

Details of the X-ray experiment, data reduction, and final least-square refinement are summarized in Table 2. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography [32]. All calculations were performed on a DEC 3000 AXP workstation with the STRUX-V [33] system, including the programs PLATON [34] SIR92 [35] and SHELXL-97 [36].

Data collection on compound **3a$_{1/2}$** was carried out on an imaging plate diffraction system (IPDS; Stoe&Cie) equipped with a rotating anode (NONIUS FR591, 50 kV, 60 mA, 3.0 kW) and graphite monochromated Mo–K_α radiation 193 K within the Θ-range of $3.14 < \Theta < 25.64°$ with an exposure time of 300 s per image (rotation scan modus from $\varphi = 0$ to 360° with $\Delta\varphi = 1.0°$). A total number of 17359 reflections was collected. After rejecting 516 systematically absent reflections and merging ($R_{int} = 0.0314$), a sum of 2210 independent reflections remained and were used for all calculations. Data were corrected for Lorentz and polarization effects. Corrections for absorption and decay effects were not applied. The unit cell parameters were obtained by full-matrix least-squares refinements of 5000 reflections with the program CELL [37]. The structure was solved by a combination of direct methods and difference-Fourier synthesis. All non-hydrogen atoms of the asymmetric unit were refined anisotropically. All hydrogen atoms were placed in ideal geometry and allowed to ride on the parent atom. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with SHELXL-97 weighting scheme and stopped at $R_1 = 0.0325$, $wR_2 = 0.0711$, GOF = 1.167, and shift/err < 0.001.

Data collection on compound **3b$_2$** was carried out on a NONIUS Kappa CCD area detection system equipped with a rotating anode (NONIUS FR591) and graphite monochromator Mo–K_α radiation at 193 K within the Θ range of $2.55 < \Theta < 25.34°$. A total number of 15741 reflections were collected. After merging ($R_{int} = 0.047$), 4742 independent reflections remained and were used to refine 316 parameters. Data were corrected for Lorentz and polarization effects [38,39]. The structure was solved by a combination of direct methods and difference-Fourier syntheses. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in ideal geometry and allowed to ride on the parent atom. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and converged with $R_1 = 0.0216$, $wR_2 = 0.0540$, GOF = 1.049 and shift/error < 0.001. The correct enantiomer (*R* configuration at C5, C6, C17, and C18) is confirmed by Flack's parameter $x = 0.007(17)$.

Table 2
Crystal data and summary of intensity data collection and structure refinement of **3a$_{1/2}$** and **3b$_2$**

	3a$_{1/2}$	**3b$_2$**
Formula	$C_{20}H_{32}I_2N_4O_2Pd$	$C_{24}H_{36}I_2N_4O_4Pd$
Formula weight	720.72	804.79
Color/shape	Yellow/fragment	Yellow/fragment
Space group	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)
a (Å)	7.4322(3)	7.7587(1)
b (Å)	8.9561(5)	10.5804(2)
c (Å)	18.8607(8)	36.3924(7)
β (°)	95.396(4)	90
λ (Å)	0.71073	0.71073
V (Å^3)	1249.9(1)	2987.46(9)
Z	2	4
ρ_{calc} (g cm^{-3})	1.915	1.789
μ (mm^{-1})	3.234	2.722
Diffractometer	STOE IPDS	NONIUS Kappa CCD
Scan type	φ-scan/rotation	φ-scan/rotation
T (K)	193	193
Reflections collected	17359	15741
Independent reflections	2210	4742
Observed reflections [$I > 2\sigma(I)$]	1991	4680
Parameters refined	145	316
R_1 [a] observed (all data)	0.0286/0.0325	0.0212/0.0216
wR_2 [b] (all data)	0.0711	0.0540
GOF [c]	1.167	1.049

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.
[c] $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(NO - NV)]^{1/2}$.

5. Supplementary material

Supporting information available. An X-ray crystallographic file in CIF format for the structure determination of complexes **3a$_{1/2}$** and **3b$_1$**, is available on the Internet (as well as with the CCDC). Access information is given on any current masthead page.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157368 (**3a$_{1/2}$**) and no. CCDC-157369 (**3b$_2$**). Copies of this data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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