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Synthesis and structure of chiral palladium(II) complexes bearing ethylene-bridged bisindolinyl- and bis(1,2,3,4-tetrahydroquinolinyl) ligands [1]

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Abstract

A series of new neutral and cationic palladium(II) complexes of type $[Pd(L-L)X_2]$ (**5**, **6**, **9**, **10**), $[Pd(L-L)Y_2](BF_4)_2$ (**7**, **8**, **11**, **12**) and $[Pd(\eta^3\text{-}C_6H_9)(L-L)](PF_6)$ (**13**, **14**), (L–L = 1,2-bis(*N*-indolinyl)ethane (BIE, **3**), 1,2-bis(*N*-1,2,3,4-tetrahydroquinolinyl)ethane (BTQE, **4**); X = Cl, NO_3; Y = MeCN, H_2O) have been prepared and characterized. These investigations show that BIE and BTQE can lead to chiral C_2-symmetric complexes, as well as to the achiral meso compounds. A nearly quantitative yield of the C_2-symmetric isomer was found for the reaction of $(PhCN)_2PdCl_2$ with BIE and BTQE. The solid state structures of the C_2-symmetric $[Pd(BIE)Cl_2]$ (**5a**) and the meso isomer of $[Pd(\eta^3\text{-}C_6H_9)(BIE)](PF_6)$ (**13b**) have been determined by X-ray structure analysis.

Keywords: Palladium; Bidentate ligands; Indolinyl ligands; Chirality; Crystal structure; Bridged complexes

1. Introduction

The use of C_2-symmetric ansa-metallocene complexes of early transition metals as catalysts for the polymerization of olefins can result in highly isotactic polymers [1]. Chiral, square-planar cationic palladium (II) complexes, stabilized by phosphine or amine ligands, have been effectively utilized as catalysts for the alternating copolymerization of carbon monoxide and olefins in organic solvents, as well as in an aqueous media [2]. The CO–styrene copolymerization leads to syndiotactic polymers with fairly high stereoregularities [3]. However, by using propene as the olefin component, a variety of different Pd(II) catalysts produce only slightly isotactic copolymers [4].

As part of our research program we study chiral and C_2-symmetric complexes of the late transition metal ions with bridged ligands that resemble the coordination mode of two indenyl fragments in ansa-metallocenes. We recently succeeded in the preparation of C_2-symmetric Fe(II)- and Co(II)-compounds, bearing a stereorigid tetradentate ligand system [5].

We now report on the synthesis and characterization of some chiral palladium(II) complexes stabilized by bridged, bidentate tertiary amine ligands bearing indoline or 1,2,3,4-tetrahydroquinoline moieties.

2. Results and discussion

2.1. Ligand and complex synthesis

The reaction of indoline (**1**) or 1,2,3,4-tetrahydroquinoline (**2**) with 1,2-dibromoethane under reflux provides a convenient one-step synthesis of the symmetric diamines **3** and **4** [6]. Stirring of **3** or **4** with $(PhCN)_2PdCl_2$ in acetone yields the corresponding dichloropalladium(II) complexes **5** and **6** respectively, in up to 92% yield (Fig. 1).

Complexes **5** and **6** exist in two diastereomeric forms: one shows both indoline or 1,2,3,4-tetrahydroquinoline fragments in a C_2-symmetric arrangement [7] (**5a**, **6a**); the other coordination mode leads to the meso structure (**5b**, **6b**). For both ligands, one complex isomer is

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[1] Dedicated to Professor Dr. M.D. Rausch on the occasion of his 65th birthday.

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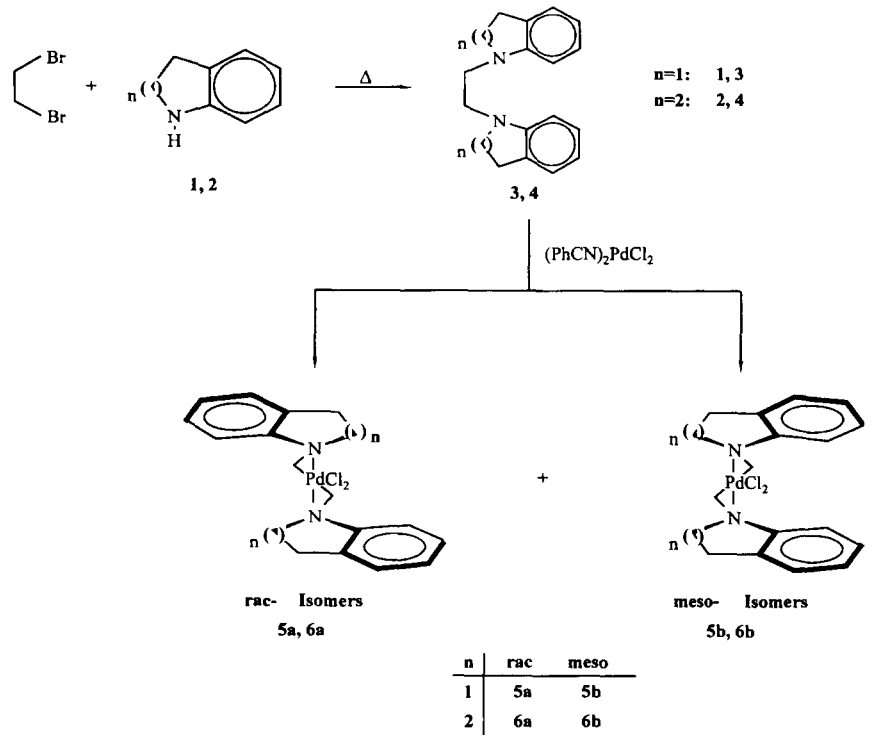

Fig. 1. Formation of bidentate nitrogen ligands and of the corresponding *rac*- and *meso*-$PdCl_2$ complexes.

formed with high diastereomeric excess ($de \approx 82\%$). The major compounds can be separated by crystallization from acetonitrile–ethyl acetate (3:1). An X-ray structure investigation (see below) performed on the indoline complex revealed the desired C_2-symmetric ligand arrangement (structure **5a**) for the major isomer.

Pd(II) complexes, like **5a** and **6a**, can be used as catalysts for CO–alkene copolymerization after conver-

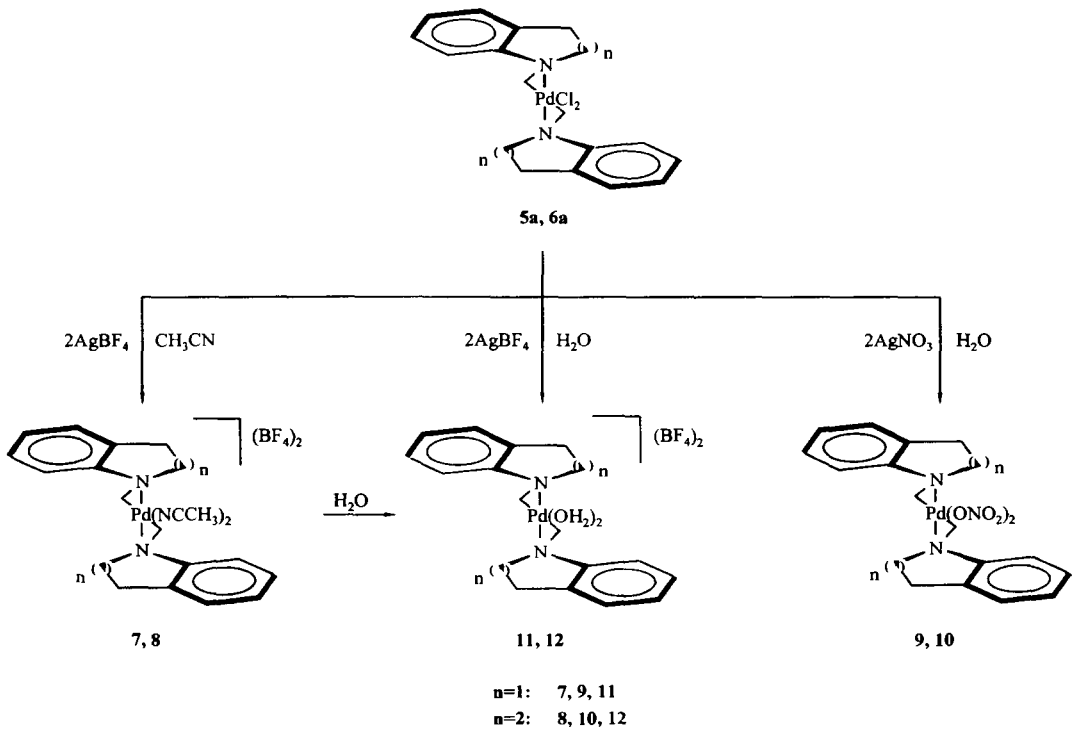

Fig. 2. C_2-symmetric, dicationic Pd(II)-complexes.

sion of the dichlorides to the solvent-stabilized dicationic species (Fig. 2) [8]. Chloride abstraction with $AgBF_4$ affords the diaquo- and diacetonitrile complexes **7**, **8** and **11**, **12** in moderate to high yields. The use of $AgNO_3$ instead of $AgBF_4$ affords the nitrato complexes **9** and **10**. From **9** we could grow crystals suitable for a preliminary X-ray structure investigation, which showed that both nitrato counterions coordinate to Pd(II). However, the quality of the crystals was unsatisfactory for a detailed analysis of the solid state structure [9].

The reaction of the dimeric cyclohexenyl palladium chloride $[Pd(\eta^3\text{-}C_6H_9)Cl]_2$ with the diamine ligands **3** and **4**, in the presence of $NaPF_6$, afforded the monocationic complexes **13** and **14** in high yield (Fig. 3) [10]. These complexes can exist in three diastereomeric forms, owing to two different orientations of the cyclohexenyl moiety (Figs. 3(a)–3(c)). In contrast to the high diastereomeric excess observed for the formation of **5a** and **6a**, the complicated ^{1}H-NMR spectrum indicates the presence of all three isomers in roughly equivalent amounts [11]. Attempts for a clean separation by crystallization were unsuccessful. However, suitable crystals for an X-ray structure determination of one meso isomer (**13b**) could be selected from a crystalline conglomerate of all three compounds (see below, Fig. 4).

2.2. *Solid state structure of* **5a** *and* **13b**

Two modes are possible for the coordination of ligands **3** and **4** to a $PdCl_2$-fragment, as outlined above. The meso compound is achiral owing to a mirror plane perpendicular to the square-planar coordination environment of the Pd(II)-center. The C_2-symmetric ligand arrangement of **5a** and **6a** is chiral. In order to assign the appropriate stereochemistry to the isolated compounds, an X-ray structure analysis was performed on the major isomer of the indoline Pd(II)-complex (Fig. 4). The results indicate the desired C_2-symmetric form (**5a**) for that major isomer. A closer investigation shows that the structure is not ideally C_2-symmetric, at least not in the solid state. This is due to the ethylene bridge which adopts an envelope conformation, so that the atoms N(1), C(2), N(2) and Pd(1) define a common plane. The distance of C(1) to that plane is 0.71 Å. However, in solution only one set of resonances for protons related by a C_2-symmetrical axis can be detected.

The complexes **13** and **14** can exist in three diastereomeric forms (Fig. 3). The X-ray structure analysis of a crystal selected from a conglomerate of the compounds **13a–c** reveals the meso arrangement of the ligands with the cyclohexenyl unit in an 'up' position (Fig. 4, **13b**) [12]. Here also, the ethylene bridge adopts an envelope conformation in the solid state. N(1), Pd(1) and N(2) define a plane. The distances of C(1) and C(2) to this plane are 0.09 Å and 0.55 Å respectively.

The Pd–C, Pd–N and C–C (allyl) bond lengths are found to be similar to those observed by Togni et al. [11] in the cation of the complex salt $([Pd(\eta^3\text{-}C_6H_9)(sparteine)][PF_6]$ and by Hegedus et al. [10a] in $[Pd(\eta^3\text{-}C_3H_5)(tmen)][Pd(\eta^3\text{-}C_3H_5)Cl_2])$ (tmen = *N,N,N′,N′*-tetramethylethylene diamine). The Pd–N(1) (2.163(5)

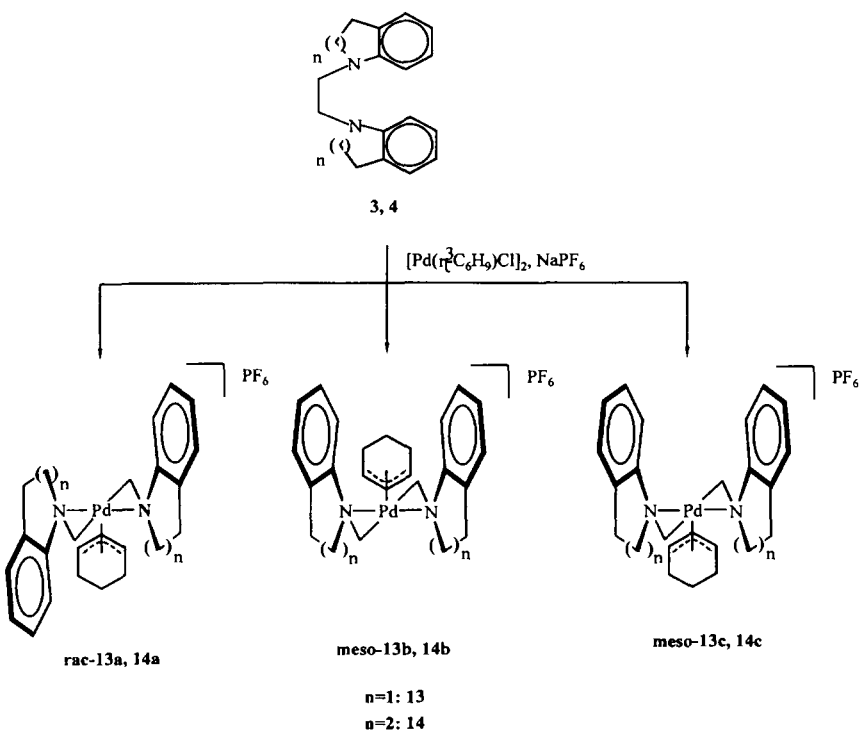

Fig. 3. Formation of *rac*- and *meso*-isomers of monocationic η^3-cyclohexenyl Pd(II) complexes.

Å) and Pd–N(2) (2.190(4) Å) bonds (Table 1) differ by about 0.03 Å and are longer than those in the dichloro complex **5a**. Obviously the trans influence of the π-allyl ligand is responsible for the long Pd–N bond lengths observed in **13b**. This discussion is supported by other structural studies [13], which have demonstrated a similar influence of π-allyl ligands on Pd–N bonds.

In a further study we intend to investigate the use of the new cationic complexes in polymerization experiments. It will be interesting to find out whether the chirality introduced by the indoline and 1,2,3,4-tetrahydroquinoline ligands can effectively influence the stereoselectivity of the carbon–carbon bond forming reaction.

3. Experimental section

All reactions were carried out under dry nitrogen by using standard Schlenk tube techniques. Reagent grade chemicals were used as-received unless otherwise stated. $(PhCN)_2PdCl_2$ [14] and $[(\eta^3\text{-}C_6H_9)PdCl]_2$ [15] were prepared according to literature procedures. The hydrocarbon and ether solvents were purified by distillation over $LiAlH_4$. CH_2Cl_2 was distilled from CaH_2. MeCN and Me_2CO were dried over K_2CO_3 and $CaSO_4$ respectively. IR spectra were measured on a Bruker IFS 48 spectrometer using KBr pellets. Other physical measurements were performed with the equipment specified previously [1g].

3.1. 1,2-Bis-(N-indolinyl)ethane (3) and 1,2-bis(1,2,3,4-tetrahydroquinolinyl)ethane (4)

A mixture of 1,2-dibromoethane (0.149 mmol) and 1,2,3,4-tetrahydroquinoline or indoline (0.892 mmol) were refluxed with continuous stirring for 3 h, after which the mixture was cooled to room temperature, hydrolyzed with saturated aqueous KOH solution and extracted with Et_2O (500 ml). The ether layer was dried

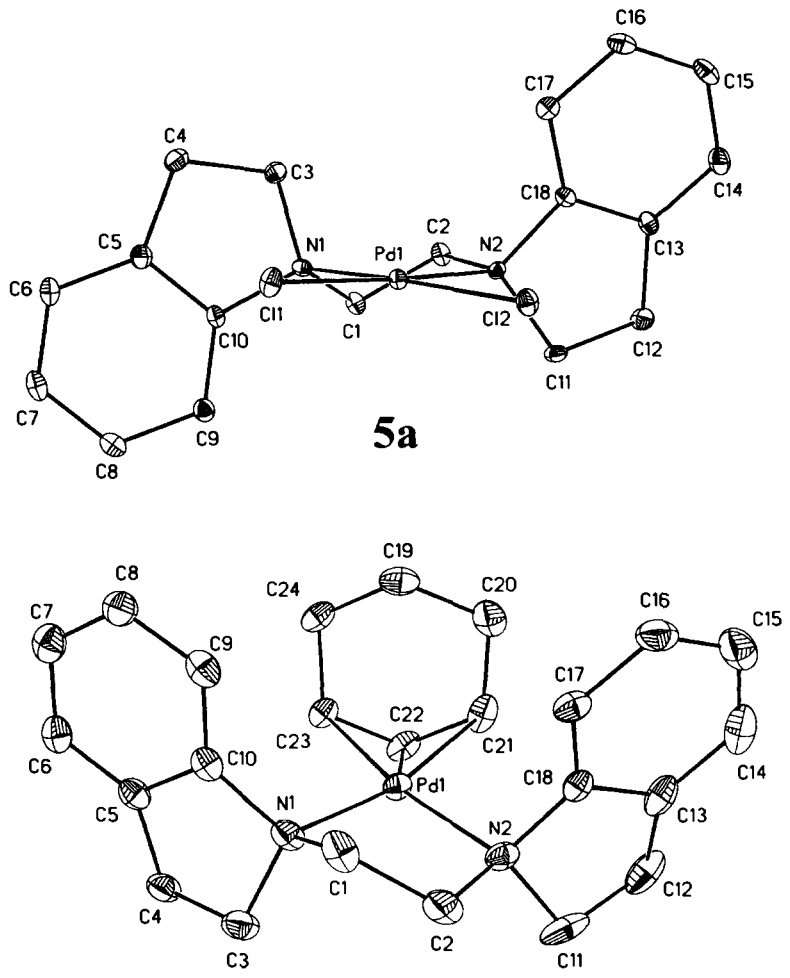

Fig. 4. Molecular structure of complex **5a** and of the monocation **13b** (the PF_6-counterion is omitted for clarity) with 20% probability thermal ellipsoids depicted.

over Na_2SO_4, filtered and evaporated under reduced pressure to give a yellow oil. Excess indoline or 1,2,3,4-tetrahydroquinoline was distilled off under vacuum. Upon addition of MeOH, (100 ml) at 0 °C with vigorous stirring, a colorless solid precipitated, which was separated by filtration, washed with MeOH (3 × 20 ml) and hexane (3 × 50 ml) and dried in vacuum.

3.1.1. 3

Yield, 36.7 g, 0.139 mmol (93%); melting point (m.p.) 88–90 °C. Anal. Found: C, 81.11; H, 7.66; N, 10.47. $C_{18}H_{20}N_2$ (264.37). Calc.: C, 81.78; H, 7.63; N, 10.59%. Mass spectrometry (MS) [field desorption (FD)]: *m/e* (rel. int.). 264.4 (100%, M^+). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.03–6.42 (m, 8H, $H_{arom.}$), 3.38 (t, 4H, $CH_{2,2\text{-indol.}}$), 3.26 (s, 4H, $CH_{2,bridge}$), 2.91 (t, 4H, $CH_{2,3\text{-indol.}}$).

3.1.2. 4

Yield, 25.3 g, 0.087 mmol (58%); m.p. 147 °C. Anal. Found: C, 81.50; H, 8.46; N, 9.25. $C_{20}H_{24}N_2$ (292.42). Calc.: C, 82.15; H, 8.27; N, 9.58%. MS (FD): *m/e* (rel. int.). 292.4 (100%, M^+). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.16–6.61 m, 8H, $H_{arom.}$), 3.39 (s, 4H, $CH_{2,bridge}$), 3.26 (t, 4H, $CH_{2,2\text{-quin.}}$), 2.66 (t, 4H, $CH_{2,4\text{-quin.}}$), 1.84 (tt, 4H, $CH_{2,3\text{-quin.}}$).

3.2. rac-Dichloro{1,2-bis(N-indolinyl)ethane}palladium(II) (5a) and rac-dichloro{1,2-bis(N-1,2,3,4-tetrahydroquinolinyl)ethane}palladium(II) (6a)

To a filtered solution of $(PhCN)_2PdCl_2$ (1.0 g, 2.61 mmol) in acetone (50 ml) was added with continuous stirring a filtered solution of the ligand (2.87 mmol) in acetone (50 ml). Upon addition, an orange-yellow solid was formed. Stirring was continued for 12 h, and the precipitate was filtered, washed with acetone (3 × 20 ml), Et_2O (3 × 20 ml) and dried in vacuum. The pure isomers **5a** and **6a** were isolated upon recrystallization from acetonitrile–ethyl acetate (3:1).

3.2.1. 5a

Yield, 1.05 g, 2.377 mmol (91%); m.p. 173 °C [decomposition, (dec.)]. Anal. Found: C, 48.36, H, 4.58; N, 6.97, Cl, 16.05. $C_{18}H_{20}Cl_2N_2Pd$ (441.69). Calc.: C, 48.95; H, 4.56; N, 6.34, Cl, 16.05%. MS [Fast atom bombardment, (FAB., 3-NOBA matrix): *m/e* (rel. int.) 407.1 (34.3%, M^+–Cl), 370.3 (87%, M^+–2Cl). ^{1}H-NMR (400 MHz, DMF-*d*7): δ 8.03–7.19 (m, 8H, $H_{arom.}$), 4.95 (m, 2H, $CH_{2,indol.}$), 3.95 (m, 2H, $CH_{2,bridge}$), 3.77 (m, 2H, $CH_{2,indol.}$), 3.20 (m, 4H, $CH_{2,indol.}$), 3.06 (m, 2H, $CH_{2,bridge}$).

3.2.2. 6a

Yield, 1.10 g, 2.34 mmol (90%); m.p. 173 °C (dec.). Anal. Found: C, 49.54, H, 5.41; N, 5.73, Cl, 15.22. $C_{20}H_{24}Cl_2N_2Pd$ (469.75). Calc.: C, 51.14; H, 5.15; N, 5.96, Cl, 15.09%. MS (FAB., 3-NOBA matrix)): *m/e* (rel. int.) 435.3 (35%, M^+–Cl), 397.3 (100%, M^+–2Cl). ^{1}H-NMR (400 MHz, DMF-*d*7): δ 8.70–6.99 (m, 8H, $H_{arom.}$), 4.37 (m, 2H, $CH_{2,quin.}$), 4.26 (m, 2H, $CH_{2,quin.}$), 3.74 (m, 2H, $CH_{2,bridge}$), 3.15 (m, 2H, $CH_{2,bridge}$), 2.71 (m, 4H, $CH_{2,quin.}$), 2.20–1.82 (m, 4H, $CH_{2,quin.}$).

Table 1
Selected distances (Å), angles (deg) and torsion angles (deg) for **5a** and **13b**

5a		**13b**	
Distances:			
Pd(1)–Cl(1)	2.283(1)	Pd(1)–C(21)	2.183(6)
Pd(1)–Cl(2)	2.298(1)	Pd(1)–C(22)	2.097(5)
Pd(1)–N(1)	2.082(3)	Pd(1)–C(23)	2.149(5)
Pd(1)–N(2)	2.082(3)	Pd(1)–N(1)	2.163(5)
N(1)–C(1)	1.499(5)	Pd(1)–N(2)	2.190(4)
N(2)–C(2)	1.514(5)	N(1)–C(1)	1.487(6)
C(1)–C(2)	1.503(5)	N(2)–C(2)	1.476(8)
		C(1)–C(2)	1.523(11)
		C(21)–C(22)	1.414(10)
		C(22)–C(23)	1.418(8)
Angles:			
Cl(1)–Pd(1)–Cl(2)	91.47(4)	C(21)–Pd(1)–C(23)	67.1(2)
N(1)–Pd(1)–N(2)	85.70(12)	N(2)–Pd(1)–C(21)	104.5(2)
N(1)–Pd(1)–Cl(1)	91.91(9)	N(2)–Pd(1)–C(22)	134.9(2)
N(2)–Pd(1)–Cl(2)	91.04(9)	N(1)–Pd(1)–C(22)	138.9(2)
		N(1)–Pd(1)–C(21)	167.1(2)
		N(2)–Pd(1)–C(23)	171.4(2)
Torsion Angle:			
N(1)–C(1)–C(2)–N(2)	61.0	N(1)–C(1)–C(2)–N(2)	53.2

3.3. *rac-Bis(acetonitrile)[1,2-bis(N-indolinyl)ethane] palladium(II) ditetrafluoroborate dihydrate (7) and rac-bis(acetonitrile)[1,2-bis(N-1,2,3,4-tetrahydroquinolinyl)-ethane]palladium(II) ditetrafluoroborate dihydrate (8)*

5a or **6a** (1.13 mmol) was mixed with $AgBF_4$ (0.45 g, 2.32 mmol) in MeCN (50 ml). After the mixture had been stirred for 3 h at room temperature, the resulting AgCl precipitate was removed by centrifugation and the supernatant solution was decanted off and evaporated under reduced pressure. The residue was redissolved in CH_2Cl_2 (40 ml) filtered and concentrated to 10 ml. The product was isolated upon slow addition of Et_2O as a yellowish solid, collected, washed with Et_2O and dried in vacuum.

3.3.1. 7

Yield, 0.37 g, 0.59 mmol (52%); m.p. 79 °C, dec. 156 °C. Anal. Found: C, 39.78; H, 4.31; N, 8.07. $C_{22}H_{30}N_4B_2F_8O_2Pd$ (662.53) calc.: C, 39.88; H, 4.56; N, 8.46%. MS (FAB., 3-NOBA matrix): *m/e* (rel. int.) 539.8 (10%, M^+-BF_4), 370.3 (96%, $M^+-C_4H_6N_2B_2F_8$). IR (KBr): ν(C≡N), 2333 (m), 2306 (m) cm^{-1}, $\nu(BF_4)$, 1063 (ssh), cm^{-1}. ^{1}H-NMR (250 MHz, CD_3CN): δ 8.30–7.47 (m, 8H, $H_{arom.}$), 5.02 (m, 2H, $CH_{2,indol.}$), 4.14 (m, 2H, $CH_{2,bridge}$), 3.68 (m, 2H, $CH_{2,indol.}$), 3.31 (m, 4H, $CH_{2,indol.}$), 3.05 (m, 2H, $CH_{2,bridge}$), 2.03 (s, 6H, CH_3CN).

3.3.2. 8

Yield, 0.42 g, 0.642 mmol (57%); m.p. 99–101 °C (dec.). Anal. Found: C, 41.21; H, 4.87; N, 7.39. $C_{24}H_{34}N_4B_2F_8O_2Pd$ (690.58). Calc.: C, 41.74; H, 4.96; N, 8.11%. MS (FAB., 3-NOBA matrix): *m/e* (rel. int.) 567.7 (10%, M^+-BF_4), 397.3 (100%, $M^+-C_4H_6N_2B_2F_8$). IR (KBr): ν(C≡N), 2333 (m), 2307 (m) cm^{-1}, $\nu(BF_4)$, 1061 (ssh) cm^{-1}. ^{1}H-NMR (250 MHz, CD_3CN): δ 8.57–7.11 (m, 8H, $H_{arom.}$), 4.54 (m, 2H, $CH_{2,quin.}$), 4.21 (m, 2H, $CH_{2,quin.}$), 3.87 (m, 2H, $CH_{2,bridge}$), 3.27 (m, 2H, $CH_{2,bridge}$), 2.99 (m, 4H, $CH_{2,quin.}$), 2.29–2.10 (m, 4H, $CH_{2,quin.}$), 2.02 (s, 6H, CH_3CN).

3.4. *rac-Dinitrato[1,2-bis(N-indolinyl)ethane]palladium(II) (9) and rac-dinitrato[1,2-bis{N-1,2,3,4-tetrahydroquinolinyl)ethane]palladium(II) hydrate* (**10**)

To a solution of **5a** or **6a** (1.13 mmol) in water (30 ml) was added $AgNO_3$ (0.38 g, 2.26 mmol) in water (5

Table 2
Crystallographic data for **5a** and **13b**

	5a	**13b**
Formula	$C_{18}H_{20}Cl_2N_2Pd^*C_4H_8O_2$	$C_{24}H_{29}F_6N_2PPd$
Formula weight	529.8	596.9
Crystal color	orange	colorless
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	7.591(2)	10.264(3)
b (Å)	10.356(4)	10.705(2)
c (Å)	14.527(4)	12.363(3)
α (deg)	78.66(3)	83.15(2)
β (deg)	76.12(3)	74.13(2)
γ (deg)	81.69(3)	66.98(2)
V (Å^3)	1081.3(6)	1202.5(5)
d_{calcd} (g cm^{-3})	1.627	1.648
Z	2	2
Crystal dimensions (mm^3)	0.50 × 0.30 × 0.10	0.5 × 0.25 × 0.05
Absorption coefficient (mm^{-1})	1.127	0.900
T (K)	173	173
Scan mode	ω	ω
Scan range (deg)	1.2	1.2
2Θ range (deg)	4–50	4–50
Scan speed (deg min^{-1})	8.37–29.30	8.37–29.30
Number of data collected	7612	8665
Number of independent data	3806	5520
Number of unique data	3197	4567
Observed criterion	$F > 4\sigma(F)$	$F > 4\sigma(F)$
Number of parameters	263	308
R [a]	0.0335	0.064
wR2 [b]	0.0932	0.168
Residual density, (e Å^{-3})	+0.84, −0.89	+3.81, −1.04

Conditions: Siemens P4 four cycle diffractometer, Mo K α-radiation, 71.073 pm, graphite monochromator. Solution: Patterson methods, all non-hydrogen atoms were refined anisotropically. [a] $R = \Sigma \| F_o \| - \| F_c \| / \Sigma | F_o |$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)]^2] / \Sigma[w(F_o^2)^2]^{1/2}$.

ml). After the suspension had been stirred for 12 h at room temperature, the resulting AgCl was removed by centrifugation, and a clear orange-solution was obtained. The supernatant liquid was filtered and the filtrate was evaporated to dryness under reduced pressure. The residue was suspended in Et_2O–hexane overnight, after which the solvent was decanted off and the product was washed with Et_2O (2 × 20 ml) and dried in vacuum.

3.4.1. 9

Yield, 0.43 g, 0.869 mmol (72%); m.p. 208 °C (dec.). Anal. Found: C, 42.96; H, 4.20; N, 10.99. $C_{18}H_{20}N_4O_6Pd$ (494.79). Calc.: C, 43.69; H, 4.07; N, 11.32%. MS (FAB., 3-NOBA matrix): *m/e* (rel. int.) 432.3 (100%, M^+-NO_3), 369.3 (60%, M^+-2NO_3). IR (KBr) $\nu(-ONO_2)$ 1271 (s) cm^{-1} [16]. ^{1}H-NMR (250 MHz, DMF-*d*7): δ 8.41–7.29 (m, 8H, $H_{arom.}$), 5.29 (m, 2H, $CH_{2,indol.}$), 4.35 (m, 2H, $CH_{2,bridge}$), 3.80 (m, 2H, $CH_{2,indol.}$), 3.25 (m, 4H, $CH_{2,indol.}$), 3.10 (m, 2H, $CH_{2,bridge}$).

3.4.2. 10

Yield, 0.38 g, 0.70 mmol (62%); m.p. 182 °C (dec.). Anal. Found: C, 44.01; H, 4.78; N, 9.76. $C_{20}H_{26}N_4O_7Pd$ (540.87). Calc.: C, 44.41; H, 4.85; N, 10.36%. MS (FAB, 3-NOBA matrix): *m/e* (rel. int.) 459.0 (100%, M^+-NO_3), 397.0 (80%, M^+-2NO_3). IR (KBr): $\nu(-ONO_2)$ 1275 (s) cm^{-1}. ^{1}H-NMR (250 MHz, DMF-*d*7, 0 °C): δ 9.06–7.11 (m, 8H, $H_{arom.}$), 4.84 (m, 2H, $CH_{2,quin.}$), 4.11 (m, 2H, $CH_{2,quin.}$), 4.05 (m, 2H, $CH_{2,bridge}$), 3.35 (m, 2H, $CH_{2,bridge}$), 2.88 (m, 4H, $CH_{2,quin.}$), 2.26–1.88 (m, 4H, $CH_{2,quin.}$).

3.5. rac-Diaquo[1,2-bis(N-indolinyl)ethane]palladium(II) ditetrafluoroborate hydrate (11) and rac-diaquo[1,2-bis(N-1,2,3,4-tetrahydroquinolinyl)ethane] palladium(II) ditetrafluoroborate (12)

Compounds **11** and **12** were prepared according to two different procedures.

(A) Starting from **5a** and **6a** procedure 3.4 was followed and $AgBF_4$ was used for chloride abstraction.

(B) The complexes were also prepared quantitatively by stirring **7** and **8** in H_2O (50 ml) for 12 h at room temperature. The solvent was evaporated and the residue was stirred in Et_2O–hexane for 12 h. After decantation of the solvent, the product was washed with Et_2O and dried in vacuum.

3.5.1. 11

Yield, 0.41 g, 0.685 mmol (61%); m.p. 154–156 °C (dec.). Anal. Found: C, 35.86; H, 4.27; N, 5.00. $C_{18}H_{26}N_2B_2F_8O_3Pd$ (598.44). Calc.: C, 36.13; H, 4.38; N, 4.68%. MS (FAB, 3-NOBA matrix): *m/e* (rel. int.) 475.3 (28%, M^+-BF_4, H_2O), 369.3 (100%, $M^+-B_2F_8H_4O_2$). IR (KBr): $\nu(BF_4)$, 1063 cm^{-1}. ^{1}H-NMR (250 MHz, CD_3OD): δ 8.38–7.38 (m, 8H, $H_{arom.}$), 4.93 (m, 2H, $CH_{2,indol.}$), 4.10 (m, 2H, $CH_{2,bridge}$), 3.68 (m, 2H, $CH_{2,indol.}$), 3.23 (m, 4H, $CH_{2,indol.}$), 2.92 (m, 2H, $CH_{2,bridge}$).

3.5.2. 12

Yield, 0.62 g, 1.02 mmol (90%); m.p. 162 °C (dec). Anal. Found: C, 40.03; H, 4.86; N, 4.69 $C_{20}H_{28}N_2B_2F_8O_2Pd$ (608.48). Calc.: C, 39.48; H, 4.64; N, 4.60%. MS (FAB, 3-NOBA matrix): *m/e* (rel. int.) 503.4 (40%, M^+-BF_4, H_2O), 397.4 (70%, $M^+-B_2F_8H_4O_2$). IR (KBr): $\nu(BF_4)$, 1063 cm^{-1}. ^{1}H-NMR (250 MHz, DMF-*d*7): δ 9.06–7.01 (m, 8H, $H_{arom.}$), 4.75 (m, 2H, $CH_{2,quin.}$), 4.05 (m, 2H, $CH_{2,quin.}$), 4.15 (m, 2H, $CH_{2,bridge}$), 3.45 (m, 2H, $CH_{2,bridge}$), 2.85 (m, 4H, $CH_{2,quin.}$), 2.26–1.86 (m, 4H, $CH_{2,quin.}$).

3.6. [η³-(Cyclohex-2-enyl)]-[1,2-bis-(N-indolinyl)ethane]palladium(II) hexafluorophosphate (13) and [η³-(cyclohex-2-enyl)]-[1,2-bis(N-1,2,3,4-tetrahydroquinolinyl)ethane]palladium(II) hexafluorophosphate (14)

A solution of the ligands (**3** or **4**) (3.78 mmol) in CH_2Cl_2 (20 ml) was added to a solution of [Pd(η³-

Table 3
Atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients ($Å^2$ × 10^3) for **5a**

Atom	*x*	*y*	*z*	U_{eq}
Pd(1)	344(1)	2588(1)	95(1)	16(1)
Cl(1)	−2256(1)	1726(1)	993(1)	25(1)
Cl(2)	−1101(1)	3568(1)	−1125(1)	23(1)
N(1)	1760(4)	1821(3)	1178(2)	18(1)
N(2)	2807(4)	3254(3)	−706(2)	16(1)
O(1)	2208(5)	4883(3)	5124(3)	40(1)
O(2)	2176(5)	2757(3)	5043(2)	33(1)
C(1)	3248(5)	2717(4)	948(3)	22(1)
C(2)	4186(5)	2722(4)	−89(3)	22(1)
C(3)	2488(6)	414(4)	1139(3)	27(1)
C(4)	1235(6)	−417(4)	1946(3)	29(1)
C(5)	437(6)	535(4)	2615(3)	25(1)
C(6)	−508(6)	321(5)	3566(3)	31(1)
C(7)	−1132(7)	1386(5)	4027(3)	35(1)
C(8)	−858(6)	2663(5)	3556(3)	32(1)
C(9)	79(6)	2892(4)	2606(3)	26(1)
C(10)	726(5)	1803(4)	2159(3)	20(1)
C(11)	2756(5)	4734(4)	−967(3)	23(1)
C(12)	4183(6)	5006(4)	−1900(3)	28(1)
C(13)	4270(5)	3772(4)	−2322(3)	23(1)
C(14)	5047(6)	3484(5)	−3235(3)	31(1)
C(15)	4950(6)	2246(5)	−3417(3)	33(1)
C(16)	4088(6)	1301(4)	−2708(3)	30(1)
C(17)	3317(5)	1573(4)	−1792(3)	24(1)
C(18)	3448(5)	2811(4)	−1629(3)	19(1)
C(19)	255(7)	3559(5)	6377(4)	39(1)
C(20)	1635(6)	3837(4)	5459(3)	30(1)
C(21)	3543(7)	2938(5)	4161(3)	34(1)
C(22)	4060(8)	1615(5)	3837(4)	42(1)

$C_6H_9)Cl]_2$ (0.77 g, 1.72 mmol) in CH_2Cl_2 (15 ml). A solution of $NaPF_6$ (0.58 g, 3.44 mmol) in MeOH (10 ml) was added and the mixture was stirred for 2 h. The mixture was filtered, the solvent was evaporated off and the solid was washed with Et_2O (2 × 25 ml). The product was dissolved in CH_2Cl_2 (40 ml) and the filtrate was evaporated to dryness, washed with Et_2O and dried in vacuum. Attempts to separate the isomers by recrystallization remained unsuccessful.

3.6.1. 13

Yield, 1.40 g, 2.35 mmol (68%); m.p. 143 °C (dec.). Anal. Found: C, 47.90; H, 5.00; N, 4.74. $C_{24}H_{29}N_2F_6PPd$ (596.65). Calc.: C, 48.27; H, 4.89; N, 4.69%. MS (FAB, 3-NOBA matrix), 451.4 (100%, M^+-PF_6), 369.3 (70%, $M^+-C_6H_9PF_6$). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.50–6.95 (m, 8H, $H_{arom.}$), 5.38–3.92 (m, 7H), 3.45–3.04 (m, 8H), 3.92 (m, 2H), 1.65–0.82 (m, 6H).

Table 4
Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2 ×10^3) for **13b**

Atom	x	y	z	U_{eq}
Pd(1)	517(1)	6874(1)	2348(1)	36(1)
P(2)	−4889(2)	12873(2)	3104(1)	47(1)
N(1)	−1803(6)	7441(5)	3079(4)	45(1)
N(2)	400(6)	7956(5)	3788(4)	43(1)
F(1)	−3178(5)	12178(7)	2781(6)	102(2)
F(2)	−5015(7)	11675(5)	3959(6)	106(3)
F(3)	−4951(8)	12115(7)	2098(5)	98(2)
F(4)	−4775(6)	14096(5)	2245(4)	73(1)
F(5)	−6639(5)	13566(6)	3418(4)	75(1)
F(6)	−4913(7)	13726(7)	4081(5)	87(2)
C(1)	−2221(7)	8634(7)	3785(6)	56(2)
C(2)	−1119(8)	8375(7)	4478(5)	58(2)
C(3)	−2161(9)	6298(7)	3755(5)	58(2)
C(4)	−2334(8)	5496(6)	2901(5)	53(1)
C(5)	−2852(6)	6570(5)	2036(5)	43(1)
C(6)	−3489(6)	6592(6)	1176(5)	50(1)
C(7)	−3799(7)	7706(7)	479(7)	58(2)
C(8)	−3511(7)	8833(5)	647(6)	55(1)
C(9)	−2879(6)	8844(5)	1500(6)	49(1)
C(10)	−2543(6)	7673(5)	2191(5)	42(1)
C(11)	1504(13)	7044(7)	4482(6)	76(3)
C(12)	2928(10)	7218(8)	3930(8)	73(2)
C(13)	2409(7)	8604(7)	3442(6)	55(2)
C(14)	3175(7)	9464(11)	3030(7)	72(2)
C(15)	2429(11)	10707(11)	2558(7)	76(3)
C(16)	997(10)	11111(7)	2523(5)	62(2)
C(17)	263(7)	10248(5)	2928(4)	45(1)
C(18)	965(5)	9004(5)	3380(4)	36(1)
C(19)	1076(9)	8114(7)	69(5)	58(2)
C(20)	2505(8)	7665(9)	438(6)	63(2)
C(21)	2701(6)	6506(8)	1268(5)	55(2)
C(22)	2204(7)	5463(6)	1206(5)	48(1)
C(23)	920(6)	5875(6)	814(4)	43(1)
C(24)	696(7)	6931(6)	−93(5)	49(1)

3.6.2. 14

Yield, 1.70 g, 2.27 mmol (79%); m.p. 125 °C (dec.). Anal. Found: C, 50.15; H, 5.25; N, 4.52. $C_{26}H_{33}N_2F_6PPd$ (624.94). Calc.: C, 49.97; H, 5.32; N, 4.48%. MS (FAB, 3-NOBA matrix), 479.2 (100%, M^+-PF_6), 397.4 (16%, $M^+-C_6H_9PF_6$). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.49–6.71 (m, 8H, $H_{arom.}$), 5.47–3.26 (m, 7H), 2.93–2.78 (m, 4H), 2.12–1.98 (m, 4H), 1.82–0.87 (m, 10H).

3.7. X-ray structure determinations [17]

Suitable crystals of **5a** and **13b** were obtained by crystallization from $CH_3CN-CH_3CO_2C_2H_5$ (5:1) and CH_2Cl_2 respectively. Samples of **5a** and **13b** were mounted on glass fibers. Graphite-monochromated Mo Kα radiation was used. Two check reflections were monitored after every 58 intensity measurements. The structures were solved by Patterson methods (SHELXL-93). Hydrogen atoms are placed in calculated positions (riding model) and phenyls were treated as rigid groups. In the crystals of **5a** a solvent molecule (ethyl acetate) was located in the asymmetric unit. The final cell parameters and specific data collection parameters are summarized in Table 2. The final atomic positional data can be found in Tables 3 (**5a**) and 4 (**13b**).

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