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Synthesis of bis(*N*-heterocyclic carbene) palladium complexes derived from (*S*,*S*)-1,2-bis(1-hydroxypropyl)benzene

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ABSTRACT

New *o*-xylylene-linked bis(benzimidazolium) salts were synthesized in six-steps from C_2-symmetric chiral 1,4-diol, 1,2-bis(1-hydroxypropyl)benzene, as a starting material. The silver complex of bis(benzimidazol-2-ylidene) was obtained on treatment of bis(benzimidazolium) salt with silver oxide. The reaction of the silver bis-NHC with $[PdCl_2(PhCN)_2]$ afforded the bis-NHC complex of palladium. The X-ray diffraction studies on Pd complexes revealed that these complexes have distorted square planar geometry around the Pd center coordinating the NHC ligand in mutually *cis*-position. The arene ring of *o*-xylylene unit hanged over the Pd center and thus these complexes showed C_1-symmetric structures. The variable temperature NMR spectroscopy revealed that these Pd complexes showed fluxional behavior between C_1- and C_2-symmetric structures in solution state.

1. Introduction

N-heterocyclic carbenes (NHCs) are now established as an important class of ligands for homogeneous catalysts, because NHCs provide an electron-rich metal center with a thermally robust metal-ligand bond [1]. The use of polydentate NHC ligands has allowed the preparation of novel complexes whose stability is entropically increased by the chelate effect [2]. Most of these polydentate NHCs reported so far are bidentate NHC ligands and there are numerous studies on their late transition metal complexes of Rh, Ir, Ni, Pd, and so on [3,4]. The C_2-symmetric chiral bidentate NHC ligands were reported firstly by Trudell [5] and RajanBabu [6], independently, in 2000, and have received much attention as promising ligands in catalytic enantioselective organic transformations [7]. The first chiral bidentate NHC ligand was derived from 2,2′-di(bromomethyl)-1,1′-binaphthyl, and C_2-symmetric structure was observed in only the *trans* isomer (**A** in Chart 1) in complexation of the ligand with transition metals [5,6]. Similar geometrical features were observed in Pd complexes derived from (*R*,*R*)-2-chloro-*N*-[2-(chloroacetylmethylamino)cyclohexyl]-*N*-methylacetamide [8] or 4,5-bis(bromoethyl)-2,2-dimethyl-1,3-dioxolane [9] probably due to the formation of 11- or 13-membered chelate ring in these complexes. Douthwaite forced a *cis* coordination mode by building the NHC moiety directly adjacent to a cyclohexane backbone and metalated with Pd to form *cis*-coordinate Pd complex derived from *N*,*N*′-diethylidene-(1*R*,2*R*)-diamino cyclohexane [10]. However, the complex showed C_1-symmetric structure because the Pd complex had strained 7-membered chelate ring. On the other hand, Shi and co-workers have reported a series of axially chiral bidentate NHC ligands derived from 1,1′-binaphthyl-2,2′-diamine and its partially saturated framework (**B** in Chart 1) [11]. In contrast to the bis-NHC ligand reported by Trudell and RajanBabu featuring 11-membered chelate ring, Shi's complex consisted of 9-membered chelate ring and thus two NHCs were *cis*-orientation with C_2-symmetry. These complexes of Rh, Ir, and Pd worked as excellent catalysts for enantioselective organic transformations.

Recently, a novel family of C_2-symmetric bidentate NHCs with dihydroethanoanthracene unit has been reported by Veige and co-workers [12]. Although two NHCs in these ligands located in *cis*-position, the complex showed C_1-symmetric structure. We have also reported novel chiral *o*-xylylene-bridged bis(imidazol-2-ylidene) ligands derived from enantiomerically pure 1,4-diol, 1,2-bis (1-hydroxypropyl)benzene (**3**), and their molybdenum complexes [13]. These molybdenum complexes showed *cis*-C_2-symmetric structure in octahedral geometry. In this paper, we wish to report a preparation of the benzimidazol-2-ylidene derivatives of the chiral *o*-xylylene-bridged bis-NHCs and their palladium complexes.

2. Results and discussion

2.1. Synthesis of ligands and complexes

As described in the Introduction, we have recently reported the preparation of chiral *o*-xylylene-bridged bis(imidazolium)

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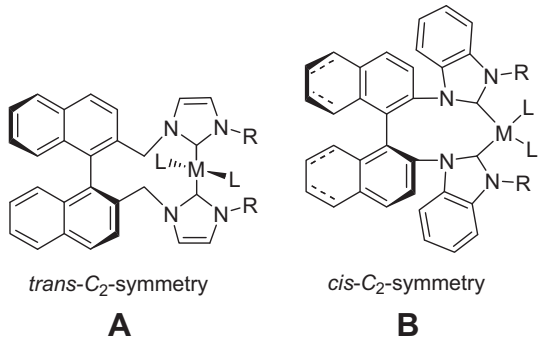
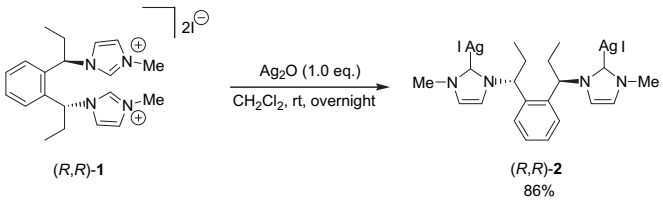


Chart 1. C_2-Symmetric chiral bis-NHC complexes.



Scheme 1. Synthesis of Ag complex with imidazol-2-ylidene.

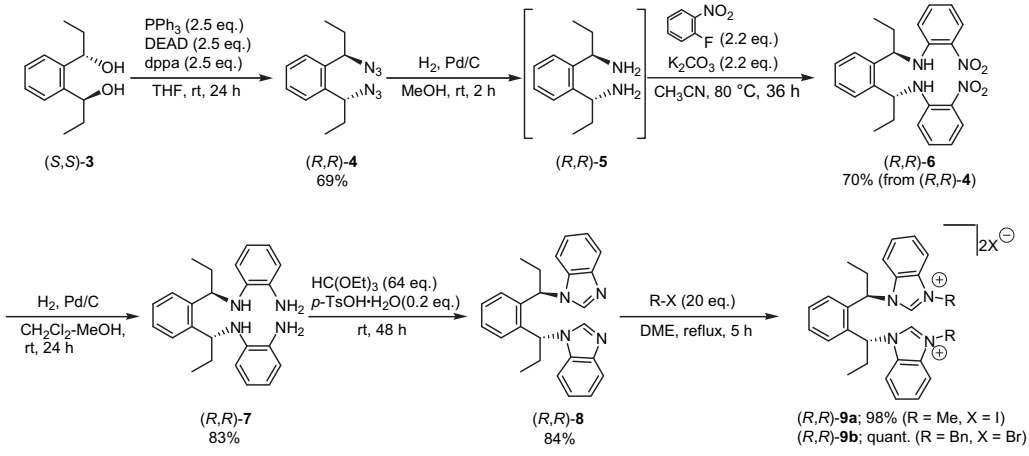
pro-ligands, which were obtained in two-steps from **3**, and their molybdenum complexes [13]. Then, we next examined the preparation of the bis(imidazol-2-ylidene) complex of palladium. The silver complex (*R,R*)-**2** was obtained in a good yield by reaction of bis(imidazolium) pro-ligand (*R,R*)-**1** with Ag_2O (Scheme 1). Although the reaction of (*R,R*)-**2** with $[PdCl_2(PhCN)_2]$ afforded a yellow solid, the ^1H NMR spectrum of the product showed the complicated result and suitable crystals for the X-ray analysis were not obtained.

Thus we began the synthesis of bis(benzimidazolium) pro-ligands (*R,R*)-**9**. Multi-step procedure for the synthesis of (*R,R*)-**9** is shown in Scheme 2. In the first place, two hydroxy groups in (*S,S*)-**3** was converted to diazide (*R,R*)-**4** by Mitsunobu reaction in 69% yield (2.5 equiv of diethyl azodicarboxylate (DEAD), PPh_3, and diphenylphosphoryl azide (dppa)). Then, (*R,R*)-**4** was hydrogenated to diamine (*R,R*)-**5**, which was used without purification in the next reaction. Dinitrodiamine (*R,R*)-**6** was obtained by the reaction of the resulting (*R,R*)-**5** and 2.2 equiv of *o*-fluoronitrobenzene in the presence of K_2CO_3 in CH_3CN at 80 °C for 36 h in 70% from (*R,R*)-**4**. The nitro groups in (*R,R*)-**6** was reduced with H_2 in mixed solvents of CH_2Cl_2 and MeOH to afford tetraamine (*R,R*)-**7** in 83% yield. Tetraamine (*R,R*)-**7** was reacted with excess of $HC(OEt)_3$ (64 equiv) in the presence of catalytic amount of *p*-toluenesulfonic acid monohydrate to give bisbenzimidazole derivative (*R,R*)-**8** in 84% yield. The resulting (*R,R*)-**8** was alkylated with excess of alkyl halide (20 equiv) to give bis(benzimidazolium) salt (*R,R*)-**9a** and (*R,R*)-**9b**, respectively.

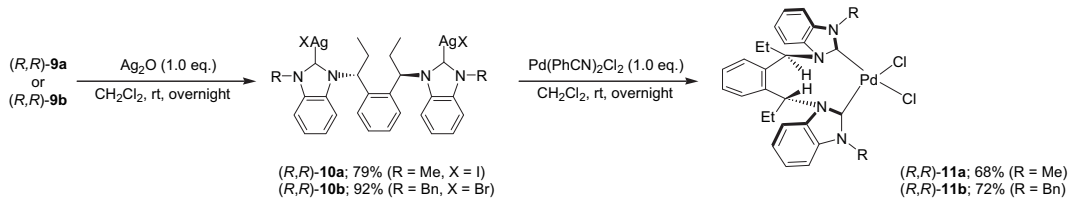
As the pro-ligands (*R,R*)-**9** were obtained, a preparation of corresponding Pd complex was examined (Scheme 3). The treatment of (*R,R*)-**9a** with 1.0 equiv of Ag_2O afforded the silver complex of bis-NHC (*R,R*)-**10a** as a pale brown powder in 79% yield. The corresponding *N*-benzyl derivative (*R,R*)-**10b** was also obtained in excellent yield from (*R,R*)-**9b**. In the ^1H NMR spectrum of (*R,R*)-**10a**, the characteristic signal of (*R,R*)-**9a** at 9.85 ppm assigned to benzimidazolium protons were disappeared. Furthermore, in the ^{13}C NMR spectrum of (*R,R*)-**10a** the signal at 200.1 ppm assigned to the carbene carbon was observed. Similar ^1H and ^{13}C NMR spectra were also obtained for (*R,R*)-**10b**. These spectroscopic features suggested the formation of silver NHC complexes (*R,R*)-**10**. In the reactions of (*R,R*)-**10a** and (*R,R*)-**10b** with $[PdCl_2(PhCN)_2]$, the NHC-transfer from silver to palladium took place to give palladium complexes (*R,R*)-**11a** and (*R,R*)-**11b**, respectively. In the ^1H NMR spectrum of (*R,R*)-**11a**, only one signal assignable to the methyl groups on the nitrogen atoms was observed at 4.29 ppm. The ethyl groups attached to the benzyl carbons showed one triplet and one broad singlet signals assignable to the methyl and methylene protons at 1.27 ppm and 2.20 ppm, respectively. The ^{13}C NMR spectrum of (*R,R*)-**11a** showed one signal assignable to the carbene carbons (172.5 ppm). The signals for methyl and methylene carbons of the ethyl groups were observed at 12.1 ppm and 25.1 ppm, respectively. These observations indicated that Pd complex has C_2-symmetric structure in solution. The ^1H NMR spectrum of complex (*R,R*)-**11b** showed somewhat broadening signals at room temperature. The variable temperature NMR spectroscopy for (*R,R*)-**11a** and (*R,R*)-**11b** was carried out. These results are discussed in the Section 2.3.

2.2. X-ray crystal structures of Pd complexes *11a* and *11b*

Unfortunately, the X-ray analyses of complexes (*R,R*)-**11a** and (*R,R*)-**11b** could not be undertaken due to the rapid deterioration of these crystals during separation of crystals and the mother liquid. However, the structures of racemic complexes **11a** and **11b** were determined by the X-ray analyses. Complexes **11a** and **11b** contained solvent molecules of CH_2Cl_2 and $CHCl_3$, respectively. The



Scheme 2. Synthesis of chiral bis(benzimidazolium) salts.



Scheme 3. Synthesis of Ag and Pd complexes with benzimidazol-2-ylidene.

ORTEP drawings of **11a** and **11b** are shown in Fig. 1. The selected bond distances and angles are listed in Table 1. These complexes have distorted square planar geometry around the Pd center coordinating the bis-NHC ligand in mutually *cis*-position, whereas the bis-NHC ligands do not adopt C_2-symmetric coordination mode suggested by the NMR spectra mentioned in the Section 2.1. The arene ring of *o*-xylylene unit hangs over the Pd center and thus these complexes show C_1-symmetric structures.

The bond distances of Pd–C (carbene) (1.990(4) and 1.949(4) Å for **11a** and 1.967(12) and 1.953(9) Å for **11b**) and Pd–Cl (2.3998(9) and 2.3715(10) Å for **11a** and 2.405(3) and 2.379(3) Å for **11b**) fall within the range found for the chelating bis-NHC palladium(II) complexes [4d]. Bite angles defined by C (carbene)–Pd–C (carbene) are 86.54 (14)° for **11a** and 87.7(4)° for **11b**, which are similar to those of the chelating bis-NHC complexes of palladium [4g]. The most characteristic feature of these complexes is the arene ring of *o*-xylylene unit locating over the Pd. The distances of Pd…C (ipso carbon of *o*-xylylene) are 3.092(4) and 2.949(4) Å for **11a** and 3.133(9) and 2.998(6) Å for **11b**. The similar structural feature was observed in the cyclophane-type bis-NHC complexes of palladium reported by Veige [12d] and Baker [4d], respectively. The arene ring containing the linker unit of bis-NHC ligands usually directed away from the metal center [4c,14]. Therefore, the existence of the interaction between π-electrons on the arene ring and the palladium metal might allow to adopt the hanged structure, in complexes **11a** and **11b**.

2.3. Spectroscopic and structural properties of Pd complexes (R,R)-*11a* and (R,R)-*11b*

As mentioned above, the conformation of the complex (*R,R*)-**11a** (and/or (*R,R*)-**11b**) in the solid state was not consistent with that in the solution state. Then, the variable temperature NMR measurements for complexes (*R,R*)-**11a** and (*R,R*)-**11b** were carried out.

The ^{1}H and ^{13}C NMR spectra of (*R,R*)-**11a** at 25 °C suggested the formation of the C_2-symmetric structure; only one signal assignable to the methyl protons on the nitrogen atoms was observed at 4.29 ppm and one signal due to the carbene carbons was observed at 172.5 ppm. As the temperature gradually decreased, the singlet assignable to N–CH_3 protons became broad and coalesced at 4 °C (277 K). The signals assignable to the hanged structure observed in the solid state became sharpe under −30 °C, and a new set of signals appeared. The new signals showed two sets of N–CH_3 protons at 4.16 and 4.44 ppm as a singlet. Furthermore, the ethyl groups attached to the benzyl carbons were observed as two triplets (1.28 and 1.30 ppm) and four multiplets (1.57, 1.99, 2.41, and 2.82 ppm) assignable to the methyl and methylene protons, respectively. Application of the coalescence formula [15] to the fluxional behavior of complex (*R,R*)-**11a** gave a $\Delta G^{\ddagger}$ (277 K) value of 13.2 kcal mol^{-1} for the methyl group exchange. Low temperature ^{13}C NMR spectrum (−70 °C) showed two signals in the region of the carbene carbons at 169.9 and 170.1 ppm. Other signals observed at −70 °C were consistent with the formation of the C_1-symmetric conformation revealed by the X-ray analysis of **11a**. In complex (*R,R*)-**11b**, similar spectroscopic features were observed in variable temperature NMR measurements [16]. These results indicated that the complexes (*R,R*)-**11a** and (*R,R*)-**11b** showed the fluxional process which may be interpreted in terms of the flipping of the *o*-xylylene unit. Similar fluxional process has been reported independently by Baker [4d,17] and Veige [12d,18], respectively (Fig. 2).

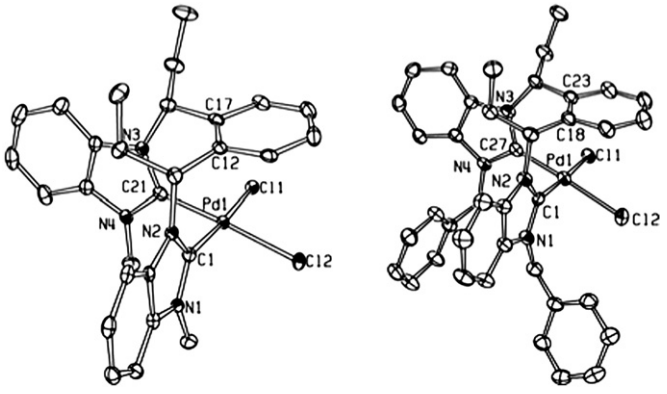


Fig. 1. ORTEP drawings of **11a** (left) and **11b** (right). Thermal ellipsoids are drawn at 50% (**11a**) and 20% (**11b**) probability level. Hydrogen atoms and solvent molecules were omitted for clarity.

3. Conclusion

In a previous paper, we have reported the synthesis of the new type of chiral C_2-symmetric bis(imidazolium) pro-ligands derived from enantiomerically pure 1,4-diol. In this study, the extension to the synthesis of chiral bis(benzimidazolium) pro-ligands and the preparation of their palladium complexes were demonstrated. In a solid state, these Pd complexes showed the interaction of the arene

Table 1
Selected bond distances (Å) and angles (°) for **11a** and **11b**.

11a		**11b**	
C1–Pd1	1.990(4)	C1–Pd1	1.967(12)
C21–Pd1	1.949(4)	C27–Pd1	1.953(9)
Cl1–Pd1	2.3998(9)	Cl1–Pd1	2.405(3)
Cl2–Pd1	2.3715(10)	Cl2–Pd1	2.379(3)
C1–N1	1.350(5)	C1–N1	1.360(10)
C1–N2	1.367(5)	C1–N2	1.397(13)
C21–N3	1.353(5)	C27–N3	1.374(9)
C21–N4	1.354(5)	C27–N4	1.364(9)
C12…Pd1	3.092(4)	C18…Pd1	3.133(9)
C16…Pd1	2.949(4)	C23…Pd1	2.998(6)
C1–Pd1–C21	86.54(14)	C1–Pd1–C27	87.7(4)
Cl1–Pd1–Cl2	95.48(3)	Cl1–Pd1–Pd2	91.81(11)
C1–Pd1–Cl1	173.19(10)	C1–Pd1–Cl1	175.0(2)
C1–Pd1–Cl2	89.97(10)	C1–Pd1–Cl2	91.8(3)
C21–Pd1–Cl1	87.93(10)	C27–Pd1–Cl1	88.5(4)
C21–Pd1–Cl2	176.38(10)	C27–Pd1–Cl2	177.04(17)
N1–C1–N2	107.0(3)	N1–C1–N2	104.3(9)
N3–C21–N4	107.0(3)	N3–C27–N4	106.1(7)

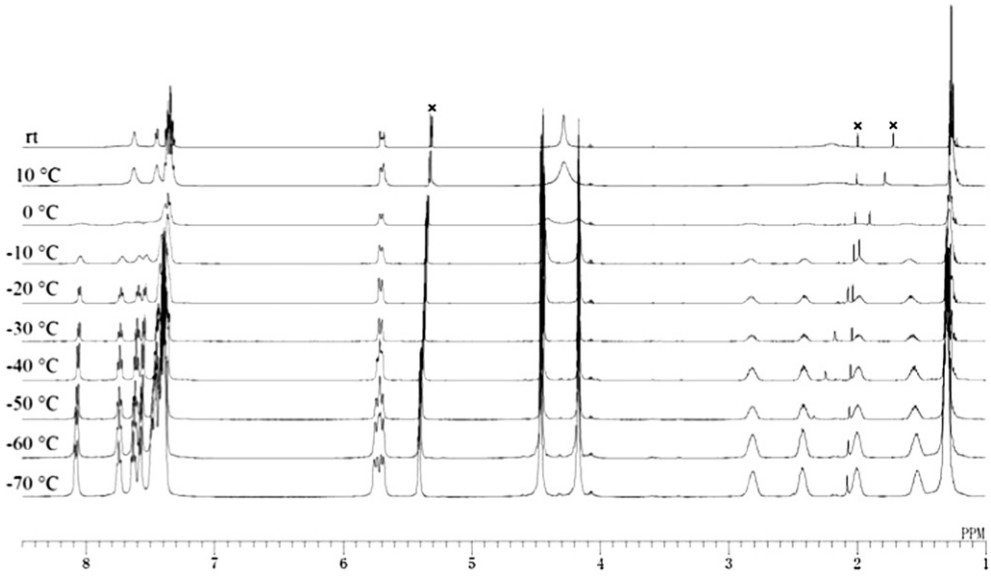


Fig. 2. Variable temperature NMR measurements of (*R*,*R*)-11a in CD_2Cl_2. × = solvent or H_2O.

ring on the linker unit with the Pd center. Variable temperature NMR spectroscopy revealed that these Pd complexes showed the fluxional behavior on the basis of the flipping motion of the *o*-xylylene unit (Chart 2). There is a possibility that these Pd complexes adopt the chiral C_2-symmetric structure in a solution state. Further investigation on the enantioselective carbon–carbon bond forming reactions catalyzed by these complexes is now in progress in our laboratory.

4. Experimental

4.1. General

All air- and moisture-sensitive experiments were carried out under an atmosphere of dry argon or nitrogen, which was purified SICAPENT (Merck Co., Inc.) by using a standard Schlenk tube or high vacuum techniques. All solvents were distilled over appropriate drying agents prior to use. All reagents were commercially available and used without further purification. Compound (*R*,*R*)-**1** was prepared according to the literature method [13]. Melting points were determined on a Stuart Scientific melting point apparatus SMP3 and are uncorrected. IR spectra were recorded on a HORIBA FT-730 spectrometer. ^{1}H and ^{13}C NMR spectra were measured on JEOL JNM-EX-270, Bruker DRX-300, JEOL AL-400, and Bruker DRX-500 spectrometers at ambient temperature unless otherwise mentioned. ^{1}H and ^{13}C NMR chemical shifts were recorded in ppm relative to internal Me_4Si. Multiplicity is indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Thin layer chromatography (TLC) was performed using Merck silica-gel 60F-254 plates. Column chromatography was performed using Silica Gel 60N (neutral, 63–210 μm, KANTO CHEMICAL CO., INC.) or Chromatorex (NH, 100–200 mesh, Fuji Silysia Chemical, Ltd.). Specific rotations were measured on a JASCO P-1010 digital polarimeter using 1-dm cell at sodium D line (589 nm) in the indicated solvent. Elemental analyses were carried out on a Vario EL Elemental analyzer. High-resolution mass spectra were recorded on a Hitachi Nano Frontier LD spectrometer.

4.2. Silver complex (*R*,*R*)-**2**

The solution of (*R*,*R*)-**1** (0.202 g, 0.350 mmol) and Ag_2O (0.081 g, 0.354 mmol) in CH_2Cl_2 (5 mL) was stirred overnight at room temperature. The mixture was filtered through Celite and the filtrate was concentrated under reduced pressure to give (*R*,*R*)-**2** as a white powder (0.239 g, 0.302 mmol, 86%). mp > 200 °C (Dec.). $[\alpha]_D^{21}$ +54.6 (*c* 0.60, CH_2Cl_2). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 0.73 (*t*, *J* = 7.6 Hz, 6H, 2 × C*H*$_3$), 2.00–2.12 (m, 2H, C*H*$_2$), 2.22–2.31 (m, 2H, C*H*$_2$), 3.91 (s, 6H, 2 × N–C*H*$_3$), 5.86 (t, *J* = 7.6 Hz, 2H, 2 × C*H*), 6.65 (d, *J* = 1.3 Hz, 2H, Im*H*), 6.90 (d, *J* = 1.3 Hz, 2H, Im*H*), 7.53–7.56 (m, 2H, Ar*H*), 7.66–7.69 (m, 2H, Ar*H*). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 11.4 (*C*H$_3$), 29.4 (*C*H$_2$), 39.5 (N–*C*H$_3$), 61.4 (*C*H), 118.6, 118.9, 128.6, 129.6 (aromatic), 186.0 (N–C–N). HRMS (ESI): calcd for $C_{20}H_{27}N_4$ $[M-2AgI+H]^+$ 323.2226, found 323.2230.

4.3. (*R*,*R*)-1,2-bis(1-azidopropyl)benzene (*R*,*R*)-**4**

DEAD (25.7 mL, 11.4 g, 65.2 mmol) was slowly added via dropping funnel to a solution of (*S*,*S*)-**3** (5.07 g, 26.1 mmol) and PPh_3 (17.1 g, 65.2 mmol) in THF (65 mL) at 0 °C and the mixture was stirred for 10 min at the temperature. A solution of dppa (17.9 g, 65.2 mmol) in THF (25 mL) was added to the reaction mixture and

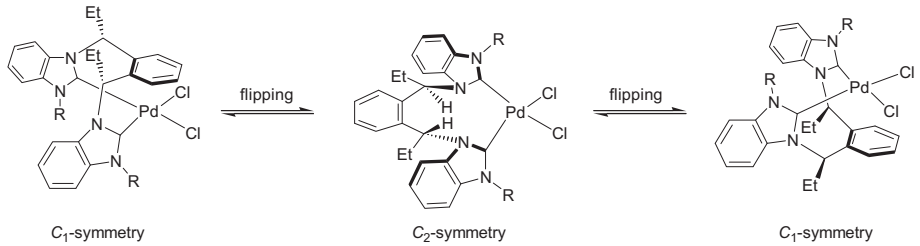


Chart 2. Flipping motion of the *o*-xylylene unit.

stirring was continued for 24 h at room temperature. The solvent was removed under reduced pressure and the resulting residue was purified by silica-gel column chromatography (Silica Gel 60N, hexane/Et_2O/CH_2Cl_2 = 70/1/2). After the solvent was removed under reduced pressure, (*R*,*R*)-**4** was obtained as a yellow oil (4.37 g, 17.9 mmol, 69%). $[\alpha]_D^{27}$ +95.0 (*c* 1.00, $CHCl_3$). IR (neat): 2098 (ν_{N3}) cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 0.99 (*t*, *J* = 7.3 Hz, 6H, 2 × C*H*$_3$), 1.73–2.01 (m, 4H, 2 × C*H*$_2$), 4.65 (dd, *J* = 8.2, 6.3 Hz, 2H, 2 × C*H*), 7.35–7.43 (m, 4H, Ar*H*). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 11.2 (*C*H$_3$), 29.3 (*C*H$_2$), 63.3 (*C*H), 127.1, 128.4, 137.3 (aromatic). Anal. Calc. for $C_{12}H_{16}N_6$: C, 59.00; H, 6.60; N, 34.40. Found: C, 58.48; H, 6.69; N, 34.01%.

4.4. (R,R)-1,2-bis(1-(2-nitroanilino)propyl)benzene (R,R)-6

To a solution of (*R*,*R*)-**4** (4.15 g, 17.0 mmol) in MeOH (55 mL) was added 5% Pd/C (1.25 g) and the mixture was stirred under H_2 atmosphere (1 atm balloon) for 2 h. The reaction mixture was filtered through Celite to remove Pd/C. The filtrate was concentrated under reduced pressure to give (*R*,*R*)-**5** as a purple oil. The diamine (*R*,*R*)-**5** was used without further purification. Then *o*-fluoronitrobenzene (5.39 g, 37.4 mmol) and K_2CO_3 (5.17 g, 37.4 mmol) were added to a solution of (*R*,*R*)-**5** in CH_3CN (20 mL) and the mixture was heated at 80 °C for 36 h. The mixture was cooled to room temperature, and water (35 mL) was added. The resulting red brown solid was collected by filtration and the solid was washed with water. Then red brown solid was dissolved in EtOH (75 mL) and the solution was stirred at 70 °C for 20 min. After cooling to 0 °C the resulting precipitate was collected by filtration and the precipitate was washed with cold EtOH to give (*R*,*R*)-**6** as a bright yellow powder (5.17 g, 11.9 mmol, 70% for 2 steps). mp 136.1–136.6 °C $[\alpha]_D^{22}$ −1059.6 (*c* 1.00, $CHCl_3$). IR (neat): 1438, 1570 (ν_{NO2}), 3344, 3359 (ν_{NH}) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 1.07 (t, *J* = 7.5 Hz, 6H, 2 × C*H*$_3$), 2.04 (m, 4H, 2 × C*H*$_2$), 4.84 (q, *J* = 6.4 Hz, 2H, 2 × C*H*), 6.58–6.64 (m, 4H, Ar*H*), 7.18–7.24 (m, 2H, Ar*H*), 7.30–7.34 (m, 2H, Ar*H*), 7.42–7.46 (m, 2H, Ar*H*), 8.12 (dd, *J* = 8.9, 1.7 Hz, 2H, Ar*H*), 8.39 (br d, *J* = 5.6 Hz, 2H, 2 × N*H*). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ 11.3 (*C*H$_3$), 30.3 (*C*H$_2$), 55.9 (*C*H), 114.2, 115.6, 126.7, 126.8, 128.4, 132.0, 135.9, 138.8, 144.3 (aromatic). Anal. Calc. for $C_{24}H_{26}N_4O_4$: C, 66.34; H, 6.03; N, 12.89; O, 14.73. Found: C, 66.17; H, 6.07; N, 12.83%.

4.5. (R,R)-1,2-bis(1-(2-aminoanilino)propyl)benzene (R,R)-7

To a solution of (*R*,*R*)-**6** (4.35 g, 10.0 mmol) in CH_2Cl_2 (25 mL) and MeOH (25 mL) was added 5% Pd/C (1.30 g) and the mixture was stirred under H_2 atmosphere (1 atm balloon) for 24 h. The reaction mixture was filtered through Celite to remove Pd/C. The filtrate was concentrated under reduced pressure and the resulting residue was purified by silica-gel column chromatography (Silica Gel 60N, hexane/EtOAc = 2/1) to give (*R*,*R*)-**7** as a pale purple powder (3.11 g, 8.31 mmol, 83%). mp 122.7–124.1 °C $[\alpha]_D^{24}$ −79.1 (*c* 1.00, $CHCl_3$). IR (neat): 1598, 1621, 3322, 3392 ($\nu_{NH,\ NH2}$) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.96 (*t*, *J* = 7.3 Hz, 6H, 2 × C*H*$_3$), 1.83–2.00 (m, 4H, 2 × C*H*$_2$), 3.18 (br s, 4H, 2 × N*H*$_2$), 3.69 (br s, 2H, 2 × N*H*), 6.46–6.48 (m, 2H, Ar*H*), 6.59–6.70 (m, 6H, Ar*H*), 7.22–7.26 (m, 2H, Ar*H*), 7.45–7.49 (m, 2H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.2 (*C*H$_3$), 29.6 (*C*H$_2$), 55.8 (*C*H), 112.6, 116.9, 118.3, 120.7, 126.5, 127.4, 134.2, 137.1, 140.8 (aromatic). Anal. Calc. for $C_{24}H_{30}N_4$: C, 76.97; H, 8.07; N, 14.96. Found: C, 77.12; H, 8.13; N, 14.88%.

4.6. (R,R)-1,2-bis(1-(2-benzimidazolyl)propyl)benzene (R,R)-8

p-Toluenesulfonic acid monohydrate (0.190 g, 1.00 mmol) was added to a solution of (*R*,*R*)-**7** (1.87 g, 5.00 mmol) in $HC(OEt)_3$ (47.4 g, 320 mmol) and the mixture was stirred for 48 h at room temperature. Excess $HC(OEt)_3$ was removed under reduced pressure and the resulting residue was purified by silica-gel column chromatography (Chromatorex, hexane/EtOAc = 1/3) to give (*R*,*R*)-**8** as a pale yellow green solid (1.65 g, 4.18 mmol, 84%). mp 215.8–216.8 °C $[\alpha]_D^{27}$ +50.5 (*c* 1.00, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 0.62 (*t*, *J* = 7.3 Hz, 6H, 2 × C*H*$_3$), 1.80–1.90 (m, 2H, C*H*$_2$), 2.14–2.24 (m, 2H, C*H*$_2$), 5.48 (*t*, *J* = 7.3 Hz, 2H, 2 × C*H*), 7.26–7.35 (m, 6H, Ar*H*), 7.47–7.51 (m, 2H, Ar*H*), 7.56–7.60 (m, 2H, Ar*H*), 7.76 (s, 2H, 2 × N=C*H*–N), 7.82–7.87 (m, 2H, Ar*H*). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ 11.1 (*C*H$_3$), 27.8 (*C*H$_2$), 56.4 (*C*H), 109.6, 120.7, 122.5, 123.1, 127.3, 129.2, 133.4, 136.8, 141.1, 143.7 (aromatic). Anal. Calc. for $C_{26}H_{26}N_4$: C, 79.16; H, 6.64; N, 14.20. Found: C, 78.85; H, 6.68; N, 13.87%.

4.7. Bis(benzimidazolium) salt (R,R)-9a

Methyl iodide (1.62 mL, 3.69 g, 26.0 mmol) was added to a solution of (*R*,*R*)-**8** (0.513 g, 1.30 mmol) in DME (15 mL) and the mixture was refluxed for 5 h. After the solvent was removed under reduced pressure, the residue was washed with hexane (10 mL × 3) and Et_2O (10 mL × 3), and dried in vacuo to give (*R*,*R*)-**9a** as a pale yellow powder (0.863 g, 1.27 mmol, 98%). mp 186.3–188.3 °C. $[\alpha]_D^{28}$ −6.2 (*c* 1.03, MeOH). ^1H NMR (400 MHz, DMSO-d_6) δ 0.88 (*t*, *J* = 7.3 Hz, 6H, 2 × C*H*$_3$), 1.92–1.99 (m, 2H, C*H*$_2$), 2.41–2.50 (m, 2H, C*H*$_2$), 4.06 (s, 6H, 2 × N–C*H*$_3$), 6.54 (t, *J* = 7.3 Hz, 2H, 2 × C*H*), 7.53–7.55 (m, 2H, Ar*H*), 7.62–7.65 (m, 2H, Ar*H*), 7.71–7.75 (m, 4H, Ar*H*), 8.02–8.04 (m, 4H, Ar*H*), 9.85 (s, 2H, 2 × N=C*H*–N) ^{13}C NMR (100 MHz, DMSO-d_6) δ 10.4 (*C*H$_3$), 27.9 (*C*H$_2$), 33.6 (N–*C*H$_3$), 58.0 (*C*H), 113.7, 113.8, 126.6, 126.8, 127.9, 130.1, 130.4, 31.9, 135.0, 141.8 (aromatic). HRMS (ESI): calcd for $C_{28}H_{32}N_4I$ $[M-I]^+$ 551.1646, found 551.1666.

4.8. Bis(benzimidazolium) salt (R,R)-9b

Compound (*R*,*R*)-**9b** was obtained from (*R*,*R*)-**8** (0.197 g, 0.500 mmol), benzyl bromide (1.71 mL, 2.46 g, 10.0 mmol), and DME (10 mL) in the same manner as that for (*R*,*R*)-**9a**. Compound (*R*,*R*)-**9b** was isolated as a pale yellow powder (quantitative yield). mp 175.2–177.7 °C $[\alpha]_D^{27}$ +50.5 (*c* 1.00, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 0.78 (*t*, *J* = 7.1 Hz, 6H, 2 × C*H*$_3$), 2.00–2.09 (m, 2H, C*H*$_2$), 2.45–2.52 (m, 2H, C*H*$_2$), 5.83 (d, *J* = 5.4 Hz, 4H, 2 × N–C*H*$_2$-Ph), 6.65 (t, *J* = 7.1 Hz, 2H, 2 × C*H*), 7.31–7.45 (m, 6H, Ar*H*), 7.53–7.55 (m, 4H, Ar*H*), 7.58–7.62 (m, 2H, Ar*H*), 7.66–7.73 (m, 6H, Ar*H*), 7.97–8.00 (m, 2H, Ar*H*), 8.09–8.11 (m, 2H, Ar*H*), 10.34 (s, 2H, 2 × N=C*H*–N) ^{13}C NMR (75.0 MHz, $CDCl_3$) δ 10.3 (*C*H$_3$), 27.9 (*C*H$_2$), 50.3 (N–*C*H$_2$–Ph), 58.6 (*C*H), 114.3, 114.4, 126.9, 127.2, 127.9, 128.1, 129.0, 130.3, 130.9, 134.0, 135.0, 141.8 (aromatic). HRMS (ESI): calcd for $C_{40}H_{40}N_4Br$ $[M-Br]^+$ 655.2440, found 655.2431.

4.9. Silver complex (R,R)-10a

The solution of (*R*,*R*)-**9a** (0.678 g, 1.00 mmol) and Ag_2O (0.238 g, 1.03 mmol) in CH_2Cl_2 (10 mL) was stirred overnight at room temperature. The mixture was filtered through Celite and the filtrate was concentrated under reduced pressure to give (*R*,*R*)-**10a** as a pale brown powder (0.709 g, 0.795 mmol, 79%). mp >175.0 °C (Dec.). $[\alpha]_D^{23}$ +57.1 (*c* 1.00, CH_2Cl_2). ^1H NMR (270 MHz, $CDCl_3$) δ 0.64 (*t*, *J* = 7.3 Hz, 6H, 2 × C*H*$_3$), 1.84–1.97 (m, 2H, C*H*$_2$), 2.25–2.42 (m, 2H, C*H*$_2$), 4.14 (s, 6H, 2 × N–C*H*$_3$), 6.42 (dd, *J* = 7.3, 5.9 Hz, 2 × C*H*), 7.04–7.13 (m, 2H, Ar*H*), 7.16–7.23 (m, 2H, Ar*H*), 7.27–7.36 (m, 3H, Ar*H*), 7.38–7.49 (m, 3H, Ar*H*), 7.81–7.84 (m, 2H, Ar*H*). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 11.8 (*C*H$_3$), 25.7 (*C*H$_2$), 36.1 (N–*C*H$_3$), 62.3 (*C*H), 111.1, 112.6, 122.9, 123.0, 128.4, 128.6, 132.3, 135.6, 137.8 (aromatic), 200.1 (N–C–N). HRMS (ESI): calcd for $C_{28}H_{31}N_4$ $[M-2AgI + H]^+$ 423.2553, found 423.2543.

4.10. Silver complex (*R,R*)-**10b**

Compound (*R,R*)-**10b** was obtained from (*R,R*)-**9b** (0.221 g, 0.300 mmol), Ag_2O (0.080 g, 0.345 mmol), and CH_2Cl_2 (10 mL) in the same manner as that for (*R,R*)-**10a**. Compound (*R,R*)-**10b** was isolated as a pale brown powder (0.263 g, 0.277 mmol, 92%). mp > 155.4 °C (Dec.). $[\alpha]_D^{27}$ +18.7 (*c* 1.00, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.71 (*t*, *J* = 7.3 Hz, 6H, 2 × C*H*$_3$), 1.07–1.88 (m, 2H, C*H*$_2$), 2.45–2.51 (m, 2H, C*H*$_2$), 5.78 (m, 4H, 2 × N–C*H*$_2$–Ph), 6.47 (dd, *J* = 7.7, 5.7 Hz, 2H, 2 × C*H*), 7.18–7.31 (m, 10H, Ar*H*), 7.33–7.41 (m, 6H, Ar*H*), 7.49–7.51 (m, 4H, Ar*H*), 7.89–7.91 (m, 2H, Ar*H*). ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.6 (*C*H$_3$), 27.1 (*C*H$_2$), 63.1 (N–*C*H$_2$–Ph), 72.2 (*C*H), 112.7, 113.4, 124.2, 128.1, 128.5, 129.0, 129.2, 129.5, 133.9, 134.9, 136.3, 138.2 (aromatic), 196.2 (N–C–N). HRMS (ESI): calcd for $C_{40}H_{39}N_4BrAg$ $[M-AgBr+H]^+$ 761.1404, found 761.1404.

4.11. Pd complex (*R,R*)-**11a**

The solution of (*R,R*)-**10a** (0.170 g, 0.120 mmol) and $PdCl_2(PhCN)_2$ (0.046 g, 0.120 mmol) in CH_2Cl_2 (5 mL) was stirred overnight at room temperature. The mixture was filtered through Celite and the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (Silica Gel 60N, acetone/EtOAc = 1/1) to give (*R,R*)-**11a** as a white solid (0.049 g, 0.082 mmol, 68%). mp > 300.0 °C (Dec.). $[\alpha]_D^{24}$ +70.3 (*c* 0.30, CH_2Cl_2). ^{1}H NMR (500 MHz, CD_2Cl_2) (−70 °C) δ 1.20–1.41 (2 × br, 6H, 2 × C*H*$_3$), 1.46–1.62 (br m, 1H, 1/2 × C*H*$_2$), 1.91–2.11 (br m, 1H, 1/2 × C*H*$_2$), 2.35–2.52 (br m, 1H, 1/2 × C*H*$_2$), 2.71–2.93 (br m, 1H, 1/2 × C*H*$_2$), 4.17 (s, 3H, N–C*H*$_3$), 4.47 (s, 3H, N–C*H*$_3$), 5.70 (br d, *J* = 10.7 Hz, 1H, C*H*), 5.75 (br d, *J* = 10.7 Hz, 1H, C*H*), 7.40–7.76 (m, 11H, Ar*H*), 8.07–8.08 (m, 1H, Ar*H*). (CD_2Cl_2) (−30 °C) δ 1.28 (*t*, *J* = 7.3 Hz, 3H, CH_3), 1.30 (t, *J* = 7.3 Hz, 3H, C*H*$_3$), 1.54–1.60 (m, 1H, 1/2 × C*H*$_2$), 1.96–2.02 (m, 1H, 1/2 × C*H*$_2$), 2.38–2.44 (m, 1H, 1/2 × C*H*$_2$), 2.79–2.86 (m, 1H, 1/2 × C*H*$_2$), 4.16 (s, 3H, N–C*H*$_3$), 4.44 (s, 3H, N–C*H*$_3$), 5.70 (br s, 1H, C*H*), 5.72 (br s, 1H, C*H*), 7.35–7.46 (m, 8H, Ar*H*), 7.55 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.60 (t, *J* = 7.9 Hz, 1H, Ar*H*), 7.73 (t, *J* = 7.9 Hz, 1H, Ar*H*), 8.06 (d, *J* = 8.2 Hz, 1H, Ar*H*). (CD_2Cl_2) (25 °C) δ 1.27 (t, *J* = 7.3 Hz, 6H, 2 × C*H*$_3$), 2.20 (br, 4H, 2 × C*H*$_2$), 4.29 (s, 6H, 2 × N–C*H*$_3$), 5.68–5.71 (m, 2H, 2 × C*H*), 7.31–7.77 (m, 12H, Ar*H*). (DMSO-d_6) (70 °C) δ 1.19 (t, *J* = 7.3 Hz, 6H, 2 × C*H*$_3$), 2.10–2.20 (br m, 4H, 2 × C*H*$_2$), 4.25 (s, 6H, 2 × N–C*H*$_3$), 5.83 (dd, *J* = 7.4, 4.7 Hz, 2H, 2 × C*H*), 7.35–7.40 (m, 4H, Ar*H*), 7.48–7.49 (m, 2H, Ar*H*), 7.58–7.61 (m, 4H, Ar*H*), 7.77–7.78 (m, 2H, Ar*H*). ^{13}C NMR (125 MHz, CD_2Cl_2) (−70 °C) δ 12.4 (*C*H$_3$), 12.6 (*C*H$_3$), 23.7 (*C*H$_2$), 26.2 (*C*H$_2$), 36.2 (N–*C*H$_3$), 37.7 (N–*C*H$_3$), 60.2 (*C*H), 67.4 (*C*H), 110.8, 111.15, 111.21, 111.3, 123.93, 123.97, 124.00, 124.3, 129.6, 130.4, 131.5, 133.2, 133.4, 134.2, 134.6, 135.17, 135.19, 136.3 (aromatic), 169.9 (N–C–N), 170.1 (N–C–N). (CD_2Cl_2) (25 °C) δ 12.1 (*C*H$_3$), 25.1 (*C*H$_2$), 36.8 (N–*C*H$_3$), 111.0, 111.2, 124.0, 124.3, 230.4, 134.2, 135.5 (aromatic), 172.5 (N–C–N). (DMSO-d_6) (70 °C) δ 11.0 (*C*H$_3$), 23.9 (*C*H$_2$), 35.8 (N–*C*H$_3$), 62.8 (*C*H), 110.7, 111.0, 123.0, 123.2, 128.9, 132.9, 133.2, 133.5, 134.2 (aromatic), 171.4 (N–C–N). Anal. Calc. for $C_{28}H_{30}N_4Cl_2Pd$: C, 56.06; H, 5.04; N, 9.34. Found: C, 55.72; H, 5.30; N, 8.99%.

4.12. Pd complex (*R,R*)-**11b**

Compound (*R,R*)-**11b** was obtained from (*R,R*)-**10b** (0.128 g, 0.135 mmol), $PdCl_2(PhCN)_2$ (0.052 g, 0.135 mmol), and CH_2Cl_2 (6 mL) in the same manner as that for (*R,R*)-**11a**. The residue was purified by silica-gel column chromatography (Silica Gel 60N, hexane/EtOAc = 2/3 ~ EtOAc) to give (*R,R*)-**11b** as a pale yellow solid (0.073 g, 0.097 mmol, 72%). mp > 220.0 °C (Dec.). $[\alpha]_D^{20}$ +183.9 (*c* 1.00, CH_2Cl_2). ^{1}H NMR (500 MHz, CD_2Cl_2) (−30 °C) δ 1.33 (t, *J* = 7.3 Hz, 3H, C*H*$_3$), 1.38 (t, *J* = 7.3 Hz, 3H, C*H*$_3$), 1.70–1.77 (m, 1H, 1/2 × C*H*$_2$), 2.15–2.20 (m, 1H, 1/2 × C*H*$_2$), 2.46–2.50 (m, 1H, 1/2 × C*H*$_2$), 2.93–3.00 (m, 1H, 1/2 × C*H*$_2$), 4.22 (d, *J* = 15.4 Hz, 1H, 1/2 × N–C*H*$_2$–Ph), 5.78–5.81 (m, 2H, 2 × C*H*), 5.85 (d, *J* = 16.7 Hz, 1H, 1/2 × N–C*H*$_2$–Ph), 6.12 (d, *J* = 16.7, 1H, 1/2 × N–C*H*$_2$–Ph), 6.44 (d, *J* = 8.2 Hz, 1H, Ar*H*), 6.51 (d, *J* = 7.2 Hz, 2H, Ar*H*), 6.68 (d, *J* = 15.4 Hz, 1H, 1/2 × N–C*H*$_2$–Ph), 6.87 (t, *J* = 7.6 Hz, 2H, Ar*H*), 7.00–7.03 (m, 4H, Ar*H*), 7.15 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.20–7.28 (m, 5H, Ar*H*), 7.42 (t, *J* = 7.9 Hz, 1H, Ar*H*), 7.45 (d, *J* = 7.9 Hz, 2H, Ar*H*), 7.62 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.66 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.77 (t, *J* = 7.6 Hz, 1H, Ar*H*), 8.13 (d, *J* = 8.2 Hz, 1H, Ar*H*). (DMSO-d_6) (70 °C) Many signals were observed as broad signal. δ 1.21 (*t*, *J* = 7.3 Hz, 6H, 2 × C*H*$_3$), 2.15–2.36 (br, 4H, 2 × C*H*$_2$), 5.60–5.68 (br, 2H, N–C*H*$_2$–Ph), 5.90–5.91 (br, 2H, 2 × C*H*), 6.04–6.11 (br, 2H, N–C*H*$_2$–Ph), 6.81–6.85 (m, 2H, Ar*H*), 6.97–7.02 (br, 2H, Ar*H*), 7.10–7.20 (m, 10H, Ar*H*), 7.33 (t, *J* = 7.9 Hz, 2H, Ar*H*), 7.50–7.54 (br, 2H, Ar*H*), 7.65–7.72 (br, 2H, Ar*H*), 7.81 (d, *J* = 7.9 Hz, 2H, Ar*H*). ^{13}C NMR (125 MHz, CD_2Cl_2) (−30 °C) δ 12.4 (*C*H$_3$), 12.5 (*C*H$_3$), 23.8 (*C*H$_2$), 26.2 (*C*H$_2$), 52.9 (N–*C*H$_2$–Ph), 54.5 (N–*C*H$_2$–Ph), 60.7 (*C*H), 68.0 (*C*H), 110.9, 111.5, 112.2, 113.3, 123.6, 123.8, 124.3, 124.5, 125.7, 127.9, 128.0, 128.5, 129.0, 129.9, 130.6, 131.5, 133.5, 134.0, 134.3, 134.5, 134.6, 135.1, 135.3, 136.4 (aromatic), 171.2 (N–C–N), 172.5 (N–C–N). (DMSO-d_6) (70 °C) δ 11.5 (*C*H$_3$), 24.3 (*C*H$_2$), 53.3 (N–*C*H$_2$–Ph), 63.5 (*C*H), 111.8, 112.1, 123.5, 127.0, 127.5, 128.2, 129.4, 133.5, 133.9, 135.2 (aromatic), 172.6 (N–C–N). Anal. Calc. for $C_{40}H_{38}N_4Cl_2Pd$: C, 63.88; H, 5.09; N, 7.45. Found: C, 63.93; H, 5.29; N, 7.30%.

4.13. Experimental procedure for X-ray analyses

Suitable single crystals were obtained by recrystallization from CH_3CN (**11a**) or $CHCl_3$/hexane (**11b**) and are mounted on glass fibers, respectively. The measurement of complex **11a** was made on a Rigaku Saturn diffractometer using graphite monochromated Mo-Kα radiation at −180 ± 1 °C. Complex **11b** was measured by the use of a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Cu-Kα radiation at 23 ± 1 °C.

Crystallographic data and the results of measurements are summarized in Table 2. The structures were solved by direct methods (SIR97) [19] and expanded using Fourier techniques. Least-square refinements were carried out using SHELXL97 [20]. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at the ideal positions and refined using the riding model. All calculations were performed using the CrystalStructure crystallographic software package [21].

Table 2
Summary of crystal data for complexes **11a** and **11b**.

	11a	**11b**
Emprical formula	$C_{30}H_{34}Cl_6N_4Pd$	$C_{41}H_{39}Cl_5N_4Pd$
Formula weight	769.74	871.45
Crystal color, habit	Pale yellow, prism	Yellow, prism
Crystal size (mm)	0.120 × 0.080 × 0.060	0.180 × 0.160 × 0.120
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	C2/c (no. 15)
Lattice parameters		
a (Å)	10.423(2)	26.724(2)
b (Å)	10.847(2)	21.4243(8)
c (Å)	14.067(3)	17.6792(10)
α (°)	96.062(3)	
β (°)	93.107(4)	129.564(2)
γ (°)	90.772(3)	
V (Å^3)	1578.9(6)	7803.2(7)
Z	2	8
D_c (g cm^{-3})	1.619	1.483
F_{000}	780.00	3552.00
μ (cm^{-1})	(Mo-Kα) 11.236	(Cu-Kα) 72.546
Reflections measured	12809	36824
Independent reflections (R_{int})	7033 (0.0229)	6693 (0.1411)
Number of variables	370	461
Reflection/parameter ration	19.01	14.52
Residuals: *R*; *R*w	0.0509; 0.1137	0.1110; 0.2905
Residuals: R_1	0.0413	0.0913
Goodness-of-fit indicator	1.046	1.142
$\delta\rho_{max,min}$ (e Å^3)	1.18, −1.25	1.31, −1.30

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Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.03.001.

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