Supporting Information for

Helicity Inversion from Left- to Right-Handed Square Planar Pd(II) Complexes: Synthesis of a Diastereomer Pair from a Single Chiral Ligand and their Structure Dynamism

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1. Measurements

¹H and ¹³C NMR spectra were recorded on Jeol LA-300 or -400 FT-NMR spectrometer at *ca*. 25°C. IR spectra were obtained with a PerkinElmer Spectrum One FT-IR spectrophotometer. Mass spectra were obtained with Jeol AX-500 or Jeol JMS-700T spectrometer. Polarization degree and melting points were recorded with a Jasco DIP-370 and Yanako MP-J3, respectively. UV-vis and CD spectra were recorded on a JASCO V-670 spectrophotometer and a JASCO J-820 spectropolarimeter at *ca*. 25°C. Microwave syntheses were done on CEM Discover BenchMate (2450MHz).

2. Synthesis of chiral Pd(II) complexes



A solution of Na₂PdCl₄ (34.2 mg, 0.116 mmol) and H₂L^{S1)} (30.0 mg, 0.116 mmol) in EtOH (15 ml) was stirred for 1 hour at room temperature. The solvent was removed *in vacuo* at *ca*. 40°C and the residue was dissolved in 5ml of CH₃OH and 1ml of CH₃CN was added. The mixed solution was concentrated to ca. 1.5ml by evaporator and an orange single crystal of N_{s} , N_{s} -[Pd(H₂L)Cl₂] was obtained by standing for 1 day (yield 33.3 mg, 0.0763 mmol, 66 %). Found: C, 33.3; N, 12.6; H, 6.01%, C₁₂H₂₆N₄O₂PdCl₂ requires C, 33.1; N, 12.9; H, 6.01%. mp=223–226 °C. FAB-MS (NBA) *m*/z=399.0, [Pd(H₂L)Cl]⁺ requires 399.1. IR v_{max}/cm⁻¹ (KCl) 3319 (s, NH), 2988 (s, NH), 2945 (s, NH), 1675 (s, C=O), 1664 (s, C=O). ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 1.27 (d, 6H, *J*=6.9 Hz, β CH₃), 2.07 (d, 2H, *J*=8.9Hz, ethylene), 2.88 (s, 6H, NCH₃), 3.06 (d, 6H, *J*=4.9Hz, NHCH₃), 4.09 (q, 2H, *J*=6.9Hz, α CH₃), 4.31 (d, 2H, *J*=8.9Hz, ethylene). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 9.08, 26.71, 45.66, 53.67, 66.07, 171.22. H_2L



 N_R, N_R -[Pd(HL)Cl]

A solution of H₂L (30.0 mg, 0.116 mmol) and Na₂PdCl₄ (34.2 mg, 0.116 mmol) in EtOH (15 ml) was heated under microwave irradiation (100W, 120°C) for 30min in sealed tube. After removal of black precipitate (6.5 mg), the filtrate was evaporated at *ca*. 40°C, and then the product (16.8 mg) was isolated as yellow powder by columnchromatography on Sephadex LH-20 with CH₃OH eluent. The light yellow single crystal of *N_R*,*N_R*-[Pd(HL)Cl] was obtained from a CH₃OH solution (yield 8.4 mg, 0.0210 mmol, 18 %). Found: C, 36.2; N, 13.7; H, 6.32 %, C₁₂H₂₅N₄O₂PdCl requires C, 36.1; N, 14.0; H, 6.31 %. M.p.=214-215 °C. ¹H NMR (300 MHz, CD₃OD): δ (ppm)=4.24 (q, 1H, *J*=7.11 Hz, αH), 3.86 (q, 1H, *J*=6.97 Hz, αH), 3.65 (m, 2H, ethylene), 3.00 (s, 3H), 2.81 (m, 2H, ethylene), 2.70 (s, 3H), 2.68 (s, 3H), 2.65 (d, 3H, *J*=0.96 Hz), 1.94 (d, 3H, *J*=6.97 Hz, βCH₃), 1.18 (d, 3H, *J*=7.11 Hz, βCH₃). IR v_{max}/cm⁻¹ (KCl) 3213 (s, NH), 1667 (s, C=O), 1595 (s, C=O). FAB-MS (NBA) *m*/z=399.0, [Pd(HL)Cl+H]⁺ requires 399.1. [α]_D²³ = -102° dm⁻¹g⁻¹cm³ (c=0.259, CH₃OH).

3. Crystallographic Studies

Yellow single crystals of N_S, N_S -[Pd(H₂L)Cl₂] with 0.35 × 0.2 × 0.15 mm and N_R, N_R -[Pd(HL)Cl] with 0.35 × 0.2 × 0.10 mm were mounted in inert oil and transferred to the cold gas stream of diffractometer (–173 °C). Their X-ray diffraction data were collected by Rigaku / MSC Mercury CCD diffractometer with graphite monochromated Mo K α radiation (λ = 0.71070 Å) to 20 max of 55.0°. Data were processed on a PC using CrystalClear software (Rigaku). The crystal structures were solved by Direct methods (Sir-97)^{S2)} and refined by full-matrix least squares on F² using *SHELXL-97*.^{S3)} All hydrogen atoms were placed on ideally geometrical positions. Non-hydrogen atoms were refined anisotropically. Absolute configuration of the complex was determined by the configuration of ligand and Flack parameter.

Crystal data for N_S, N_S -[Pd(H₂L)Cl₂]: C₁₂H₂₆Cl₂N₄O₂Pd, *M*= 435.67, orthorhombic, *a* = 10.2009(10), *b* = 12.1922(15), *c* = 13.7244(16) Å, *U* = 1706.9(3) Å³, *T* = 100 K, space group *P*2₁2₁2₁ (no.19), *Z* = 4, 17076 reflections measured, 3883 unique (R_{int} = 0.0340) which were used in all calculations. The final *wR*(F₂) was 0.0449 (all data). Flack parameter was -0.003(19). Selected bond length (Å) and bond angles (deg) Pd1-N1=2.0797(18), Pd1-N2=2.0885(18), Pd1-Cl1=2.3069(6), Pd1-Cl2=2.3182(5), N1-Pd1-N2=85.34(7), Cl1-Pd1-Cl2=90.11(2).

Crystal data for N_R , N_R -[Pd(HL)Cl]: C₁₂H₂₅ClN₄O₂Pd, M= 399.21, orthorhombic, a = 7.0991(10), b = 14.147(2), c = 15.733(2) Å, U = 1580.1(4) Å³, T = 100 K, space group $P2_12_12_1$ (no.19), Z = 4, 15637 reflections measured, 3592 unique (R_{int} = 0.0303) which were used in all calculations. The final $wR(F_2)$ was 0.0545 (all data). Flack parameter was -0.03(3). Selected bond length (Å) and bond angles (deg)Pd1-N1=2.031(2), Pd1-N2=2.116(2), Pd1-N3=1.997(2), Pd1-Cl1=2.3196(7), N1-Pd1-N2=87.14(9), N1-Pd1-N3=81.15(9), N1-Pd1-Cl1=175.20(7), N2-Pd1-N3=167.63(9).

4. **DFT calculations.**

The geometry optimizations were performed for Pd(II) complexes using Gaussian03 $(D.01)^{S4}$ starting from coordinates based on the crystal structure of the Pd(II) complexes for N_S, N_S -[Pd(H₂L)Cl₂] and N_R, N_R -[Pd(HL)Cl], and from the inverted structure of N_R, N_R -[Pd(HL)Cl] for N_S, N_S -[Pd(HL)Cl]. These optimizations were confirmed that no imaginary frequencies were arisen at calculated structure by frequency calculation. The calculation was performed on a single electronic state. The method used was B3LYP with LANL2DZ as the basis set.

5. References

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6. Figures



Figure S1. CD spectra of N_S , N_S -[Pd(H₂L)Cl₂]at room temperature. (a) KBr pellet: the KBr pellet was made from the mixture of the complex (0.3 mg) and KBr (27 mg). The pellet was rotated 60 degree to eliminate the linear dichroism of the sample pellet by averaging the spectra. (b) CH₃OH solution: [complex] = 2.5×10^{-3} mol dm⁻³, 10 mm cuvette.



Figure S2. ¹H NMR changes of N_5 , N_5 -[Pd(H₂L)Cl₂] upon microwave irradiation for (a) 10 min, (b) 20 min, (c) 40 min and (d) 90 min at 120°C in C₂D₅OD. (e) ¹H NMR spectra of N_R , N_R -[Pd(HL)Cl] in the presence of 50 mM NaClO₄ in C₂D₅OD. [complex] = 2.5×10^{-3} mol dm⁻³. [CHCl₃]= 3.8×10^{-3} mol dm⁻³ as an internal standard. *; solvent and water.



Figure S3. CD spectra of N_R , N_R -[Pd(HL)Cl]at room temperature. (a) KBr pellet: the KBr pellet was made from the mixture of the complex (2.2 mg) and KBr (28 mg) for 290-600 nm, 3.0 mg of which was further diluted by 14 mg of KBr for 230-290 nm. The pellet was rotated 60 degree to eliminate the linear dichroism of the sample pellet by averaging the spectra. (b) CH₃OH solution: [complex] = 2.5×10^{-3} mol dm⁻³, 0.5 mm cuvette for 200-290 nm, 10 mm cuvette for 290-600 nm.



Figure S4. ¹H NMR changes of N_S, N_S -[Pd(H₂L)Cl₂] at 120°C for (a) 1 hour, (b) 10 hours, (c) 24 hours and (d) 34 hours in C₂D₅OD. [complex] = 2.5×10^{-3} mol dm⁻³. [CHCl₃]= 3.8×10^{-3} mol dm⁻³ as an internal standard. *; solvent and water.



Figure S5. CD and absorption spectra of N_S, N_S -[Pd(HL)Cl] complex generated by mixing N_S, N_S -[Pd(H₂L)Cl₂] complex and one equivalent of C₂H₅N in CD₃OD at ca. 25 °C (blue). After 5 min heating at 100 °C (red). Dashed lines indicate CD and absorption spectra of N_R, N_R -[Pd(HL)Cl]. (Right) Time traces of CD spectral changes at 322 nm. [complex] = 2.5×10^{-3} mol dm⁻³, 0.5 mm cuvette for 200-290 nm, 10 mm cuvette for 290-600 nm.



Figure S6. Molecular structures of (a) N_S , N_S -[Pd(HL)Cl] and (b) N_R , N_R -[Pd(HL)Cl] optimized by DFT calculation. Most hydrogen atoms are omitted for simplification.