

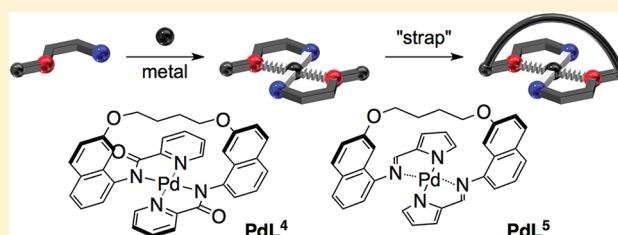
Planar-Chiral Metal Complexes Comprised of Square-Planar Metal and Achiral Tetradentate Ligands: Design, Optical Resolution, and Thermodynamics

Hidetoshi Goto, Teppei Hayakawa, Kanako Furutachi, Hiroshi Sugimoto,* and Shohei Inoue

Department of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science, 12-1 Ichigaya-funagawara, Shinjuku, Tokyo 162-0826, Japan

S Supporting Information

ABSTRACT: Planar-chiral palladium complexes $\{[N,N'-[1,4\text{-butanediylbis}(\text{oxy-7,1-naphthalenediyl})]\text{bis}(2\text{-pyridinecarboxamidato})[(2-)\text{-}\kappa N_1,\kappa N_1',\kappa N_2,\kappa N_2']\text{palladium}(\text{PdL}^4)] \text{ and } [[2,2'-[1,4\text{-butanediylbis}[(\text{oxy-7,1-naphthalenediyl})\text{imino}]\text{methyl}]]\text{dipyrrolato}[(2-)\text{-}\kappa N_1,\kappa N_1',\kappa N_2,\kappa N_2']\text{palladium}(\text{PdL}^5)]\}$ were synthesized from achiral tetradentate ligands $N,N'-[1,4\text{-butanediylbis}(\text{oxy-7,1-naphthalenediyl})]\text{bis}(2\text{-pyridinecarboxamide}) (\text{H}_2\text{L}^4)$ and $N,N'-\text{bis}[(1H\text{-pyrrol-2-yl})\text{methylidene}]-7,7'-(1,4\text{-butanedioldioxy})\text{bis}-(1\text{-naphthalenamine}) (\text{H}_2\text{L}^5)$ bearing two dissymmetric bidentate units at both ends and a Pd^{II} ion, respectively. The palladium complexes were crystallized in the monoclinic space group $P2_1/n$ with the unit cell parameters $a = 16.5464(6) \text{ \AA}$, $b = 11.3534(4) \text{ \AA}$, $c = 17.6697(7) \text{ \AA}$, $\beta = 115.5300(10)^\circ$, and $Z = 4$ for PdL^4 and $a = 17.2271(8) \text{ \AA}$, $b = 10.1016(5) \text{ \AA}$, $c = 17.9361(9) \text{ \AA}$, $\beta = 105.6310(10)^\circ$, and $Z = 4$ for PdL^5 . The planar-chiral structures of PdL^4 and PdL^5 were confirmed by single-crystal X-ray analyses, resulting in the fact that the crystals were racemic mixtures. The racemic mixtures were successfully resolved by using chiral high-performance liquid-chromatography techniques. Racemizations of the complexes were found to be drastically dependent on the arrangement of the charged or uncharged metal-binding N atoms of the ligands.



■ INTRODUCTION

Chiral metal complexes as represented by metalloporphyrins vertically coordinated by imidazole, thiol, and phenol residues assignable to amino acid units (histidine, cysteine, and tyrosine) in proteins are ubiquitous in nature and play many roles including O_2 activation and utilization (cytochrome P450 and cytochrome oxidase) and covalent-bond cleavage and formation (hydrolase and lyase).¹ These have prompted chemists to develop artificial chiral metal complexes from the aspect of not only unique three-dimensional structures^{2–5} and their chiroptical properties⁶ but also potential applications to catalysts for asymmetric syntheses,^{7,8} catalysts for stereospecific polymerizations,⁹ sensors^{10–12} and selectors^{13–15} for chiral discriminations, and chiral dopants for liquid crystals.¹⁶

Optically active compounds having metal-binding functional groups and asymmetric sources such as asymmetric tetrahedral C atoms, which are chiral sources of naturally occurring products (proteins, sugars, and so on), have been widely used for construction of the chiral complexes.^{7,17} On the other hand, achiral ones such as ethylenediamine, 2,2'-bipyridine, and acetylacetonate salts have been frequently employed to build the chiral metal complexes dependent upon coordination geometries of metals, in particular of four and six coordination numbers.^{2,18} Since Werner reported syntheses and optical resolutions of chiral octahedral, six-coordinate cobalt complexes, so-called "Werner complexes", having three achiral bidentate ligands (ethylenediamine) about a century ago,¹⁹ a

variety of chiral octahedral complexes having achiral multidentate ligands such as bi-, tri-, or hexadentate have been synthesized^{19–21} and applied to chiral discrimination reagents^{14,15} and chiral capsules.^{8a,c,e} It is known that tetrahedral, four-coordinate complexes tend to be labile and even stereochemical isomers of the complexes having bi-²² or tetradentate²³ ligands transform into the other antipodes rather quickly. Nevertheless, optical resolutions of chiral tetrahedral complexes with two dissymmetric bidentate²⁴ or four distinct monodentate²⁵ ligands were accomplished. Some helicates composed of tetrahedral complexes as repeating units were successfully separated into enantiomerically pure compounds.²⁶ Chiral square-planar, four-coordinate complexes were sophisticatedly designed, and those optical resolutions were achieved as well.^{27,28} In contrast with the tetra- and octahedral complexes mentioned above, the square-planar complexes needed two kinds of bidentate ligands.²⁷ We expected to constitute a chiral square-planar complex from two of the same bidentate ligands and a four-coordinate metal, as below (Figure 1): (1) two dissymmetric bidentate ligands are coordinated to metal at trans positions to each other (trans effect) to generate a complex having an enantiotopic plane; (2) when a strap unit is introduced to the trans square-planar complex, the strap unit covers one face of the enantiotopic plane. Such a complex is

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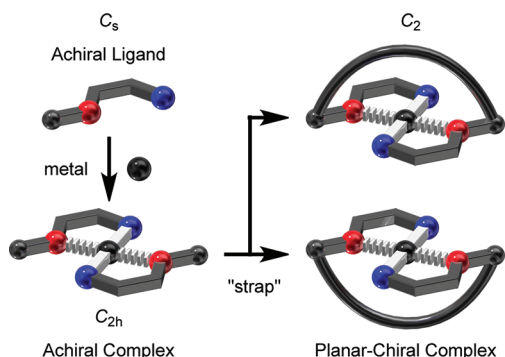


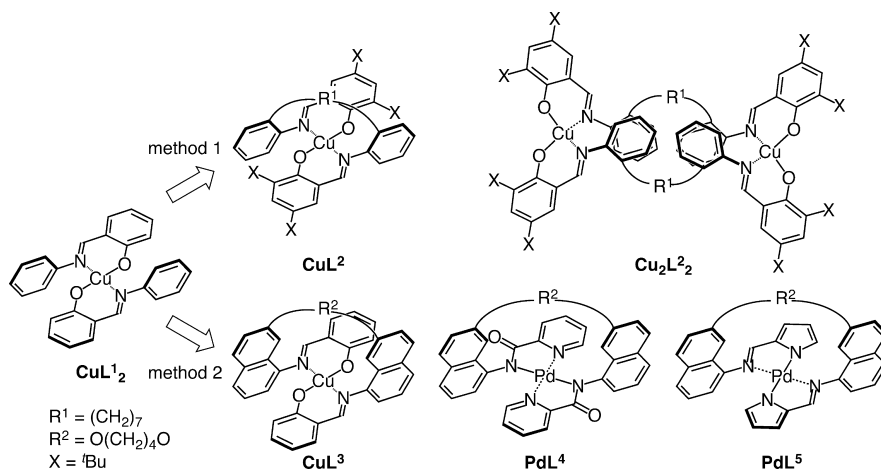
Figure 1. Concept of a planar-chiral metal complex (black sphere, metal; red and blue spheres, metal-binding site; white tube, coordinate bond; gray tube, covalent bond). Two C_s -symmetric bidentate ligands are coordinated to the metal to form a C_{2h} -symmetric square-planar complex. Cross-linking between two bidentate ligands generates a pair of enantiomers of the planar-chiral complex.

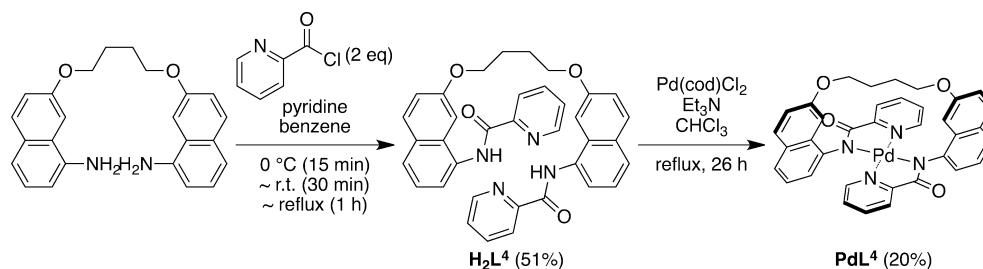
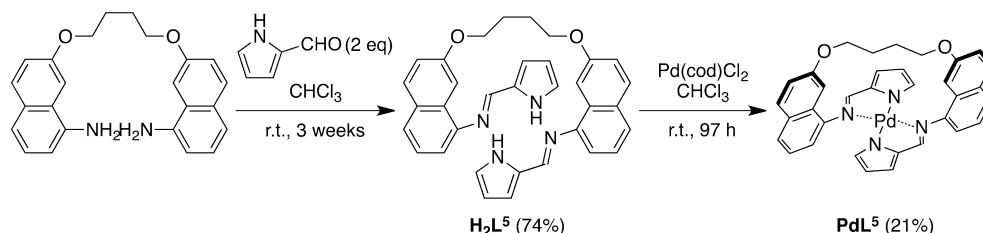
planar-chiral. Some research groups have hitherto developed planar-chiral complexes with strap chains called chiral “fly-over” complexes.^{29–31} Since the first chiral “fly-over” complex by Schlesinger in 1927,^{29a} Martin presented a rational design and an undoubted structure of chiral-strapped complexes by X-ray crystallography in 1979.^{29b,c} Some chiral “fly-over” complexes have been reported since then, and a few optical resolutions of such complexes have been accomplished by Naota and our groups, individually.^{30,31}

In our and others’ laboratories, metal complexes of planar-chiral porphyrins obtained by intramolecular cross-linkings of *achiral* tetradentate porphyrins having enantiotopic faces (C_{2h} or C_{4h} symmetry) were found to serve as effective chiral catalysts for asymmetric oxidations^{32,33} and as effective selectors for biomolecules.^{34–36} In the beginning of our research on chiral square-planar complexes different from the metalloporphyrins,³⁷ our platform, based on the design concept as described above, was the bis[2-[(*N*-phenylimino)methyl]phenolate]copper complex (CuL^1 ; Chart 1), of which two *N*-phenyl groups were roughly orthogonal to the plane of the copper(II) square-planar geometry.⁴⁵ Unfortunately, the mixture of copper(II) and 2,2'-[1,7-heptanediy]bis[[1,2-phenylenediyl]imino]methyl]]bis(4,6-di-*tert*-butylphenolate)-(2- (L^2) having a heptamethylene group (R^1) as a flexible

spacer bridging two *N*-phenyl groups of two L^1 at the ortho positions formed not a planar-chiral complex with a 1:1 stoichiometric ratio, [[2,2'-[1,7-heptanediy]bis[[1,2-phenylenediyl]imino]methyl]]bis(4,6-di-*tert*-butylphenolate)]-(2-)- $\kappa\text{N}_2,\kappa\text{N}_2',\kappa\text{O}_1,\kappa\text{O}_1'$ copper (CuL^2), but an achiral (meso) ladder complex with a 2:2 composition {bis[2,2'-[1,7-heptanediy]bis[[1,2-phenylenediyl]imino]methyl]]bis(4,6-di-*tert*-butylphenolate)]dicopper complex, Cu_2L^2_2 }, confirmed by single-crystal X-ray analysis.³¹ The flexibility of R^1 was considered to be one of factors to inhibit the formation of the planar-chiral structure (CuL^2). So, [[2,2'-[1,4-butanediyl]bis-[[1,2-phenylenediyl]imino]methyl]]bis(phenolate)]-(2-)- $\kappa\text{N}_2,\kappa\text{N}_2',\kappa\text{O}_1,\kappa\text{O}_1'$ copper (CuL^3) comprised of copper(II) and a newly employed ligand {2,2'-[1,4-butanediyl]bis-[[1,2-phenylenediyl]imino]methyl]]bis(phenolate)]-(2-), L^3 } bearing a more rigid “naphthalene” unit and a shorter “ R^2 ” spacer was focused on as an alternative platform.^{29b,c} Such complexes are reported to form planar-chiral structures in crystals,^{29b,c,f–i,30,31} while the isomerization behaviors of the chiral structures have never been investigated to date. Our optical resolution of CuL^3 using chiral high-performance liquid chromatography (HPLC) was unsuccessful (Scheme S1 and Figure S1 in the Supporting Information). We herein report the synthesis, optical resolution, and thermodynamic investigation of novel planar-chiral complexes {[[[*N,N'*-[1,4-butanediyl]bis-(oxy-7,1-naphthalenediyl)]bis(2-pyridinecarboxamido)]-(2-)- $\kappa\text{N}_1,\kappa\text{N}_1',\kappa\text{N}_2,\kappa\text{N}_2'$]palladium (PdL^4) and [[2,2'-[1,4-butanediyl]bis-[[1,2-phenylenediyl]imino]methyl]]bis(phenolate)]-(2-)- $\kappa\text{N}_1,\kappa\text{N}_1',\kappa\text{N}_2,\kappa\text{N}_2'$]palladium (PdL^5); Chart 1}.³¹ Palladium(II) is one of the representative square-planar coordinate metals and was used for the construction of planar-chiral complexes with two [NN]-bidentate ligands.^{27c,d} The dissymmetric [NN]-bidentate units [*N*-phenyl-2-pyridinecarboxamido⁴⁶ and 2-(*N*-phenylimino)methyl-1*H*-pyrrolato⁴⁷] in *N,N'*-[1,4-butanediyl]bis(oxy-7,1-naphthalenediyl)]bis(2-pyridinecarboxamido)(2- (L^4) and 2,2'-[1,4-butanediyl]bis-[[1,2-phenylenediyl]imino]methyl]]dipyrrolato(2- (L^5) have a monovalent negative charge similar to that of 2-[(*N*-phenylimino)methyl]phenolate in L^3 . Although the synthesis and optical resolution of PdL^4 ahead of PdL^5 was accomplished, racemization of PdL^4 proceeded at ambient temperature. Our idea to suppress racemization of the complex was to exchange the positions of the neutral and negative charges. In fact, no racemization of PdL^5 was observed under

Chart 1. Structures of Planar-Chiral Metal Complexes



Scheme 1. Synthesis of PdL^4 Scheme 2. Synthesis of PdL^5 

the same condition as that of PdL^4 . The details will be described hereinafter.

RESULT AND DISCUSSION

Syntheses and Characterizations of PdL^4 and PdL^5

Two palladium complexes (PdL^4 and PdL^5) were synthesized according to Schemes 1 and 2. 7,7'-(1,4-Butanedioldioxy)bis(1-naphthalenamine)^{29b} as a starting material in both schemes was reacted with picolinoyl chloride⁴⁸ or 1*H*-pyrrole-2-carbaldehyde⁴⁹ to obtain the corresponding compounds H_2L^4 and H_2L^5 , respectively. The reactions of the compounds with dichloro(1,5-cyclooctadiene)palladium(II) ($\text{Pd}(\text{cod})\text{Cl}_2$)⁵⁰ were followed by ^1H NMR spectroscopy (Figures S2 and S3 in the Supporting Information). Upon the addition of H_2L^4 or H_2L^5 to $\text{Pd}(\text{cod})\text{Cl}_2$, the signals assignable to the amide (NH for H_2L^4) and pyrrole (NH for H_2L^5) at 10–12 ppm became gradually smaller, as we expected. Furthermore the obtained product from palladium(II) and H_2L^4 showed signals in the fast atom bombardment mass spectrometry (FAB-MS) spectrum that were identical to those of a 1:1 complex of palladium(II) and the corresponding anionic ligand ($[\text{L}^4]^{2-}$). In the case of H_2L^5 , the signals assignable to the 1:1 complex of palladium(II) and $[\text{L}^5]^{2-}$ were observed as well.

The single-crystal X-ray analyses of PdL^4 and PdL^5 also revealed the planar-chiral formations with the 1:1 stoichiometric ratios of tetradentate ligands/palladium(II) (Table 1 and Figures 2 and S4 and S5 in the Supporting Information). PdL^4 was crystallized as a racemic mixture in a monoclinic system with a space group of $P2_1/n$. Two independent molecules, which are *pR* and *pS* forms, were found in the dissymmetric unit. Two pyridylamido groups of H_2L^4 were coordinated to the Pd^{II} ion in a trans geometry: Pd–N distances in the range of 2.03–2.06 Å, N–N distances in the ranges of 2.61–2.62 and 3.14–3.16 Å, and N–Pd–N angles in the ranges of 79.30–79.33° and 100.2–100.8° (cis) and 174.7–175.3° (trans), exhibiting that, strictly speaking, the palladium complex formed slightly distorted square-planar geometries bearing enantiotopic planes (C_2 symmetry). Two naphthalene rings covalently bonded to the amido N atoms were orthogonally distorted to the Pd–ONNO planes: dihedral angles in the range of 84.8–87.1°. Furthermore, each 1,4-butanedioldioxy group connected to

Table 1. Crystal Data and Structure Refinement for PdL^4 and PdL^5

	PdL^4	PdL^5
formula	$[\text{C}_{36}\text{H}_{28}\text{N}_4\text{O}_4]\text{Pd}$	$[\text{C}_{34}\text{H}_{28}\text{N}_4\text{O}_2]\text{Pd}(\text{CH}_2\text{Cl}_2)$
fw	687.02	714.92
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
<i>T</i> /K	90	90
<i>a</i> /Å	16.5464(6)	17.2271(8)
<i>b</i> /Å	11.3534(4)	10.1016(5)
<i>c</i> /Å	17.6697(7)	17.9361(9)
α /deg	90	90
β /deg	115.5300(10)	105.6310(10)
γ /deg	90	90
<i>V</i> /Å ³	2995.29(19)	3005.8(3)
<i>Z</i>	4	4
$\rho_{\text{calcd}}/\text{g cm}^{-3}$	1.524	1.580
$\mu(\text{Mo K}\alpha)/\text{mm}^{-1}$	0.668	0.836
<i>F</i> (000)	1400	1452
cryst size/mm	0.50/0.20/0.20	0.50/0.40/0.10
θ range/deg	2.20–27.52	1.92–28.35
reflns collected	20554	21947
indep reflns [<i>R</i> _{int}]	6868 [0.0228]	7482 [0.0295]
max, min transmn	0.8780, 0.7313	0.956236, 0.784376
data/restraints/param	6868/0/406	7482/0/397
final <i>R</i> 1 [<i>wR</i> 2]	0.0308 [0.0783]	0.0276 [0.0766]
final <i>R</i> 1 [<i>wR</i> 2] (all data)	0.0353 [0.0812]	0.0349 [0.0816]
largest diff peak, hole/e Å ^{−3}	1.805, −0.305	0.672, −0.554

the two naphthalene rings crossed over one face of the enantiotopic plane with 1:1 possibility. Each molecule of the planar-chiral complex had a C_2 axis perpendicular to the Pd–ONNO plane. These results indicate the formation of the planar-chiral complex from H_2L^4 and palladium(II) with a 1:1 stoichiometric ratio.⁴⁶ PdL^5 was also crystallized as a racemic mixture in a monoclinic system with a space group of $P2_1/n$ and formed a planar-chiral structure similar to PdL^4 : Pd–N distances in the range of 2.01–2.04 Å, N–N distances in the ranges of 2.61–2.62 and 3.07–3.10 Å, N–Pd–N angles in the

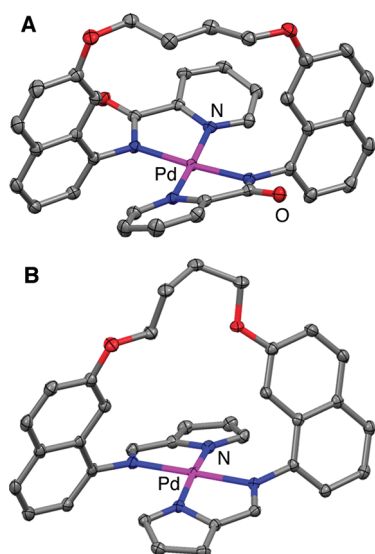


Figure 2. Ball-and-stick drawings of PdL^4 (A) and PdL^5 (B) with thermal ellipsoids at 50% probability (carbon, gray; nitrogen, blue; oxygen, red; palladium, pink). Each one of the independent complexes is shown here. H atoms (for A and B) and solvent molecules (for B) are omitted for clarity.

ranges of $80.5\text{--}80.6^\circ$ and $99.0\text{--}99.8^\circ$ (cis) and $172.3\text{--}178.8^\circ$ (trans), and $\text{Pd}\text{--}\text{N}\text{--}\text{C}_{\text{naph}}\text{--}\text{C}_{\text{naph}}$ dihedral angles in the range of $61.4\text{--}71.6^\circ$.⁴⁷

The chiral conformations of PdL^4 and PdL^5 in solutions were suggested by ^1H NMR spectroscopy. The ^1H NMR spectrum of PdL^4 exhibited 10 distinct signals in the aromatic region, meaning that PdL^4 adopted a single conformation in solution. In addition, the signals assignable to the oxymethylene protons (OCH_2) of PdL^4 were observed as two signals at 4–4.5 ppm, while those attributed to the other methylene protons (CH_2) near 2 ppm just became slightly broader than those of H_2L^4 . These results indicate that the geminal protons of the oxymethylene group are diastereotopic, meaning that PdL^4 adopts a cyclic structure in solution of which intramolecular rotations are under restriction. The changes between the ^1H NMR spectra of H_2L^5 and PdL^5 were similar to those of H_2L^4 and PdL^4 : 4.29 (H_2L^5) to 4.15–4.30 and 4.40–4.50 (PdL^5) ppm for oxymethylene protons.

Optical Resolutions and Thermodynamics of PdL^4 and PdL^5 . The optical resolutions of the planar-chiral complexes were carried out by using HPLC with SUMICHIRAL OA-4600 as a chiral column (Figure 3). A chromatogram of PdL^4 showed two peaks with comparable peak areas in 3.42 (the first fraction) and 3.74 (the second fraction) min. ^1H NMR and MS spectra of the component of the first fraction separated by chiral HPLC were identical with those of the second fraction. On the other hand, a circular dichroism (CD) spectrum of the component (the first fraction) exhibited a negative peak at 350 nm [$(-)\text{PdL}^4$], which has a maximum intensity in the long-wavelength region [$(-)\text{PdL}^4$ denotes the sign of the peak at 350 nm, vide infra], whereas the second fraction showed a positive peak [$(+)\text{PdL}^4$]. These CD patterns were complete mirror images in the range of 200–500 nm (Figure 4A). These results indicate that the two components [$(-)\text{PdL}^4$ and $(+)\text{PdL}^4$] are a pair of enantiomers of PdL^4 . In a similar fashion, PdL^5 was also separated successfully to a pair of enantiomers of PdL^5 : one is $(-)\text{PdL}^5$ (the first fraction, 9.32 min), and the other is

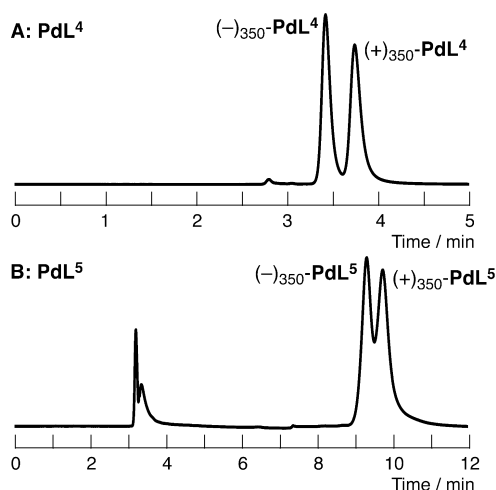


Figure 3. Chromatographic resolution of stereoisomers of PdL^4 (A) and PdL^5 (B) on SUMICHIRAL OA-4600. Column: 25×0.46 (i.d.) cm. Eluent: chloroform/ethanol (50:1, v/v) (A); hexane/ethanol (100:1, v/v) (B). Flow rate: 1 mL min^{-1} .

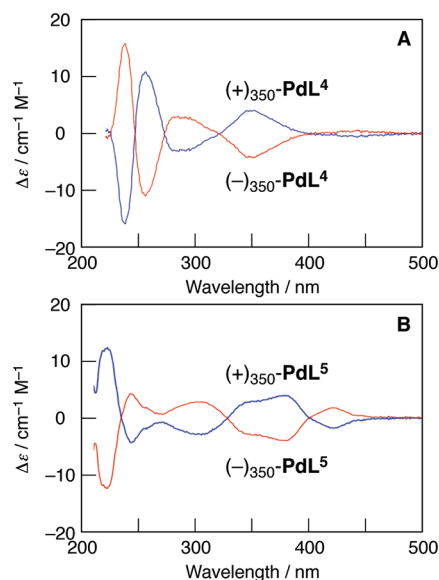


Figure 4. CD spectra of fractions of PdL^4 (A) and PdL^5 (B) (red line, $(-)\text{PdL}$ isomers; blue line, $(+)\text{PdL}$ isomers) in 1,2-dichloroethane at room temperature. $[\text{Pd complex}] = 0.28$ (PdL^4) and 0.89 (PdL^5) mM.

$(+)\text{PdL}^5$ (the second fraction, 9.75 min) (Figure 4B). Enantiomeric excesses (ee's) of the enantiomers were estimated to be more than 99% based on their chiral HPLC analyses (Figure S6 in the Supporting Information).

Finally, we investigated the stability of the planar-chiral complexes toward racemization (Figures 5 and S7 in the Supporting Information). The ee's of the complexes were periodically estimated by chiral HPLC after the solutions of $(-)\text{PdL}^4$ and $(-)\text{PdL}^5$ were kept at room temperature (ca. $22\text{--}24^\circ\text{C}$) for a predetermined amount of time. The peak of the chromatogram for $(-)\text{PdL}^4$ gradually became lower over time, while that for $(+)\text{PdL}^4$ became higher. No other peaks were observed during incubation of the solution. Furthermore, the ^1H NMR spectra of the solutions before and after incubation were completely identical. These results indicate that racemization of PdL^4 only proceeded under this condition. The first-order kinetic constant (k) and the half-life

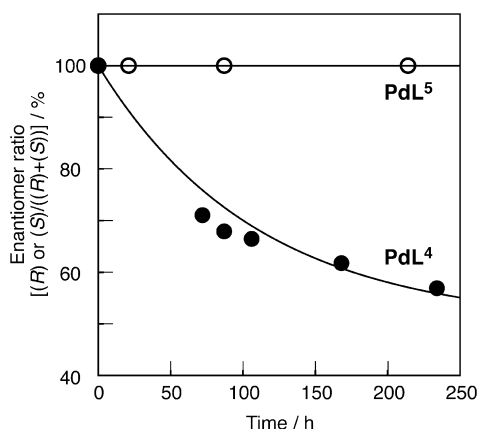


Figure 5. Racemization behaviors of PdL^4 (full circles) in chloroform/ethanol (50:1, v/v) and PdL^5 (opened circles) in hexane/ethanol (100:1, v/v) at room temperature. The black solid curve is calculated using the first-order rate equation.

period ($\tau_{1/2}$) of racemization were estimated to be $1.27 \times 10^{-6} \text{ s}^{-1}$ and 76 h, respectively. In addition, the Gibbs' free-energy change ($\Delta G^\ddagger$) of the rotational barrier around the Pd–N bond of the complex was calculated as 106 kJ mol^{-1} using the Eyring equation.⁵¹ On the other hand, no racemization of $(-)\text{-}_{350}\text{-PdL}^5$ was observed under the same condition as that of $(-)\text{-}_{350}\text{-PdL}^4$; assuming that a small amount (1.0 mol %) of $(-)\text{-}_{350}\text{-PdL}^5$ is racemized, the values can be calculated as follows: $k < 1.31 \times 10^{-8} \text{ s}^{-1}$, $\tau_{1/2} > 7350 \text{ h}$, and $\Delta G^\ddagger > 117 \text{ kJ mol}^{-1}$. Both complexes were built using two kinds of Pd–N bonds: ionic and nonionic coordination bonds, of which the arrangements were different from each other. A linear dianion derived from H_2L^4 has nonionic pyridyl groups at both ends, while that from H_2L^5 has anionic pyrrolato groups at both ends. A dianionic, linear compound having four metal-binding [N_2O_2] sites was recently reported to play a role as not a tetradentate but a bidentate ligand to adopt a metal complex, in which the two anionic O atoms at both ends of the ligand strand were coordinated to the metal while the two nonionic N atoms

(imine units), being in the middle of the ligand, were nonconnected.⁵² On the basis of these results, the racemization mechanisms of the planar-chiral metal complexes were proposed, as shown in Scheme 3. Because the N atoms are dissociated from the Pd–N bonds in one enantiomer of PdL^4 and PdL^5 at the first step (a, a' or d, d'), the cleavages of the nonionic Pd–N bonds (a, a') preferentially proceed because the binding forces are weaker than those of the ionic Pd–N bonds. Subsequently, the dissociated N atoms at both ends of the ligands (b, e') are rotated faster around the remaining Pd–N bonds than those in the middle of the ligands. Thereafter, the dissociated N atoms are associated with the metal to generate the others (c, c' or f, f'). In other words, PdL^4 is racemized via the reaction pass of Scheme 3a–c, which proceeds more easily than that of PdL^5 .

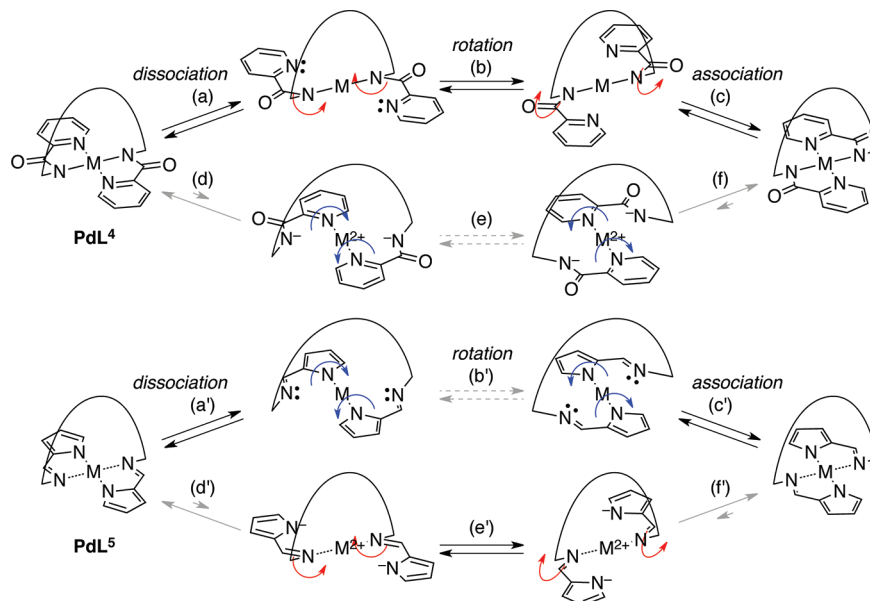
CONCLUSIONS

We have designed and synthesized planar-chiral palladium(II) complexes (PdL^4 and PdL^5) consisting of *achiral*, four-coordinate compounds (H_2L^4 and H_2L^5) bearing two dissymmetric bidentate binding sites at both ends. The single-crystal X-ray analyses revealed the planar-chiral structures of the compounds of which crystals were racemic mixtures. Both enantiomers of the compounds were successfully resolved by chiral HPLC. Racemization of the compounds was found to proceed via cleavage of the Pd–uncharged N bond and subsequent intramolecular rearrangements. These optically active, planar-chiral complexes are expected to be applicable to chiral recognition agents^{32,33} and catalysts for asymmetric synthesis^{34–36} such as planar-chiral metalloporphyrins, as was previously reported by our group and others. This project is now in progress in our laboratory.

EXPERIMENTAL SECTION

1. Materials. 2-Hydroxybenzaldehyde and pyridine-2-carboxylic acid were purchased from Tokyo Chemical Industry (Japan). Copper(II) acetate monohydrate was purchased from Kanto Chemicals (Japan). Triethylamine and benzene were dried with calcium hydride (CaH_2) and then distilled over sodium benzophenone

Scheme 3. Possible Mechanism of Racemization



ketyl under nitrogen. Pyridine was dried with CaH_2 and then distilled over CaH_2 under nitrogen. Thionyl chloride was purified by fractional distillation under nitrogen. Copper(II) acetate monohydrate was twice recrystallized from acetic acid. Pyridine-2-carboxylic acid was recrystallized from benzene. Other reagents were used without purification. 7,7'-(1,4-Butanedioldioxy)bis(1-naphthalenamine),^{29b} 1H-pyrrole-2-carbaldehyde,⁴⁹ and $\text{Pd}(\text{cod})\text{Cl}_2$ ⁵⁰ were synthesized according to literatures, respectively.

2. Synthesis. *Synthesis of N,N'-[1,4-Butanediylbis(oxy-7,1-naphthalenediyl)]bis(2-pyridinecarboxamide) (H_2L^4).* A solution of thionyl chloride (2.0 mL, 28 mmol) in benzene (3 mL) was dropwise added to a suspension of picolinic acid (0.752 g, 6.11 mmol) in benzene (3 mL) at 0 °C over 15 min under nitrogen. The mixture was stirred for 30 min at room temperature and subsequently heated under reflux for 60 min. After removal of excess thionyl chloride and benzene under high vacuum, the residue was dissolved in benzene (3 mL). The solution was added to a solution of 7,7'-(1,4-butanedioldioxy)bis(1-naphthalenamine) (0.811 g, 2.18 mmol) in pyridine (2.0 mL) at room temperature. After heating under reflux for 3 h, the mixture was cooled at room temperature. Chloroform was added to the mixture, and a chloroform-insoluble fraction was removed by filtration. After the filtrate was washed with saturated $\text{NaHCO}_3(\text{aq})$, the organic layer was dried with Na_2SO_4 and concentrated under high vacuum. The crude product was purified by silica gel chromatography with chloroform ($R_f = 0.50$) and subsequent recrystallization from chloroform/hexane to afford H_2L^4 as a slightly yellow needle crystal (0.640 g, 1.10 mmol, 50.5%). Mp: 143.5–146.0 °C. ^1H NMR (CDCl_3): δ 2.12 (m, 4H, CH_2), 4.26 (m, 4H, OCH_2), 7.20 (dd, $J = 8.8$ and 2.4 Hz, 2H, Ar–H), 7.34 (d, $J = 2.4$ Hz, 2H, Ar–H), 7.40 (t, $J = 8.0$ Hz, 2H, Ar–H), 7.44 (ddd, $J = 7.2$, 4.8, and 1.2 Hz, 2H, Ar–H), 7.64 (d, $J = 8.0$ Hz, 2H, Ar–H), 7.78 (d, $J = 8.8$ Hz, 2H, Ar–H), 7.90 (td, $J = 7.2$ and 1.6 Hz, 2H, Ar–H), 8.23 (d, $J = 8.0$ Hz, 2H, Ar–H), 8.33 (dd, $J = 7.2$ and 1.2 Hz, 2H, Ar–H), 8.60 (dd, $J = 4.8$ and 1.6 Hz, 2H, Ar–H), 10.63 (br, 2H, NH). IR (KBr, cm^{-1}): 3363 ($\nu_{\text{N-H}}$), 1693 ($\nu_{\text{C=O}}$), 1543 ($\nu_{\text{N-C=O}}$), 1234 ($\nu_{\text{C-O-C}}$). FAB-MS: m/z 583.3 [calcd for $\text{C}_{36}\text{H}_{31}\text{N}_4\text{O}_4$ ($[\text{M} + \text{H}]^+$): m/z 583.2]. Anal. Calcd for $\text{C}_{36}\text{H}_{30}\text{N}_4\text{O}_4$: C, 74.21; H, 5.19; N, 9.62. Found: C, 73.85; H, 5.27; N, 9.63.

Synthesis of [[N,N'-[1,4-Butanediylbis(oxy-7,1-naphthalenediyl)]bis(2-pyridinecarboxamidato)](2-)- $\kappa\text{N}_1,\kappa\text{N}_1',\kappa\text{N}_2,\kappa\text{N}_2'$]palladium (PdL^4). A solution of H_2L^4 (290 mg, 498 μmol) in chloroform (25 mL) was added to a solution of $\text{Pd}(\text{cod})\text{Cl}_2$ (143 mg, 501 μmol) in chloroform (50 mL). After the addition of triethylamine (1.4 mL, 10 mmol), the mixture was heated under reflux for 26 h. During heating, the mixture gradually changed to a reddish-brown suspension. After filtration of the suspension, the filtrate was concentrated under high vacuum to leave a crude product. The product was purified by silica gel chromatography with ethyl acetate and subsequent recrystallization from dichloromethane/diethyl ether to afford PdL^4 as an orange needle crystal (68.6 mg, 99.8 μmol , 20.0%). ^1H NMR (CDCl_3): δ 1.95–2.15 (m, 4H, CH_2), 4.20–4.30 (m, 2H, OCH_2), 4.35–4.50 (m, 2H, OCH_2), 6.48 (d, $J = 5.6$ Hz, 2H, Ar–H), 6.68 (ddd, $J = 7.6$, 5.6, and 1.6 Hz, 2H, Ar–H), 7.11 (dd, $J = 8.8$ and 2.4 Hz, 2H, Ar–H), 7.46 (t, $J = 7.6$ Hz, 2H, Ar–H), 7.58 (d, $J = 7.6$ Hz, 2H, Ar–H), 7.72 (td, $J = 7.6$ and 1.6 Hz, 2H, Ar–H), 7.78 (d, $J = 8.8$ Hz, 2H, Ar–H), 7.82 (d, $J = 7.6$ Hz, 2H, Ar–H), 7.99 (dd, $J = 7.6$ and 1.6 Hz, 2H, Ar–H), 8.31 (d, $J = 2.4$ Hz, 2H, Ar–H). IR (KBr, cm^{-1}): 1628 ($\nu_{\text{C=O}}$), 1250 ($\nu_{\text{C-O-C}}$). FAB-MS: m/z 686.0 (calcd for $\text{C}_{36}\text{H}_{28}\text{N}_4\text{O}_4\text{Pd}$ ($[\text{M}]^+$): m/z 686.1). Anal. Calcd for $\text{C}_{36}\text{H}_{28}\text{N}_4\text{O}_4\text{Pd}$: C, 62.93; H, 4.11; N, 8.15. Found: C, 62.98; H, 4.35; N, 8.01.

Synthesis of N,N'-Bis[(1H-pyrrol-2-yl)methylidene]-7,7'-(1,4-butanedioldioxy)bis(1-naphthalenamine) (H_2L^5).^{29b} Na_2SO_4 was added to a solution of 1H-pyrrole-2-carbaldehyde (0.51 g, 5.4 mmol) and 7,7'-(1,4-butanedioldioxy)bis(1-naphthalenamine) (0.502 g, 1.35 mmol) in chloroform (20 mL). After the suspension was stirred at room temperature for 3 weeks, a chloroform-insoluble fraction was removed by filtration. The crude product obtained by concentration of

the filtrate was purified by silica gel chromatography with chloroform/ethyl acetate (10:1, v/v) and subsequent recrystallization from chloroform/hexane to afford H_2L^5 as a slightly yellow crystal (0.528 g, 1.00 mmol, 74.4%). ^1H NMR (CDCl_3): δ 2.07 (m, 4H, CH_2), 4.29 (m, 4H, OCH_2), 5.82 (br, 2H, Ar–H), 6.00 (dd, $J = 3.6$ and 2.4 Hz, 2H, Ar–H), 6.61 (dd, $J = 2.4$ and 1.2 Hz, 2H, Ar–H), 7.08 (d, $J = 7.2$ Hz, 2H, Ar–H), 7.21 (dd, $J = 8.8$ and 2.4 Hz, 2H, Ar–H), 7.38 (t, $J = 7.2$ Hz, 2H, Ar–H), 7.70 (d, $J = 8.8$ Hz, 2H, Ar–H), 7.80 (d, $J = 7.2$ Hz, 2H, Ar–H), 7.81 (d, $J = 2.4$ Hz, 2H, Ar–H), 8.28 (s, 2H, C(=N)H), 11.18 (br, 2H, NH). IR (KBr, cm^{-1}): 1620 ($\nu_{\text{C=N}}$), 1250 ($\nu_{\text{C-O-C}}$). FAB-MS: m/z 527.2 (calcd for $\text{C}_{34}\text{H}_{31}\text{N}_4\text{O}_2$ ($[\text{M} + \text{H}]^+$): m/z 527.2).

Synthesis of [[2,2'-[1,4-Butanediylbis[(oxy-7,1-naphthalenediyl)imino]methyl]]dipyrrolato](2-)- $\kappa\text{N}_1,\kappa\text{N}_1',\kappa\text{N}_2,\kappa\text{N}_2'$]palladium (PdL^5). A solution of H_2L^5 (263 mg, 499 μmol) in chloroform (25 mL) was added to a solution of $\text{Pd}(\text{cod})\text{Cl}_2$ (142 mg, 497 μmol) in chloroform (50 mL), and the mixture was stirred at room temperature for 26 h. The crude product obtained by concentration of the mixture was purified by silica gel chromatography with chloroform and subsequent recrystallization from dichloromethane/hexane to afford PdL^5 as a yellow plate crystal (66.3 mg, 105 μmol , 21.1%). ^1H NMR (CDCl_3): δ 1.95–2.15 (m, 4H, CH_2), 4.15–4.30 (m, 2H, OCH_2), 4.40–4.50 (m, 2H, OCH_2), 4.68 (br, 2H, Ar–H), 5.74 (dd, $J = 3.6$ and 2.4 Hz, 2H, Ar–H), 6.67 (d, $J = 3.6$ Hz, 2H, Ar–H), 7.18 (dd, $J = 8.8$ and 2.4 Hz, 2H, Ar–H), 7.34 (d, $J = 7.6$ Hz, 2H, Ar–H), 7.40 (t, $J = 7.6$ Hz, 2H, Ar–H), 7.47 (s, 2H, C(=N)H), 7.83 (d, $J = 8.8$ Hz, 2H, Ar–H), 7.85 (d, $J = 7.6$ Hz, 2H, Ar–H), 8.07 (d, $J = 2.4$ Hz, 2H, Ar–H). IR (KBr, cm^{-1}): 1583 ($\nu_{\text{C=N}}$). FAB-MS: m/z 630.0 (calcd for $\text{C}_{34}\text{H}_{28}\text{N}_4\text{O}_2$ ($[\text{M}]^+$): m/z 630.1). Calcd for $\text{C}_{34}\text{H}_{28}\text{N}_4\text{O}_2\text{Pd}\cdot\text{CH}_2\text{Cl}_2\cdot\text{H}_2\text{O}$: 0.4C₆H₁₄: C, 58.46; H, 4.93; N, 7.29. Found: C, 58.62; H, 4.61; N, 6.98.

3. Optical Resolutions. A typical procedure for optical resolutions of PdL^4 and PdL^5 is described as follows. A stock solution (1 mg mL^{-1}) of PdL^4 in a mixture of chloroform/ethanol (50:1, v/v) was prepared. A 1.5 mL aliquot of the PdL^4 solution was injected into an HPLC system [eluent, chloroform/ethanol (50:1, v/v); flow speed, 6.5 mL min^{-1}] with a SUMICHIRAL OA-4600 [25×2 (i.d.) cm] to collect fractions. The solvents of the fractions were removed under reduced pressure at low temperature (less than 20 °C). The same operations were repeatedly carried out 10 times to give enantiometrically pure (–)₃₅₀- PdL^4 (the first eluent) and (+)₃₅₀- PdL^4 (the second eluent) as white powders. The optical purities of the collected fractions were estimated to be more than 99% ee by chiral HPLC analyses.

PdL^5 was also resolved using the same column with a different eluent: hexane/ethanol (100:1, v/v).

4. CD Measurements. In order to measure CD spectra of the isolated stereoisomers of the palladium complexes, each stock solution of the palladium complexes in 1,2-dichloroethane [1.90 mg/10 mL (2.77×10^{-4} mM) for PdL^4 and 6.35 mg/10 mL (8.87×10^{-4} mM) for PdL^5] was prepared in measuring flasks. Each stock solution was transferred to a 0.1 cm quartz cell by a pipet (ca. 0.5 mL). CD spectra of the stereoisomers of the complexes were measured at the range of 210–500 nm at room temperature (ca. 22–24 °C).

5. Thermodynamic Investigations. A typical procedure for investigation of the thermal stabilities of the isolated stereoisomers of the palladium complexes is described as follows. The solution of (–)₃₅₀- PdL^4 in a mixture of hexane/ethanol (9:1, v/v) was prepared and then kept at 50 °C for a predetermined amount of time. At each predetermined time, a 100 μL aliquot of the solution was injected into the chiral HPLC system to estimate an enantiomeric population of PdL^4 . The enantiomer populations were plotted versus time, and then an initial rate constant (k_T) of isomerization was calculated. Further, the isomerization barrier ($\Delta G^\ddagger$) of PdL^4 was calculated by using k_T and the Eyring equation.⁵¹

6. Instruments. NMR measurements (400 MHz for ^1H and 100 MHz for ^{13}C) were performed with CDCl_3 as the solvent at 30 °C on a Bruker BioSpin DPX-400 spectrometer with respect to tetramethylsilane (TMS; δ 0.00). IR spectra were recorded using a Horiba FT-720 spectrometer. FAB-MS spectra were measured using a JEOL JMX-AX505H mass spectrometer. Absorption measurements were

performed on a JASCO V-550 spectrometer. CD measurements were carried out with a JASCO J-720 spectropolarimeter. Melting points were measured using a MEL-TEMP II melting point apparatus (Laboratory Devices, MA). Elemental analyses were performed by using a Yanaco MT-6 CHN analyzer. HPLC experiments for estimations of enantiomeric excesses were carried out on a Hitachi instrument (L-7610 degasser, L-6000 pump, L-7400 UV detector, and D-2500 integrator) with a SUMICHIRAL OA-4600 [25 × 0.46 (i.d.) cm, 5 μm particle; Sumika Chemical Analysis Service, Osaka, Japan]. HPLC experiments for separations and isolations of stereoisomers were performed on a Hitachi instrument (L-7110 pump, L-7250 autosampler, L-4000H UV detector, L-5200 fraction collector, and D-2500 integrator) with a SUMICHIRAL OA-4600 [25 × 2 (i.d.) cm, 5 μm particle]. Single-crystal X-ray analyses were conducted using a Bruker AXS SMART X-ray diffractometer equipped with a CCD area director and Mo K α radiation (λ = 0.71073 Å).

■ ASSOCIATED CONTENT

■ Supporting Information

X-ray crystallographic data in CIF format, synthesis of CuL³, single-crystal X-ray data of CuL³, PdL⁴, and PdL⁵, and chiral HPLC profiles on racemization investigations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hrssgmt@rs.kagu.tus.ac.jp.

Notes

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- (37) In our laboratory, metalloporphyrins have frequently been employed not only as catalysts for precision macromolecular syntheses (polymethacrylates, polyesters, polyethers, polycarbonates, and so on)³⁸ but also as chiral catalysts for asymmetric syntheses^{32,33} and chiral selectors for biomolecules.^{34–36} In addition, a first clear example of an enantiomer-selective polymerization of a racemic epoxide with chiral initiator systems was reported to afford an optically active polyether in our former laboratory.³⁹ Thereafter, Jacobsen and Coates reported chiral Schiff base/metal complexes as effective catalysts for enantiomer-selective reactions and polymerizations of racemic epoxides to afford optically active diols and their analogues,⁴⁰ polyethers,⁴¹ and polycarbonates⁴² generated by using alternating copolymerization with carbon dioxide. In general, chiral metalloporphyrins⁴³ and salen-type [N₂O₂]-Schiff base/metal complexes⁴⁴ utilized as asymmetric catalysts were composed of chiral tetradentate ligands “porphyrins” or “salen-type Schiff bases” and octahedrally coordinated metals to preferentially adopt square-planar structures due to rigidity of the ligands. Other tetradentate compounds such as porphyrins and salen-type Schiff bases are expected to be effective ligands for asymmetric syntheses. Because achiral tetradentate compounds with the aid of four- or six-coordinate metals form chiral square-planar metal complexes such as chiral metalloporphyrins, the complexes adopt unique “fly-over” structures, being planar-chiral. Therefore, in this report, we focus our attention on the chiral structures of new “strapped” square-planar complexes comprised of flexible tetradentate ligands and square-planar-coordinated metals.
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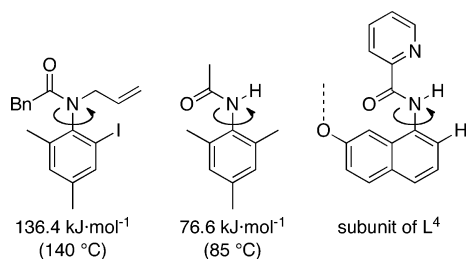
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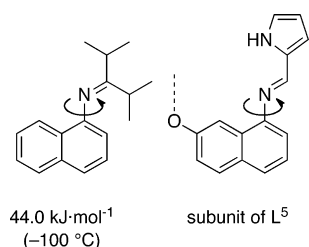
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