Inorganic Chemistry

Article

pubs.acs.org/IC

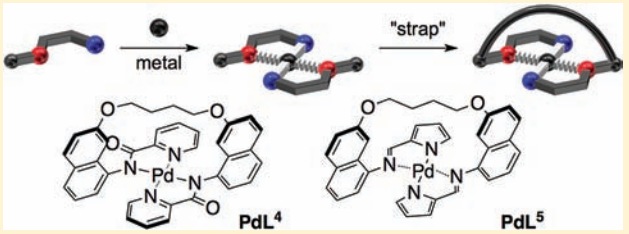
Planar-Chiral Metal Complexes Comprised of Square-Planar Metal and Achiral Tetradentate Ligands: Design, Optical Resolution, and Thermodynamics

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

Supporting Information

ABSTRACT: Planar-chiral palladium complexes {[[*N*,*N*′-[1,4-butanediylbis(oxy-7,1-naphthalenediyl)]bis(2-pyridinecarboxamidato)](2−)-κN_1,$\kappa N_1'$,κN_2,$\kappa N_2'$]palladium (**PdL^4**) and [[2,2′-[1,4-butanediylbis[[(oxy-7,1-naphthalenediyl)imino]methyl]]dipyrrolato](2−)-κN_1,$\kappa N_1'$,κN_2,$\kappa N_2'$]palladium (**PdL^5**)} were synthesized from *achiral* tetradentate ligands *N*,*N*′-[1,4-butanediylbis(oxy-7,1-naphthalenediyl)]bis(2-pyridinecarboxamide) (**H$_2$L^4**) and *N*,*N*′-bis[(1*H*-pyrrol-2-yl)methylidene]-7,7′-(1,4-butanediyldioxy)bis-(1-naphthalenamine) (**H$_2$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) Å, b = 11.3534(4) Å, c = 17.6697(7) Å, β = 115.5300(10)°, and Z = 4 for **PdL^4** and a = 17.2271(8) Å, b = 10.1016(5) Å, c = 17.9361(9) Å, β = 105.6310(10)°, 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 properties[6] 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 tetradentate[23] ligands transform into the other antipodes rather quickly. Nevertheless, optical resolutions of chiral tetrahedral complexes with two dissymmetric bidentate[24] or four district monodentate[25] 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

Received: November 18, 2011
Published: March 21, 2012

   dx.doi.org/10.1021/ic2024742 | *Inorg. Chem.* 2012, 51, 4134−4142

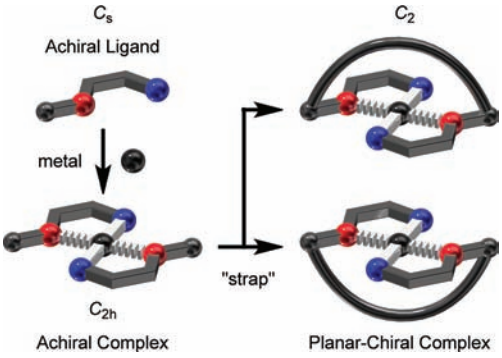
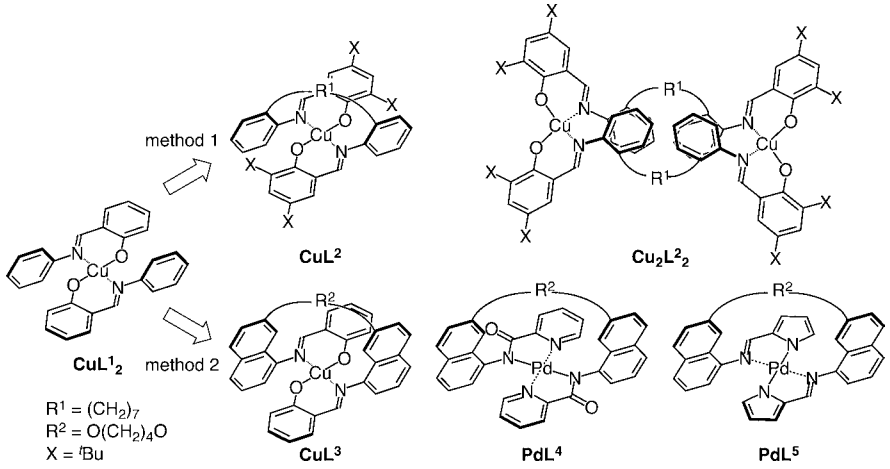


Figure 1. Concept of a planar-chiral metal complex (black sphere, metal; red and blue spheres, metal-binding site; white tube, coordinate bond; gray tube, covalent bond). Two C_s-symmetric bidentate ligands are coordinated to the metal to form a C_{2h}-symmetric square-planar complex. Cross-linking between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

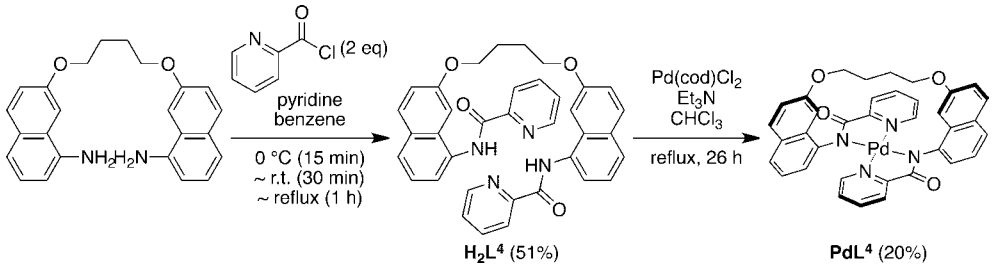
In our and others' laboratories, metal complexes of planar-chiral porphyrins obtained by intramolecular cross-linkings of *achiral* tetradentate porphyrins having enantiotopic faces (C_{2h} or C_{4h} symmetry) were found to serve as effective chiral catalysts for asymmetric oxidations[32,33] and as effective 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$^1_2$**; 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-heptanediylbis[[(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-heptanediylbis[[(1,2-phenylenediyl)imino]methyl]]bis(4,6-di-*tert*-butylphenolate)]-(2−)-$\kappa N_2,\kappa N_2',\kappa O_1,\kappa O_1'$]copper (**CuL^2**), but an achiral (meso) ladder complex with a 2:2 composition {bis[2,2′-[1,7-heptanediylbis[[(1,2-phenylenediyl)imino]methyl]]bis(4,6-di-*tert*-butylphenolate)]dicopper complex, **Cu$_2$L$^2_2$**}, 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-butanediylbis-[[(oxy-7,1-naphthalenediyl)imino]methyl]]bis(phenolate)]-(2−)-$\kappa N_2,\kappa N_2',\kappa O_1,\kappa O_1'$]copper (**CuL^3**) comprised of copper-(II) and a newly employed ligand {2,2′-[1,4-butanediylbis-[[(oxy-7,1-naphthalenediyl)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-butanediylbis-(oxy-7,1-naphthalenediyl)]bis(2-pyridinecarboxamidato)]-(2−)-$\kappa N_1,\kappa N_1',\kappa N_2,\kappa N_2'$]palladium (**PdL^4**) and [[2,2′-[1,4-butanediylbis[[(oxy-7,1-naphthalenediyl)imino]methyl]]-dipyrrolato](2−)-$\kappa N_1,\kappa N_1',\kappa N_2,\kappa N_2'$]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-pyridinecarboxamido[46] and 2-(*N*-phenylimino)methyl-1*H*-pyrrolato[47]] in *N*,*N*′-[1,4-butanediylbis(oxy-7,1-naphthalenediyl)]bis(2-pyridinecarboxamidato)(2−) (**L^4**) and 2,2′-[1,4-butanediylbis-[[(oxy-7,1-naphthalenediyl)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

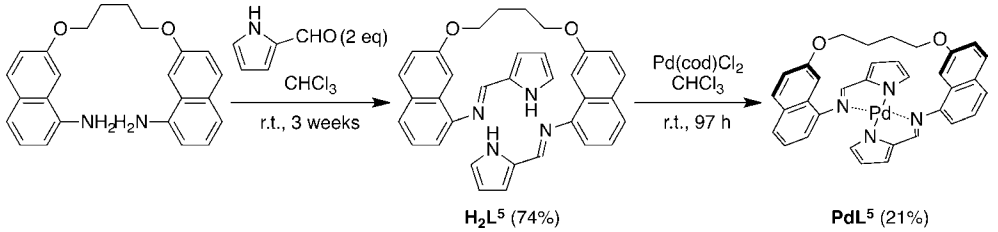


dx.doi.org/10.1021/ic2024742 | *Inorg. Chem.* 2012, 51, 4134−4142

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-Butanediyldioxy)bis(1-naphthalenamine)[29b] as a starting material in both schemes was reacted with picolinoyl chloride[48] or 1*H*-pyrrole-2-carbaldehyde[49] to obtain the corresponding compounds **H$_2$L^4** and **H$_2$L^5**, respectively. The reactions of the compounds with dichloro(1,5-cyclooctadiene)palladium(II) (Pd(cod)Cl$_2$)[50] were followed by ^{1}H NMR spectroscopy (Figures S2 and S3 in the Supporting Information). Upon the addition of **H$_2$L^4** or **H$_2$L^5** to Pd(cod)Cl$_2$, the signals assignable to the amide (NH for **H$_2$L^4**) and pyrrole (NH for **H$_2$L^5**) at 10−12 ppm became gradually smaller, as we expected. Furthermore the obtained product from palladium(II) and **H$_2$L^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 ([**L^4**]$^{2-}$). In the case of **H$_2$L^5**, the signals assignable to the 1:1 complex of palladium(II) and [**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$_2$L^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_{2h} 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-butylenedioxy group connected to 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$_2$L^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

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

	PdL^4	PdL^5
formula	$[C_{36}H_{28}N_4O_4]Pd$	$[C_{34}H_{28}N_4O_2]Pd$ (CH_2Cl_2)
fw	687.02	714.92
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
T/K	90	90
a/Å	16.5464(6)	17.2271(8)
b/Å	11.3534(4)	10.1016(5)
c/Å	17.6697(7)	17.9361(9)
α/deg	90	90
β/deg	115.5300(10)	105.6310(10)
γ/deg	90	90
V/Å^3	2995.29(19)	3005.8(3)
Z	4	4
ρ_{calcd}/g cm^{-3}	1.524	1.580
μ(Mo Kα)/mm^{-1}	0.668	0.836
F(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 [R_{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 R1 [wR2]	0.0308 [0.0783]	0.0276 [0.0766]
final R1 [wR2] (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

dx.doi.org/10.1021/ic2024742 | Inorg. Chem. 2012, 51, 4134−4142

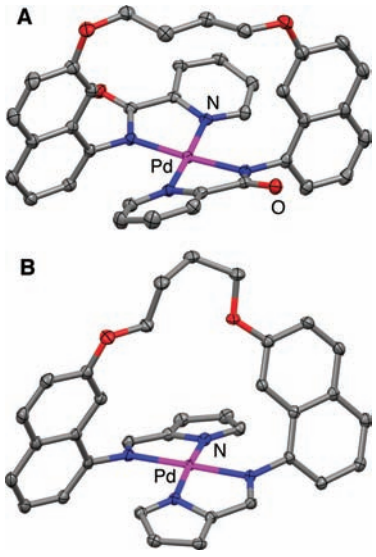


Figure 2. Ball-and-stick drawings of **PdL^4** (A) and **PdL^5** (B) with thermal ellipsoids at 50% probability (carbon, gray; nitrogen, blue; oxygen, red; palladium, pink). Each one of the independent complexes is shown here. H atoms (for A and B) and solvent molecules (for B) are omitted for clarity.

ranges of 80.5−80.6° and 99.0−99.8° (cis) and 172.3−178.8° (trans), and Pd−N−C_{naph}−C_{naph} dihedral angles in the range of 61.4−71.6°.[47]

The chiral conformations of **PdL^4** and **PdL^5** in solutions were suggested by ^{1}H NMR spectroscopy. The ^{1}H 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 ^{1}H 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. ^{1}H 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 [$(-)_{350}$-**PdL^4**], which has a maximum intensity in the long-wavelength region ["$(-)_{350}$" denotes the sign of the peak at 350 nm, vide infra], whereas the second fraction showed a positive peak [$(+)_{350}$-**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 [$(-)_{350}$- and $(+)_{350}$-**PdL^4**'s] 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^4**: one is $(-)_{350}$-**PdL^5** (the first fraction, 9.32 min), and the other is

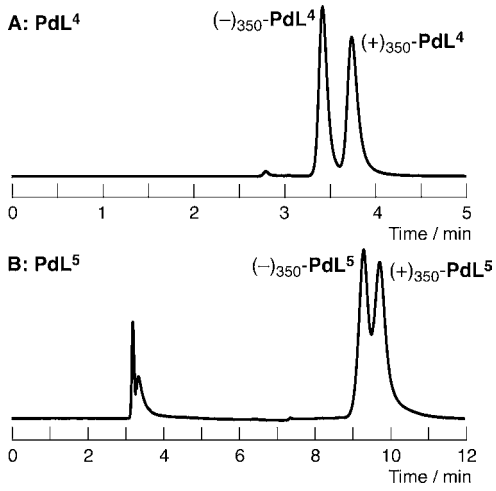


Figure 3. Chromatographic resolution of stereoisomers of **PdL^4** (A) and **PdL^5** (B) on SUMICHIRAL OA-4600. Column: 25 × 0.46 (i.d.) cm. Eluent: chloroform/ethanol (50:1, v/v) (A); hexane/ethanol (100:1, v/v) (B). Flow rate: 1 mL min^{-1}.

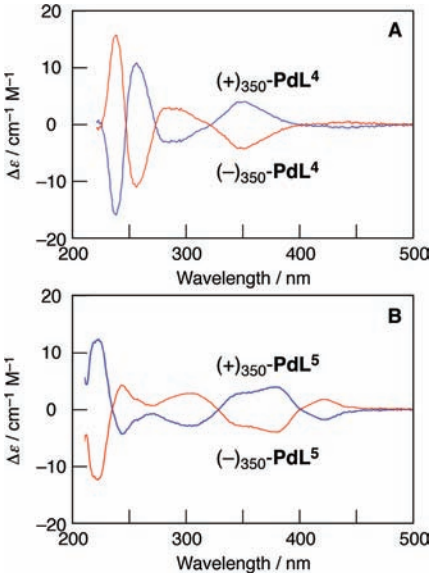


Figure 4. CD spectra of fractions of **PdL^4** (A) and **PdL^5** (B) (red line, $(-)_{350}$ isomers; blue line, $(+)_{350}$ isomers) in 1,2-dichloroethane at room temperature. [Pd complex] = 0.28 (**PdL^4**) and 0.89 (**PdL^5**) mM.

$(+)_{350}$-**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 $(-)_{350}$-**PdL^4** and $(-)_{350}$-**PdL^5** were kept at room temperature (ca. 22−24 °C) for a predetermined amount of time. The peak of the chromatogram for $(-)_{350}$-**PdL^4** gradually became lower over time, while that for $(+)_{350}$-**PdL^4** became higher. No other peaks were observed during incubation of the solution. Furthermore, the ^{1}H 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

dx.doi.org/10.1021/ic2024742 | Inorg. Chem. 2012, 51, 4134−4142

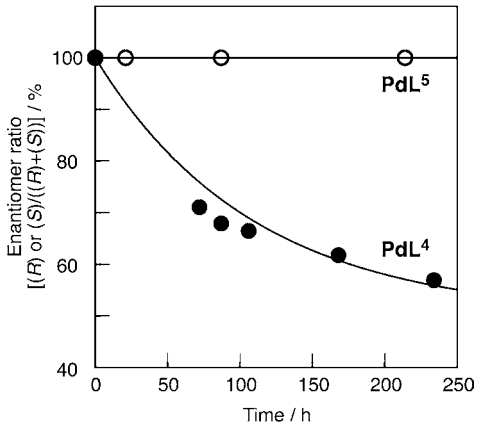


Figure 5. Racemization behaviors of **PdL^4** (full circles) in chloroform/ethanol (50:1, v/v) and **PdL^5** (opened circles) in hexane/ethanol (100:1, v/v) at room temperature. The black solid curve is calculated using the first-order rate equation.

period ($\tau_{1/2}$) of racemization were estimated to be 1.27×10^{-6} 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 $(-)_{350}$-**PdL^5** was observed under the same condition as that of $(-)_{350}$-**PdL^4**; assuming that a small amount (1.0 mol %) of $(-)_{350}$-**PdL^5** is racemized, the values can be calculated as follows: $k < 1.31 \times 10^{-8}$ s^{-1}, $\tau_{1/2} > 7350$ h, and $\Delta G^{\ddagger} > 117$ 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**.

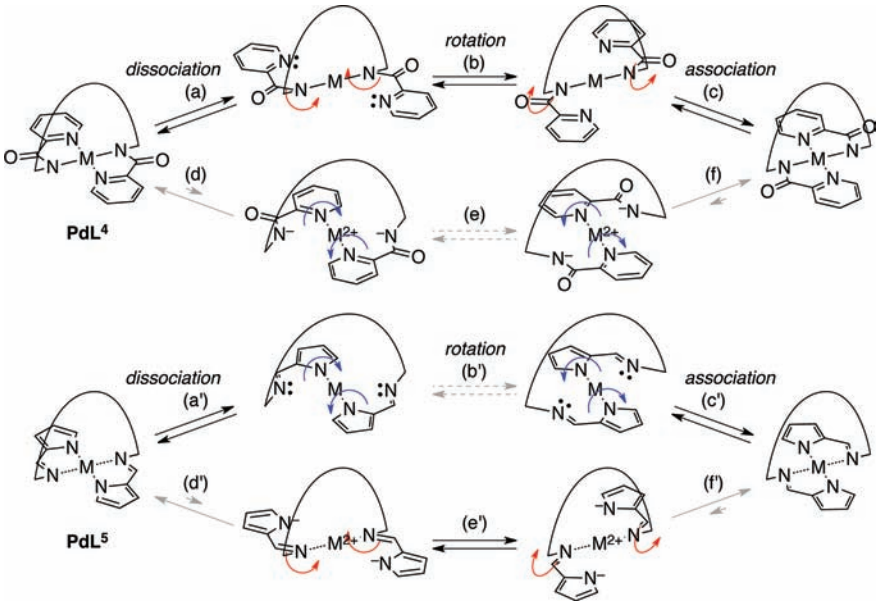
CONCLUSIONS

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



dx.doi.org/10.1021/ic2024742 | *Inorg. Chem.* 2012, 51, 4134−4142

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-Butanediyldioxy)bis(1-naphthalenamine),[29b] 1*H*-pyrrole-2-carbaldehyde,[49] and Pd(cod)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-butanediyldioxy)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 $NaHCO_3$(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. ^{1}H 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, N*H*). IR (KBr, cm^{-1}): 3363 (ν_{N-H}), 1693 ($\nu_{C=O}$), 1543 ($\nu_{N-C=O}$), 1234 (ν_{C-O-C}). FAB-MS: m/z 583.3 [calcd for $C_{36}H_{31}N_4O_4$ ([M + H]$^+$): m/z 583.2]. Anal. Calcd for $C_{36}H_{30}N_4O_4$: 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−)-κN_1,κN_1′,κN_2,κN_2′]palladium (**PdL^4**).* A solution of **H_2L^4** (290 mg, 498 μmol) in chloroform (25 mL) was added to a solution of Pd(cod)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%). ^{1}H 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 ($\nu_{C=O}$), 1250 (ν_{C-O-C}). FAB-MS: m/z 686.0 (calcd for $C_{36}H_{28}N_4O_4Pd$ ([M]$^+$): m/z 686.1). Anal. Calcd for $C_{36}H_{28}N_4O_4Pd$: 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-butanediyldioxy)bis(1-naphthalenamine) (**H_2L^5**).*[29b] Na_2SO_4 was added to a solution of 1*H*-pyrrole-2-carbaldehyde (0.51 g, 5.4 mmol) and 7,7′-(1,4-butanediyldioxy)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%). ^{1}H 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, N*H*). IR (KBr, cm^{-1}): 1620 ($\nu_{C=N}$), 1250 (ν_{C-O-C}). FAB-MS: m/z 527.2 (calcd for $C_{34}H_{31}N_4O_2$ ([M + H]$^+$): m/z 527.2).

*Synthesis of [[2,2′-[1,4-Butanediylbis[[(oxy-7,1-naphthalenediyl)-imino]methyl]]dipyrrolato](2−)-κN_1,κN_1′,κN_2,κN_2′]palladium (**PdL^5**).* A solution of **H_2L^5** (263 mg, 499 μmol) in chloroform (25 mL) was added to a solution of Pd(cod)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%). ^{1}H 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 ($\nu_{C=N}$). FAB-MS: m/z 630.0 (calcd for $C_{34}H_{28}N_4O_2$ ([M]$^+$): m/z 630.1). Calcd for $C_{34}H_{28}N_4O_2Pd\cdot CH_2Cl_2\cdot H_2O\cdot 0.4C_6H_{14}$: 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 enantiomerically 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 ^{1}H 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

dx.doi.org/10.1021/ic2024742 | *Inorg. Chem.* 2012, 51, 4134−4142

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 Kα radiation (λ = 0.71073 Å).

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format, synthesis of **CuL**^{3}, single-crystal X-ray data of **CuL**^{3}, **PdL**^{4}, and **PdL**^{5}, 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

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Prof. Y. Nagao, Dr. K. Kozawa, Prof. K. Miyamura, and K. Ueji of our university for single-crystal X-ray crystallographic analyses.

■ REFERENCES

(1) (a) Lippard, S. J.; Berg, J. M. *Principles of Bioinorganic Chemistry*; University Science Books: Mill Valley, CA, 1994. (b) Fraústo da Silva, J. J. R.; Williams, R. J. P. *The Biological Chemistry of the Elements: The Inorganic Chemistry of Life*, 2nd ed.; Oxford University Press: Oxford, U.K., 2001. (c) *Biological Inorganic Chemistry: Structure & Reactivity*; Bertini, I., Gray, H. B., Stiefel, E. I., Valentine, J. S., Eds.; University Science Books: Sausalito, CA, 2007. (d) Ochiai, E. *Bioinorganic Chemistry: A Survey*; Academic Press: Burlington, MA, 2008.

(2) Reviews on stereochemistry of chiral metal complexes: (a) *Stereochemistry of Optically Active Transition Metal Compounds*; Douglas, B. E., Saito, Y., Eds.; American Chemical Society: Washington DC, 1980. (b) Amouri, H.; Gruselle, M. *Chirality in Transition Metal Chemistry*; John Wiley & Sons: West Sussex, U.K., 2008; Chapters 1−3 and 5, pp 1−97 and 121−178. (c) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*, 2nd ed.; John Wiley & Sons: West Sussex, U.K., 2009; Chapter 10, pp 591−706.

(3) Reviews on chiral aggregates of metal complexes: (a) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975−982. (b) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853−908. (c) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483−3537. (d) Stoddart, J. F.; Lindoy, L. F.; Atkinson, I. M. *Self-Assembly in Supramolecular Systems*; The Royal Society of Chemistry: Cambridge, U.K., 2000; Chapter 7, pp 185−219. (e) Seeber, G.; Tiedemann, B. E. F.; Raymond, K. N. *Top. Curr. Chem.* **2006**, *265*, 147−183. (f) Pluth, M. D.; Raymond, K. N. *Chem. Soc. Rev.* **2007**, *36*, 161−171. (g) Lee, S. J.; Lin, W. *Acc. Chem. Res.* **2008**, *41*, 521−537. (h) Scarso, A.; Borsato, G. In *Chirality at the Nanoscale*; Amabilino, D. B., Ed.; Wiley-VCH-Verlag: Weinheim, Germany, 2009; Chapter 2, pp 29−65.

(4) Reviews on helicates: (a) Piguet, C.; Bernardinelli, G.; Hopfgartner, G. *Chem. Rev.* **1997**, *97*, 2005−2062. (b) Stoddart, J. F.; Lindoy, L. F.; Atkinson, I. M. *Self-Assembly in Supramolecular Systems*; The Royal Society of Chemistry: Cambridge, U.K., 2000; Chapter 6, pp 119−184. (c) Albrecht, M. *Chem. Rev.* **2001**, *101*, 3457−3497. (d) Albrecht, M. *Top. Curr. Chem.* **2004**, *248*, 105−140.

(5) Reviews on helical coordination polymers: (a) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629−1658. (b) Batten, S. R.; Neville, S. M.; Turner, D. R. *Coordination Polymers: Design, Analysis and Application*; The Royal Society of Chemistry: Cambridge, U.K., 2009. Chapter 11, pp 345−374. (c) Leong, W. L.; Vittal, J. J. *Chem. Rev.* **2011**, *111*, 688−764.

(6) (a) Autschbach, J.; Nitsch-Velasquez, L.; Rudolph, M. *Top. Curr. Chem.* **2011**, *298*, 1−98. (b) Yang, G.; Xu, Y. *Top. Curr. Chem.* **2011**, *298*, 189−236.

(7) Reviews on chiral metal complexes for asymmetric reactions: (a) *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, Germany, 1995. (b) *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer Verlag: Berlin, 1999. (c) Fu, G. C. *Acc. Chem. Res.* **2000**, *33*, 412−420. (d) Knowles, W. S. *Angew. Chem., Int. Ed.* **2002**, *41*, 1998−2007. (e) Noyori, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008−2022. (f) Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2024−2032. (g) Satyanarayana, T.; Abraham, S.; Kagan, H. B. *Angew. Chem., Int. Ed.* **2009**, *48*, 456−494. (h) *Catalytic Asymmetric Synthesis*, 3rd ed.; Ojima, I., Ed.; John Wiley & Sons: Hoboken, NJ, 2010.

(8) Reviews on chiral supramolecular metal complexes for asymmetric reactions: (a) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 349−358. (b) Lin, W. In *Supramolecular Catalysis*; van Leeuwen, P. W. N. M., Ed.; Wiley-VCH-Verlag: Weinheim, Germany, 2008; Chapter 4, pp 93−111. (c) Pluth, M. D.; Bergman, R. G.; Raymond, K. N. In *Supramolecular Catalysis*; van Leeuwen, P. W. N. M., Ed.; Wiley-VCH-Verlag: Weinheim, Germany, 2008; Chapter 7, pp 165−197. (d) Takacs, J. M.; Moteki, S. A.; Reddy, D. S. In *Supramolecular Catalysis*; van Leeuwen, P. W. N. M., Ed.; Wiley-VCH-Verlag: Weinheim, Germany, 2008; Chapter 9, pp 235−253. (e) Pluth, M. D.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2009**, *42*, 1650−1659. (f) Wang, C.; Zheng, M.; Lin, W. *J. Phys. Chem. Lett.* **2011**, *2*, 1701−1709.

(9) (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170. (b) Kuran, W. *Principles of Coordination Polymerization*; John Wiley and Sons: West Sussex, U.K., 2001; Chapter 3, pp 43−245. (c) Suzuki, N. *Top. Organomet. Chem.* **2005**, *8*, 177−216.

(10) (a) Borovkov, V. V.; Hembury, G. A.; Inoue, Y. *Acc. Chem. Res.* **2004**, *37*, 449−459. (b) Borovkov, V. V.; Inoue, Y. *Top. Curr. Chem.* **2006**, *265*, 89−146. (c) Hembury, G. A.; Borovkov, V. V.; Inoue, Y. *Chem. Rev.* **2008**, *108*, 1−73.

(11) (a) Shinkai, S.; Ikeda, M.; Sugasaki, A.; Takeuchi, M. *Acc. Chem. Rev.* **2001**, *34*, 494−503. (b) Takeuchi, M.; Ikeda, M.; Sugasaki, A.; Shinkai, S. *Acc. Chem. Rev.* **2001**, *34*, 865−873. (c) James, T. D.; Phillips, M. D.; Shinkai, S. *Boronic Acids in Saccharide Recognition*; The Royal Society of Chemistry: Cambridge, U.K., 2006.

(12) (a) Tsukube, H.; Shinoda, S. *Chem. Rev.* **2002**, *102*, 2389−2403. (b) Kubo, Y.; Ishii, Y. *J. Nanosci. Nanotechnol.* **2006**, *6*, 1489−1509. (c) Anslyn, E. V. *J. Org. Chem.* **2007**, *72*, 687−699. (d) Joyce, L. A.; Maynor, M. S.; Dragna, J. M.; da Cruz, G. M.; Lynch, V. M.; Canary, J. W.; Anslyn, E. V. *J. Am. Chem. Soc.* **2011**, *133*, 13746−13752.

(13) (a) Wenzel, T. J. *Discrimination of Chiral Compounds Using NMR Spectroscopy*; John Wiley & Sons: Hoboken, NJ, 2007; Chapter 9, pp 331−398. (b) Amouri, H.; Gruselle, M. *Chirality in Transition Metal Chemistry*; John Wiley & Sons: West Sussex, U.K., 2008; Chapter 4, pp 99−120.

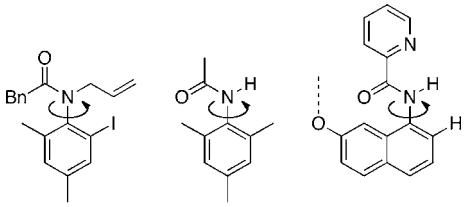
(14) (a) Lacour, J.; Hebbe-Viton, V. *Chem. Soc. Rev.* **2003**, *32*, 373−382. (b) Constant, S.; Lacour, J. *Top. Curr. Chem.* **2005**, *250*, 1−41. (c) Lacour, J.; Moraleda, D. *Chem. Commun.* **2009**, 7073−7089.

(15) (a) Masuda, Y.; Yamatera, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 58−62. (b) Yamagishi, A. *J. Coord. Chem.* **1987**, *16*, 131−211. (c) Bergman, S. D.; Kol, M. *Inorg. Chem.* **2005**, *44*, 1647−1654.

(16) Amouri, H.; Gruselle, M. *Chirality in Transition Metal Chemistry*; John Wiley & Sons: West Sussex, U.K., 2008; Chapter 6, pp 189−204.

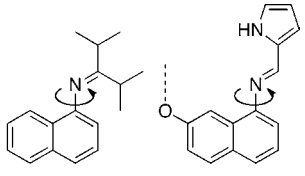
(17) (a) Knof, U.; von Zelewsky, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 302−322. (b) von Zelewsky, A.; Mamula, O. *J. Chem. Soc., Dalton Trans.* **2000**, 219−231.
(18) (a) Bailar, J. C. Jr. *J. Chem. Educ.* **1981**, *58*, 674−681. (b) Bailar, J. C. Jr. *Coord. Chem. Rev.* **1990**, *100*, 1−27.
(19) (a) Werner, A. *Z. Anorg. Allg. Chem.* **1893**, *3*, 267−330. (b) Werner, A. *Ann.* **1912**, *386*, 1−272. (c) Karrer, P. *Helv. Chim. Acta* **1920**, *3*, 196−232. (d) Morral, F. R. *Adv. Chem. Ser.* **1967**, *62*, 70−77.
(20) For chiral octahedral complexes having hexadentate ligands, see: (a) Dwyer, F. P.; Lions, F. *J. Am. Chem. Soc.* **1947**, *69*, 2917−2918. (b) Dwyer, F. P.; Gyarfas, E. C.; Mellor, D. P. *J. Phys. Chem.* **1954**, *59*, 296−297. (c) *Chelating Agents and Metal Chelates*; Dwyer, F. P., Mellor, D. P., Eds.; Academic Press: New York, 1964; references cited therein. (d) Busch, D. H.; Bailar, J. C. Jr. *J. Am. Chem. Soc.* **1953**, *75*, 4574−4575. (e) Das Sarma, B.; Bailar, J. C. Jr. *J. Am. Chem. Soc.* **1955**, *77*, 5476−5480. (f) Curry, J. D.; Busch, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 592−594.
(21) (a) Hunter, C. A.; Mayers, P. C. *Nature* **2001**, *411*, 763. (b) Guo, J.; Mayers, P. C.; Breault, G. A.; Hunter, C. A. *Nat. Chem.* **2010**, *2*, 218−222.
(22) Desvergnes-Breuil, V.; Hebbe, V.; Dietrich-Buchecker, C.; Sauvage, J.-P.; Lacour, J. *Inorg. Chem.* **2003**, *42*, 255−257.
(23) For tetrahedral metal complexes having tetradentate ligands, see: (a) Graf, E.; Graff, R.; Hosseini, M. W.; Huguenard, C.; Taulelle, F. *Chem. Commun.* **1997**, 1459−1451. (b) Green, S.; Nelson, A.; Warriner, S.; Whittaker, B. *J. Chem. Soc., Perkin Trans. 1* **2000**, 4403−4408.
(24) Tetrahedral metal complexes having bidentate ligands. For beryllium complexes, see: (a) Mills, W. B.; Gotts, R. A. *J. Chem. Soc.* **1926**, 3121−3131. (b) Busch, D. H.; Bailar, J. C. Jr. *J. Am. Chem. Soc.* **1954**, *76*, 5352−5353. For a zinc complex, see: (c) Liu, J. C. I.; Bailar, J. C. Jr. *J. Am. Chem. Soc.* **1951**, *73*, 5432−5433.
(25) For tetrahedral metal complexes having four distinct monodentate ligands, see: (a) Brunner, H.; Schindler, H.-D. *J. Organomet. Chem.* **1970**, *24*, c7−c10. (b) Brunner, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 249−260. (c) Jaouen, G.; Meyer, A.; Simonneaux, G. *Tetrahedron* **1975**, *31*, 1889−1895. (d) Flood, T. C.; DiSanti, F. J.; Miles, D. L. *Inorg. Chem.* **1976**, *15*, 1910−1918. (e) Leblanc, J. C.; Moise, C.; Tirouflet, J. *J. Organomet. Chem.* **1978**, *148*, 171−178. (f) Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 151−206 and references cited therein..
(26) For optical resolutions of copper(I) helicates, see: (a) Woods, C. R.; Benaglia, M.; Cozzi, F.; Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1830−1833. (b) Annunziata, R.; Benaglia, M.; Cinquini, M.; Cozzi, F.; Woods, C. R.; Siegel, J. S. *Eur. J. Org. Chem.* **2001**, 173−180. (c) Furusho, Y.; Goto, H.; Itomi, K.; Katagiri, H.; Miyagawa, Y.; Yashima, E. *Chem. Commun.* **2011**, *47*, 9795−9797.
(27) Square-planar complexes having achiral tetradentate ligands. For platinum complexes, see: (a) Mills, W. H.; Quibell, T. H. H. *J. Chem. Soc.* **1935**, 839−846. (b) Habu, T.; Bailar, J. C. Jr. *J. Am. Chem. Soc.* **1966**, *88*, 1128−1130. For palladium complexes, see: (c) Lindstone, A. G.; Mills, W. H. *J. Chem. Soc.* **1939**, 1754−1759. (d) Nakamura, K.; Komorita, T.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1056−1062.
(28) Helical conformations of square-planar complexes having achiral bi- or tetradentate ligands. For an optical resolution using crystallization, see: (a) Zhang, F.; Bai, S.; Yap, G. P. A; Tarwade, V.; Fox, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 10590−10599. For optical resolutions using chiral selectors, see: (b) Deuschel-Cornioley, C.; Stoeckli-Evans, H.; von Zelewsky, A. *J. Chem. Soc., Chem. Commun.* **1990**, 121−122. (c) O, W. W. N.; Lough, A. J.; Morris, R. H. *Organometallics* **2009**, *28*, 6755−6761.
(29) For examples on chiral "fly-over" complexes, see: (a) Schlesinger, N. *Ber* **1925**, *58*, 1877−1889. (b) Hendrickson, A. R.; Hope, J. M.; Martin, R. L. *J. Chem. Soc., Dalton Trans.* **1979**, 1497−1502. (c) Baker, A. T.; Martin, R. L.; Taylor, D. *J. Chem. Soc., Dalton Trans.* **1979**, 1503−1511. (d) Kraihanzel, C. S.; Sinn, E.; Gray, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 960−962. (e) Bailey, N. A.; Barrass, A.; Fenton, D. E.; Leal Gonzalez, M. S.; Moody, R.; Rodriguez de Barbarin, C. O. *J. Chem. Soc., Dalton Trans.* **1984**, 2741−2746. (f) Ransohoff, S.; Adams, M. T.; Dzugan, S. J.; Busch, D. H. *Inorg. Chem.* **1990**, *29*, 2945−2947. (g) Liu, Z.-C.; Shao, M.-C.; Tang, Y.-Q. *Gaodeng Xuexiao Huaxue Xuebao* **1990**, *11*, 58−61 (Chinese). (h) Khandar, A. A.; Cardin, C.; Hosseini-Yazdi, S. A.; McGrady, J.; Abedi, M.; Zarei, S. A.; Gan, Y. *Inorg. Chim. Acta* **2010**, *363*, 4080−4087. (i) Komiya, N.; Okada, M.; Fukumoto, K.; Jomori, D.; Naota, T. *J. Am. Chem. Soc.* **2011**, *133*, 6493−6496.
(30) For examples on optical resolutions of chiral "fly-over" complexes, see: (a) Naota, T.; Koori, H. *J. Am. Chem. Soc.* **2005**, *127*, 9324−9325. (b) Komiya, N.; Muraoka, T.; Iida, M.; Miyanaga, M.; Takahashi, K.; Naota, T. *J. Am. Chem. Soc.* **2011**, *133*, 16054−16061.
(31) Our researches on this theme have preliminarily been presented in a presymposium of an international symposium and in an international symposium. (a) Hayakawa, T.; Sugimoto, H.; Inoue, S. Poster PA-12 at Symposium on Molecular Chirality, Shizuoka, Japan, 2003. (b) Goto, H.; Hayakawa, T.; Furutachi, K.; Sugimoto, H.; Inoue, S. Poster PB-89 at the 22nd International Symposium on Chirality (ISCD-22), Sapporo, Japan, 2010.
(32) (a) Chiang, L.-C.; Konishi, K.; Aida, T.; Inoue, S. *J. Chem. Soc., Chem. Commun.* **1992**, 254−256. (b) Konishi, K.; Oda, K.; Nishida, K.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1992**, *114*, 1313−1317.
(33) Ito, A.; Konishi, K.; Aida, T. *Tetrahedron Lett.* **1996**, *37*, 2585−2588.
(34) Konishi, K.; Yahara, K.; Toshishige, H.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1994**, *116*, 1337−1344.
(35) (a) Konishi, K.; Kimata, S.; Yoshida, K.; Tanaka, M.; Aida, T. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2823−826. (b) Zheng, J.-Y.; Konishi, K.; Aida, T. *Tetrahedron* **1997**, *53*, 9115−9122. (c) Ishida, Y.; Konishi, K.; Aida, T.; Nagamume, T. *Chem.—Eur. J.* **1998**, *4*, 1148−1153. (d) Shoji, Y.; Tashiro, K.; Aida, T. *J. Am. Chem. Soc.* **2006**, *128*, 10690−10691. (e) Shoji, Y.; Tashiro, K.; Aida, T. *Chirality* **2008**, *20*, 420−424. (f) Shoji, Y.; Tashiro, K.; Aida, T. *J. Am. Chem. Soc.* **2010**, *132*, 5928−5929.
(36) (a) Kuroda, Y.; Kato, Y.; Higashioji, T.; Ogoshi, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 723−724. (b) Kuroda, Y.; Kato, Y.; Higashioji, T.; Hasegawa, J.; Kawanami, S.; Takahashi, M.; Shiraishi, N.; Tanabe, K.; Ogoshi, H. *J. Am. Chem. Soc.* **1995**, *117*, 10950−10958. (c) Mizutani, T.; Kurahashi, T.; Murakami, T.; Matsumi, N.; Ogoshi, H. *J. Am. Chem. Soc.* **1997**, *119*, 8991−9001.
(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 polycarbonates[42] generated by using alternating copolymerization with carbon dioxide. In general, chiral metalloporphyrins[43] and salen-type $[N_2O_2]$-Schiff base/metal complexes[44] 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.
(38) Aida, T.; Inoue, S. *The Porphyrin Handbook Vol. 6: Applications: Past, Present and Future*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Chapter 42, pp 133−156.

(39) (a) Inoue, S.; Tsuruta, T.; Furukawa, J. *Makromol. Chem.* **1962**, *53*, 215−218. (b) Tsuruta, T.; Inoue, S.; Yoshida, M.; Furukawa, J. *Makromol. Chem.* **1962**, *55*, 230−231.
(40) Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997**, *277*, 935−938.
(41) Hirahata, W.; Thomas, R. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2008**, *130*, 17658−17659.
(42) Qin, Z.-Q.; Thomas, C. M.; Lee, S.; Coates, G. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5484−5487.
(43) Marchon, J.-C.; Ramasseul, R. *The Porphyrin Handbook, Vol. 11: Bioinorganic and Bioorganic Chemistry*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2003; Chapter 64, pp 75−132.
(44) Jacobsen, E. N. *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon, New York, 1995; Vol. *12*, pp 1097−1135.
(45) Wei, L.; Stogsdill, R. M.; Lingafelter, E. C. *Acta Crystallogr.* **1964**, *17*, 1058−1062.
(46) Square-planar metal complexes of *N*-phenyl-2-pyridinecarboxamide derivatives as dissymmetric bidentate ligands. For copper(II): (a) Ray, M.; Mukherjee, R.; Richrdson, J. F.; Mashuta, M. S.; Buchanan, R. M. *J. Chem. Soc., Dalton Trans.* **1994**, 965−969. (b) Sunatsuki, Y.; Matsumoto, T.; Fukushima, Y.; Mimura, M.; Hirohata, M.; Matsumoto, N.; Kai, F. *Polyhedron* **1998**, *17*, 1943−1952. For platinum(II): (c) Zhang, J.-Y.; Liu, Q.; Duan, C.-Y.; Shao, Y.; Ding, J.; Miao, Z.-H.; You, X.-Z.; Guo, Z.-J. *Dalton Trans.* **2002**, 591−597. Although 1-naphthalenamide subunits of $\mathbf{H_2L^4}$ essentially possess axial chirality, it is probably difficult that the single subunit is optically resolved at ambient temperature because of an expectedly low rotational barrier: (d) Curran, D. P.; Chen, C. H.-T.; Geib, S. J.; Lapierre, A. J. B. *Tetrahedron* **2004**, *60*, 4413−4424. (e) Kessler, H.; Rieker, A. *Liebigs Ann. Chem.* **1967**, *708*, 57−68.



136.4 kJ·mol^{-1} (140 °C) 76.6 kJ·mol^{-1} (85 °C) subunit of L^4

(47) Square-planar metal complexes of 2-(*N*-phenylimino)methyl-1*H*-pyrrole derivatives as dissymmetric bidentate ligands. For copper(II): (a) Castro, J. A.; Romero, J.; Garcia-Vazquez, J. A.; Castineiras, A.; Duran, D. L.; Sousa, A. *Z. Anorg. Allg. Chem.* **1992**, *615*, 155−160. (b) Grushin, V. V.; Marshall, W. J. *Adv. Synth. Catal.* **2004**, *346*, 1457−1460. For palladium(II): (c) Yeh, K.-N.; Barker, R. H. *Inorg. Chem.* **1967**, *6*, 830−833. (d) Liang, H.; Liu, J.-G.; Li, X.-F.; Li, Y.-S. *Polyhedron* **2004**, *23*, 1619−1627. Although *N*-alkylidene-1-naphthalenamine subunits of $\mathbf{H_2L^5}$ essentially possess axial chirality as well, it is significantly difficult that the single subunit is optically resolved at ambient temperature because of an expectedly low rotational barrier: (e) Guerra, A.; Lunazzi, L. *J. Org. Chem.* **1995**, *60*, 7959−7965.



44.0 kJ·mol^{-1} (−100 °C) subunit of L^5

(48) Rowland, J. M.; Thornton, M. L.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **2001**, *40*, 1069−1073.
(49) Silverstein, R. M.; Ryskiewicz, E. E.; Chaikin, S. W. *J. Am. Chem. Soc.* **1953**, *76*, 4485−4486.
(50) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1972**, *13*, 47−55.
(51) The free activation energy for the racemization process was determined according to the Eyring equation: $\Delta G_T^{\ddagger} = -RT \ln(k_T h/\kappa k_B T)$, where R is the universal gas constant (=8.31441 J K^{-1} mol^{-1}), T the absolute temperature (K), k_T the kinetic rate constant, h Plank's constant (=6.626176 × 10^{-34} J s), κ the transition factor (κ = 0.5), and k_B Boltzmann's constant (=1.380662 × 10^{-23} J K^{-1}). (a) Trapp, O.; Trapp, G.; Kong, J.-W.; Hahn, U.; Vögtle, F.; Schurig, V. *Chem.—Eur. J.* **2002**, *8*, 3629−3634. (b) Osswald, P.; Würthner, F. *J. Am. Chem. Soc.* **2007**, *129*, 14319−14326. (c) Wolf, C. *Dynamic Stereochemistry of Chiral Compounds*; The Royal Society of Chemistry: Cambridge, U.K., 2008; Chapter 4, pp 136−179.
(52) For an example of a salen-type [N_2O_2] Schiff base playing a role as a bidentate ligand binding to a transition metal: (a) Na, S. J.; S, S.; Cyriac, A.; Kim, B. E.; Yoo, J.; Kang, Y. K.; Han, S. J.; Lee, C.; Lee, B. Y. *Inorg. Chem.* **2009**, *48*, 10455−10465. For examples on complexes having N atoms noncoordinated to metals, see: (b) Kaye, P. T.; Nyokong, T.; Watkins, G. M.; Wellington, K. W. *Arkivoc* **2002**, No. ix, 9−18. (c) Wellington, K. W.; Kaye, P. T.; Watkins, G. M. *Arkivoc* **2009**, No. xiv, 301−313. (d) Kose, M.; Mckee, V. *Acta Crystallogr.* **2011**, *E67*, m149.