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Article

Chiral Variation of a Hybrid Bis(carbene-amido) Ligand System

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A simple synthetic strategy starting from a chiral amino acid was used to prepare a unique chiral tetradentate hybrid dianionic bis(carbene-amido) ligand precursor, which was subsequently used for the generation of a chiral nickel complex.

Introduction

In recent years, the development of bi- or polydentate ligand precursors based on functionalized imidazolium salts incorporating more "classical heteroatom" donor(s) has attracted considerable attention.[1] In this context, heteroatom-functionalized carbene ligand precursors containing phosphine,[2] pyridine, pyrimidine, or amine,[3] amido,[4] alkoxy, aryloxy, phenoxyimine, or enolate,[5] and oxazoline[6] donor functions have been synthesized. Their reactions with various bases have produced a new versatile class of hybrid, potentially hemilabile NHC ligands, whereas some of their complexes have been applied in valuable catalytic transformations.[2f,g,3a,3e−3k,4d,4e,5b,5d,7]

During the past few years, we have worked on tetradentate ligands such as salens[8] and more recently on hybrid N-functionalized bis(NHC) systems.[9] In this context, we recently reported photoluminescent dinuclear bis(NHC) gold(I) and gold(III) complexes, in which the two NHCs are functionalized by alcohol pendant arms. During the course of these syntheses, we became interested in potentially tetradentate ligands incorporating easily deprotonatable donor functions, susceptible to stabilize mononuclear complexes. The

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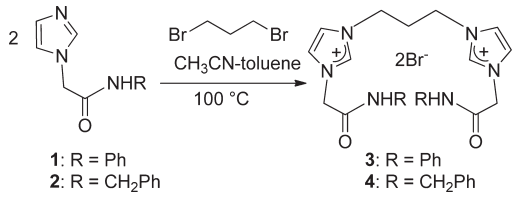
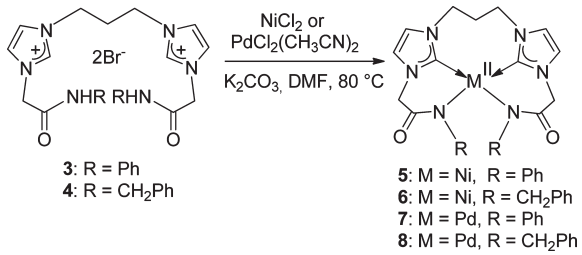
Scheme 1. Synthesis of Amide-Functionalized Bis-Imidazolium Salts 3 and 4



Scheme 2. Synthesis of Complexes 5−8



chelating effect of tetradentate ligands is indeed prone to enhance the robustness of the corresponding precatalysts and to prevent catalyst decomposition under harsh reaction conditions. Recently, Yagyu et al. reported the synthesis of a dianionic tetradentate bis(carbene) ligand containing aryloxy moieties, a motif very similar to that for salen ligands.[10] Salens and porphyrins represent the most famous examples of dianionic tetradentate systems, particularly well-known for applications in asymmetric catalysis.[11] However, to date no chiral equivalents of such ligands based on bis(carbene) have been reported.

In the present report, we disclose the preparation of various amido-functionalized bis-imidazolium salts, in which the two imidazolium rings are held together by a flexible C3 chain, and their subsequent complexation with Ni(II) and Pd(II) leading to the first chiral archetype of this family.

Results and Discussion

The amide-functionalized bis-imidazolium salts **3** and **4** were obtained in quantitative yields by quaternization of **1** or **2**[4d] with $^1/_2$ equiv of 1,3-dibromopropane (Scheme 1).

Lee et al. reported the successful synthesis of mononuclear bis(bidentate) nickel(II) and palladium(II) complexes, involving amido-NHC ligands, via direct reaction between imidazolium salts, $NiCl_2$ or $PdCl_2$, and K_2CO_3, in either DMF or pyridine.[4d,7g] Following this procedure, the palladium(II) and nickel(II) complexes **5**−**8** were prepared from equimolar amounts of bis-imidazolium salts **3** or **4** with a slight excess of K_2CO_3 as a base in dry DMF at 80 °C and isolated as yellow solids (56−87%) (Scheme 2).

All the synthesized complexes are highly stable toward air and moisture. For complexes **5**−**8**, the most notable features of the symmetrical ^{1}H spectra are the absence of the resonance for the imidazolium and the amide protons, attesting

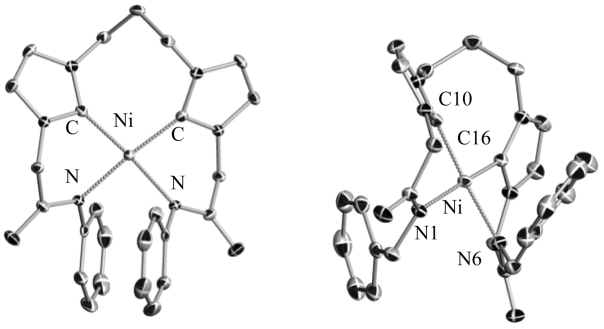
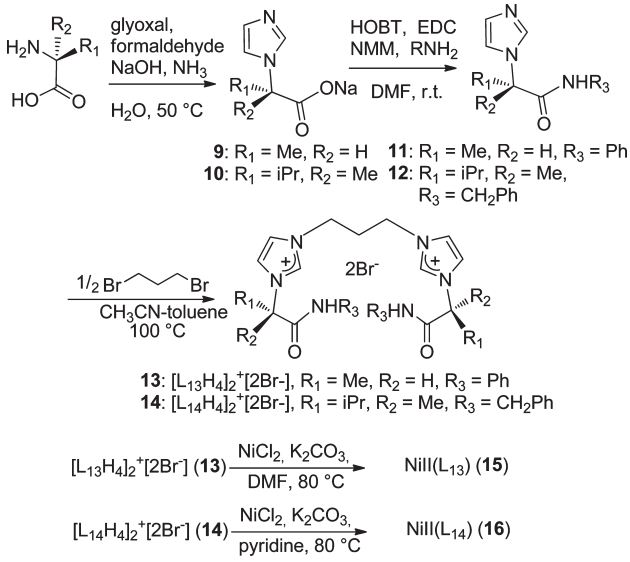


Figure 1. Molecular structures (50% probability level for the thermal ellipsoids) of complexes **5** (left) and **6** (right). Hydrogen atoms and anions have been omitted. Selected bond lengths (Å) and angles (deg): for **5**, Ni−C = 1.867(3), Ni−N = 1.936(2), C−Ni−C = 99.2(2), C−Ni−N = 87.7(2), N−Ni−N = 88.6(2); for **6**, Ni−C10 = 1.885(2), Ni−C16 = 1.886(2), Ni−N1 = 1.943(2), Ni−N6 = 1.932(2), C−Ni−C = 97.72(10), C10−Ni−N1 = 86.66(9), C16−Ni−N6 = 88.19(9), N−Ni−N = 89.44(8).

Scheme 3. Synthesis of Bis-Imidazolium Salts 13 and 14 and of the Complexes 15 and 16



to the successful formation of tetradentate bis(amido-carbene) complexes. In ^{13}C NMR spectra of **5**−**8**, the two downfield quaternary signals have been unambiguously attributed, using HMBC experiments, which enable the assignments of the more upfield signals for the carbenic carbons (161.2−162.2 ppm) and the more downfield ones for the carbonyl carbons (166.6−170.2 ppm). These values are in the range of those reported by Lee et al. for related nickel(II) and palladium(II) complexes.[4d,7g] Elemental analysis and FAB-MS spectra of **5**−**8** are in agreement with neutral monomeric species.

Single crystals of nickel(II) complexes were grown at room temperature by slow evaporation of a methanol solution of complex **5** or by slow diffusion of diethyl ether into a solution of **6** in chloroform (Figure 1).

In further work, we became interested in a synthesis of the corresponding chiral ligand system. For this purpose, another strategy starting from amino acids was applied (see Scheme 3). The sodium L-2-(1-imidazolyl)alkanoic acids **9**

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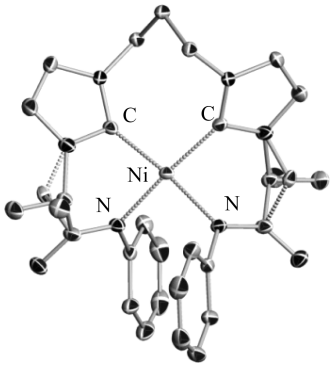

Figure 2. Molecular structure (50% probability level for the thermal ellipsoids) of the racemic complex **15**. Hydrogen atoms and anions have been omitted. Disorders of the parts concerning the asymmetric carbon atoms are illustrated. Selected bond lengths (Å) and angles (deg): Ni−C = 1.886(2), Ni−N = 1.941(2); C−Ni−C = 98.11(9), C−Ni−N = 87.33(6), N−Ni−N = 89.57(8).

and **10** were prepared by a one-pot condensation strategy.[12] A subsequent peptidic coupling between **9** and aniline or **10** and benzylamine, involving HOBT and EDC as coupling agents, gave the corresponding imidazole precursors **11** and **12**, respectively, obtained in moderate yields (44 and 27%). In order to verify if **13** conserved the stereochemical information of the starting amino acid, the corresponding system starting from a racemic mixture of the amino acid has been prepared. Both **13** and the racemic proligand have been studied by HPLC experiments using a chiral column (Chirobiotic T), confirming that **13** is at 93% the desired enantiomer. Very similar values obtained by the measurements of optical rotations for the bis-imidazolium salts **13** and **14** confirmed also the formation of chiral proligands ($[\alpha]_D^{20}$ = +51.9° (**13**), +53.2° (**14**)). The nickel complexes were then generated by using the same protocol as described above (albeit with pyridine as the solvent for **16**), yielding yellow powders (78% (**15**), 52% (**16**)).

Slow evaporation of a methanol solution of **15** gave single crystals (Figure 2). The structure analysis revealed that the racemization of the two stereogenic centers of the ligand occurred during complexation, which is accompanied by a dramatic decrease of α_D ($[\alpha]_D^{20}$ = +8.5°) and important changes in the spectroscopic data.[13] This racemization is probably due to the mobility of the H atoms on the asymmetric carbons, under the drastic complexation conditions. Attempts to obtain **15** in an enantiomerically pure form, by lowering the temperature reaction (60 °C) or by using other bases (pyridine or $NHCO_3$) failed.

In order to better protect the chiral centers, we choose a non-racemizable system bearing a methyl and an isopropyl group on the asymmetric carbon atoms (**14**), starting from a disubstituted chiral amino acid. In that case, the resulting nickel(II) complex must be optically pure, which is also reflected in a very high $[\alpha]_D^{20}$ value (+85.8°).

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(13) In the ^{1}H and ^{13}C NMR data for **15**, four distinct peaks for each type of proton or carbon atom are observed. This is in agreement with a racemization of the two asymmetric carbon centers, leading to two pairs of enantiomers, where each one forms two types of conformers, which interchange slowly relative to the NMR time scale. The presence of two conformers for each diastereoisomer has been confirmed by NMR ROESY analysis.

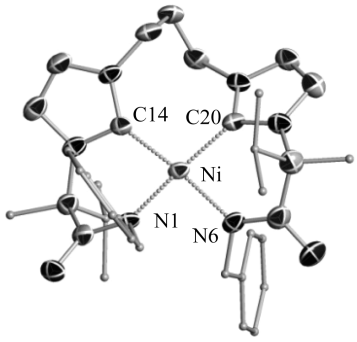


Figure 3. Molecular structure (50% probability level for the thermal ellipsoids) of complex **16**. Only one of the two independent molecules in the asymmetric unit is shown. Hydrogen atoms and anions have been omitted. Selected bond lengths (Å) and angles (deg): Ni−C14 = 1.887(4), Ni−C20 = 1.888(4), Ni−N1 = 1.928(4), Ni−N6 = 1.946(4); C−Ni−C = 97.0(2), C14−Ni−N1 = 86.9(2), C20−Ni−N6 = 87.2(2), N−Ni−N = 89.8(2).

The spectroscopic data of **16** are quite similar to those of **5** and **6**. Single crystals were obtained by slow diffusion of diethyl ether into a solution of **16** in chloroform (Figure 3).

All four complexes presented here are mononuclear neutral species, in which the ligands are tetradentate. The two carbenes and the two amido groups are in a cis disposition. In all cases the Ni centers are distorted from the ideal square-planar coordination geometry, with all four bond angles at the metal center deviating significantly from 90°. The C−Ni−C angles are larger than the N−Ni−N angles, mainly due to the steric constraints imposed by the trimethylene chain. The Ni−C bonds (1.87−1.89 Å) are shorter than the Ni−N bonds (1.94 Å), as observed by Lee et al. for bis-(amido-NHC) nickel complexes.[13]

Conclusion

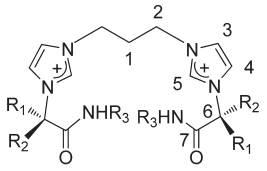
In summary, we prepared new tetradentate NHC ligands consisting of soft carbene and hard amido moieties, suitable for the formation of air- and water-stable Pd(II) and Ni(II) complexes. The structures of the square-pyramidal complexes **5**, **6**, **15**, and **16** were determined by single-crystal X-ray diffraction. Furthermore, the nickel complex **16** represents the first structurally characterized example of a complex containing a chiral dianionic tetradentate bis-(carbene) ligand.

Experimental Section

Unless otherwise stated, all reactions were performed under an atmosphere of argon using standard Schlenk techniques. Solvents were freshly distilled from standard drying agents and kept under argon. 2-(1*H*-imidazol-1-yl)-*N*-phenylacetamide (**1**)[14] and L-sodium 2-(1-imidazolyl)propanoic acid (**9**) were prepared by following literature procedures.[12] All other reagents were used as received from commercial suppliers. ^{1}H (250, 300, or 500 MHz) and ^{13}C NMR (63, 75, or 125 MHz) spectra were recorded at 298 K on Bruker ARX250, Bruker DPX300, and Bruker AV500 spectrometers in DMSO-d_6,

(14) Liao, C.-Y.; Chan, K.-T.; Zeng, J.-Y.; Hu, C.-H.; Tu, C.-Y.; Lee, H. M. *Organometallics* **2007**, *26*, 1692.

CD_3OD, and $CDCl_3$ as solvents. Elemental analyses were carried out by the "Service de Microanalyse du Laboratoire de Chimie de Coordination" (Toulouse, France). Mass spectrometry analyses were performed on a Nermag R1010 apparatus (FAB^+/*m*-nitrobenzyl alcohol (MNBA) in DMSO) by the "Service de Spectrométrie de Masse de Chimie UPS-CNRS" (Toulouse, France). Optical rotations were measured with a Perkin-Elmer 241 polarimeter.



Numbering scheme for NMR data

Preparation of Amide-Functionalized Diimidazolium Salts. *N*-Benzyl-2-(1*H*-imidazol-1-yl)acetamide (2). A mixture of imidazole (1.02 g, 15.0 mmol) and 2-chloro-*N*-benzylacetamide (0.567 g, 3.0 mmol) in toluene (10 mL) was heated to 110 °C overnight. After cooling, the solvent was removed and the residue was extracted with dichloromethane (15 mL). The organic phase was washed with water (12 mL) and dried over Na_2SO_4. After evaporation of the solvent and drying under vacuum, **2** was obtained as a white solid (0.380 g, 60%). Anal. Calcd for $C_{12}H_{13}N_3O$: C, 66.96; H, 6.09; N, 19.52. Found: C, 66.65; H, 5.95; N, 19.35. ^{1}H NMR (250 MHz, DMSO-d_6): δ 8.64 (t, 1H, N*H*), 7.61 (s, 1H, H_5), 7.32 (m, 5H, H_{Ar}), 7.13 (s, 1H, H_{Im}), 6.90 (s, 1H, H_{Im}), 4.74 (s, 2H, H_6), 4.32 (d, 2H, NCH_2, ^3J = 5.8 Hz). ^{13}C NMR (63 MHz, DMSO-d_6): δ 167.3 (1C, *C*=O), 139.4 (1C, C_5), 138.6 (1C, C_{Ar}), 128.8 (2C, C_{Ar}), 128.5 (1C, C_{Im}), 127.8 (2C, C_{Ar}), 127.4 (1C, C_{Ar}), 120.9 (1C, C_{Im}), 49.1 (1C, C_6), 42.8 (1C, NCH_2). MS (FAB): *m*/*z* 216 $[M + H^+]^+$.

1,1′-(1,3-Propanediyl)bis[3-(2-anilino-2-oxoethyl)-1*H*-imidazol-3-ium] Dibromide (3). A solution of 2-(1*H*-imidazol-1-yl)-*N*-phenylacetamide (0.804 g, 4.0 mmol) and 1,3-dibromopropane (0.203 mL, 2.0 mmol) in a mixture of acetonitrile and toluene (2 mL/2 mL) was stirred at 100 °C overnight. After the mixture was cooled to room temperature, the solvents were evaporated. The product was dried under vacuum to afford **3** as a white solid (1.208 g, 100%). Anal. Calcd for $C_{25}H_{28}N_6O_2Br_2$: C, 49.69; H, 4.67; N, 13.91. Found: C, 49.65; H, 4.69; N, 13.93. ^{1}H NMR (250 MHz, DMSO-d_6): δ 10.57 (bs, 2H, N*H*), 9.23 (s, 2H, H_5), 7.85 (d, 2H, H_{Im}, $^{3,4}J$ = 1.7 Hz), 7.83 (d, 2H, H_{Im}, $^{3,4}J$ = 1.5 Hz), 7.59 (d, 4H, H_9, ^3J = 7.5 Hz), 7.35 (t, 4H, H_{10}, ^3J = 7.5 Hz), 7.11 (t, 2H, H_{11}, ^3J = 7.5 Hz), 5.25 (s, 4H, H_6), 4.34 (t, 4H, H_2, ^3J = 7.0 Hz), 2.46 (m, 2H, H_1). ^{13}C NMR (63 MHz, DMSO-d_6): δ 164.1 (2C, *C*=O), 138.7 (2C, C_5), 138.2 (2C, C_8), 129.5 (4C, $C_{9\ or\ 10}$), 124.8 (2C, C_{Im}), 124.4 (2C, C_{Im}), 122.2 (2C, C_{11}), 119.6 (4C, $C_{9\ or\ 10}$), 51.8 (2C, C_6), 46.5 (2C, C_2), 30.0 (1C, C_1). MS (FAB): *m*/*z* 523 $[M - Br^-]^+$ and 443 $[M - 2Br^- - H^+]^+$.

1,1′-(1,3-Propanediyl)bis{3-[(2-benzylamino)-2-oxoethyl]-1*H*-imidazol-3-ium} Dibromide (4). A solution of *N*-benzyl-2-(1*H*-imidazol-1-yl)acetamide (**2**; 0.364 g, 1.7 mmol) and 1,3-dibromopropane (0.086 mL, 0.84 mmol) in a mixture of acetonitrile and toluene (1 mL/1 mL) was stirred at 100 °C overnight. After the mixture was cooled to room temperature, the solvents were evaporated. The product was dried under vacuum to afford **4** as a white solid (0.531 g, 100%). Anal. Calcd for $C_{27}H_{32}N_6O_2Br_2 \cdot 1.6H_2O$: C, 49.04; H, 5.37; N, 12.71. Found: C, 49.07; H, 5.32; N, 12.70. ^{1}H NMR (250 MHz, DMSO-d_6): δ 9.24 (s, 2H, H_5), 8.98 (pseudot, 2H, N*H*), 7.83 (bs, 2H, H_{Im}), 7.79 (bs, 2H, H_{Im}), 7.34 (m, 10H, H_{Ar}), 5.10 (s, 4H, H_6), 4.36 (d, 4H, NCH_2, ^3J = 5.8 Hz), 4.31 (t, 4H, H_2, ^3J = 7.0 Hz), 2.45 (m, 2H, H_1). ^{13}C NMR (75 MHz, DMSO-d_6): δ 165.4 (2C, *C*=O), 139.0 (2C, C_5), 138.1 (2C, C_{Ar}), 128.8 (4C, C_{Ar}), 127.8 (4C, C_{Ar}), 127.5 (2C, C_{Ar}), 124.5 (2C, C_{Im}), 122.2 (2C, C_{Im}), 51.1 (2C, C_6), 46.3 (2C, C_2), 42.9 (2C, C_8), 30.0 (1C, C_1). MS (FAB): *m*/*z* 551 $[M - Br^-]^+$, 471 $[M - 2Br^- - H^+]^+$.

(2*S*)-2-(1*H*-Imidazol-1-yl)-*N*-phenylpropanamide (11). To a solution of sodium (2*S*)-2-(1*H*-imidazol-1-yl)propanoate (0.486 g, 3.0 mmol) and *N*-methylmorpholine (1.011 g, 10 mmol) in dry DMF (15 mL) was successively added EDC (0.767 g, 4.0 mmol), HOBT (0.542 g, 4.0 mmol), and aniline (0.186 g, 2 mmol). The resulting mixture was stirred at room temperature for 24 h, and the solvent was completely removed under vacuum. The residue was then extracted with dichloromethane (50 mL). The organic phase was washed with a saturated $NaHCO_3$ solution (75 mL) and dried over Na_2SO_4. The crude product was further purified by column chromatography (4/96 methanol/dichloromethane), to give a hydroscopic white powder (0.190 g, 44%). Anal. Calcd for $C_{12}H_{13}N_3O$: C, 66.96; H, 6.09; N, 19.52. Found: C, 67.03; H, 6.15; N, 19.61. ^{1}H NMR (250 MHz, DMSO-d_6): δ 10.31 (bs, 1H, N*H*), 7.75 (bs, 1H, H_5), 7.60 (d, 2H, $H_{Ar,}$ ^3J = 8.0 Hz), 7.33 (t, 2H, H_{Ar}, ^3J = 7.8 Hz), 7.27 (bs, 1H, H_{Im}), 7.09 (t, 1H, H_{Ar}, ^3J = 7.5 Hz), 6.91 (bs, 1H, H_{Im}), 5.11 (m, 1H, H_6, ^3J = 7.0 Hz), 1.68 (d, 3H, H_{Me}, ^3J = 7.2 Hz). ^{13}C NMR (75 MHz, DMSO-d_6): δ 168.8 (2C, *C*=O), 139.0 (2C, C_{Ar}), 136.9 (2C, C_5), 129.3 (4C, C_{Ar}), 128.6 (4C, C_{Ar}), 124.3 (2C, C_{Im}), 119.9 (2C, C_{Ar}), 118.9 (2C, C_{Im}), 56.0 (2C, C_6), 18.9 (1C, C_{Me}). MS (FAB): *m*/*z* 216 $[M + H^+]^+$.

(2*S*)-*N*-Benzyl-2-(1*H*-imidazol-1-yl)-2,3-dimethylbutanamide (12). A formaldehyde−water solution (36%, 0.142 g, 1.7 mmol) and glyoxal water solution (32%, 0.38 g, 1.7 mmol) were added in a 50 mL, three-necked flask provided with a stirrer and reflux condenser. While the mixture was heated at 50 °C with stirring, a mixture of (2*S*)-2-amino-2,3-dimethylbutyric acid (0.223 g, 1.7 mmol), ammonia solution (32%, 0.09 g, 1.7 mmol), and sodium hydroxide solution (10%, 0.680 g, 1.7 mmol) was added in small portions over 0.5 h. After the mixture was stirred for an additional 4 h at 50 °C, acetone (20 mL) was added and the solvents were removed under reduced pressure. The resulting residue (**10**) was dried under vacuum. ^{1}H NMR (250 MHz, CD_3OD): δ 7.94 (s, 1H, H_5), 7.01 (s, 1H, H_3), 6.97 (s, 1H, H_4), 2.66 (m, 1H, C*H*Me$_2$, ^3J = 6.8 Hz), 1.69 (s, 3H, CH_3), 0.94 (d, 3H, CH(CH_3)$_2$, ^3J = 6.8 Hz), 0.76 (d, 3H, CH(CH_3)$_2$, ^3J = 6.7 Hz).

To a solution of **10** (0.350 g, 1.7 mmol) and *N*-methylmorpholine (0.759 g, 7.5 mmol) in dry DMF (6 mL) were successively added EDC (0.576 g, 3.0 mmol), HOBT (0.406 g, 3.0 mmol), and benzylamine (0.348 g, 1.5 mmol). The solution was stirred at room temperature for 24 h, and the solvent was completely removed under vacuum. The residue was then extracted with dichloromethane (50 mL). The organic phase was washed with a saturated $NaHCO_3$ solution (75 mL), separated, and dried with anhydrous Na_2SO_4. The crude product was further purified by column chromatography (4/96 methanol/dichloromethane) to give a hygroscopic white powder (0.110 g, 27% yield). Anal. Calcd for $C_{16}H_{21}N_3O$: C, 70.82; H, 7.80; N, 15.49. Found: C, 70.47; H, 7.62; N, 15.61. ^{1}H NMR (250 MHz, DMSO-d_6): δ 8.36 (bs, 1H, *NH*), 7.74 (bs, 1H, H_5), 7.27 (m, 6H, H_{Ar} and H_{Im}), 6.91 (bs, 1H, H_{Im}), 4.27 (d, 2H, NCH_2, ^3J = 5.9 Hz), 2.70 (m, 1H, C*H*Me$_2$, ^3J = 6.7 Hz), 1.67 (s, 3H, H_{Me}), 0.82 (d, 3H, CH(CH_3)$_2$, ^3J = 6.7 Hz), 0.62 (d, 3H, CH(CH_3)$_2$, ^3J = 6.7 Hz). ^{13}C NMR (63 MHz, DMSO-d_6): δ 171.5 (1C, C_7), 139.7 (1C, C_5), 136.2 (1C, C_{Ar}), 128.7 (2C, C_{Ar}), 128.3 (1C, C_{Im}), 127.5 (2C, C_{Ar}), 127.2 (1C, C_{Ar}), 118.7 (1C, C_{Im}), 67.2 (1C, C_6), 43.1 (1C, NCH_2), 34.4 (1C, *C*H(CH$_3$)$_2$), 18.0 (1C, C_{Me}), 16.9 (1C, CH(*C*H$_3$)$_2$), 16.7 (1C, CH(*C*H$_3$)$_2$). MS (FAB): *m*/*z* 271 $[M + H^+]^+$.

3,3′-(1,3-Propanediyl)bis{1-[(1*S*)-2-anilino-1-methyl-2-oxoethyl]-3*H*-imidazol-1-ium} Dibromide (13). A solution of **11** (0.260 g, 1.2 mmol) and 1,3-dibromopropane (0.121 g, 0.6 mmol) in acetonitrile/toluene (0.5−0.5 mL) was stirred at 100 °C overnight. After the mixture was cooled to room temperature, the solvents were evaporated. The product was dried under vacuum to afford the desired white solid (0.381 g, 100%). Anal. Calcd for

$C_{27}H_{32}N_6O_2Br_2 \cdot 2H_2O$: C, 48.52; H, 5.43; N, 12.57. Found: C, 48.65; H, 4.91; N, 12.79. ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.57 (bs, 2H, *NH*), 9.45 (s, 2H, H_5), 7.97 (bs, 2H, H_{Im}), 7.86 (bs, 2H, H_{Im}), 7.61 (d, 4H, H_{Ar}, ^3J = 7.5 Hz), 7.35 (t, 4H, H_{Ar}, ^3J = 7.5 Hz), 7.13 (t, 2H, H_{Ar}, ^3J = 7.5 Hz), 5.41 (m, 2H, H_6), 4.31 (t, 4H, H_2, ^3J = 7.0 Hz), 1.84 (d, 6H, H_{Me}, ^3J = 7.1 Hz). ^{13}C NMR (63 MHz, DMSO-d_6): δ 167.1 (2C, C_7), 138.6 (2C, C_5), 137.1 (2C, C_{Ar}), 129.4 (4C, C_{Ar}), 124.7 (2C, C_{Im}), 123.2 (2C, C_{Im}), 122.3 (2C, C_{Ar}), 119.9 (4C, C_{Ar}), 58.8 (2C, C_6), 46.6 (2C, C_2), 29.7 (1C, C_1), 18.7 (2C, C_{Me}). MS (FAB$^+$): *m*/*z* 552 [M − Br^-]$^+$ and 471 [M − 2Br^- − H^+]$^+$. $[\alpha]^{20}_D$ = +51.9° (589 nm, 20 °C, 5.01 × 10^{-3} g/cm^3 in MeOH, 10 cm path). HPLC (Chirobiotic T, MeOH, 1 mL/min, UV): RT = 8.555 (93.74%, UV 241.5 nm), 10.356 (6.26%, UV 240.4 nm); racemic system RT = 8.583 (49.83%, UV 241.5 nm), 9.743 (47.81%, UV 241.5 nm).

3,3′-(1,3-Propanediyl)bis(1-{(1*S*)-1-[(benzylamino)carbonyl]-1,2-dimethylpropyl}-3*H*-imidazol-1-ium) Dibromide (14). A solution of **12** (0.110 g, 0.4 mmol) and 1,3-dibromopropane (0.041 g, 0.2 mmol) in acetonitrile/toluene (0.3−0.3 mL) was stirred at 100 °C overnight. After the mixture was cooled to room temperature, the solvents were evaporated. The product was dried under vacuum to afford the desired white solid (0.153 g, 100%). Anal. Calcd for $C_{35}H_{48}N_6O_2Br_2 \cdot 2H_2O$: C, 53.85; H, 6.71; N, 10.77. Found: C, 53.96; H, 6.41; N, 10.79. ^{1}H NMR (250 MHz, DMSO-d_6): δ 9.51 (bs, 2H, H_5), 8.87 (s, 2H, *NH*), 7.94 (bs, 2H, H_{Im}), 7.91 (bs, 2H, H_{Im}), 7.28 (m, 10H, H_{Ar}), 4.31 (m, 8H, H_2 and NCH_2), 2.70 (m, 2H, CH(CH$_3$)$_2$), 1.83 (d, 6H, H_{Me}), 0.84 (d, 6H, CH(CH_3)$_2$, ^3J = 6.6 Hz), 0.75 (d, 6H, CH(CH_3)$_2$, ^3J = 6.6 Hz). ^{13}C NMR (75 MHz, DMSO-d_6): δ 169.6 (2C, C_7), 139.2 (2C, C_{Ar}), 137.1 (2C, C_5), 128.8 (4C, C_{Ar}), 127.8 (4C, C_{Ar}), 127.4 (2C, C_{Ar}), 122.4 (2C, C_{Im}), 122.2 (2C, C_{Im}), 71.3 (2C, C_6), 46.7 (2C, NCH$_2$), 43.5 (2C, C_2), 34.8 (2C, CH(CH$_3$)$_2$), 30.1 (1C, C_1), 17.5 (2C, C_{Me}), 17.4 (2C, CH(CH_3)$_2$), 16.9 (2C, CH(CH_3)$_2$). MS (FAB$^+$): *m*/*z* 663 [M − Br^-]$^+$ and 583 [M − 2Br^- − H^+]$^+$. $[\alpha]^{20}_D$ = +53.2° (589 nm, 20 °C, 6.02 × 10^{-3} g/cm^3 in MeOH, 10 cm path).

Synthesis of Complexes. Complex 5. A mixture of ligand **3** (0.604 g, 1.0 mmol), K_2CO_3 (0.690 g, 5 mmol), and $NiCl_2$ (0.130 g, 1.0 mmol) in dry DMF (25 mL) was heated at 80 °C overnight. After it was cooled to room temperature, the solution was filtered through a pad of Celite; a yellow solid precipitated by addition of diethyl ether (100 mL). After filtration, the precipitate was dissolved in chloroform (100 mL) and the organic layer was washed with water (50 mL). The water was extracted twice with chloroform (50 mL), and the combined organic layers were dried over Na_2SO_4. After removal of the solvent and drying under vacuum, complex **5** was obtained as a yellow solid (0.434 g, 87%). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a methanol solution of **5**. Anal. Calcd for $C_{25}H_{24}N_6O_2Ni \cdot 2H_2O$: C, 56.10; H, 5.27; N, 15.70. Found: C, 55.85; H, 5.21; N, 15.71. ^{1}H NMR (250 MHz, DMSO-d_6): δ 7.75 (d, 4H, H_{Ar}, ^3J = 7.5 Hz), 7.59 (d, 2H, H_{Im}, $^{3,4}J$ = 1.8 Hz), 7.28 (d, 2H, H_{Im}, $^{3,4}J$ = 1.8 Hz), 7.15 (t, 4H, H_{Ar}, ^3J = 7.3 Hz), 6.89 (t, 2H, H_{Ar}, ^3J = 7.2 Hz), 5.19 (d, 2H, H_{6a}, ^2J = 14.4 Hz), 4.11 (m, 4H, H_{6b} and H_{2b}), 3.43 (m, 2H, H_{2a}), 1.82 (m, 2H, H_1). ^{13}C NMR (63 MHz, DMSO-d_6): δ 166.6 (2C, C=O), 161.8 (2C, C_5), 148.1 (2C, C_{Ar}), 126.9 (4C, C_{Ar}), 126.6 (4C, C_{Ar}), 124.5 (2C, C_{Im}), 121.9 (2C, C_{Ar}), 121.4 (2C, C_{Im}), 56.7 (2C, C_6), 44.6 (2C, C_2), 36.3 (1C, C_1). MS (FAB): *m*/*z* 499 [M + H^+]$^+$, 537 [M + K^+]$^+$.

Complex 6. A mixture of **4** (0.630 g, 1.0 mmol), K_2CO_3 (0.690 g, 5 mmol), and $NiCl_2$ (0.130 g, 1.0 mmol) in dry DMF (25 mL) was heated at 80 °C overnight. After it was cooled to room temperature, the solution was filtered through a pad of Celite and the solvent was removed under vacuum. The residue was dissolved in chloroform (100 mL) and was washed with water (50 mL). The water was extracted twice with chloroform (50 mL), and the combined organic layers were dried over Na_2SO_4. After removal of the solvent and drying under vacuum, complex **6** was obtained as a yellow solid (0.510 g, 81%). Crystals suitable for X-ray diffraction analysis were grown by diffusion of diethyl ether into a solution of **6** in chloroform. Anal. Calcd for $C_{27}H_{28}N_6O_2Ni \cdot 0.2CHCl_3$: C, 59.28; H, 5.16; N, 15.25. Found: C, 59.00; H, 5.07; N, 15.19. ^{1}H NMR (250 MHz, CD_3OD): δ 7.35 (m, 10H, H_{Ar}), 7.26 (d, 2H, H_{Im}, $^{3,4}J$ = 1.8 Hz), 7.09 (d, 2H, H_{Im}, $^{3,4}J$ = 1.8 Hz), 4.79 (d, 2H, NCH_{2a}, ^2J = 15.5 Hz), 4.01 (m, 4H, NCH_{2b} and H_{2a}), 3.63 (m, 4H, H_6), 3.13 (m, 2H, H_{2b}), 1.79 (m, 2H, H_1). ^{13}C NMR (63 MHz, CD_3OD): δ 170.2 (2C, C=O), 161.2 (2C, C_5), 142.6 (2C, C_{Ar}), 128.1 (4C, C_{Ar}), 127.7 (4C, C_{Ar}), 126.4 (2C, C_{Ar}), 123.5 (2C, C_{Im}), 120.8 (2C, C_{Im}), 54.0 (2C, C_6), 48.3 (2C, NCH$_2$), 44.0 (2C, C_2), 31.5 (1C, C_1). MS (FAB): *m*/*z* 527 [M + H^+]$^+$, 565 [M + K^+]$^+$.

Complex 7. A mixture of **3** (0.121 g, 0.2 mmol), K_2CO_3 (0.138 g, 1 mmol), and $PdCl_2(CH_3CN)_2$ (0.052 g, 0.2 mmol) in dry DMF (6 mL) was heated at 55 °C for 2 h and then at 80 °C overnight. After it was cooled to room temperature, the solution was filtered through a pad of Celite, and a yellow solid precipitated by addition of diethyl ether (60 mL). After filtration and drying under vacuum, complex **7** was obtained as a yellow solid (0.261 g, 79%). Anal. Calcd for $C_{25}H_{24}N_6O_2Pd$: C, 54.90; H, 4.42; N, 15.37. Found: C, 54.76; H, 4.31; N, 15.26. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.65 (d, 2H, H_4, $^{3,4}J$ = 1.8 Hz), 7.42 (d, 2H, H_3, $^{3,4}J$ = 1.8 Hz), 7.11 (d, 4H, H_{Ar}, ^3J = 7.4 Hz), 6.96 (t, 4H, H_{Ar}, ^3J = 7.4 Hz), 6.79 (t, 2H, H_{Ar}, ^3J = 7.3 Hz), 4.93 (d, 2H, H_{6a}, ^2J = 14.1 Hz), 4.26 (d, 2H, H_{6b}, ^2J = 14.2 Hz), 4.19 (m, 2H, H_{2a}), 3.58 (m, 2H, H_{2b}), 1.92 (m, 2H, H_1). ^{13}C NMR (125 MHz, DMSO-d_6): δ 166.6 (2C, C=O), 162.1 (2C, C_5), 148.4 (2C, C_{Ar}), 127.0 (4C, C_{Ar}), 126.2 (4C, C_{Ar}), 124.1 (2C, C_4), 121.1 (2C, C_{Ar}), 119.6 (2C, C_3), 58.0 (2C, C_6), 45.0 (2C, C_2), 32.5 (1C, C_1). MS (FAB): *m*/*z* 547 [M + H^+]$^+$.

Complex 8. A mixture of **4** (0.127 g, 0.2 mmol), K_2CO_3 (0.138 g, 1 mmol), and $PdCl_2(CH_3CN)_2$ (0.052 g, 0.2 mmol) in dry DMF (6 mL) was heated at 55 °C for 2 h and then at 80 °C overnight. After it was cooled to room temperature, the solution was filtered through a pad of Celite, and a yellow solid precipitated by addition of diethyl ether (60 mL). After filtration and drying under vacuum, complex **8** was obtained as a yellow solid (0.065 g, 56%). Anal. Calcd for $C_{27}H_{28}N_6O_2Pd \cdot H_2O$: C, 54.69; H, 5.10; N, 14.17. Found: C, 54.92; H, 4.82; N, 14.25. ^{1}H NMR (500 MHz, CD_3OD): δ 7.32 (d, 2H, H_4, $^{3,4}J$ = 1.9 Hz), 7.21 (m, 6H, H_{Ar}), 7.18 (d, 2H, H_3, $^{3,4}J$ = 1.9 Hz), 7.10 (m, 4H, H_{Ar}), 5.09 (d, 2H, NCH_{2a}, ^2J = 14.6 Hz), 4.08 (m, 4H, H_{6b} and H_{2a}, ^2J = 14.8 Hz), 3.96 (d, 2H, NCH_{2b}, ^2J = 14.5 Hz), 3.81 (d, 2H, H_{6a}, ^2J = 14.8 Hz), 3.30 (m, 2H, H_{2b}), 1.89 (m, 2H, H_1). ^{13}C NMR (125 MHz, CD_3OD): δ 169.7 (2C, C=O), 162.1 (2C, C_5), 142.2 (2C, C_{Ar}), 128.0 (4C, C_{Ar}), 127.8 (4C, C_{Ar}), 126.1 (2C, C_{Ar}), 123.1 (2C, C_4), 120.2 (2C, C_3), 55.6 (2C, C_6), 50.3 (2C, NCH$_2$), 44.4 (2C, C_2), 31.8 (1C, C_1). MS (FAB): *m*/*z* 575 [M + H^+]$^+$.

Complex 15. A mixture of ligand **13** (0.127 g, 0.2 mmol), K_2CO_3 (0.138 g, 1 mmol), and $NiCl_2$ (0.026 g, 0.2 mmol) in dry DMF (6 mL) was heated at 80 °C overnight. After it was cooled to room temperature, the solution was filtered through a pad of Celite, and a yellow solid precipitated by addition of diethyl ether (15 mL). After filtration, the precipitate was dissolved in chloroform (20 mL) and the organic layer was washed with water (15 mL). The water was washed twice with chloroform (15 mL), and the combined organic layers were dried over Na_2SO_4. After removal of the solvent and drying under vacuum, complex **15** was obtained as a yellow solid (0.082 g, 78%). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a methanol solution of **15**. Anal. Calcd for $C_{27}H_{28}N_6O_2Ni \cdot H_2O$: C, 59.47; H, 5.55; N, 15.41. Found: C, 59.31; H, 5.31; N, 15.27. Variable-temperature NMR experiments have been carried out (in CD_3OD between 223 and 323 K and in DMSO-d_6 between 298 and 363 K) to discard the possibility of conformational equilibrium. For the strongly affected methyl group on position 6, no fusion of the four signals and no significant simplification of the spectra could be observed. Only the room-temperature data are given here.

Table 1. Crystal Data for 5, 6, 15, and 16

	5·2MeOH	**6**·$CHCl_3$·H_2O	**15**·2MeOH	**16**·0.25$CHCl_3$·0.5CH_2Cl_2·0.5Et_2O·0.75H_2O
empirical formula	$C_{27}H_{32}N_6NiO_4$	$C_{28}H_{31}Cl_3N_6NiO_3$	$C_{29}H_{36}N_6NiO_4$	$C_{37.75}H_{51.75}Cl_{1.75}N_6NiO_{3.25}$
formula wt	563.30	664.65	591.35	762.35
temp (K)	173(2)	193(2)	193(2)	193(2)
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
space group	*C*2/*c*	$P2_1/c$	*C*2/*c*	$P2_12_12_1$
a (Å)	14.774(1)	10.5437(2)	15.4796(4)	14.9787(3)
b (Å)	16.001(1)	14.9883(3)	18.1846(4)	19.8518(4)
c (Å)	12.392(1)	19.1501(4)	10.6625(2)	28.4798(6)
β (deg)	112.797(4)	100.537(1)	104.303(1)	
V (Å^3)	2700.6(3)	2975.3(1)	2908.4(2)	8468.6(3)
Z	4	4	4	8
ρ_{calcd} (Mg m^{-3})	1.385	1.484	1.351	1.196
μ (mm^{-1})	0.763	0.963	0.712	0.609
F(000)	1184	1376	1248	3232
cryst size (mm^3)	0.1 × 0.1 × 0.1	0.4 × 0.2 × 0.2	0.4 × 0.4 × 0.3	0.6 × 0.4 × 0.3
θ range for data collecn (deg)	5.13−25.35	1.96−26.85	5.11−26.37	5.12−25.35
no. of rflns collected	11 542	28 389	10 994	89 914
no. of indep rflns	2453	6339	2956	15 341
R(int)	0.0989	0.0392	0.0217	0.0358
max/min transmissn	0.9276/0.7153	0.8308/0.6994	0.8149/0.7639	0.8384/0.7114
no. of data/restraints/params	2453/0/175	6339/0/378	2956/53/203	15 341/572/1123
goodness of fit on F^2	1.004	1.052	1.078	1.071
R1 ($I > 2\sigma(I)$)	0.0443	0.0394	0.0298	0.0541
wR2 ($I > 2\sigma(I)$)	0.0762	0.1059	0.0720	0.1426
R1 (all data)	0.0836	0.0563	0.0328	0.0781
wR2 (all data)	0.0884	0.1156	0.0736	0.1640
$\Delta\rho_{max/min}$ (e Å^{-3})	0.356/−0.360	0.523/−0.462	0.347/−0.261	0.655/−0.390

^{1}H NMR (500 MHz, DMSO-d_6): δ 7.85 (d, H_{Ara}, ^3J = 7 Hz), 7.65 (d, $H_{Arb'}$, ^3J = 6.9 Hz), 7.56 (d, H_{4b}, ^{3,4}J = 1.6 Hz), 7.52 (bs, H_{4a}), 7.49 (bs, $H_{4a'}$), 7.47 (bs, $H_{4b'}$), 7.34 (d, $H_{Ara'}$, ^3J = 7.4 Hz), 7.30 (d, H_3, ^3J = 1.5 Hz), 7.17 (m, H_{Arb} and H_{Ar}), 7.06 (m, H_{Ar}), 6.91 (m, H_{Ar}), 5.81 (q, $H_{6a'}$), 5.52 (q, $H_{6b'}$), 4.47 (q, H_{6b}), 4.40 (q, H_{6a}), 4.10 (m, H_2), 3.45 (m, H_2), 3.37 (m, H_2), 3.24 (m, H_2), 3.10 (m, H_2), 2.42 (d, H_{Meb}, ^3J = 7.2 Hz), 2.08 (d, H_{Mea}, ^3J = 7.5 Hz), 1.78 (d, H_1), 1.42 (d, $H_{Mea'}$ and $H_{Meb'}$). ^{13}C NMR (125 MHz, DMSO-d_6): δ 170.3 (C_{7b}), 170.0 (C_{7a}), 169.5 ($C_{7a'}$), 168.7 ($C_{7b'}$), 163.2 ($C_{5b'}$), 162.8 ($C_{5a'}$), 159.4 (C_{5a}), 159.4 (C_{5b}), 148.9 (C_{Ar}), 148.5 (2C, C_{Ar}), 148.3 (C_{Ar}), 148.0 (C_{Ar}), 129.0 (C_{Arb}), 128.3 ($C_{Ara'}$), 127.7 ($C_{Ara'}$), 127.0 ($C_{Arb'}$), 126.8 (C_{Ara}), 126.7 ($C_{Arb'}$), 126.5 (C_{Ara}), 126.1 (C_{Arb}), 124.0 (C_{4b}), 123.7 (C_{4a}), 123.4 (C_{Arb}), 122.5 (C_{Ara}), 122.3 (C_{3b}), 122.2 ($C_{Ara'}$), 122.1 ($C_{Arb'}$), 122.0 (C_{3a}), 121.1 ($C_{3b'}$), 121.0 ($C_{3a'}$), 120.7 ($C_{4a'}$), 120.6 ($C_{4b'}$), 62.9 (C_{6a}), 62.8 (C_{6b}), 58.9 ($C_{6a'}$), 58.7 ($C_{6b'}$), 45.1 (C_{2b}), 44.9 (C_{2a}), 44.8 ($C_{2a'}$), 44.7 ($C_{2b'}$), 32.3 ($C_{1b'}$), 32.2 (C_{1a}), 31.3 (C_{1b}), 30.9 ($C_{1a'}$), 24.6 (C_{Meb}), 24.3 (C_{Mea}), 14.4 ($C_{Meb'}$), 14.1 ($C_{Mea'}$). MS (FAB$^+$): *m*/*z* 527 [M + H$^+$]$^+$. $[\alpha]^{20}_D$ = +8.5° (589 nm, 20 °C, 5.31 × 10^{-3} g/cm^3 in MeOH, 10 cm path).

Complex 16. A mixture of **14** (0.270 g, 0.36 mmol), K_2CO_3 (0.250 g, 1.8 mmol), and $NiCl_2$ (0.047 g, 0.36 mmol) in dry pyridine (3 mL) was heated at 80 °C overnight. After the mixture was cooled to room temperature, the solvent was removed under vacuum. The residue was dissolved in dichloromethane (15 mL) and was washed with water (15 mL). The water was washed twice with chloroform (15 mL), and the combined organic layers were dried over Na_2SO_4. After removal of the solvent, the crude solid was washed with THF (10 mL). After drying under vacuum, complex **16** was obtained as a yellow solid (0.120 g, 52%). Crystals suitable for X-ray diffraction analysis were grown by diffusion of diethyl ether into a solution of **16** in dichloromethane. Anal. Calcd for $C_{35}H_{44}N_6O_2Ni$: C, 65.74; H, 6.94; N, 13.14. Found: C, 65.70; H, 6.79; N, 13.13. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.17 (bs, 2H, H_{Im}), 7.04 (m, 10H, H_{Ar}), 6.80 (bs, 2H, H_{Im}), 5.64 (m, 2H, C*H*(CH$_3$)$_2$, ^3J = 5.5 Hz), 5.01 (d, 2H, NCH_{2a}, ^2J = 16 Hz), 3.99 (m, 2H, H_{2a}), 3.90 (m, 2H, NCH_{2b}, ^2J = 15.9 Hz), 3.41 (m, 2H, H_{2b}), 1.73 (m, 2H, H_1), 1.56 (s, 6H, H_{Me}), 0.71 (m, 12H, CH(CH_3)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.1 (2C, C_7), 165.1 (2C, C_5), 143.3 (2C, C_{Ar}), 127.6 (4C, C_{Ar}), 126.0 (4C, C_{Ar}), 125.0 (2C, C_{Ar}), 121.9 (2C, C_{Im}), 118.9 (2C, C_{Im}), 71.0 (2C, C_6), 49.7 (2C, NCH_2), 44.8 (2C, C_2), 43.3 (2C, *C*H(CH$_3$)$_2$), 32.6 (1C, C_1), 18.0 (2C, CH(*C*H$_3$)$_2$), 16.01 (2C, CH(*C*H$_3$)$_2$), 15.06 (2C, C_{Me}). MS (FAB$^+$): *m*/*z* 639 [M + H$^+$]$^+$. $[\alpha]^{20}_D$ = +85.8° (589 nm, 20 °C, 8.00 × 10^{-3} g/cm^3 in MeOH, 10 cm path).

Experimental Crystallographic Data for 5, 6, 15, and 16. Details of the crystal data for all structures are presented in Table 1. All data were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS APEX2 diffractometer with Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods,[15] and all non-hydrogen atoms were refined anisotropically using the least-squares method on F^2.[16] A racemic disorder of the group concerning the asymmetric carbon atom in **15** has been refined with the help of ADP and distance restraints. Two molecules of compound **16** and some partial occupied and disordered solvent molecules are present in the independent unit of **16**. Only one of the complexes shows disorders of the phenyl rings. The ether molecule has been refined on two positions, and a mixture of dichloromethane and trichloromethane has been refined on the same position. As in **15**, all disorders could be refined with help of ADP and distance restraints. With regard to **16**, the absolute structure parameter has been refined to −0.032(14).[17] Crystallographic data in CIF format for **5**, **6**, **15**, and **16** are available in the Supporting Information.

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Supporting Information Available: Text giving additional experimental details and CIF files giving crystallographic data for **5**, **6**, **15**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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