Binucleating Ligands: Synthesis of Acyclic Achiral and Chiral Schiff Base−Pyridine and Schiff Base−Phosphine Ligands

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5-*tert*-Butyl-3-(2′-pyridyl)salicyaldehyde and 5-*tert*-butyl-3-(diphenylphosphino)salicyaldehyde were synthesized from 4-*tert*-butylphenol in good overall yields. Condensation of the salicyaldehydes with 2,3-diamino-2,3-dimethylbutane afforded the desired dinucleating Schiff base−pyridine and Schiff base−phosphine ligands, respectively. 5-*tert*-Butyl-3-(2′-pyridyl)salicyaldehyde reacted with optically active 1,2-diaminocyclohexanes to give chiral dinucleating Schiff base−pyridine ligands.

Introduction

The synthesis of dinucleating ligands capable of binding metal ions in close proximity has continued to arouse interest among chemists. Since 1970,[1,2] the preparation of dinucleating ligands plays a central role in bimetallic chemistry which is currently the area of extensive investigation due to its importance in the fields of bioinorganic chemistry, homogeneous catalysis, and magnetic exchange processes.[3] The design of dinucleating system determines the nature of metal ions to be incorporated, coordination environment, and metal−metal separation of the bimetallic complexes. Several kinds of dinucleating ligands have been reported[1,2] to afford binuclear complexes. Previous efforts have been focused on the synthesis and complexation of a vast array of symmetrical dinucleating macrocycles due to the relative ease of their synthesis.[4] However, this kind of ligand is usually more useful in the preparation of homobimetallic complexes while the synthesis of heterobimetallic complexes is better accomplished by using the heteroditopic ligands.[5] An important category of the heteroditopic ligands is the Schiff base-crown ether macrocyclic compounds.[6] The Schiff base−crown ether ligands have been demonstrated to complex soft and hard metal ions in their soft (Schiff base) and hard (crown ether) cavities.

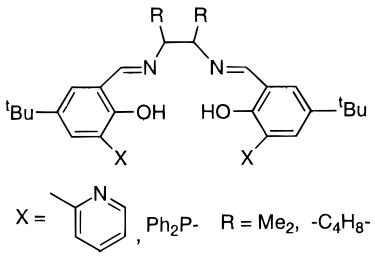

Figure 1.

Another type is the acyclic Schiff base−carboxylic acids which were reported to complex soft and hard metal ions selectively.[7] While the aforementioned heteroditopic ligands bear hard binding sites coupled to the Schiff base moieties, here we report the synthesis of achiral and chiral acyclic side-off Schiff base−pyridine and Schiff base−phosphine ligands containing the relatively softer pyridyl and phosphino groups which may allow complexation of low valent transition metal ions.[8] The general structure of the dinucleating ligands is shown in Figure 1.

As shown in Figure 1, in these phenolic bridged dinucleating ligands, the Schiff base moieties provide the internal salen type N_2O_2 cavity while the functional groups X serve as the extra binding ends to constitute the external O_2X_2 donor set. Schiff base ligands are well known to afford stable transition metal complexes,[9] and their monometallic chemistry has been extensively studied.[10] The dinucleating properties of our Schiff base system are attributed to the donor groups X (X = 2-pyridyl or diphenylphosphino) at 3′-positions giving rise to the external O_2X_2 binding sites. While the O_2N_2 sites of the pyridyl derivative are expected to bind first row transition metal ions, the O_2P_2 system of the Schiff base−phosphine ligand can complex the softer second and third row transition metal ions as well.[11] In order to enhance the solubility of the ligands and their bimetallic complexes in organic solvents, the lipophilic *tert*-butyl groups and the tetramethylethylene bridge are introduced in our

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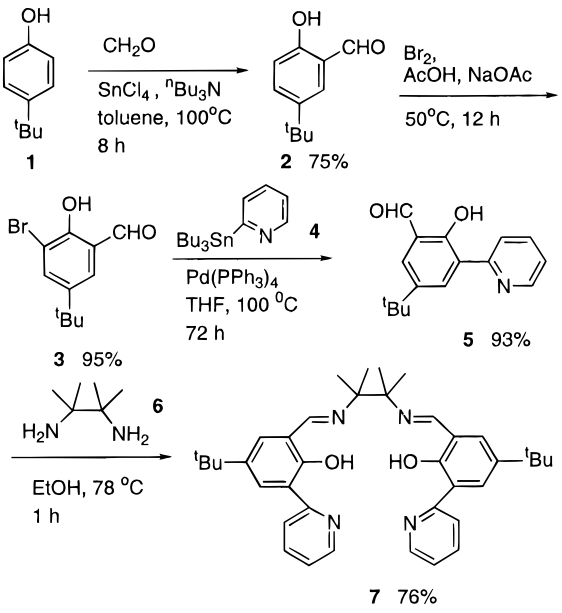
Scheme 1



ligand design. 1,2-Diaminocyclohexanes, readliy available chiral diamines, are employed for the synthesis of chiral ligands.

The class of chiral dinucleating ligands is especially interesting since the asymmetric induction coupled with bimetallic cooperativity in a multiple redox reaction for these heterobimetallic complexes would be promising biomimetics as well as potential asymmetric catalysts such as aerobic oxidation catalysts.[12] We now disclose our full results in the synthesis of acyclic achiral and chiral Schiff base−pyridine and achiral Schiff base−phosphine ligands.[13]

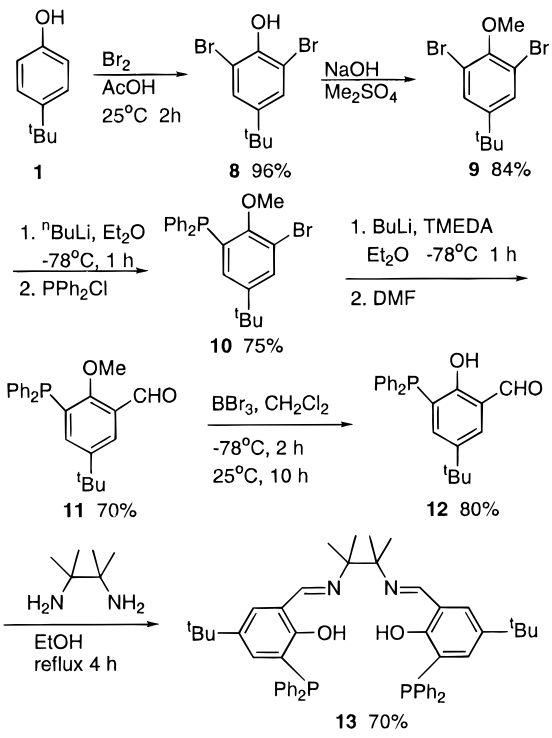
Results and Discussion

The dinucleating ligands **7** and **13** were prepared by the condensation of 2,3-diamino-2,3-dimethylbutane and optically active 1,2-diaminocyclohexanes with 5-*tert*-butyl-3-(2′-pyridyl)salicyaldehyde and 5-*tert*-butyl-3-(diphenylphosphino)salicyaldehyde which were synthesized according to Schemes 1 and 2.

As shown in Scheme 1, the ligand **7** was synthesized from 4-*tert*-butylphenol in four steps in 50% overall yield. Formylation of 4-*tert*-butylphenol with formaldehyde[14] in the presence of $SnCl_4$ afforded the salicyaldehyde **2** which was then brominated with Br_2/AcOH[15] to give 3-bromo-5-*tert*-butylsalicyaldehyde (**3**) in 95% yield. Stille type palladium-catalyzed cross coupling[16] of **3** with 2-(tri-*n*-butylstannyl)pyridine[17] in THF produced 5-*tert*-butyl-3-(2′-pyridyl)salicyaldehyde (**5**) in 93% yield. Condensation of **5** with 2,3-diamino-2,3-dimethylbutane[18] afforded the desired dinucleating ligand **7** in 76% yield.

Similarly, ligand **13** was prepared by the condensation reaction with 5-*tert*-butyl-3-(diphenylphosphino)salicyaldehyde (**11**) in six steps starting from 4-*tert*-butylphenol

Scheme 2



as shown in Scheme 2. Bromination of 4-*tert*-butylphenol (**1**) gave a 96% yield of the dibromophenol **8** which was then methylated with Me_2SO_4 to afford the dibromoanisole **9** in 94% yield. Lithiation of **7** with n-BuLi in Et_2O at −78 °C followed by quenching with PPh_2Cl produced (3-bromo-5-*tert*-butyl-2-anisyl)diphenylphosphine (**10**) in 75% yield. **9** was lithiated with n-BuLi/TMEDA in Et_2O at −78 °C and was subsequently quenched with anhydrous DMF to afford the *o*-methoxybenzaldehyde **11** in 70% yield. Without the addition of TMEDA, no aldehyde **11** was formed even though the lithiation was succcessful as evidenced by the formation of deuteriated arene upon trapping reaction with D_2O. Demethylation of **11** with BBr_3 yielded the salicyaldehyde **11** in 80% yield which was then condensed with 2,3-diamino-2,3-dimethylbutane to afford ligand **13** in 70% yield.

The enantiomeric pair of chiral acyclic pyridine ligands was prepared via the condensation of 5-*tert*-butyl-3-(2′-pyridyl)salicyaldehyde (**5**) with either (*R*,*R*)- and (*S*,*S*)-1,2-diaminocyclohexanes in the form of mono(+)-tartrates[19] in 85 and 86% yield, respectively (Scheme 3). **16** and **17** showed equal but opposite sign of optical rotation confirming their enantiomeric relationship.

The characteristic functionalities of Schiff base ligands include the hydrogen bonded hydroxyl groups and the azomethine groups (-C═N-). These functional groups were identified in **7**, **13**, **16**, and **17** by comparing the spectroscopic data with literature values of similar systems.[1a,6] Broad peaks were observed in the range 3600−2400 cm^{-1} in their IR spectra which strongly suggested the presence of hydrogen bonded OH groups. Low field broad singlets appeared at δ 14.76, 14.37, 14.14, and 14.14 in the ^1H NMR spectra of **7**, **13**, **16**, and **17** respectively, and supported hydrogen bonded phenolic protons. In the IR spectra of these compounds, strong

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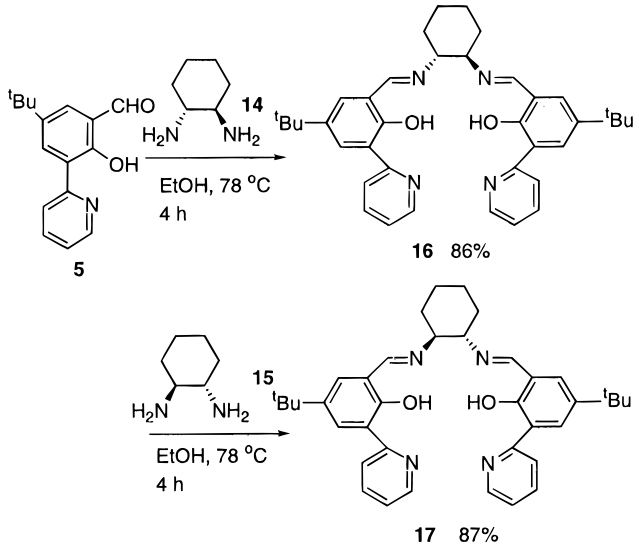
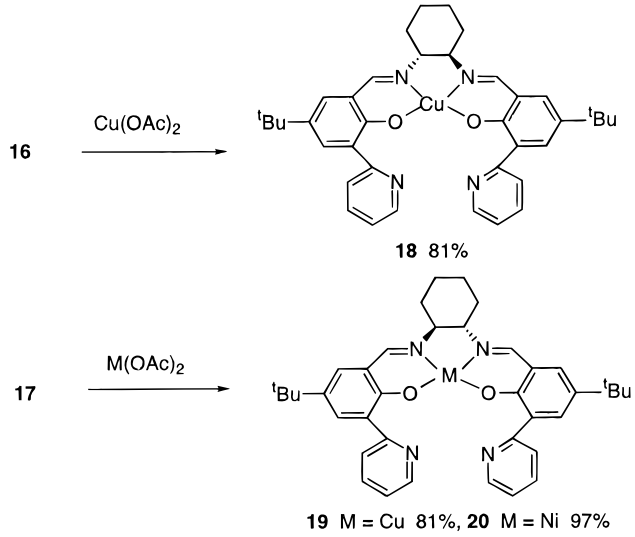
Scheme 3



Scheme 4



signals at 1620−1630 cm^{-1} were observed and likely arose from the C═N stretch of the imine linkage. The singlets at δ 8.3−8.4 in their NMR spectra, indicating the presence of azomethine protons,[20] substantiated the IR assignment.

Compounds **7** and **13** also exhibited characteristic UV-vis spectra of Schiff base ligands. Schiff base ligands exhibit two absorption peaks at a lower energy region (>300 nm). Bosnich[21] has made general assignments of the electronic transitions. The stronger, higher energy peak is attributed to the $\pi \rightarrow \pi^*$ transition of the azomethine chromophore while the weaker and less energetic peak is assigned to the n $\rightarrow \pi^*$ transition involving the promotion of the lone pair electron of azomethine nitrogen atom to the antibonding π orbital associated with the azomethine group. Both **7** and **13** exhibited a pair of absorption bands in their electronic spectra. The strong peak at 340−350 nm and the less intense peak at 430−440 nm corresponded well to the expected $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ transitions of Schiff base derivatives.

Preliminary studies showed that both ligands **16** and **17** formed mononuclear metal complexes with copper and nickel ions in high yields (Scheme 4). Both homo and hetero binuclear complexes were prepared, and the full characterization by X ray crystallography as well as their catalytic activity are in progress.

Conclusion

In conclusion, we have synthesized acyclic chiral and achiral dinucleating ligands of Schiff bases of pyridine and phosphine groups. Preliminary complexation studies show that these ligands formed heterobimetallic complexes with Ni and Cu.[22] Further studies of the bimetallic chemistry of these ligands are in progress.

Experimental Section

UV-vis spectra were recorded using CH_2Cl_2 as the solvent. IR spectra were recorded on a FT-IR spectrophotometer as neat film on KBr plates. ^1H NMR spectra were recorded either at 250 MHz. Chemical shifts (δ) were reported in ppm downfield from internal standard tetramethylsilane, and coupling constants (J) were reported in hertz. ^{13}C Spectra were obtained at 62.9 or 125 MHz. Mass spectra (EI) were obtained at 70 eV, and FABMS was recorded using *m*-nitrobenzyl alcohol (NBA) as the matrix at National Tsing Hua University, Taiwan. Elemental analyses were performed by the Medac Ltd, Department of Chemistry, Brunel University, United Kingdom. Specific rotation were determined on a polarimeter.

Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. 2-(Tributylstannyl)pyridine (**4**),[17] 2,3-diamino-2,3-dimethylbutane (**6**),[18] 2,6-dibromo-4-*tert*-butylphenol (**8**),[23] 2,6-dibromo-4-*tert*-butylanisole (**9**),[24] (*R*,*R*)-1,2-diammoniocyclohexane mono-(+)-tartrate,[19] and (*S*,*S*)-1,2-diammoniocyclohexane mono-(−)-tartrate salt (**5**)[19] were prepared according to the literature methods. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl immediately prior to use. Hexane was distilled over calcium chloride, and toluene was distilled from sodium. Silica gel (70−230 mesh) was used for column chromatography. Thin layer chromatography was performed on Merck precoated silica gel 60 F254 plates. All melting points were uncorrected.

3-Bromo-5-*tert*-butyl-2-hydroxybenzaldehyde (3). To a solution of **2**[19] (0.52 g, 2.93 mmol) and sodium acetate (0.44 g, 5.37 mmol) in glacial acetic acid (13 mL), was added bromine (0.47 g, 2.93 mmol) in acetic acid (5 mL) dropwise within 0.5 h. The mixture was heated at 50 °C for 12 h. The solvent was removed in vacuo, and the residue was poured into water and then extracted with dichloromethane. The organic layer was washed with $Na_2S_2O_5$ and $NaHCO_3$ solution and dried ($MgSO_4$). The solvent was removed, and the crude product was purified by column chromatography using hexane/ethyl acetate (5:1) as the eluent (R_f = 0.70) to give pale yellow solids of **15** (0.71 g, 95%): mp 81−83 °C (CH_2Cl_2/hexane); ^1H NMR ($CDCl_3$, 250 MHz) δ 1.30 (s, 9 H), 7.48 (d, 1 H, J = 2.2 Hz), 7.79 (d, 1 H, J = 2.2 Hz), 9.82 (s, 1 H), 11.39 (s, 1 H); mass spectrum *m*/*e* (% relative intensity) 258 (M^+ + 2, 35), 256 (M^+, 35), 243 (100), 241 (100); IR (film) 3600−3200, 2958, 1656, 1456, 736, 724 cm^{-1}. Anal. Calcd for $C_{11}H_{13}BrO_2$: C, 51.38; H, 5.10. Found: C, 51.20; H, 5.08.

3-(2′-Pyridyl)-5-*tert*-butyl-2-hydroxybenzaldehyde (5). Salicyaldehyde **3** (0.040 g, 0.156 mmol), 2-(tri-*n*-butylstannyl)-pyridine (0.17 g, 0.468 mmol), and $Pd(PPh_3)_4$ (0.018 g, 0.0156 mmol) were dissolved in anhydrous THF (5 mL). The mixture was degassed by the freeze-thaw-pump method (three cycles)

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and then heated at 100 °C under nitrogen for 72 h. The solvent was removed at reduced pressure, and the residue was purified by column chromatography using hexane/ethyl acetate (10:1) as the eluent to give yellow solids (R_f = 0.20) as the product (0.037 g, 93%): mp 89−91 °C (CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.37 (s, 9 H), 7.30 (m, 1 H), 7.89 (td, 1 H, J = 1.8, 8.3 Hz), 7.90 (d, 1 H, J = 2.5 Hz), 7.99 (d, 1 H, J = 8.3 Hz), 8.09 (d, 1 H, J = 2.5 Hz), 8.56 (d, 1 H, J = 4.3 Hz), 10.60 (s, 1 H) 15.09 (bs, 1 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.30, 34.24, 119.57, 120.10, 122.01, 124.25, 127.13, 129.75, 137.93, 140.05, 145.89, 157.00, 161.20, 190.80; mass spectrum *m*/*e* (% relative intensity) 255 (M^+, 8), 240 (22), 227 (100), 212 (56); IR (film) 3600−2400, 1680, 1597, 1480, 1255 cm^{-1}. Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 74.89; H, 6.60; N, 5.42.

Bis[5′-*tert*-butyl-3′-(2″-pyridyl)salicylidene]-1,1,2,2-tetramethylethylenediamine (7). To a solution of **5** (0.042 g, 0.165 mmol) in refluxing absolute ethanol (5 mL) was added slowly in 20 min 2,3-diamino-2,3-dimethylbutane (**6**) (0.0096 g, 0.083 mmol) in absolute ethanol (5 mL) to yield a yellow solution. The solution was refluxed for 1 h. After cooling, yellow crystals were collected by filtration. The rest of product was obtained by cooling the filtrate at 0 °C for several hours followed by filtration to afford totally 0.037 g of bright yellow solids as the product (76%): mp 218−220 °C (ethanol); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.35 (s, 18 H), 1.41 (s, 12 H), 7.15−7.20 (m, 2 H), 7.33 (d, 2 H, J = 2.5 Hz), 7.69 (td, 2 H, J = 1.9, 7.5 Hz), 7.96 (d, 2 H, J = 2.5 Hz), 8.05 (d, 2 H, J = 8.3 Hz), 8.44 (s, 2 H), 8.68 (d, 2 H, J = 4.3 Hz), 14.76 (bs, 2 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 23.63, 32.14, 34.77, 65.82, 119.67, 122.15, 125.31, 127.66, 129.86, 131.51, 136.45, 141.57, 149.81, 156.65, 158.57, 162.48; mass spectrum *m*/*e* (% relative intensity) 590 (M^+, 11); IR (film) 3600−2400, 2962, 1628, 1598, 1469, 1257 cm^{-1}; UV-vis [λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})] 342 (21.5 × 10^3), 434 (1.65 × 10^3). Anal. Calcd for $C_{38}H_{46}N_4O_2 \cdot 1/_2\ H_2O$: C, 76.09; H, 7.90; N, 9.34. Found: C, 76.13; H, 7.85; N, 9.35.

(3-Bromo-5-*tert*-butyl-2-methoxyphenyl)diphenylphosphine (10). To a solution of **9**[24] (5.01 g, 15.6 mmol) in anhydrous ether (20 mL) under nitrogen −78 °C was added n-BuLi (1.6 M, 10 mL, 16.0 mmol) dropwise. The mixture was stirred for 0.5 h at −78 °C to give a yellow solution to which PPh_2Cl (3.44 g, 15.6 mol) in anhydrous ether (10 mL) was added dropwise at −78 °C under nitrogen. The solution was allowed to warm up to room temperature and stirred for 2 h. Dilute HCl (10 mL) was added to the solution at 5 °C. The mixture was extracted with ether, and the organic layer was collected and dried over $MgSO_4$. After removal of solvent, a pale yellow oil was obtained. White crystals were collected by crystallization from ethanol, and the crude product from the mother liquor was purified by column chromatography using hexane/ethyl acetate (10:1) as the eluent (R_f = 0.70) to give totally 5.0 g of **10** (75%): mp 101−103 °C (CH_2C_2/hexane); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.08 (s, 9 H), 3,77 (s, 3 H), 6.64 (dd, 1 H, J = 2.5, 4.2 Hz), 7.20−7.36 (m, 10 H), 7.50 (d, 1 H, J = 2.5 Hz); mass spectrum *m*/*e* (% relative intensity) 428 (M^+ + 2, 98), 426 (M^+, 100). IR (film) 3069, 2962, 1474, 1267 cm^{-1}. Anal. Calcd for $C_{23}H_{24}BrOP$: C, 64.65; H, 5.66. Found: C, 64.95; H, 5.69.

5-*tert*-Butyl-3-(diphenylphosphino)-2-methoxybenzaldehyde (11). To a well-stirred solution of **10** (2.94 g, 6.9 mmol) and TMEDA (1.04 g, 9.0 mmol) in anhydrous ether (10 mL) at −78 °C was added n-BuLi (1.6 M, 4.4 mL, 7.0 mmol) dropwise under nitrogen. The orange solution was stirred at −78 °C for 1 h. Distilled DMF (2.52 g, 34.5 mmol) was added to the solution via a syringe at −78 °C under nitrogen. The mixture was allowed to warm up to room temperature and stirred for 2 h. Dilute HCl was slowly added to the reaction mixture until pH = 2. After stirring for 1−2 h, the mixture was extracted with dichloromethane, and the organic layer was dried (Na_2SO_4) to afford yellow oil after removal of solvent. The crude product was purified by column chromatography (hexane/ethyl acetate = 10:1) to give white solids of **22** (1.82 g, 70%): R_f = 0.55; mp 125−126 °C (CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.10 (s, 9 H), 3.86 (s, 3 H), 7.01 (m, 1 H), 7.24−7.35 (m, 10 H), 7.82 (d, 1 H, J = 2.3 Hz), 10.35 (s, 1 H); MS *m*/*e* (relative intensity) 376 (M^+, 88), 348 (97), 185 (14); IR (film) 2963, 1687, 1586, 1247 cm^{-1}. Anal. Calcd for $C_{24}H_{25}O_2P$: C, 76.58; H, 6.69. Found: C, 76.61; H, 6.73.

5-*tert*-Butyl-3-(diphenylphosphino)-2-hydroxybenzaldehyde (12). To a solution of **11** (0.83 g, 2.2 mmol) in anhydrous CH_2Cl_2 (20 mL) at −78 °C under nitrogen, was added slowly BBr_3 (2.8 g, 11 mmol) in anhydrous CH_2Cl_2 (20 mL) via a syringe. The yellow solution was stirred at −78 °C under nitrogen for 2 h and allowed to stir for further 10 h at room temperature. The mixture was added to ice−water and extracted with CH_2Cl_2. The aqueous layer was neutralized by saturated $NaHCO_3$ and extracted with CH_2Cl_2. The dichloromethane extract was dried over Na_2SO_4 to give a yellow oil which was purified by column chromatography (hexane−ethyl acetate 10:1) to afford a pale yellow solid (0.63 g, 80%): R_f = 0.60; mp 110−112 °C (CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.28 (s, 9 H), 7.06 (dd, 1 H, J = 2.5, 4.8 Hz), 7.37 (m, 10 H), 7.54 (d, 1 H, J = 2.5 Hz), 9.90 (s, 1 H), 11.43 (d, 1 H, J = 2.8 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 30.87, 33.99, 119.34, 122.47, 125.62 (d, J_{CP} = 25.2 Hz), 127.53, 128.48 (d, J_{CP} = 6.9 Hz), 128.72 (d, J_{CP} = 22.0 Hz), 130.72 (d, J_{CP} = 14.5 Hz), 133.81 (d, J_{CP} = 20.8 Hz), 135.79 (d, J_{CP} = 11.3 Hz), 138.94, 172.77, 161.13 (d, J_{CP}= 17.0 Hz), 199.80; mass spectrum *m*/*e* (relative intensity) 362 (M^+, 36), 334 (100); calcd for $C_{23}H_{23}O_2P$: 362.1436; found: 362.1410; IR (film) 3600−3200, 2963, 1651 cm^{-1}.

Bis[5′-*tert*-butyl-3′-(diphenylphosphino)salicylidene]-1,1,2,2-tetramethylethylenediamine (13). To a solution of **12** (0.20 g, 0.55 mmol) in refluxing absolute ethanol (10 mL), was added slowly in 20 min 2,3-diamino-2,3-dimethylbutane (**6**) (0.033 g, 0.28 mmol) in absolute ethanol (10 mL) to yield a yellow solution. The ethanolic solution was refluxed for 4 h. After cooling, yellow crystals were collected after filtration to afford **13** (0.155 g, 70%): mp 186−189 °C (ethanol); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.07 (s, 18 H), 1.34 (s, 12 H), 6.76 (dd, 2 H, J = 2.5, 4.5 Hz), 7.19 (d, 2 H, J = 2.0 Hz), 7.32 (m, 20 H), 8.31 (s, 2 H), 14.37 (bs, 2 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 23.19, 31.17, 33.98, 65.21, 117.16, 124.20 (d, J_{CP} = 13.2 Hz), 128.32 (m), 129.25, 133.83 (d, J_{CP} = 19.5 Hz), 134.60, 136.99 (d, J_{CP} = 11.3 Hz), 140.81, 162.11 (m); FABMS *m*/*e* (% relative intensity) 805 (M+1$^+$, 85); IR (film) 3600−2400, 2962, 1625, 1598, 1435 cm^{-1}; UV-vis [λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})] 340 (7.77 × 10^3), 436 (1.15 × 10^3). Anal. Calcd for $C_{52}H_{58}N_2O_2P_2.3/_2H_2O$: C, 75.07; H, 7.39; N, 3.37. Found: C, 75.06; H, 7.31; N, 3.25.

Bis[5′-*tert*-butyl-3′-(2″-pyridyl)salicylidene]-(*R*,*R*)-1,2-cyclohexanediamine (16). (*R*,*R*)-1,2-Diammoniocyclohexane mono-(+)-tartrate[19] (0.132 g, 0.5 mmol), K_2CO_3 (0.138 g, 1.0 mmol), and distilled water (0.7 mL) were stirred together to form a solution, and then ethanol (2.7 mL) was added. The resulting mixture was heated to reflux, and a solution of aldehyde **5** (0.132 g, 0.5 mmol) in ethanol (1.3 mL) was added dropwise. The funnel was rinsed with ethanol (0.2 mL), and the yellow solution was stirred at refluxed for 4 h. Water (0.7 mL) was added, and the stirred mixture was cooled to rt. The mixture was extracted with CH_2Cl_2. The extracted mixture was washed with water (2 × 1.5 mL) and brine (1.5 mL). After drying over Na_2SO_4, the solvent was removed under vaccum, and the residue was recrystallized from hexane to give yellow solids (0.25 g, 85% yield): mp 170−1 °C, (phase change 118−119 °C). R_f = 0.32 (hexane/ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.29 (s, 18 H), 1.40−2.10 (m, 8 H), 3.33 (m, 2 H), 7.22 (dd, 2 H, J = 5.2, 7.0 Hz), 7.26 (d, 2 H, J = 2.5 Hz), 7.73 (ddd, 2 H, J = 1.8, 7.0, and 7.8 Hz), 7.85 (d, 2 H, J = 2.5 Hz), 7.96 (d, 2 H, J = 7.8 Hz), 8.38 (s, 2 H), 8.71 (d, 2 H, J = 5.2 Hz), 14.14 (bs, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$), 24.19, 31.38, 33.13, 34.05, 72.59, 118.91, 121.56, 124.44, 126.60, 128.97, 130.59, 135.82, 141.13, 149.21, 156.10, 156.93, 164.87; mass spectrum, *m*/*e* (% relative intensity), 588 (M^+, 32), 334 (70), 294 (5), 254 (100), 212 (9), IR (neat film), 733, 796, 1256, 1451, 1565, 1596, 1629, 1633, 2862, 2936, 2960, 2400−3600 cm^{-1}. $[\alpha]^{20}_D$ = −518° (c = 1.0, CH_2Cl_2); UV-vis [λ_{max}, nm (L mol^{-1} cm^{-1})] 342 (16.6 × 10^3). Anal. Calcd for $C_{38}H_{44}N_4O_2$: C, 77.52; H, 7.53; N, 9.52. Found: C, 77.38, H, 7.56; N, 9.46.

Bis[5′-*tert*-butyl-3′-(2″-pyridyl)salicylidene]-(*S*,*S*)-1,2-cyclohexanediamine (17). (*S*,*S*)-1,2-Diammoniocyclohexane mono-(−)-tartrate[19] (0.132 g, 0.5 mmol), K_2CO_3 (0.138 g, 1.0 mmol), and distilled water (0.7 mL) were stirred until dissolu-

tion was achieved, and then ethanol (2.7 mL) was added. The resulting mixture was heated to reflux, and a solution of aldehyde **5** (0.132 g, 0.5 mmol) in ethanol (1.1 mL) was added dropwise. The funnel was rinsed with ethanol (0.2 mL), and the yellow solution was stirred at reflux for 4 h before heating was discontinued. Water (0.7 mL) was added, and the stirred mixture was cooled to rt. The mixture was extracted with CH_2Cl_2. Then the extracted mixture was washed with water (2 × 1.5 mL) and brine (1.5 mL) and dried over Na_2SO_4. The solvent was removed under vaccum, and the residue was recrystallized in hexane to give the yellow solid (0.253 g, 86% yield): mp 169−70 °C (phase change 118−119 °C); $R_f = 0.32$ (hexane/ethyl acetate: 5:1); ^{1}H NMR ($CDCl_3$, 250 MHz): 1.29 (s, 18 H), 1.40−2.10 (m, 8 H), 3.33 (m, 2 H), 7.22 (d, 2 H, J = 5.2, 7.0 Hz), 7.26 (d, 2 H, J =2.5 Hz), 7.73 (ddd, 2 H, J = 1.8, 7.0, and 7.8 Hz), 7.85 (d, 2 H, J = 2.5 Hz), 7.96 (d, 2 H, J = 7.8 Hz), 8.38 (s, 2 H), 8.71 (d, 2 H, J = 5.2 Hz),14.14 (bs, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$), 24.20, 31.38, 33.14, 34.05, 72.59, 118.91, 121.57, 124.44, 126.60, 128.97, 130.60, 135.83, 141.14, 149.21, 156.10, 156.93, 164.88; mass spectrum, *m*/*e* (% relative intensity), 588 (M^+, 22), 334 (73), 294 (9), 254 (100), 212 (11); IR (neat film) 734, 796, 1256, 1451, 1565, 1596, 1630, 1634, 2935, 2960, 2400−3600 cm^{-1}; $[\alpha]^{20}_D = +517°$ (c = 1.0, CH_2Cl_2); UV-vis [λ_{max}, nm (L mol^{-1} cm^{-1})] 342 (16.1 × 10^3). Anal. Calcd for $C_{38}H_{44}N_4O_2$: C, 77.52; H, 7.53; N, 9.52. Found: C, 76.04, H, 7.64; N, 9.22.

Copper(II) Bis[5′-*tert*-butyl-3′-(2″-pyridyl)salicylidene]-(*R*,*R*)-1,2-cyclohexanediamine (18). To a refluxing solution of (*R*,*R*) Schiff base **16** (50 mg, 0.085 mmol) in ethanol (10 mL) was added dropwise $Cu(OAc)_2 \cdot H_2O$ (17 mg, 0.085 mmol), dissolved in hot ethanol (10 mL), within 20 min. The resulting brown suspension was refluxed for 1 h. After the mixture was cooled, the precipitate was filtered and recrystallized in $CHCl_3$/EtOH to give 90 mg of brown solid (yield 81%): mp 352−353 °C; IR (neat film) 2949, 2927, 1622, 1536, 1444, 1429, 1249, 1226, 797 cm^{-1}; $[\alpha]^{20}_D = -1.1 \times 10^{3°}$ (c = 0.02, CH_2Cl_2), UV-vis [λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})] 387 (21.0 × 10^3). Anal. Calcd for $C_{38}H_{42}N_4O_2Cu$: C, 70.23; H, 6.52; N, 8.63. Found: C, 69.96, H, 6.66; N, 8.50. HRMS calcd 650.2682, found 650.2745.

Copper(II) Bis[5′-*tert*-butyl-3′-(2″-pyridyl)salicylidene]-(*S*,*S*)-1,2-cyclohexanediamine (19). To a refluxing solution of (*S*,*S*) Schiff base **17** (50 mg, 0.085 mmol) in ethanol (10 mL) was added dropwise $Cu(OAc)_2 \cdot H_2O$ (17 mg, 0.085 mmol), dissolved in hot ethanol (10 mL), within 20 min. The resulting brown suspension was refluxed for 1 h. After the mixture was cooled, the precipitate was filtered and recrystallized in $CHCl_3$/EtOH to give 90 mg of brown solid (yield 81%): mp 352−353 °C; IR (neat film) 2949, 2927, 1622, 1536, 1444, 1429, 1249, 1226, 798 cm^{-1}. $[\alpha]^{20}_D = 1.1 \times 10^{3o}$ (c = 0.02, CH_2Cl_2), UV-vis [λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})] 388 (20.4 × 10^3). Anal. Calcd for $C_{38}H_{42}N_4O_2Cu$: C, 70.23; H, 6.52; N, 8.63. Found: C, 70.29, H, 6.52; N, 8.63. HRMS calcd 650.2682, found 650.2705.

Nickel(II) Bis[5′-*tert*-butyl-3′-(2″-pyridyl)salicylidene]-(*S*,*S*)-1,2-cyclohexanediamine (20). To a refluxing solution of (*S*,*S*) Schiff base **17** (50 mg, 0.085 mmol) in ethanol (10 mL) was added dropwise $Ni(OAc)_2 \cdot 4H_2O$ (21 mg, 0.085 mmol), dissolved in hot ethanol (10 mL), within 20 min. The yellow precipitate appeared, and the mixture was refluxed for 1 h. After cooling, the precipitate was filtered and recrystallized in $CHCl_3$/EtOH to give 53.4 mg of a muddy yellow solid (yield 97%): mp 380−381 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) 1.32 (s, 18 H), 1.62 (br, 2 H), 1.76 (br, 4 H), 2.36 (br, 2 H), 3.24 (br, 2 H), 6.94 (dd, 2 H, J = 7.6, 7.8 Hz), 7.01 (dd, 2 H, J = 6.9, 7.6 Hz), 7.09 (s, 2 H), 7.46 (s, 2 H), 8.17 (d, 2 H, J = 2.2 Hz), 8.21 (d, 2H, J = 7.8 Hz), 8.57 (d, 2H, J = 2.2 Hz); IR (neat film) 2949, 2927, 1622, 1537, 1445, 1251, 797 cm^{-1}; $[\alpha]^{20}_D = 1.1 \times 10^{3o}$ (c = 0.05, CH_2Cl_2); UV-vis [λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})] 425 (13.6 × 10^3), 329 (16.3 × 10^3). Calcd for $C_{38}H_{42}N_4O_2Ni$: HRMS calcd 645.2739, found 645.2743.

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