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Synthesis of Dinucleating Phenanthroline-Based Ligands

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Abstract: The phenolic bridged dinucleating phenanthroline-pyridine, phenanthroline-phosphine, phenanthroline-alcohol, and phenanthroline-imine ligands have been synthesized from 1,10-phenanthroline via key Stille and Suzuki cross couplings.

INTRODUCTION

Bimetallic complexes have found importance in the fields of bioinorganic chemistry, homogeneous catalysis and magnetic exchange processes.[1,2,3] Notable examples include models for dinitrogen reduction,[4] oxidation chemistry,[5] epoxide ring opening,[6] and hydroformylation.[7] The synthesis of bimetallic complexes depends heavily on the availablity of properly designed binucleating ligands capable of binding metal ions in close proximity.[1,2] Although one of the commonly studied binucleating ligands is the Schiff base type ligands,[1] the Schiff base bears an oxidation and hydrolysis sensitive imine functionality which may give the metal complexes limited catalytic efficiency.[8] Incorporating the imine into part of an aromatic nucleus such as pyridine or 1,10-phenanthroline (Phen) which has been widely applied in catalytic oxidation,[9] catalytic polymerization,[10] and catalytic amination,[11] should enhance the robustness of the ligands towards degradation. We now report our full results on the synthesis of three types of acyclic Phen-based binucleating ligands with pendant pyridine, phosphine, and hydroxyl groups, as well as a novel macrocyclic Schiff base derivative.[12]

RESULTS AND DISCUSSION

The synthesis of phenanthroline-pyridine ligand **9** was accomplished via regioselective nucleophilic aromatic substitution and Stille cross coupling reaction[13] (Scheme 1). The aryl bromide **3**[14] was lithiated with lithium metal to generate the corresponding aryl lithium which then underwent nucleophilic aromatic substitution with Phen followed by oxidative rearomatization with MnO_2 to produce **5** in 80% yield in a similar manner to the Sauvage method.[15] Regioselective bromination of the methoxy-substituted and more electron rich aromatic ring at the *ortho* positions yielded the bromide **6** in 80% yield which was then cross coupled with 2-pyridyltributylstannane (**7**)[16] in Stille cross coupling[13] under prolonged super-heating in THF at 120 °C to form **8** in 86% yield. The potentially chelating interference of the Phen moiety did not seem to affect the coupling. Subsequent demethylation with BBr_3 generated the final target **9** in 80% yield (Scheme 1).

In comparison to the straightforward synthetic route to the dipyridyl derivative **9**, the synthesis of phosphino derivative **15** encountered more complications. Attempted dilithiation of the dibromide **6** with BuLi in Et_2O or THF was not successful. At -78°C or above, lithiation afforded an unidentified complex mixture while the reaction was very slow at -90 to -100 °C. The complication may be due to the nucleophilic attack on the phenanthroline ring by BuLi or the aryl lithio species generated *in situ* . Grignard reagent preparation has

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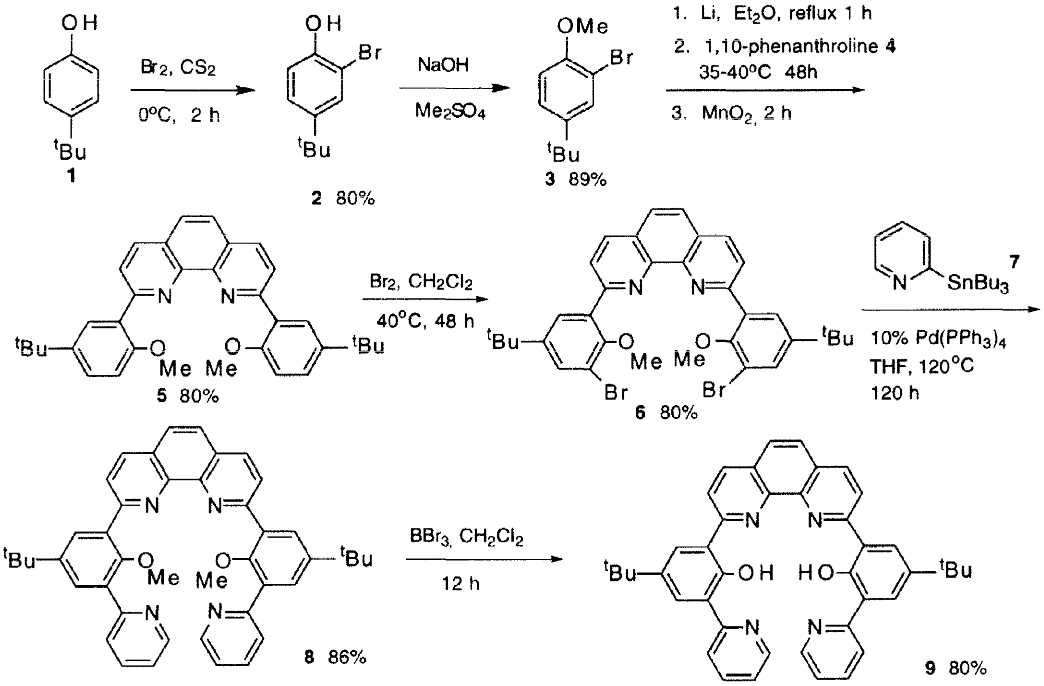
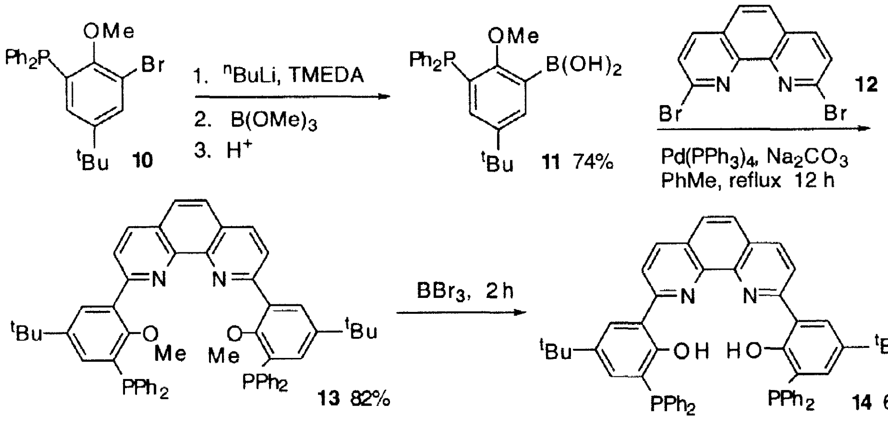
also been considered as an alternative to the lithium compound. However, attempted preparation of aryl magnesium bromide from **6** and subsequent reaction with PPh_2Cl afforded only unidentified product. Stille and Tunney[17] have reported the Pd-catalyzed cross coupling of aryl halides with Me_3SiPPh_2 as an alternative route for phosphination. However, this method did not work for our system as reduction of **6** rather than coupling product was observed. The dibromide may be too unreactive to couple with Me_3SiPPh_2 but the reason for the preference of reduction to coupling is unclear.



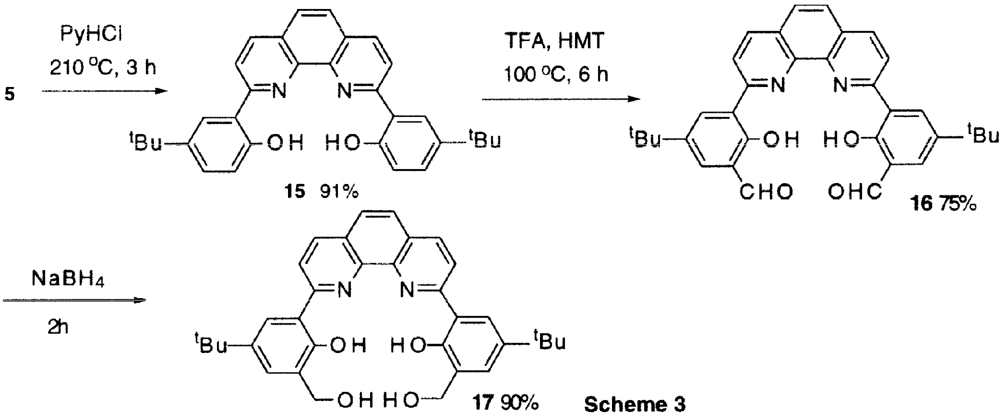
Scheme 1

As phosphination of the 2,9-bis(*o*-anisyl)-1,10-phenanthroline **6** was not successful, the construction of the dinucleating framework required strategic modification. Initial attempts at the direct nucleophilic attack of the lithium agent derived from **10** on 1,10-phenanthroline were not successful probably due to a reduction of nucleophilicity by chelation with phosphine. Therefore, activation was required. Since 2,9-dibromo-1,10-phenanthroline **12** has been demonstrated to couple with aryl boronic acids affording 2,9-diaryl-1,10-phenanthroline in good yields.[18] Hence we embarked on the synthesis of the phosphine ligand via coupling of phosphino boronic acid **11** with 2,9-dibromo-1,10-phenanthroline **12** (Scheme 2).

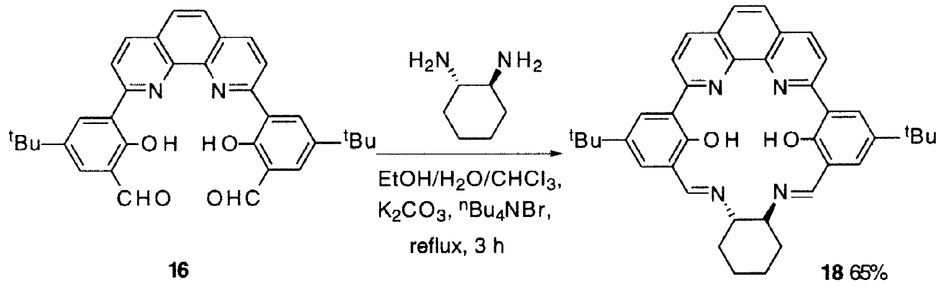


Scheme 2

Lithiation of **10** with the BuLi-TMEDA-Et_2O system afforded the corresponding activated lithium reagent which was then trapped by trimethylborate to give the desired boronic acid **11** in 74% yield after hydrolysis. It is noteworthy that a much lower yield of the boronic acid **11** (< 40%) was obtained during the lithiation of **10** in the absence of TMEDA, probably due to the aforementioned low reactivity of the lithio species. The diphosphine **13** was obtained in 82% yield by Suzuki type[19] palladium-catalyzed cross coupling of boronic acid **11** with 2,9-dibromo-1,10-phenanthroline **12** under classical reaction conditions.[19] Demethylation of **13** under mild conditions with BBr_3 gave the dinucleating ligand **14** in 60% yield.



Scheme 3



(1)

The Phen-alcohol **17** and Phen-imine **18** were prepared via functionalization at the phenol moiety. The Phen-alcohol **17** was prepared conveniently from anisole **5** (Scheme 3). **5** was firstly demethylated with PyHCl to produce 91% yield of phenol **15** which was then formylated with hexamethylene tetramine (HMT) /TFA[22] to give aldehyde **16** in 75% yield. It should be mentioned that Na^+ coordination to **15** was observed from electrospray mass spectrum if $NaHCO_3$ or Na_2CO_3 solution was used in the work up procedure. The problem was avoided by the use of dilute aq ammonia instead during workup. Reduction of **16** with $NaBH_4$ afforded the desired alcohol **17** in 90% yield. The optically active imine **18** was prepared condensation with *trans*-1,2-diaminocyclohenxane in 65% yield using phase-transfer condition to improve reaction efficiency (eq 1). Without the addition of phase transfer agent Bu_4NBr, no product formation was observed.

9, **14** and **17** bear the same dianionic N_2O_2 cavity derived from the 2,9-bis(*o*-phenolic)-1,10-phenanthroline system. This binding site was characterized by the downfield proton signals at 15.70, 14.16 and 15.26 ppm respectively in their ^1H NMR spectra indicating the presence of hydrogen bonded phenolic hydroxy protons, similar to that observed in salen type ligands. In a preliminary study, the ligand **9** formed both homobimetallic complexes of nickel (Ni-Ni) as well as heterobimetallic complex (Ni-Cu).

We have demonstrated that the binucleating Phen-pyridine **9** and Phen-phosphine **14**, Phen-alcohol **17** and Phen-chiral imine **18** ligands can be conveniently synthesized from readily available starting materials. Further investigation of the chemistry of the binuclear complexes is underway.

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EXPERIMENTAL SECTION

Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl immediately prior to use. Hexane was distilled over calcium chloride. Toluene was distilled from sodium and dichloromethane was distilled over calcium hydride. Thin layer chromatography was performed on precoated silica gel plates. Silica gel (70-230 and 230-400 mesh) was used for column chromatography.

Melting points are uncorrected. IR spectra were recorded as neat film on KBr plates. ^1H NMR spectra were recorded either at 250, 300 or 500 MHz. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.24 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as internal standard. Chemical shifts (δ) are reported as part per million (ppm) in δ scale down-field from TMS. Coupling constant (J) are reported in Hertz (Hz). ^{13}C NMR spectra were obtained at 62.89, 75 or at 125 MHz and referenced to the residual $CHCl_3$ (δ 77.00 ppm) in $CDCl_3$. Mass spectra were recorded either in electron ionization or in FAB mode using *m*-nitrobenzyl alcohol (NBA) as the matrix. Elemental Analyses were performed by the Medac Ltd., Department of Chemistry, Brunel University, United Kingdom.

2,9-Bis (5-*tert*-butyl-2-methoxyphenyl)-1,10-phenanthroline (5).[19] The anisole **3**[14] (15.5 g, 0.064 mol) in anhydrous ether (20 mL) was transferred slowly to freshly cut lithium metal (0.98 g, 0.14 mol) in anhydrous ether (10 mL) via a cannular . The mixture was refluxed for 1 h under nitrogen and the aryl lithio reagent was then transferred dropwise to 1,10-phenanthroline (1.44 g, 8.0 mmol) in anhydrous toluene (15 mL) via a cannular under nitrogen to give a red solution. The mixture was allowed to stirred for 48 h at 40°C. The solution was then cooled to 5°C and water (30 mL) was added under nitrogen to hydrolyze the reaction mixture. The organic layer was collected and the aqueous layer was extracted with CH_2Cl_2. MnO_2 (5.0 g, 57 mmol) was added to the organic solution and the mixture was stirred for 8 h and then dried over $MgSO_4$. After filtration and removal of solvent, a brown oil was collected and purified by column chromatography (hexane/ethyl acetate 3 : 1) to give white solids (3.2 g, 80%) as the product. $R_f = 0.30$; mp 115-118°C (CH_2Cl_2/hexane); ^1H NMR ($CDCl_3$, 250 MHz) δ 1.37 (s, 18 H), 3.81 (s, 6 H), 6.95 (d, 2 H, $J = 8.8$ Hz), 7.40 (dd, 2 H, $J = 2.4$, 8.8 Hz), 7.78 (s, 2 H), 8.04 (d, 2 H, $J = 2.4$ Hz), 8.06 (d, 2 H, $J = 8.5$ Hz), 8.20 (d, 2 H, $J = 8.5$ Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.68, 34.22, 55.94, 111.22, 125.26, 125.96, 126.84, 127.42, 128.97, 129.74, 135.01, 143.60, 155.13, 157.23; MS *m/e* (% rel intensity) 504 (M^+, 69), 503 (100), 486 (61); Calcd. for $C_{34}H_{36}N_2O_2$: 504.2777. Found: 504.2777.

2,9-Bis(3-bromo-5-*tert*-butyl-2-methoxyphenyl)-1,10-phenanthroline (6). To a solution of **5** (0.314 g, 0.621 mmol) in CH_2Cl_2 (10 mL), a solution of bromine (0.60 g, 3.7 mmol) in CH_2Cl_2 (10 mL) was added slowly within 20 min. The mixture was stirred at 40°C for 48 h. $Na_2S_2O_5$ solution, sat. $NaHCO_3$ solution and sat. NaCl solution were successively added to wash the cooled mixture. Extraction of the mixture with CH_2Cl_2 afforded a brown solution. A dark brown oil was obtained after removal of solvent. Purification by column chromatography (hexane/ethyl acetate 3 : 1) gave white solids of **6** (0.33 g, 80%). $R_f =$ 0.60; mp 202-204°C (CH_2Cl_2/hexane); ^1H NMR ($CDCl_3$, 250 MHz) δ 1.36(s, 18 H), 3.66 (s, 6 H), 7.64 (d, 2 H, J = 2.5 Hz), 7.86 (s, 2 H), 7.94 (d, 2 H, J = 2.5 Hz), 8.17 (d, 2 H, J = 8.4 Hz), 8.31 (d, 2 H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) d 32.14, 35.33, 62.42, 118.26, 125.27, 127.13, 128.60, 129.07, 131.83, 136.36, 136.73, 147.09, 149.36, 153.69, 157.28; MS *m/e* (rel intensity) 660 (M^+, 100); Anal. Calcd. for $C_{34}H_{34}Br_2N_2O_2$: C, 61.64; H, 5.17; N, 4.23. Found: C, 61.18; H, 5.18; N, 4.06.

2,9-Bis(5-*tert*-butyl-2-methoxy-3-pyridylphenyl)-1,10-phenanthroline (8). The dibromide **6** (0.166 g, 0.25 mmol), 2-tri-n-butylstannyl pyridine (**7**) (0.368 g, 1.0 mmol) and $Pd(PPh_3)_4$ (0.029 g, 0.025 mmol) were dissolved in anhydrous THF (5 mL). The mixture was degassed by the freeze-pump-thaw method (3 cycles) and then stirred at 120°C under nitrogen for 120 h in a sealed tube. The solvent was removed at reduced pressure and the residue was purified by column chromatography (hexane/ethyl acetate = 1 : 1) to give white solids (0.142 g, 86%) as the product. R_f = 0.20; mp 286-287°C (CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.42 (s, 18 H), 3.40 (s, 6 H), 7.26 (m, 2 H), 7.74 (td, 2 H, J = 1.9, 7.5 Hz), 7.81 (d, 2 H, J = 2.6 Hz), 7.86 (s, 2 H), 7.88 (d, 2 H, J = 8.0 Hz), 8.10 (d, 2 H, J = 2.6 Hz), 8.25 (d, 2 H, J = 8.4 Hz), 8.31 (d, 2 H, J = 8.4 Hz), 8.76 (m, 2 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.60, 34.66, 62.08, 121.72, 124.82, 126.18, 127.66, 129.02, 129.74, 133.58, 134.54, 135.65, 135.81, 146.48, 147.05, 149.49, 154.20, 157.05, 157.36; MS *m/e* (rel intensity) 658 (M^+, 100), 657 (98); UV-VIS [λ_{max}, nm (ε, L mol^{-1}cm^{-1})] 298 (12.4x10^3); Anal. Calcd. for $C_{44}H_{42}N_4O_2$: C, 80.21; H, 6.43; N, 8.50. Found: C, 79.93; H, 6.34; N, 8.49.

2,9-Bis(5-*tert*-butyl-2-hydroxy-3-pyridylphenyl)-1,10-phenanthroline (9). The phenanthroline **8** (0.330 g, 0.50 mmol) was dissolved in CH_2Cl_2 (10 mL) and the solution was degassed by the freeze-pump-thaw method (3 cycles). Then BBr_3[21] (1.26 g, 5.0 mmol) in CH_2Cl_2 (10 mL) was added slowly to the solution at -78°C under nitrogen. The mixture was stirred for 1 h at -78°C followed by stirring for a further 12 h at room temperature under nitrogen. The yellow solution was added to the ice water and the crude product was extracted with CH_2Cl_2. The organic layer was collected and the aqueous layer was neutralized by $NaHCO_3$ and extracted with CH_2Cl_2. The organic solution was combined and dried over $MgSO_4$. The solvent was removed and the residue was purified by column chromatography using ethyl acetate as the eluent to give yellow solids of **9** (0.316 g, 80%). R_f = 0.70; mp 280 °C (dec. CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.38 (s, 18 H), 7.19 (m, 2 H), 7.61 (t, 2 H, J = 7.0 Hz), 7.76 (s, 2 H), 7.95 (d, 2 H, J = 2.4 Hz), 8.11 (d, 2 H, J = 8.1 Hz), 8.21 (d, 2 H, J = 2.4 Hz), 8.29 (d, 2 H, J = 8.7 Hz), 8.41 (d, 2 H, J = 8.7 Hz), 8.63 (m, 2 H), 15.70 (brs, 2 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 32.29, 34.98, 121.93, 122.27, 123.36, 124.08, 125.63, 126.31, 127.72, 127.87, 129.13, 137.12, 141.66, 143.80, 148.35, 157.43,. 158.11, 158.30; MS *m/e* (% rel intensity) 630 (M^+, 100), 629 (10), 615 (98), 599 (28); IR (film) 3400-3200 cm^{-1}; UV-VIS [λ_{max}, nm (ε, L mol^{-1}cm^{-1})] 308 (18.9x10^3), 354 (17.9x10^3); Anal. Calcd. for $C_{42}H_{38}N_4O_2$: C, 79.97; H, 6.07; N, 8.88. Found: C, 79.70; H, 5.99; N, 8.70.

5-*tert*-Butyl-2-methoxy-3-diphenylphosphinophenyl boronic acid (11). To a solution of **10**[25] (2.15 g, 5.05 mmol) and TMEDA (0.76 g, 6.56 mmol) in anhydrous ether (10 mL), BuLi (1.6 M, 3.2 mL, 5.12 mmol) was added dropwise at -78°C under nitrogen. The orange solution was stirred at -78°C under nitrogen for 1 h. Trimethyl borate (0.79 g, 7.58 mmol) was added to the lithio reagent at -78°C under nitrogen. The mixture was allowed to stir at -78°C for 1 h followed by stirring at room temperature for 6 h. Dilute HCl was added to the reaction mixture until pH < 2. The mixture was stirred for 1/2 h and then extracted with CH_2Cl_2. The dichloromethane solution was dried over Na_2SO_4 and yellow solids were obtained after removal of solvent. The crude product was purified by column chromatography (hexane/ethyl acetate 10 : 1) to afford white solids as product **11** (1.98 g, 74 %). $R_f = 0.26$; mp 182-185°C (CH_2Cl_2/hexane); ^1H NMR ($CDCl_3$, 250 MHz) δ 1.12 (s, 9 H), 3.87 (s, 3 H), 6.25 (bs, 2 H), 6.91 (dd, 1 H, $J = 2.7, 4.8$ Hz), 7.24-7.84 (m, 10 H), 7.85 (d, 1 H, $J = 2.7$ Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.03, 34.28, 63.25 (d, $J_{CP} = 7.5$ Hz), 128.30 (d, $J_{CP} = 5.7$ Hz), 128.46 (d, $J_{CP} = 15.1$ Hz), 129.14 (d, $J_{CP} = 15.1$ Hz), 131.58, 133.59 (d, $J_{CP} = 20.1$ Hz), 134.39, 135.02, 136.73 (d, $J_{CP} = 10.7$ Hz), 147.05, 166.28 (d, $J_{CP} = 18.2$ Hz); MS *m/e* (rel intensity) 392 (M^+, 14), 335 (51), 169 (100); IR (film) 3416 cm^{-1}; Anal. Calcd. for $C_{23}H_{26}BO_3P$: C, 70.43; H, 6.68. Found: C, 70.44; H, 6.78.

2,9-Bis(5-*t*-butyl-3-diphenylphosphino-2-methoxyphenyl)-1,10-phenanthroline (13). 2,9-Dibromo-1,10-phenanthroline[20] (**12**) (0.079 g, 0.23 mmol) and $Pd(PPh_3)_4$ (0.021 g, 0.023 mmol) were dissolved in toluene (2 mL) under nitrogen. Na_2CO_3 (0.109 g, 1.03 mmol) in water (1 mL) and **11** (0.202 g, 0.51 mmol) in ethanol (2 mL) were added to the toluene solution. The mixture was degassed by the freeze-pump-thaw method (3 cycles) and refluxed under nitrogen for 12 h. After cooling, the mixture was extracted with ether followed by CH_2Cl_2. After removal of solvent, the crude product was purified by column chromatography (hexane/ethyl acetate 3 : 1) to afford the product **13** as white solids (0.166 g, 82%). $R_f = 0.50$; mp 145-147 °C (CH_2Cl_2/hexane); ^1H NMR ($CDCl_3$, 250 MHz) δ 1.17 (s, 18 H), 3.21 (s, 6 H), 6.82 (dd, 2 H, $J = 2.5, 4.1$ Hz), 7.35 (m, 20 H), 7.80 (s, 2 H), 8.05 (d, 2 H, $J = 2.5$ Hz), 8.22 (s, 4 H); FABMS *m/e* (rel intensity) 873 ($M+1^+$, 75); Anal. Calcd. for $C_{58}H_{54}N_2O_2P_2$: C, 79.80; H, 6.23; N, 3.21. Found: C, 79.70; H, 6.25; N, 3.17.

2,9-Bis(5-*t*-butyl-3-diphenylphosphino-2-hydroxyphenyl)-1,10-phenanthroline (14). The phosphine **13** (0.098 g, 0.11 mmol) was dissolved in CH_2Cl_2 (10 mL) and the solution was degassed by the freeze-pump-thaw method (3 cycles). Then BBr_3 (0.28 g, 1.1 mmol) in CH_2Cl_2 (10 mL) was added dropwise to the solution at -78 °C under nitrogen. The mixture was stirred for 1 h at -78 °C followed by stirring for a further 2 h at room temperature under nitrogen. The yellow solution was added to the ice water and the crude product was extracted with CH_2Cl_2. The organic layer was collected and the aqueous layer was neutralized by $NaHCO_3$ and extracted with CH_2Cl_2. The organic solution was combined and dried over Na_2SO_4. The solvent was removed and the residue was purified by column chromatography (hexane/ethyl acetate 3 : 1) to give yellow solids (0.057 g, 60%) as the product. $R_f = 0.30$; mp 276 °C (dec. CH_2Cl_2/hexane); ^1H NMR ($CDCl_3$, 250 MHz) δ 1.18 (s, 18 H), 6.95 (dd, 2 H, $J = 2.0, 3.9$ Hz), 7.24-7.50 (m, 22 H), 7.76 (d, 2 H, $J = 2.0$ Hz), 7.97 (d, 2 H, $J = 8.0$ Hz), 8.04 (d, 2 H, $J = 8.0$ Hz), 14.16 (s, 2 H); FABMS *m/e* (rel intensity) 845 ($M+1^+$, 75); IR (film) 3600-3400 cm^{-1}. Anal. Calcd. for $C_{56}H_{50}N_2O_2P_2$: C, 79.60; H, 5.96; N, 3.32. Found: C, 79.16; H, 6.01; N, 3.34.

2, 9-Bis (5-^{t}butyl- 2-hydroxyphenyl)-1, 10-phenanthroline (15)[23] Pyridine (16 mL) was placed in a 100 mL two-necked round-flask fitted with a thermometer and a funnel. With rapid stirring conc. hydrochloride acid (17.6 mL) was added . The flask was equipped for distillation, and water was distilled from the mixture until its internal temperature rose to 210 °C. After cooling to 140 °C, 2, 9-bis (5-^{t}butyl-2-

methoxyphenyl)-1, 10-phenanthroline (**5**) was added as a solid and the reaction flask was fitted with a reflux condenser connected to a source of nitrogen. The yellow mixture was stirred and refluxed for 3 h (210 ^{o}C). To cooled mixture 70 mL of water was added and extracted with $CHCl_3$, washed with saturated NaCl solution, dried with $MgSO_4$. After removal of solvent a yellow solid was collected as product (4.3 g), 91% yield. R_f = 0.6 (hexane/ethyl acetate = 2:1) was collected; mp 150-152 ^{o}C (hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.40 (s, 18 H), 7.22 (s, 2 H), 7.44 (s, 2 H), 7.60 (s, 2 H), 7.85 (s, 2 H), 8.07 (d, 2 H, J = 8.7 Hz), 8.15 (d, 2 H, J = 8.7 Hz), 14.26 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.22, 34.82, 118.84, 119.30, 120.00, 123.74, 126.41, 127.68, 130.19, 138.04, 141.74, 142.02, 158.66, 158.71; UV-Vis ($CHCl_3$, nm, log ε): 364 (4.78); IR (neat film, cm^{-1}): 3412 (υ_{O-H}); MS m/e (rel intensity): 476 (M^+, 92), 461 (98), 445 (26), 433 (13), 405 (14), 377 (6). Anal. Calcd. for $C_{32}H_{32}N_2O_2$: C, 80.64; H, 6.77 N, 5.88. Found: C, 80.00; H, 6.92; N, 5.71.

2,9-Bis(5-^{t}butyl-3-formyl-2-hydroxyphenyl)-1,10-phenanthroline (16)[22] A stirred mixture containing **15** (0.5 g, 1.1 mmol), hexamethylene tetramine (0.368 g, 2.62 mmol) and trifluoroacetic acid (5 mL) was heated at 100 ^{o}C for 6 h. The reaction was cooled to 75 ^{o}C and 33% (w/w) aqueous H_2SO_4 (10 mL) was added. The stirred mixture was heated at reflux for 1 h. After cooling down, it was neturalized with ammonia and extracted with CH_2Cl_2, then organic layer was collected, washed with brine, dried over anhydrous Na_2SO_4. After removal of the solvent, a yellow solid was obtained (0.41 g), 75 % yield. R_f = 0.33 (CH_2Cl_2). mp 228-230 ^{o}C (decomposed, CH_2Cl_2/hexane). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.41 (s, 18 H), 7.84 (s, 2 H), 8.10 (d, J = 2.8 Hz, 2 H), 8.30 (dd, J = 8.8, 12.0 Hz, 4 H), 8.44 (d, J = 2.3 Hz, 2 H), 10.42 (s, 2 H), 14.70 (br s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.37, 34.45, 121.40, 122.76, 123.25, 126.12, 127.51, 128.78, 129.17, 130.86, 132.83, 137.14, 141.90, 142.91, 156.15, 160.94, 193.24; IR (neat film, cm^{-1}): 3425; FABMS (m/e, % rel intensity): 533 (M^+, 55), 517 (98), 501 (34); HRMS calcd. for $C_{34}H_{32}N_2O_4$: 532.2356, found 532.2378.

2,9-Bis(5-^{t}butyl-3-hydroxymethyl-2-hydroxyphenyl)-1,10-phenanthroline (17) A mixture of **16** (0.5 g, 0.94 mmol) and $NaBH_4$ (0.11 g, 2.84 mmol) in methanol (30 mL) was stirred at rt for 2h, then H_2O (30 mL) was added and extracted with CH_2Cl_2. The organic layer was washed with water and dried over anhydrous Na_2SO_4, evaporated in vacuo to give a yellow solid (0.45 g, 90 %). R_f = 0.20 (CH_2Cl_2) mp 244-246 ^{o}C (CH_2Cl_2/hexane). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.38 (s, 18 H), 2.92 (br s, 2 H), 4.87 (s, 4 H), 7.42 (s, 2 H), 7.74 (s, 2 H), 7.83 (s, 2 H), 8.31 (d, 2 H, J = 8.5 Hz), 8.17 (d, 2 H, J = 8.5 Hz), 15.26 (br s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.58, 34.29, 63.15, 118.17, 119.80, 122.70, 125.87, 127.21, 129.25, 129.50, 137.74, 141.11, 141.34, 156.46, 158.26; IR (neat film, cm^{-1}): 3434 (br, υ_{O-H}), 1530; FABMS m/e (rel intensity): 537 (M^+, 9), 523 (41), 471 (11). HRMS calcd. for $C_{34}H_{36}N_2O_4$: 536.2669, found 536.2616.

2,9-(*R*,*R*)-N,N'-Bis(5-tert-butylsalicylidene)-1,2-cyclohexanediamine-1,10-phenanthroline (18) (*R*,*R*)-1,2-diaminecyclohexane mono-(+)-tartrate salt[22] (0.04 g, 0.15 mmol), K_2CO_3 (0.084 g, 0.6 mmol) and BuN_4Br (0.005 g) were dissolved in distilled water (2 mL), then EtOH (10 mL) was added. A solution of **16** (0.08 g, 0.15 mmol) in $CHCl_3$ (10 mL) was added dropwise into the above solution, the resulting yellow mixture was heated to reflux for 3 h. Water (20 mL) was added and the mixture was extracted with CH_2Cl_2. It was washed with water (2 x 20 mL). The solvent was removed under vacuum and the residue was recrystallized from hexane/$CHCl_3$ to give yellow solid (0.059 g, 65 %). R_f = 0.24 (CH_2Cl_2). mp 159-161 ^oC ($CHCl_3$/hexane). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.15 (s, 18 H), 1.38 (s, 4 H), 1.64 (s, 4 H), 1.80 (m, 2 H), 3.23 (t, J = 4.0 Hz, 2 H), 7.04 (d, J = 2.1 Hz, 2 H), 7.20 (s, 2 H), 7.56 (d, J = 4.5 Hz, 2 H), 7.70 (s, 2 H), 8.18 (s, 2 H), 13.08 (br s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.11, 31.29, 33.12, 33.82, 72.71, 116.14, 117.87, 123.01. 126.45, 127.84, 129.38, 135.92, 141.15, 146.14, 150.23, 158.52, 164.92; IR (neat film, cm^{-1}): 3401, 1765, 1666; FABMS m/e (rel intensity): 611 (M^+, 99), 271(7), 595 (11), 529 (22), 484 (22); HRMS Calcd. for $C_{40}H_{42}N_4O_2$: 611.3302, found 611.3312. $[\alpha]_D^{20}$ = +300.20 (c=0.25, CH_2Cl_2).

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