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Synthesis, structure, and properties of oligo-tridentate ligands; covalently assembled precursors of coordination arrays

Garry S. Hanan, Ulrich S. Schubert, Dirk Volkmer, Emmanuel Rivière, Jean-Marie Lehn, Nathalie Kyritsakas, and Jean Fischer

Abstract: Oligo-tridentate ligands based on alternating pyridines and pyrimidines were synthesised by Stille-type carbon–carbon bond-forming reactions. The terpyridine-like sites are designed to coalign upon metal complexation, giving rise to organized and rigidly spaced metal ions. Peripheral functionalization of the basic bis-tridentate framework was explored. The heterocycles in the ligands are in an all-*trans* conformation about the interannular bonds as indicated by comparison of their ^{1}H NMR spectra. An X-ray crystal structure analysis of the nonchiral tris-tridentate ligand **2***a* reveals a helical structure in the solid state. The seven heterocycles form a helical structure with resulting overlap of the terminal pyridines. Their centroid-to-centroid distance is 4.523 Å with 38.8° between the planes. NMR investigations support a helical conformation in solution as well. Electrochemical and UV absorption measurements indicate that the LUMO resides on the pyrimidine moiety of the ligands.

Key words: nitrogen-containing ligands, Stille coupling, helical structure, supramolecular chemistry.

Résumé : Nous avons développé une route synthétique pour la synthèse de ligands oligo-tridentates basée sur le couplage carbone–carbone de Stille. La disposition des sites tridentates a été conçue en vue de la complexation d'ions métalliques de façon colinéaire. La structure de base a été fonctionalisée de manière à construire des systèmes plus étendus. La structure rayons-X du ligand tris-tridentate **2***a* révèle sa forme hélicoidale. Les groupes pyridine terminaux s'empilent l'un sur l'autre à une distance centre–centre de 4.523 Å avec un angle de 38.8° entre les planes. Le spectre de RMN du proton est en accord avec l'existence de la forme hélicoidale aussi en solution. Les études d'électrochimie et d'absorption d'UV indiquent que la plus basse orbitale inoccupée est localisée principalement sur le groupe pyrimidine.

Mots clés : ligands azoté hétérocycliques, couplage Stille, structure hélicoidale, chimie supramoléculaire.

Introduction

Recent work that exploits hydrogen-bonding (1–3), metal–ligand (4, 5), and cation–π (6) interactions has demonstrated that information stored into molecular components may be read out by various non-covalent interactions to bring about a desired structure (7). Functional supramolecular structures are of current interest for the development of molecular-level devices (8, 9). Interesting structures exploiting metal–ligand interactions based on commercially available compounds have been constructed; however, most contain infinite lattices and some only exist in the solid state (10, 11). Increasingly, chemists must look to more and more complex components to assemble structures presenting desired properties. Molecular components with repeating sub-units simplify the overall synthesis of relatively complex target molecules (12) and this approach has been exploited here to synthesize oligo-tridentate ligands capable of binding metal ions in a predetermined arrangement (13).

We sought to develop models for information storage based on coordination *arrays*, multimetallic complexes of precise nuclearity and geometry, in particular inorganic architectures of two-dimensional geometries and $[m \times n]$ nuclearity. The basic geometries may be termed *racks* $[n]$R, *ladders* $[2n]$L, and *grids* $[m \times n]$G (Fig. 1), where the nuclearity of the R, L, and G species is given by $[n]$, $[2n]$, and $[m \times n]$, in sequence of increasing complexity. In addition to serving as centres for ligand binding and positioning, metal ions also introduce a range of electrochemical, photochemical, and reactional properties.

The metal-directed self-assembly of molecules of rack, ladder, and grid type requires judicious choice of metal and binding site. Transition metal ions with octahedral coordination geometry are expected to cover a wider range of elements and properties than ladder- (14) and grid-type (15) complexes with tetrahedral metal ions. The two ligand moieties, therefore, must be tridentate to maintain an orthogonal disposition about an octahedral metal ion (16). Terpyridine (tpy) forms stable complexes with a wide variety of octahedral metals (17) and is a well-suited tridentate motif. It also sustains a variety of oxidative and reductive conditions (18, 19), and has accessible π^* orbitals (20).

Linking tpy's together in the 4, 3′ positions as depicted in Fig. 2*a* would produce a ligand strand where the individual tpy

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Fig. 1. Inorganic architectures of rack (left), ladder (center), and grid (right) type.

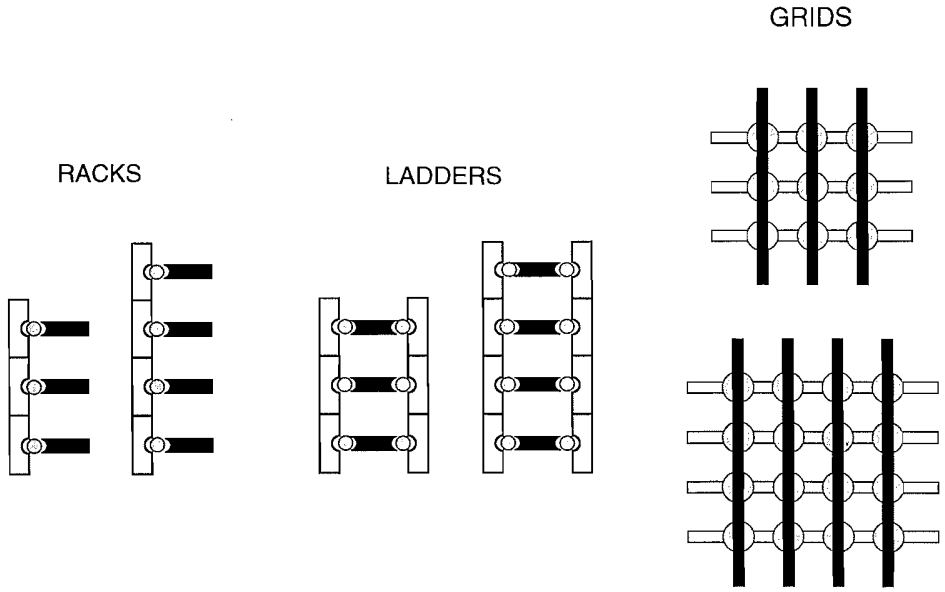
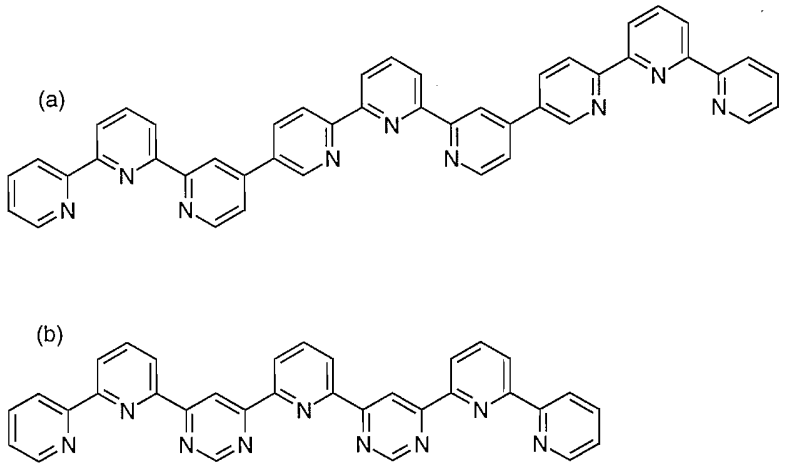


Fig. 2. Types of oligo-tridentate ligands for the assembly of metal ion arrays.



sub-units may not coalign properly in the complex due to rotation about the interannular bonds. To enforce alignment and to promote metal–metal interaction (21), a condensed-ring structure was chosen by using bridging pyrimidines (Fig. 2*b*). The synthesis and characterization of the bis-tridentate (**1***a–f*) and tris-tridentate ligands (**2***a–c*) based on pyridine and pyrimidine is presented in the present work.

Experimental

2,2′-Bipyridine-*N*-oxide (22), 6-chloro-2,2′-bipyridine (23), 2-tributylstannylpyridine (24), 2-bromo-5-methylpyridine (25), and 4,6-dichloro-2-phenylpyrimidine (26) were prepared as described. Materials were obtained from commercial suppliers and used without further purification. Dimethylformamide (DMF) was purchased anhydrous from Aldrich Chemical Company. Diethyl ether (ether) and tetrahydrofuran (THF) were distilled under argon from sodium–benzophenone immediately prior to use in lithiation reactions. Dichloromethane (DCM) was dried over CaH_2. Organic extracts were dried over $MgSO_4$. Chromatography was carried out on Merck 60 silica gel (0.040–0.063 mm), Merck, activity II-III, alumina (0.063–0.200 mm). ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 200 and 50 MHz, respectively, on a Bruker AC 200 spectrometer in $CDCl_3$. ^1H NMR spectra were also recorded at 400 MHz on a Bruker AM 400 spectrometer in $CDCl_3$ where indicated. The chemical shifts were calibrated to the residual solvent peak. Melting points were measured on a digital Thomas–Hoover (Electrotherma) apparatus. Infrared absorption spectra were measured on a Perkin Elmer 1600 series FTIR spectrometer as KBr disks. Electronic absorption spectra were measured on a Cary 219 spectrometer in DCM, with λ_{max} in nm and 10^{-4} ε/dm^3 mol^{-1} cm^{-1}. Cyclic voltammograms were measured using a EDT potentiostat/galvanostat

with a Tacussel IG5-LN integrator and IFELEC-IF 3802 recorder: the working electrode was a platinum disc, the auxiliary electrode was a coiled platinum wire, and the reference electrode was a SCE.

Preparation of 6-bromo-2,2′-bipyridine (*6a*)

(i) Via 6-chloro-2,2′-bipyridine (5)

To 6-chloro-2,2′-bipyridine **5** (2.00 g, 10.5 mmol) was added phosphorous tribromide (50 mL) and the reaction mixture was stirred at 165°C for 5 h. The reaction mixture was cooled to room temperature, poured on crushed ice, carefully basicified with ammonia to basic pH (**Caution:** *exothermic reaction, continuous addition of crushed ice required*), and extracted with ether (4 × 50 mL). The combined organic phases were dried and evaporated. The black residue was extracted with pentane (2 × 100 mL) and the pentane was evaporated. The resulting pale, yellow solid was sublimed (0.75 Torr (1 Torr = 133.3 Pa), 75°C) giving **6***a* (2.30 g, 93%) as a white solid.

(ii) Via 2,6-dibromopyridine (9)

To 2-(tributylstannyl)pyridine **8***a* (43.0 g, 0.117 mol), 2,6-dibromopyridine **9** (48.0 g, 0.205 mol), and tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) (1.86 g, 1.4 mol%) was added THF (100 mL) and the reaction mixture was stirred at reflux for 72 h. The solvent was evaporated and HCl (6 M, 100 mL) was added to the remaining tar. The aqueous phase was extracted with DCM (5 × 100 mL) and basified with ammonia. To the aqueous solution was added $NiCl_2 \cdot 6H_2O$ until a deep-green colour persisted. The aqueous solution was reextracted with DCM (7 × 200 mL) and the latter organic phases were combined, dried, and evaporated. Sublimation (0.75 Torr, 75°C) of the residue gave **6***a* (10.0 g, 36%) as a white solid, mp 70–71°C (lit. (23) mp 70–71°C). ^{1}H NMR, δ (ppm): 8.67 (d, $H_{6'}$, J = 4.7 Hz, 1H), 8.41 (dt, $H_{3'}$, J = 7.9, 0.9 Hz, 1H), 8.37 (dd, $H_{3\text{ or }5}$, J = 7.6, 0.9 Hz, 1H), 7.82 (td, $H_{4'}$, J = 7.6, 1.7 Hz, 1H), 7.67 (t, H_4, J = 7.8 Hz, 1H), 7.49 (dd, $H_{3\text{ or }5}$, J = 7.8, 0.9 Hz, 1H), 7.33 (ddd, $H_{5'}$, J = 7.5, 4.8, 1.2 Hz, 1H). ^{13}C{^{1}H} NMR (DEPT), δ (ppm): 149.0, 139.3, 137.4, 128.1, 124.4, 121.7, 119.9. MS *m/z*+ (EI): 235 (M+1, 6%), 234 (M, 52%), 155 (M−79 (−Br), 100%), 128 (M−107 (−CNH, Br), 14%). R_f: 0.68 on alumina (DCM).

Preparation of 2-tributylstannyl-5-methylpyridine (*8b*)

To a solution of 2-bromo-5-methylpyridine **7***a* (10.00 g, 0.058 mol) in THF (150 mL) was added *n*-butyllithium (37.6 mL, 1.6 M, 0.060 mol) while the solution temperature was kept at −78°C. After stirring 75 min at −78°C, tributyltin chloride (18.5 mL, 0.068 mol) was added during 15 min to the reaction mixture, which was further stirred for 4 h at −78°C. The temperature was left to rise to room temperature, at which time water (50 mL) was added and the phases separated. The aqueous phase was extracted with ether (3 × 100 mL) and the combined organic phases were dried and evaporated. The residue was distilled (Kugelrohr, 0.5 Torr, 130–135°C) and chromatographed on alumina, eluting with DCM, to afford **8***b* (5.09 g, 84%) as a colourless oil. ^{1}H NMR, δ (ppm): 8.58 (d, H_6, J = 0.5 Hz, 1H), 7.30 (dd, $H_{3\text{ or }4}$, J = 8.0, 0.5 Hz, 1H), 7.30 (d, $H_{3\text{ or }4}$, J = 1.2 Hz, 1H), 2.28 (s, H_{methyl}, 3H), 1.57 (m, H_{CH_2}, 6H), 1.37 (m, H_{CH_2}, 6H), 1.15 (m, H_{CH_2}, 6H), 0.87 (t, H_{CH_3}, 9H). ^{13}C{^{1}H} NMR, δ (ppm): 169.5, 151.3, 134.0, 131.8, 131.1, 29.1, 27.3, 18.5, 13.7, 9.7. MS *m/z*+ (FAB): 384 (M + 1, 11%), 326 (M − 58 (Bu + H), 17%), 268 (M − 112 (−2 Bu), 14%), 212 (M − 170 (−3 Bu), 100%). Anal. calcd. for $C_{18}H_{33}NSn$: C 56.57, H 8.70, N 3.67; found: C 56.29, H 8.53, N 3.64. R_f: 0.79 on alumina (CH_2Cl_2).

Preparation of 6-bromo-5′-methyl-2,2′-bipyridine (*6b*)

To 2-tributylstannyl-5-methylpyridine **8***b* (18.69 g, 0.049 mol), 2,6-dibromopyridine **9** (27.25 g, 0.116 mol), and $Pd(PPh_3)_4$ (1.84 g, 2.7 mol%) was added toluene (150 mL) and the reaction mixture was stirred at reflux for 72 h. The solvent was evaporated and HCl (6 M, 50 mL) was added to the remaining tar. The aqueous phase was extracted with DCM (5 × 100 mL) and basified with ammonia. To the aqueous solution was added $NiCl_2 \cdot 6H_2O$ until a deep-green colour persisted. The aqueous solution was reextracted with DCM (5 × 200 mL) and the latter organic phases were combined, dried, and evaporated. Chromatography of the residue on silica (CH_2Cl_2:CH_3OH 99:1) gave **6***b* (8.82 g, 72%) as a white solid, mp 126–128°C. ^{1}H NMR, δ (ppm): 8.48 (d, $H_{6'}$, J = 1.6 Hz, 1H), 8.33 (d, H_5, J = 7.8 Hz, 1H), 8.29 (d, $H_{3'}$, J = 7.8 Hz, 1H), 7.64 (t, H_4, J = 7.8 Hz, 1H), 7.61 (dd, $H_{4'}$, J = 7.8, 1.6 Hz, 1H), 7.45 (d, H_3, J = 7.8 Hz, 1H), 2.39 (s, H_{methyl}, 3H). ^{13}C{^{1}H} NMR (DEPT), δ (ppm): 157.5, 152.0, 149.7, 141.5, 139.1, 137.9, 134.1, 127.6, 121.0, 119.4, 18.4. MS *m/z*+ (FAB): 249 (M, 100%), 169 (M−79 (−Br), 28%). Anal. calcd. for $C_{11}H_9BrN_2$: C 53.04, H 3.64, N 11.25; found: C 53.09, H 3.59, N 11.39. R_f: 0.86 on alumina (DCM).

Preparation of 6-tributylstannyl-2,2′-bipyridine (*10a*)

To a solution of 6-bromo-2,2′-bipyridine **6***a* (3.02 g, 0.0128 mol) in ether (80 mL) was added *n*-butyllithium (8.0 mL, 1.6 M, 0.0128 mol) while the solution temperature was maintained at −90°C. After stirring 30 min, tributyltin chloride (3.63 mL, 0.0128 mol) was added to the reaction mixture over 10 min. The temperature of the solution was left to rise to room temperature, at which time water (30 mL) was added and the phases separated. The aqueous phase was extracted with ether (3 × 50 mL). The combined organic phases were dried and evaporated. The residue was distilled (0.5 Torr, 135–140°C) to afford **10***a* (5.09 g, 89%) as a pale brown oil. IR (neat): 2925, 1574, 1549, 1421, 1074, 770, 691. ^{1}H NMR, δ (ppm): 8.66 (d, $H_{6'}$, J = 4.8 Hz, 1H), 8.53 (d, $H_{3'}$, J = 8.0, 1.0 Hz, 1H), 8.25 (d, $H_{3\text{ or }5}$, J = 8.0, 1.3 Hz, 1H), 7.80 (td, $H_{4'}$, J = 7.6, 1.8 Hz, 1H), 7.63 (dd, H_4, J = 8.0, 7.3 Hz, 1H), 7.40 (dd, $H_{3\text{ or }5}$, J = 7.3, 1.3 Hz, 1H), 7.27 (ddd, $H_{5'}$, J = 7.6, 4.8, 1.2 Hz, 1H), 1.62 (m, H_{CH_2}, 6H), 1.37 (m, H_{CH_2}, 6H), 1.16 (m, H_{CH_2}, 6H), 0.90 (t, H_{CH_3}, 9H). ^{13}C{^{1}H} NMR, δ (ppm): 173.2, 157.0, 155.9, 136.6, 134.0, 132.3, 123.4, 121.1, 119.2, 119.1, 29.1, 27.3, 13.7, 10.1. MS *m/z*+ (FAB): 447 (M + 2, 90%), 389 (M − 58 (Bu + H), 65%), 333 (M − 112 (−2 Bu), 18%), 275 (M − 175 (bpy), 100%). Anal. calcd. for $C_{22}H_{34}N_2Sn$: C 59.34, H 7.71, N 6.29; found: C 59.04, H 7.66, N 6.44. R_f: 0.78 on alumina (5% $CH_3CN - CHCl_3$).

Preparation of 6-tributylstannyl-5′-methyl-2,2′-bipyridine (*10b*)

To a solution of 6-bromo-5′-methyl-2,2′-bipyridine **6***b* (6.94 g, 0.028 mol) in THF (200 mL) was added *n*-butyllithium (18.2 mL, 1.6 M, 0.029 mol) while the solution temperature was maintained at −90°C. After stirring 45 min, tributyltin

chloride (8.34 mL, 0.029 mol) was added to the reaction mixture over 15 min, while the solution warmed up to −78°C. The temperature of the solution was left to rise to room temperature, at which time water (100 mL) was added. Ether (50 mL) was added and the phases separated. The aqueous phase was extracted with ether (5 × 100 mL). The combined organic phases were dried and evaporated. The residue was distilled (Kugelrohr, 0.5 Torr, 150–155°C) and chromatographed on alumina, eluting with DCM to afford **10***b* (10.55 g, 82%) as a colourless oil. ^{1}H NMR, δ (ppm): 8.48 (dd, $H_{6'}$, J = 2.0, 0.8 Hz, 1H), 8.42 (d, $H_{3'}$, J = 8.1 Hz, 1H), 8.20 (ddd, H_5, J = 8.1, 8.0, 1.2 Hz, 1H), 7.61 (td, H_4, J = 8.0, 7.3 Hz, 1H), 7.61 (ddd, $H_{4'}$, J = 8.0, 2.0, 0.8 Hz, 1H), 7.37 (ddd, H_3, J = 8.0, 7.3, 1.2 Hz, 1H), 2.39 (s, H_{methyl}, 3H), 1.62 (m, H_{CH_2}, 6H), 1.37 (m, H_{CH_2}, 6H), 1.15 (m, H_{CH_2}, 6H), 0.89 (t, H_{CH_3}, 9H). ^{13}C{^{1}H} NMR, δ (ppm): 173.1, 156.0, 154.5, 149.3, 137.3, 134.0, 133.0, 132.0, 120.7, 118.9, 29.1, 27.4, 18.4, 13.7, 10.0. MS *m/z*+ (FAB): 461 (M+1, 48%), 403 (M − 58, 46%), 289 (M − 170, 100%). Anal. calcd. for $C_{23}H_{36}N_2Sn$: C 60.15, H 7.90, N 6.10; found: C 59.92, H 7.78, N 5.99. R_f: 0.73 on alumina (CH_2Cl_2).

Preparation of 4,6-dichloro-2-methylpyrimidine (11*b*)

A solution of 2-methyl-4,6-dihydroxypyrimidine (4.11 g, 32.6 mmol) in $POCl_3$ (170 mL) was heated to reflux for 5 h. The $POCl_3$ was evaporated, water (100 mL) was added to the residue, and the mixture was extracted with ether (4 × 50 mL). The combined organic phases were dried and evaporated. The crude solid was sublimed (0.1 Torr, 40°C) to afford **11***b* (3.40 g, 64%) as a white solid, mp 46–47°C (lit. (32) mp 46–48°C). ^{1}H NMR, δ (ppm): 7.20 (s, H_5, 1H), 2.65 (s, H_a, 3H). ^{13}C{^{1}H} NMR, δ (ppm): 169.7, 161.5, 118.3, 25.6.

Preparation of 2-(9-anthryl)-4,6-dichloropyrimidine (11*d*)

To 9-bromoanthracene (5.42 g, 0.0211 mol) in a two-necked, 250 mL, round-bottom flask fitted with a low-temperature thermometer and Ar inlet was added diethyl ether (150 mL). The mixture was cooled to −10°C and *n*-butyllithium (13.8 mL, 0.0221 mol) was added while maintaining the temperature below 0°C. The solution was stirred at 0°C for 20 min and then was cooled to −35°C. To this mixture was added 4,6-dichloropyrimidine (2.99 g) in diethyl ether (30 mL) over 15 min. After stirring at −30°C for 20 min, the temperature was left to rise to 0°C. To this mixture was added acetic acid (1.2 mL), water (0.2 mL), and THF (4 mL) followed by DDQ (4.50 g) in THF (20 mL). The solution was stirred at room temperature for 10 min, brought to 0°C, and NaOH (3 M, 8 mL) was added while vigorously stirring the solution. Water (20 mL) was added to the solution, the phases were separated, and the aqueous phase was extracted with ether (3 × 50 mL). The combined organic phases were dried, concentrated, and chromatographed on alumina, eluting with DCM to afford **11***d* (2.58 g, 40%) as a pale-yellow solid, mp 188.8–190.8°C. IR: 1529, 1306, 1276, 1106, 894, 862, 847, 820, 730, 637. UV–VIS: 249 (11.1), 256 (15.0), 366 (1.01), 385 (1.04). ^{1}H NMR, δ (ppm): 8.60 (s, H_{A10}, 1H), 8.06 (m, H_{A1}, 2H), 7.60 (m, H_{A4}, 2H), 7.59 (s, H_5, 1H), 7.52–7.43 (m, $H_{A2,A3}$, 4H). ^{13}C{^{1}H} NMR (DEPT), δ (ppm): 168.5, 162.4, 131.2, 129.6, 129.5, 128.7, 127.0, 125.3, 124.8, 119.7. MS *m/z*+ (CI): 325.2 (M+H, 100%), 289.2 (M−35 (Cl), 10%). Anal. calcd. for $C_{18}H_{10}N_2Cl_2$: C 66.48, H 3.11, N 8.62; found: C 66.42, H 8.53, N 3.25. R_f: 0.46 on silica (DCM/hexane, 1:1).

General procedure for the in situ preparation of 6-tributylstannyl-2,2′-bipyridines (10*a*,*b*)

To a stirred solution of **6***a* or **6***b* (1 equiv.) in THF at −90°C was added *n*-butyllithium (1.05 equiv.) over 15 min. The temperature of the mixture was maintained at −90°C for another 30 min and was brought to −70°C during the addition of tributyltin chloride (1.05 equiv. over 10 min). The mixture was stirred at −50°C for another 30 min. The THF was evaporated and the residue was used without purification in subsequent reactions. The estimated yield of **10***a*,*b* was 90%.

General procedure for the preparation of the bis-tridentate ligands (1*a*,*e*)

To the residue of **10***a* or **10***b* (2.1 equiv., prepared in situ, vide supra) was added 4,6-dichloro-2-*R*-pyrimidine (1 equiv.), bis(triphenylphosphine)dichloropalladium $Pd(PPh_3)_2Cl_2$ (0.1 equiv.), and dry DMF. The reaction mixtures were stirred at the temperatures and for the times indicated below. The reaction mixtures were cooled and the DMF was evaporated under reduced pressure. The resulting black residues were purified by the procedures described below.

*Preparation of 4,6-bis(2″,2′-bipyrid-6′-yl)pyrimidine (1*a*)*

To 6-tributylstannyl-2,2′-bipyridine **10***a* (prepared in situ from **6***a* (2.00 g, 8.51 mmol), *n*-butyllithium (5.6 mL, 1.6 M, 8.96 mmol), and tributyltin chloride (2.92g, 8.96 mmol)), 4,6-dichloropyrimidine (0.54 g, 3.65 mmol), and $Pd(PPh_3)_2Cl_2$ (0.54 g, 9 mol%) was added DMF (8 mL) and the reaction mixture was stirred at 100°C for 15 h. The DMF was evaporated and the residue was extracted with acetone–methanol (1:1, 3 × 25 mL). The remaining solid was recrystallized from acetonitrile–chloroform to afford **1***a* (0.34 g, 24%) as a off-white solid. The combined filtrates were concentrated and chromatographed on alumina, eluting with DCM to give more **1***a* (0.36 g, 25%). Total yield: 0.70 g (49%); mp: 233–236°C. IR: 1560, 1532, 1474, 1429, 1380, 827, 763, 653. ^{1}H NMR (400 MHz), δ (ppm): 9.78 (d, H_5, J = 1.3 Hz, 1H), 9.40 (d, H_2, J = 1.3 Hz, 1H), 8.79 (dt, $H_{3''}$, J = 8.0, 0.9 Hz, 2H), 8.75 (d, $H_{6''}$, J = 4.7 Hz, 2H), 8.61 (dd, $H_{3' \text{ or } 5'}$, J = 7.9, 1.0 Hz, 2H), 8.57 (dd, $H_{3' \text{ or } 5'}$, J = 7.8, 1.0 Hz, 2H), 8.05 (t, $H_{4'}$, J = 7.8 Hz, 2H), 7.89 (dt, $H_{4''}$, J = 7.7, 1.8 Hz, 2H), 7.39 (ddd, $H_{5''}$, J = 7.6, 4.8, 1.2 Hz, 2H). ^{13}C{^{1}H} NMR, δ (ppm): 164.0, 158.6, 155.9, 155.8, 153.4, 149.3, 138.2, 136.7, 124.0, 122.6, 121.7, 121.2, 114.0. MS *m/z*+ (EI): 389 (M+1, 12%), 388 (M, 57%), 387 (M−1, 100%), 360 (M−28 (CNH), 4%), 310 (M–78 (py), 3%). Anal. calcd. for $C_{24}H_{16}N_6$: C 74.20, H 4.16, N 21.64; found: C 73.95, H 4.02, N 21.43. R_f: 0.06 on alumina (DCM).

Preparation of 4,6-bis(2″,2′-bipyrid-6′-yl)-2-methylpyrimidine (1b)

To 6-tributylstannyl-2,2′-bipyridine **10***a* (prepared in situ from **6***a* (2.10 g, 8.93 mmol), *n*-butyllithium (6.1 mL, 1.6 M, 9.883 mmol), and tributyltin chloride (3.20 g, 9.83 mmol)), 4,6-dichloro-2-methylpyrimidine **11***b* (0.62 g, 3.83 mmol), and $Pd(PPh_3)_2Cl_2$ (0.56 g, 10 mol%) was added DMF (4 mL) and the reaction mixture was stirred at 110°C for 20 h. During this time, a precipitate formed and, upon cooling to 4°C, more solid precipitated out of solution. The solid was collected by filtration, washed with methanol (3 × 25 mL), dissolved in boiling chloroform, and filtered. The filtrate was evaporated and the unreacted starting material and by-products were sub-

limed (10^{-5} Torr, 180°C) and the residue was resublimed (10^{-5} Torr, 200°C) to give **1***b* (0.73 g, 48%) as a white solid, mp 274–276°C. IR: 2922, 1599, 1560, 1542, 1475, 1432, 1385, 993, 789, 764, 653. ^{1}H NMR, δ (ppm): 9.55 (s, H_5, 1H), 8.80 (d, $H_{3''}$, J = 8.0 Hz, 2H), 8.74 (d, $H_{6''}$, J = 4.8 Hz, 2H), 8.58 (d, $H_{3',5'}$, J = 7.8 Hz, 4H), 8.03 (t, $H_{4'}$, J = 7.8 Hz, 2H), 7.89 (td, $H_{4''}$, J = 1.8, 7.8 Hz, 2H), 7.38 (ddd, $H_{5''}$, J = 7.5, 4.8, 1.1 Hz, 2H), 2.94 (s, CH_3, 3H). ^{13}C{^{1}H} NMR (DEPT, CH), δ (ppm): 149.3, 138.2, 136.8, 124.1, 122.5, 121.8, 121.3, 111.1. MS m/z^+ (FAB): 403.2 (M+1, 100%). Anal. calcd. for $C_{25}H_{18}N_6$: C 74.60, H 4.52, N 20.88; found: C 74.57, H 4.49, N 20.79. R_f: 0.73 on alumina (5% CH_3CN–$CHCl_3$); 0.41 on alumina ($CHCl_3$).

*Preparation of 4,6-bis(2″,2′-bipyrid-6′-yl)-2-phenylpyrimidine (**1**c)*

To 6-tributylstannyl-2,2′-bipyridine **10***a* (prepared in situ from **6***a* (0.99 g, 4.21 mmol), *n*-butyllithium (2.8 mL, 1.6 M, 4.43 mmol), and tributyltin chloride (1.39 g, 4.43 mmol)), 4,6-dichloro-2-phenylpyrimidine **11***c* (0.406 g, 1.804 mmol), and $Pd(PPh_3)_2Cl_2$ (0.266 g, 9 mol%) was added DMF (5 mL) and the reaction mixture was stirred at 100°C for 15 h. The DMF was evaporated and the residue was washed with methanol (3 × 25 mL). The remaining solid was recrystallized from DCM giving **1***c* (0.43 g, 51%) as an off-white solid. The combined filtrates were concentrated and chromatographed on alumina, eluting with DCM to give more **1***c* (0.043 g, 5.1%). Total yield: 0.473 g (56%); mp 242–243°C. IR: 1551, 1531, 1475, 1430, 1376, 781, 753, 693, 651. ^{1}H NMR, δ (ppm): 9.69 (s, H_5, 1H), 8.84 (dt, $H_{3''}$, J = 0.9, 8.0 Hz, 2H), 8.78 (m, H_o, 2H), 8.78–8.74 (m, $H_{6'',3' \text{ or } 5'}$, 4H), 8.62 (dd, $H_{3' \text{ or } 5'}$, J = 7.9, 1.0 Hz, 2H), 8.08 (t, $H_{4'}$, J = 7.9 Hz, 2H), 7.91 (td, $H_{4''}$, J = 7.8, 1.8 Hz, 2H), 7.62–7.55 (m, $H_{m,p}$, 3H), 7.40 (ddd, $H_{5''}$, J = 7.5, 4.8, 1.2 Hz, 2H). ^{13}C{^{1}H} NMR (DEPT, CH), δ (ppm): 149.4, 138.2, 136.8, 130.8, 128.7, 128.5, 124.1, 122.6, 121.9, 121.4, 111.8. MS *m/z*+ (CI): 465.4 (M+H, 63%). Anal. calcd. for $C_{30}H_{20}N_6$: C 77.56, H 4.35, N 18.09; found: C 77.48, H 4.34, N 18.20. R_f: 0.65 on alumina ($CHCl_3$).

*Preparation of 2-(9-anthryl)-4,6-bis(2″,2′-bipyrid-6′-yl)-pyrimidine (**1**d)*

To 6-tributylstannyl-2,2′-bipyridine **10***a* (4.60 g, 0.0103 mol), 2-(9-anthryl)-4,6-dichloropyrimidine **11***d* (1.60 g, 0.00492 mol), and $Pd(PPh_3)_2Cl_2$ (0.72 g, 9 mol%) was added DMF (30 mL) and the reaction mixture was stirred at 105°C. After 36 h, TLC indicated the presence of starting material as well as product. Another aliquot of $Pd(PPh_3)_2Cl_2$ (0.20 g, 2 mol%) was added to the reaction mixture. After an additional 24 h, the DMF was evaporated and the resulting residue was extracted with boiling chloroform (8 × 25 mL) and filtered. The combined filtrates were evaporated and the resulting solid was washed with boiling ethanol (3 × 25 mL) and filtered. The solid was recrystallized from chloroform–hexane to afford **1***d* (1.66 g, 60%) as a pale-yellow solid. The filtrates were combined, concentrated, and filtered, giving more pure **1***d* (0.15 g, 5.4%) as a pale-yellow solid. Total yield: (1.81 g, 65%); mp 270–274°C. IR: 1560, 1531, 1474, 1430, 1379, 1262, 1080, 773, 742, 698, 653. ^{1}H NMR, δ (ppm): 9.92 (s, H_5, 1H), 8.90 (dt, $H_{3''}$, J =8.0 Hz, 2H), 8.78 (d, $H_{6''}$, J = 4.7 Hz, 2H), 8.64 (s, H_{A10}, 1H), 8.61 (dd, $H_{3' \text{ or } 5'}$, J = 8.0, 0.9 Hz, 2H), 8.57 (d, $H_{3' \text{ or } 5'}$, J = 7.7, 1.0 Hz, 2H), 8.11 (d, H_{A1}, J = 7.7 Hz, 2H), 7.96 (t, $H_{4'}$, J = 7.9 Hz, 2H), 7.95 (td, $H_{4''}$, J = 7.9, 1.3 Hz, 2H), 7.86 (d, H_{A4}, J = 8.8 Hz, 2H), 7.45 (m, $H_{5'', A2, A3}$, 6H). ^{13}C{^{1}H} NMR, δ (ppm): 167.0, 164.8, 156.1, 155.9, 153.7, 149.4 (CH), 138.3 (CH), 136.9 (CH), 134.2, 131.6, 130.0, 128.7 (CH), 128.3 (CH), 126.2 (CH), 126.1 (CH), 125.3 (CH), 124.1 (CH), 122.8 (CH), 122.4 (CH), 121.3 (CH), 112.0 (CH). MS *m/z*+ (FAB): 565.1 (M+1, 100%), Anal. calcd. for $C_{38}H_{24}N_6$: C 80.82, H 4.29, N 14.89; found: C 80.81, H 4.35, N 14.78. R_f: 0.48 on alumina (DCM).

*Preparation of 4,6-bis(5″-methyl-2″,2′-bipyrid-6′-yl)pyrimidine (**1**e)*

To 6-tributylstannyl-5′-methyl-2,2′-bipyridine **10***b* (prepared in situ from **6***b* (6.94 g, 0.028 mol), *n*-butyllithium (18.2 mL, 1.6 M, 0.029 mol), and tributyltin chloride (9.95 g, 0.029 mol)), 4,6-dichloropyrimidine (1.82 g, 0.012 mol), and $Pd(PPh_3)_2Cl_2$ (1.75 g, 9 mol%) was added DMF (20 mL) and the reaction mixture was stirred at 100°C for 24 h. The DMF was evaporated and the residue was chromatographed on silica (DCM with 1–5% MeOH) and alumina (DCM), giving **1***e* (2.45 g, 49%); mp 239–241°C. ^{1}H NMR, δ (ppm): 9.62 (d, H_5, J = 1.3 Hz, 1H), 9.31 (d, H_2, J = 1.3 Hz, 1H), 8.79 (dt, $H_{3''}$, J = 8.0, 0.9 Hz, 2H), 8.75 (d, $H_{6''}$, J = 4.7 Hz, 2H), 8.61 (dd, $H_{3' \text{ or } 5'}$, J = 7.9, 1.0 Hz, 2H), 8.57 (dd, $H_{3' \text{ or } 5'}$, J = 7.8, 1.0 Hz, 2H), 8.05 (t, $H_{4'}$, J = 7.8 Hz, 2H), 7.94 (t, $H_{4'}$, J = 7.8, 2H), 7.39 (ddd, $H_{5''}$, J = 7.6, 4.8, 1.2 Hz, 2H), 2.40 (s, H_{CH_3}, 3H). ^{13}C{^{1}H} NMR, δ (ppm): 165.9, 158.4, 155.7, 153.3, 153.2, 149.6, 137.9, 137.1, 133.6, 122.2, 121.2, 120.6, 113.8, 18.4. MS *m/z*+ (FAB): 417 (M+1, 100%). Anal. calcd. for $C_{26}H_{20}N_6$: C 74.98, H 4.84, N 20.18; found: C 74.70, H 4.83, N 20.35. R_f: 0.41 on alumina (DCM with 1% MeOH).

*Preparation of 4,6-bis(5″-(bromomethyl)-2″,2′-bipyrid-6′-yl)-pyrimidine (**1**f)*

A mixture of 4,6-bis(5″-methyl-2″,2′-bipyrid-6′-yl)pyrimidine **1***e* (0.106 g, 0.25 mmol), *N*-bromosuccinimide (0.460 g, 0.0026 mol), and 2,2′-azobis(2-methylpropionitrile) (0.0021 g, 0.13 mmol) in 20 mL carbon tetrachloride was heated under reflux for 70 min (monitored by TLC). The mixture was filtered hot and the filtrate was cooled to 0°C. The white precipitate was collected and chromatographed on silica (DCM with 1–5% MeOH), giving **1***f* (39 mg, 27%); mp 231–233°C. ^{1}H NMR, δ (ppm): 9.72 (d, H_5, J = 1.2 Hz, 1H), 9.40 (d, H_2, J = 1.2 Hz, 1H), 8.75 (d, $H_{6''}$, J = 2.3 Hz, 2H), 8.75 (d, $H_{3''}$, J = 7.7 Hz, 2H), 8.60 (dd, $H_{3' \text{ or } 5'}$, J = 7.7, 0.9 Hz, 2H), 8.57 (dd, $H_{3' \text{ or } 5'}$, J = 7.7, 0.3 Hz, 2H), 8.05 (t, $H_{4'}$, J = 7.7 Hz, 2H), 7.94 (dd, $H_{4'}$, J = 7.7, 2.1, 2H), 4.61 (s, H_{CH_2}, 4H). ^{13}C{^{1}H} NMR, δ (ppm): 163.0, 158.6, 155.8, 155.2, 153.5, 149.3, 138.3, 137.5, 134.0, 122.8, 121.9, 121.2, 114.1, 29.7. MS *m/z*+ (FAB): 575 (M+1, 100%), 496 (M − Br, 29%), 415 (M − 2 Br, 24%), 242 (45%). HRMS (M^+) calcd. for $C_{26}H_{18}N_6Br_2$: 573.0039; found: 573.0036. R_f: 0.42 on alumina (DCM with 1% MeOH).

Preparation of 4-(2″,2′-bipyrid-6′-yl)-6-chloropyrimidine (12*a*)

To 6-tributylstannyl-2,2′-bipyridine **10***a* (prepared in situ from **6***a* (1.01 g, 4.30 mmol), *n*-butyllithium (2.65 mL, 1.6 M, 4.73 mmol), and tributyltin chloride (1.54 g, 4.73 mmol)), 4,6-dichloropyrimidine **11***a* (1.15 g, 7.74 mmol), and $Pd(PPh_3)_2Cl_2$ (0.27 g, 10 mol%) was added DMF (10 mL); the reaction mixture was stirred at 90°C for 10 h and subsequently

cooled to room temperature. To the mixture was added a saturated aqueous solution of KF (20 mL) and ether (30 mL). The mixture was stirred vigorously for 1 h. Water (100 mL) was added and the mixture was extracted with diethyl ether (3 × 50 mL). The combined organics were washed with water (3 × 50 mL), dried, and evaporated. The residue was chromatographed on alumina, eluting with DCM to afford pure **12***a* (0.476 g, 41%) as a white solid, mp 151.8–152.2°C. IR: 1561, 1530, 1447, 1428, 1350, 769, 760. ^{1}H NMR, δ (ppm): 9.08 (d, H_2, J = 1.0 Hz, 1H), 8.72 (d, $H_{6''}$, J = 4.0 Hz, 1H), 8.62–8.50 (m, $H_{5,3',5',3''}$, 4H), 8.03 (t, $H_{4'}$, J = 7.9 Hz, 1H), 7.91 (td, $H_{4''}$, J = 7.8, 1.7 Hz, 1H), 7.38 (ddd, $H_{5''}$, J = 7.5, 4.7, 1.1, 1H). ^{13}C{^{1}H} NMR, δ (ppm): 158.7, 149.3, 138.3, 137.0, 124.2, 123.4, 122.1, 121.2, 118.0. MS *m/z*+ (EI): 268 (M, 100%), 240 (M–28 (CHN), 5%), 233 (M−35 (Cl), 36%), 206 (M−62 (Cl + CHN), 34%), 155 (M−113 (py + Cl), 13%), 78 (M−190 (bpy+ Cl), 21%). Anal. calcd. for $C_{14}H_9ClN_4$: C 62.57, H 3.38, N 20.85; found: C 62.58, H 3.35, N 20.91. R_f: 0.36 on alumina (DCM).

Preparation of 4-(2″,2′-bipyrid-6′-yl)-6-chloro-2-methylpyrimidine (12*b*)

To 6-tributylstannyl-2,2′-bipyridine **10***a* (prepared in situ from **6***a* (3.76 g, 16.0 mmol), *n*-butyllithium (10.5 ml, 1.6 M, 16.8 mmol), and tributyltin chloride (5.21 g, 16.0 mmol)), 4,6-dichloro-2-methylpyrimidine **11***b* (2.77 g, 17.0 mmol), and $Pd(PPh_3)_2Cl_2$ (1.0 g, 9 mol%) was added DMF (25 mL); the reaction mixture was stirred at 90°C for 14 h and subsequently cooled to room temperature. To the mixture was added a saturated aqueous solution of KF (50 mL) and ether (100 mL). The mixture was stirred vigorously for 2 h. Water (300 mL) was added and the mixture was extracted with diethyl ether (3 × 150 mL). The combined organics were washed with water (3 × 50 mL), dried, and evaporated. The residue was filtered over a short alumina column, eluting with DCM to afford a crude yellow powder. Recrystallization from acetonitrile afforded white needles of **12***b* (2.83 g, 67%), mp 142°C. IR: 1561, 1537, 1472, 1424, 1393, 1344, 1324, 1260, 1154, 1068, 876, 848, 834, 787, 761, 740, 666. ^{1}H NMR, δ (ppm): 8.69 (d, $H_{6''}$, J = 4.7 Hz, 1H), 8.55 (d, $H_{3'}$, $H_{5'}$, J = 7.8 Hz, 2H), 8.48 (dd, $H_{3''}$, J = 7.8, 1.0 Hz, 1H), 8.35 (s, H_5, 1H), 7.97 (t, $H_{4'}$, J = 7.8 Hz, 1H), 7.87 (dt, $H_{4''}$, J = 7.8, 1.7 Hz, 1H), 7.34 (ddd, $H_{5''}$, J = 7.3, 4.7, 1.2 Hz, 1H), 2.79 (s, CH_3, 3H). ^{13}C{^{1}H} NMR, δ (ppm): 168.9, 164.6, 162.0, 155.9, 155.5, 152.2, 149.2, 138.1, 136.9, 124.1, 123.1, 122.0, 121.2, 114.6, 25.9. MS *m/z*+ (FAB): 283.1 (M+H, 100%), 206.1 (M−76 (py), 6%). Anal. calcd. for $C_{15}H_{11}ClN_4$: C 63.72, H 3.92, N 19.82; found: C 63.61, H 3.68, N 19.90. R_f: 0.66 on alumina (DCM).

Preparation of 4-(2″,2′-bipyrid-6′-yl)-6-chloro-2-phenylpyrimidine (12*c*)

To 6-tributylstannyl-2,2′-bipyridine **10***a* (prepared in situ from **6***a* (1.42 g, 6.04 mmol), *n*-butyllithium (4.15 mL, 1.6 M, 6.64 mmol), and tributyltin chloride (2.16 g, 6.64 mmol)), 4,6-dichloro-2-phenylpyrimidine **11***b* (0.42 g, 6.04 mmol), and $Pd(PPh_3)_2Cl_2$ (0.42 g, 10 mol%) was added DMF (25 mL); the reaction mixture was stirred at 90°C for 13.5 h and subsequently cooled to room temperature. To the mixture was added a saturated aqueous solution of KF (20 mL) and ether (30 mL). The mixture was stirred vigorously for 1 h. Water (100 mL) was added and the mixture was extracted with diethyl ether (3 × 50 mL). The combined organics were washed with water (3 × 50 mL), dried, and evaporated. The residue was chromatographed on alumina, eluting with DCM–hexane 1:1 to afford **12***c* (1.00 g, 48%) as a white solid, mp 187–189°C. IR: 1559, 1546, 1530, 1430, 1374, 1332, 1077, 826, 785, 754, 696, 650. ^{1}H NMR, δ (ppm): 8.73 (d, $H_{6''}$, J = 4.7 Hz, 1H), 8.69 (dd, $H_{3'}$ or $H_{5'}$, J = 7.8, 0.9 Hz, ^{1}H), 8.64–8.58 (m, $H_{3'}$ or $H_{5'}$, $H_{3'',o}$, 4H), 8.45 (s, H_5, 1H), 8.05 (t, $H_{4'}$, J = 7.8 Hz, 1H), 7.91 (td, $H_{4''}$, J = 7.8, 1.7 Hz, 1H), 7.58–7.51 (m, $H_{m,p}$, 3H), 7.38 (ddd, $H_{5''}$, J = 7.5, 4.8, 1.1 Hz, 1H). ^{13}C{^{1}H} NMR, δ (ppm): 165.1, 164.7, 162.7, 156.0, 155.6, 152.4, 149.3, 138.2, 137.0, 136.4, 131.5, 128.7, 124.2, 123.2, 122.2, 121.3, 115.3 (missing one C). MS *m/z*+ (EI): 344 (M, 100%), 309 (M−35 (Cl), 83%), 242 (M+H−103 (C_6H_5+CN), 6%), 206 (M−138 (C_6H_5+CN+Cl), 60%), 155 (M+H−190 (bpy+ Cl), 32%). Anal. calcd. for $C_{20}H_{13}ClN_4$: C 69.66, H 3.81, N 16.25; found: C 69.88, H 3.94, N 16.22. R_f: 0.48 on alumina (DCM/hexane, 1:1).

Preparation of 2,6-bis(tributylstannyl)pyridine (13)

To 2,6-dibromopyridine **9** (17.3 g, 0.0730 mol) in THF (240 mL) was added *n*-butyllithium (28 mL, 10.0 M, 0.28 mol) dropwise over 2 h while the solution temperature was maintained below −90°C. The solution was stirred for 2 h at −90°C and tributyltin chloride (75 mL, 0.28 mol) was added over 1 h while the solution temperature was kept below −75°C. The solution temperature was allowed to rise to room temperature and the THF was evaporated. Water (30 mL) was added to the residue and the aqueous phase was extracted with DCM (3 × 20 mL). The combined organic phases were dried and evaporated. The residue was purified by two Kugelrohr distillations (5 × 10^{-6} Torr, 140–150°C) to afford **13** (8.15 g, 17%) as a pale-brown oil. ^{1}H NMR, δ (ppm): 7.30–7.20 (m, $H_{3,4}$, 3H), 1.70–1.55 (m, CH_2, 6H), 1.46–1.21 (m, CH_2, 6H), 1.16–1.04 (m, CH_2, 6H), 0.92 (t, CH_3, 9H). ^{13}C{^{1}H} NMR, δ (ppm): 174.51 (C_2, J_{Sn-C} = 255, 28 Hz), 130.63 (C), 130.33 (C), 29.25 (CH2, J_{Sn-C} = 10.8 Hz), 27.48 (CH_2, J_{Sn-C} = 27.4 Hz), 13.81 (CH_3), 10.05 (CH_2, J_{Sn-C} = 37.2, 7.2 Hz). MS *m/z*+ (EI): 597 (M−58 (H + butyl), 100%), 540 (M−115 (H, 2 × butyl), 18%). Anal. calcd. for $C_{29}H_{57}NSn_2$: C 52.99, H 8.76, N 2.13; found: C 53.20, H 8.91, N 2.34. R_f: 0.80 on alumina ($CHCl_3$).

Preparation of 2,6-bis(6′-(2‴,2″-bipyrid-6″-yl)-pyrimidin-4′-yl)-pyridine (2*a*)

To 2,6-bis(tributylstannyl)pyridine **13** (0.4586 g, 0.6978 mmol), 4-(2′,2″-bipyrid-6′-yl)-6-chloropyrimidine **12***a* (0.4125 g, 1.535 mmol), and $Pd(PPh_3)_2Cl_2$ (0.108 g, 10 mol%) was added DMF (5 mL); the reaction mixture was stirred at 120°C for 48 h. The DMF was evaporated, DCM (50 mL) was added to the residue, and the organic phase was extracted with aqueous HCl (5 × 50 mL). The combined aqueous phases were extracted with DCM (4 × 50 mL), basified, and reextracted with DCM (5 × 75 mL). The latter organic phases were combined, dried, and evaporated. The residue was chromatographed on alumina, eluting with DCM to afford **2***a* (0.118 g, 31%) as a white solid, mp 292–293°C. IR: 1601, 1576, 1564, 1531, 1468, 1457, 1431, 1372, 1247, 1273, 990, 827, 771, 661. ^{1}H NMR (400 MHz), δ (ppm): 9.99 (d, H_5, J = 1.3 Hz, 2H), 9.44 (d, H_2, J = 1.3 Hz, 2H), 8.70 (d, $H_{3'''}$, J = 7.8 Hz, 2H), 8.62 (dd, $H_{3' \text{ or } 5'}$, J = 7.7, 1.0 Hz, 2H), 8.38 (dd, $H_{3' \text{ or } 5'}$, J

= 7.9, 1.0 Hz, 2H), 8.33 (d, $H_{6''}$, J = 4.8 Hz, 2H), 8.31 (dt, $H_{3''}$, J = 7.7, 1.0 Hz, 2H), 8.14 (t, $H_{4'''}$, J = 7.8 Hz, 1H), 8.02 (t, $H_{4'}$, J = 7.8 Hz, 2H), 6.85 (ddd, $H_{5''}$, J = 7.4, 4.7, 1.2 Hz, 2H), 6.72 (td, $H_{4''}$, J = 7.6, 1.9 Hz, 2H). $^{13}C\{^1H\}$ NMR, δ (ppm): 164.2, 163.8, 158.8, 156.0, 154.8, 153.9, 153.1, 148.5, 138.6, 138.0, 135.8, 123.7, 123.2, 122.7, 121.3, 121.2, 114.0. MS *m/z*+ (EI): 544 (M+1, 22%), 543 (M, 38%), 542 (M−1, 86%), 543 (M−2, 46%), 515 (M−27 (CNH), 4%), 465 (M−77 (py), 86%), 388 (M−154 (bpy), 6%); HRMS *m/z* calcd. for $C_{33}H_{22}N_9$ (MH^+): 544.1998; found: 544.1985. Anal. calcd. for $C_{33}H_{21}N_9$: C 72.90, H 3.90, N 23.19; found: C 71.96, H 3.72, N 23.14. R_f: 0.16 on alumina ($CHCl_3$).

Preparation of 2,6-bis(6′-(2‴,2″-bipyrid-6″-yl)-2′-methylpyrimidin-4′-yl)-pyridine (2*b*)

To 2,6-bis(tributylstannyl)pyridine **13** (1.45 g, 2.2 mmol), 4-(2″,2′-bipyrid-6′-yl)-6-chloro-2-methylpyrimidine **12***b* (1.30 g, 4.6 mmol), and $Pd(PPh_3)_2Cl_2$ (0.25 g, 16 mol%) was added DMF (15 mL); the reaction mixture was stirred at 120°C for 44 h and subsequently cooled to room temperature. The solid precipitate was filtered off and it was washed thoroughly, first with DMF and then with acetonitrile. The combined filtrates were evaporated to dryness. The remaining residue was treated with a mixture of ether and hexane (1/1) to yield a second crop of the desired product. The crude product was suspended in chloroform and refluxed for 12 h. Filtration of the hot mixture yields **2***b* as an off-white powder (0.56 g, 45%), mp 334°C. IR: 1599, 1538, 1474, 1429, 1371, 1259, 1131, 1095, 1070, 993, 826, 788, 766, 742, 634. ^1H NMR, δ (ppm): 9.80 (s, H_5, 2H), 8.65 (d, $H_{3'''}$, J = 7.7 Hz, 2H), 8.63 (dd, $H_{3'}$ or $H_{5'}$, J = 7.9, 1.0 Hz, 2H), 8.40 (dd, $H_{3'}$ or $H_{5'}$, J = 7.9, 1.0 Hz, 2H), 8.37–8.34 (m, $H_{6''}$, $H_{3''}$, 4H), 8.10 (t, $H_{4'''}$, J = 7.7 Hz, 1H), 8.00 (t, $H_{4'}$, J = 7.7 Hz, 2H), 6.86 (ddd, $H_{5''}$, J = 7.4, 4.6, 1.2 Hz, 2H), 6.77 (td, $H_{4''}$, J = 7.9, 1.8 Hz, 2H), 2.97 (s, CH_3, 6H). $^{13}C\{^1H\}$ NMR, δ (ppm): insufficiently soluble. MS *m/z*+ (FAB): 572.1 (M+H, 100%), 493.1 (M−78 (py), 5%). HRMS *m/z*+ calcd. for $C_{35}H_{26}N_9$ (MH+): 572.2309; found: 572.2322. Anal. calcd. for $C_{35}H_{25}N_9$: C 73.54, H 4.41, N 22.05; found: C 73.73, H 4.11, N 22.27. R_f: 0.12 on alumina ($CHCl_3$).

Preparation of 2,6-bis(6′-(2‴,2″-bipyrid-6″-yl)-2′-phenylpyrimidin-4′-yl)-pyridine (2*c*)

To 2,6-bis(tributylstannyl)pyridine **13** (0.194 g, 0.29 mmol), 4-(2′,2″-bipyrid-6′-yl)-6-chloro-2-phenylpyrimidine **12***c* (0.200 g, 0.580 mmol), and $Pd(PPh_3)_2Cl_2$ (0.06 g, 10 mol%) was added DMF (10 mL); the reaction mixture was stirred at 110°C for 60 h. The DMF was evaporated and the residue was washed with methanol (3 × 25 mL). The remaining solid was recrystallized from chloroform to afford **2***c* (0.0606 g, 30%) as a white solid. The combined filtrates were evaporated and the residue was washed with boiling diethyl ether and recrystallized from chloroform to give more pure **2***c* (0.0553 g, 27%). Total yield: 0.116 g (57%); mp 262–264°C. IR: 1560, 1538, 1476, 1429, 1368, 1261, 992, 823, 788, 757, 697, 652, 634. ^1H NMR (400 MHz), δ (ppm): 9.97 (s, H_5, 2H), 8.93 (d, $H_{3'''}$, J = 7.9 Hz, 2H), 8.85 (dd, $H_{3'\text{ or }5'}$, J = 7.7, 1.0 Hz, 2H), 8.83 (dd, H_o, J = 8.0, 1.8 Hz, 4H), 8.43 (d, $H_{3'\text{ or }5'}$, J = 8.2 Hz, 2H), 8.41 (d, $H_{3''}$, J = 7.6 Hz, 2H), 8.35 (d, $H_{6''}$, J = 5.0 Hz, 2H), 8.21 (t, $H_{4'''}$, J = 7.8 Hz, 1H), 8.07 (t, $H_{4'}$, J = 7.9 Hz, 2H), 7.65–7.58 (m, $H_{m,p}$, 6H), 6.87 (ddd, $H_{5''}$, J = 7.3, 5.0, 1.2 Hz, 2H), 6.78 (td, $H_{4''}$, J = 7.3, 1.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (DEPT): δ (ppm): 148.5, 138.4, 139.0, 135.9, 130.9, 128.7, 128.6, 123.7, 123.2, 122.6, 121.5, 121.4, 111.8. MS *m/z*+ (FAB): 696.2 (M+H, 100%), 617 (M−78 (py), 4%); HRMS *m/z* calcd. for $C_{45}H_{30}N_9$ (MH^+): 696.2624; found: 696.2618. Anal. calcd. for $C_{45}H_{29}N_9 \cdot H_2O$: C 75.71, H 4.39, N 17.66; found: C 76.06, H 4.57, N 17.39. R_f: 0.33 on alumina (DCM).

Crystal structure determination

X-Ray data for **2**: ($C_{33}H_{21}N_9$), M = 543.6; colourless crystals; monoclinic; a = 12.396(3), b = 12.307(3), c = 17.358(5) Å, ß = 95.49(2)°, V = 2636.0 Å^3, Z = 4, ρ_{calc} = 1.370, μ = 6.502 cm^{-1}, space group *C*2/*c*. A suitable crystal of **2**, (0.28 × 0.20 × 0.14 mm^3) was mounted on the end of a glass fibre: 2891 + $h \pm k \pm l$ reflections were collected on a Philips PW1100/16 instrument at 20°C with Cu graphite monochromated radiation (λ = 1.5418 Å), θ/2θ flying step scans, step width = 0.03°, scan speed = 0.020° s^{-1}, scan width = 0.80 + 0.14 tg(θ)°, 3° < θ < 52°. Three standard reflections measured every hour during the data collection period showed no significant trend. The raw data were converted to intensities and corrected for Lorentz and polarization factors. The structure was solved using direct methods: 1036 independent reflections with $I > 3\sigma(I)$ were used to determine and refine the structure. Hydrogen atoms were introduced as fixed contributors by their computed coordinates (C—H = 0.95 Å) and isotropic temperature factors such as $B_H = 1.3\ B_{eqv}(C)$ Å^2. Empirical absorption corrections were applied (DIFABS): Molen on a Vax computer was used for all calculations. Final $R(F)$ = 0.035. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Results and discussion

The basic ligand design is shown in Fig. 2*b*. Modification of the substituent in the pyrimidine 2-position will influence the metal-binding properties as well as the shape of the ligand upon metal complexation. Various R groups (hydrogen, methyl, phenyl, and 9-anthryl) were incorporated into the framework by attaching bipyridyl subunits onto substituted pyrimidines by carbon–carbon bond-forming reactions. To use such ligands as building blocks for larger systems requires the functionalization of the terminal pyridines; this was done by introducing a functionalized methyl group in the 5-position of the terminal pyridine ring, so as not to interfere with metal complexation.

The key material, 6-bromo-2,2′-bipyridine **6***a*, was synthesized in two different ways. In the first approach (Fig. 3), bipyridine (bpy) **3** and *m*-CPBA gave 2,2′-bipyridine-*N*-oxide **4** in 46% yield (22). Excess $POCl_3$ and **4** gave two chlorobipyridine isomers, 4-chloro-2,2′-bipyridine and 6-chloro-2,2′-bipyridine **5** in 99% yield (27). The 6-isomer is isolated by selectively complexing the 4-isomer with $Ni(II)Cl_2 \cdot 6H_2O$ in water (28). The bpy **5** is extracted into DCM and isolated in 45% yield and is converted to 6-bromo-2,2′-bipyridine **6***a* in 93% yield with excess PBr_3 heated to reflux. The overall yield of **6***a* from bpy over the four steps is 19% (Fig. 3).

We investigated whether **6***a* could be prepared by organotin chemistry in good yields in the steps outlined in Fig. 3. Other direct methods to synthesize **6***a* resulted in moderate yields or multistep procedures (29–31). 2-Tributylstannylpyridine (24)

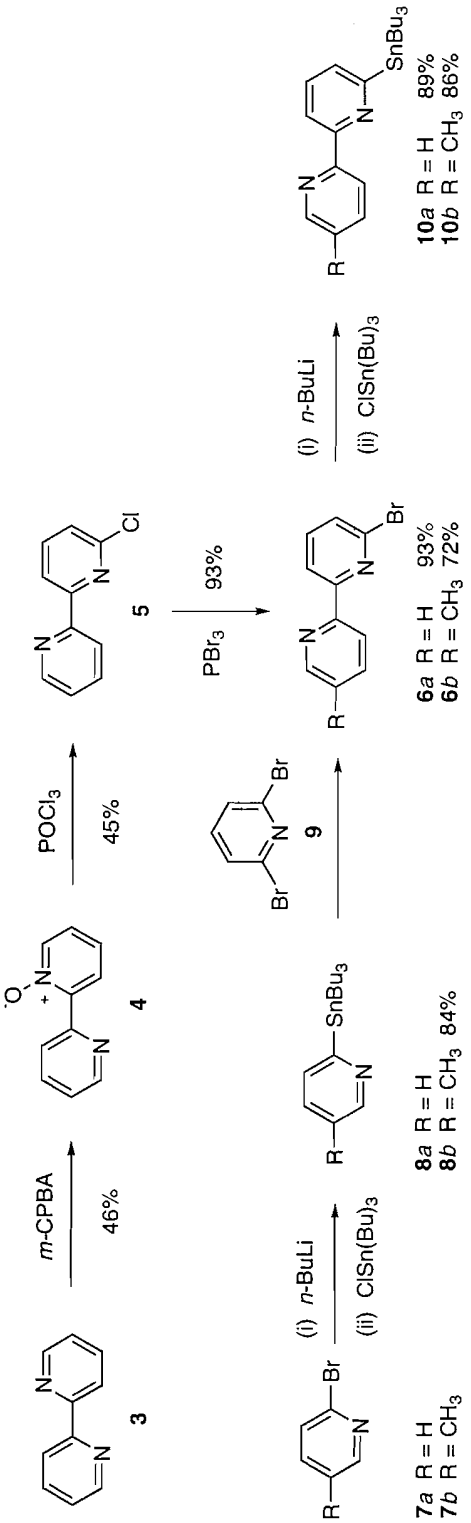


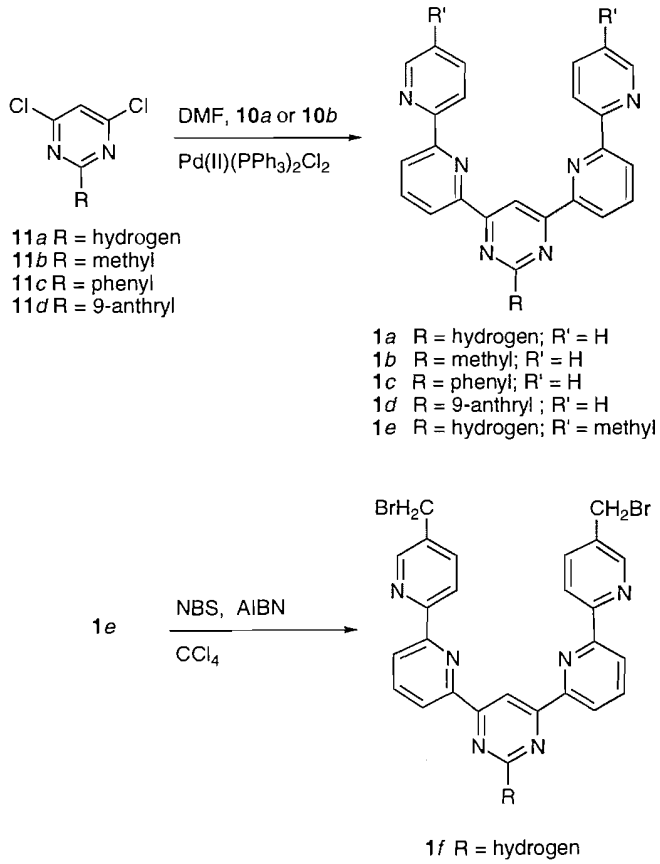
Fig. 3. Synthesis of 6-tributylstannyl-2,2′-bipyridines **10***a,b* from 2,2′-bipyridine and stannyl pyridines **8***a,b*.

Table 1. Reaction conditions for the synthesis of the bipyridine derivative **6***a* via Stille-type coupling.

	Reagent ratio[a]	
Conditions	1:1	1:2
Toluene 70°C, 73 h	35%	—
Toluene 90°C, 24 h	54%	67%
THF 67°C, 24 h	29%	36%
Dioxane 90°C, 21 h	43%	—
Dimethoxy ethylene glycol 70°C, 71 h	56%	—

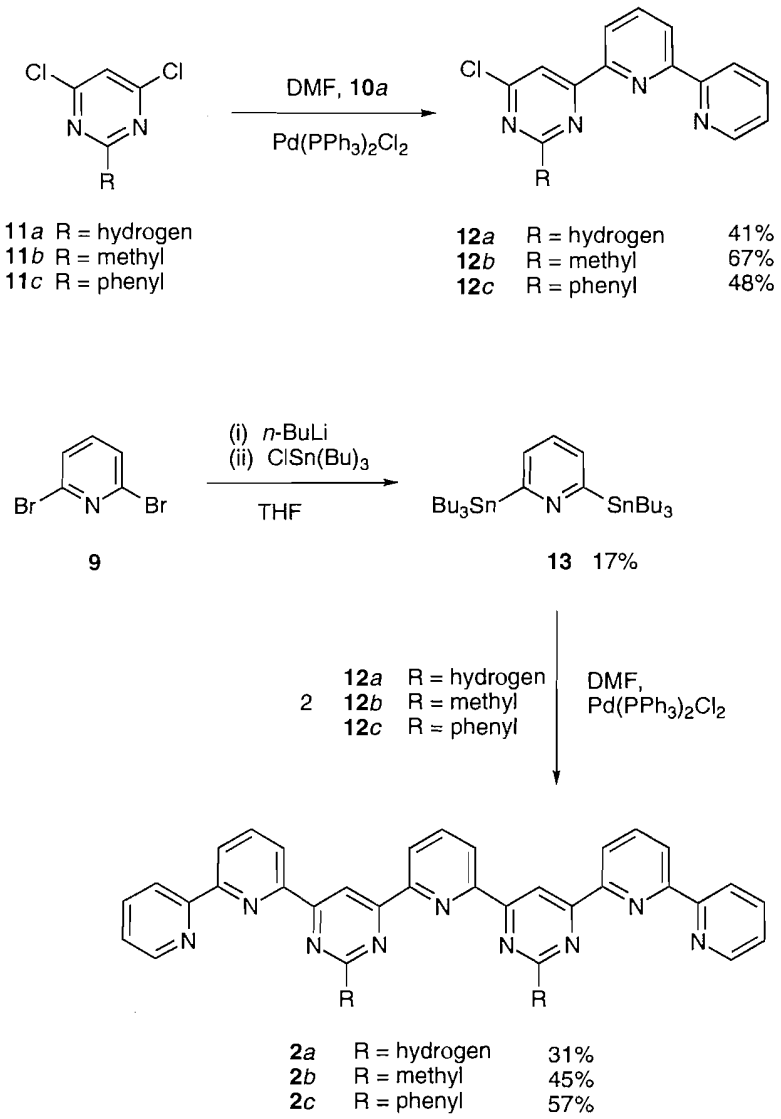
[a]Ratio of **8***a* to **9**, 5 mol% $Pd(PPh_3)_4$ for all reactions except in THF, where 5 mol% $Pd(PPh_3)_2Cl_2$ was used.

Fig. 4. Synthesis of the bis-tridentate ligands **1***a–e* and of the bromo-substituted ligand **1***f*.



8*a* and 2,6-dibromopyridine **9** are heterocoupled using the conditions listed in Table 1. The bpy **6***a* is easily separated from the starting materials and organotin by-products by acidification of the reaction mixture and subsequent extraction with organic solvents. Stannylpyridine **8***a*, 2,6-dibromopyridine **9**, and tributyltin chloride are extracted into the organic phase of a 1 M HCl – DCM mixture, whereas **6***a* and the side-product tpy are not. Nickel dichloride hexahydrate, added to the neutralized aqueous phase, separates tpy from **6***a* quantitatively following extraction with DCM. Excess **9** favours the formation of **6***a* over tpy. Unreacted **9** is recovered by column

Fig. 5. Synthesis of tris-tridentate ligands **2***a–c*.



chromatography along with the tributyltin bromide formed as a by-product. The synthesis can also be performed in a single procedure. The lithiation of 2-bromopyridine in THF at −78°C with *n*-butyllithium followed by the addition of tributyltin chloride gives pyridine **8***a*. After adding an excess of **9** and palladium catalyst, the reaction mixture is heated to reflux for 2 days. The bpy **6***a* and tpy are isolated as described above. Reaction times are shorter if one removes the THF under reduced pressure and replaces it with higher boiling solvents (Table 1).

To obtain 2-bromo-5-methyl-2,2′-bipyridine **6***b* we used a similar strategy starting from 2-bromo-5-methylpyridine, which is easily obtained from commercially available 2-amino-5-methylpyridine (25). Low-temperature lithiation and reaction with tributyltin chloride gave 2-tributylstannylpyridine **8***b*, which was heterocoupled with 2,6-dibromopyridine **9** to afford **6***b* in 72% yield. The reaction conditions and work-up procedures are similar to those described for **6***a*.

Following low-temperature lithiation of **6***a,b* with *n*-butyllithium, the lithiobipyridine is quenched with tributyltin chloride. Purification by distillation affords the 6-tributylstannyl functionalized bipyridines **10***a,b* in yields of 89 and 86%, respectively. Upon prolonged standing, small quantities of the dimerization product of **10***a*, 2,2′:6′,2″:6″,2‴-quaterpyridine, solidify out of the oil.

The pyrimidines are all synthesized in one step from commercially available materials. Reacting 4,6-dihydroxy-2-methylpyrimidine with $POCl_3$ gives 4,6-dichloro-2-methylpyrimidine **11***b*. Purification in an analogous fashion to that of **5**, followed by sublimation (instead of fractional distillation as reported (32)) affords **11***b* in 64% yield. 4,6-Dichloro-2-phenylpyrimidine **11***c* is produced by the addition of phenyllithium to **11***a*, followed by oxidation of the addition product with DDQ (26). In an analogous fashion, 9-lithioanthracene, generated by treatment of 9-bromoanthracene with *n*-butyllithium, reacts with **11***a* to afford 2-(9-anthryl)-4,6-dichloropyrimidine **11***d* in 40% yield. The reaction of two equivalents of bpy **10***a* with the 2-substituted-4,6-dichloropyrimidines

Table 2*a*. ^{1}H NMR chemical shifts for the various ligands (in ppm).[a,d]

	6″	5″	4″	3″	5′	4′	3′	5	2	3‴	4‴
11*a*								7.44	8.81		
12*a*	8.72	7.38	7.91	8.56[b]	8.56[b]	8.03	8.56[b]	8.56[b]	9.08		
1*a*	8.75	7.39	7.89	8.79	8.61[c]	8.05	8.57[c]	9.78	9.40		
12*a*	8.33	6.85	6.72	8.31	8.62[c]	8.02	8.38[c]	9.99	9.44	8.70	8.14
11*b*								7.20			
12*b*	8.69	7.34	7.87	8.48	8.55	7.97	8.55	8.35			
1*b*	8.74	7.38	7.89	8.80	8.58	8.03	8.58	9.55			
2*b*	8.36[b]	6.86	6.77	8.36[b]	8.63[c]	8.00	8.40[c]	9.80		8.65	8.10
11*c*								7.27			
12*c*	8.73	7.38	7.91	8.61[b]	8.69[c]	8.05	8.61[b,c]	8.45			
1*c*	8.76[b]	7.40	7.91	8.84	8.76[b,c]	8.08	8.62[c]	9.69			
2*c*	8.35	6.87	6.78	8.41	8.85[c]	8.07	8.43[c]	9.97		8.93	8.21
11*d*								7.59			
1*d*	8.78	7.45[b]	7.95	8.90	8.61[c]	7.96	8.57[c]	9.92			
1*e*	8.49		8.58	8.57	8.50[c]	7.94	8.46[c]	9.62	9.31		
1*f*	8.75		7.94	8.75	8.60[c]	8.05	8.57[c]	9.72	9.40		
tpy	8.69	7.35	7.88	8.64	8.47	7.96					

[a]In $CDCl_3$.
[b]Denotes central position of multiplet.
[c]Uncertainty in peak assignment.
[d]^{1}H labelling in Fig. 6.

Table 2*b*. ^{1}H NMR chemical shifts for the R groups of the various ligands and their precursors (in ppm).[a,b]

	H_{Me}	H_o	H_m	H_p	A_{10}	A_1	A_2	A_3	A_4
11*b*	2.65								
12*b*	2.79								
1*b*	2.94								
2*b*	2.97								
11*c*		8.44	7.51[c]	7.51[c]					
12*c*		8.61[c]	7.54[c]	7.54[c]					
1*c*		8.78	7.59[c]	7.59[c]					
2*c*		8.83	7.52[c]	7.52[c]					
11*d*					8.60	8.07	7.48[c]	7.48[c]	7.60[c]
1*d*					8.64	8.11	7.45[c]	7.45[c]	7.86

[a]In $CDCl_3$.
[b]R group labelling in Fig. 6.
[c]Denotes central position of multiplet.

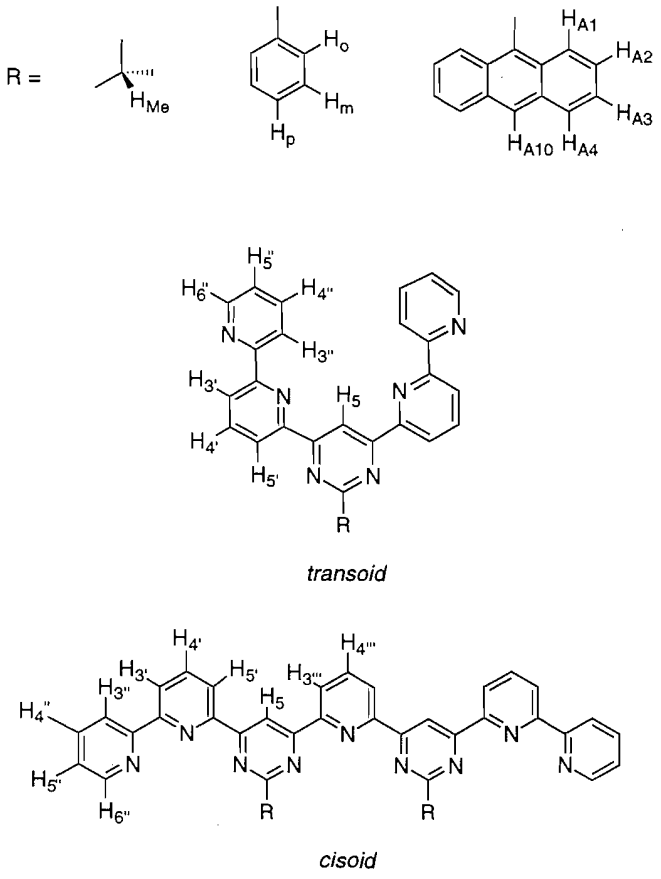
11*a–d* in DMF with $Pd(II)(PPh_3)_2Cl_2$ as catalyst yields the bis-tridentate ligands **1***a–d* in 49, 48, 56, and 65% yield, respectively (Fig. 4). Similarly, the terminal pyridine methyl-substituted bis-tridentate ligand **1***e* can be obtained in 49% yield. Further functionalization with NBS resulted in a mixture of different brominated products. The bisbromomethyl ligand **1***f* was isolated via column chromatography in 27% yield (Fig. 4).

2,6-Bis(tributylstannyl)pyridine **13** is obtained via transmetallation of 2,6-dilithiopyridine (33) with tributyltin chloride in 17% yield (Fig. 5). 4-(2′,2″-Bipyrid-6′-yl)-6-chloropyrimidines **12***a–c* are synthesized in an analogous manner to the bis-tridentate ligands (Fig. 5). The bpy **10***a* and an excess of pyrimidines **11***a–c* are reacted in DMF with $Pd(II)(PPh_3)_2Cl_2$ as the catalyst, giving **12***a–c* in yields of 41, 67, and 48%, respectively. The reaction of **13** with **12***a–c* proceeded under similar conditions to yield 31, 45, and 57% of the respective tris-tridentate ligands **2***a–c*.

Solution structure of 1*a–f* and 2*a–c*

Information concerning the orientation of the bis- and tris-tridentate ligands in solution was deduced from ^{1}H NMR chemical shifts (Fig. 6, Table 2). In the *cisoid* conformation, $H_{3''}$ would have no nitrogen lone pairs in proximity, whereas in the *transoid* conformation, $H_{3''}$ is close to two nitrogen lone pairs, accounting for its deshielding relative to H_3 in tpy. The chemical shifts of $H_{3'}$ and $H_{5'}$ are similar (a single doublet in **1***b* at 200 MHz), demonstrating that the pyrimidine N lone pair has

Fig. 6. Labelling of the *transoid* bis-tridentate and *cisoid* tris-tridentate ligands.



a similar deshielding effect to that of the pyridine N lone pair. The minor differences in the chemical shifts of H_2 in **11***a*, **12***a*, **1***a*, and **2***a* suggests that there is no intramolecular interaction between H_2 and the rest of the molecule. Intramolecular interactions involving H_5 are demonstrated by significant changes in its chemical shift in the aforementioned compounds. The greatest deshielding of H_2 and H_5 occurs after the addition of the first and second bipyridyl moieties to **11***a* (for **12***a*: +0.27 and +1.12, respectively; for **1***a*: +0.32 and +1.22 ppm, respectively). In **2***a*, the deshielding of H_2 (+0.04 ppm) and H_5 (+0.21 ppm) is modest relative to **1***a*. Evidently, the proximity of more nitrogen lone pairs deshields H_5. Although three nitrogen lone pairs point into a central cavity in **2***a*, one is far from H_5, resulting in only minor deshielding effects when compared to **1***a*.

The large upfield shift of the terminal pyridine protons in **2***a–c* may be attributed to shielding effects resulting from π–π interactions between the two terminal pyridines. Significant upfield shifts are observed when comparing **1***a* to **2***a*: −0.44, −0.54, −1.17, and −0.48 ppm for $H_{6''}$–$H_{3''}$, respectively. Similar upfield shifts occur between **1***b* and **2***b* (−0.38, −0.52, −1.12, and −0.44 ppm for $H_{6''}$–$H_{3''}$, respectively) and **1***c* and **2***c* (−0.41, −0.53, −1.13, and −0.43 ppm for $H_{6''}$–$H_{3''}$, respectively), suggestings similar environments for the terminal pyridines. The ^{1}H NMR spectra of **2***a–c* indicate similar solution structures.

The ^{1}H ROESY NMR spectrum of **2***a* reveals no interannular NOE interactions between adjacent heterocycles, supporting an all-*trans* conformation. The only prevalent NOE interaction occurs between $H_{3''}$ and H_5, indicating partial curling up of the ligand. The symmetry of the molecule on the NMR time scale does not allow differentiation of the three-ring (partial curling-up of the ligand) and five-ring (full curling-up of the ligand) interactions between $H_{3''}$ and H_5. No NOE interactions between $H_{3'''}$ and H_5 are observed, further supporting a *transoid* conformation at the central tridentate site.

The overlap between the terminal pyridines requires that the nonchiral linear molecule be curled up into a helical shape. Three basic features dictate this behaviour: (*a*) an alternating sequence of pyridine and pyrimidine units; (*b*) linkage of these units at appropriate positions; (*c*) *transoid* conformation around the linkage bonds based on the preference for a *trans* orientation of nitrogen sites and concomitant *cis* orientation of CH and N sites as found in 2,2′-bipyridine (12).

Solid state structure of 2*a*

X-ray crystallographic studies indicate a helical structure in the solid state (Figs. 7 and 8). The unit cell is centrosymmetric and contains the two enantiomeric helices. The molecule has a twofold rotation axis passing through the central pyridine N and C-4. Molecule **2***a* adopts an overall helical conformation in which the nitrogen sites have the expected *transoid* orientation about the interannular bonds. The interior of the helical strand is lined with alternating CH and N sites. The central cavity is 5.42 Å across and of a size comparable to that in cyclosexipyridine and 18-crown-6.

$H_{3''}$ is directed into the cavity formed by the helix, with a distance of 3.0 and 3.4 Å between $H_{3''}$ and H_5 for the three-ring and five-ring interaction, respectively. The angle between the least-squares planes (16.5 (2)°) is greatest between the pyrimidine (ring C) and central pyridine (ring D) (Fig. 8). The most coplanar rings are B and C (3.8 (8)°). The angle (8.6 (3)°) between the pyridine rings in the bipyridyl moieties is slightly greater than that found in terpyridine (5.1° and 7.1°) (34).

The interannular bond lengths in molecule **2***a* are typical of C—C single bonds between sp^2 hybridized carbon atoms, and lie between 1.484 (3) and 1.489 (4) Å. The pyridine and pyrimidine C—N bond lengths range from 1.334 (3) to 1.346 (4) Å and from 1.329 (4) to 1.344 (3) Å, respectively. The angles about the interannular bonds fall into two separate sets for the pyridines and pyrimidines: those which include a nitrogen atom and those which include a carbon atom. The C-C-C angles are between 3.5° and 9.2° greater than the N-C-C angles.

The interlamellar distance in graphite (3.354 Å) (35) is a reference for an optimal π-stacking distance. The terminal pyridines in **2***a* lie between an edge-to-face and a face-to-face orientation with a least-squares-planes angle of 38.8° and a centroid-to-centroid distance of 4.523 Å. The closest interactions between the terminal pyridines are those of C-3–C-3 (3.600 Å) and C-2-C-3 (3.755 Å), although C-3 and C-4 of the terminal pyridine are closer to the nitrogen of pyridine ring B, at 3.559 and 3.598 Å, respectively. The terminal pyridines are, therefore, slightly offset from one another, and are partially

Fig. 7. Solid state structure of **2***a*.

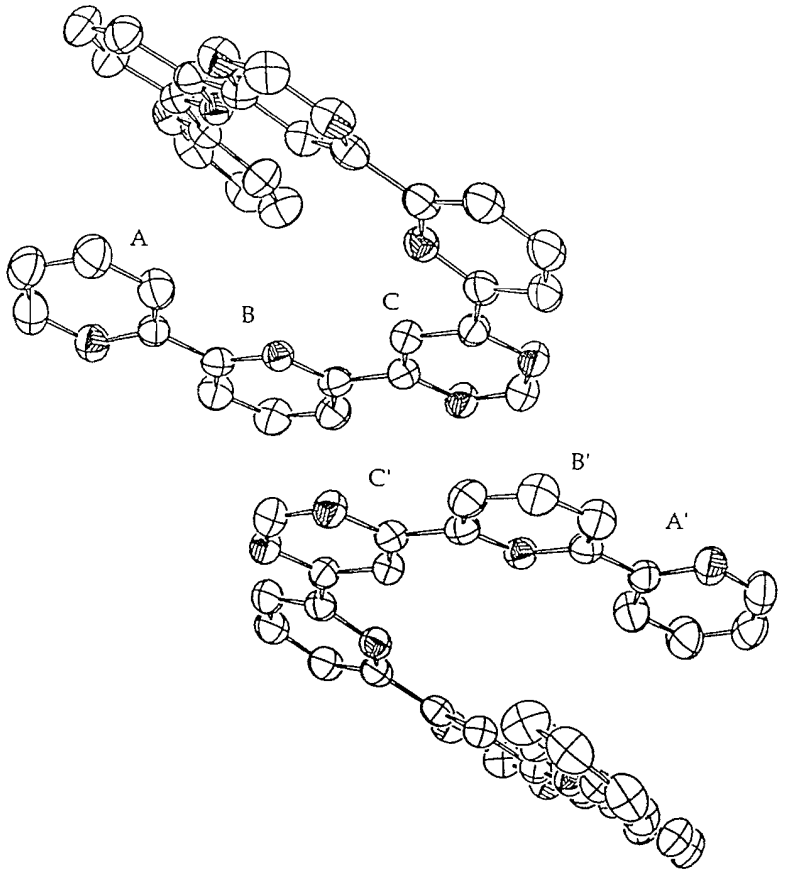


Table 3. Electrochemical reduction potentials $E^{\circ\prime}$ of the bis- and tris-tridentate ligands.[a,b]

	1*a*	**1***b*	**1***c*	**1***d*	**1***e*	**1***f*	**2***a*	**2***c*
$E^{\circ\prime}$ (1)	−1.44 (70)	−1.49 (60)	−1.43 (60)	−1.46 (70)	−1.54 (90)	−1.32[c]	−1.38 (70)	−1.41 (60)
$E^{\circ\prime}$ (2)	−2.07[c]	−2.17[c]	−2.06[c]	−1.96[c]	−2.22[c]	−1.46 (80)	−1.62 (70)	−1.64 (80)
$E^{\circ\prime}$ (3)				−2.06[c]				

[a]In DMF vs. SCE, except **1***e* and **1***f* vs. ferrocene (+0.45 V). The difference between cathodic and anodic peak potentials (mV) is given in parentheses.
[b]**2***b* not soluble enough for accurate measurements.
[c]Irreversible wave.

above the B rings (least-squares-planes angle = 33.2(1)°). $H_{4''}$ is directed above the B ring, whereas $H_{3''}$, $H_{5''}$, and $H_{6''}$ are above the other terminal pyridine. These interactions lead to the significant upfield shift of the ^{1}H NMR signals of these protons (36).

Ring B and ring C′ from each of the two enantiomeric helices have a centroid-to-centroid distance of 3.79 Å (Fig. 7). The least-squares-planes angle between the rings is 3.8 (7)°. The rings are slightly offset from one another, which may lead to favourable π–π interaction (36). Based on the above observations, we conclude that the solid state and solution structures of this molecule are helical and similar.

Heterocyclic ligands exhibit electrochemical reduction potentials that approximate their relative π* levels (37). The bis-tridentate ligands **1** present a reversible pyrimidine-based reduction (between −1.43 and −1.49 V; $E^{\circ\prime}_{\text{pyrimidine}} = -1.87$ V (38)) followed by an irreversible pyridine-based reduction (between −2.06 and −2.17 V; $E^{\circ\prime}_{\text{pyridine}} = -2.09$ V (38)) in DMF (Table 3). The 9-anthryl substituted ligand **1***d* also shows another irreversible reduction at −1.96 V in DMF, presumably due to the 9-anthryl moiety ($E^{\circ\prime}_{\text{anthracene}} = -1.92$ V, 2.5 V (39)).

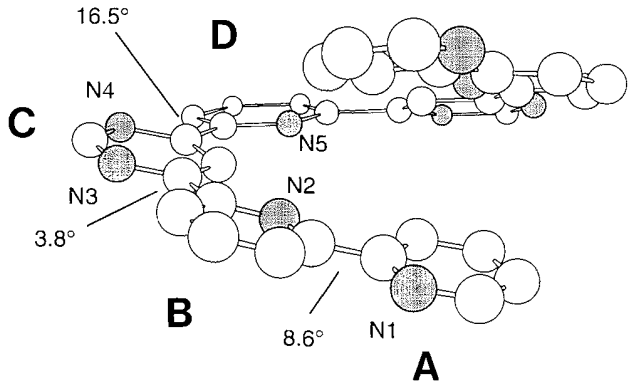
The tris-tridentate ligands **2***a* and **2***c* exhibit two reversible reductions, the first near −1.40 V and the second near −1.63 V (Table 3), which may be considered as pyrimidine based, with the first lower and the second higher in energy than the first reduction of the bis-tridentate ligands **1**. Clearly, the pyrimidine moieties provide electronic communication that may involve extended delocalization through the central pyridine and electrostatic interaction. No subsequent reductions of the

Table 4. Electronic spectra of the bis- and tris-tridentate ligands **1** and **2**.[a]

Compound	Absorption bands (λ_{max}, nm (ε, 10^4 dm^{-3} mol cm^{-1}))
1*a*	236 (3.8), 286 (3.3), 308 (2.6), 320 (3.2)
1*b*	237 (4.9), 284 (3.0), 304 (2.5), 322 (1.9)
1*c*	236 (4.8), 256 (3.2), 275 (3.8), 284 (sh, 3.5), 322 (1.4), 333 (1.0)
1*d*	236 (sh, 14), 250 (20), 257 (28), 285 (5.6), 320 (sh, 3.6), 348 (1.4), 366 (2.0), 386 (1.8)
1*e*	241 (5.7), 289 (4.0), 298 (sh, 3.5), 312 (sh, 2.4), 322 (sh, 2.0)
1*f*	244 (5.55), 295 (5.1), 321 (sh, 2.4)
2*a*	232 (7.7), 281 (sh, 3.5), 294 (3.9), 318 (sh, 2.4)
2*b*	233 (8.8), 291 (sh, 5.2), 302 (5.3), 320 (sh, 3.3)
2*c*	230 (8.3), 255 (5.1), 273 (5.5), 311 (2.4), 332 (1.5)

[a]In CH_2Cl_2.

Fig. 8. Angles between the least-squares planes between heterocyclic rings A–D in **2***a*.



pyridyl groups are observed. The poor solubility of **2***b* precluded determination of its reduction potentials.

The absorption spectra of the bis-tridentate ligands **1***a–f* (Table 4) display high-energy absorption bands like those found in pyridine (251, 270 nm) and pyrimidine (243, 298 nm) (40). They contain common absorption bands near 236, 286, 308, and 320 nm. The lowest energy band is ascribed to a pyrimidine-based transition, while the high-energy ones may be due to either pyridine- or pyrimidine-based absorptions. The low-energy absorption is expected to occur at lower energies than those of pyridine and pyrimidine, as bpy and tpy low-energy bands are at lower energies than those of pyridine (41). The same was found in other polyaromatic compounds, where conjugative interaction gives an extended π-system with a lowered HOMO–LUMO energy gap (42).

The phenyl- (**1***c*) and 9-anthryl-substituted (**1***d*) ligands exhibit additional UV bands (256 and 333 nm; and 250, 257, 348, 366, and 386 nm, respectively) that correspond reasonably well to the absorption bands of benzene (204, 256 nm) and anthracene (221, 256, 375 nm) (40). The molar absorptivity of **1***d* is higher than that of the other bis-tridentate ligands at all the common wavelengths as the 9-anthryl moiety has higher ε values than the other R groups at these wavelengths. As for the absorption maxima, the molar absorptivities for the chromophoric components in the ligands are approximately additive.

The tris-tridentate ligands **2***a–c* exhibit absorption spectra similar to those of their bis-tridentate counterparts **1***a–c*. The molar absorptivities of the transitions are more intense due to the greater number of heterocycles present and the λ_{max} positions are closer together.

Conclusion

We have developed a synthetic pathway for the synthesis of bis- and tris-tridentate ligands for metal complexation based on pyridine and pyrimidine units. The stepwise synthesis of the ligands proceeded via Stille carbon–carbon bond-forming reactions. The solution structures of the ligands were deduced by ^{1}H NMR, exemplified by pronounced deshielding of the protons adjacent to the interannular bond. When seven alternating pyridine–pyrimidine heterocycles are connected together, a helical structure is formed, as indicated by solution and solid state data. Longer multisite versions of these ligands are being investigated. The ligands **1***e–f*, functionalized at the terminal pyridine, represent potential building blocks for more extended systems.

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