Diversification of ligand families through ferroin–neocuproin metal-binding domain manipulation

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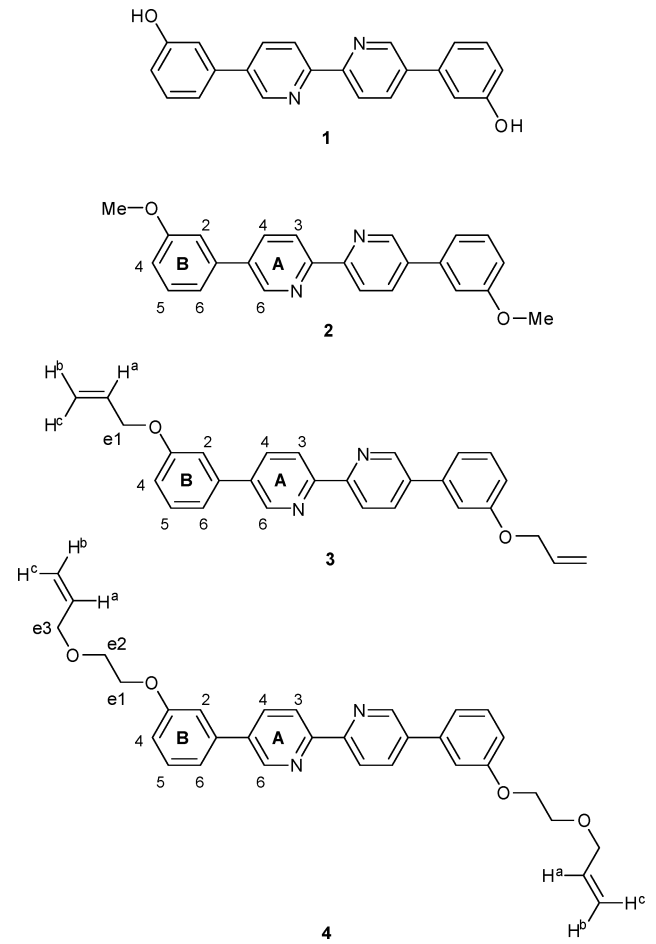
Derivatization of 5,5′-bis(3-hydroxyphenyl)-2,2′-bipyridine to give two new ligands, **3** and **4**, which possess terminal alkene functionalities is described. The syntheses and characterization of the palladium(II) complexes $[Pd(\mathbf{3})_2][BF_4]_2$ and $[Pd(\mathbf{4})_2][BF_4]_2$, and the related $[Pd(\mathbf{2})_2][BF_4]_2$ in which **2** is 5,5′-bis(3-methoxyphenyl)-2,2′-bipyridine are reported. The labile nature of the ligand leads to $[Pd(\mathbf{2})_2][BF_4]_2$ co-crystallizing with the free ligand as $[Pd(\mathbf{2})_2][BF_4]_2\cdot\mathbf{2}$; in the solid state, the ligands in the $[Pd(\mathbf{2})_2]^{2+}$ cation distort (a 'bow-incline' distortion) to alleviate bpy $H^6\cdots H^6$ repulsions. Compound **2** has been converted to 5,5′-bis(3-methoxyphenyl)-6-methyl-2,2′-bipyridine (**5**) and 5,5′-bis(3-methoxyphenyl)-6,6′-dimethyl-2,2′-bipyridine (**6**) to produce ligands suited to forming air-stable, copper(I) complexes of type $[CuL_2]^+$. $[Cu(\mathbf{5})_2][PF_6]$ and $[Cu(\mathbf{6})_2][PF_6]$ have been prepared and characterized, and the single crystal structures of **6** and $[Cu(\mathbf{5})_2][PF_6]\cdot 0.1C_2H_4Cl_2\cdot 0.15CH_2Cl_2$ are described. By altering the conditions under which **2** is methylated, competitive formation of 5,5′,5″,5‴-tetrakis(3-methoxyphenyl)-2,2′:3′,3″:2″,2‴-quaterpyridine occurs.

Introduction

Diaryl-functionalized 2,2′-bipyridines (bpy), 1,10-phenanthrolines (phen) and 2,2′:6′,2″-terpyridines are commonly utilized scaffolds in metallosupramolecular chemistry. The aryl groups bear substituents which can be further elaborated or which contain desired functionalities, and the metal-binding domain provides the recognition features for interaction with specific metal centres. The development of the metal-ion templated synthesis of catenanes, knots and other topologically complex systems[1] was predicated on the organization of 6,6′-disubstituted bpy (or 2,9-disubstituted phen) ligands about tetrahedral copper(I) or silver(I) centres. Although the substituents adjacent to the nitrogen (neocuproin structure type) are critical for the stability of copper(I) complexes,[2,3] formation of stable complexes with octahedral metal centres requires that the aryl substituents are attached to other positions (ferroin structure type). The synthesis of families of ligands with neocuproin or ferroin metal-binding domains is time-consuming and we have developed strategies for the direct conversion of ferroin metal-binding domains to the neocuproin type.

We have previously reported ligands **1** and **2**[4] (Scheme 1), and the complexation of **1** with silver(I).[5] We have also used **1** as a building block for the formation of a heterotopic ligand in which the central bpy domain is linked by polyethyleneoxy spacers to two 2,2′:6′,2″-terpyridine (tpy) units. The flexibility of this ligand permits the binding of iron(II) and formation of a [1 + 1] ferramacrocycle.[6] Apart from these studies, the complexation of **1** and **2** remains unexplored. In this paper, we report the formation of two ligands, **3** and **4** (Scheme 1), which possess terminal alkene functionalities that are ideally suited to



Scheme 1 Structure of ligands **1** to **4**, and numbering schemes for NMR spectra.

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Grubbs' coupling and the assembly of polymeric or macrocyclic species. We extend the diversity in coordination space beyond commonly studied 1 : 2 tetrahedral and 1 : 3 octahedral species to 1 : 2 square planar metal centres and describe the preparation and characterization of palladium(II) complexes of ligands **2–4**. We have made proof-of-principle conversion of **2** to ligands containing substituents adjacent to the nitrogen donors and describe the air-stable copper(I) complexes of these new ligands.

Experimental

^{1}H and ^{13}C NMR spectra were recorded at room temperature on Bruker Avance DRX-500 and DPX-400 MHz spectrometers; chemical shifts are relative to residual solvent peaks with TMS δ 0 ppm for ^{1}H and ^{13}C, and relative to $CF^{35}Cl_3$ in $CDCl_3$ for ^{19}F (external reference). Infrared spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer with solid samples on a Golden Gate diamond ATR accessory. Electrospray ionisation (ESI) mass spectra were recorded using Finnigan MAT LCQ or Bruker esquire 3000^{plus} instruments, and FAB (NBA matrix) and electron impact (EI) mass spectra using Finnigan MAT 312 and VG 70-250 instruments, respectively. Electronic absorption spectra were recorded on a Varian-Cary 5000 spectrophotometer. Microwave reactions were carried out in a Biotage Initiator 8 reactor. Solvents were distilled before use, and reactions were carried out under N_2.

Electrochemical measurements were carried out using an Eco Chemie Autolab PGSTAT 20 with a platinum working electrode, a platinum mesh for the counter electrode, and a silver wire as the reference electrode. Solutions of the compounds in dry and degassed MeCN were used in the presence of 0.1 M [*n*-Bu_4N][PF_6]. The scan rate for the CV was 150 mV s^{-1} and ferrocene was added as an internal standard at the end of every experiment.

First generation Grubbs' and Hoveyda–Grubbs' catalysts and $[Pd(CH_3CN)_4][BF_4]_2$ were purchased from Aldrich, MeLi from Acros. Compound **1** was prepared by our previously reported method.[4]

Ligand 2

Ligand **2** was prepared according to the literature procedure.[4] For comparison with the palladium(II) complex, NMR data were recorded in DMSO-d_6. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 9.06 (d, J = 2.1 Hz, 2H, H^{A6}), 8.51 (d, J = 8.3 Hz, 2H, H^{A3}), 8.28 (dd, J = 8.3, 2.3 Hz, 2H, H^{A4}), 7.40 (t, J = 7.8 Hz, 2H, H^{B5}), 7.37 (m, 4H, H^{B2+B6}), 7.03 (dd, J = 8.1, 1.7 Hz, 2H, H^{B4}), 3.86 (s, 6H, H^{Me}).

[Pd(2)$_2$][BF$_4$]$_2$

A solution of **2** (227 mg, 617 μmol) in CH_2Cl_2 (10 cm^3) was added to a solution of $[Pd(CH_3CN)_4][BF_4]_2$ (137 mg, 308 μmol) in CH_3CN (10 cm^3) and stirred at room temperature for 24 h. The solution turned pale yellow and a yellow precipitate was formed. Solvent was removed under vacuum to give [Pd(**2**)$_2$][BF_4]$_2$ as a yellow solid (313 mg, 308 μmol, 100%). ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) 9.15 (s, 4H, H^{A6}), 8.90 (br, 8H, H^{A3+A4}), 7.43 (m, 8H, H^{B2+B6}), 7.39 (t, J = 7.8 Hz, 4H, H^{B5}), 7.13 (d, J = 7.4 Hz, 4H, H^{B4}), 3.73 (s, 12H, H^{Me}). ^{13}C NMR (126 MHz, DMSO-d_6) δ (ppm) 160.1 (C^{B3}), 154.5 (C^{A2}), 149.5 (C^{A6}), 140.1 (C$^{A3/A4}$), 139.2 (C^{A5}), 135.6 (C^{B1}), 130.5 (C^{B5}), 124.3 (C$^{A3/A4}$), 119.7 (C^{B6}), 115.4 (C^{B4}), 112.8 (C^{B2}), 55.2 (C^{Me}). ^{19}F NMR (376 MHz, DMSO-d_6) δ (ppm) −148.7 (s). FAB MS m/z 861.1 [Pd(**2**)$_2$ + F]$^+$ (calc. 861.2), 842.1 [Pd(**2**)$_2$]$^+$ (calc. 842.2), 474.0 [Pd(**2**)]$^+$ (calc. 474.1), 369.1 [**2** + H]$^+$ (calc. 369.2). IR (solid, ν (cm^{-1})) 3005 w, 2932 w, 2856 w, 1738 m, 1605 m, 1576 m, 1464 m, 1452 s, 1435 m, 1300 m, 1231 m, 1205 m, 1063 m, 1016 m, 843 m, 837 m, 779 s, 692 s. Found C, 56.53; H, 4.10; N, 5.41; $C_{48}H_{40}B_2F_8N_4O_4Pd$ requires C, 56.69; H, 3.96; N, 5.51%.

Ligand 3

Compound **1** (88.4 mg, 260 μmol), allyl bromide (1.0 cm^3, 11.5 mmol) and Cs_2CO_3 (350 mg, 1.07 mmol) were heated in THF at 100 °C in a microwave reactor for 45 min. Purification by column chromatography (SiO_2, CH_2Cl_2 : MeOH 100 : 1) gave **3** as a colourless solid (106 mg, 252 μmol, 96%). Mp 135–137 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.91 (d, J = 1.7 Hz, 2H, H^{A6}), 8.48 (d, J = 8.2 Hz, 2H, H^{A3}), 8.00 (dd, J = 8.3, 2.4 Hz, 2H, H^{A4}), 7.40 (t, J = 7.9 Hz, 2H, H^{B5}), 7.18 (d, J = 7.9 Hz, 2H, H^{B6}), 7.14 (m, 2H, H^{B2}), 6.91 (ddd, J = 8.2, 2.4, 0.8 Hz, 2H, H^{B4}), 6.03 (m, 2H, H^{a}), 5.40 (m, 2H, H^{c}), 5.26 (m, 2H, H^{b}), 4.56 (m, 4H, H^{e1}). ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 9.00 (d, J = 1.7 Hz, 2H, H^{A6}), 8.59 (d, J = 8.3 Hz, 2H, H^{A3}), 8.21 (dd, J = 8.3, 2.4 Hz, 2H, H^{A4}), 7.40 (t, J = 8.1 Hz, 2H, H^{B5}), 7.37 (m, 4H, H^{B2+B6}), 7.04 (dd, J = 8.2, 2.4 Hz, 2H, H^{B4}), 6.12 (m, 2H, H^{a}), 5.47 (m, 2H, H^{c}), 5.28 (m, 2H, H^{b}), 4.71 (m, 4H, H^{e1}). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 159.1 (C^{B3}), 154.7 (C^{A2}), 147.7 (C^{A6}), 139.0 (C^{B1}), 136.2 (C^{A5}), 135.2 (C^{A4}), 133.1 (C^{a}), 130.1 (C^{B5}), 120.9 (C^{A3}), 119.6 (C^{B6}), 117.9 (C$^{b/c}$), 114.3 (C^{B4}), 113.7 (C^{B2}), 68.9 (C^{e1}). IR (solid, ν (cm^{-1})) 2874 m, 2869 m, 1605 m, 1578 s, 1460 s, 1435 m, 1362 w, 1297 m, 1278 m, 1201 s, 1175 w, 1113 m, 1099 m, 1068 m, 1016 m, 947 m, 934 m, 937 m, 918 m, 841 m, 779 s. EI MS m/z 421.2 [M]$^+$ (calc. 421.2). Found C, 79.13; H, 6.10; N, 6.31; $C_{28}H_{24}N_2O_2 \cdot 0.2H_2O$ requires C, 79.30; H, 5.80; N, 6.61%.

[Pd(3)$_2$][BF$_4$]$_2$

The procedure was as for [Pd(**2**)$_2$][BF_4]$_2$ using **3** (64.1 mg, 152 μmol) and $[Pd(CH_3CN)_4][BF_4]_2$ (34.2 mg, 77.0 μmol). [Pd(**3**)$_2$][BF_4]$_2$ was isolated as a yellow solid (85.1 mg, 75.9 μmol, 99.9%). ^{1}H NMR (500 MHz, CD_3COCD_3) δ (ppm) 9.33 (s, 4H, H^{A6}), 8.86 (m, 8H, H^{A3+A4}), 7.45 (m, 4H, H^{B2}), 7.41 (m, 8H, H^{B5+B6}), 7.14 (m, 4H, H^{B4}), 6.04 (m, 4H, H^{a}), 5.39 (m, 4H, H^{c}), 5.24 (m, 4H, H^{b}), 4.60 (dt, J = 1.5, 5.2 Hz, 8H, H^{e1}). ^{13}C NMR (126 MHz, CD_3COCD_3) δ (ppm) 160.5 (C^{B3}), 156.2 (C^{A2}), 150.3 (C^{A6}), 141.3 (C^{A5}), 141.0 (C$^{A3/A4}$), 137.0 (C^{B1}), 134.4 (C^{Ha}), 131.6 (C^{B5}), 125.3 (C$^{A3/A4}$), 120.7 (C^{B6}), 117.8 (C$^{Hb/c}$), 117.1 (C^{B2}), 114.5 (C^{B4}), 69.5 (C^{e1}). ^{19}F NMR (376 MHz, CD_3COCD_3) δ (ppm) −152.2 (s). IR (solid, ν (cm^{-1})) 3070 m, 2924 m, 2168 m, 2037 w, 1736 w, 1582 w, 1466 m, 1373 w, 1304 m, 1250 m, 1211 m, 1026 s, 918 m, 841 m, 779 m, 687 m. ESI-MS m/z 1033.9 [Pd(**3**)$_2$$BF_4$]$^+$ (calc. 1032.3), 965.1 [Pd(**3**)$_2$F]$^+$ (calc. 965.3), 473.3 [Pd(**3**)$_2$]$^{2+}$ (calc. 473.2). Found C, 60.64; H, 4.49; N, 4.80; $C_{56}H_{48}B_2F_8N_4O_4Pd$ requires C, 60.00; H, 4.32; N, 5.00%.

Ligand 4

Compound **1** (1.63 g, 4.79 mmol), 3-(2-bromoethoxy)prop-1-ene (1.57 g, 9.63 mmol) and Cs_2CO_3 (6.24 g, 19.0 mmol) were dissolved in dry DMF (200 cm^3). The reaction mixture was heated at 120 °C

for 4 d. Solvent was removed and the product purified by column chromatography (SiO_2, CH_2Cl_2 : MeOH 66 : 1). After filtration over Al_2O_3, **4** was isolated as a colourless crystalline solid (2.17 g, 4.27 mmol, 89%). Mp 96–98 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.97 (d, J = 2.1 Hz, 2H, H^{A6}), 8.54 (d, J = 8.2 Hz, 2H, H^{A3}), 8.06 (dd, J = 2.3, 8.3 Hz, 2H, H^{A4}), 7.45 (t, J = 7.9 Hz, 2H, H^{B5}), 7.29 (m, 4H, H^{B2+B6}), 7.03 (dd, J = 8.2, 2.2 Hz, 2H, H^{B4}), 6.00 (m, 2H, H^{a}), 5.37 (m, 2H, H^{c}), 5.27 (m, 2H, H^{b}), 4.27 (m, 4H, H^{e1}), 4.18 (m, 4H, H^{e3}), 3.88 (m, 4H, H^{e2}). ^{1}H NMR (400 MHz, CD_3CN–$CDCl_3$) δ (ppm) 8.88 (d, J = 2.1 Hz, 2H, H^{A6}), 8.46 (d, J = 8.3 Hz, 2H, H^{A3}), 8.03 (dd, J = 2.4, 8.3 Hz, 2H, H^{A4}), 7.39 (t, J = 7.9 Hz, 2H, H^{B5}), 7.24 (m, 2H, H^{B6}), 7.20 (m, 2H, H^{B2}), 6.95 (ddd, J = 8.3, 2.5, 0.8 Hz, 2H, H^{B4}), 5.91 (m, 2H, H^{a}), 5.29 (m, 2H, H^{c}), 5.17 (m, 2H, H^{b}), 4.19 (m, 4H, H^{e1}), 4.07 (m, 4H, H^{e3}), 3.80 (m, 4H, H^{e2}). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 159.3 (C^{B3}), 154.7 (C^{A2}), 147.7 (C^{A6}), 138.9 (C^{B1}), 136.2 (C^{A5}), 135.2 (C^{A4}), 134.5 (C^{a}), 130.1 (C^{B5}), 120.9 (C^{A3}), 119.7 (C^{B6}), 117.4 ($C^{b/c}$), 114.0 (C^{B4}), 113.6 (C^{B2}), 72.4 (C^{e3}), 68.4 (C^{e2}), 67.5 (C^{e1}). EI MS m/z 508.2 $[M]^+$ (calc. 508.2), 424.2 $[M - C_5H_8O]^+$ (calc. 424.2), 340.1 $[M - 2C_5H_8O]^+$ (calc. 340.1). IR (solid, ν (cm^{-1})) 3005 w, 2932 w, 2856 w, 1605 m, 1576 s, 1464 m, 1452 s, 1441 m, 1358 m, 1300 m, 1279 m, 1205 s, 1142 m, 1130 m, 1099 m, 1068 m, 1016 m, 947 m, 937 m, 918 m, 835 m, 781 s, 694 s. Found C, 75.54; H, 6.50; N, 5.39; $C_{32}H_{32}N_2O_2$ requires C, 75.57; H, 6.34; N, 5.51%.

$[Pd(4)_2][BF_4]_2$

The procedure was as for $[Pd(\mathbf{2})_2][BF_4]_2$ using **4** (100 mg, 197 µmol) and $[Pd(CH_3CN)_4][BF_4]_2$ (44.1 mg, 99.3 µmol). $[Pd(\mathbf{4})_2][BF_4]_2$ was isolated as a yellow solid (129 mg, 99.4 µmol, 100%). ^{1}H NMR (500 MHz, CD_3CN–$CDCl_3$) δ (ppm) 8.76 (s, 4H, H^{A6}), 8.46 (s, 8H, H^{A3+A4}), 7.30 (t, J = 7.9 Hz, 4H, H^{B5}), 7.17 (s, 4H, H^{B2}), 7.14 (d, J = 7.6 Hz, 4H, H^{B6}), 7.00 (dd, J = 8.3, 1.4 Hz, 4H, H^{B4}), 5.86 (m, 4H, H^{a}), 5.25 (m, 4H, H^{c}), 5.14 (m, 4H, H^{b}), 4.07 (m, 8H, H^{e1}), 4.01 (d, J = 5.5 Hz, 8H, H^{e3}), 3.72 (m, 8H, H^{e2}). ^{13}C NMR (126 MHz, CD_3CN–$CDCl_3$) δ (ppm) 160.0 (C^{B3}), 155.0 (C^{A2}), 148.9 (C^{A6}), 140.1 ($C^{A3/A4}$), 136.0 ($C^{A5/B1}$), 135.8 ($C^{A5/B1}$), 134.8 (C^{Ha}), 131.0 (C^{B5}), 124.7 ($C^{A3/A4}$), 119.9 (C^{B6}), 117.2 ($C^{Hb/c}$), 116.6 (C^{B4}), 113.4 (C^{B2}), 72.3 (C^{e3}), 68.6 (C^{e2}), 67.9 (C^{e1}). ^{19}F NMR (376 MHz, CD_3COCD_3) δ (ppm) –152.6 (s). ESI-MS m/z 1157.6 $[PdL_2Cl]^+$. IR (solid, ν (cm^{-1})) 3072 w, 2928 w, 2864 w, 1719 m, 1600 m, 1581 m, 1471 s, 1436 m, 1373 w, 1302 m, 1251 w, 1211 m, 1035 s, 1028 s, 936 m, 840 m, 781 s, 690 m. Found C, 60.03; H, 5.15; N, 4.36; $C_{64}H_{64}B_2F_8N_4O_4Pd$ requires C, 59.26; H, 4.97; N, 4.32%.

Attempted ring-closing metathesis

In a typical reaction, $[Pd(\mathbf{4})_2][BF_4]_2$ or $[Pd(\mathbf{5})_2][BF_4]_2$ (20 µmol) and Grubbs' catalyst (first generation or Hoyveda–Grubbs catalyst second generation) (2 µmol) were dissolved in CH_2Cl_2 (20 cm^3) and stirred at room temperature (5–7 days) or heated at reflux overnight. In additional trials, the solvent was CH_3NO_2 under the same conditions. Reactions were also attempted in a microwave reactor at 60 °C for 1.5 h in CH_2Cl_2. See text.

Ligand 5

Compound **2** (1.28 g, 3.47 mmol) was dissolved in toluene (250 cm^3). The solution was cooled to –78 °C and MeLi (2.4 cm^3, 1.6 M solution in hexane, 3.82 mmol) was added dropwise resulting in an orange coloration. The reaction mixture was allowed to warm slowly to room temperature and left to stand overnight after which time the colour became an intense blue-violet. The reaction mixture was then stirred at 100 °C for 30 min and the resulting orange solution was cooled to room temperature and extracted with H_2O (200 cm^3). The aqueous phase was extracted with CH_2Cl_2 (3 × 20 cm^3) and the combined organic layers were dried over $MgSO_4$, filtered and stirred in the presence of MnO_2 (10 g) for 6 h. Filtration and removal of solvents yielded **5** as a white solid (1.09 g, 2.85 mmol, 82%). Mp 143–144 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.91 (d, J = 2.1 Hz, 1H, H^{A6}), 8.52 (d, J = 8.2 Hz, 1H, H^{A3}), 8.28 (d, J = 8.0 Hz, 1H, H^{C3}), 8.00 (dd, J = 8.2, 2.3 Hz, 1H, H^{A4}), 7.66 (d, J = 8.0 Hz, 1H, H^{C4}), 7.40 (t, J = 7.9 Hz, 1H, H^{B5}), 7.36 (t, J = 7.9 Hz, 1H, H^{D5}), 7.23 (d, J = 7.5 Hz, 1H, H^{B6}), 7.17 (m, 1H, H^{B2}), 6.94 (m, 3H, $H^{B4+D4+D6}$), 6.91 (m, 1H, H^{D2}), 3.88 (s, 3H, OMe^{B}), 3.84 (s, 3H, OMe^{D}), 2.62 (s, 3H, Me). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 160.4 (C^{B3}), 159.7 (C^{D3}), 155.6 (C^{A2}), 155.4 (C^{C2}), 154.3 (C^{C6}), 147.9 (C^{A6}), 141.6 (C^{D1}), 139.4 (C^{B1}), 138.2 (C^{C4}), 137.0 (C^{C5}), 136.3 (C^{A5}), 135.4 (C^{A4}), 130.4 (C^{B5}), 129.7 (C^{D5}), 121.7 (C^{D6}), 121.2 (C^{A3}), 119.7 (C^{B6}), 118.5 (C^{C3}), 115.0 (C^{D4}), 113.6 (C^{B4}), 113.1 (C^{D2}), 113.0 (C^{B2}), 55.6 ($C^{B\text{-}OMe}$), 55.5 ($C^{D\text{-}OMe}$), 23.9 (C^{Me}). ESI MS: m/z 382.2 $[M]^+$ (calc. 382.2). IR (solid, ν (cm^{-1})) 3060 w, 2993 w, 2929 w, 2832 w, 1606 m, 1578 m, 1458 s, 1439 m, 1432 m, 1418 m, 1295 m, 1283 s, 1209 s, 1178 m, 1167 m, 1048 m, 1035 m, 1019 m, 841 s, 697 s. Found C, 78.34; H, 5.98; N, 7.13; $C_{25}H_{22}N_2O_2$ requires C, 78.51; H, 5.80; N, 7.32%.

Ligand 6

Compound **5** (102 mg, 267 µmol) was dissolved in toluene (30 cm^3). The solution was cooled to –20 °C. MeLi (180 µL, 1.6 M solution in hexane, 293 µmol) was added dropwise and an intense blue coloration appeared. The reaction mixture was stirred for 1 h at this temperature, allowed to warm to room temperature and H_2O (5 cm^3) was added. The aqueous phase was separated and extracted with CH_2Cl_2 (3 × 10 cm^3). The combined organic layers were treated with MnO_2 (2 g) and stirred for 5 h at room temperature. Column chromatography (Al_2O_3, CH_2Cl_2) yielded a colourless fraction from which solid **6** was isolated (58.3 mg, 147 µmol, 55%). Mp 185–188 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.30 (d, J = 7.9 Hz, 2H, H^{C3}), 7.64 (d, J = 7.9 Hz, 2H, H^{C4}), 7.36 (t, J = 7.8 Hz, 2H, H^{D5}), 6.93 (overlapping m, 6H, $H^{D2+D4+D6}$), 3.84 (s, 6H, H^{OMe}), 2.60 (s, 6H, H^{Me}). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 159.5 (C^{B3}), 155.2 (C^{A2}), 154.6 (C^{A6}), 141.5 (C^{B1}), 137.9 (C^{A4}), 136.6 (C^{A5}), 129.4 (C^{B5}), 121.5 (C^{B6}), 118.4 (C^{A3}), 114.9 (C^{B4}), 112.7 (C^{B2}), 55.3 (C^{OMe}), 23.7 (C^{Me}). ESI MS m/z 397.4 $[M + H]^+$ (calc. 397.2), 419.2 $[M + Na]^+$ (calc. 419.2), 815.6 $[2M + Na]^+$ (calc. 815.4). IR (solid, ν (cm^{-1})) 3077 w, 3052 w, 2989 m, 2959 m, 2924 m, 2832 m, 1606 m, 1575 m, 1456 m, 1289 m, 1209 s, 1179 m, 1049 m, 1018 m, 879 w, 841 s, 781 s. Found C, 76.12; H, 6.15; N, 6.70; $C_{26}H_{24}N_2O_2 \cdot 0.75H_2O$ requires C, 76.17; H, 6.27; N, 6.83%.

Compound 7

Compound **2** (1.92 g, 5.21 mmol) was dissolved in toluene (250 cm^3). MeLi (3.9 cm^3, 1.6 M solution in hexane, 6.25 mmol) was added dropwise at room temperature resulting in a blue-violet solution which was stirred for 30 min at room temperature. Water

(40 cm^3) was added and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 and the combined organic layers were dried over $MgSO_4$, filtered and stirred in the presence of MnO_2 (25 g) for 6 h. After filtration, spot thin layer chromatography showed the presence of two components. These were separated by column chromatography (Al_2O_3, CH_2Cl_2 changing to CH_2Cl_2 : MeOH 20 : 1). After removal of solvent, **5** (first fraction, 668 mg, 1.75 mmol, 34%) and **7** (second fraction, 621 mg, 814 µmol, 31%) were isolated as colourless solids. Compound **7**: Mp 102–104 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.67 (dd, J = 2.3, 0.7 Hz, 2H, H^{A6}), 7.71 (dd, J = 8.2, 2.3 Hz, 2H, H^{A4}) 7.54 (d, J = 8.2 Hz overlapping s, 4H, H^{A3+E4}), 7.34 (t, J = 7.9 Hz, 2H, H^{B5}), 7.27 (t, J = 7.9 Hz, 2H, H^{F5}), 7.14 (ddd, J = 7.7, 1.4, 0.8 Hz, 2H, H^{B6}), 7.09 (m, 2H, H^{B2}), 6.90 (ddd, J 8.3, 2.5, 0.7 Hz, 2H, H^{B4}), 6.86 (m, 4H, H^{F4+F6}), 6.79 (m, 2H, H^{F2}), 3.81 (s, 6H, $H^{B\text{-}OMe}$), 3.72 (s, 6H, $H^{F\text{-}OMe}$), 2.62 (s, 6H, H^{Me}). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 160.1 (C^{B3}), 159.4 (C^{F3}), 156.5 (C^{A2}), 154.5 (C^{E6}), 153.3 ($C^{E2/3}$), 147.2 (C^{A6}), 140.6 (C^{F1}), 140.4 (C^{E4}), 139.1 (C^{B1}), 136.1 (C^{E5}), 134.9 (C^{A5}), 134.4 (C^{A4}), 131.9 ($C^{E3/2}$), 130.1 (C^{B5}), 129.3 (C^{F5}), 124.2 (C^{A3}), 121.5 (C^{F6}), 119.5 (C^{B6}), 114.7 (C^{F2}), 113.2 (C^{B4}), 113.0 (C^{F4}), 112.9 (C^{B2}), 55.3 ($C^{B\text{-}OMe}$), 55.2 ($C^{F\text{-}OMe}$), 23.3 (C^{Me}). ESI MS: m/z 763.4 $[M + H]^+$ (calc. 763.3). IR (solid, ν (cm^{-1})) 3001 w, 2932 w, 2831 w, 1599 s, 1578 s, 1450 m, 1424 s, 1363 w, 1285 m, 1211 s, 1163 m, 1037 m, 1013 m, 844, 777 s, 690 s. Found C, 77.36; H, 5.70; N, 7.22; $C_{50}H_{42}N_4O_4{\cdot}0.75H_2O$ requires C, 77.35; H, 5.65; N, 7.22%.

[Cu(5)$_2$][PF$_6$]

Ligand **5** (32.0 mg, 83.7 µmol) was dissolved in CH_2Cl_2 (5 cm^3) and a solution of $[Cu(NCMe)_4][PF_6]$ (15.7 mg, 42.0 µmol) in CH_3CN (5 cm^3) was added. The red solution was stirred for 30 min at room temperature, filtered over Al_2O_3, and then the solvent was removed *in vacuo*. [Cu(**5**)$_2$][PF$_6$] was isolated as a red solid (40.1 mg, 41.2 µmol, 98%). ^{1}H NMR (500 MHz, CD_3CN) δ (ppm) 8.91 (d, J = 1.7 Hz, 2H, H^{A6}), 8.48 (d, J = 8.4 Hz, 2H H^{A3}), 8.30 (d, J = 8.1 Hz, 2H, H^{C3}), 8.24 (dd, J = 8.3, 1.4 Hz, 2H, H^{A4}), 7.83 (d, J = 8.0 Hz, 2H, H^{C4}), 7.39 (t, J = 8.0 Hz, 2H, H^{B5}), 7.37 (t, J = 7.9 Hz, 4H, H^{D5}), 7.25 (d, J = 7.8 Hz, 2H, H^{B6}), 7.22 (m, 2H, H^{B2}), 7.00–6.94 (overlapping, 6H, $H^{B4+D4+D6}$), 6.93 (m, 2H, H^{D2}), 3.81 (s, 6H, $H^{B\text{-}OMe}$), 3.80 (s, 6H, $H^{D\text{-}OMe}$), 2.39 (s, 6H, H^{Me}). ^{13}C NMR (126 MHz, CD_3CN) δ (ppm) 161.4 (C^{B3}), 160.7 (C^{D3}), 156.3 (C^{C6}), 153.7 (C^{A2}), 152.7 (C^{C2}), 148.5 (C^{A6}), 141.5 (C^{D1}), 139.6 (C^{C4}), 139.3 (C^{C5}), 139.0 (C^{B1}), 138.4 (C^{A5}), 136.7 (C^{A4}), 131.4 ($C^{B5/D5}$), 130.7 ($C^{D5/B5}$), 122.5 (C^{A3}), 122.3 (C^{D6}), 120.4 (C^{B6}), 119.9 (C^{C3}), 115.8 (C^{D2}), 115.2 (C^{D4}), 114.3 (C^{B4}), 113.6 (C^{B2}), 56.1 ($C^{B\text{-}OMe}$), 56.05 ($C^{D\text{-}OMe}$), 24.6 (C^{Me}). ^{19}F NMR (376 MHz, CD_3CN) δ (ppm) –74.03 (d, J = 707). ESI MS: m/z 827.4 $[M - PF_6]^+$ (calc. 827.3). IR (solid, ν (cm^{-1})) 3062 w, 2954 w, 2922 m, 2850 w, 1599 m, 1581 m, 1470 m, 1447 m, 1435 m, 1377 w, 1300 m, 1251 w, 1224 m, 1045 s, 1021 s, 837 s, 786 s, 690 m. UV/VIS (CH_2Cl_2) λ_{max} (nm) 468 (ε/6000 dm^3 mol^{-1} cm^{-1}), 319 (61 000), 277 (50 500). Emission (CH_2Cl_2, λ_{ex} 350 nm) λ_{max} (nm) 379. Found C, 61.39; H, 4.75; N, 5.54; $C_{50}H_{44}CuN_4O_4PF_6$ requires C, 61.69; H, 4.56; N, 5.76%.

[Cu(6)$_2$][PF$_6$]

The method was as for [Cu(**5**)$_2$][PF$_6$] starting with **6** (40.0 mg, 101 µmol) and $[Cu(NCMe)_4][PF_6]$ (19 mg, 50.9 µmol). [Cu(**6**)$_2$][PF$_6$] was isolated as a red solid (48.1 mg, 48.0 µmol, 94%). ^{1}H NMR (500 MHz, CD_3CN) δ (ppm) 8.35 (d, J = 7.1 Hz, 4H, H^{C3}), 7.98 (d, J = 7.3 Hz, 4H, H^{C4}), 7.39 (t, J = 7.8 Hz, 4H, H^{D5}), 6.99 (m, 12H, $H^{D2+D4+D6}$), 3.80 (s, 12H, OMe), 2.32 (s, 12H, Me). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 159.7, 154.7, 150.5, 139.4, 139.3, 129.8, 129.4, 121.3, 119.9, 114.8, 113.6, 55.4 (C^{OMe}), 24.3 (C^{Me}). ^{19}F NMR (376 MHz, CD_3CN) δ (ppm) –74.1 (d, J = 703 Hz). ESI MS: m/z 856.0 $[M - PF_6]^+$ (calc. 855.3) UV/VIS (CH_2Cl_2) λ_{max} (nm) 467 (ε/6100 dm^3 mol^{-1} cm^{-1}), 320 (61 000), 277 (50 600). Emission (CH_2Cl_2, λ_{ex} 350 nm) λ_{max} (nm) 383. IR (solid, ν (cm^{-1})) 3057 w, 2972 w, 2918 w, 2842 w, 1589 m, 1448 m, 1230 w, 1223 m, 1047 w, 1022 m, 831 s, 787 m, 702 m. $E°$(MeCN)/V *vs.* Fc/Fc$^+$: +0.40 (irreversible). Found C, 62.96; H, 4.95; N, 5.58; $C_{52}H_{48}CuF_6N_6O_6P$ requires C, 62.36; H, 4.83; N, 5.59%.

Crystal structure determination

Data were collected on a Bruker-Nonius Kappa CCD or Stoe IPDS instrument; data reduction, solution and refinement used the programmes Stoe IPDS software[7] or COLLECT,[8] and then DENZO/SCALEPACK,[9] SIR92,[10] and CRYSTALS.[11] The structures have been analysed using Mercury v. 1.4.2.[12] The ORTEP figures drawn using Ortep-3 for Windows.[13]

[Pd(2)$_2$][BF$_4$]$_2$·2

$C_{72}H_{60}B_2F_8N_6O_6Pd$, M = 1385.31, yellow plate, triclinic, space group P-1, a = 8.7623(2), b = 11.1136(2), c = 16.3282(3) Å, α = 75.890(1), β = 77.905(1), γ = 89.117(1)°, U = 1506.78(5) Å^3, Z = 1, D_c = 1.527 Mg m^{-3}, μ(Mo Kα) = 0.396 mm^{-1}, T = 173 K, 13 865 reflections collected (7175 unique). Refinement of 5977 reflections (430 parameters) with $I > 3\sigma(I)$ converged at final R_1 = 0.0274 (R_1 all data = 0.0356), wR_2 = 0.0285 (wR_2 all data = 0.0351), R_{int} = 0.023, gof = 1.1096.

Ligand 6

$C_{26}H_{24}N_2O_2$, M = 396.49, colourless block, monoclinic, space group $P2_1/c$, a = 10.0276(2), b = 8.1544(1), c = 12.9843(2) Å, β = 111.960(1)°, U = 984.68(3) Å^3, Z = 2, D_c = 1.337 Mg m^{-3}, μ(Mo Kα) = 0.085 mm^{-1}, T = 123 K, 25 410 reflections collected (4279 unique). Refinement of 2689 reflections (136 parameters) with $I > 3\sigma(I)$ converged at final R_1 = 0.0512 (R_1 all data = 0.0728), wR_2 = 0.0533 (wR_2 all data = 0.0608), R_{int} = 0.036, gof = 1.0661.

[Cu(5)$_2$][PF$_6$]·0.1C$_2$H$_4$Cl$_2$·0.15CH$_2$Cl$_2$

$C_{50.35}H_{44.70}Cl_{0.50}CuF_6N_4O_4P$, M = 996.07, red plate, triclinic, space group P-1, a = 10.3190(8), b = 15.078(1), c = 16.603(1) Å, α = 90.627(7), β = 98.169(6), γ = 106.230(7)°, U = 2451.7(4) Å^3, Z = 2, D_c = 1.349 Mg m^{-3}, μ(Mo Kα) = 0.575 mm^{-1}, T = 173 K, 59 962 reflections collected (16 938 unique). Refinement of 7730 reflections (757 parameters) with $I > 2\sigma(I)$ converged at final R_1 = 0.0916 (R_1 all data = 0.1710), wR_2 = 0.0858 (wR_2 all data = 0.1181), R_{int} = 0.128, gof = 1.0181.

Results and discussion

Ligands for palladium(II) complexes

Ligands **3** and **4** were prepared using caesium-directed Williamson's methodology by treating **1** with allyl bromide or 3-(2-bromoethoxy)prop-1-ene, respectively, in the presence of Cs_2CO_3 in DMF. For **3**, the reaction was carried out in a microwave reactor at 100 °C and was complete in less than an hour. For **4**, the reaction mixture was heated at 120 °C for 4 d. Both ligands were obtained in high yield. The EI mass spectrum of each compound exhibited a parent ion (*m*/*z* 421.2 for **3** and 508.2 for **4**), and the appearance of the solution ^{1}H and ^{13}C NMR spectra of **3** and **4** confirmed the formation of symmetrical ligands. The spectra have been assigned using COSY, DEPT, HMQC and HMBC techniques. With the exception of the appearance of signals for the additional methylene groups in **4**, the ^{1}H NMR spectra for **3** and **4** are almost identical, as are their ^{13}C NMR spectra. However, whereas in **3**, the signals for protons H^{B2} and H^{B6} (Scheme 1) appear at δ 7.14 and 7.18 ppm, in **4**, they overlap at δ 7.29 ppm. Since the ^{13}C NMR spectroscopic signatures for the aromatic domain of the two ligands are virtually superimposable, the assignments of signals for C^{B2} and C^{B6} in **4** have been made by comparison with those of **3**, assigned from the HMQC spectrum.

Palladium(II) complexes: synthesis and solution characterization

The reaction of $[Pd(CH_3CN)_4][BF_4]_2$ with two equivalents of ligand **2** in CH_3CN produced analytically pure $[Pd(\mathbf{2})_2][BF_4]_2$ as a yellow solid. The highest mass peaks in the FAB mass spectrum came at *m*/*z* 861.1 and 842.1, and were assigned to $[Pd(\mathbf{2})_2 + F]^+$ and $[Pd(\mathbf{2})_2]^+$, respectively. Fragmentation by ligand loss was also observed. The complex was poorly soluble in most common solvents, and the NMR spectra were recorded in DMSO-d_6. Compared to signals for the free ligand in DMSO-d_6, the most diagnostic indication of complex formation is the large shift to higher frequency for the signal for bpy proton H^{A4}. This presumably reflects the fact that in the square planar Pd(II) environment, the presence of the methoxy substituents restricts rotation about the C_{py}–C_{Ph} bond, and the aryl ring twists out of the plane of the bpy unit (this is confirmed in the crystal structures of ligand and complex described below). The bpy protons most affected by this will be those facing the aryl π-cloud, *i.e.* H^{A4} and H^{A6} (Fig. 1). As Fig. 1 shows, the peaks for the bpy unit are rather broad compared to those of the free ligand in the same solvent. Addition of free ligand to an NMR sample of $[Pd(\mathbf{2})_2][BF_4]_2$ resulted in further broadening of the signal assigned to H^{A3+A4} as well as broadening of the resonance for H^{B4} and loss of resolution for the signals for H^{B2+B6}/H^{B5}. In spectra recorded for $[Pd(\mathbf{2})_2][BF_4]_2$ plus half and one equivalent of ligand, no signals arising from the free ligand were observed. This observation is consistent with that observed by Milani *et al.*, in the DMSO-d_6 solution ^{1}H NMR spectrum of $[Pd(bpy)_2][PF_6]_2$, indicating that exchange occurs between the free and the coordinated ligand on the NMR spectroscopic timescale.[14]

Structural characterization of $[Pd(2)_2][BF_4]_2\cdot 2$

A solution of analytically pure $[Pd(\mathbf{2})_2][BF_4]_2$ in a mixture of DMF and Et_2O in a vial surrounded by Et_2O was left at 4 °C for several weeks after which time, X-ray quality yellow plates had grown. Interestingly, the complex co-crystallized with the free ligand (which must have originated from the complex) and the single crystal structure of $[Pd(\mathbf{2})_2][BF_4]_2\cdot\mathbf{2}$ determined. Fig. 2(a) and Fig. 3 show the centrosymmetric structures of the $[Pd(\mathbf{2})_2]^{2+}$ cation and ligand **2**, respectively. Bond distances and angles within the bpy and phenyl rings are unexceptional. As expected, the free ligand adopts a *transoid* conformation, but flips to a *cisoid* arrangement upon binding to palladium(II). The C–O bond distances and C–O–C bond angles in both ligand and complex (see figure caption) are consistent with delocalization of π-character from the phenyl ring to the oxygen atom. Two features of the structure deserve note: the ligand distortion in $[Pd(\mathbf{2})_2]^{2+}$, and the packing. In $[M(bpy)_2]^{n+}$ complexes and in

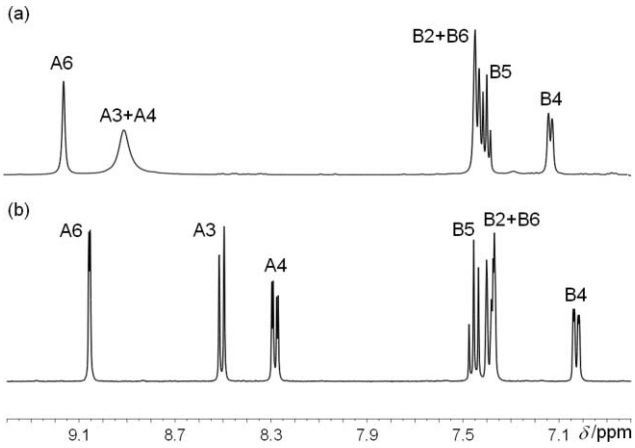


Fig. 1 500 MHz NMR spectra of DMSO-d_6 solutions of (a) $[Pd(\mathbf{2})_2][BF_4]_2$ and (b) ligand **2**.

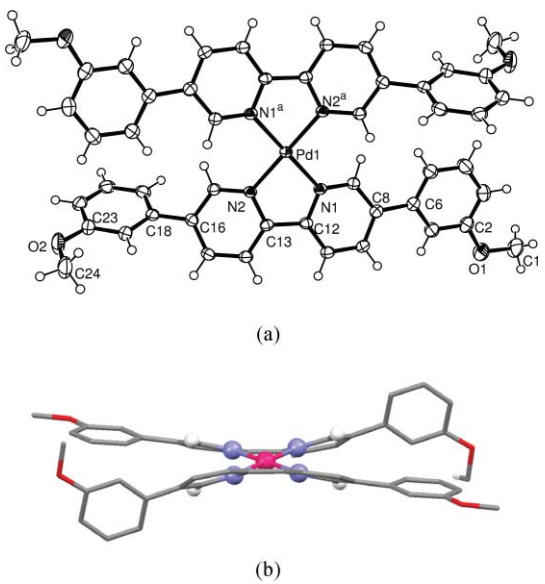


Fig. 2 (a) Molecular structure of the $[Pd(\mathbf{2})_2]^{2+}$ cation in $[Pd(\mathbf{2})_2][BF_4]_2\cdot\mathbf{2}$ with ellipsoids plotted at 50% probability level. Symmetry code a = $-x$, $-y$, $-z$. Selected bond parameters: Pd1–N1 = 2.033(1), Pd1–N2 = 2.022(1), C1–O1 = 1.427(2), C2–O1 = 1.362(2), C23–O2 = 1.361(2), C24–O2 = 1.428(2) Å; N1–Pd1–N2 = 79.21(5), $N2^a$–Pd1–N1 = 100.79(5), C1–O1–C2 = 118.3(2), C24–O2–C23 = 117.5(1)°. (b) Distortion of the bpy units alleviates steric hindrance between H^6 protons.

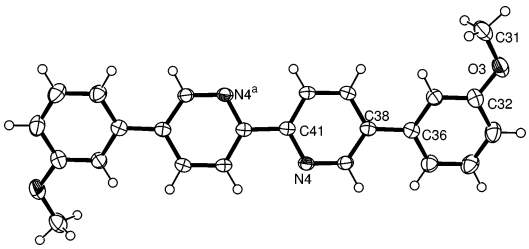
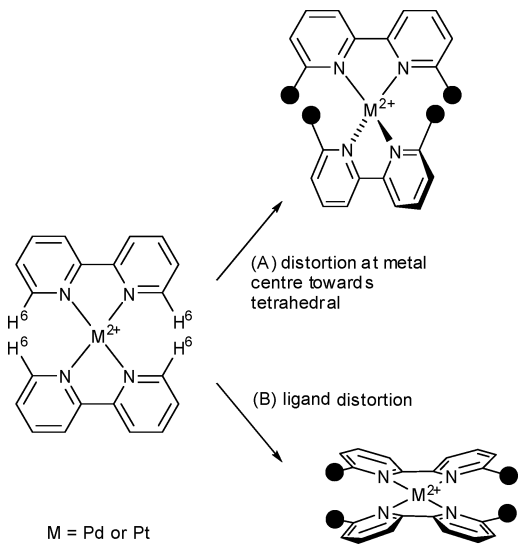


Fig. 3 Molecular structure of the free ligand **2** in $[Pd(\mathbf{2})_2][BF_4]_2 \cdot \mathbf{2}$ with ellipsoids plotted at 50% probability level. Symmetry code a = $-x, -y, -z$. Selected bond parameters: C41–C41^a = 1.478(3), C36–C38 = 1.482(2), C32–O3 = 1.363(2), C31–O3 = 1.427(3) Å; C31–O3–C32 = 117.4(2)°.

the absence of electronic factors (*i.e.* crystal field stabilization energy), the metal ion is typically in a tetrahedral environment. However, a square planar environment is preferred for a d^8 metal centre such as palladium(II) or platinum(II). In such a bis(bpy) complex, steric interactions between the H^6 protons on adjacent ligands lead to one of the two types of distortion illustrated in Scheme 2.[15] A search of the Cambridge Structural Database (v. 5.30)[16] using Conquest[12] revealed 24 structures containing either a $[Pd(bpy)_2]^{2+}$ or $[Pt(bpy)_2]^{2+}$ motif, including substituted derivatives and $[M(phen)_2]^{2+}$ (phen = 1,10-phenanthroline).[14,17–34] Excluded from this set are compounds in which adjacent bpy domains are connected directly[35–37] or indirectly[38] through the six-positions. Of the 24 structures, twelve distort at the metal centre (distortion A in Scheme 2) and twelve undergo ligand distortion (B in Scheme 2, the so-called 'bow-incline' distortion). These distortions have been discussed in detail by Marzilli *et al.*,[31] but with a sample size of only six complexes. In $[Pd(\mathbf{2})_2]^{2+}$, $H^6 \cdots H^6$ repulsions are relieved by distortion B as shown in Fig. 2(b).



Scheme 2 Modes of distortion in $[Pd(bpy)_2]^{2+}$, $[Pt(bpy)_2]^{2+}$ and related cations.

In ligand **2** (Fig. 3), the bpy unit is planar, and the phenyl substituent is twisted 23.44(9)° with respect to this plane. This compares to 32.2(6) and 32.4(6)° in the two independent molecules of **2** in the previously determined structure of the ligand alone.[4] In $[Pd(\mathbf{2})_2][BF_4]_2 \cdot \mathbf{2}$ the MeO group is oriented on the side opposite the N atom of the adjacent pyridine ring (Fig. 3), whereas in the previous structure of **2**,[4] it lies on the same side of the molecule as the N atom. This difference probably originates from packing effects. In **2**,[4] molecules interact through weak $C–H_{methyl} \cdots O$ hydrogen bonds to form interconnected, undulating chains; offset face-to-face π-stacking occurs between adjacent bpy domains and between adjacent phenyl rings. In $[Pd(\mathbf{2})_2][BF_4]_2 \cdot \mathbf{2}$, ligands and $[Pd(\mathbf{2})_2]^{2+}$ cations are interleaved to form stacks (Fig. 4(a)) with the pyridine ring containing atom N1 in $[Pd(\mathbf{2})_2]^{2+}$ is π-stacked over the bpy unit of the free ligand at a distance of 3.33 Å. The stacks are connected by non-classical hydrogen bonds between atom O3 of a free ligand and C24H241 of a methyl group of a $[Pd(\mathbf{2})_2]^{2+}$ cation ($C24H241 \cdots O3^i$ = 2.50 Å, $C24 \cdots O3^i$ = 3.258(2) Å, $C24H241 \cdots O3^i$ = 135°, symmetry code i = $-1 + x, 1 + y, -1 + z$) (Fig. 4(b)).

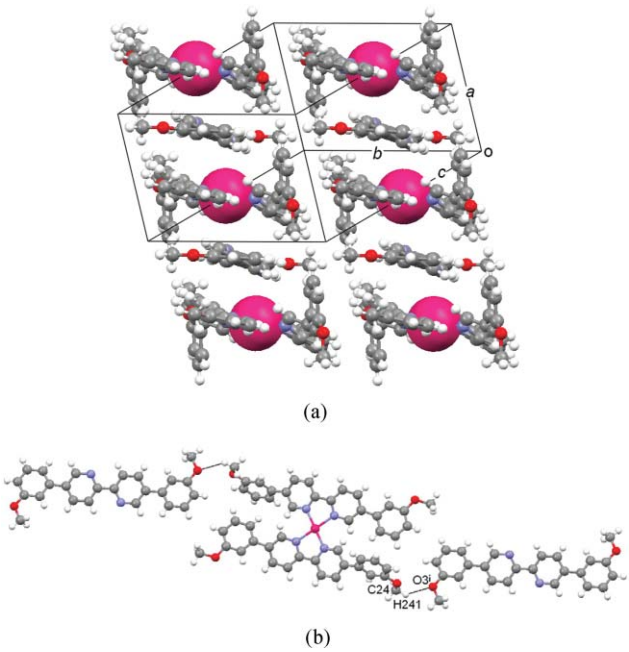


Fig. 4 (a) Stacking of $[Pd(\mathbf{2})_2]^{2+}$ cations and ligands **2** in$[Pd(\mathbf{2})_2][BF_4]_2 \cdot \mathbf{2}$. (b) Hydrogen bonding between free ligands and cations (see text).

Introduction of terminal alkene functionalities

The reaction of $[Pd(CH_3CN)_4][BF_4]_2$ with two equivalents of either **3** or **4** resulted in the formation of $[Pd(\mathbf{3})_2][BF_4]_2$ or $[Pd(\mathbf{4})_2][BF_4]_2$, respectively, each isolated as a yellow solid. The two complexes were characterized by NMR spectroscopic and mass spectrometric methods, and by elemental analyses. A comparison of the ^{1}H NMR spectrum of acetone-d_6 solutions of ligand **3** and of the palladium(II) complex showed that the most significant changes were in the chemical shifts of the signals (assigned by 2D techniques) arising from protons H^{A4} (δ 9.00 to 9.33 ppm) and H^{A6} (δ 8.21 to 8.86 ppm), consistent with the formation of a square planar palladium(II) complex (see earlier discussion). A comparison of the ^{1}H NMR spectra of **4** and $[Pd(\mathbf{4})_2][BF_4]_2$ was made using CD_3CN–$CDCl_3$ solutions of the compounds, and the change in the chemical shift of proton H^{A4} (δ 8.03 to 8.46 ppm) was indicative of coordination. Attempts to grow X-ray quality crystals of $[Pd(\mathbf{3})_2][BF_4]_2$ and $[Pd(\mathbf{4})_2][BF_4]_2$ were unsuccessful. Our interest in these complexes is the reactivity of

the terminal alkene functionalities. The application of Grubbs' catalysts to the formation of macrocyclic species have included the formation of macrocycles, catenanes and knots templated within a metal coordination sphere.[39–48] Molecular modelling† indicated that in both $[Pd(\mathbf{3})_2]^{2+}$ and $[Pd(\mathbf{4})_2]^{2+}$, the terminal alkene chains are long enough to permit ring-closing metathesis with concomitant formation of a palladium(II)-bound macrocyclic ligand. However, attempts at ring closure were unsuccessful with both first generation Grubbs' and Hoveyda–Grubbs' catalysts in CH_2Cl_2 or CH_3NO_2 at room temperature or reflux, and also under microwave heating conditions. In each case, the ^{1}H NMR spectrum of the crude mixture indicated no signs of the formation of a new double bond. The ^{1}H NMR spectrum of the crude mixture showed the presence of the unreacted palladium(II) complex. We propose that the problem lies in the lability of the palladium(II) complexes which release free ligands capable of poisoning the catalyst. Although ruthenium carbene catalysts exhibit an exceptional tolerance towards many functional groups, catalyst inhibition by complex-formation involving the reagents is known to be problematical.[49,50]

An obvious way to circumvent the problem of ligand lability is to use the more inert platinum(II) analogues of the palladium(II) complexes described above. We began by attempting to prepare $[Pt(\mathbf{2})_2][BF_4]_2$ by reaction of K_2PtCl_4 with ligand **2** in deionized water, following the procedure reported for the synthesis of $[Pt(bpy)_2][BF_4]_2$.[51] However, only starting materials were recovered. The reaction was repeated under more rigorous conditions (microwave reactor, heating the aqueous mixture at 165 °C for 1 h) and this led to the formation of a yellow-brown residue that was completely insoluble in common solvents. Finally, the solvent was changed to DMF (microwave reactor, 220 °C, 1 h) and this gave rise to a yellow solid, which was partly soluble in DMSO but otherwise insoluble in common organic solvents. Because of the difficulties encountered in characterizing this product, we did not pursue the syntheses of platinum(II) complexes of ligands **3** and **4**.

The ferroin–cuproin interconversion

In order to broaden the scope of our investigation of 4-coordinate complexes with ligands related to **2**, we turned our attention to the preparation of copper(I) complexes. The crucial factor for the isolation of air-stable complexes containing an $\{Cu(bpy)_2\}^+$ core is the presence of substituents in the 6- and 6′-positions.[2] We describe here the syntheses of ligands **5** and **6**, and their reactions with copper(I).

Ligand **5** was prepared by methylation of **2** using MeLi adapting the procedure reported for the methylation of 1,10-phenanthrolines and 2,2′-bipyridines.[52–55] The optimum yield of **5** (82%) was obtained when MeLi (one equivalent) was added at –78 °C, and the reaction then carried out at room temperature followed by a period of heating. After quenching the reaction with water, oxidation with MnO_2 resulted in the formation of **5**. Ligand **6** was subsequently synthesized by methylation of **5**. Attempts to prepare **6** directly by the reaction of **2** with two or more equivalents of MeLi were unsuccessful. The highest mass peak in the ESI MS of each ligand corresponded to the parent ion. The symmetrical appearance of the ^{1}H and ^{13}C NMR spectra of **6** was consistent with methylation at both the 6- and 6′-positions, and this is confirmed by the disappearance of the signal assigned to H^{A6} on going from **2** to **6** (Fig. 5(a) and (b)). Fig. 5(a) and (b) also illustrate that the introduction of the methyl substituents causes the signals for the remaining bpy protons and the *ortho*-protons of the phenyl substituent (H^{D2} and H^{D6}) to shift to lower frequency. This can be rationalized in terms of a change in the relative orientations of pyridine and aryl rings (see structural details below) which results in the ring protons lying over the π-cloud of the adjacent ring. The resonances for the aryl protons remote from the bpy unit and for the methoxy protons are only slightly affected by methylation. The ^{1}H NMR spectrum of **5** (Fig. 5(c)) is readily assigned by comparison with those of **2** and **6** (Fig. 5(a),(b)), and the assignments have been confirmed by 2D techniques.

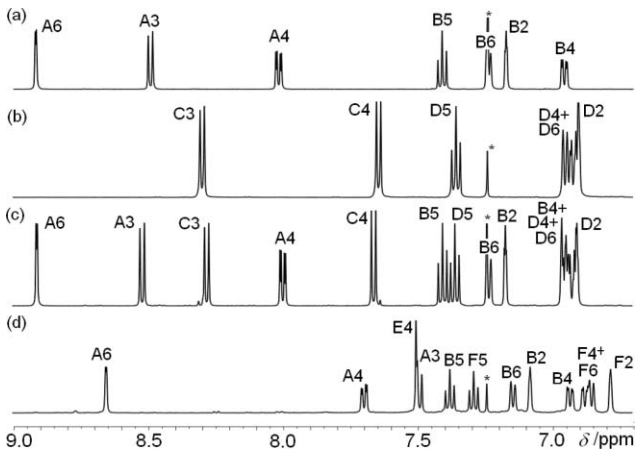


Fig. 5 Room temperature 500 MHz NMR spectra of $CDCl_3$ solutions of (a) **2**, (b) **6**, (c) **5** and (d) **7**; * = residual $CHCl_3$. Proton labelling is given in Schemes 1 and 3.

Single crystals of **6** were grown by slow evaporation of a $CDCl_3$ solution of the ligand. The centrosymmetric molecular structure of **6** is shown in Fig. 6(a). The plane of the aryl substituent deviates 55.16(6)° from the plane of the bpy unit, and so, as expected, 6,6′-dimethyl substitution results in a significantly greater twist of the 3-anisyl groups than is observed in **2** (Fig. 3). This deviation affects the way in which the molecules are able to pack. In **2**, π-stacking is important,[4] whereas in **6**, there is no analogous stacking, and the molecules pack so that each 6-methyl or 6′-methyl substituent points obliquely towards a pyridine ring on an adjacent molecule (Fig. 6(b)).

In our initial attempts to synthesize the monomethyl derivative **5**, one equivalent of MeLi was added to **2** at room temperature. After quenching the reaction in water, and oxidation of the intermediate using MnO_2, spot thin layer chromatography showed the presence of two products. These colourless compounds were separated by column chromatography, and the first fraction was identified as **5**. The highest mass peak in the ESI MS of the second product, **7**, was observed at m/z 763.4 (*i.e.* approximately twice the molecular mass of **5**). The $CDCl_3$ solution ^{1}H NMR spectrum of **7** showed the presence of two MeO signals (δ 3.81 and 3.72 ppm, relative integrals 1 : 1), both shifted to lower frequency with respect

† Spartan '04, Wavefunction Inc.; geometry optimization of the palladium complex used the crystallographically determined structure of $[Pd(\mathbf{2})_2]^{2+}$ as a starting point.

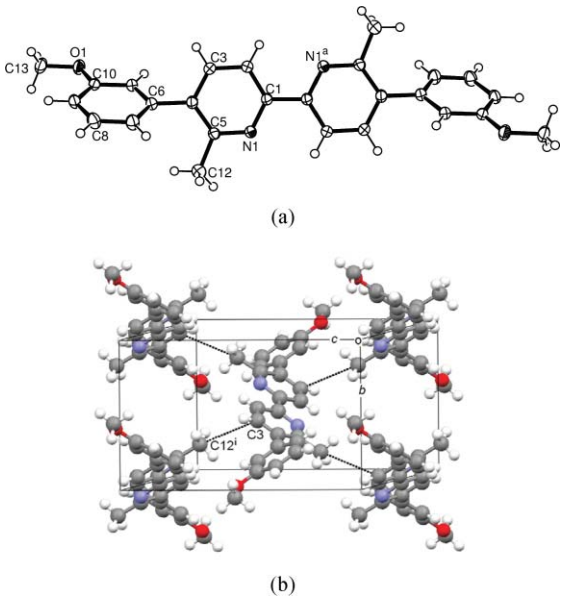
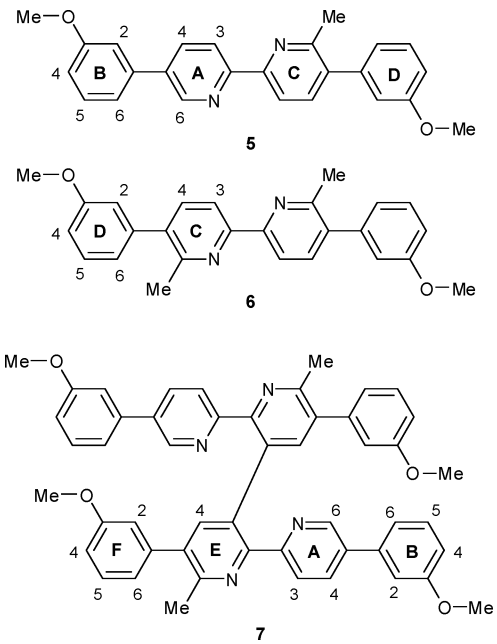


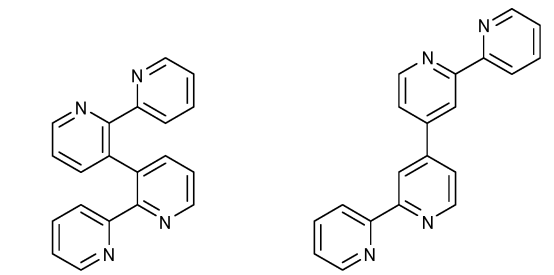
Fig. 6 (a) Molecular structure of **6** with ellipsoids plotted at 50% probability. Symmetry operator a = 1 − *x*, 1 − *y*, 1 − *z*. Selected bond parameters: C1–C1^{a} = 1.484(2), C4–C6 = 1.484(2), C5–C12 = 1.496(2), C10–O1 = 1.367(2), C13–O1 = 1.429(2) Å; C13–O1–C10 = 117.6(1), C1–N1–C5 = 119.22(9)°. (b) Packing of molecules of **6**; symmetry code i = x, $\frac{3}{2} - y$, $\frac{1}{2} + z$.

to those in **5** (δ 3.88 and 3.84 ppm). A singlet at δ 2.62 ppm (relative integral with respect to each OMe = 1 : 1) replicated that in **5**. Fig. 5(d) shows the aromatic region of the ^{1}H NMR spectrum of **7** (see Scheme 3 for atom labelling). Crucial observations that aid the identification of **7** are a similarity between the phenyl regions of the spectra of **5** and **7**, the appearance of a singlet at δ 7.54 ppm, significant changes in the chemical shifts of signals for the bpy protons, and the loss of one bpy signal with respect



Scheme 3 Compounds **5–7** with ring and atom labelling for NMR spectroscopic assignments.

to the number of resonances in **5**. A comparison of the ^{13}C and DEPT NMR spectra revealed the presence of ten quaternary ^{13}C nuclei in **7** compared to nine in **5**. The NMR and ESI MS data are consistent with C–C bond formation between two bpy units of **5** to produce **7**. The equivalence of the bpy units deduced from the ^{1}H and ^{13}C NMR spectra gave two possibilities: the formation of a tetramethoxyphenyl derivative of 2,2′:3′,3″:2″,2‴-quaterpyridine or 2,2′:4′,4″:2″,2‴-quaterpyridine (Scheme 4). The singlet in the ^{1}H NMR spectrum can be assigned to either H^{E3} or H^{E4}, and the appearance in the NOESY spectrum of a cross peak from this singlet to the signal for H^{F2} confirms an assignment of H^{E4} (Fig. 7). Single crystals of **7** were not forthcoming, but Fig. 8 shows an optimized structure† which indicates C_1 symmetry, *i.e.* ligand **7** is chiral. To date, attempts at metal complexation using **7** have been unsuccessful.



Scheme 4 Structures of two isomers of quaterpyridine.

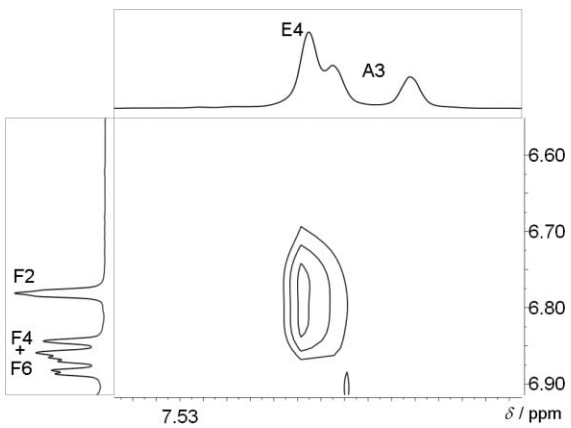


Fig. 7 Part of the 500 MHz NMR NOESY spectrum of **7** showing the H^{E4}–H^{F2} cross peak.

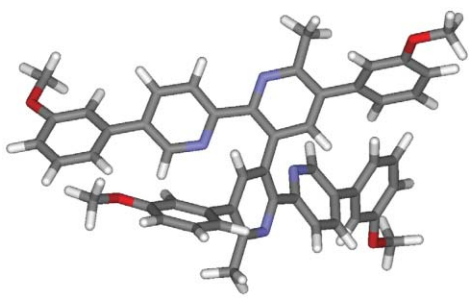


Fig. 8 Optimized C_1 structure of **7**.

Copper(I) complexes

Treatment of $[Cu(NCMe)_4][PF_6]$ with either ligands **5** or **6** led to the formation of red $[Cu(\mathbf{5})_2][PF_6]$ or $[Cu(\mathbf{6})_2][PF_6]$, respectively. The highest mass envelopes in the ESI mass spectra of the products were assigned to $[M - PF_6]^+$ in each case, with isotope distributions matching those calculated. The diagnostic changes in the ^{1}H NMR spectrum on going from **5** (in $CDCl_3$) to $[Cu(\mathbf{5})_2]^+$ (in CD_3CN) involve the signals for protons H^{A4} and H^{C4}. Both signals are shifted to higher frequency (δ 8.00 to 8.24 ppm for H^{A4}, and δ 7.66 to 7.83 ppm for H^{C4}), while the remaining signals are little affected. Similarly, on going from **6** to $[Cu(\mathbf{6})_2]^+$, the signal assigned to H^{C4} is the only resonance to undergo significant perturbation (δ 7.64 to 7.98 ppm). This mirrors the effects described earlier for coordination of ligands **2** and **3** to palladium(II).

Crystals of $[Cu(\mathbf{5})_2][PF_6]\cdot 0.1C_2H_4Cl_2\cdot 0.15CH_2Cl_2$ of X-ray quality were grown by vapour diffusion of Et_2O into a solution of the complex in a mixture of CH_2Cl_2 and 1,2-$C_2H_4Cl_2$. Fig. 9 depicts the structure of the $[Cu(\mathbf{5})_2]^+$ cation. The structure suffers from disorders in the cation, anion and solvent molecules. In the cation, the methyl group of one ligand is disordered over two sites modelled with 70% (atom C50 in Fig. 9) and 30% occupancies. In the other ligand, one methoxyphenyl unit (the one containing atom O11, Fig. 9) is disordered and has been modelled over two sites with 70–30% occupancies. Despite the problems associated with the structure, it confirms that the coordination geometry of the copper(I) centre is distorted tetrahedral (angle between the least squares planes of the two bpy domains = 70.0(1)°). In the ligand containing atoms N1 and N2, the phenyl ring containing atom C21 is approximately coplanar with the bpy rings (angles between the least squares planes of the rings = 6.5(2) and 11.9(5)°), while the second phenyl ring is twisted through 67.7(2)° with respect to the bpy unit. The coplanar rings are π-stacked with those of adjacent cations (alternating distances between least squares planes = 3.49 and 3.66 Å). Extensive C–$H_{phenyl}\cdots$O, C–$H_{methyl}\cdots$O and C–$H_{bpy}\cdots$F hydrogen bonding contribute to the solid state packing.

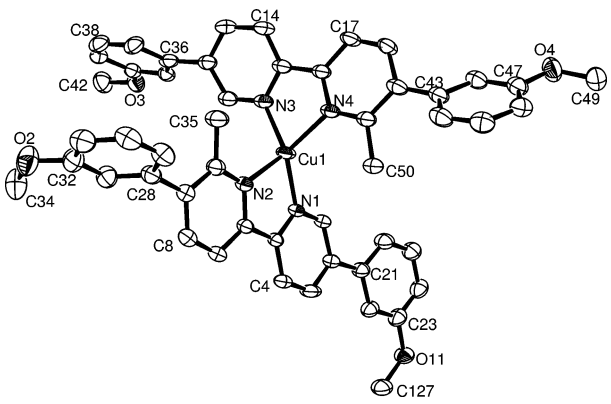


Fig. 9 Molecular structure of the $[Cu(\mathbf{5})_2]^+$ cation in $[Cu(\mathbf{5})_2][PF_6]\cdot 0.1C_2H_4Cl_2\cdot 0.15CH_2Cl_2$ with ellipsoids plotted at 30% probability; hydrogen atoms are omitted. For disordered sites (see text), only the major occupancy atoms are shown. Selected bond parameters: Cu1–N1 = 2.014(2), Cu1–N2 = 2.088(3), Cu1–N3 = 2.031(3), Cu1–N4 = 2.069(3) Å; N1–Cu1–N2 = 82.1(1), N1–Cu1–N3 = 134.9(1), N2–Cu1–N3 = 115.0(1), N1–Cu1–N4 = 126.4(1), N2–Cu1–N4 = 121.7(1), N3–Cu1–N4 = 81.5(1)°.

Conclusions

We have described the preparation of two ligands, **3** and **4**, which possess bpy domains terminated in alkene functionalities, and the syntheses and characterization of $[Pd(\mathbf{3})_2][BF_4]_2$ and $[Pd(\mathbf{4})_2][BF_4]_2$. For the related complex $[Pd(\mathbf{2})_2][BF_4]_2$ in which **2** is 5,5′-bis(3-methoxyphenyl)-2,2′-bipyridine, the labile nature of the ligand leads to co-crystallization with the free ligand to give $[Pd(\mathbf{2})_2][BF_4]_2\cdot\mathbf{2}$ in the solid state; rather than undergoing distortion in the coordination sphere towards a tetrahedral geometry, the $H^6\cdots H^6$ repulsions between the two bpy domains in $[Pd(\mathbf{2})_2]^{2+}$ are alleviated by a 'bow-incline' distortion within each ligand. Compound **2** has been converted to 5,5′-bis(3-methoxyphenyl)-6-methyl-2,2′-bipyridine (**5**) and 5,5′-bis(3-methoxyphenyl)-6,6′-dimethyl-2,2′-bipyridine (**6**) to produce ligands capable of forming air-stable copper(I) complexes. We have described the syntheses of $[Cu(\mathbf{5})_2][PF_6]$ and $[Cu(\mathbf{6})_2][PF_6]$, and the single crystal structures of **6** and $[Cu(\mathbf{5})_2][PF_6]\cdot 0.1C_2H_4Cl_2\cdot 0.15CH_2Cl_2$. By altering the conditions under which **2** is methylated, competitive formation of 5,5′,5″,5‴-tetrakis(3-methoxyphenyl)-2,2′:3′,3″:2″,2‴-quaterpyridine occurs.

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