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Functionalised 2,2′-bipyridine ligands for the preparation of metallostars; X-ray structures of free ligands and preparation of copper(I) and silver(I) complexes

Edwin C. Constable *, Catherine E. Housecroft *, Markus Neuburger, Ingo Poleschak, Margareta Zehnder

Department of Chemistry, University of Basel, Spitalstrasse 51, CH 4056 Basel, Switzerland

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Abstract

2,2-Bipyridine ligands bearing functionalised aryl substituents have been prepared with the aim of subsequent functionalisation and the preparation of multinuclear metallostars. The key intermediates are compounds containing 4-methoxyphenyl substituents which may be converted to 4-hydroxyphenyl substituted ligands. Copper(I) and silver(I) complexes of 4,4′-di(methoxyphenyl)-6,6′-dimethyl-2,2′-bipyridine have been prepared and structurally characterised as have the ligands 4,4′-di(methoxyphenyl)-6,6′-dimethyl-2,2′-bipyridine and 4,4′-di(methoxyphenyl)-2,2′-bipyridine.

Keywords: Copper; Silver; Ruthenium; 2,2′-Bipyridine; Metallostar; X-ray

1. Introduction

Many contemporary approaches to the construction of photoconversion devices are based upon multinuclear complexes which act either as photocollecting arrays or as multifunctional devices, which both collect light energy and transform it into stored chemical energy [1–4]. Increasing knowledge of the molecular detail of the biological photoconversion systems has served to emphasise that a key feature in the successful design of artificial photoconversion devices will be the precise control of the spatial arrangement of the individual functional elements [5]. These constraints on the spatial arrangement of components in photoactive assemblies have led us and others to develop strategies for the synthesis of metallodendrimers incorporating, in particular, ruthenium(II), osmium(II), rhodium(III) and iridium(III) centres [6–10]. Many of these metallodendrimers are based upon multiple $\{M(bpy)_3\}$ motifs which, particularly in the case of ruthenium(II) complexes, have near optimal photophysical properties (long excited state lifetimes, absorption maxima near the energy maximum of the solar energy spectrum, suitable redox properties) [11]. However, the $\{M(bpy)_3\}$ motif is chiral and can exist as Δ or Λ configurations [12,13]. In general, synthetic procedures for the preparation of metallodendrimers are regiospecific but not diastereospecific and compounds with multiple $\{M(bpy)_3\}$ motifs will be formed as ill-defined mixtures of diastereoisomers [13]. As the precise spatial control of the photoactive subunits is of prime importance in the design of photoconversion devices, we and others adopted the achiral $\{M(tpy)_2\}$ motif in preference [14,15] and have recently addressed the poor photophysical properties of $\{Ru(tpy)_2\}$ domains through ligand design [16–18]. Constraints upon the growth of dendrimers as they approach the de Gennes generation limit [19], have led us to propose the use of metallostars rather than metallodendrimers. In a metallostar, the primary branching occurs in the core zeroth generation and subsequent growth is linear [20]. By definition, first generation metallostars and metallodendrimers are synonymous. In this paper, we further develop the

* Corresponding authors. Tel.: +41-61-267-1001; fax: +41-61-267-1015
E-mail address: edwin.constable@unibas.ch (E.C. Constable).

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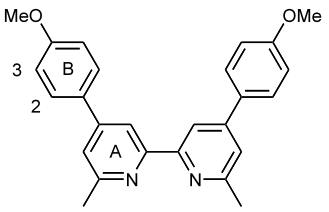
synthesis of heptanuclear first generation metallostars in which the core motif is a single $\{M(bpy)_3\}$ domain and in which the pendant metal centres are found in $\{M(tpy)_2\}$ substructures. A characteristic feature of the design of these new metallostars is the replacement of some of the ether linkages present in our prototype systems by stable, conjugated C–C bonds [21–26].



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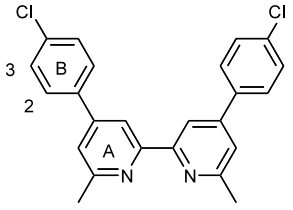

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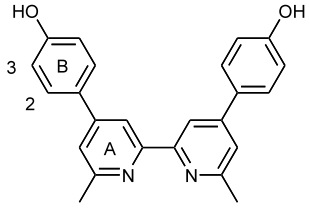

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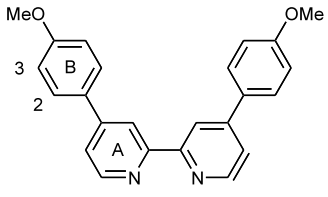

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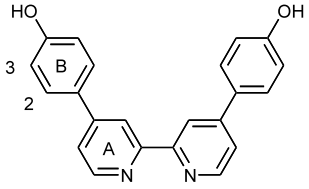

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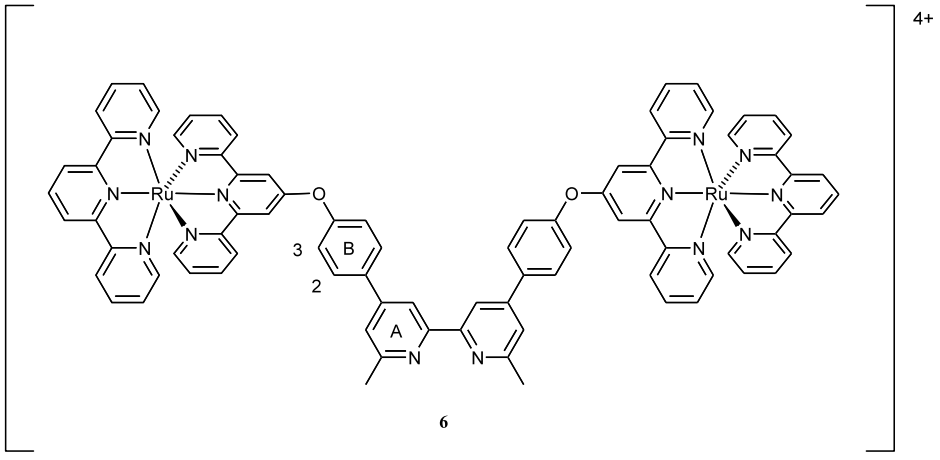

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2. Experimental

2.1. General procedures

Infrared spectra were recorded on a Mattson Genesis Fourier-transform spectrophotometer with samples in compressed KBr discs. ^{1}H NMR spectra were recorded on Bruker AM 250 or 400 MHz spectrometers. UV–Vis measurements were performed using a Perkin Elmer Lambda 19 spectrophotometer and were recorded in acetonitrile at a concentration of 5×10^{-5} M. FAB and EI mass spectra were recorded on a Kratos MS50 instrument. Time of flight (MALDI) spectra were recorded using a PerSeptive Biosystems Voyager-RP Biospectrometry Workstation. Electrochemical measurements were performed with an Amel model 553 potentiostat connected to an Amel model 567 function generator and an Amel model 560/A interface or an Eco Chemie Autolab PGSTAT 20 system using platinum bead working and auxiliary electrodes with an Ag/AgCl electrode as reference. The experiments were conducted using purified acetonitrile as solvent and 0.1 M $[Bu^n_4N][BF_4]$ as supporting electrolyte; ferrocene was

added at the end of each experiment as an internal reference. The compounds 1-pyridiniopropanone bromide [27], $[Pd(PPh_3)_4]$ [28], $[Ru(tpy)(Cltpy)][PF_6]_2$ [29] and $[Cu(MeCN)_4][PF_6]$ [30] were prepared by the literature methods; all other compounds were used as supplied commercially.

2.2. Synthesis of 4,4′-di(4-methoxyphenyl)-6,6′-dimethyl-2,2′-bipyridine (*1*)

A mixture of 4-methoxybenzaldehyde (13.6 g, 100 mmol), butane-2,3-dione (4.3 g, 50 mmol), EtOH (50 cm^3) and piperidine (0.5 cm^3) were heated to reflux for 2 h and then the solution allowed to cool. After 24 h in the refrigerator, orange–yellow crystals of 1,6-di(4-methoxyphenyl)hexa-1,5-diene-3,4-dione were collected by filtration and washed with a little cold MeOH. This dione (0.322 g, 1.0 mmol), 1-pyridiniopropanone bromide (0.432 g, 2.0 mmol) and NH_4OAc (2 g) in EtOH (10 cm^3) were heated to reflux for 4 h. On cooling, 4,4′-di(4-methoxyphenyl)-6,6′-dimethyl-2,2′-bipyridine (**1**) crystallised and was collected by filtration. The product was washed with MeOH, dried under reduced pressure and recrystallised from EtOH/pentane to give colourless needles of 4,4′-di(4-methoxyphenyl)-6,6′-dimethyl-2,2′-bipyridine (**1**) (0.130 g, 35%), m.p. 250–252 °C (Anal. Found: C, 76.6; H, 6.1; N 6.75. $C_{26}H_{24}N_2O_2 \cdot 2/3H_2O$ requires C, 76.5; H, 6.25; N, 6.86%); δH ($CDCl_3$) 8.82 (2H, d, $J_{3A,5A}$ 1.4 Hz, H^{3A}), 7.78 (4H, d, $J_{2B,3B}$ 8.8 Hz, H^{2B}), 7.42 (2H, d, $J_{3A,5A}$ 1.4 Hz, H^{5A}), 7.03 (4H, d, $J_{2B,3B}$ 8.8 Hz, H^{3B}), 3.88 (6H, s, OCH_3), 2.75 (6H, s, CH_3); δC ($CDCl_3$) 160.6, 158.1, 155.4, 149.6, 130.6, 128.5, 120. 9, 116.8, 114.4, 55.4, 24.4; $\bar{\nu}_{max}$ (cm^{-1}) 2961w, 2919w, 2838w, 1609s, 1534s, 1548m, 1513s, 1460m, 1438m, 1383m, 1365w, 1291m, 1241s, 1208w, 1175s, 1112w, 1073w, 1029s, 832s, 795w, 576m, 526w, 510w (KBr); *m/z* 396 (M^+) (EI); λ_{max}, nm, ($CHCl_3$) 243 (ε, $M^{-1}\,cm^{-1}$, 17 700), 269 (34 300), 291 (32 800).

2.3. Synthesis of 4,4′-di(4-chlorophenyl)-6,6′-dimethyl-2,2′-bipyridine (*2*)

A mixture of 4-chlorobenzaldehyde (14.0 g, 100 mmol), butane-2,3-dione (4.3 g, 50 mmol), EtOH (50 cm^3) and piperidine (0.5 cm^3) were heated to reflux for 2 h and then the solution was allowed to cool. After 24 h in the refrigerator, orange–yellow crystals of 1,6-di(4-chlorophenyl)hexa-1,5-diene-3,4-dione were collected by filtration and washed with a little cold MeOH. This dione (0.330 g, 1.0 mmol), 1-pyridiniopropanone bromide (0.432 g, 2.0 mmol) and NH_4OAc (2 g) in EtOH (10 cm^3) were heated to reflux for 4 h. On cooling, 4,4′-di(4-chlorophenyl)-6,6′-dimethyl-2,2′-bipyridine (**2**) crystallised and was collected by filtration. The product was washed with MeOH, dried under reduced pressure and recrystallised from $CHCl_3$/ether to give colourless needles of 4,4′-di(4-chlorophenyl)-6,6′-dimethyl-2,2′-bipyridine (**2**) (0.200 g, 50%), m.p. 230-234 °C (Anal. Found: C, 70.6; H, 4.8; N 6.8. $C_{24}H_{18}N_2Cl_2$ requires C, 71.1; H, 4.5; N, 6.9%); δH ($CDCl_3$) 8.47 (2H, d, $J_{3A,5A}$ 1.4 Hz, H^{3A}), 7.71 (4H, d, $J_{2B,3B}$ 8.8 Hz, H^{2B}), 7.48 (4H, d, $J_{2B,3B}$ 8.8 Hz, H^{3B}), 7.37 (2H, d, $J_{3A,5A}$ 1.4 Hz, H^{5A}), 2.78 (6H, s, CH_3); δC ($CDCl_3$) 159.0, 156.9, 148.7, 137.7, 135.4, 129.6, 128.9, 121.3, 116.8, 25.2; $\bar{\nu}_{max}$ (cm^{-1}) 1600s, 1547s, 1492 s, 1382m, 1093s, 1013m, 829s, 757m, 478m (KBr); *m/z* 404/406/408 (M^+), 369/371 (M–Cl), 202 (M^{2+}) (EI); λ_{max}, nm, ($CHCl_3$) 254 (ε, $M^{-1}\,cm^{-1}$, 51 900), 303 (17 000).

2.4. Synthesis of 4,4′-di(4-hydroxyphenyl)-6,6′-dimethyl-2,2′-bipyridine (*3*)

Concentrated hydrochloric acid (5.5 cm^3) was added with vigorous stirring to pyridine (6.0 cm^3) cooled to 0 °C. After the addition was complete, the mixture was heated and water distilled off until the internal temperature reached 200 °C ($\sim$3 cm^3 volume). The resultant pyridinium chloride was cooled to 140 °C and **1** (0.200 g, 0.50 mmol) was added in one portion. An immediate colour change to green occurred and heating to reflux was resumed for 4 h. The mixture was then allowed to cool to 100 °C, when water (100 cm^3) was added and the mixture stirred for 12 h at room temperature. The green precipitate that resulted was collected by filtration, washed well with water and chloroform and dried under vacuum to give **3** as a green powder (0.180 g, 97%) m.p. >270 °C (Anal. Found: C, 77.9; H, 5.8; N, 7.3. $C_{24}H_{20}N_2O_2$ requires C, 78.2; H, 5.5; N, 7.6%); δH (CD_3SOCD_3) 8.67 (2H, d, $J_{3A,5A}$ 1.4 Hz, H^{3A}), 8.03 (2H, d, $J_{3A,5A}$ 1.4 Hz, H^{5A}), 7.78 (4H, d, $J_{2B,3B}$ 8.8 Hz, H^{2B}), 6.98 (4H, d, $J_{2B,3B}$ 8.8 Hz, H^{3B}), 2.78 (6H, s, CH_3); δC (CD_3SOCD_3) 161.7, 152.5, 148.0, 146.3, 129.5, 127.1, 122.9, 120.0, 114.8, 55.5; $\bar{\nu}_{max}$ (cm^{-1}) 3145br, 1630m, 1587s, 1519s, 1477m, 1406m, 1278s, 1210s, 1184s, 1111w, 994w, 825s, 570m (KBr); *m/z* 369/371 (MH^+) (EI); λ_{max}, nm, (CD_3SOCD_3) 272 (ε, $M^{-1}\,cm^{-1}$, 26 500), 291 (26 700).

2.5. Synthesis of 4-methoxyphenylboronic acid

Magnesium turnings (1.20 g, 50 mmol) and a few grains of iodine were heated under argon with a heat gun until violet fumes were evolved. Diethyl ether (5 cm^3) was then added to the cooled flask and 9.6 cm^3 of a solution of freshly distilled 4-bromoanisole (9.40 g, 50 mmol) in diethyl ether (10 cm^3) was added. The reaction was initiated by warming gently, after which the remaining 4-bromoanisole solution was added dropwise at such a rate that gentle reflux was maintained. Finally, the mixture was warmed to 40 °C for 30 min after which the solution was transferred dropwise into a solution of $(^iPrO)_3B$ (7.70 g, 55 mmol, 8.3 cm^3) in THF

(30 cm^3) at −78 °C. After stirring for 30 min a white precipitate formed. The mixture was then stirred overnight and allowed to warm to room temperature after which hydrochloric acid (4 M, 20 cm^3) was added and the clear solution stirred for 1 h. The phases were separated and the organic phase extracted twice with 4:1 NH_4Cl (saturated aqueous solution): 4 M NaOH. The combined aqueous phases were acidified with hydrochloric acid (4 M) and extracted three times with EtOAc. The combined organic phases were then dried over $MgSO_4$ and the solvent was evaporated. The crude 4-methoxyphenylboronic acid was obtained as a light brown solid and was used without further purification (1.50 g, 20%) m.p. 106–108 °C (dec.); δH (CD_3OD) 8.17 (d, *J* 8.4 Hz, 2H, H^{2A}), 7.02 (d, *J* 8.4, 2H, H^{3A}), 3.88 (s, 3H, Me).

2.6. Synthesis of 4,4′-di(4-methoxyphenyl)-2,2′-bipyridine (*4*)

2.6.1. By Stille coupling

4-Bromoanisole (1.60 g, 8.5 mmol, 2.4 cm^3) was dissolved in THF (100 cm^3) and the solution cooled to −90 °C after which *n*-BuLi (5.5 cm^3, 8.8 mmol, 1.6 M in hexanes) was added dropwise and the mixture stirred at this temperature for 30 min. The solution was then allowed to warm to −70 °C and tri-*n*-butylchlorostannane (2.80 g, 8.5 mmol) in THF (20 cm^3) was added. The solution was then raised in temperature to −50 °C and stirred for 1 h after which it was allowed to warm to room temperature overnight. The solvent was then evaporated in vacuo and DMF (75 cm^3) added to the yellow oil containing 4-tri-*n*-butylstannylanisole; finally, 4,4′-dibromo-2,2′-bipyridine (1.30 g, 4.0 mmol) and $[Pd(PPh_3)_4]$ (0.30 g, 3 mol%) were added and the mixture stirred at 120 °C for 2 d. The solvent was then removed under high vacuum, the residue treated with H_2O:MeOH (1:1, 30 cm^3) and the off-white precipitate collected by filtration, washed with a small amount of cold MeOH and recrystallised from EtOH/$CHCl_3$ to give white needles of **4** (0.270 g, 18%) m.p. 205–207 °C.

2.6.2. By Suzuki coupling

4,4′-Dibromo-2,2′-bipyridine (0.60 g, 2.0 mmol) was dissolved in toluene (40 cm^3) and aqueous Na_2CO_3 solution (2 M, 25 cm^3) added. The biphasic mixture was purged with Ar and $[Pd(PPh_3)_4]$ (0.11 g, 5.0 mol%) was added under argon. Finally an Ar-purged solution of 4-methoxyphenylboronic acid (0.76 g, 5.0 mmol) in EtOH (20 cm^3) was added slowly and the mixture refluxed at 110 °C for 2 d. The resulting dark solution was diluted with water (30 cm^3) and toluene (30 cm^3); EtOH was removed in vacuo and the phases were separated. The aqueous phase was extracted twice with $CHCl_3$ (30 cm^3). The combined organic phases were washed with saturated aqueous sodium chloride solution twice, dried over $MgSO_4$ and the solvent removed in vacuo. The residue was recrystallised from EtOH/$CHCl_3$ to give a first crop of **4** as colourless needles (0.34 g). The mother liquor was chromatographed (SiO_2, hexanes:$CHCl_3$:MeOH saturated with ammonia, 10:5:1 R_f 0.51) to give another 0.21 g of **5** (0.550 g, 75%) m.p. 206–208 °C (Anal. Found: C, 77.25; H, 5.7; N, 7.5. $C_{24}H_{40}N_2O_2 \cdot 1/4H_2O$ requires C, 77.3; H, 5.5; N, 7.5%); δH ($CDCl_3$) 8.71 (d, *J* 5.2 Hz, 2H, H^{6A}), 8.69 (d, *J* 1.8 Hz, 2H, H^{3A}), 7.76 (d, *J* 8.9 Hz, 4H, H^{2B}), 7.53 (dd, *J* 5.2, 1.8 Hz, 2H, H^{5A}), 7.03 (d, *J* 8.9 Hz, 4H, H^{3B}), 3.89 (s, 6H, CH_3); δC ($CDCl_3$) 160.6, 156.7, 149.6, 148.8, 130.6, 128.4, 121.1, 118.5, 114.5, 55.4; *m/z* 369.4 (M^+) (ESMS); λ_{max}, nm, ($CHCl_3$) 237 (ε, $M^{-1}\,cm^{-1}$, 33 000), 264 (62 900), 284 (59 700); $\lambda_{emission}$, nm, (λ_{irrad} 284 nm, $CHCl_3$, 298 K) 365, 692; $\bar{\nu}_{max}$ (cm^{-1}) 1608m, 1592s, 1542m, 1515s, 1458s, 1446m, 1301m, 1285m, 1253s, 1186s, 1040m, 1019m, 826m, 574m (KBr).

2.7. Synthesis of 4,4′-di(4-hydroxyphenyl)-2,2′-bipyridine (*5*)

2.7.1. Method 1

Concentrated hydrochloric acid (5.5 cm^3) was added cautiously to vigorously stirred pyridine (6.0 cm^3) after which the mixture was heated until the internal temperature had reached 200 °C. The resultant pyridinium chloride was then cooled to 140 °C, **4** (0.180 g, 0.49 mmol) added and the temperature raised to 200 °C for 4 h, after which the reaction mixture was cooled to 100 °C and treated with H_2O (100 cm^3). After stirring overnight, the green solid precipitate was filtered off, washed well with water and dried in vacuo to give **5**. HCl (0.161 g, 97%) (Found: C, 67.1; H, 4.9; N, 7.5. $C_{22}H_{17}N_2O_2Cl \cdot H_2O$ requires C, 66.9; H, 4.85; N, 7.1%).

2.7.2. Method 2

A solution of **4** (0.400 g, 1.1 mmol) in $CHCl_3$ (30 cm^3) was cooled to 0 °C and treated with BBr_3 (1.2 cm^3, 1.0 M solution in CH_2Cl_2). The reaction mixture was then stirred overnight and allowed to warm to room temperature, after which H_2O (10 cm^3) was added and the precipitate filtered off, washed well with $CHCl_3$, H_2O, MeOH and dried in vacuo to give **5** (0.356 g, 96%) m.p. >270 °C. *m/z* 341 (M^+) (ESMS); $\bar{\nu}_{max}$ (cm^{-1}) 3144br, 3063w, 1631m, 1606s, 1586s, 1518m, 1476m, 1454w, 1404w, 1332w, 1276s, 1209s, 1185s, 823s, 662m, 502w (KBr); δ_H (CD_3SOCD_3) 10.40 (br s, 2H, OH), 8.97 (s, 2H, H^{3A}), 8.78 (d, *J* 6.0 Hz, 2H, H^{6A}), 8.08 (d, *J* 6.0 Hz, 2H, H^{5A}), 8.00 (d, *J* 8.4 Hz, 4H, H^{2B}), 7.01 (d, *J* 8.4 Hz, 4H, H^{3B}); δ_C (CD_3SOCD_3) 160.5, 152.3, 148.8, 146.6, 129.4, 125.6, 122.2, 119.3, 116.3; λ_{max}, nm, (CH_3SOCH_3) 254 (ε, $M^{-1}\,cm^{-1}$, 21 900), 272 (29 400), 294 (32 100).

2.8. Synthesis of the bisruthenated ligand **6** $[PF_6]_4$

The complex $[Ru(tpy)(Cltpy)][PF_6]_2$ (0.065 g, 0.073 mmol) was dissolved in MeCN (40 cm^3) and K_2CO_3 (0.400 g) and several crystals of NaI were added. The suspension was heated to 60 °C and a solution of **3** (0.013 g, 0.035 mmol) in CD_3SOCD_3 (4 cm^3) was added dropwise. After the addition was complete, the suspension was stirred at 80 °C for 24 h and the progress of the reaction monitored by TLC. The reaction mixture was then cooled and poured into water (100 cm^3) and $[NH_4][PF_6]$ added until there was no further precipitation. The crude red product was collected over Celite, washed well with water and dissolved in aqueous MeCN (MeCN:H_2O; 9:1). After evaporation of the solvent, the complex was purified by chromatography (SiO_2, MeCN–saturated aqueous KNO_3–H_2O 20:0.5:1). The product was collected as a band with $R_f = 0.23$ and treated with water (20 cm^3) and a small amount of $[NH_4][PF_6]$. The MeCN was removed in vacuo and the red solid product was collected over Celite. After washing with water the complex was redissolved in aqueous MeCN (MeCN:H_2O; 9:1), filtered and the solvent removed in vacuo to give a red solid that was dried under high vacuum (0.029 g, 40%) (Anal. Found: C 47.36, H 3.2, N 9.4. $C_{84}H_{60}N_{14}O_2Ru_2P_4F_{24}\cdot 2H_2O$ requires C, 47.7; H, 3.1; N, 9.3%); *m/z* 894.3 $(M-2PF_6)^{2+}$, 548.4 $(M-3PF_6)^{3+}$, 372.7 $(M-4PF_6)^{4+}$ (ESMS); δH (CD_3CN) 8.75 (d, *J* 8.1 Hz, 4H, H^{3F}), 8.64 (d, *J* 1.2 Hz, 2H, H^{5A}), 8.50 (d, *J* 8.0 Hz, 4H, H^{3E}), 8.42 (s, 4H, H^{3C}), 8.40 (d, *J* 8.2 Hz, 4H, H^{3D}), 8.38 (t, *J* 8.1 Hz, 2H, H^{4F}), 8.13 (d, *J* 8.8 Hz, 4H, H^{2B}), 7.92 (ddd, *J* 15.7, 7.8, 1.5 Hz, 4H, H^{4E}), 7.86 (ddd, *J* 15.7, 7.8, 1.5 Hz, 4H, H^{4D}), 7.74 (d, *J* 1.2 Hz, 2H, H^{3A}), 7.65 (d, *J* 8.8 Hz, 4H, H^{3B}), 7.47 (d, *J* 4.9 Hz, 4H, H^{6E}), 7.32 (d, *J* 4.9 Hz, 4H, H^{6D}), 7.21 (ddd, *J*13.2, 5.6, 1.3 Hz, 4H, H^{5E}), 7.13 (ddd, *J* 13.2, 5.6, 1.3 Hz, 4H, H^{5D}), 2.83 (s, 6H, CH_3); λ_{max}, nm, (MeCN) 272 (ε, $M^{-1}\,cm^{-1}$, 69 900), 305 (85 300), 480 (20 000); $\bar{\nu}_{max}$, cm^{-1}, 1600m, 1508w, 1465w, 1449w, 1434w, 1405m, 1384s, 1286w, 1227m, 1189w, 841s, 788w, 767w, 588m (KBr).

2.9. Synthesis of $[Cu(\mathbf{1})_2][PF_6]$

A solution of $[Cu(MeCN)_4][PF_6]$ (0.019 g, 0.05 mmol) in EtOH (10 cm^3) was added dropwise to a solution of **1** (0.040 g, 0.10 mmol) in EtOH (40 cm^3) and the mixture stirred for 2 h at room temperature after which H_2O (50 cm^3) was added and the organic solvent removed in vacuo. The precipitate was collected over Celite, washed with water and redissolved in MeCN and purified by recrystallisation from acetone/ether to give dark red crystals of $[Cu(\mathbf{1})_2][PF_6]$ (0.0342 g, 66%) (Anal. Found: C, 61.85; H, 3.2; N 9.4. $C_{52}H_{48}N_4O_4CuPF_6\cdot 1/2H_2O$ requires C, 61.8; H, 4.9; N, 5.5%); δH (CD_3CN) 8.64 (s, 4H, H^{3A}), 7.95 (d, *J* 8.9, 8H, H^{2B}), 7.78 (s, 4H, H^{5A}), 7.14 (d, *J* 8.9, 8H, H^{3B}), 3.90 (s, 12H, OCH_3), 2.12 (s, 12H, CH_3); *m/z* 855 ($M-PF_6$), 397 (I) (ESMS); λ_{max}, nm, (MeCN) 210 (ε, $M^{-1}\,cm^{-1}$, 61 800), 280 (90 700), 482 (9600); $\lambda_{emission}$, nm, (λ_{irrad} 482 nm, MeCN, 298 K) 619; $\bar{\nu}_{max}$ (cm^{-1}) 1603 s, 1580w, 1544m, 1519s, 1460w, 1439w, 1394w, 1254s, 1293m, 1182s, 1030m, 844w, 829s, 584w, 557m (KBr).

2.10. Synthesis of $[Ag(\mathbf{1})_2][PF_6]$

A solution of $Ag[BF_4]$ (0.010 g, 0.05 mmol) in EtOH (10 cm^3) was added dropwise to a solution of I (0.040 g, 0.10 mmol) in EtOH (40 cm^3) and the mixture stirred for 2 h at room temperature after which H_2O (50 cm^3) and ammonium hexafluorophosphate were added and the organic solvent removed in vacuo. The precipitate was collected over Celite, washed with water and redissolved in acetone and purified by recrystallisation from acetone/ether to give orange yellow cubes of $[Ag(\mathbf{1})_2][PF_6]$ (0.0393 g, 75%) (Anal. Found: C, 59.2; H, 4.8; N 5.3. $C_{52}H_{48}N_4O_4AgPF_6$ 1/2H_2O requires C, 59.2; H, 4.7; N, 5.3%); δH (CD_3CN) 8.42 (s, 4H, H^{3A}), 7.84 (d, *J* 8.9, 8H, H^{2B}), 7.69 (s, 4H, H^{5A}), 7.07 (d, *J* 8.9, 8H, H^{3B}), 3.85 (s, 12H, OCH_3), 2.55 (s, 12H, CH_3); *m/z* 901 ($M-PF_6$); λ_{max}, nm, (MeCN) 268 (ε, $M^{-1}\,cm^{-1}$, 85 100), 283 (83 100); $\lambda_{emission}$, nm, (λ_{irrad} 283 nm, MeCN, 298 K) 381; $\bar{\nu}_{max}$ (cm^{-1}) 2956w, 2934w, 2911w, 2838w, 1600s, 1548s, 1515s, 1461s, 1439w, 1395w, 1292s, 1252s, 1220m, 1181s, 1031s, 840s, 578m, 558m (KBr).

2.11. Synthesis of $[Ru(bpy)_2(\mathbf{L})][PF_6]_2$ (**L** = **1**,**2** or **3**)

2.11.1. Method 1, thermal

A suspension of $[Ru(bpy)_2Cl_2]$ (0.048 g, 0.10 mmol) and the appropriate ligand (0.10 mmol) in 1,2-ethanediol (40 cm^3) was treated with *N*-ethylmorpholine (1 drop) and the mixture stirred at 110 °C for 24 h, after which the red solution was treated with water (120 cm^3). The solution was then filtered to remove any particulate matter and then treated with ammonium hexafluorophosphate to give a red precipitate. This precipitate was collected over Celite, washed well with water and then dissolved in acetonitrile and purified by chromatography over silica gel using MeCN–saturated aqueous KNO_3 solution–water 20:0.5:1 as the mobile phase. In each case, the major red fraction was collected and the product precipitated with ammonium hexafluorophosphate. Recrystallisation from acetonitrile or acetonitrile-diethyl ether yielded the desired compounds as analytically pure red solids.

2.11.2. Method 2, microwave

A suspension of $[Ru(bpy)_2Cl_2]$ (0.048 g, 0.10 mmol) and the appropriate ligand heated to reflux for 6 min in a modified domestic microwave oven. After this period, the reaction mixture was worked up as described above.

*2.11.3. [Ru(bpy)$_2$(**1**)][PF$_6$]$_2$*

Yield: thermal, 0.020 g, 17%; microwave, 0.068 g 60%. (Anal. Found: C 48.75, H 4.1, N 7.3. $C_{46}H_{40}N_6O_2RuP_2F_{12}\cdot 2H_2O$ requires C, 48.7; H, 3.9; N, 7.4%); *m/z* 956 $(M-PF_6)^+$ (MALDI TOF); δH (CD_3CN) 8.64 (d, *J* 1.2 Hz, 2H, H^{3A}), 8.51 (dd, *J* 8.0, 1.4 Hz, 2H, H^{3LA}), 8.43 (dd, *J* 8.0, 1.4 Hz, 2H, H^{3LB}), 8.10 (dt, *J* 8.0, 1.4 Hz, 2H, H^{4LA}), 8.05 (dd, *J* 5.6, 1.3 Hz, 2H, H^{6LA}), 7.95 (dt, *J* 8.0, 1.4 Hz, 2H, H^{4LB}), 7.93 (d, *J* 8.8 Hz, 4H, H^{2B}), 7.65 (dd, *J* 5.6, 1.3 Hz, 2H, H^{6LB}), 7.58 (d, *J* 1.2 Hz, 2H, H^{5B}), 7.49 (ddd, *J* 8.0, 5.6, 1.4 Hz, 2H, H^{5LA}), 7.23 (ddd, *J* 8.0, 5.6, 1.4 Hz, 2H, H^{5LB}), 7.13 (d, *J* 8.8 Hz, 4H, H^{3B}), 3.87 (s, 6H, OCH_3), 1.71 (s, 6H, CH_3); λ_{max}, nm, (MeCN) 242 (ε, $M^{-1}\,cm^{-1}$, 29,300), 252 (25,600), 282 (85,000) 424 (13,900); $\bar{\nu}_{max}$ (cm^{-1}) 1605m, 1517w, 1466w, 1447w, 1253w, 1227m, 1183w, 842s, 764m, 558m (KBr); $E_{1/2}$+1.06 (V versus ferrocene/ferrocenium, MeCN, cyclic voltammetry), −1.75, −1.96, −2.17).

*2.11.4. [Ru(bpy)$_2$(**2**)][PF$_6$]$_2$*

Yield: thermal, 0.020 g, 18%; microwave, 0.060 g 52%. (Anal. Found: C 44.2, H 3.4, N 8.35. $C_{44}H_{34}N_6Cl_2RuP_2F_{12}\cdot KNO_3$ requires C, 43.7; H, 2.8; N, 8.10%); *m/z* 967 $(M-PF_6)^+$ (MALDI TOF); δH (CD_3CN) 8.66 (d, *J* 1.2 Hz, 2H, H^{3A}), 8.52 (dd, *J* 8.0, 1.4 Hz, 2H, H^{3LA}), 8.43 (dd, *J* 8.0, 1.4 Hz, 2H, H^{3LB}), 8.11 (dt, *J* 8.0, 1.4 Hz, 2H, H^{4LA}), 8.03 (dd, *J* 5.6, 1.3 Hz, 2H, H^{6LA}), 7.97 (dt, *J* 8.0, 1.4 Hz, 2H, H^{4LB}), 7.92 (d, *J* 8.8 Hz, 4H, H^{2B}), 7.65 (dd, *J* 5.6, 1.3 Hz, 2H, H^{6LB}), 7.64 (d, *J* 1.2 Hz, 2H, H^{5B}), 7.63 (d, *J* 8.8 Hz, 4H, H^{3B}), 7.49 (ddd, *J* 8.0, 5.6, 1.4 Hz, 2H, H^{5LA}), 7.25 (ddd, *J* 8.0, 5.6, 1.4 Hz, 2H, H^{5LB}), 1.71 (s, 6H, CH_3); λ_{max}, nm, (MeCN) 252 (ε, $M^{-1}\,cm^{-1}$, 85,300), 283 (97,100) 427 (12,300); $\bar{\nu}_{max}$ (cm^{-1}) 1606w, 1468w, 1449m, 1428w, 840s, 763m, 731w, 558m (KBr); $E_{1/2}$+1.05 (V versus ferrocene/ferrocenium, MeCN, cyclic voltammetry), −2.08, −2.27, −2.69).

*2.11.5. [Ru(bpy)$_2$(**3**)][PF$_6$]$_2$*

Yield: thermal, 0.015 g, 14%; microwave, 0.047 g 44%. (Anal. Found: C 45.9, H 4.0, N 8.6. $C_{44}H_{36}N_6O_2RuP_2F_{12}\cdot KNO_3$ requires C, 45.1; H, 3.1; N, 8.3%); *m/z* 967 $(M-PF_6)^+$ (MALDI TOF); δH (CD_3CN) 8.59 (d, *J* 1.2 Hz, 2H, H^{3A}), 8.51 (dd, *J* 8.0, 1.4 Hz, 2H, H^{3LA}), 8.43 (dd, *J* 8.0, 1.4 Hz, 2H, H^{3LB}), 8.08 (dt, *J* 8.0, 1.4 Hz, 2H, H^{4LA}), 8.03 (dd, *J* 5.6, 1.3 Hz, 2H, H^{6LA}), 7.94 (dt, *J* 8.0, 1.4 Hz, 2H, H^{4LB}), 7.81 (d, *J* 8.8 Hz, 4H, H^{2B}), 7.63 (d, *J* 8.8 Hz, 4H, H^{3B}), 7.54 (d, *J* 1.2 Hz, 2H, H^{5B}), 7.46 (ddd, *J* 8.0, 5.6, 1.4 Hz, 2H, H^{5LA}), 7.21 (ddd, *J* 8.0, 5.6, 1.4 Hz, 2H, H^{5LB}), 6.98 (dd, *J* 5.6, 1.3 Hz, 2H, H^{6LB}), 1.67 (s, 6H, CH_3); λ_{max}, nm, (MeCN) 256 (ε, $M^{-1}\,cm^{-1}$, 29,600), 289 (56,400) 428 (8,000); $\bar{\nu}_{max}$ (cm^{-1}) 3433 s br, 1608s, 1543w, 1520m, 1464w, 1446m, 1385m, 1277w, 1221w, 1180w, 842s, 764m, 733w, 558m (KBr); $E_{1/2}$+0.96 (V versus ferrocene/ferrocenium, MeCN, cyclic voltammetry), −1.92, −2.01, −2.26).

2.12. Crystal structure determinations

The structures were solved and refined by direct methods using standard techniques as indicated in Table 1 using the programmes CRYSTALS [31], SHELXS-86 [32],

Table 1
Crystal data for **1**, **4**, [Ag(**1**)$_2$][PF$_6$], [Ag(**1**)(MeCN)][BF$_4$]·MeCN and [Ru(bpy)$_2$(**2**)][PF$_6$]$_2$·3MeCN·0.5H$_2$O

Compound	**1**	**4**	[Ag(**1**)$_2$][PF$_6$]	[Ag(**1**)(MeCN)][BF$_4$]·MeCN	[Ru(bpy)$_2$(**2**)][PF$_6$]$_2$·3MeCN·0.5H$_2$O
Formula	$C_{26}H_{24}N_2O_2$	$C_{24}H_{10}N_2O_2$	$C_{52}H_{48}AgN_4O_4PF_6$	$C_{60}H_{60}Ag_2B_2F_8N_8O_4$	$C_{50}H_{44}RuN_9Cl_2P_2F_{12}O_{0.5}$
M (g mol^{-1})	396.49	368.44	1045.81	1346.52	1240.88
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$
μ (mm^{-1})	0.60	0.64	0.51	0.748	0.52
Final *R* (observed)	0.0491	0.0494	0.0485	0.0429	0.0944
Final R_w (observed)	0.0659	0.0658	0.0446	0.1129	0.0831
a (Å)	9.542(1)	10.896(2)	17.118(4)	13.934(4)	20.9764(8)
b (Å)	10.401(1)	5.382(1)	14.778(3)	7.9270(10)	12.3992(6)
c (Å)	11.772(1)	15.927(2)	19.621(6)	27.179(8)	21.939(1)
α (°)	98.451(8)	90	90	90	90
β (°)	103.156(8)	19.18(1)	98.37(4)	102.60(3)	105.138(3)
γ (°)	109.633(8)	90	90	90	90
V (Å$^{3)}$	1039.3(2)	922.1(3)	4911.0(9)	2929.8(13)	5508.22
T (K)	293	293	293	190(1)	193(1)
Z	2	2	4	2	4
F(0 0 0)	420	388	2144	1368	2508
No. reflections	4176	1834	9355	14776	209927
No. independent reflections	3918	1661	8938	6178	19579
No. observed reflections	3506	1453	5431	5231	11783
	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$

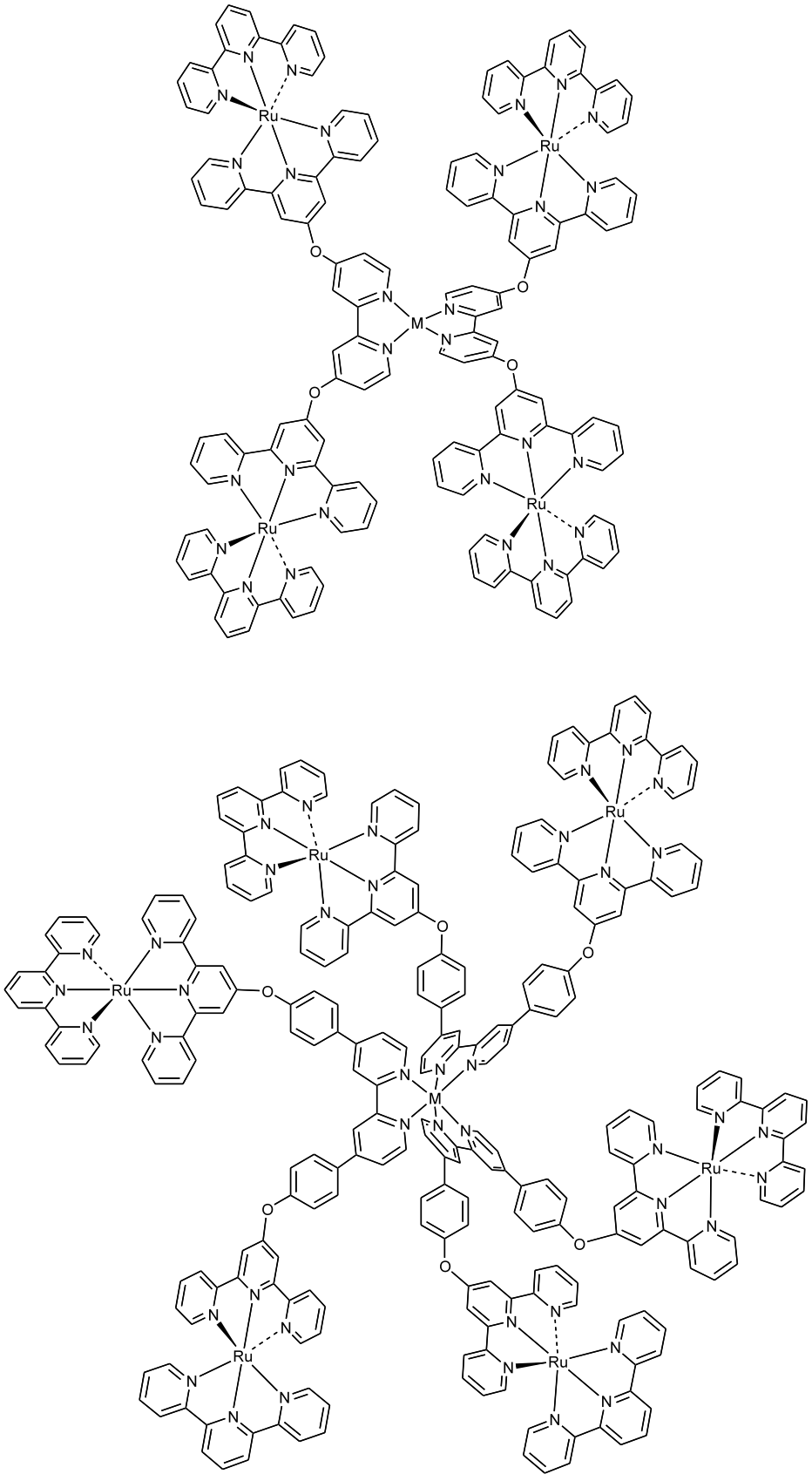


Fig. 1. Pentanuclear and heptanuclear metallostars based upon $\{M(bpy)_2\}$ and $\{M(bpy)_3\}$ core motifs.

SHELXS-93 [33] and SHELXS-97 [34]. Diagrams and supplementary material were prepared using the above programmes together with ORTEP-3 for Windows [35], PLATON [36], and CAMERON [37].

3. Results and discussion

3.1. Strategy

We have previously reported the preparation of a series of 1,6-diarylhexa-1,5-diene-3,4-diones from the condensation of butane-2,3-dione with 4-substituted benzaldehydes and their subsequent conversion to 4′,4″-diaryl-2,2′:6′,2″:6″,2‴-quaterpyridines [38]. We have now used these precursor compounds to prepare 4,4′-diaryl-2,2′-bipyridines in which the aryl substituents bear substituents which can be used in subsequent chemical manipulation. Specifically, we have prepared compounds with 4-chlorophenyl and 4-hydroxyphenyl substituents as representative electrophilic and nucleophilic substituents. Although fully aware that halobenzene derivatives are normally inactive as electrophiles in reactions with simple nucleophiles, we hoped that the inductive effects associated with the coordination of a metal ion to the bpy domain would be transmitted to the 4-chlorophenyl substituents, leading to activation in the same way that reactions of 4-halopyridines with nucleophiles are dramatically enhanced upon coordination [39,40]. In the case of ligand **2**, this hope has proved unfounded and in no case have we observed any activation towards nucleophilic attack upon coordination. The 4-hydroxyphenyl substituents provide an alternative approach in which reaction with electrophiles will allow subsequent structural development. In either case, the aim was the synthesis of a bis(ruthenated) ligands which could be used for the convergent assembly of pentanuclear or heptanuclear metallostars based upon $\{M(bpy)_2\}$ or $\{M(bpy)_3\}$ core motifs (Fig. 1). The bpy metal-binding domain can be optimised for the formation of complexes with metal ions possessing either tetrahedral or octahedral coordination preferences by the introduction of substituents at the 6 and 6′-positions [41]. These metallostars would differ from our prototype systems by the presence of a hydrolytically stable C–C bond linking the aryl ring to the bpy domain, in contrast to the benzyl ethers introduced in our earlier work [23].

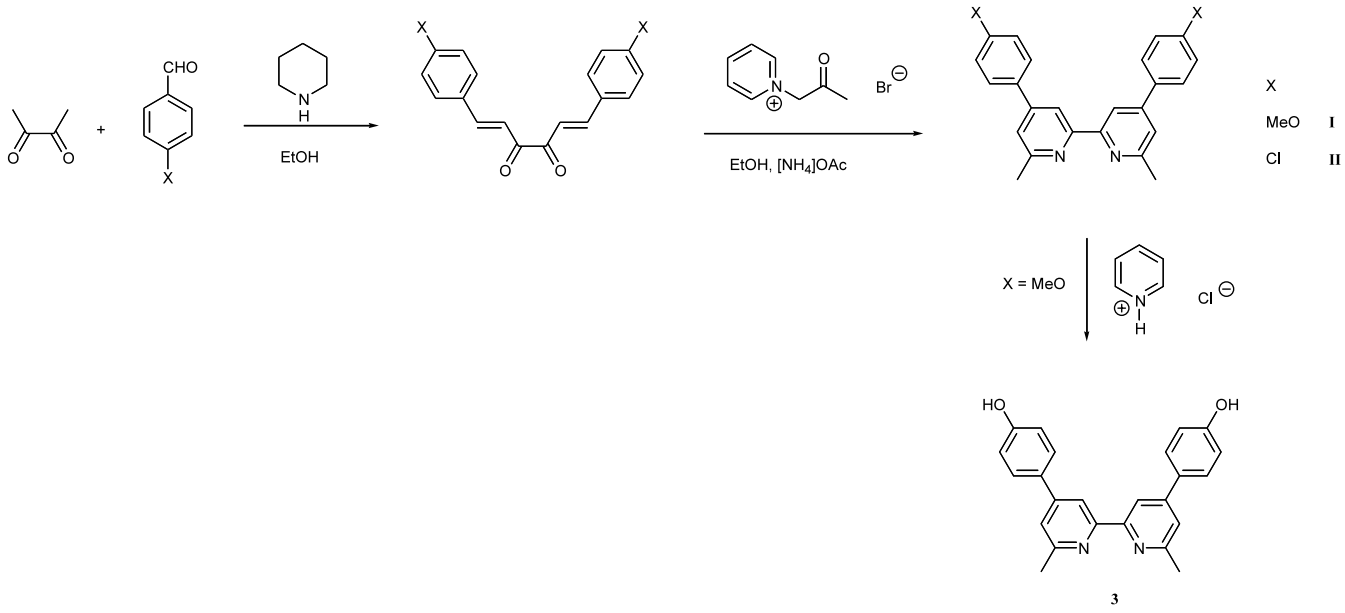
3.2. Ligand synthesis-6,6′-dimethyl-4,4′-diaryl-2,2′-bipyridine metal-binding domains

The introduction of methyl substituents into the 6 and 6′-positions of a bpy ligand stabilises complexes with tetrahedral centres such as copper(I) and silver(I) and destabilises *tris* complexes with metals adopting an octahedral coordination geometry. The compounds 1,6-bis(4-methoxyphenyl)-hexa-1,5-diene-3,4-dione and 1,6-bis(4-chlorophenyl)-hexa-1,5-diene-3,4-dione were prepared as orange solids from the reaction of butane-2,3-dione with 4-methoxybenzaldehyde or 4-chlorobenzaldehyde respectively in the presence of piperidine [38]. Subsequent Krohnke reaction [42] of these 1,6-diarylhexa-1,5-diene-3,4-diones with 1-pyridiniopropan-2-one bromide (acetonylpyridinium bromide prepared by the reaction of bromoacetone with pyridine [27]) and ammonium acetate in ethanol gave the desired ligands 4,4′-di(4-methoxyphenyl)-6,6′-dimethyl-2,2′-bipyridine **1** and 4,4′-di(4-chlorophenyl)-6,6′-dimethyl-2,2′-bipyridine **2** as colourless needles in 35–50% yield. The compounds were fully characterised and exhibited the expected spectroscopic properties (see Section 2). The ligand 4,4′-di(4-hydroxyphenyl)-6,6′-dimethyl-2,2′-bipyridine **3** was prepared as a green solid in near-quantitative yield by the demethylation of **1** by heating with molten pyridinium chloride at 140 °C [43,44]. Once again, the new ligand **3** was fully characterised. The synthetic routes to ligands **1**, **2** and **3** are summarised in Scheme 1.

3.3. Ligand synthesis-4,4′-diaryl-2,2′-bipyridine metal-binding domains

Building upon our preliminary studies with the 6,6′-dimethyl substituted systems, we concentrated upon the preparation of nucleophilic ligands bearing 4-hydroxyphenyl substituents. We investigated a number of routes for the preparation of the nucleophilic ligand **5**, all of which involved the deprotection of the methoxy compound **4** in the last reaction step. The bisenones are not useful intermediates for the synthesis of 2,2′-bipyridines with only hydrogen substituents at the 6- and 6′-positions. Initially we attempted to prepare **4** by Stille coupling which is a powerful method for the preparation of heteroaryls [45] and we selected 4,4′-dibromo-2,2′-bipyridine, which is readily prepared in a four-step procedure from 2,2′-bipyridine [46], as the key synthetic intermediate. Lithiation of 4-bromoanisole with *n*-BuLi in THF followed by reaction with tri-*n*-butylchlorotin gave a solution containing 4-tri-*n*-butylstannylanisole. The solvent was removed and the crude stannyl compound dissolved in DMF and reacted directly with 4,4′-dibromo-2,2′-bipyridine in the presence of $[Pd(PPh_3)_4]$. After work-up, the desired ligand **4** was obtained in 18% yield. The low yield was disappointing, and quenching experiments indicated that the difficulty arose from side-reactions involving the 4-lithioanisole [47].

We finally adopted a method for the synthesis of **4** based upon the Suzuki coupling [48] of 4-methoxyphenylboronic acid with 4,4′-dibromo-2,2′-bipyridine. Commercially available 4-bromoanisole was converted



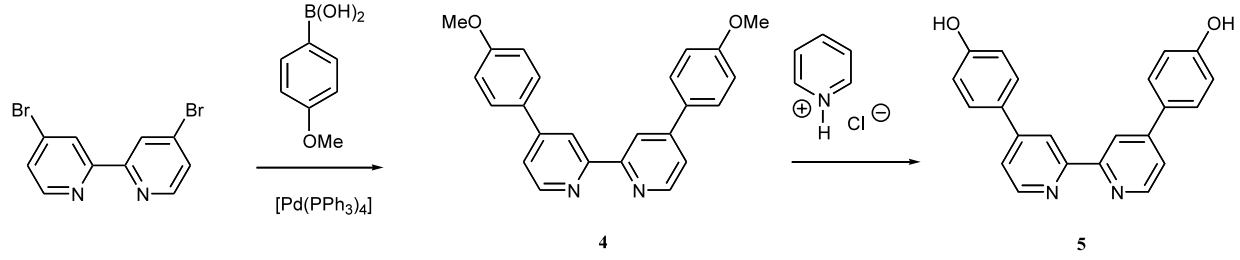
Scheme 1.

to 4-methoxyphenylboronic acid by reaction with magnesium to give a Grignard reagent followed by treatment with tri(isopropyl)borate and subsequent hydrolysis [49]. Initial attempts to conduct Suzuki reactions of 4-methoxyphenylboronic acid with the more readily available 4,4′-dichloro-2,2′-bipyridine gave only very low yields of **4** and resulted in the formation of significant amounts of the monofunctionalised product 4-chloro-4′-(4-methoxyphenyl)-2,2′-bipyridine. Accordingly, we returned to the more activated compound 4,4′-dibromo-2,2′-bipyridine. The reaction of 4,4′-dibromo-2,2′-bipyridine with 4-methoxyphenylboronic acid proceeded smoothly in a biphasic toluene-aqueous sodium carbonate medium in the presence of $[Pd(PPh_3)_4]$ to give **4** as colourless needles in 75% overall yield. The compound was fully characterised and its properties generally resembled those of **1**, although there is a blue-shifting of the maxima in the electronic absorption spectra of ≈ 6 nm between **1** and **4**.

Two methods were investigated for the demethylation of **4** to give **5**. Initially, we used molten pyridinium chloride, which has proved to be effective for the conversion of a number of methoxy oligopyridine derivatives to hydroxy analogs including that of **1** to **3** above and obtained **5** in 97% yield (Scheme 2). For convenience, we later adopted a milder method of deprotection involving treatment with BBr_3 in $CHCl_3$ [43,50] at 0 °C which gave **5** in 96% yield.

3.4. Solid state structures of *1* and *4*

In order to obtain metrical data for subsequent use in modelling and to quantify the effects of introducing the methyl substituents into the 6,6′-positions, we have determined the solid state structure of the ligands **1** and **4**. The solid state structure of **1** is shown in Fig. 2. The bpy domain adopts the expected *trans* conformation and is essentially planar with an angle of 1.15° between the least squares planes of the two rings. The 4-methoxyphenyl substituents are crystallographically independent and are twisted with respect to the directly bonded pyridine ring (least squares planes, 29.52°, 38.81°). The carbon and oxygen atoms of the methoxy groups lie close to the plane of the directly bonded phenyl ring (torsion angles 0.8°–1.8°). Adjacent bpy domains are parallel and stacked with a shortest interplanar distance of 3.5 Å.



Scheme 2.

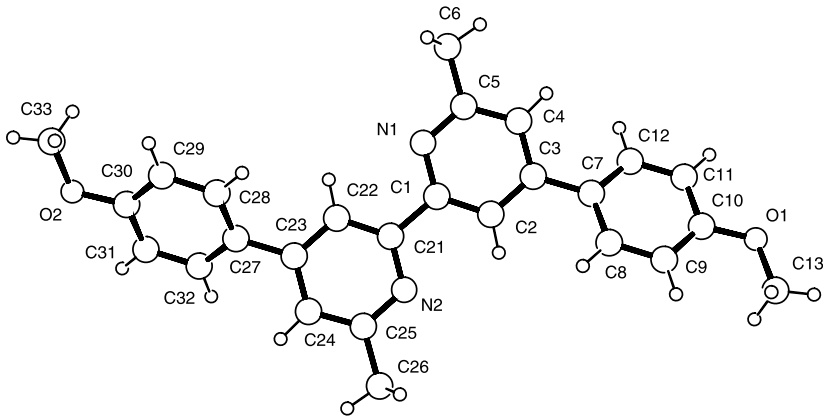


Fig. 2. Molecular structure of **1** showing the numbering scheme adopted. Selected bond lengths (Å) and angles (°): N1–C1 1.346(1); N1–C5 1.337(2); N2–C21 1.346(2); N2–C25 1.341(2); C5–C6 1.505(2); C25–C26 1.503(2); C30–O2 1.369(1); O2–C33 1.414(2); C1–N1–C5 117.4(1); C21–N2–C25 117.6(1); C30–O2–C33 118.0(1); N1–C5–C6. 116.6(1); N2–C25–C26. 116.5(1).

The molecular structure of **4** closely resembles that of **1** with the pyridine rings adopting a *trans* conformation. The phenyl rings and the directly bonded pyridine ring are near coplanar with an interplanar angle of 4.60° in marked contrast to the significantly greater angles in **1**. The carbon and oxygen atoms of the methoxy groups lie close to the plane of the directly bonded phenyl ring with a torsion angle of 2.0°. In the lattice, there are stacking interactions with ≈3.5 Å distances between parallel planes (Fig. 3).

3.5. Coordination chemistry of *1* with copper(I) and silver(I)

As mentioned in Section 3.2, ligand **1** is expected to form stable 2:1 complexes with copper(I) and silver(I) whereas **4** will form 3:1 complexes with octahedral metal centres. The reaction of **1** with $[Cu(MeCN)_4][PF_6]$ or $Ag[BF_4]$ in ethanol gave solutions from which the 2:1 complexes $[M(\mathbf{1})_2][PF_6]$ could be isolated by the addition of ammonium hexafluorophosphate. The ^1H NMR spectra of CD_3CN solutions of the complexes exhibited four aromatic and two methyl resonances indicating that on the NMR time-scale the two ligands are equivalent and that the ligands remain symmetrical about the interannular C–C bond. The red copper(I) complex exhibits an MLCT absorption at 482 nm with an associated emission at 619 nm which are typical for copper(I) bis(diimine) chromophores and lumophores [51–55].

Good quality pale orange crystals of $[Ag(\mathbf{1})_2][PF_6]$ were obtained by the slow diffusion of diethyl ether vapour into an acetone solution of the complex and the X-ray solid state structure was determined. The structure of the $[Ag(\mathbf{1})_2]^+$ cation present in $[Ag(\mathbf{1})_2][PF_6]$ is shown in Fig. 4. The silver is in a very irregular four coordinate environment in which it is bonded to the four nitrogen donors of the two ligands. The distortion from a regular tetrahedral geometry is illustrated in Fig. 5. The four Ag–N bonds vary considerably and lie in the range 2.259(3)–2.372(4) Å although the bite angles of 71.8(1)° and 71.3(1)° are typical. The two ligands are not orthogonal but make least squares planes angles of 78.8° with each other. The distortion from a tetrahedral geometry is significant but is in accord with that observed in other copper(I) and silver(I) bis(2,2′-bipyridine) and bis(1,10-phenanthroline) complexes [56,57]. The only other close contact to the silver centre is the oxygen atom of a methoxy group from an adjacent cation which shows an O···Ag contact of 4.114 Å; this

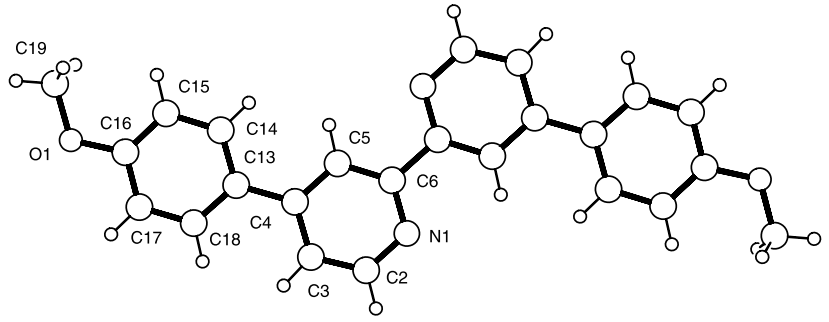


Fig. 3. Molecular structure of **4** showing the numbering scheme adopted. Selected bond lengths (Å) and angles (°): N1–C2 1.332(2); N1–C6 1.339(2); O1–C16 1.365(2); O1–C19 1.423(2); C2–N1–C6 116.5(1); C16–O1–C19 117.4(1).

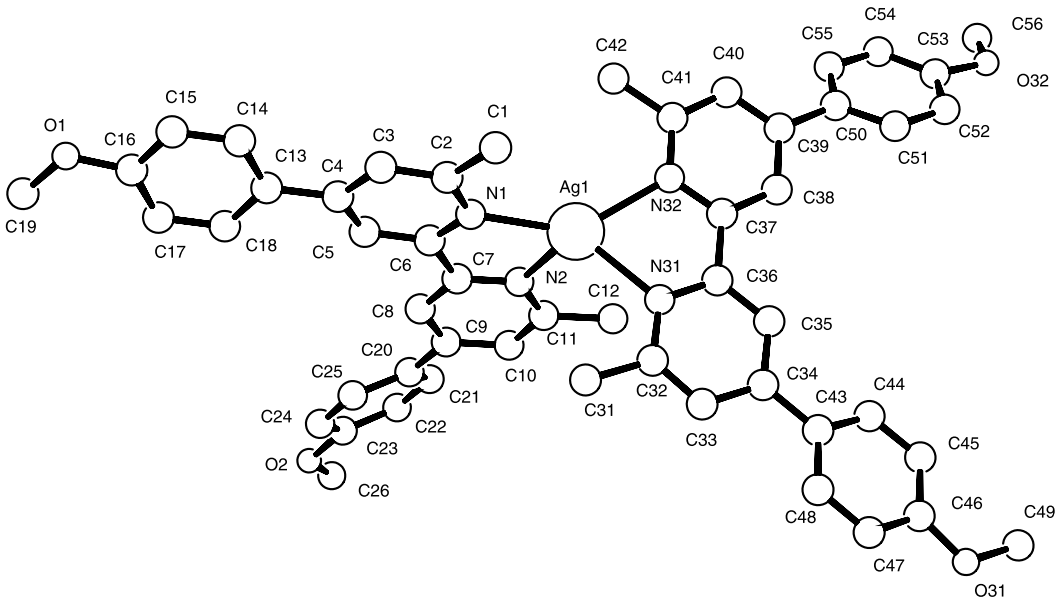


Fig. 4. Molecular structure of the $[Ag(\mathbf{1})_2]^+$ cation present in $[Ag(\mathbf{1})_2][PF_6]$ showing the numbering scheme adopted. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1–N1 2.259(3); Ag1–N2 2.372(4); Ag1–N31 2.321(3); Ag1–N32 2.301(3); N1–C2 1.347(5); N1–C6 1.349(5); N2–C7 1.341(4); N2–C11 1.351(5); N31–C32 1.333(6); N31–C36 1.340(5); N32–C37 1.347(5); N32–C41 1.336(6); O1–C16 1.372(4); O1–C19 1.412(6); O2–C23 1.369(7); O2–C26 1.369(9); O31–C46 1.374(6); O31–C49 1.405(8); O32–C53 1.376(5); O32–C56 1.405(8); N1–Ag1–N2 71.8(1); N1–Ag1–N31 142.8(1); N2–Ag1–N31 105.9(1); N1–Ag1–N32 141.4(1); N2–Ag1–N32 125.6(1); N31–Ag1–N32 71.3(1); C16–O1–C19 117.9(4); C23–O2–C26 119.5(6); C46–O31–C49 117.7(5); C53–O32–C56 117.2(5).

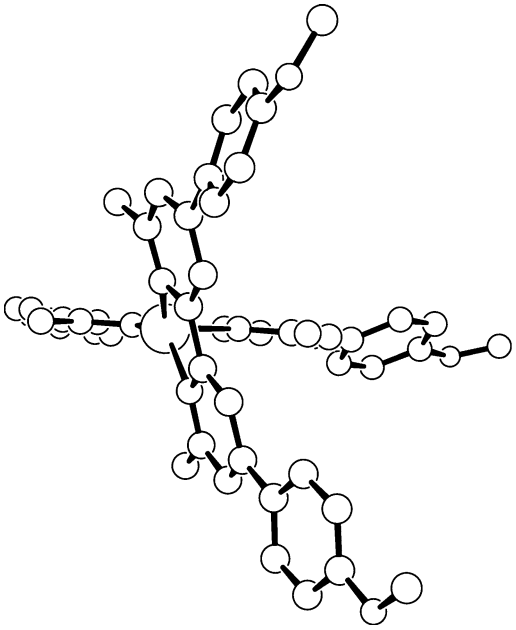


Fig. 5. A representation of the structure of the $[Ag(\mathbf{1})_2]^+$ cation showing the distortion from ideal D_{2d} symmetry.

methoxyphenyl group is stacked with one of the ligands coordinated to the silver. The silver atom is effectively encapsulated by the 6,6′-methyl substituents of the **1** ligands and although the coordination geometry is very irregular, there is little opportunity for the silver to increase its coordination number. The distortion from ideal D_{2d} symmetry in copper(I) bis(diimine) complexes has been discussed and paramaterised but in our case the deviation from ideality is so great that the Dobson angle is not a particularly useful parameter [58]. The starting point for a description of the geometry is a trigonal plane described by N1, N31 and N32 (sum of the three N–Ag–N angles, 355.4°) with the remaining N2 occupying an off-axis axial site. The Ag1–N2 distance of 2.372(4) Å is the longest of the silver–nitrogen distances. The bpy metal-binding domains are approximately planar (torsion angles 2.57° and 3.13°) but each ligand shows a small torsion angle (11.94°, 16.92°) to one methoxyphenyl substituent and a larger one (31.62°, 33.87°) to the other. The short Ag···O distance of 4.114 Å is to the methoxyphenyl substituents with the greatest twisting with respect to the pyridine ring. As with the free ligands, the carbon and oxygen atoms of the methoxy groups lie within the plane of the attached phenyl ring.

In the course of our studies on the silver complex, we also prepared the tetrafluoroborate salt $[Ag(\mathbf{1})_2][BF_4]$ and slow recrystallisation from acetonitrile by the diffusion of diethyl ether vapour into the solution gave a new compound $[Ag(\mathbf{1})(MeCN)][BF_4]\cdot MeCN$. We have observed the displacement of bpy metal-binding domains by acetonitrile in our earlier studies of silver(I) 2,2′:6′,2″-quaterpyridine complexes [59–62] and on the basis of these we anticipated a three coordinate silver complex. In order to confirm this proposal and to investigate any silver–silver interactions we have also determined the X-ray structure of $[Ag(\mathbf{1})(MeCN)][BF_4]\cdot$

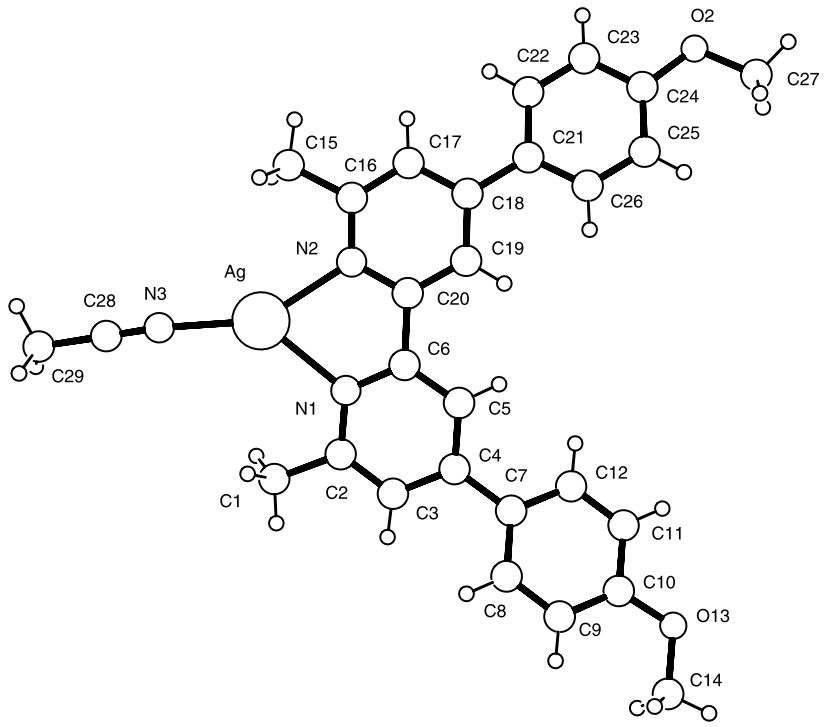


Fig. 6. Molecular structure of the $[Ag(\mathbf{1})(MeCN)]^+$ cation present in $[Ag(\mathbf{1})(MeCN)][BF_4]$ showing the numbering scheme adopted. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag–N3 2.121(2); Ag–N2 2.259(2); Ag–N1 2.296(2); C10–O13 1.356(3); O13–C14 1.423(4); O2–C27 1.417(4); C24–O2 1.365(3); N1–C6 1.349(3); N1–C2 1.350(3); N2–C16 1.341(4); N2–C20 1.343(3); N3–C28 1.131(3); N3–Ag–N2 150.64(9); N3–Ag–N1 136.73(9); N2–Ag–N1 72.49(8); C6–N1–C2 118.8(2); C16–N2–C20 119.0(2); C24–O2–C27 118.1(2); N3–C28–C29 179.7(4); C10–O13–C14 117.0(2).

MeCN. The structure of the $[Ag(\mathbf{1})(MeCN)]^+$ cation is presented in Fig. 6. The silver is three-coordinate and bonded to the two nitrogen donors of **1** and the nitrogen of an acetonitrile ligand. The remaining acetonitrile is found as a solvent molecule in the lattice with no interaction with silver. The bite angle N1–Ag1–N2 is 72.49(8)° and the remaining angles in the coordination sphere are 136.73(9)° (N1–Ag1–N3) and 150.64(9)° (N2–Ag1–N3); the sum of these three angles is 359.86° indicating that the compound is correctly described as trigonal planar. The planes of the methoxyphenyl substituents make torsions of 6° and 24° with the directly bonded pyridine rings and the bpy domain shows a small torsion of 2° between the two pyridine rings. The silver–nitrogen distances are typical (Ag1–N1 2.296(2) Å, Ag1–N2 2.259(2) Å, Ag1–N3 2.121(2) Å. The shortest Ag···Ag contact between adjacent molecules is 4.876 Å and so there are no significant silver–silver interactions.

3.6. Ruthenium(II) complexes of 6,6′-dimethyl substituted ligands

As discussed earlier, the presence of substituents in the 6,6′-position of a diimine ligand (the *cuproin* motif) allows the preparation of air-stable copper(I) complexes. Conversely, their presence results in a very great steric destabilisation of octahedral complexes in which three of these ligands are coordinated to the same centre.

An initial attempt to force three **1** ligands to coordinate to a ruthenium centre was unsuccessful and reaction of four equivalents of **1** with $RuCl_3 \cdot 3H_2O$ in 1,2-ethanediol at 120° or 140° for period of up to 48 h gave no evidence for the formation of $[Ru(\mathbf{1})_3]^{2+}$ species. On the basis of literature precedent [63,64], we argued that it should be possible to coordinate at least one of the sterically hindered ligands to a $\{Ru(bpy)_2\}$ motif and accordingly prepared these compounds. Two synthetic methods were investigated, both involving the reaction of $[Ru(bpy)_2Cl_2]$ with the appropriate ligand. The compounds were obtained either by prolonged thermal reaction (24 h at 110 °C) in 1,2-ethanediol or by reaction for 6 min in 1,2-ethanediol in a modified domestic microwave oven. In all cases, the yields were significantly higher for the reactions under microwave irradiation. After chromatographic purification, the three complexes $[Ru(bpy)_2(\mathbf{L})][PF_6]_2$ ($\mathbf{L} = \mathbf{1}$, **2** or **3**) were isolated as red solids.

The red colour arises from an MLCT absorption and these have maxima ≈ 425 nm for the three complexes $[Ru(bpy)_2(\mathbf{L})][PF_6]_2$. The MLCT band is blue-shifted with respect to $[Ru(bpy)_3]^{2+}$ salts which typically have an absorption maximum at 452 nm [65]. The origin of this blue-shifting is not obvious, since related complexes

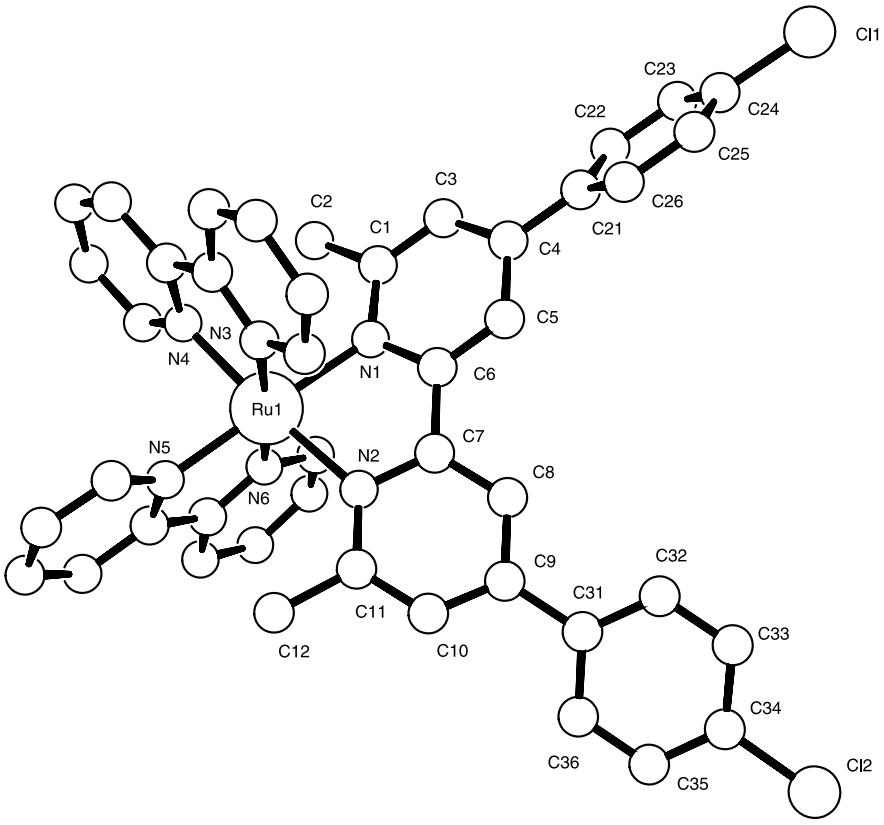
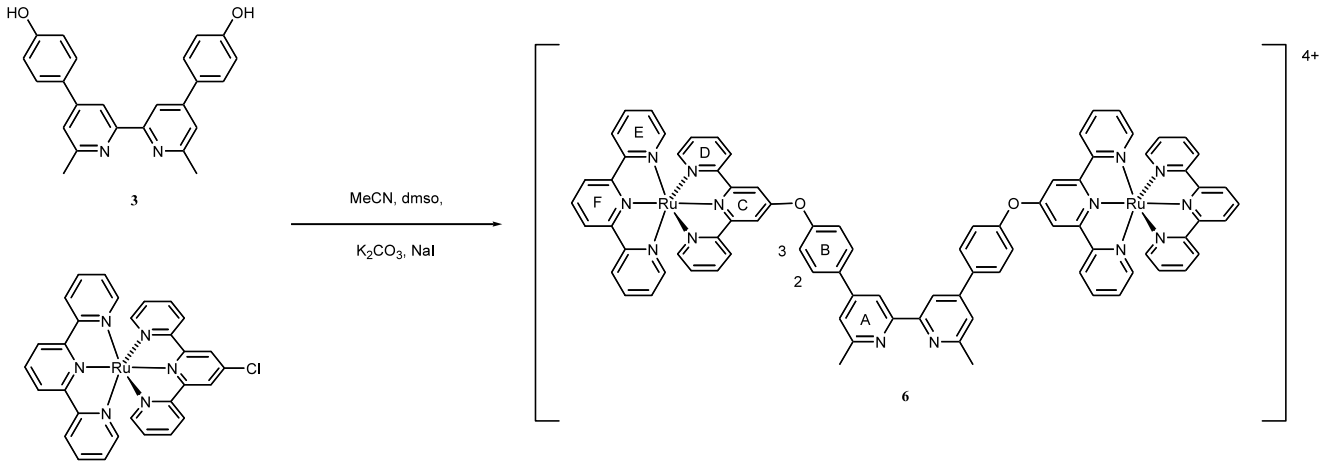


Fig. 7. Molecular structure of the Λ-$[Ru(bpy)_2(\mathbf{2})]^{2+}$ cation present in $[Ru(bpy)_2(\mathbf{2})][PF_6]$ showing the numbering scheme adopted. Both Λ and Δ enantiomers are present in the lattice. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°):Ru1–N1 2.116(3); Ru1–N2 2.139(3); Ru1–N3 2.082(3); Ru1–N4 2.049(3); Ru1–N5 2.055(3); Ru1–N6 2.066(3); N1–Ru1–N2 79.4(1); N1–Ru1–N3 84.3(1); N2–Ru1–N3 94.3(1); N1–Ru1–N4 98.0(1); N2–Ru1–N4 172.5(1); N3–Ru1–N4 78.5(1); N1–Ru1–N5 176.6(1); N2–Ru1–N5 100.4(1); N3–Ru1–N5 99.1(1); N4–Ru1–N5 82.7(1); N1–Ru1–N6 97.7(1); N2–Ru1–N6 90.5(1); N3–Ru1–N6 175.1(1); N4–Ru1–N6 96.8(1); N5–Ru1–N6 78.9(1).

are reported as having maxima closer to 450 nm, although in all cases the absorptions are broad and show a second feature at ≈430 nm [66–69]. In contrast to $[Ru(bpy)_3]^{2+}$ salts, the three complexes show only very weak or no emission upon excitation in the MLCT absorption, as observed for other 6,6′-disubstituted bpy complexes [70]. The ^1H NMR spectra of these complexes are of some interest. The two rings of each bpy ligand are expected to be magnetically inequivalent depending upon whether they are *trans* to another bpy ligand or the ligand **L**. This is observed in the ^1H NMR spectrum, which shows four subspectra in the aromatic region, corresponding to the two different magnetically inequivalent bpy rings, the pyridine of the ligand **L** and the aryl substituent of the **L** ligand. To date, we have been unable to distinguish between the two bpy rings on the basis of NOESY spectra. The complexes are redox active and all exhibit a ruthenium(II)/(III) process close to +1.0 V versus ferrocene/ferrocenium, indicating that the remote substituent on the phenyl substituent has little influence at the metal. The ligand reduction processes are much more sensitive to these substituents.

We have determined the solid state structure of the complex $[Ru(bpy)_2(\mathbf{2})][PF_6]_2$ to provide model data for the construction of molecular wires based upon this as a central unit. Suitable crystals were obtained by the diffusion of diethyl ether vapour into an acetonitrile solution of the complex; the structure of one of the pair of Δ and Λ enantiomers of the chiral *tris*chelate cations present in the crystal of $[Ru(bpy)_2(\mathbf{2})][PF_6]_2 \cdot 3CH_3CN \cdot 0.5H_2O$ is presented in Fig. 7. The two bpy ligands are typical and approximately planar (torsion angles 2°–4°) with Ru–N distances in the range 2.049(3)–2.082(3) Å similar to those observed in other $[Ru(bpy)_3]^{2+}$ salts [71]. All three of the coordinated bpy domains exhibit bite angles between 78.5° and 79.4°, typical of a 2,2′-bipyridine coordinated to a second or third row transition metal centre [72]. Potential interactions between the 6,6′-dimethyl substituents of **2** with the metal centre and the other bpy ligands result in a lengthening of the Ru–N bonds to this ligand (Ru1–N1 2.116(3) Å, Ru1–N2 2.139(3) Å). The two pyridine rings of the bpy domain of **2** are not coplanar but exhibit a torsion angle of 21.2°, the chlorophenyl substituents are also substantially



Scheme 3.

twisted with respect to the pyridine rings and form torsion angles of 25° and 39°. The presence of the methyl substituents results in a significant distortion of the geometry from ideality, but there are no short contacts between the cations and other lattice species.

3.7. The bisruthenated metallostar precursor

The bisphenolic ligands **3** and **5** are the key to the preparation of metallostars and we have established that it is possible to metallate **3** to give a diruthenated species. The complex $[Ru(tpy)(Cltpy)][PF_6]_2$ (Cltpy = 4′-chloro-2,2′:6′,2″-terpyridine) [29] contains a Cltpy ligand that is activated towards nucleophilic attack by coordination to the ruthenium(II) centre. The reaction of **3** with $[Ru(tpy)(Cltpy)][PF_6]_2$ proceeded smoothly in acetonitrile-dmso containing potassium carbonate and sodium iodide to give a deep red solution from which the compound **6**$[PF_6]_4$ was isolated in 40% yield after chromatographic purification (Scheme 3). The electrospray mass spectrum of the product exhibited clusters of peaks corresponding to the isotopomers of the ions $\{\mathbf{6}(PF_6)_2\}^{2+}$, $\{\mathbf{6}(PF_6)\}^{3+}$ and $\{\mathbf{6}\}^{4+}$ and the ^1H NMR spectrum provides confirmatory evidence for the formulation of the product. The singlet assigned to H^{3C} is characteristic and precludes the possibility of mixtures of the starting materials. The assignments presented in Section 2 are on the basis of COSY and NOESY spectroscopy. The red compound exhibits an MLCT absorption with a maximum at 480 nm but like the majority of $\{Ru(tpy)_2\}$ chromophores is virtually non-luminescent in fluid solution. The complex shows a single two-electron ruthenium(II)/(III) process at +0.85 V versus ferrocene/ferrocenium and a series of ligand reductions. The ruthenium(II)/(III) process is at a very similar potential to the model compound $[Ru(tpy)(EtOtpy)][PF_6]_2$ (EtOtpy = 4′-ethoxy-2,2′:6′,2″-terpyridine) [29].

All attempts to prepare **6**$[PF_6]_4$ from **2** or $[Ru(bpy)_2(\mathbf{2})][PF_6]_2$ by reaction with HOtpy or $[Ru(tpy)(HOtpy)][PF_6]_2$ (HOtpy = 2,2′:6′,2″-terpyridin-4′(1′*H*)-one) [29] under a variety of conditions were unsuccessful.

4. Conclusions

We have prepared a series of ligands which can be further structurally elucidated to give metallostars with octahedral or tertrahedral metal centres. The most useful of these is the hydroxy compound **3**, which has bee ruthenated at the periphery to give the immediate precursor for the metallostars. The coordination behaviour of the new ligands has been studied and X-ray crystallographic studies have confirmed the anticipated coordination geometries in the metal complexes and which will lead to the metallostars. In a future publication, we will describe the preparation of metallostars from these ligand systems.

5. Supplementary material

All crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos 185693 (**1**), 185692 (**4**), 185691 ($[Ag(\mathbf{1})(MeCN)][BF_4]$), 185694 ($[Ag(\mathbf{1})_2][PF_6]$), 189355 ($[Ru(bpy)_2(\mathbf{2})][PF_6]_2$). Copies of this information may be obtained free of charge from The Director, CCDC 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-366033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www/ccdc.cam.ac.uk.

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