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Metallostars containing {Ru(bpy)$_3$} motifs

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Abstract

Two new ligands designed to act as the core for metallostars based upon multiple bpy (bpy = 2,2′-bipyridine) metal-binding domains have been prepared. The first ligand **6** consists of a 1,3,5-triazine bearing three bpy metal-binding domains and was prepared inter alia using Stille methodology. All attempts to form complexes of **6** were unsuccessful. In contrast, a non-planar core compound based upon a tetraphenylmethane moiety bearing four bpy domains, also prepared using Stille couplings, was shown to form a tetraruthenametallostar complex containing four {Ru(bpy)$_3$} motifs. Each of the {Ru(bpy)$_3$} motifs is chiral, possessing Δ or Λ chirality and detailed NMR studies indicate that the complex is formed with little or no diastereoselectivity leading to a mixture of diastereomers and a fuzzy stereochemistry.

Keywords: Oligopyridines; Metallostars; Ruthenium complexes; Bipyridine complexes

1. Introduction

Dendrimers and metallodendrimers are often utilised as polyfunctional compounds or as precursors to highly functional species prepared in subsequent decoration steps [1]. Although dendrimers are aesthetically pleasing and are being successfully applied in fields as diverse as catalysis, biomolecule recognition and polymer synthesis [2], they also have a number of inherent disadvantages. Progressive steric congestion at the surface means that fractal growth through infinite generations is not possible and the De Gennes packing model relates the point at which defects start to appear in the topology and length of the dendron [3]. Furthermore, defects within individual generations are rapidly promulgated and lead to polydispersivity in contrast to the ideal monodispersed dendrimer structure. These difficulties led us and others to consider the synthesis of multinuclear compounds in which the growth of multiple arms from a central core occurs in a linear rather than a branching manner. We have termed these compounds metallostars. Metallostars possess many similarities to dendrimers and it is convenient to adopt the nomenclature based upon cores and generations to describe these compounds. We have previously reported metallostars with metal ions at the centre [4–9] together with a series based upon organometallic derivatives with organic cores [10–13]. In this article, we report the synthesis of three- and four-armed cores bearing 2,2′-bipyridine (bpy) metal-binding motifs and of a metallostar in which each arm bears a {Ru(bpy)$_3$} motif.

2. Experimental

Infrared spectra were recorded on a Mattson Genesis Fourier-transform spectrophotometer with samples in compressed KBr discs. ^{1}H NMR spectra were recorded on a Bruker AM 250 MHz spectrometer. Time of flight (MALDI) spectra were recorded using a PerSeptive Biosystems Voyager-RP Biospectrometry Workstation. Electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT 20 system using platinum or glassy carbon working and auxiliary electrodes with an Ag | AgCl electrode as reference using purified acetonitrile as solvent and 0.1 M [^{n}Bu$_4$N][BF$_4$] as supporting electrolyte; ferrocene was added at the end of each experiment as an internal reference. The compounds tetra(4-bromophenyl)methane [14], 6-bromo-

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2,2′-bipyridine [15], $[Pd(PPh_3)_4]$ [16] and $[Ru(bpy)_2Cl_2]$ [17] were prepared by the literature methods. The complex $[Ru(bpy\text{-}d_8)_2Cl_2]$ was prepared as for $[Ru(bpy)_2Cl_2]$ but using bpy-d_8.

2.1. *N*-{3-(4-Bromophenyl)-3-oxopropyl}-*N*,*N*-dimethylammonium chloride (**1**)

N,*N*-Dimethylammonium chloride (1.20 g, 15 mmol), paraformaldehyde (3.52 g, 59 mmol) and 4-bromoacetophenone (2.78 g, 14 mmol) were heated to reflux in EtOH (40 ml) for 4 h after which an additional quantity of paraformaldehyde (0.71 g, 0.012 mol) was added and heating continued for a further 4 h. The clear yellow solution so obtained was concentrated in vacuo to 10 ml volume and treated with acetone (120 ml) to give a white suspension. This was cooled to −18°C for 12 h after which the Mannich salt **1** was collected by filtration (2.79 g, 68%). *Anal.* Found: C, 45.32; H, 5.08; N, 4.83. Calc. for $C_{11}H_{15}NBrOCl$: C, 45.15; H, 5.17; N, 4.79%. Mass spectrum (+ve FAB) *m*/*z*: 293 (with isotopomers) $\{HM\}^+$, 256 (with isotopomers $\{M-Cl\}^+$. IR (KBr cm^{-1}): 2957 m, 2938 m, 2910 m, 1681 s, 1601 s, 1476 m, 1464 m, 1411 m, 1383 m, 1297 m, 1019 m, 951 m, 823 m, 782 m.

2.2. 6-(4-Bromophenyl)-2,2′-bipyridine (**2**)

A mixture of $[NH_4][OAc]$ (4.20 g, 55 mmol) and 2-(2-pyridyl)-2-oxoethylpyridinium iodide (1.41 g, 4.32 mmol) was heated to reflux for 10 min in EtOH (10 ml) under dinitrogen. After this period **1** (1.26 g, 4.32 mmol) was added and the mixture refluxed for a further 4.5 h. The suspension was then cooled and the beige precipitate of **2** collected by filtration. Recrystallisation from EtOH gave **2** as an off-white solid (0.47 g, 92%). M.p. 89.2°C. *Anal.* Found: C, 61.9; H, 4.2; N, 8.8. Calc. for $C_{16}H_{11}N_2Br$: C, 61.8; H, 3.8; N, 9.0%. Mass spectrum (+ve FAB) *m*/*z*: 310, 312 $\{M\}^+$. IR (KBr cm^{-1}): 1582 m, 1560 m, 1430 m, 1008 m, 771 s, 745 m, 510 m. ^1H NMR ($CDCl_3$): δ 8.70 (1H, d, H^{6A}), 8.58 (1H, d, H^{3A}), 8.39 (1H, d, H^{3B}), 8.02 (2H, d, H^o), 7.85 (2H, dd, $H^{4A,4B}$), 7.70 (1H, d, H^{5B}), 7.62 (2H, d, H^m), 7.32 (1H, ddd, H^{5A}). ^{13}C NMR ($CDCl_3$): δ 156.1, 155.8, 155.2, 149.1, 138.2, 137.8, 136.8, 131.8, 128.4, 123.8, 123.4, 121.2, 119.9, 119.6.

2.3. *N*-{3-(4-Cyanophenyl)-3-oxopropyl}-*N*,*N*-dimethylammonium chloride (**3**)

N,*N*-Dimethylammonium chloride (0.39 g, 4.8 mmol), paraformaldehyde (0.65 g, 22.2 mmol) and 4-cyanoacetophenone (0.69 g, 4.8 mmol) were heated to 60°C in DMF (15 ml) for 5 h after which acetone (75 ml) was added and the mixture left at −18°C overnight to precipitate the salt **3** (0.25 g, 68%). *Anal.* Found: C, 60.2; H, 6.4; N, 11.8. Calc. for $C_{12}H_{15}N_2OCl$: C, 60.4; H, 6.3; N, 11.7%. IR (KBr cm^{-1}): 2222 w.

2.4. 6-(4-Cyanophenyl)-2,2′-bipyridine (**4**)

2.4.1. Method 1

A mixture of 2-(2-pyridyl)-2-oxoethylpyridinium iodide (1.37 g, 4.2 mmol) and $[NH_4][OAc]$ (3.24 g, 42.1 mmol) in EtOH (50 ml) was refluxed for 10 min after which **3** (1.00 g, 4.2 mmol) was added and heating continued for a further 6 h. Addition of water to the reaction mixture followed by overnight cooling resulted in the precipitation of a small amount of **4** as a white solid (0.043 g, 4%).

2.4.2. Method 2

A mixture of **2** (1.1 g, 4.8 mmol) and CuCN (0.43 g, 5.2 mmol) in DMF (2 cm^3) was heated at 145°C for 24 h. The reaction mixture was then poured into an excess of concentrated aqueous potassium cyanide solution and allowed to stand overnight. The resulting precipitate was filtered off, dried and extracted with toluene. The organic extract was then evaporated to dryness in vacuo and then recrystallised from MeOH to give **4** (0.70 g, 57%). M.p. 135–136°C. *Anal.* Found: C, 78.9; H, 3.9; N, 16.4. Calc. for $C_{17}H_{11}N_3$: C, 79.4; H, 4.3; N, 16.3%. Mass spectrum (TOF; 1,8,9-trihydroxyanthracene matrix): *m*/*z* 257 $\{M\}^+$, 231 $\{M-CN\}^+$. IR (KBr cm^{-1}): 2926 m, 2222 m, 1725 s, 1581 s, 1561 s, 1452 s, 1429 s, 1282 s, 1138 m, 1071 m, 821 m, 773 s, 744 s, 548 m. ^1H NMR ($CDCl_3$): δ 8.70 (1H, d, H^{6A}), 8.58 (1H, d, H^{3A}), 8.39 (1H, d, H^{3B}), 8.10 (2H, d, H^o), 7.85 (2H dd, $H^{4A,4B}$), 7.75 (1H, d, H^{5B}), 7.71 (2H, d, H^m), 7.32 (1H, ddd, H^{5A}).

2.5. 6-(4-Tri-*n*-butylstannylphenyl)-2,2′-bipyridine (**5**)

2 (0.30 g, 0.97 mmol) was dissolved in THF (40 ml) under dinitrogen and cooled to −100°C (liquid dinitrogen/MeOH) after which n-butyllithium (0.73 ml, 1.6 M solution in hexane, 1.17 mmol) was added dropwise to the stirred solution which turned deep crimson-red. The mixture was stirred at −100°C for 40 min after which n-Bu_3SnCl (0.48 g, 0.40 ml, 1.46 mmol) was added over 3 min. The solution became green–blue and was stirred for 75 min and then allowed to warm to −10°C when H_2O (5 ml) was added. The THF was removed in vacuo and the residue extracted into CH_2Cl_2 (2 × 150 ml). The extracts were dried (Na_2SO_4) and evaporated to give a pale yellow oil which was

purified by column chromatography (SiO_2, 4:1 hexanes:EtOAc) to give **5** as an oil (92%, 0.47 g).

Mass spectrum (TOF, 1,8,9-trihydroxyanthracene matrix): m/z 520 $\{M\}^+$. IR (KBr cm^{-1}): 2959 m, 1579 w, 1428 w, 1260 w, 1074 w, 777 w, 726 w, 691 w, 655 w, 587 w, 433 vs. ^1H NMR ($CDCl_3$): δ 8.68 d, H^{6A}), 8.63 (1H, d, H^{3A}), 8.38 (1H, d, H^{3B}), 8.11 (2H, d, H^{2C}), 7.87 (2H, m, $H^{4A,\ 4B}$), 7.78 (1H, d, H^{5B}), 7.63 (2H, d, H^{3C}), 7.31 (1H, dd, H^{5A}), 1.57 (6H, m, $SnCH_2$), 1.37 (6H, m, $SnCH_2CH_2$), 1.12 (6H, m, CH_2CH_3), 0.92 (9H, m, CH_3). ^{13}C NMR ($CDCl_3$): δ 156.7, 156.5, 155.7, 149.1, 143.5, 139.0, 137.6, 136.9, 136.8, 126.3, 123.7, 121.3, 120.3, 119.3, 29.2, 27.5, 13.8, 9.7.

2.6. 2,4,6-Tris(4-(2,2′-bipyridin-6-yl)phenyl)-1,3,5-triazine (6)

2.6.1. Method 1

A solution of **4** (0.5 g, 1.9 mmol) in PhMe (3 ml) was added slowly over 3 h to $ClSO_3H$ (0.38 ml, 5.83 mmol) maintained at −6°C (ice-salt bath). The reaction mixture changed through yellow and orange finally forming a deep viscous red suspension. The reaction flask was removed from the ice bath and cooled to 3°C overnight after which H_2O was cautiously added and the resulting orange–red product mixture was extracted with CH_2Cl_2. The organic layer was washed with H_2O (3 × 10 ml), dried ($MgSO_4$) and then evaporated to dryness in vacuo. Purification by flash column chromatography (SiO_2, 7:3 40–60° petroleum ether: EtOAc) removed the organic impurities leaving **5** as a yellow band at the top of the column which was eluted with the highly polar solvent mixture MeCN:saturated KNO_3:H_2O (14:2:1). The yellow fraction was collected, extracted with CH_2Cl_2 and the extract washed with H_2O, dried ($MgSO_4$) and evaporated to dryness to give **6** (0.015 g, 3%).

2.6.2. Method 2

5 (0.30 g, 0.58 mmol), $[Pd(PPh_3)_4]$ (0.013 g, 0.012 mmol) and 2,4,6-trichloro-1,3,5-triazine (0.027 g, 0.15 mmol) were dissolved in toluene freshly distilled over sodium wire (10 ml) when a rapid reaction ensued and precipitation of **6** began after 2 h. The reaction was left overnight and then diethyl ether (20 ml) was added and the product filtered off (0.10 g, 87%). *Anal.* Found: C, 79.6; H, 4.4; N, 16.7. Calc. for $C_{51}H_{33}N_9$: C, 79.4; H, 4.3; N, 16.3%. Mass spectrum (+ve FAB): m/z 771 $\{M\}^+$. IR (KBr cm^{-1}): 2923 m, 1648 s, 1619 m, 1581 s, 1561 m, 1454 m, 1430 s, 774 s. ^1H NMR ($CDCl_3$) δ 8.79 (2H, d, H^{2C}), 8.72 (1H, d, H^{6A}), 8.67 (1H, d, H^{3A}), 8.46 (1H, d, H^{3B}), 8.36 (2H, d, H^{3C}), 7.95 (1H, m, H^{4B}), 7.90 (1H, m, H^{4B}), 7.34 (1H, m, H^{5B}), 7.17 (1H, m, H^{5A}). ^{13}C NMR ($CDCl_3$): δ 152.3, 149.6, 143.3, 139.3, 137.4, 136.6, 132.5, 128.7, 127.9, 125.0, 124.7, 124.4, 124.0, 121.8, 118.4. UV ($CDCl_3$): λ_{max} (ε/dm^3 mol^{-1} cm^{-1}) 259 (33 800), 326.4 nm (105 700).

2.7. 6-Tri-n-butylstannyl-2,2′-bipyridine (7)

Freshly distilled (Na, Ph_2CO) diethyl ether (4 ml) was placed in a flame-dried apparatus under an atmosphere of argon and cooled to −100°C and a solution (1.6 M) of ^{n}BuLi in hexanes (1.06 cm^3, 1.70 mmol). A solution of 6-bromo-2,2′-bipyridine (0.040 g, 1.70 mmol) in freshly distilled diethyl ether (4 ml) was immediately added to give a deep red solution which was stirred for 5 min. After this period, (n-Bu_3)SnCl (0.46 ml, 1.70 mmol) was added and the mixture stirred whilst the temperature was allowed to rise to 0°C. The resultant yellow suspension was treated with H_2O to give a clear solution which was extracted with diethyl ether (100 ml). The organic phase was separated and dried over $MgSO_4$ and then purified by chromatography over SiO_2 (Et_2O/hexanes mobile phase) to give 6-tri-n-butylstannyl-2,2′-bipyridine (**7**) as a green oil (0.498 g, 65.9%) that was not further purified. ^1H NMR ($CDCl_3$): δ 8.65 (1H, ddd, $J = 6.0$ Hz, H^{6A}), 8.53 (1H, d, $J = 7.8$ Hz, H^{3A}), 8.25 (1H, dd, $J = 7.8$, 1.2 Hz, H^{3B}, subspectrum with $^5J_{Sn-H}$ 8.0 Hz), 7.80 (1H, td, $J = 7.8$, 1.2 Hz, H^{4A}), 7.63 (1H, t, $J = 7.8$ Hz, H^{4B}, subspectrum with $^4J_{Sn-H}$ 14.2 Hz), 7.40 (1H, dd, $J = 7.8$, 1.2 Hz, H^{5B}, subspectrum with $^3J_{Sn-H}$ 15.5 Hz), 7.63 (1H, ddd, $J = 7.8$, 6.0, 1.2 Hz, H^{5A}), 1.61 (6H, m, $SnCH_2$), 1.36 (6H, m, $SnCH_2CH_2$), 1.56 (6H, m, CH_2CH_3), 0.89 (9H, t, CH_3). Mass spectrum (MALDI-TOF): m/z 447 $\{M\}^+$, 390 $\{M-C_4H_9\}^+$. IR (KBr cm^{-1}): 2956 m, 1544 m, 1420 s, 770 s.

2.8. Tetrakis(4-{6-[2,2-bipyridyl]phenyl)methane (8)

A mixture of **7** (2.56 g, 5.75 mmol), tetra(4-bromophenyl)methane (0.827 g, 1.30 mmol), $[Pd(PPh_3)_4]$ (0.120 g, 0.104 mmol) in DMF (5 ml) was heated to 90°C and stirred for 110 h to give a dark-coloured reaction mixture. Chromatographic purification (SiO_2, CH_2Cl_2/acetone mobile phase) followed by recrystallisation from CH_2Cl_2/EtOH gave tetrakis(4-{6-[2,2-bipyridyl]}phenyl)methane (**8**) as white crystals (0.376 g, 30.8%). M.p. > 300°C. *Anal.* Found: C, 82.9; H, 4.8; N, 11.5. Calc. for $C_{65}H_{44}N_8$: C, 83.3; H, 4.7; N, 12.0%. ^1H NMR ($CDCl_3$): δ 8.68 (4H, ddd, $J = 6.0$ Hz, H^{6A}), 8.62 (4H, d, $J = 7.8$ Hz, H^{3A}), 8.37 (1H, dd, $J = 7.8$, 1.2 Hz, H^{3B}), 8.12 (8H, d, $J = 8.8$ Hz, H^o), 7.89 (4H, t, $J = 7.8$ Hz, H^{4B}), 7.81 (1H, td, $J = 7.8$, 1.2 Hz, H^{4A}), 7.78 (4H, dd, $J = 7.8$, 1.2 Hz, H^{5B}), 7.56 (8H, d, H^m), 7.31 (4H, ddd, $J = 7.8$, 6.0, 1.2 Hz, H^{5A}). ^{13}C NMR ($CDCl_3$): δ 156.3 (4C, $C^{2A/2B/6B}$), 156.0 (4C, $C^{2A/2B/6B}$), 155.7 (4C, $C^{2A/2B/6B}$), 149.0 (4C, C^{6A}), 147.4 (4C, C^{ipso}), 137.7 (4C, C^{4B}), 137.2 (4C, C^p), 136.8 (4C, C^{4A}), 131.5 (8C, C^o), 126.3 (8C, C^m), 123.7 (4C, C^{3A}), 121.3 (4C, C^{5A}), 120.2 (4C, $C^{3B/5B}$), 119.3 (4C, $C^{3B/5B}$), 64.8 (1C, C^{centre}). UV–Vis (CH_2Cl_2): λ_{max} (ε/dm^3 mol^{-1} cm^{-1}) 272 (8700), 292 (7360), 311 (5820) nm. IR (KBr cm^{-1}): 3052 m, 1581 m,

1561 s, 1454 m, 1429 s, 1320 w, 1258 w, 1157 w, 1099 w, 1038 w, 1015 m, 989 w, 814 m, 776 s, 748 m, 712 w, 618 w cm^{-1}. Mass spectrum (MALDI-TOF): *m/z* 937 $\{M\}^+$, 783 $\{M-C_{10}H_7N_2\}^+$, 705 $\{M\text{-}C_6H_4C_{10}H_7N_2\}^+$, 474 $\{M\text{-}2(C_6H_4C_{10}H_7N_2)\}^+$.

2.9. 2,2′-Bipyridine-d_8

2,2′-Bipyridine (1.0 g, 6.4 mmol) was heated at 200°C in a sealed glass tube with D_2O (5 ml) and palladium-charcoal (10%, 0.05 g) for 5 d. After this period, the tube was cooled, opened and sufficient Me_2CO added to dissolve all organics. The mixture was filtered through celite and concentrated in vacuo to give a white solid shown by ^1H NMR spectroscopy to be $\approx$90% deuterated. The deuteration procedure was repeated to give fully deuterated 2,2′-bipyridine-d_8 as white crystals (0.83 g, 85%).

2.10. [**8**{Ru(bpy)$_2$}$_4$][PF$_6$]$_8$

A mixture of **8** (0.050 g, 0.053 mmol) and $[Ru(bpy)_2Cl_2]$ (0.114 g, 0.235 mmol) was suspended in ethane-1,2-diol (2.5 ml) and refluxed under microwave irradiation (440 W, 10 min.) for 10 min. The orange reaction mixture was cooled and then stirred with $[NH_4][PF_6]$ (0.900 g) and sufficient H_2O to give an essentially mother liquor and an orange precipitate. The precipitate was collected by filtration, dissolved in the minimum amount of MeCN, purified by chromatography (SiO_2, MeCN:saturated aqueous KNO_3:H_2O, 7:1:0.5 v/v) and finally precipitated by $[NH_4][PF_6]$. Recrystallisation from acetone gave red crystals of [**8**{Ru(bpy)$_2$}$_4$][PF$_6$]$_8$ (0.131 g, 65.2%). *Anal.* Found: C, 44.6; H, 3.4; N, 8.7. Calc. for $C_{145}H_{108}N_{24}F_{48}P_8Ru_4\cdot 8H_2O$: C, 44.85; H, 3.4; N, 8.7%. ^1H NMR (CD_3CN): See Table 1. ^{13}C NMR ($CDCl_3$): δ 167.2 (4C, C^{6B}), 158.95, 158.9, 158.4, 158.2, 158.0, 157.3, 153.6 (24C, $C^{2A,2B,2D,2E,2F,2G}$), 153.6, 153.0, 152.7, 152.5, 151.8 (20C, $C^{6A,6D,6E,6F,6G}$), 144.5 (4C, C^{ipso}), 139.0 (3C), 138.9, 138.8, 128.7, 137.3 (24C, $C^{4A,4B,4D,4E,4F,4G,p}$) 131.5, 128.9, 128.8, 128.7, 128.3, 128.2, 126.8, 125.9, 125.5, 125.2, 124.9, 124.6, 123.5, 123.7 (64C, $C^{3A,5A,3B,5B,3D,5D,3E,5E,3F,5F,3G,5G,m,o}$), 64.4 (1C, C^{centre}). UV–Vis (MeCN): λ_{max} 244, 290, 451 nm: IR (KBr cm^{-1}): 1604 w, 1466 w, 1448 m, 1426 w, 841 s, 765 m, 731 w, 558 m. Mass spectrum (MALDI-TOF): *m/z* 3607 $\{M-PF_6\}^+$, 2909 $\{M-Ru(bpy)_2-3PF_6\}^+$.

Table 1
^1H NMR data for the ligand **8** in [**8**{Ru(bpy)$_2$}$_4$][PF$_6$]$_8$ and ligand **9** in [Ru(bpy)$_2$(**9**)][PF$_6$]$_2$ [a]

	[**8**{Ru(bpy-d_8)$_2$}$_4$][PF$_6$]$_8$	[Ru(bpy)$_2$(**9**)][PF$_6$]$_2$
A6 (dd)	7.54	7.55
A5	7.32	7.30
A4 (t)	8.06	8.10
A3 (d)	8.55	8.60
B5 (dd)	7.42	7.35
B4 (td)	8.20	8.15
B3 (d)	8.61	8.65
C	6.40*	6.7*
C	7.30*	7.2*
C	5.90*	7.0*
C	6.09*	6.0*
D6	7.15	6.95
D5	6.33	6.80
D4	7.20	7.55
D3	7.70	8.00
E6	7.86	7.80
E5	7.43	7.45
E4	8.10	8.10
E3	8.10	8.37
F6	7.27	7.30
F5	7.20	7.25
F4	7.92	7.90
F3	8.32	8.30
G6	8.00	8.05
G5	7.56	7.50
G4	8.11	8.10
G3	8.41	8.40

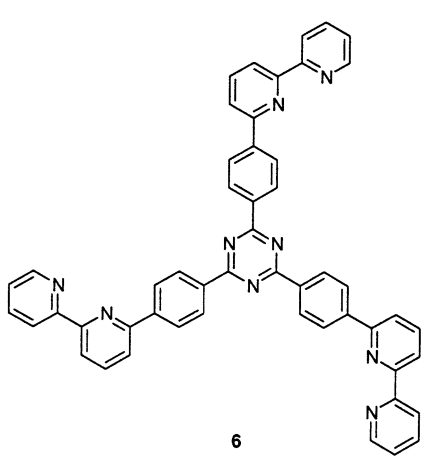
[a] All data for CD_3CN solutions. Unambiguous assignments for the C-ring protons have not been made (see text).

3. Results and discussion

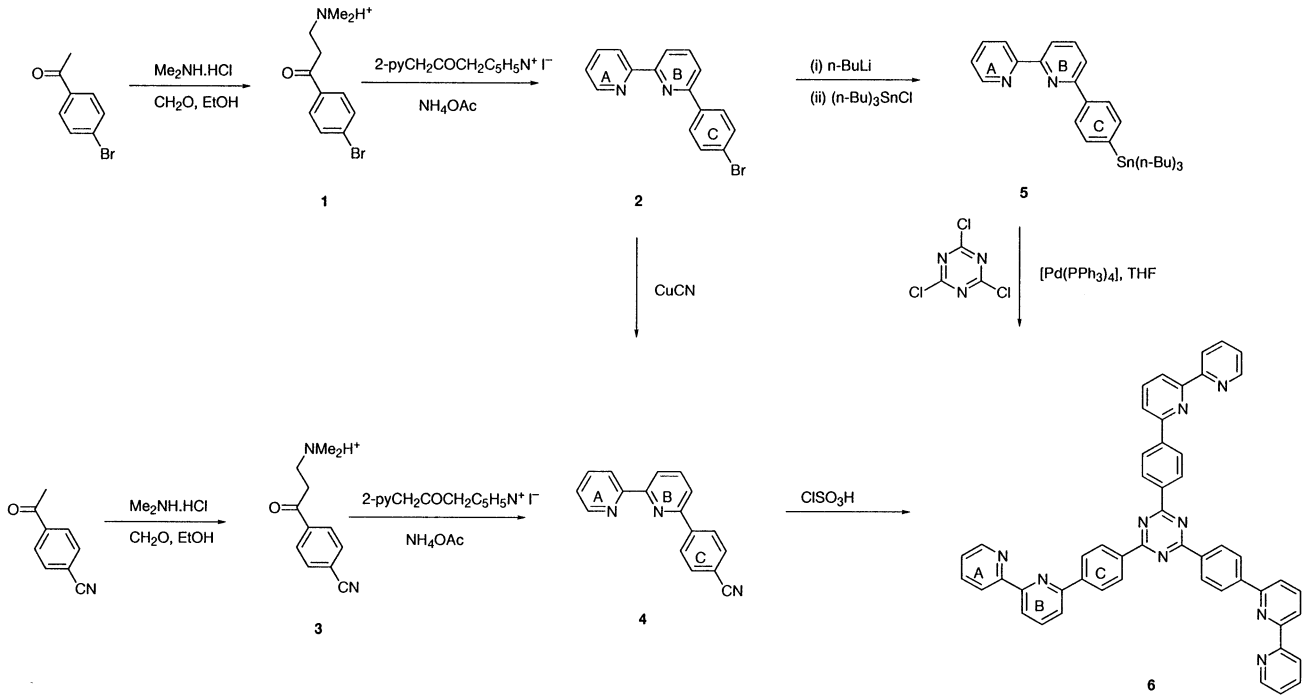
3.1. Ligand synthesis and characterisation

3.1.1. The three-armed 1,3,5-triazine ligand

The aim of this study was to develop new cores for use in metallodendrimers and metallostars. The initial motif that we considered was a 2,4,6-trifunctionalised 1,3,5-triazine as a planar core with three pendant arms. We adopted this choice for two reasons: (i) the triazine can be prepared in a convergent sense from three precursor molecules and (ii) the spatial arrangement of the substituents is reasonably well-defined.



6



Scheme 1.

The target molecule was 2,4,6-tris(4-(2,2′-bipyridin-6-yl)phenyl)-1,3,5-triazine (**6**) in which three bpy metal-binding domains are attached to the 1,3,5-triazine through *para*-phenylene spacers. The original approach that we developed was based upon the cyclotrimerisation of 6-(4-cyanophenyl)-2,2′-bipyridine (**4**). This latter compound was prepared as indicated in Scheme 1. Initially, we prepared the Mannich salt *N*-{3-(4-cyanophenyl)-3-oxopropyl}-*N*,*N*-dimethylammonium chloride (**3**) from 4-cyanoacetophenone under standard conditions. The salt was isolated in 68% yield and was fully characterised. We used Krohnke methodology [18] to convert **3** to **4** by reaction with 2-(2-pyridyl)-2-oxoethylpyridinium iodide and ammonium acetate. Despite investigating a range of reaction conditions, the best yield that we achieved in this conversion was 4%, which we considered to be unacceptable.

In a second approach to **4**, we decided to make a functional group interconversion in the final step to introduce the nitrile late in the synthesis. The conversion of 4-bromoacetophenone to the Mannich salt **1** was achieved under standard conditions to give **1** in 68% yield as a white solid which was fully characterised. The salt exhibits a characteristic carbonyl absorption at 1681 cm^{-1} in its IR spectrum. The reaction of **1** with ammonium acetate and the Krohnke reagent 2-(2-pyridyl)-2-oxoethylpyridinium iodide [18] in EtOH gave 6-(4-bromophenyl)-2,2′-bipyridine (**2**) as a white solid in excellent yield. The compound **2** exhibits a pair of parent ions in its mass spectrum at m/z 310/312 corresponding to the two isotopomers. The ^{1}H NMR spectrum was well-resolved and typical for a 6-substituted 2,2′-bipyridine. The conversion of **2** to **4** was achieved by heating with copper(I) cyanide in DMF to give **4** as a white solid in 57% yield. The IR spectrum of **4** exhibits a typical ν(CN) mode at 2222 cm^{-1}.

Acid-mediated trimerisation of nitriles is a standard preparative method for 1,3,5-triazines [19] and the reaction of **4** with chlorosulfonic acid at -5°C gave **6** in optimised 3% yield.

A significantly better route for the preparation of **4** was subsequently adopted based upon a Stille coupling reaction (Scheme 1). The starting point was the previously prepared bromo compound **2**. Lithiation with n-BuLi in THF followed by reaction with n-Bu_3SnCl gave the stannylated compound 6-(4-tri-n-butylstannylphenyl)-2,2′-bipyridine (**5**) in 92% yield as a pale yellow oil. The presence of the tin gives rise to characteristic ^{117}Sn and ^{119}Sn satellites on both the aliphatic and aromatic resonances in the ^{1}H NMR spectrum. Figs. 1 and 2 present the aromatic region of a $CHCl_3$ solution of **5** showing the coupling to H^{3C} of the phenylene. Stille coupling [20] of **5** with commercially available 2,4,6-trichloro-1,3,5-triazine in toluene in the presence of $[Pd(PPh_3)_4]$ gave the desired ligand **6** as an extremely insoluble white solid in 87% yield. The high yield is somewhat surprising in view of the presence of bpy metal-binding domains in both **5** and **6** which could coordinate to palladium. The new ligand **6** was fully characterised (see Section 2). Ligand **6** proved to be extremely insoluble, compatible with extensive π-

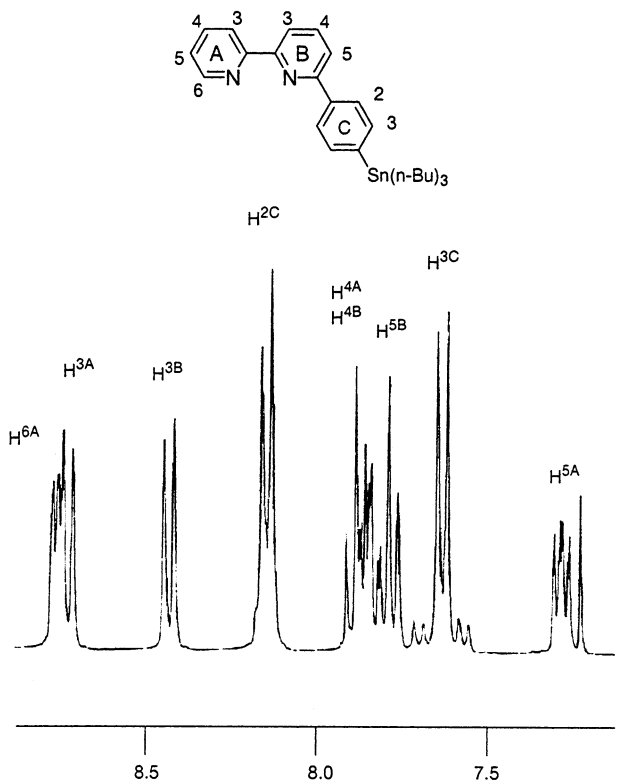
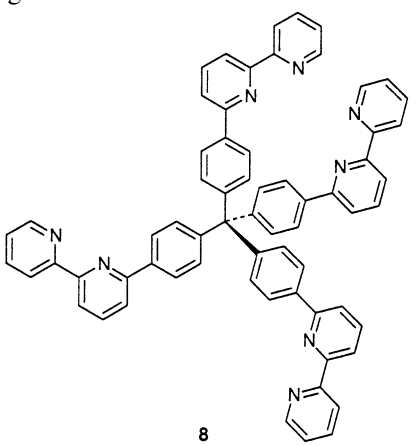


Fig. 1. 250 MHz ^{1}H NMR spectrum of a $CDCl_3$ solution of 6-(4-tri-n-butylstannylphenyl)-2,2′-bipyridine (**5**) showing the assignments and the numbering scheme adopted.

stacking in the solid state, as expected for a highly conjugated, and most likely planar, system. We decided to design a second ligand in which the core structure orients the metal binding domains in such a way that extensive solid state stacking is not possible.

3.1.2. The four-armed tetraphenylmethane ligand

The non-planar ligand was to be based upon a tetrahedral tetraphenylmethane core. This latter motif has been used by Wuest and co-workers as an extended tetrahedral *tecton* for the synthesis of novel materials and in crystal engineering [21,22]. We planned to structurally develop the tetraphenylmethane core by functionalisation with a metal-binding domain and our planned ligand was **8**.



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In view of the success in the synthesis of **6**, we hoped to use palladium-catalysed Stille reactions for the attachment of stannylated metal-binding domains to halogenated tetraphenylmethane derivatives (Scheme 2). Commercially available tetraphenylmethane was converted to tetrakis(4-bromophenyl)methane by reaction with bromine using the literature methods [14]. Once again, the metal-binding domain of choice was bpy which was to be introduced via the known compound 6-bromo-2,2′-bipyridine. Lithiation of 6-bromo-2,2′-bipyridine with n-BuLi proceeded smoothly at low

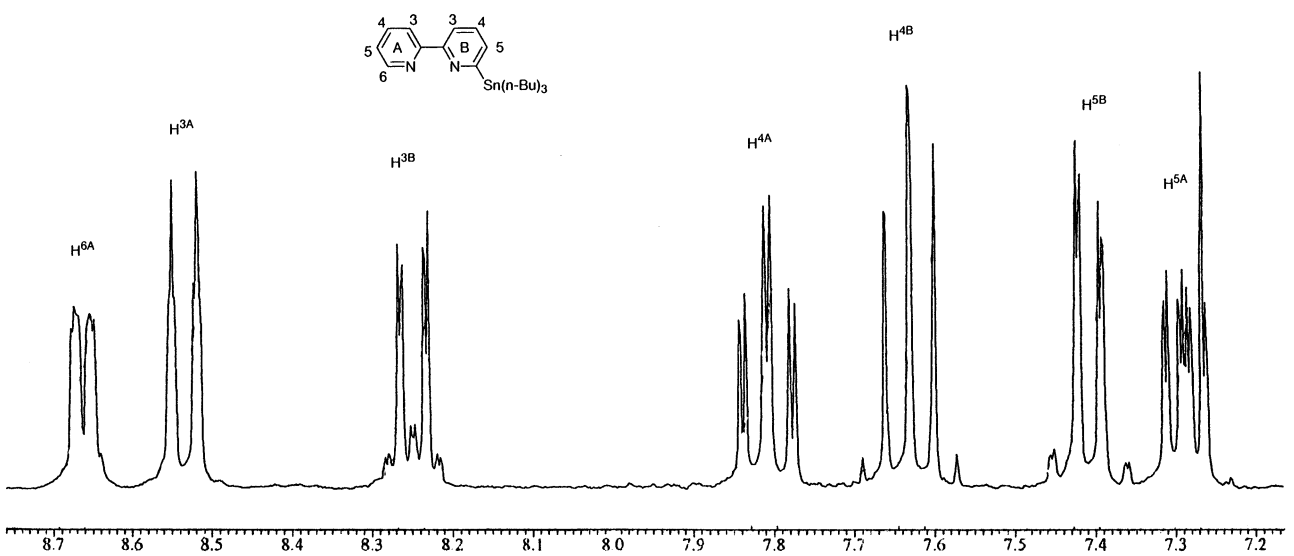
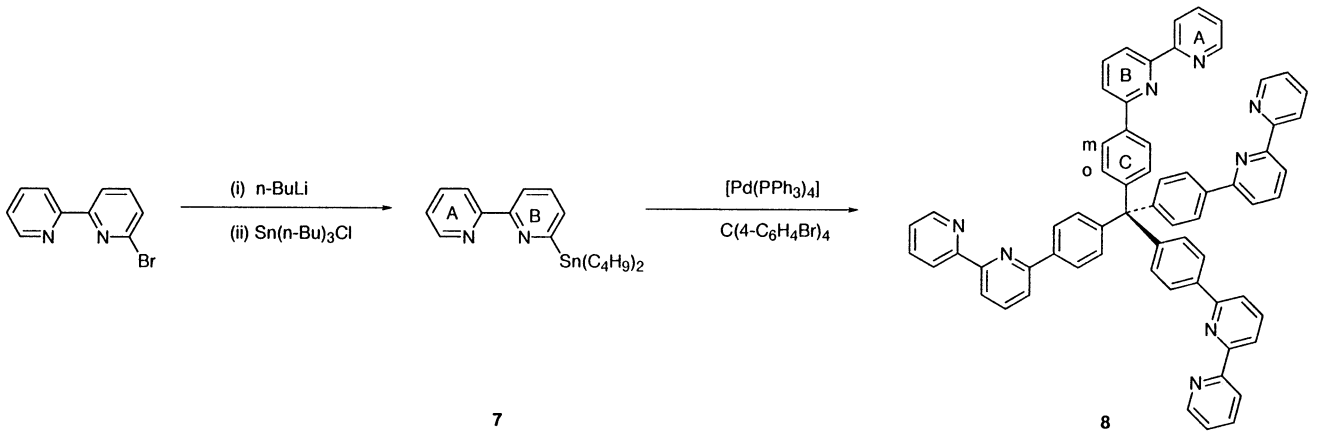


Fig. 2. 250 MHz ^{1}H NMR spectrum of a $CDCl_3$ solution of 6-(4-tri-n-butylstannyl)-2,2′-bipyridine (**7**) showing the assignments and the numbering scheme adopted.



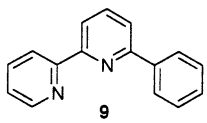
Scheme 2.

temperature and subsequent reaction of the 6-lithio-2,2′-bipyridine with n-Bu_3SnCl gave the stannyl derivative 6-tri-n-butylstannyl-2,2′-bipyridine (**7**) as an oil in 66% yield. The compound was characterised by conventional methods. Once again, the observation of coupling to the ^{117}Sn and ^{119}Sn nuclei of the protons at the stannylated pyridine ring in the ^1H NMR spectrum, confirms the formation of the desired metallated compound.

The Stille coupling of 6-tri-n-butylstannyl-2,2′-bipyridine with tetrakis(4-bromophenyl)methane proceeded smoothly in DMF to give the desired ligand tetrakis(4-{6-[2,2′-bipyridyl]}phenyl)methane (**8**) as a white crystalline solid in 31% yield. The compound exhibited a parent ion at m/z 937 in its mass spectrum and the high symmetry led to a simple ^1H NMR spectrum which was fully assigned on the basis of COSY methods (Fig. 3).

3.2. Coordination behaviour of the new core ligands

After investing a considerable effort in preparing ligand **6** we were extremely disappointed to find that we were unable to prepare any coordination complexes with it! The ligand gives no coloration with solutions of either iron(II) or copper(I) salts and would not react with $[Ru(bpy)_2Cl_2]$ in a variety of solvents (MeOH, EtOH, n-BuOH, MeOH-CH_2Cl_2). Attempted reaction with $[Ru(bpy)_2Cl_2]$ in boiling ethane-1,2-diol under microwave irradiation resulted in the formation of a deep violet solution of $[Ru(bpy)_2(HOCH_2CH_2OH)]Cl_2$ and an insoluble residue of **6**! Molecular modelling indicates that no serious steric interactions beyond those in the known complex $[Ru(bpy)_2(\mathbf{9})]^{2+}$ are anticipated in a complex such as $[\mathbf{6}\{Ru(bpy)_2\}_3]^{6+}$. In part, the insolubility of the ligand, which contains 10 conjugated aromatic rings which can stack in the crystal lattice, contributes to its low reactivity.



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In contrast, the more soluble ligand **8** reacted smoothly with slightly more than four equivalents of $[Ru(bpy)_2Cl_2]$ in ethane-1,2-diol under microwave irradiation to give a deep orange solution from which the red crystalline compound $[\mathbf{8}\{Ru(bpy)_2\}_4][PF_6]_8$ was isolated in 65% yield after chromatographic purification (Scheme 3). The compound exhibited a single spot on TLC analysis in a variety of mobile phases. The new tetranuclear metallostar exhibited a peak in its MALDI-TOF mass spectrum corresponding to $\{[\mathbf{8}\{Ru(bpy)_2\}_4][PF_6]_7\}^+$ together with a fragmentation peak corresponding to the loss of a $\{Ru(bpy)_2\}$ unit assigned to $\{[\mathbf{8}\{Ru(bpy)_2\}_3][PF_6]_5\}^+$. The orange colour is typical of the $\{Ru(bpy)_3\}$ chromophore and arises from an MLCT band at 451 nm. The absorption is significantly blue-shifted with respect to $[Ru(bpy)_3]^{2+}$, presumably as a result of the distortion of the idealised D_3 symmetry upon introducing the 6-substituent on one of the bpy rings. A similar blue shift is seen in $[Ru(bpy)_2(\mathbf{9})]^{2+}$ which has λ_{max} 447 nm [23,24]. The complex $[\mathbf{8}\{Ru(bpy)_2\}_4][PF_6]_8$ is strongly luminescent and irradiation in MeCN solution at 451 nm results in an emission at 616 nm (compared to 615 nm for $[Ru(bpy)_3]^{2+}$ in MeCN at 298 K). The complex is electrochemically active and exhibits a single, reversible ($E_a - E_c = 66$ mV) ruthenium(II)/(III) process at $+0.92$ V (vs. Fc/Fc^+). This is shifted slightly to more positive potential with respect to the model compound $[Ru(bpy)_2(\mathbf{9})]^{2+}$ which shows a ruthenium(II)/(III) process at $+0.85$ V [23,24]. In addition, a reversible ($E_a - E_c = 96$ mV) ligand centred reduction is observed at -1.68 V together with a second reduction at -1.91 V with an associated stripping peak on the return wave. These are comparable to the reductions at -1.76 and -1.91 V observed for $[Ru(bpy)_2(\mathbf{9})]^{2+}$ [23,24].

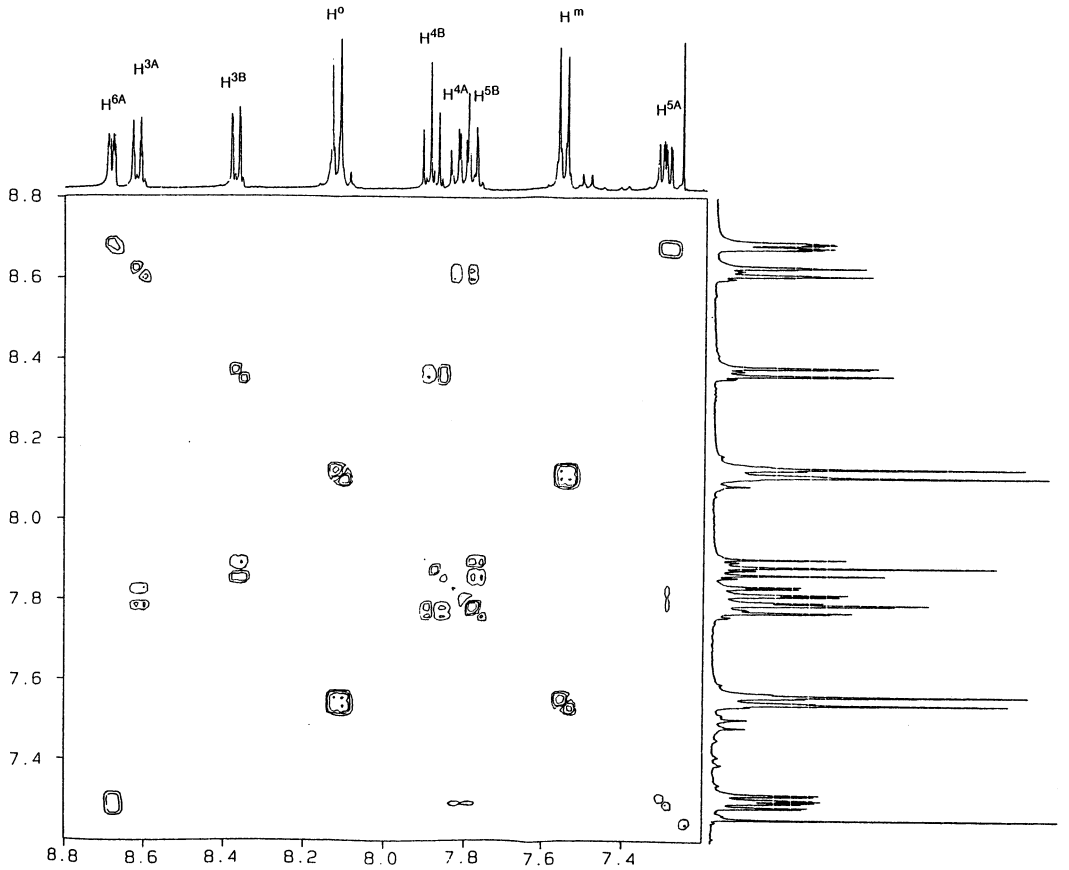
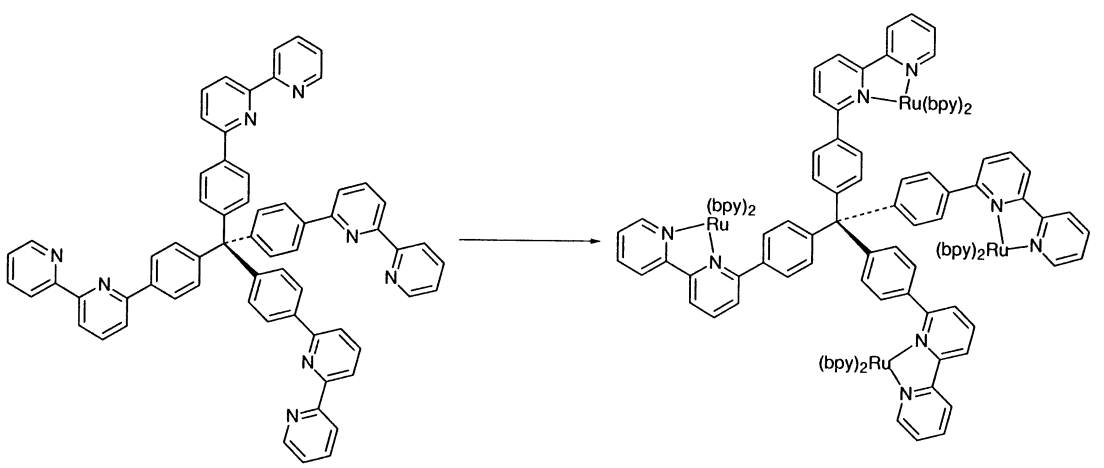


Fig. 3. 250 MHz ^{1}H NMR COSY spectrum of a CD_3CN solution of **8** showing the assignments and the numbering scheme adopted.



Scheme 3.

3.2.1. Stereochemistry of the tetraruthenametallostar

A pseudo-octahedral *tris*chelate complex is chiral [25] and each of the {Ru(bpy)$_3$} motifs in the tetraruthenametallostar [**8**{Ru(bpy)$_2$}$_4$][PF$_6$]$_8$ represents a chiral centre. Using the conventional nomenclature for such centres, five diastereomers, denoted (ΔΔΔΔ), (ΔΔΔΛ), (ΔΔΛΛ), (ΔΛΛΛ) and (ΛΛΛΛ) are possible. Of these, the (ΔΔΔΔ) and (ΛΛΛΛ) pair are related as enantiomers, as are the (ΔΔΔΛ) and (ΛΛΛΔ) pair. The remaining diastereomer, (ΔΔΛΛ), is an achiral *meso* form with S_4 symmetry. The question was, whether any diastereoselectivity is observed or whether a product with fuzzy stereochemistry consisting of a mixture of the possible diastereomers had been obtained. Chro-

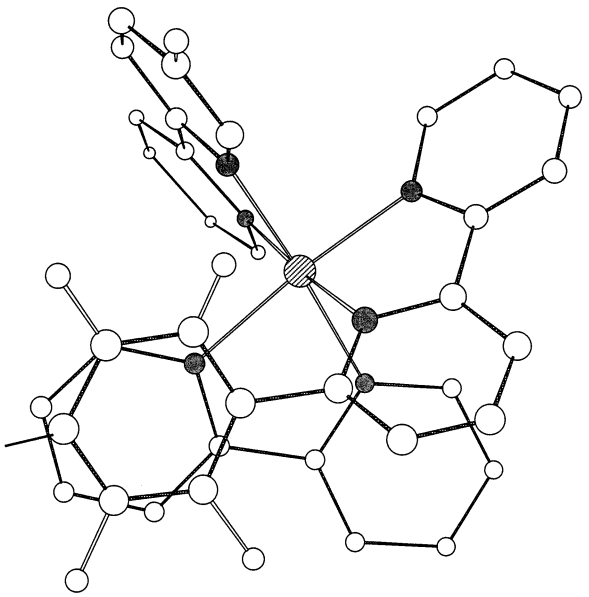


Fig. 4. A view of a single $\{Ru(bpy)_3\}$ unit in $[\mathbf{8}\{Ru(bpy)_2\}_4][PF_6]_8$ showing how the stacking of the C and D rings (Fig. 5) leads to the magnetic non-equivalence of the phenylene protons. All protons except those attached to the phenylene ring have been removed for clarity.

matography indicated the presence of a single species, although the various diastereomers might be expected to exhibit very similar characteristics.

The ^{13}C NMR spectrum of $[\mathbf{8}\{Ru(bpy)_2\}_4][PF_6]_8$ exhibits a total of 35 resonances, as expected for a single diastereomer with magnetically equivalent (or indistinguishable) arms, although the signals tentatively assigned to the phenylene spacer were broadened and showed signs of additional, very poorly resolved, splitting. A single resonance at δ 64.4 is observed for the central carbon atom. This argues for diastereoselective formation of a single diastereomer (or pair of enantiomers).

In order to simplify the initial analysis of the ^1H NMR spectrum, we prepared the analogous compound $[\mathbf{8}\{Ru(bpy\text{-}d_8)_2\}_4][PF_6]_8$ from $[Ru(bpy\text{-}d_8)_2Cl_2]$. The ^1H NMR spectrum of this complex will only exhibit resonances due to the ligand **8**. As far as the protons associated with the various bpy metal-binding domains are concerned, the spectrum is consistent with a single solution species, in accord with the ^{13}C NMR data. Table 1 presents the ^1H NMR data for ligand **8** in $[\mathbf{8}\{Ru(bpy\text{-}d_8)_2\}_4][PF_6]_8$ and for comparison includes

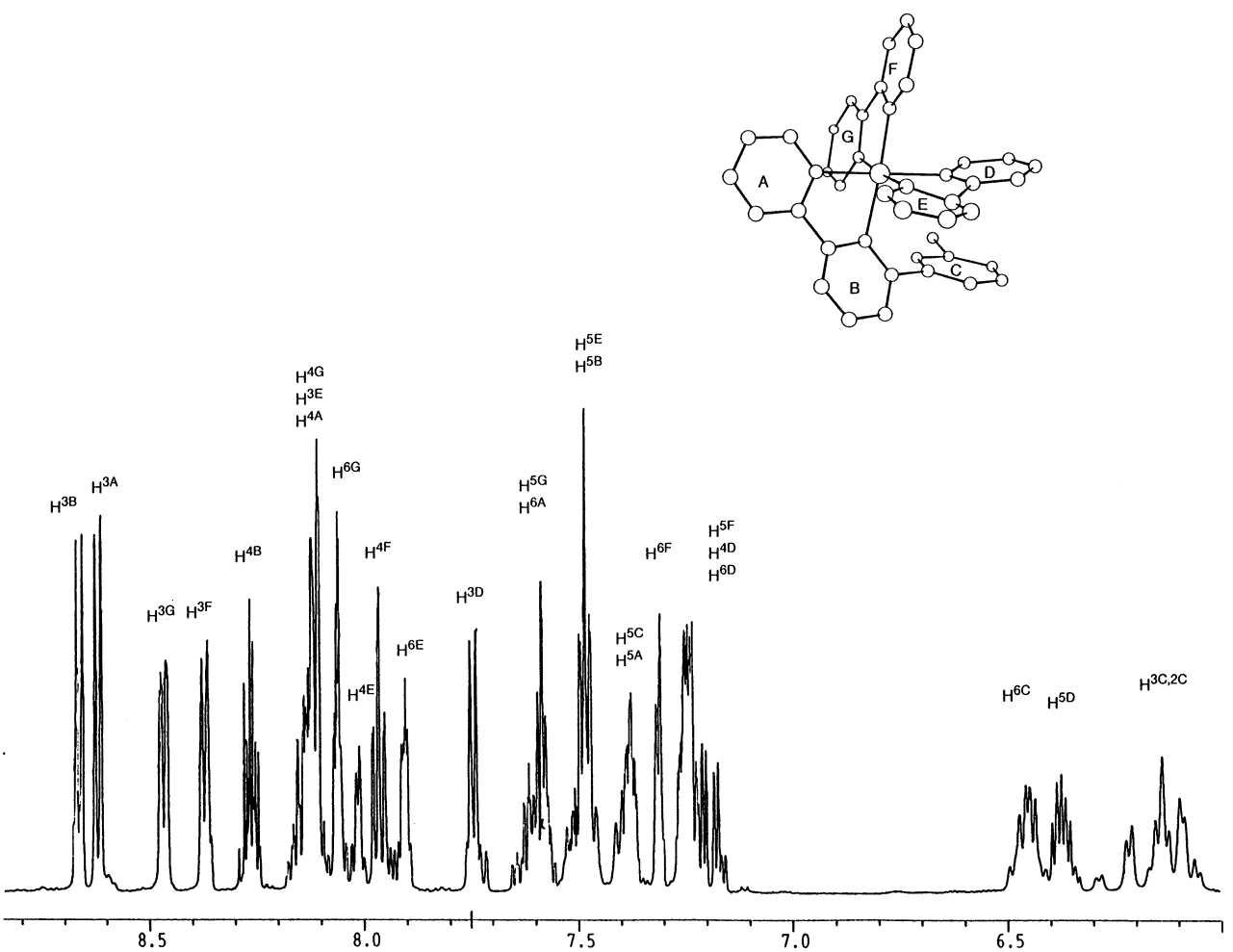


Fig. 5. 600 MHz ^1H NMR spectrum of a CD_3CN solution of $[\mathbf{8}\{Ru(bpy)_2\}_4][PF_6]_8$ showing the assignments and the numbering scheme adopted.

data for the mononuclear model compound $[Ru(bpy)_2(\mathbf{9})]^{2+}$; all assignments were made on the basis of COSY spectroscopy. It is remarkable how closely the two sets of data correlate with each other — the only significant differences arise with the phenylene ring C. Firstly, it is also apparent that the four protons of the phenylene ring appear as four separate resonances. We have commented upon this phenomenon in earlier discussions of the spectrum of $[Ru(bpy)_2(\mathbf{9})]^{2+}$ salts. Ring C is stacked and approximately coplanar with the bpy ring D (Fig. 4). The consequence is that the two *ortho* and the two *meta* protons of ring C are no longer magnetically equivalent. One *ortho* and one *meta* proton lie on the 'outside' of the bpy ring, whilst the other two are on the 'inside'. Initial assignments of the phenylene protons were made on the basis of COSY spectra; the δ 6.40 and 7.30 resonances were strongly coupled and showed only very weak cross peaks to the δ 5.90 and 6.09 peaks, which were also strongly coupled to one another. However, inspection of the spectrum at various fields (250, 300 and 600 MHz) reveals that each of the signals assigned to the phenylene ring protons is a cluster of three or four overlapping resonances. We have been unable to assign the protons unambiguously. Even at 600 MHz we have been unable to resolve the various sub-spectra, but this observation provides extremely strong evidence for a random assembly of Δ and Λ units to give a complex with fuzzy stereochemistry.

The 600 MHz ^{1}H NMR spectrum is presented in Fig. 5 showing the final assignments made on the basis of COSY experiments and illustrating the multiple subspectra observed for the phenylene protons. The final assignments are compared with those for in Table 1. Overall, the similarity of the spectra of the two compounds is remarkable.

Molecular modelling studies (Fig. 6) indicate that the tetraruthenastar compound possesses a diameter of about 25 Å. The overall structure does not obviously vary greatly as the relative stereochemistry at the metal centres is varied and in no diastereomer are there serious steric interactions between the $\{Ru(bpy)_3\}$ motifs.

4. Conclusions

We have prepared two core compounds for the preparation of metallostars based upon bpy metal-binding motifs. The highly conjugated structure **6** did not coordinate to iron(II), copper(I) or ruthenium(II) centres. In contrast, the non-planar tetrakis(bpy) ligand **8** gave a tetraruthenametallostar containing four $\{Ru(bpy)_3\}$ motifs. NMR data indicate that a fuzzy assembly process has occurred to give a random mixture of diastereoisomers. The $\{Ru(bpy)_3\}$ motifs are sufficiently remote from each other that they behave as essentially independent sub-units and are to all intents and purposes isochronous. Only the phenylene spacer groups are sensitive to the asymmetric environment and act as spectators for the fuzziness.

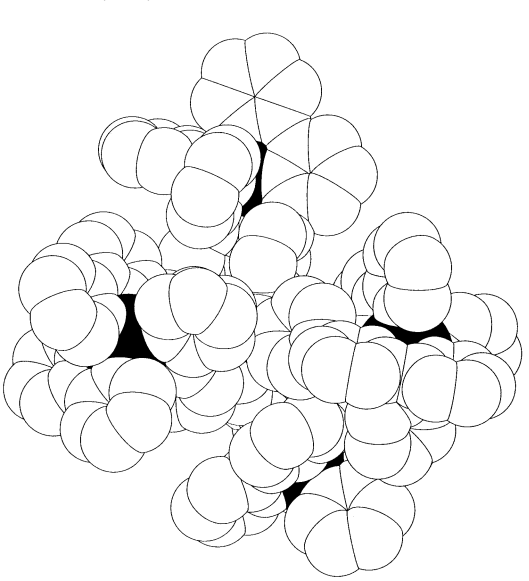


Fig. 6. Modelled structure of $[\mathbf{8}\{Ru(bpy)_2\}_4][PF_6]_8$. The homochiral complex is shown, although the heterochiral systems do not exhibit any significant interactions between the $\{Ru(bpy)_3\}$ motifs.

Acknowledgements

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