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Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
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Carboranyl cluster-functionalised ligands for metallosupramolecular chemistry

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To cite this Article Armspach, Dominique , Constable, Edwin C. , Housecroft, Catherine E. , Neuburger, Markus and Zehnder, Margareta(1996) 'Carboranyl cluster-functionalised ligands for metallosupramolecular chemistry', Supramolecular Chemistry, 7: 2, 97 — 100
To link to this Article: DOI: 10.1080/10610279608035181
URL: http://dx.doi.org/10.1080/10610279608035181

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SUPRAMOLECULAR CHEMISTRY, Vol. 7, pp. 97–100
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COMMUNICATION

Carboranyl cluster-functionalised ligands for metallosupramolecular chemistry

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(Received April 18, 1995)

A series of 2,2':6',2''-terpyridine ligands bearing *ortho*-carboranyl substituents have been prepared by a variety of routes, and the crystal structure of one such compound determined (monoclinic, $P2_1/n$, a = 12.796(1). b = 9.624(1), c = 19.097(1)Å, β = 92.687(6)°, V = 2349.2(3) Å^3, R_w = 0.051).

The incorporation of main-group element or metal clusters into defined supramolecular assemblies offers a challenge to the synthetic chemist and holds the promise of accessing novel materials.[1] We have recently become interested in boron-rich supramolecules, and have developed our metallosupramolecular methodology[2] to include cluster-functionalised ligands; such ligands can then be used to form metallosupramolecules of known nuclearity containing a defined number of spatially separated clusters in a precisely coded manner. In this communication we describe our prototype cluster-functionalised ligands in which *ortho*-carboranyl groups are covalently linked to 2,2':6',2''-terpyridine (tpy) metal-binding domains.[3] This work is conceptually different from the numerous studies of metalloboranes with direct cluster-metal interactions,[4] and to the best of our knowledge there are very few systematic studies of the coordination behaviour of cluster compounds bearing metal-binding substituents.[5]

The *ortho*-carborane unit is conveniently prepared from the reaction of an alkyne with $B_{10}H_{14}$. We considered two approaches: a) preparation of alkynyl-substituted tpy ligands and subsequent reaction with $B_{10}H_{14}$ and b) preparation of a functionalised *ortho*-carborane followed by attachment of the tpy. Initially we pursued approach a. The reaction of **1**[6] with $HC{\equiv}CCH_2Br$ gave **2** as a white solid in 56% yield,[7] but the subsequent reaction of **2** with $B_{10}H_{14}$ gave **3** in less than 1% yield. Although analogues of **2** could be prepared by the treatment of **1** with $HC{\equiv}C(CH_2)_nBr$, their reactions with $B_{10}H_{14}$ were equally low-yielding. (Scheme 1)

We then considered approach b, in which a pre-formed *ortho*-carborane is attached to the tpy domain. The reaction of $HC{\equiv}C(CH_2)_3Cl$ with $B_{10}H_{14}$ followed by metathesis with NaI in acetone gave the 3-iodopropyl-substituted *ortho*-carborane **4** in 52% yield.[8] This electrophilic *ortho*-carborane derivative reacts with **1** to give 5% yield of 3-*ortho*-carboranylpropoxy-2,2':6',2''-terpyridine (**5**) as a white crystalline solid.[9] In order to unambiguously establish the formation of **5** we have determined its crystal and molecular structure[10] (Fig. 1a).[2] The tpy adopts the expected[11] *trans,trans* arrangement of the pyridine rings about the interannular C-C bonds and is approximately planar. The cluster unit is ordered, and the structural analysis confirms the presence of the *ortho*-carboranyl substituent. All of the B-B and B-C bond distances and angles within the cluster are within the normal limits.[12] In the solid state a particularly beautiful structure is adopted, in which the tpy and carborane domains partition to give columns of stacked tpy units and channels of hydrophobic carborane groups (Fig. 1b).

Although we had reached our target of a carboranyl substituted ligand, the yields were unacceptably low. Accordingly, we wondered whether it might be more profitable to investigate reactions of *coordinated* tpy domains rather than the free ligands. Initially we considered an extension of approach a. Attempts to coordinate the ligand **2** to a ruthenium(II) centre prior to reaction with $B_{10}H_{14}$ were also unsuccessful. Although the complex $[RuCl_3(\mathbf{2})]$ could be isolated, reaction of this with a further equivalent of **2** resulted in partial hydrolysis of the propargylic ether. The ruthenium complex $[Ru(\mathbf{1})_2][PF_6]_2$ is readily prepared and reacts smoothly with

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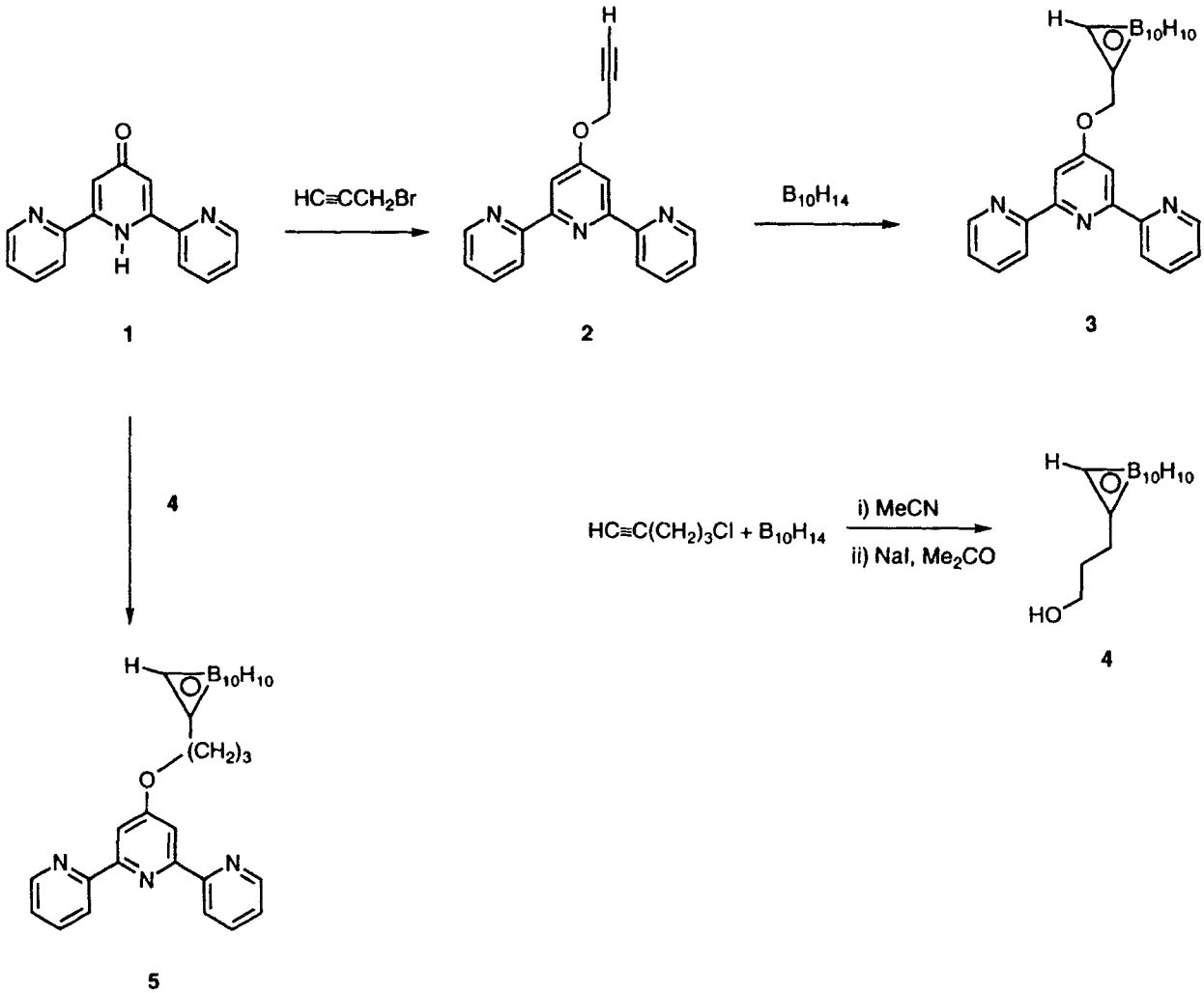

Scheme 1

$HC{\equiv}CCH_2Br$ to give the complex $[Ru(\mathbf{2})_2][PF_6]_2$ in 82% isolated yield. Conversion of the coordinated ligand **2** to **3** by reaction with $B_{10}H_{14}$ was successful, and the complex $[Ru(\mathbf{3})_2][PF_6]_2$ was isolated in 27% yield. Although this represents a considerable improvement over the 1% yield of the free ligand **3**, the success is not unqualified, and in addition to $[Ru(\mathbf{3})_2][PF_6]_2$, significant amounts of the compounds $[Ru(\mathbf{3})(\mathbf{1})][PF_6]_2$ (41%) and $[Ru(\mathbf{1})_2][PF_6]_2$ (6%), arising from reductive cleavage of the propargylic ether, were isolated.[13]

Finally, we adapted route b to reactions of coordinated tpy ligands. The reaction of $[Ru(\mathbf{1})_2][PF_6]_2$ with **4** gave the complex $[Ru(\mathbf{5})_2][PF_6]_2$ in 31% isolated yield. Interestingly, this reaction also gave 25% of a second complex which we have characterised as $[Ru(\mathbf{5})(\mathbf{6})][PF_6]$ in which one of the *ortho*-carborane groups has undergone a boron extrusion process to generate an anionic *nido* cluster. Much of the remainder of the ruthenium may be accounted for in the neutral *bis*(*nido*) complex $[Ru(\mathbf{6})_2]$. This extremely insoluble, Zwitterionic, species may also be prepared directly by the treatment of $[Ru(\mathbf{5})_2][PF_6]_2$ or $[Ru(\mathbf{5})(\mathbf{6})][PF_6]$ with base.[14] We have observed a similar pattern of reactivity in a second generation of ligands in which the carborane cluster is directly attached to the tpy domain.[15] (Scheme 2)

Each of these ruthenium complexes is electrochemically active. In acetonitrile solution, $[Ru(\mathbf{5})_2][PF_6]_2$ exhibits a reversible ruthenium(II)/(III) process at +0.75 V *vs* Fc/Fc^+. This is strictly comparable to the model complex $[Ru(EtOtpy)_2][PF_6]_2$ (EtOtpy = 4'-ethoxy-2,2':6',2"-terpyridine) which exhibits a ruthenium(II)/(III) process at +0.742 V. In other words, the presence of the carborane does not significantly perturb the metal-centred redox processes. The complex with a single anionic *nido* ligand, $[Ru(\mathbf{5})(\mathbf{6})][PF_6]$ shows a ruthenium (II)/(III) process which is modestly shifted to lower potential (+0.72 V *vs* Fc/Fc^+). This provides further support for the suggestion that the spatial separation between the metal and the carborane is such that there is no significant perturbation of the metal-centred energy levels.

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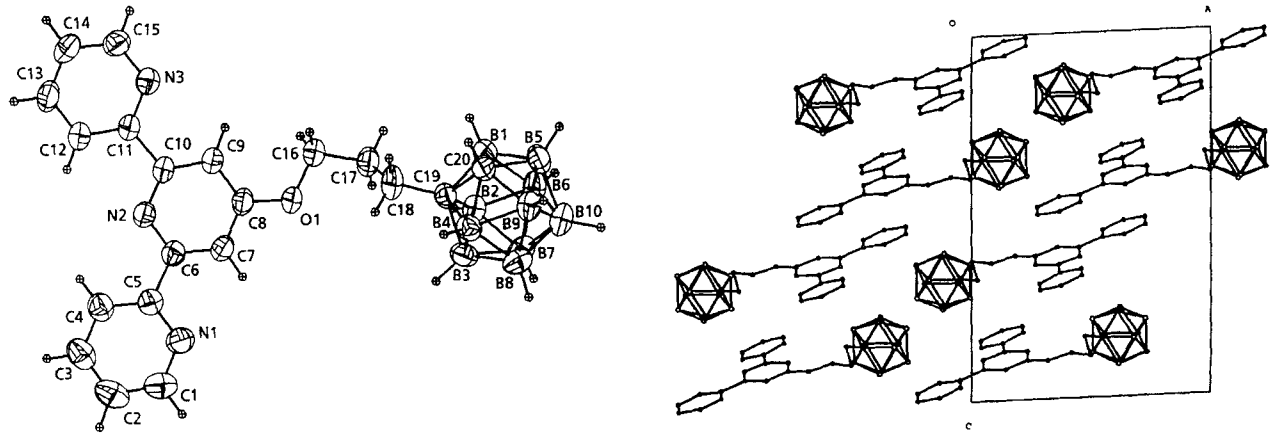
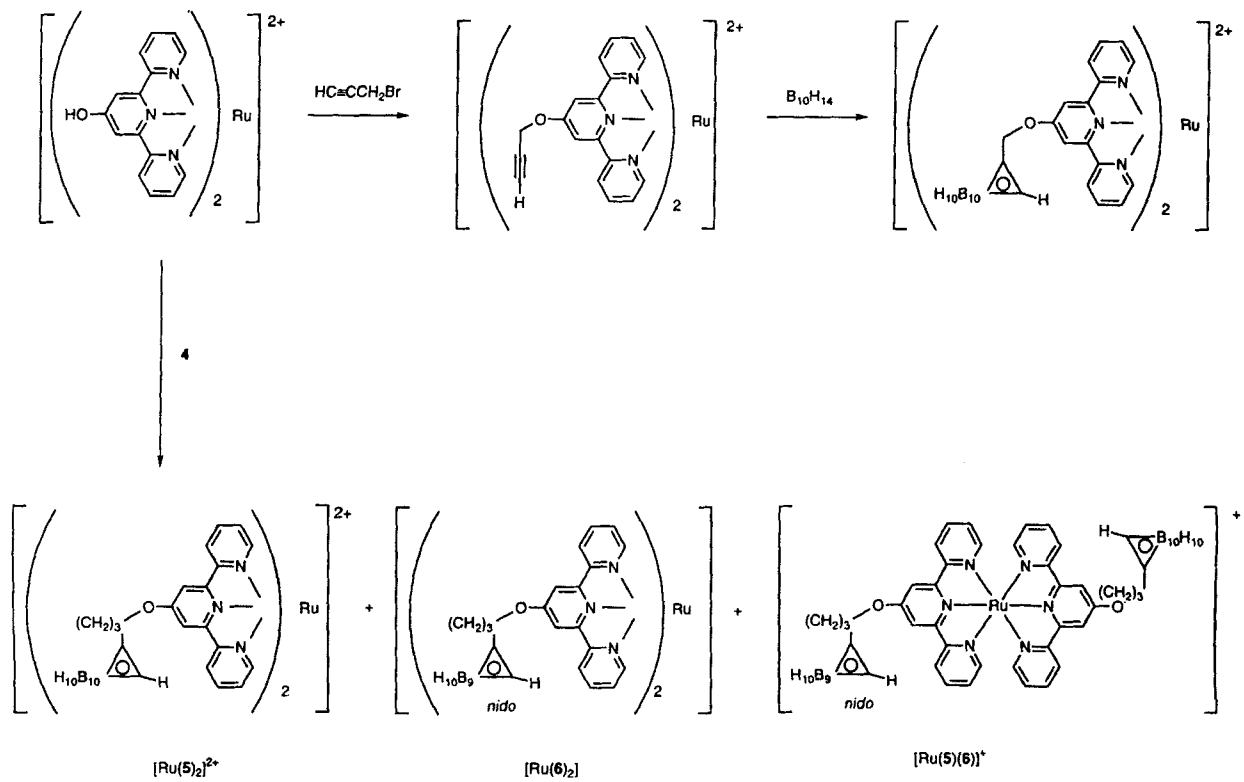


Figure 1 (a) Crystal structure of **5**. Selected distances [Å] and angles [°]: C(19)-B(1), 1.718(2), C(19)-B(2), 1.706(2), C(19)-B(3), 1.700(2), C(19)-B(4), 1.727(2), C(20)-B(1). 1.711(2), C(20)-B(4), 1.696(2), C(20)-B(5), 1.692(2), C(20)-B(9), 1.693(2); B(1)-C(19)-B(2), 62.08(8), C(18)-C(19)-B(3), 121.5(1), C(20)-C(19)-B(3), 109.18(9), B(1)-C(19)-B(3), 113.57(9), B(2)-C(19)-B(3), 62.82(8), C18-C(19)-B(4), 115.02(9), C(20)-C(19)-B(4), 60.16(7), B(1)-C(19)-B(4), 112.80(9), B(2)-C(19)-B(4), 113.36(9), B(3)-C(19)-B(4), 61.86(8), C(19)-C(20)-B(1), 61.34(7), C(19)-C(20)-B(4), 62.00(7), B(1)-C(20)-B(4), 114.70(9), C(19)-C(20)-B(5), 112.01(9), B(1)-C(20)-B(5), 62.76(8), B(4)-C(20)-B(5), 115.1(1), C(19)-C(20)-B(9), 112.34(9), B(1)-C(20)-B(9), 115.34(9), B(4)-C(20)-B(9), 62.56(8), B(5)-C(20)-B(9), 63.46(8), and (b) a view along *b* showing the stacked tpy domains and the hydrophobic carborane channels in the lattice.

In conclusion, we have demonstrated the viability of using metal-directed reactions of coordinated tpy ligands for the preparation of cluster-functionalised complexes. We are currently exploring dendritic systems incorporating significant numbers of such ligands, and alternative routes for the synthesis of tpy domains bearing carboranyl and other cluster moieties as substituents.

ACKNOWLEDGEMENTS

This research was supported by the Schweizerischer Nationalfonds zur Förderung der wissenenschaftlichen Forschung (Grant numbers 21-37325.93 and 21-42027.94) and the University of Basel for financial support.



Scheme 2

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7 All new compounds were fully characterised and will be described in detail in a full paper.

8 **4**: A solution of decaborane (2.000 g, 16.35 mmol) in anhydrous acetonitrile (25 mL) was refluxed under argon for 2 h whereupon the solvent was removed by distillation. The yellow residue was then suspended in dry toluene (25 mL) and 5-chloro-1-pentyne (2.400 g, 23.35 mmol) was added. The reaction mixture was refluxed for 12 h. Evaporation of the solvent gave an yellow oily residue which was redissolved in CH_2Cl_2 and extracted with deionised water. The organic phase was then dried over $MgSO_4$ before being evaporated to dryness *in vacuo*. The residue was subjected to column chromatography [SiO_2, Hexane-CH_2Cl_2 (4:2)] to afford a colourless solid (2.100 g) which was dissolved in dry acetone (20 mL). Sodium iodide (1.400 g, 9.34 mmol) was added to the solution and the reaction mixture was refluxed for 12 h. After cooling to room temperature, the NaCl precipitate was removed by filtration, and the filtrate was evaporated to dryness *in vacuo*. Recrystallisation of the residue from heptane afforded **4** (2.700 g, 53%) as a colourless solid. [M. p. 55.5–56°C; ^{1}H NMR ($CDCl_3$): δ 1.1–3.3 (br m, 10H); 1.78–2.00 (m, 2H), 2.52–2.71 (m, 2H), 3.10 (t, ^3J = 6.0 Hz, 2H), 3.55 (br s, 1H); ^{13}C NMR ($CDCl_3$): δ 3.65, 32.34, 38.87, 61.52, 74.10; ^{11}B NMR ($CDCl_3$): δ-13.1 (d, 2B), −12.2 (d, 2B), −11.8 (d, 2B), −9.3 (d, 2B), −5.7 (d, 1B), −2.3 (d, 1B); MS (EI):*m/z* 311 [M^+], 183 [M-I^-]].

9 **5**: A stirred solution of **1** (0.500 g, 2.01 mmol) in acetonitrile (10 mL) was treated with potassium carbonate (2.5 g, 10.7 mmol), followed by **4** (0.627 g, 2.01 mmol). The suspension was heated at 60°C under nitrogen for 12 h whereupon it was filtered over celite. The filtrate was evaporated to dryness *in vacuo* to give a white residue which was subjected to column chromatography [SiO_2, CH_2Cl_2-MeOH-concentrated aqueous NH_3 solution (88:11:1)] to afford **5** (0.050 g, 6%) as colourless crystals after recrystallisation from CH_2Cl_2-pentane. [M. p. 179–180°C; ^{1}H NMR ($CDCl_3$): δ 1.2–3.2 (br m, 10H); 1.94–2.05 (m, 2H), 2.40–2.48 (m, 2H), 3.61 (br s, 1H); 4.17 (t, ^3J = 6.1 Hz, 2H), 7.29–7.33 (m, 2H), 7.83 (dt, ^3J = 1.9 Hz, ^3J = 7.5 Hz, 2H), 7.94 (s, 2H), 8.59 (d, ^3J = 8.0 Hz, 2H), 8.65 (d, ^3J = 4.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 28.85, 34.96, 61.60, 66.32, 74.55, 107.10, 121.34, 123.96, 136.86, 149.03, 155.86, 157.23, 166.62; ^{11}B NMR ($CDCl_3$): δ −13.0 (d, 2B), −11.8 (d, 4B), −9.2 (d, 2B), −5.7 (d, 1B), −2.2 (d, 1B); MS (FAB): *m/z* 434 [M+H^+]].

10 X-ray structure analysis of **5**: $C_{20}H_{27}B_{10}N_3O$, monoclinic, space group $P\,2_1/n$, a = 12.796(1), b = 9.624(1), c = 19.097(1)Å, β = 92.687(6)°, V = 2349.2(3) Å^3, M_r = 433.57, Z = 4, ρ_{calc} = 1.23 g cm^{-3}, F(000) 906, Enraf-Nonius CAD4 diffractometer, Cu-K_α radiation, λ = 1.54178 Å, μ = 4.897 cm^{-1}. ω/2θ scan technique, 5297 independent reflections, 4167 reflections used in refinement, final R = 0.043, R_w = 0.051, Chebychev weighting scheme (J.R. Carruthers, D.J. Watkin, *Acta Crystallogr., Sect. A*, **1979**, *35*, 698). Diffraction absorption correction was determined by φ scans. The hydrogen atoms were included in calculated positions. The structure was solved by direct methods using SIR92 (C. Giacovazzo, University of Bari, 1992) and refined using CRYSTALS (CRYSTALS, Issue 9, Watkin, D.; Chemical Crystallography Laboratory, Oxford, 1990)

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13 [Ru(**3**)$_2$][PF_6]$_2$: A solution of decaborane (0.015 g, 0.12 mmol) in anhydrous acetonitrile (2 mL) was refluxed under argon for 2 h whereupon [Ru(**2**)$_2$][PF_6]$_2$ (0.050 g, 0.05 mmol) was added. The reaction mixture was then refluxed for 12 h. Removal of the solvent in vacuo afforded a red solid which was subjected to column chromatography [SiO_2, MeCN-saturated aqueous KNO_3 solution (9:1)] to afford in order of their elution and after ion-exchange [Ru(**3**)$_2$][PF_6]$_2$ (0.017 g, 27%), [Ru(**3**)(**1**)][PF_6]$_2$ (0.025 g, 41%) and [Ru(**1**)$_2$][PF_6]$_2$ (0.003 g, 6%). [[Ru(**3**)$_2$][PF_6]$_2$: ^{1}H NMR (CD_3CN): δ 1.1–3.5 (br m, 20H), 4.70 (br s, 2H), 5.04 (s, 4H), 7.14–7.19 (m, 4H), 7.33 (d, ^3J = 4.8 Hz, 4H), 7.91 (dt, ^3J = 1.4 Hz, ^3J = 8.0 Hz, 4H), 8.32 (s, 4H), 8.43 (d, ^3J = 8.2 Hz, 4H); ^{13}C NMR (CD_3CN): δ 61.80, 71.31, 98.08, 112.10, 125.38, 128.57, 138.91, 153.53, 157.57, 158.91, 165.34; ^{11}B NMR (CD_3CN): δ −12.5 (d, 4B), −11.1 (d, 8B), −8.9 (d, 4B), −4.0 (d, 2B), −2.5 (d, 2B); MS (FAB): 1057 [M-[PF_6]$^+$], 911 [M-2×[PF_6]$^+$], 755 [M-2×[PF_6]-[$CH_2C_2B_{10}H_{11}$]$^+$], 598 [M-2×[PF_6]-2×[$CH_2C_2B_{10}H_{11}$]$^+$]].

14 [Ru(**5**)$_2$][PF_6]$_2$: A stirred solution of [Ru(**1**)$_2$][PF_6]$_2$ (0.200 g, 0.22 mmol) in acetonitrile (20 mL) was treated with potassium carbonate (0.200 g, 1.45 mmol), followed by **4** (0.155 g, 0.50 mmol). The suspension was heated at 60°C under nitrogen for 24 h whereupon it was filtered over celite. Water (10 mL) and saturated methanolic [NH_4][PF_6] solution (5 mL) was added to the filtrate. Partial removal of the solvents *in vacuo* caused a red solid to precipitate. The product was collected by filtration, washed with a mixture of water and ethanol, and diethyl ether. The mixture of complexes was subjected to preparative thin-layer chromatography [SiO_2, MeCN-saturated aqueous KNO_3 solution (7:1)] to afford in order of their elution, and after ion-exchange [Ru(**5**)(**6**)][PF_6] (0.060 g, 24%) and [Ru(**5**)$_2$][PF_6]$_2$ (0.085 g, 30%). [Ru(**5**)$_2$][PF_6]$_2$: ^{1}H NMR (CD_3CN): δ 1.1–3.5 (br m, 20H), 2.15–2.23 (m, 4H), 2.63–2.69 (m, 4H), 3.59 (br s, 2H), 4.47 (t, ^3J = 6.1 Hz, 4H), 7.13–7.17 (m, 4H), 7.36 (d, ^3J = 4.8 Hz, 4H), 7.88 (dt, ^3J = 1.4 Hz, ^3J = 7.8 Hz, 4H), 8.26 (s, 4H), 8.45 (d, ^3J = 7.5 Hz, 4H); ^{13}C NMR (CD_3CN): δ 29.55, 34.74, 63.70, 69.50, 76.68, 111.87, 125.26, 128.37, 138.71, 153.45, 157.40, 159.20, 166.52; ^{11}B NMR (CD_3CN) δ −12.5 (d, 4B), −11.4 (d, 8B), −9.4 (d, 4B), −5.7 (d, 2B), −2.6 (d, 2B); MS (FAB): 1113 [M-[PF_6]$^+$], 967 [M-2×[PF_6]$^+$], 783 [M-[PF_6]-[$(CH_2)_3C_2B_{10}H_{11}$]$^+$], 598 [M-[PF_6]-2×[$(CH_2)_3C_2B_{10}H_{11}$]$^+$]].

15 Armspach D.; Constable E.C.; Housecroft C.E.; König, M. Unpublished results.

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