Electronic Supporting Information

Thermochromic organometallic complexes: experimental and theoretical studies of 16- to 18-electron interconversions of adducts of arene Ru(II) carboranes with pyridines

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S.1. EXPERIMENTAL

S.1. Materials

$RuCl_3.3H_2O$ was purchased from Alfa-Aesar. Anhydrous quality of ethanol, tetrahydrofuran and dichloromethane were used (Aldrich). 1,2-dicarba-*closo*-dodecarborane was purchased from Katchem and used as received. Pyridine and imidazole derivatives and all other reagents were obtained from commercial suppliers and used as received. The preparations of the starting material $[Ru(\eta^6\text{-}p\text{-cym})Cl_2]_2$,[1] of the 16-electron precursor $[Ru(\eta^6\text{-}p\text{-cym})$(1,2-dicarba-*closo*-dodecaborane-1,2-dithiolato)] (**1**)[2] and of the 18-electron complex $[Ru(\eta^6\text{-}p$-cym)(1,2-dicarba-*closo*-dodecaborane-1,2-dithiolato)(pyridine)] (**7**)[2] were based on previous reports.

S.2. Instrumentation

NMR Spectroscopy. ^1H, ^{11}B, $^{11}B\{^1H\}$, ^{13}C, and 2D ^1H-^1H spectra were acquired in 5 mM NMR tubes at 298 K on either Bruker DPX-400 or Bruker DRX-500 spectrometers (frequencies: ^1H NMR: 400 MHz, ^{11}B NMR: 160 MHz, ^{13}C NMR: 125 MHz). ^1H NMR and ^{13}C NMR chemical shifts were internally referenced to TMS using $CHCl_3$ (7.27 ppm), and ^{11}B NMR chemical shifts were internally referenced to BF_3–OEt_2 at 0.0 ppm. All data processing was carried out using TOPSPIN version 2.0 (Bruker U.K. Ltd.).

UV-visible spectroscopy. UV-visible absorption spectra were recorded on a temperature-controlled Varian CARY 300 Biospectrophotometer using 1-cm path-length quartz cuvettes (0.5 mL).

Infrared spectroscopy. Infrared spectra of the solids were recorded as powder on a Perkin-Elmer Spectrum One FT-IR spectrometer.

Elemental analysis. Elemental analysis (carbon, hydrogen, nitrogen) was carried out by Warwick Analytical Service using an Exeter analytical elemental analyser (CE440).

S.1.3. Synthesis of complexes 2–6

A mixture of complex **1** (60 mg, 0.14 mmol), with the pyridine or imidazole derivative (4-dimethylaminopyridine: 16.6 mg (**2**); nicotinamide: 16.6 mg (**3**), 3-ethynylpyridine: 14.0 mg (**4**), *N*-metylimidazole: 11.2 mg (**5**), or 4-cyanopyridine: 14.2 mg (**6**)) in dry dichloromethane (30 mL) under a nitrogen atmosphere was stirred at ambient temperature for 24 h. The solvent was then evaporated, the residue was dissolved in dichloromethane (2 mL), and hexane was slowly added to precipitate a yellow solid which was filtered and dried under vacuum.

[Ru(*p*-cym)(1,2-dicarba-*closo*-dodecaborane-1,2-dithiolato)(4-dimethylaminopyridine)] (2): Yield: 59.7 mg, (78 %). UV-vis (1.0×10^{-4} M, CH_2Cl_2): λ_{max} 352 nm ($\varepsilon = 3.86 \times 10^3$ $M^{-1}\cdot cm^{-1}$), λ_{max} 454 nm ($\varepsilon = 0.89 \times 10^3$ $M^{-1}\cdot cm^{-1}$), λ_{max} 632 nm ($\varepsilon = 0.64 \times 10^3$ $M^{-1}\cdot cm^{-1}$). IR: ν = 2980 (s, $CH_{aromatic}$), 2569 (m, BH), 2568 (m, BH), 2567 (m, BH), 1385 (w, $CN_{aromatic}$) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, ^3J (H,H) = 7.1 Hz, 2 H, H_a), 6.41 (d, 2 H, H_b), 5.17 (m, 2 H, $H_{p\text{-cym}}$), 5.03 (m, 2 H, $H_{p\text{-cym}}$), 2.56 (sept, ^3J (H,H) = 6.9 Hz, 1 H, C**H**$(CH_3)_2$), 2.00 (s, 3 H, CH_3), 1.16 (d, 6 H, CH(C**H**$_3)_2$) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = -8.02 ($B_{3,6}$, 2 B); -8.55 ($B_{4,5,7,11}$, 4 B); -11.22 ($B_{8,10}$ and $B_{9,12}$, 4 B) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 154.4 (**C**H_a), 153.5 (**C**H_b), 107.3 (**C**$_{p\text{-cym}}$), 93.9 (**C**$_{carborane}$), 84.9 (**C**$H_{p\text{-cym}}$), 84.5 (**C**$H_{p\text{-cym}}$), 39.2 (**C**$H(CH_3)_2$), 22.5 (CH(**C**$H_3)_2$), 18.1 (**C**H_3) ppm. Elemental analysis calcd (%) for [$C_{19}H_{34}B_{10}N_2RuS_2$ + ½CH_2Cl_2]: C 38.63, H 5.82, N 4.62; found: C 38.46, H 5.83, N 4.84.

[Ru(*p*-cym)(1,2-dicarba-*closo*-dodecaborane-1,2-dithiolato)(nicotinamide)] (3): Yield: 54.4 mg, (71 %). UV-vis (1.0×10^{-4} M, CH_2Cl_2): λ_{max} 352 nm ($\varepsilon = 8.89 \times 10^3$ $M^{-1}\cdot cm^{-1}$), λ_{max}

454 nm (ε = 0.70 × 10^3 $M^{-1}\cdot cm^{-1}$), λ_{max} 632 nm (ε = 1.98 × 10^3 $M^{-1}\cdot cm^{-1}$). IR: ν = 2979 (s, $CH_{aromatic}$), 2901 (s, $CH_{aromatic}$), 2576 (m, BH), 1694 (s, CO_{amide}), 1393 (w, $CN_{aromatic}$) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.08 (s, 1 H, H_a), 8.83 (m, 1 H, H_b), 8.18 (m, 1 H, H_c), 7.40 (m, 1 H, H_d), 5.41 (m, 2 H, $H_{p\text{-cym}}$), 5.37 (m, 2 H, $H_{p\text{-cym}}$), 2.54 (m, 1 H, C**H**$(CH_3)_2$), 2.11 (s, 3 H, CH_3), 1.21 (d, ^3J (H,H) = 6.9 Hz, 6 H, CH(C**H**$_3)_2$) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): -7.97 ($B_{3,6}$, $B_{4,5,7,11}$ and $B_{8,10}$, 8 B); -10.59 ($B_{9,12}$, 2 B) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 136.2 (**C**H_a), 129.6 (**C**H_b), 123.9 (**C**H_c), 118.4 (**C**H_d), 93.5 (**C**$_{carborane}$), 82.9 (**C**$H_{p\text{-cym}}$), 82.9 (**C**$H_{p\text{-cym}}$), 31.3 (**C**H$(CH_3)_2$), 22.9 (CH(**C**$H_3)_2$), 19.5 (**C**H_3) ppm. Elemental analysis calcd (%) for [$C_{18}H_{30}B_{10}N_2ORuS_2$ + 1CH_2Cl_2]: C 35.18, H 4.97, N 4.32; found: C 34.61, H 4.86, N 4.92.

[Ru(*p*-cym)(1,2-dicarba-*closo*-dodecaborane-1,2-dithiolato)(3-ethynylpyridine)] (4): Yield: 51.1 mg, (69 %). UV-vis (1.0 × 10^{-4} M, CH_2Cl_2): λ_{max} 352 nm (ε = 9.22 × 10^3 $M^{-1}\cdot cm^{-1}$), λ_{max} 454 nm (ε = 0.42 × 10^3 $M^{-1}\cdot cm^{-1}$), λ_{max} 632 nm (ε = 2.09 × 10^3 $M^{-1}\cdot cm^{-1}$). IR: ν = 3295 (m, CH_{alkyne}), 2962 (s, $CH_{aromatic}$), 2910 (s, $CH_{aromatic}$), 2580 (m, BH), 2578 (m, BH), 2576 (m, BH), 1381 (w, $CN_{aromatic}$) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.78 (s, 1 H, H_a), 8.64 (m, 1 H, H_b), 7.80 (d, ^3J (H,H) = 7.6 Hz, 1 H, H_c), 7.29 (m, 1 H, H_d), 5.51 (m, 2 H, $H_{p\text{-cym}}$), 5.50 (m, 2 H, $H_{p\text{-cym}}$), 3.26 (s, 1 H, $H_{C\equiv CH}$), 2.62 (m, 1 H, C**H**$(CH_3)_2$), 2.19 (s, 3 H, CH_3), 1.28 (d, ^3J (H,H) = 6.6 Hz, 6 H, CH(C**H**$_3)_2$) ppm. ^{11}B NMR (100 MHz, $CDCl_3$): δ = -7.85 ($B_{3,6}$ and $B_{8,10}$, 4 B); -8.21 ($B_{4,5,7,11}$, 4 B); -10.57 ($B_{9,12}$, 2 B) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 139.4 (**C**H_a), 131.7 (**C**H_b), 123.5 (**C**H_c), 123.1 (**C**H_d), 120.6 (**C**$_{C\equiv CH}$), 108.2 (**C**$_{p\text{-cym}}$), 93.2 (**C**$_{carborane}$), 89.1 (**C**$_{C\equiv CH}$), 82.3 (**C**$H_{p\text{-cym}}$), 81.0 (**C**$H_{p\text{-cym}}$), 24.1 (**C**H$(CH_3)_2$), 20.9 (CH(**C**$H_3)_2$), 18.0 (**C**H_3) ppm. Elemental analysis calcd (%) for [$C_{19}H_{29}B_{10}NRuS_2$ + 6$CHCl_3$]: C 23.81, H 2.80, N 1.11; found: C 23.95, H 3.12, N 1.42.

[Ru(*p*-cym)(1,2-dicarba-*closo*-dodecaborane-1,2-dithiolato)(*N*-methylimidazole)] (5): Yield: 54.1 mg, (76 %). UV-vis (1.0×10^{-4} M, CH_2Cl_2): λ_{max} 352 nm ($\varepsilon = 4.04 \times 10^3$ $M^{-1}\cdot cm^{-1}$), λ_{max} 454 nm ($\varepsilon = 0.76 \times 10^3$ $M^{-1}\cdot cm^{-1}$), λ_{max} 632 nm ($\varepsilon = 1.12 \times 10^3$ $M^{-1}\cdot cm^{-1}$). IR: ν = 2973 (s, $CH_{aromatic}$), 2901 (s, $CH_{aromatic}$), 2570 (m, BH), 2568 (m, BH), 1378 (w, $CN_{aromatic}$) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.83 (s, 1 H, H_a), 7.13 (m, 1 H, H_b), 6.85 (m, 1 H, H_c), 5.22 (m, 2 H, $H_{p\text{-cym}}$), 5.11 (m, 2 H, $H_{p\text{-cym}}$), 3.74 (s, 3 H, H_{Me}), 2.53 (m, 1 H, C**H**$(CH_3)_2$), 2.08 (s, 3 H, CH_3), 1.14 (d, ^3J (H,H) = 6.9 Hz, 6 H, CH(C**H**$_3)_2$) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = -8.13 ($B_{3,6}$, $B_{8,10}$, and $B_{4,5,7,11}$, 8 B); -11.25 ($B_{9,12}$, 2 B) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 125.6 (**C**H_a), 120.8 (**C**H_b), 120.7 (**C**H_c), 94.1 (**C**$_{carborane}$), 84.7 (**C**$H_{p\text{-cym}}$), 84.7 (**C**$H_{p\text{-cym}}$), 34.7 (**C**$_{Me}$), 30.5 (**C**$H(CH_3)_2$), 22.5 (CH(**C**$H_3)_2$), 17.9 (**C**H_3) ppm. Elemental analysis calcd (%) for [$C_{16}H_{30}B_{10}N_2RuS_2$ + 1CH_2Cl_2]: C 33.55, H 5.03, N 4.62; found: C 33.34, H 5.28, N 4.87.

[Ru(*p*-cym)(1,2-dicarba-*closo*-dodecaborane-1,2-dithiolato)(4-cyanopyridine)] (6): Yield: 51.9 mg, (70 %). UV-vis (1.0×10^{-4} M, CH_2Cl_2): λ_{max} 352 nm ($\varepsilon = 8.22 \times 10^3$ $M^{-1}\cdot cm^{-1}$), λ_{max} 454 nm ($\varepsilon = 0.77 \times 10^3$ $M^{-1}\cdot cm^{-1}$), λ_{max} 632 nm ($\varepsilon = 1.82 \times 10^3$ $M^{-1}\cdot cm^{-1}$). IR: ν = 2970 (s, $CH_{aromatic}$), 2558 (m, BH), 2241 (w, $CN_{nitrile}$), 1383 (w, $CN_{aromatic}$) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.88 (d, ^3J (H,H) = 6.1 Hz, 2 H, H_a), 7.51 (d, 2 H, H_b), 5.46 (d, ^3J (H,H) = 6.0 Hz, 2 H, $H_{p\text{-cym}}$), 5.43 (d, 2 H, $H_{p\text{-cym}}$), 2.57 (sept, ^3J (H,H) = 6.9 Hz, 1 H, C**H**$(CH_3)_2$), 2.14 (s, 3 H, CH_3), 1.23 (d, 6 H, CH(C**H**$_3)_2$) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = -7.62 ($B_{3,6}$ and $B_{8,10}$, 4 B); -8.52 ($B_{4,5,7,11}$, 4 B); -10.45 ($B_{9,12}$, 2 B) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 151.7 (**C**H_a), 125.3 (**C**H_b), 116.2 (**C**H_c), 93.7 (**C**$_{carborane}$), 82.2 (**C**$H_{p\text{-cym}}$), 80.3 (**C**$H_{p\text{-cym}}$), 31.6 (**C**$H(CH_3)_2$), 22.9 (CH(**C**$H_3)_2$), 19.9 (**C**H_3) ppm. Elemental analysis calcd (%) for [$C_{18}H_{28}B_{10}N_2RuS_2$ + 4CH_2Cl_2]: 29.84, H 4.10, N 3.16; found: C 29.92, H 4.07, N 3.68.

S.1.4. Methods

DFT Calculations. All calculations used the restricted Kohn-Sham density functional theory approach implemented in the ORCA program system version 2.9.1.[3] The Becke-Perdew exchange/correlation functional was employed in conjunction with the resolution of identity approximation, Ahlrich's TZVP basis sets,[4] a conductor-like screening model (COSMO[5-7]) correction for solvation effects, and Grimme's empirical dispersion energy term.[8] The COSMO term used the predefined parameters appropriate to dichloromethane. Geometries of the metal complexes and isolated ligands were optimised to the default convergence limits with Gibbs free energies estimated *via* the usual statistical mechanical procedures. To evaluate the electronic spectroscopic data, the lowest 80 singlet states were computed via time dependent DFT using the same methodology as above save that the exchange-correlation kernel employed the local density approximation. The computed data were analyzed and visualised via ChemCraft.[9]

X-ray Crystallography. X-ray diffraction data for [Ru(*p*-cym)(1,2-dicarba-*closo*-dodecaborane-1,2-dithiolato)(4-dimethylaminopyridine)] (**2**) and [Ru(*p*-cym)(1,2-dicarba-*closo*-dodecaborane-1,2-dithiolato)(*N*-methylimidazole)] (**5**) were obtained on an Oxford Diffraction Gemini four-circle system with a Ruby CCD area detector using Mo K_α radiation.[10] Absorption corrections were carried out using ABSPACK. The crystals were mounted in oil and held at 150(2) K (**2**) and 100(2) K (**5**) with the Oxford Cryosystem Cryostream Cobra. The structure was solved by direct methods using SHELXS (TREF) with additional light atoms found by Fourier methods[11] and refined with SHELXL 97[12] (refinement of F^2 against ALL reflections). Hydrogen atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms. H-atoms were given isotropic displacement parameter equal to 1.2 (or

1.5 for methyl H-atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached. Drawings were made with Ortep-3.

Job plots. All the solutions for obtaining the Job plots were prepared at 10^{-4} M in dichloromethane by successive dilutions in order to minimise the weighting errors. For instance, 10^{-4} M solution of **1** (A) was prepared by dilution (1 mL into 9 mL of dichloromethane) of a 10^{-3} M solution of **1** (4.5 mg of solid **1** dissolved into 10 mL of dichloromethane). A 10^{-4} M solution (B) of the ligand was prepared following the same procedure. The total concentration [**1**] + [ligand] was kept constant at 10^{-4} M, but [**1**]/[ligand] varied and, for each variation (2-x) mL of solution A + x mL of solution B, a UV-visible spectrum was recorded at 298 K. Finally, $X(A-A_0)$ *versus* X was plotted, where X is defined by X = [**1**]/([**1**]+[ligand]), A is the absorbance for the value $0 \leq X \leq 1$, A_0 is the absorbance for X = 0.

UV-visible titrations. All the solutions for UV-visible titrations were prepared at 10^{-4} M in dichloromethane by successive dilutions in order to minimise the weighting errors. For instance, 10^{-4} M solution of **1** (A) was prepared by dilution (1 mL into 9 mL) of a 10^{-3} M solution of **1** (4.5 mg of solid **1** dissolved into 10 mL of dichloromethane). The 10^{-4} M solution (B) of ligand was prepared by adding 20 mol equiv of solid ligand into 8 mL of the 10^{-4} M solution of **1** (A). The solutions were left to equilibrate for 2 minutes before recording the spectra, at 298 K.

Determination of K. From the UV-visible titrations, the binding constants were determined by using the non-linear ThordarsonFittingProgram with MatLab.[13] The files were prepared by using the *fitting1to1uv4*, which is adapted for determination from UV-visible spectra of binding constants for a 1/1 binding process (4 different wavelengths were used in order to

increase the precision of the calculations: 350, 475, 560 and 635 nm were chosen). Each titration was repeated three times, to give an average value of K and standard error.

Determination of ΔG°. The Gibbs free energies were calculated from the Gibbs equation[14] $\Delta G^\circ = - RT\ln(K)$, using the value of K obtained form UV-visible titrations.

S.2. TABLES S1-S5

Table S1. X-ray crystallographic data for complexes **2** and **5**·1.5$CHCl_3$

	2	**5**·1.5$CHCl_3$
Empirical formula	$C_{19}H_{34}B_{10}N_2RuS_2$	$C_{16}H_{30}B_{10}N_2RuS_2$
Crystal size [mm]	0.35×0.24×0.08	0.14×014×0.06
Formula weight	563.77	702.76
Crystal system	monoclinic	triclinic
Space group	P2(1)/n	P-1
a [Å]	12.63006(16)	12.8296(2)
b [Å]	13.44521(15)	14.3571(3)
c [Å]	15.6629(2)	16.7253(4)
α [º]	90.00	87.0579(19)
β [º]	95.8996(11)	89.9426(17)
γ [º]	90.00	76.9564(17)
Volume [$Å^3$]	2645.69(6)	2997.12(11)
Temperature [K]	150(2)	100(2)
Z	4	4
μ [mm^{-1}]	0.763	9.326
Reflections collected	24007	33861
Independent reflections [R_{int}]	6762	33861
*R*1, *wR*2 [$I>2\sigma(I)$]	0.0238, 0.0553	0.0344, 0.0850
*R*1, *wR*2 (all data)	0.0276, 0.0568	0.0384, 0.0877
GOF	1.062	1.032
Δρ max and min /e$Å^{-3}$	0.395, -0.315	1.360, -0.945

Table S2. Selected bond lengths (Å) for complexes **2** and **5**

	Ru1-S33	Ru1-S20	Ru1-N1	S20-C21	C32-S33
2					
	2.3822(4)	2.3827(4)	2.1311(12)	1.7827(16)	1.7823(16)
	Ru1-S130	Ru1-S117	Ru1-N104	S130-C129	S117-C118
5					
	2.3885(6)	2.3782(6)	2.113(2)	1.790(3)	1.782(3)

Table S3. Selected bond angles (°) for complexes **2** and **5**

	N1 Ru1 S20	N1 Ru1 S33	S33 Ru1 S20	C21 S20 Ru1	C32 S33 Ru1
2					
	89.84(3)	87.34(4)	89.744(13)	106.82(5)	106.29(5)
	N104 Ru1 S117	N104 Ru1 S130	S117 Ru1 S130	C118 S117 Ru1	C129 S130 Ru1
5					
	86.53(6)	88.31(6)	89.45(2)	106.88(9)	106.56(9)

Table S4. Wavelengths and extinction coefficients of local maxima of the UV-visible spectra of complexes **1 – 7** in dichloromethane

	λ_{max} (nm)	ε (10^3 L·mol^{-1}·cm^{-1})
1	352; 632	9.9; 2.1
2	353; 436; 632	0.4; 0.9; 0.6
3	352; 631	8.9; 1.9
4	352; 632	9.2; 2.1
5	352; 426; 632	4.0; 0.8; 1.1
6	349; 632	8.2; 1.8
7	352; 426; 632	7.1; 0.5; 1.6

Table S5. Molecular orbital transitions involved in the main bands (352 and 632 nm) of the UV-visible spectrum of complex **1** and their relative weights determined by TD-DFT calculations. The molecular orbitals are shown in Figure 7

Band (λ_{max}/nm)	E (cm^{-1})	f	Main MOs	Relative weights
632	16359.4	0.021	110 → 111	0.88
	17109.2	0.008		
	22123.3	0.000		
	24160.5	0.001		
352	26190.3	0.059	107 → 111	0.58
	26459.9	0.001		
	26915.4	0.023	106 → 111	0.64
	28558.0	0.000		
	28643.4	0.024	109 → 112	0.87
	28951.0	0.043	110 → 114	0.70
	29249.4	0.001		

S.3. Figures S1-S4

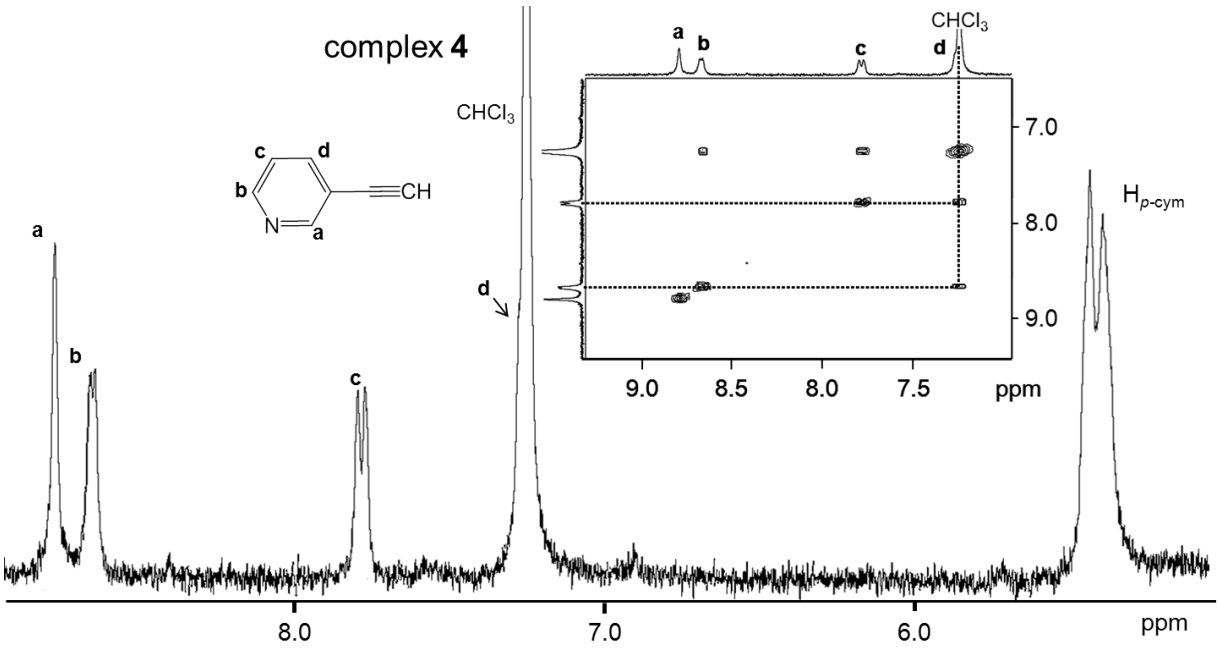

Figure S1. The aromatic region of the ^{1}H NMR spectrum of 5 mM complex **4** in $CDCl_3$. Inset: ^{1}H-^{1}H 2D COSY NMR spectrum showing the correlation between the signal of H_d and the signals of H_a and H_b. The labelling of protons on the ligand is shown.

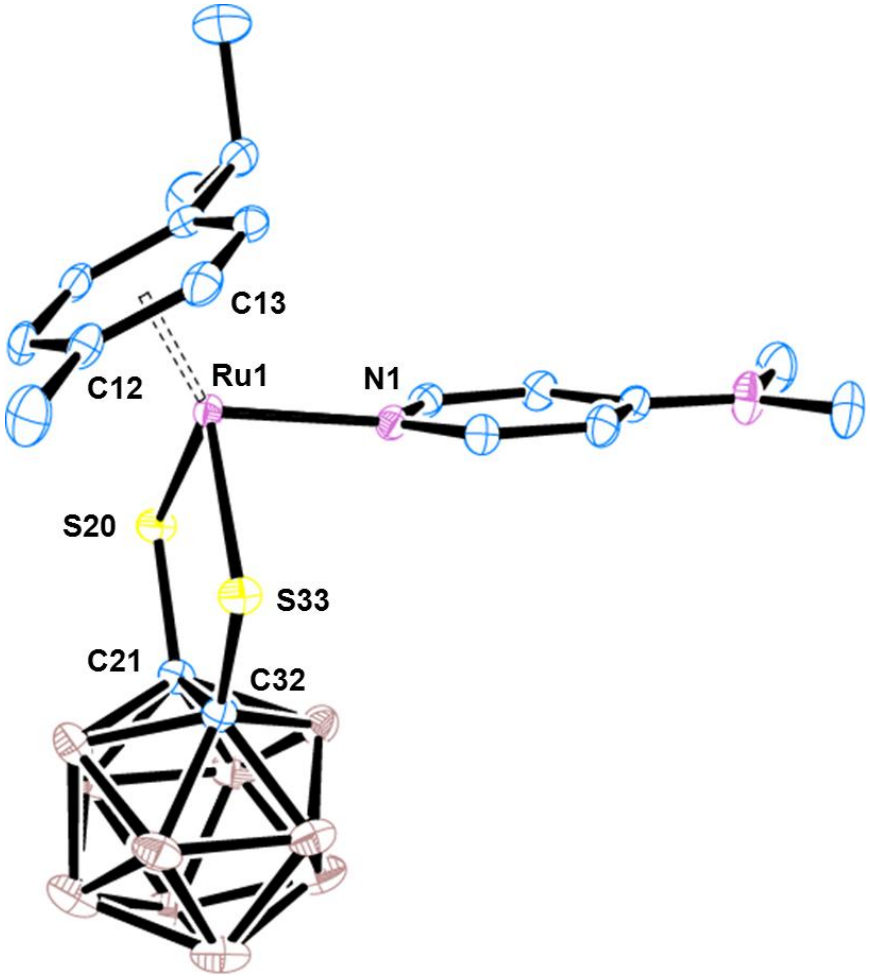

Figure S2. ORTEP drawing of [Ru(p-cym)(1,2-dicarba-closo-dodecaborane-1,2-dithiolato)(p-NMe2py)] (**2**) at the 50% probability level. Hydrogen atoms are omitted for clarity.

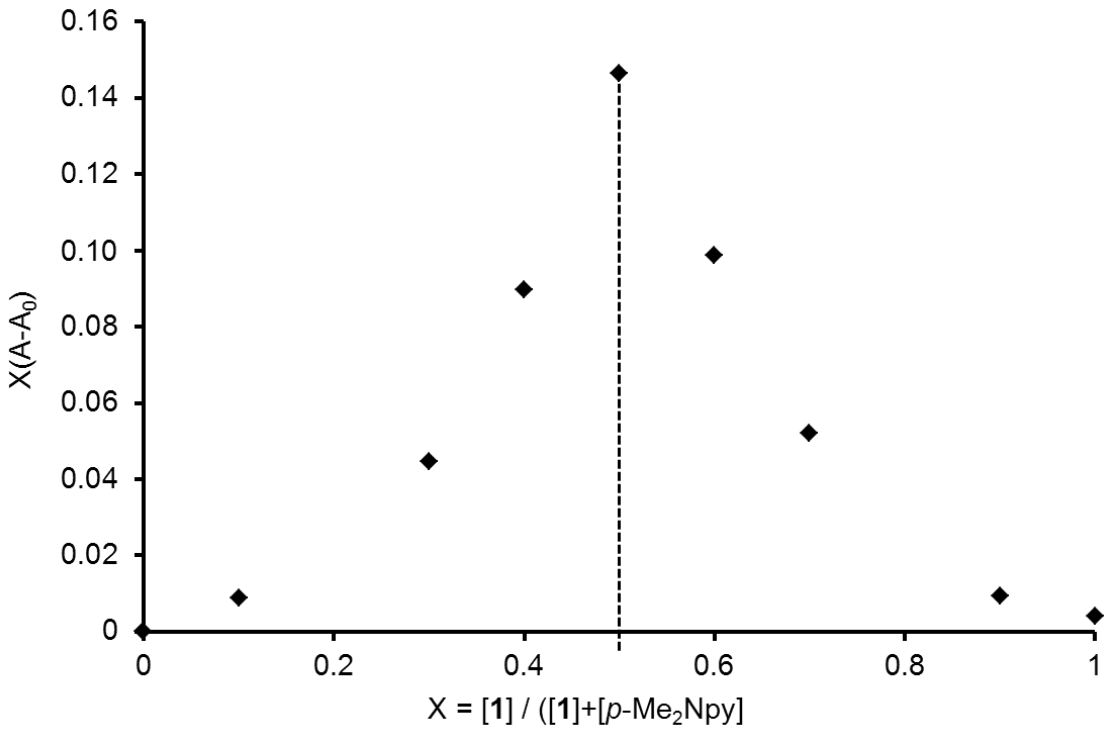

Figure S3. Job plot for the binding of *p*-NMe_2py to complex **1** (10^{-4} M) monitored by the change in absorption at 303 nm in dichloromethane. X is defined by X = [**1**]/([**1**]+[*p*-Me_2py]), A is the absorbance for the value $0 \leq X \leq 1$, A_0 is the absorbance for X = 0 ([**1**] = 0 mol·L^{-1}).

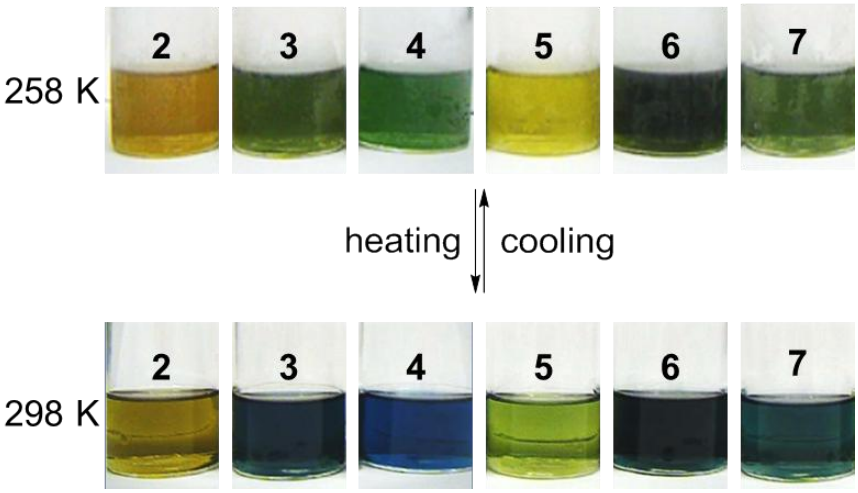

Figure S4. Reversible thermochromism exhibited by solutions of **2 – 7** in dichloromethane (10^{-4} M) between 258 K and 298 K.

S.4. References

1. M. A. Bennett, T.-N. Huang, T. W. Matheson and A. K. Smith, *Inorg. Synth.,* 1982, **21**, 74–76.

2. M. Herberhold, H. Yan and W. Milius, *J. Organomet. Chem.,* 2000, **598**, 142–149.

3. F. Neese, U. Becker, D. Ganiouchine, S. Koßmann, T. Petrenko, C. Riplinger and F. Wennmohs, ORCA 2.9.1 ed.; University of Bonn: Bonn, 2012.

4. A. Schaefer, H. Horn and R. Ahlrichs, *J. Chem. Phys.,* 1992, **97**, 2571–2577.

5. A. Klamt, *J. Phys. Chem.,* 1995, **99**, 2224–2235.

6. A. Klamt and V. Jones, *J. Chem. Phys.,* 1996, **105**, 9972–9981.

7. A. Klamt and G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2,* 1993, 799–805.

8. S. Grimme, *J. Comput. Chem.,* 2006, **27**, 1787–1799.

9. G. A. Zhurko, ChemCraft 1.6 (Build 350); http://www.chemcraftprog.com

10. *CrysAlis PRO*, Oxford Diffraction Ltd., Abington, Oxfordshire, U.K., 2007.

11. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 467–473.

12. G. M. Sheldrick, *SHELX97, Programs for Crystal Structure Analysis (Release 97-92)*, University of Göttingen, Germany, 1997.

13. P. Thordarson, *Chem. Soc. Rev.,* 2011, **40**, 1305–1323.

14. P. Thordarson, in *Supramolecular Chemistry: From Molecules to Nanomaterials (*Eds.: J. W. Steed and P. A. Gale), John Wiley & Sons, 2012, pp. 239–274.