Electronic Supplementary Material (ESI) for RSC Advances.

Stepwise synthesis of mixed-metal assemblies using pre-formed Ru(II) 'complex ligands' as building blocks

Alexander J. Metherell and Michael D. Ward*

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK

SUPPORTING INFORMATION

Characterisation data for $[Ru(L^{th})_3](PF_6)_2$

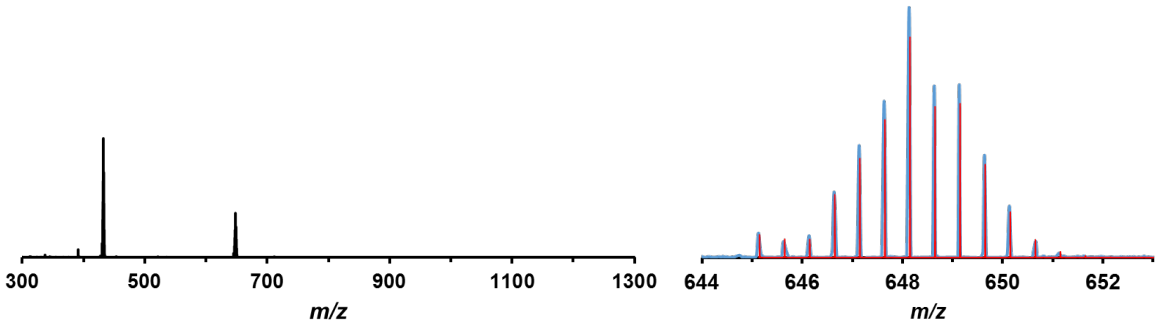


Fig. S1. Electrospray mass spectrum of $[Ru(L^{th})_3](PF_6)_2$ showing the $[RuL_3H]^{3+}$ and $[RuL_3]^{2+}$ peaks(left); expansion of the $[RuL_3]^{2+}$ peak (right), blue = experimental, red = predicted.

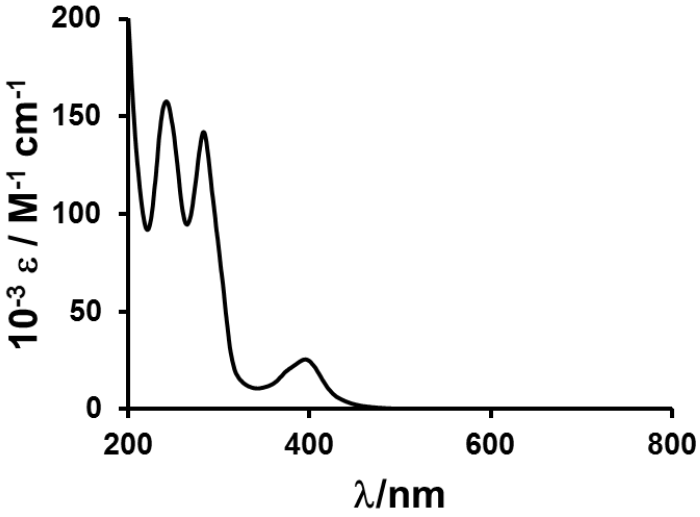


Fig. S2. UV vis spectrum (MeCN) of $[Ru(L^{th})_3](PF_6)_2$

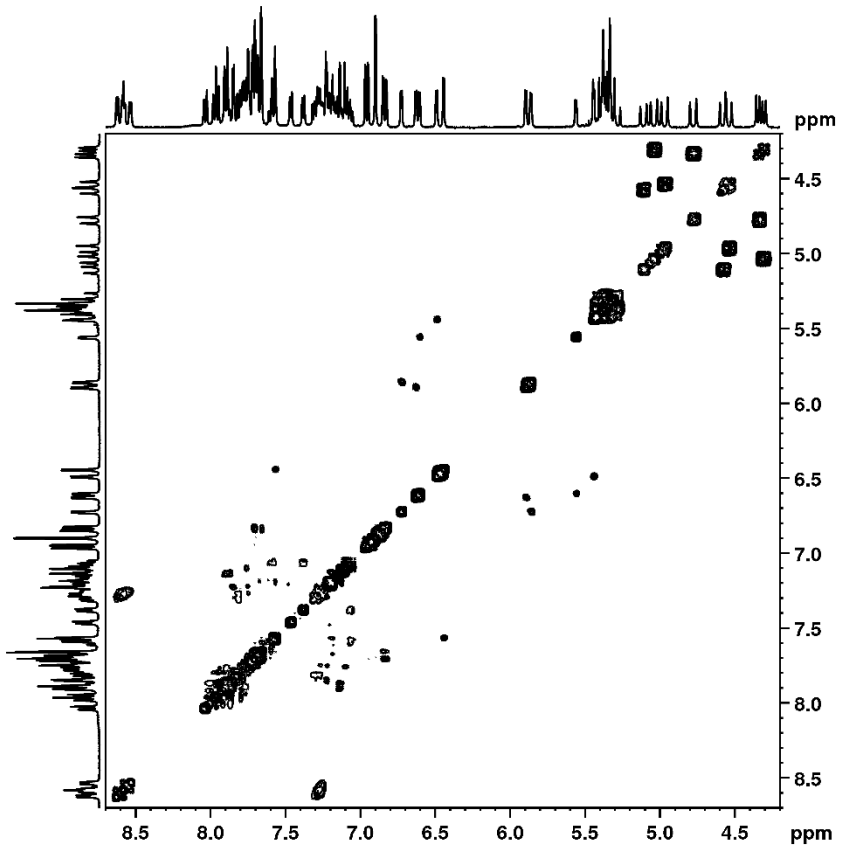


Fig. S3: COSY spectrum (in CD_3CN, 400 MHz) of $[Ru(L^{th})_3](PF_6)_2$ – note 4 pairs of thiophene doublets, and 4 of the CH_2 pairs.

Characterisation data for $[Ru_2Co_2(L^{th})_6](BF_4)_4(PF_6)_4$

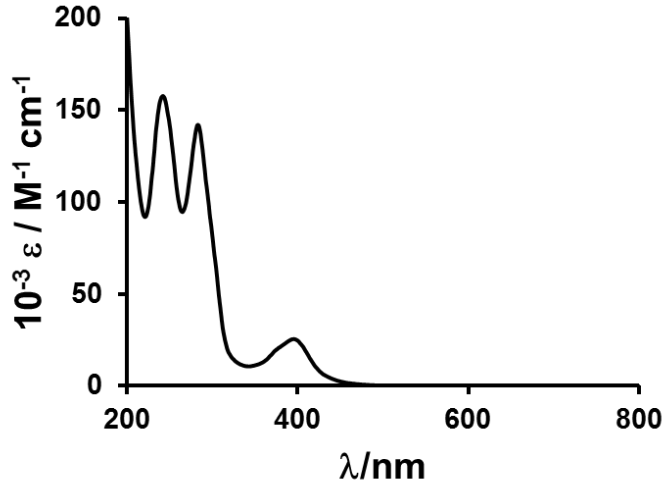


Fig. S4. UV vis spectrum (MeCN) of $[Ru_2Co_2(L^{th})_6](BF_4)_4(PF_6)_4$.

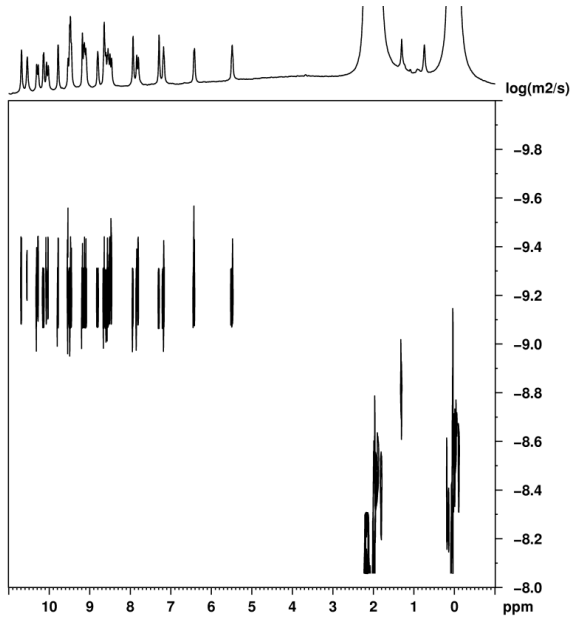


Fig. S5. DOSY spectrum (400 MHz, CD_3CN) of the diamagnetic region of $[Ru_2Co_2(L^{th})_6](BF_4)_4(PF_6)_4$.

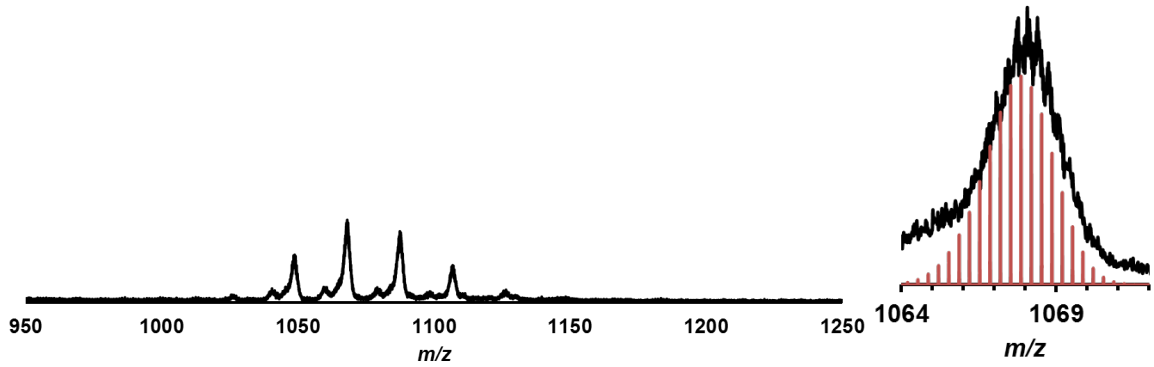


Fig. S6. Electrospray mass spectrum of $[Ru_2Co_2(L^{th})_6](BF_4)_4(PF_6)_4$ showing the series of $\{[Ru_2Co_2(L^{th})_6]X_5\}^{3+}$ peaks(left); expansion of the $\{[Ru_2Co_2(L^{th})_6](BF_4)_4(PF_6)\}^{3+}$ peak (right), black = experimental, red = predicted.

Characterisation data for $\{[CdRu(L^{th})_3](ClO_4)_2(PF_6)_2\}_\infty$

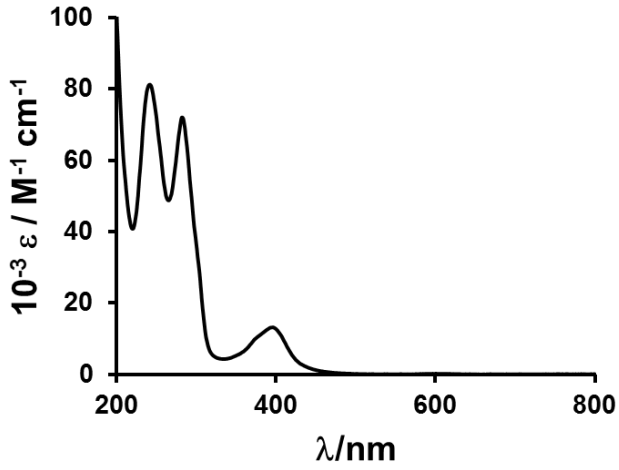


Fig. S7. UV vis spectrum (MeCN) of $\{[CdRu(L^{th})_3](ClO_4)_2(PF_6)_2\}_\infty$.

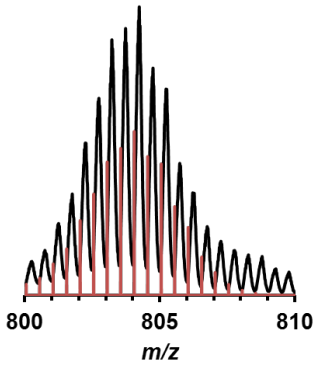


Fig. S8. Expansion of the ESMS of $\{[CdRu(L^{th})_3](ClO_4)_2(PF_6)_2\}_\infty$ showing the $\{[RuCd(L^{th})_3](ClO_4)_2\}^{2+}$ peak at 804, black = experimental, red = predicted.

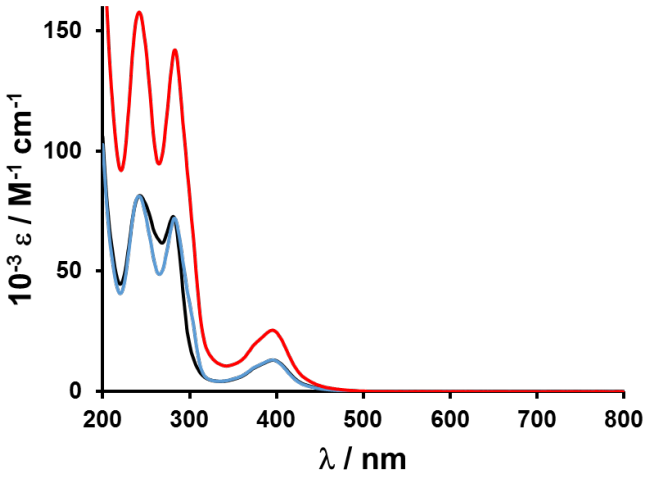


Fig. S9. Overlay of UV vis spectra of: $[Ru(L^{th})_3](PF_6)_2$ (black), $\{[CdRu(L^{th})_3](ClO_4)_2(PF_6)_2\}_\infty$ (blue) and $[Ru_2Co_2(L^{th})_6](BF_4)_4(PF_6)_4$ (red), all in MeCN

Synthesis of *4:1*-$Ru(L^{ph})_3](PF_6)_2$

A solution of L^{Ph} (0.24 g, 0.62 mmol, 5.9 eq) was stirred rapidly in refluxing ethylene glycol (25 cm^3) until dissolved. To this was added a solution of $RuCl_2(dmso)_4$ (0.05 g, 0.11 mmol) in H_2O / ethylene glycol (1 : 12, 65 cm^3) by dropping funnel over 3 hours, and then the orange mixture was stirred at reflux for 40 h. The solution was cooled to 25 ^oC and excess saturated $KPF_{6\,(aq)}$ was added. The product was extracted with dichloromethane, dried over $MgSO_4$ and evaporated to dryness.

The product was purified by repeated column chromatography on silica. Elution with MeCN–water–saturated aqueous KNO_3 (100 : 10 : 1) resulted in two yellow bands moving down the column – the second major band was collected, and purified further by another column. After removing acetonitrile by rotary evaporation, excess saturated aqueous KPF_6 was added and the product was extracted from the suspension into dichloromethane. The organic layer was separated, dried over $MgSO_4$, and the solvent removed in vacuo to yield $[Ru(L^{ph})_3](PF_6)_2$, 4 : 1 *mer:fac* isomers, as a yellow solid. Yield: 0.10 g, 61 %. ESMS *m/z* 1423 $(M - PF_6)^+$, 639 $(M - 2PF_6)^{2+}$, 426 $(M + H - 2PF_6)^{3+}$. UV/Vis in MeCN [λ_{max}/nm(10^{-3} ε/M^{-1} cm^{-1})]: 397 (14.6), 282 (79.2), 248 (76.3).

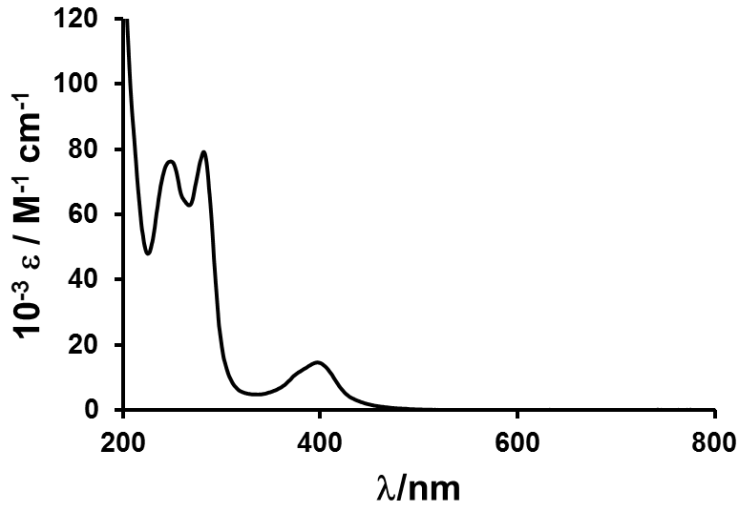


Fig. S10. UV vis spectrum (MeCN) of $[Ru(L^{ph})_3](PF_6)_2$, 4 : 1 *mer:fac* isomers.

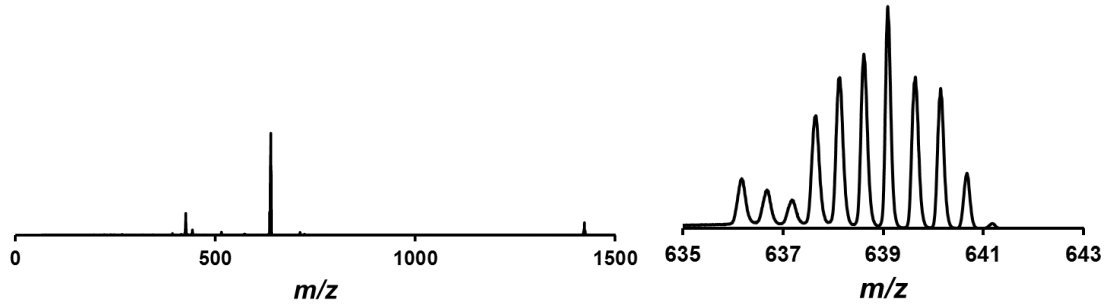


Fig. S11. Electrospray mass spectrum of $[Ru(L^{ph})_3](PF_6)_2$, 4 : 1 *mer:fac* isomers.

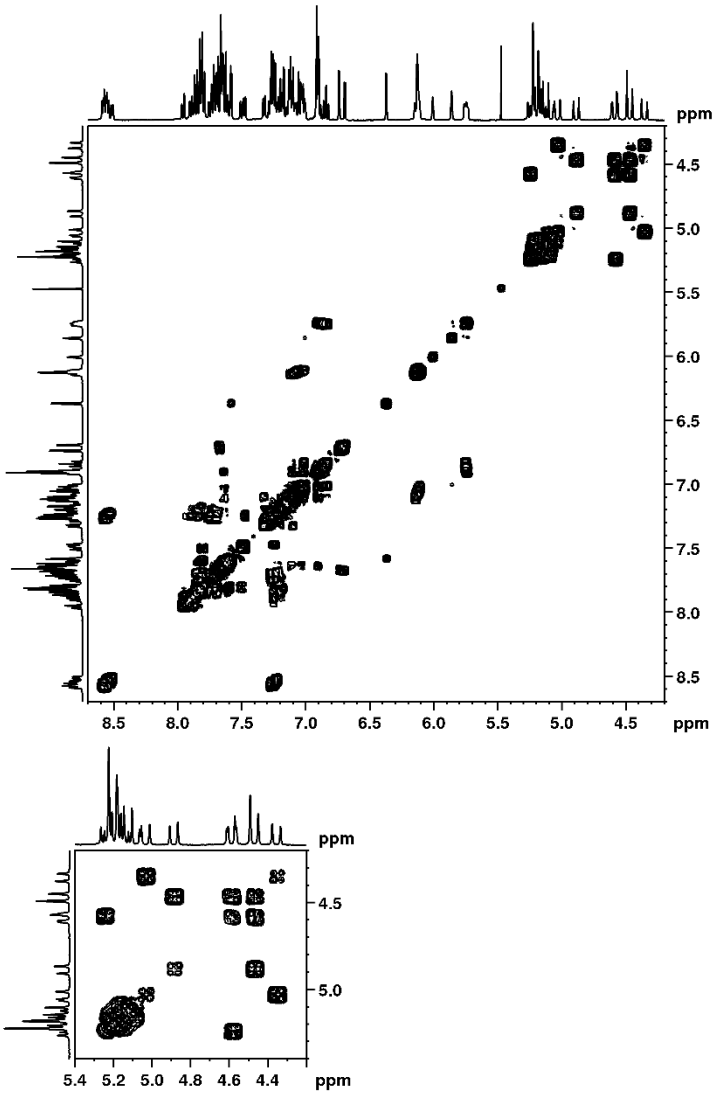


Fig. S12. COSY spectrum (400 MHz, CD_3CN) of $[Ru(L^{ph})_3](PF_6)_2$, 4 : 1 *mer:fac* isomers.

$[Ru_3Co_3(L^{ph})_9](BF_4)_8(PF_6)_8$

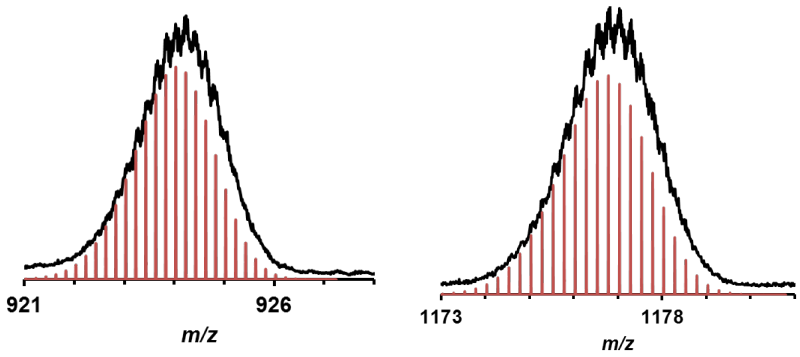


Fig. S13. Expansions of the electrospray mass spectrum of $[Ru_3Co_3(L^{ph})_9](BF_4)_{12}$ showing the $\{[Ru_3Co_3(L^{ph})_9](BF_4)_7\}^{5+}$ and $\{[Ru_3Co_3(L^{ph})_9](BF_4)_8\}^{4+}$ peaks (m/z = 924 and 1177, respectively), black = experimental, red = predicted.

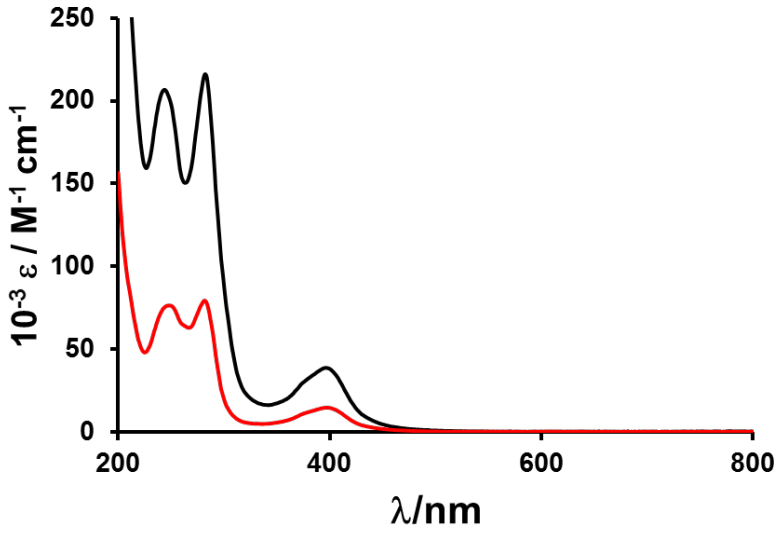
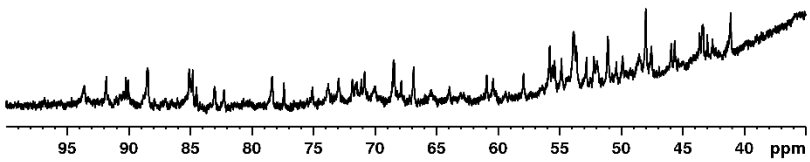


Fig. S14. UV vis spectrum (MeCN) of $[Ru_3Co_3(L^{ph})_9](BF_4)_{12}$ (black) compared to RuLph3 (red)



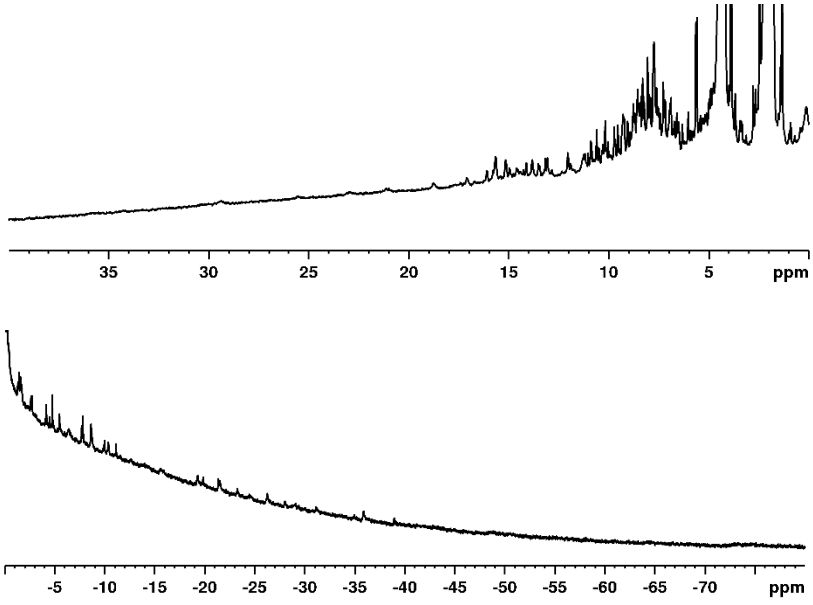


Fig. S15. Paramagnetic ^{1}H NMR spectrum (400MHz, CD_3CN) of redissolved crystals of $[Ru_3Co_3(L^{ph})_9](BF_4)_{12}$.

$[Ru_4Co_4(L^{ph})_{12}](BF_4)_8(PF_6)_8$

Site	**Label**	**Isotropic thermal parameter, U (Å²)**	**Average M-N bond length (Å)**
mer	Ru	0.033	2.07*
fac	Co	0.038	2.14
mer	Co	0.003	2.06**
fac	Ru	0.086	2.14

Table 1. Table summarising the key crystallographic information for correct* and deliberate mis-assignment** of the different metal sites.

* Correct assignment of metals gives sensible thermal parameters.
** Deliberate mis-assignment of metals with physically unreasonable thermal parameters.