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Anion Binding and Luminescent Sensing using Cationic Ruthenium(II) Aminopyridine Complexes

Sara Jane Dickson,[a] Martin J. Paterson,[b] Charlotte E. Willans,[a] Kirsty M. Anderson,[a] and Jonathan W. Steed*[a]

Abstract: The synthesis of a series of ruthenium(II) based anion sensors of the type $[Ru(\eta^6\text{-}C_6H_4MeCHMe_2)\text{-}Cl(L)_2][BF_4]$ (**2**) is reported in which ligand L represents a series of substituted pyridinylmethyl–amine derivatives. The carbazole based ligand $\mathbf{L^3}$ exhibits a fluorescent intraligand charge-transfer (ILCT) state that is quenched by ligand-to-metal charge transfer (LMCT) upon coordination to ruthenium in the 1:1 complex $[Ru(\eta^6\text{-}C_6H_4MeCHMe_2)Cl_2(\mathbf{L^3})]$ (**1c**). The 1:2 complex **2c** is fluorescent, however, and acts as a fluorescent anion sensor because of the mixing of an anion-dependent charge-transfer component into the excited state. The 1:2 complexes of type **2** all exhibit interesting low symmetry ^{1}H NMR spectra that also are a useful handle on anion complexation. The electronic structures of $\mathbf{L^3}$, **1c** and **2c** have been probed by time-dependent DFT calculations.

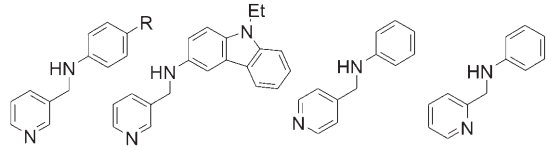
Keywords: anion binding · density functional calculations · fluorescence · ruthenium · sensors

Introduction

Metal ions are important structural and signalling elements in anion-binding and sensing systems.[1–10] The metal may play either i) a structural role,[11–15] ii) it may form a key component of the anion binding site[3,16,17] or iii) it may act as part of a redox, luminescent or colourimetric reporter group.[7,10,18–23] Generally inert metal-containing fragments such as metallocenes, arene complex of d^6 metals, or tris(bipyridyl) type complexes have been used predominantly in a reporting role.[9,10,24,25] More recently there has been a trend toward self-assembling systems in which a more labile metal, along with the anion and a series of multifunctional ligands together form a complex under thermodynamic control.[26–29] Within this context the semilabile (arene)ruthenium(II) piano stool type complexes represent a readily synthesised scaffold that has proved useful in anion binding studies.[30,31] In the presence of an anionic ligand a molecular cleft can be created in which the single overall positive charge on the metal fragment complements monovalent anions bound within a binding pocket engineered by ligand design. In the present paper we report the synthesis, structure, anion binding and fluorescent properties of a series of such metal-based receptors. Part of this work has appeared in a preliminary communication.[32]

Results and Discussion

Synthesis and characterisation: Ligands $\mathbf{L^1}$–$\mathbf{L^5}$ were prepared by reaction of the appropriate pyridine carboxaldehyde with the relevant amine. The simple synthetic procedure involves a condensation step followed by the reduction of the imine, using $NaBH_4$, to produce a secondary amine. Reactions were carried out in 1,2-dichloroethane at reflux for 6 h and products were fully characterised. Reaction of li-



L^1: R = H
L^2: R = NO_2
L^3 L^4 L^5

[a] S. J. Dickson, Dr. C. E. Willans, Dr. K. M. Anderson, Prof. J. W. Steed
Department of Chemistry, Durham University
South Road, Durham, DH1 3LE (UK)
Fax: (+44) 191-384-4737
E-mail: jon.steed@durham.ac.uk

[b] Dr. M. J. Paterson
Department of Chemistry
School of Engineering and Physical Sciences
Heriot-Watt University, Edinburgh, EH14 4AS (UK)

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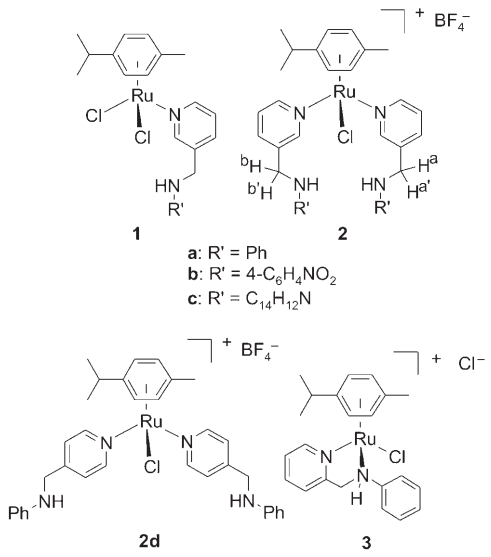


gands $\mathbf{L^1}$–$\mathbf{L^4}$ with the chloro-bridged dimer $[\{Ru(\eta^6\text{-}C_6H_4MeCHMe_2)Cl(\mu\text{-}Cl)\}_2]$,[33] gave mono-adducts of type $[Ru(\eta^6\text{-}C_6H_4MeCHMe_2)Cl_2(L)]$ (L = $\mathbf{L^1}$–$\mathbf{L^4}$, compounds **1a**–**d**) similar to known analogous compounds.[34] Further reaction of these mono-adducts with one equivalent of $AgBF_4$ and an additional ligand in methanol/acetone (1:1, v/v) solvent mixture gave monocationic Ru(II) complexes $[Ru(\eta^6\text{-}C_6H_4MeCHMe_2)Cl(L)_2][BF_4]$ (L = $\mathbf{L^1}$–$\mathbf{L^4}$, compounds **2a**–**d**).

The new complexes were fully characterised by elemental analysis, ESI-MS, IR spectroscopy (nujol) and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. For compound **2c** it proved very difficult to remove traces of $[Ru(\eta^6\text{-}C_6H_4MeCHMe_2)Cl(H_2O)(\kappa\text{-}N\text{-}\mathbf{L^3})][BF_4]$ (identified by the diastereotopic nature of its ^1H NMR spectrum), which was present as a $\approx$10% impurity in the samples studied. In contrast to $\mathbf{L^1}$–$\mathbf{L^4}$, the reaction of $[\{Ru(\eta^6\text{-}C_6H_4MeCHMe_2)Cl(\mu\text{-}Cl)\}_2]$ with $\mathbf{L^5}$ (1:1 ratio of $\mathbf{L^5}$/Ru) did not result in a product of type **1**, but gave a cationic chelate complex $[Ru(\eta^6\text{-}C_6H_4MeCHMe_2)Cl(\kappa\text{-}N,N'\text{-}\mathbf{L^5})]Cl$ (**3**). In contrast to compounds of type **1**, which retain two chloride ligands in the mass spectrum, the ES+ mass spectrum of **3** shows a peak at $m/z = 455$ assigned to the molecular cation. The ^1H NMR spectrum of **3** provides clear evidence for the chirality of the metal centre with separate signals for the diastereotopic methyl groups on the isopropyl substituent, a characteristic diastereotopic AA′BB′ pattern for the *p*-cymene aromatic ring, and a doublet of doublets for the methylene protons of $\mathbf{L^5}$. In contrast, analysis of the ^1H NMR spectra of type **1** compounds does not show diastereotopic splitting, thus confirming that the metal centre is not chiral. The chemical shift of the NH resonance at $\delta = 11.50$ ppm in **3** is also very significantly different from compounds of type **1** in which the NH resonance occurs at $\delta \approx 4$–6 ppm ($\delta = 4.40$ ppm in compound **1a**, for example). The ionic nature of **3** was confirmed by counter anion metathesis with $NaBPh_4$ in methanol, which gave a precipitate of $[Ru(\eta^6\text{-}C_6H_4MeCHMe_2)Cl(\kappa\text{-}N,N'\text{-}\mathbf{L^5})][BPh_4]$. The 1:1 ratio between the complex cation in **3** and BPh_4^- ion was confirmed by ^1H NMR spectroscopy. In DMSO, the formation of a further chiral product from **3** was observed by ^1H NMR spectroscopy that lacked the very low field resonance assigned to the NH proton in **3**. This product most likely arises from displacement of the secondary amine by the coordinating solvent to give chiral $[Ru(\eta^6\text{-}C_6H_4MeCHMe_2)Cl(DMSO)(\kappa\text{-}N\text{-}\mathbf{L^5})][BPh_4]$.

In the ^1H NMR spectra there is a significant difference in the chemical shift values for the NH resonance of the free ligands compared to adducts of **1** and to cations of type **2**. For example, the NH resonance in the free ligand $\mathbf{L^2}$, occurs at $\delta = 4.92$ ppm, in the mono-adduct **1b** at $\delta = 5.94$ ppm and in the monocationic host **2b** at $\delta = 6.67$ ppm. In addition to effects arising from the coordination to the Ru(II) centre the downfield chemical shift of this resonance suggests enhanced hydrogen bonding in **2b** compared to the free ligand and **1b**, and presumably arises from hydrogen bonding to the BF_4^- ion.

Interestingly, the ^1H NMR spectra of complexes **2a**–**c** all exhibit an AB quartet resonance assigned to the methylene protons, $H^{a,a'}$ and $H^{b,b'}$, for example, in **2a** at $\delta = 4.40$ and 4.32 ppm, with $^2J = 17.2$ Hz, consistent with geminal coupling (in some cases further split by vicinal coupling to NH). Although this splitting is also observed in **3** it is not evident in the ^1H NMR spectra of the free ligands or monoadducts of type **1**. As compounds **2a**–**c** are not chiral (no splitting of the *p*-cymene ligand resonances is observed), the inequivalence of protons H^a and H^b must arise from the fact that the molecule is point group C_s and H^a and H^b are not related to one another by the mirror symmetry of the molecule. Instead, the mirror plane relates H^a to $H^{a'}$ and H^b to $H^{b'}$ and hence H^a and H^b are diastereotopic. Note that the protons are diastereotopic even without invoking any restricted rotation, for example arising from intramolecular NH···Cl or CH···Cl hydrogen bonding—indeed molecular models suggest that any such association is unfeasible. In principle diastereotopic protons should also be observed for the *para* isomer **2d** (prepared as a control), however, only a broad doublet resonance (NH coupling) is observed for the methylene protons, which are perhaps too far away from the metal centre for the magnetic inequivalence to be observed. A dilution study on compound **2a** in $CDCl_3$ shows that the NH and methylene resonances remain essentially unchanged across the concentration range 1.9–31.0 mol dm^{-3} ruling out any intermolecular association as an alternative explanation of the magnetic inequivalence.

Attempts were made to characterise the new complexes by X-ray crystallography, however in every case crystals were not forthcoming. However, changing the *p*-cymene ligand for hexamethylbenzene by reaction of $\mathbf{L^1}$ with $[\{Ru(\eta^6\text{-}C_6Me_6)Cl(\mu\text{-}Cl)\}_2]$ did yield a sample of the hexamethylbenzene analogue of **1a**, $[Ru(\eta^6\text{-}C_6Me_6)Cl_2(\mathbf{L^1})]$ (**4**) that was characterised by X-ray crystallography. The structure is shown in Figure 1 and comprises the usual piano-stool geometry with two terminal chloride ligands and a single unidentate pyridyl *N*-bound aminomethylpyridine ligand. Bond lengths and angles are within the normal ranges. The amine

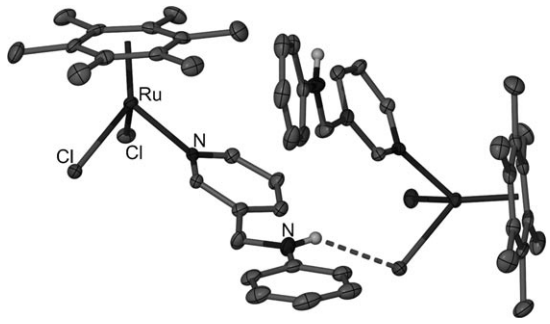


Figure 1. X-ray crystal structure of $[Ru(\eta^6\text{-}C_6Me_6)Cl_2(\mathbf{L^1})]$ (**4**) showing the NH···Cl hydrogen bonding, N···Cl 3.436(3) Å (50% displacement ellipsoids).

NH proton is engaged in a single NH···Cl interaction[35–37] to an adjacent molecule.

Anion binding: The anion complexation ability of the new host complexes **2a**, **2b** and **2c** was determined by ^{1}H NMR spectroscopic titration with the tetrabutylammonium salts of a number of common anions in $CDCl_3$. Anion binding by **1a** and **1b** was also studied as a control. Anion binding constants for the formation of 1:1 and 2:1 host/guest complexes are given in Table 1. The use of both 1:1 and 2:1 stoichiometry models for complexes **2a** and **2b** is consistent with previous work on 3-aminopyridine derivatives, which showed the formation of compounds in which a single anion is sandwiched between two hosts.[31] The inclusion of this second equilibrium resulted in a much improved fit to the titration data compared to a 1:1 model alone. Job plot analysis of **2a** binding Br^- also confirmed the 2:1 host/guest stoichiometry and an ESI mass spectrum of **2a** in the presence of half an equivalent of NBu_4Br gave a peak at m/z 1357, corresponding to $[(\mathbf{2a})_2Br]^+$. In contrast, the Job plot for the analogous chloride complex suggested a 1:1 stoichiometry despite the fact that a better fit to the titration data was obtained for the model including both 1:1 and 2:1 complexes (Figure 2). The fact that the second binding constant is small may explain the anomaly.

Table 1. Anion binding constants (log β) for 1:1, 1:2 and 2:1 host/guest complexes in $CDCl_3$ at 20 °C. Anions added as NBu_4^+ salts, host concentration 0.006 mol dm^{-3} (hyphen indicates not measured).

			log β		
Anion	**1a**	**1b**	**2a**	**2b**	**2c**[b]
Cl^-	≈0	β_{11} 2.00(2)	β_{11} 3.64(3) β_{21} 6.01(9)	β_{11} 4.04(3) β_{21} 6.66(9)	β_{11} 3.95(3) β_{12} 7.03(4)
Br^-	–	–	β_{11} 3.28(2) β_{21} 5.32(9)	β_{11} 3.71(3) β_{21} 6.30(9)	β_{11} 3.38(3) β_{12} 5.69(9)
NO_3^-	≈0	–	β_{11} 2.06(14) β_{21} 3.92(7)	β_{11} 3.44(4) β_{21} 6.11(9)	β_{11} 3.23(6)
$MeCO_2^-$	–	–	β_{11} 3.53(10) β_{21} 2.06[a]	β_{11} 4.14(2) β_{21} 7.11(12)	β_{11} 3.41(2) β_{12} 6.20(2)
HSO_4^-	–	–	β_{11} 3.40[a] β_{21} 5.11[a]	[c]	–
$H_2PO_4^-$	–	–	β_{11} 3.67(11) β_{21} 6.18(15)	[c]	–
$CF_3SO_3^-$	≈0	–	β_{11} 1.94[a] β_{21} 2.19[a]	β_{11} 2.30(7) β_{21} 4.54(5)	≈0

[a] Large error. [b] Corrected for the presence of $[Ru(\eta^6\text{-}C_6H_4MeCHMe_2)Cl(H_2O)(\kappa\text{-}N\text{-}\mathbf{L^3})][BF_4]$. [c] Precipitate.

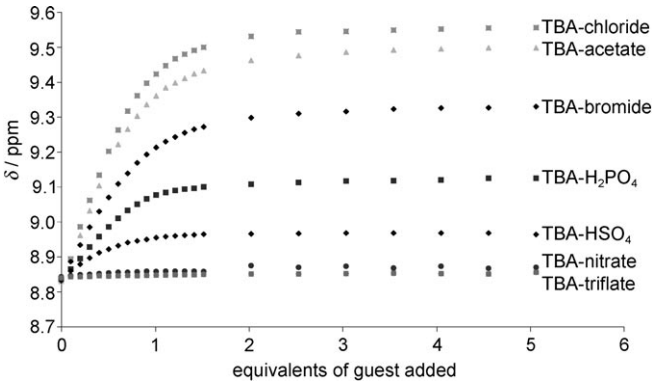
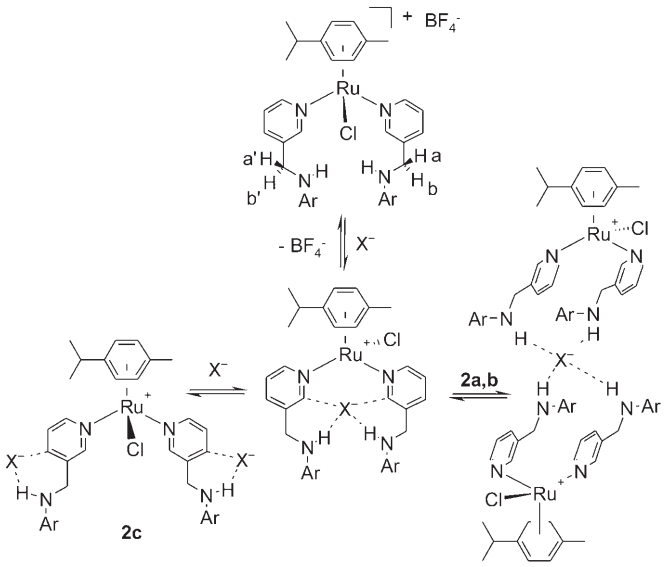


Figure 2. Titration data showing chemical shift changes of the pyridyl-H resonances for **2a**.

Binding by hosts **2a** and **2b** is strongest with chloride, the most densely charged anion, followed by $H_2PO_4^-$ in the case of **2a** and acetate, the most basic anions, followed by bromide and then the relatively charge-diffuse nitrate anion. There is a significant enhancement in all binding constants on moving to the nitro-substituted host **2b** consistent with the electron withdrawing nature of the nitro substituent and consequent increased H-bond acidity of the secondary amine NH protons. Titrations were attempted with HSO_4^- and $H_2PO_4^-$ with **2b**, but resulted in precipitation. Unlike **2a** and **2b**, a 1:1 and 2:1 host/guest model fitted the data for **2c** very poorly. However, a model involving the binding of two anions by a single host gave good agreement to the data. It is likely that the much larger size of the carbazole substituent prevents two hosts from encapsulating a single anion in this case. In terms of affinity, however, the compound proved similar to **2a** and **2b** with modest selectivity for chloride and acetate. Nitrate binding is relatively weak and inclusion of a 1:2 complex in the model did not result in any significant improvement in the fit. The control compounds of type **1** proved to have essentially no anion affinity, highlighting the importance of the charge and anion chelate effect in hosts **2** despite the need to compete with the BF_4^- counterion in the latter compounds. Virtually no displacement of the unidentate pyridyl ligands was observed

during the titrations even in the presence of nucleophilic anions such as Cl^-, in contrast to previous work on 3-aminopyridine derivatives.[31] The possible displacement of $\mathbf{L^3}$ by one equivalent of chloride in **2a** to give **1a** was studied as a function of time. After one hour, a very small amount of **1a** is evident (≈2%), After 5 h about a 10% conversion is observed rising to 40% of the mixture after ≈40 h. The anion-binding equilibria are summarised in Scheme 1.



Scheme 1. Anion binding by complexes **2** forms both 1:1 and 2:1 host/guest complexes.

Surprisingly, on addition of strongly bound anions, the resonances assigned to the diastereotopic methylene protons H^a and H^b in the ^1H NMR spectra of compounds **2a**, **2b** and **2c** gradually collapsed to a singlet. In contrast, weakly interacting anions such as $CF_3SO_3^-$ do not affect the appearance of the resonance even after the addition of a fivefold excess, Figure 3. Generally the ^1H NMR spectroscopic resonances assigned to the methylene protons H^a and H^b of the nitro host **2b** coalesced into a singlet with less added anion than for **2a**. In both cases (**2b** and **2a**) the anion/host ratio required is approximately inversely proportional to the anion binding constant. For example compound **2a** gives a singlet methylene resonance after the addition of only 0.4 equivalents of Cl^-, whereas 0.8 equivalents of acetate and two equivalents of nitrate are required to achieve coalescence. It took more equivalents still to collapse the AB quartet to a singlet for **2c** than for both **2a** and **2b**, thus the loss of the geminal coupling appears to correspond with the strength of interaction with the anions in each case. To remove the inequivalence of protons H^a and H^b in complexes of type **2**, anion binding must either induce a time-averaged plane of symmetry running along the N-Ru-N axis or involve temporary dissociation of the pyridyl ligand. The latter explanation seems relatively unlikely because we have shown that the displacement of the ligand to regenerate **1a** in the presence of chloride takes hours to days (see above). The magnetic equivalence is also unlikely to occur by anion association to form a transient 20-electron complex since this would not result in increased symmetry in any case other than Cl^- binding. In our view the most likely explanation is chloride loss to form a transient 16-electron complex in which the two pyridyl ligands can become co-planar. We suggest therefore strong anion association in hosts **2** leading to increased lability of the coordinated chloride ligand as a result of electrostatic repulsion, such that in the presence of tightly bound anions X^- the complex is rapidly interconverting between the 18-electron $[Ru(\eta^6\text{-}C_6H_4MeCHMe_2)Cl(\mathbf{L^{1-3}})_2]^+ \cdot X^-$ and the transient 16-electron $[Ru(\eta^6\text{-}C_6H_4MeCHMe_2)(\mathbf{L^{1-3}})_2]^{2+} \cdot X^- \cdot Cl^-$. Sixteen electron Ru(II) intermediates are well known in the substitution chemistry of 6-coordinte 18 electron species.[38] We present this explanation tentatively since we cannot rule out the possibility that anion binding induces a conformational change that moves the methylene group just far enough away from the metal centre on average to render the splitting unobservable even though the methylene protons remain formally inequivalent. Such a situation appears to be the case for the *para* isomer **2d** which does not exhibit splitting despite the formal magnetic inequivalence of the methylene protons.

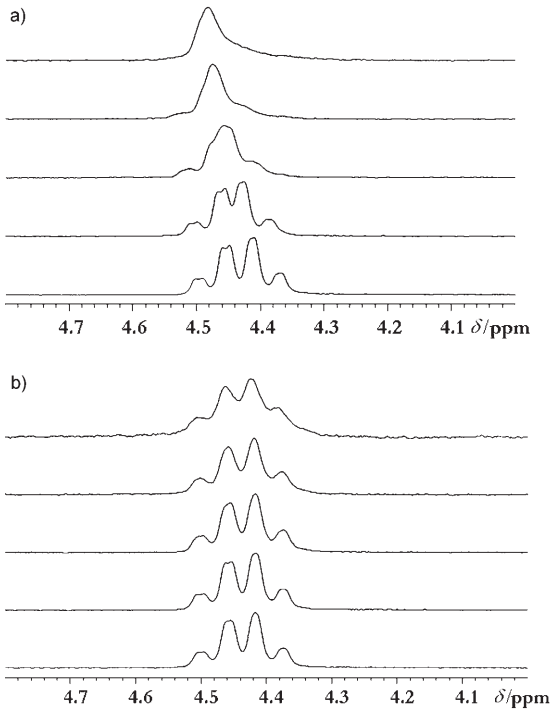


Figure 3. ^1H NMR spectra of the methylene region of host **2a** in $CDCl_3$ as a function of a) added $NBu_4^+Br^-$ and b) added $NBu_4^+CF_3SO_3^-$ (bottom to top 0, 0.2, 0.5, 1.0 and 5.0 equivalents of anion).

Photophysical binding studies: The carbazole derivative **2c** was designed as a fluorescent anion chemosensor. The free ligand $\mathbf{L^3}$ in acetonitrile exhibits a single band in its UV/Vis spectrum at $\lambda = 377$ nm and in its fluorescence spectrum a

broad emission centred on $\lambda = 430$ nm. To understand the photophysical properties of the system we undertook time-dependent DFT calculations, which suggested that the first excited state of the ligand gives rise to a broad band at about $\lambda = 350$ nm ($\lambda = 377$ nm observed in acetonitrile) and involve charge transfer from the carbazole to the pyridyl group. The dominant single particle–hole configuration ($c_i = 0.690$) of the first excited state is seen in Figure 4 and can be ascribed to intraligand charge transfer (ILCT).

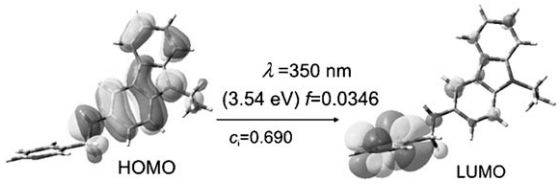


Figure 4. Electronic transition to the dominant configuration of the first excited state of $\mathbf{L}^4$.

Coordination of $\mathbf{L}^3$ to ruthenium(II) to give **1c** results in complete quenching of this ILCT emission and the complex is essentially non-emissive, even though both **1c** and **2c** give rise to a similar absorption at $\lambda = 377$ nm (with a significantly higher extinction coefficient for **2c**). Titration of **1c** with $NBu_4^+Cl^-$ does not result in any restoration of the fluorescence. Complex **2c**, however, exhibits a broad emission at longer wavelength ($\lambda = 474$ nm) compared to the free ligand (Figure 5).

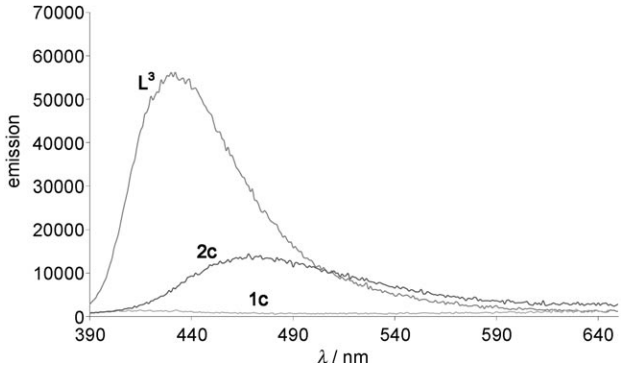


Figure 5. Fluorescent emission spectra (1.03×10^{-4} M, MeCN, $\lambda_{ex} = 375$ nm) of $\mathbf{L}^3$, **1c** and **2c**.

The ability of **2c** to act as a fluorescent anion sensor was probed by spectrofluorimetric titration with a number of different anions in acetonitrile. Addition of the non-coordinating $CF_3SO_3^-$ resulted in a slight increase in the emission intensity, but no change in wavelength (see the Supporting Information), consistent with the fact that this anion is extremely weakly bound by these types of host. In contrast, addition of Cl^-, Br^-, NO_3^- and $MeCO_2^-$ all resulted in partial quenching of the fluorescence (factor of ≈ 2.5) and a shift to shorter wavelength ($\lambda = 447$ nm for Cl^-, Br^- and $MeCO_2^-$; $\lambda = 456$ nm for NO_3^-), but not to the same wavelength as the free ligand ($\lambda = 430$ nm), Figure 6. In each case

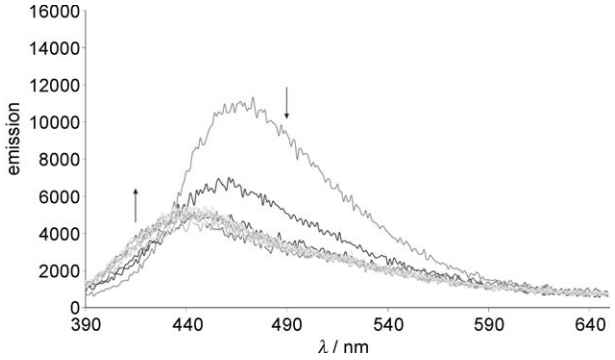


Figure 6. Emission spectrum of **2c** (1.03×10^{-4} M, MeCN, $\lambda_{ex} = 375$ nm) upon addition of up to 10 mole equivalents of tetrabutyl ammonium acetate. The arrows indicate emission after an increase in molar equivalents. The equivalents were increased in a stepwise approach: 0, 0.5, 1, and in integer steps from 2–10.

changes were complete after addition of one equivalent of anion. This suggests that the quenching is a result of solely the 1:1 complex. The chemical shift data obtained by NMR spectroscopic titration strongly suggests that hydrogen bonding of a pyridyl CH group (Figure 2) as well as the amine NH donor to these anions, and hence the interaction of anions with the pyridyl unit, may reduce its electron acceptor ability, and hence lower the emission wavelength.

The structural and electronic properties of **1c**, **2c** and **2c**·Cl^- were also probed by time-dependent DFT calculations using benzene as a model for *p*-cymene. In the case of **1c** the calculations indicate a broad absorption band around $\lambda = 350$ nm assignable to an ILCT transition very similar to that observed in the free ligand $\mathbf{L}^3$ consistent with the observed similarity in their absorption spectra. In **1c** there are three electronic states which give rise to this broad band. States 2 and 3 (see the Supporting Information) are dominated by ILCT configurations. State 1 is an interesting mixed state consisting of two dominant configurations involving a charge redistribution around the metal centre with some ligand-to-metal charge transfer (LMCT) component. State 1 (Figure 7) also has a significant ($c \approx 0.1$) component of ILCT character similar to states 2 and 3. Thus, although absorption gives rise to a similar ILCT band in $\mathbf{L}^3$ and **1c**, state mixing in **1c** means that the system can relax in a state involving a ruthenium d-orbital. This LMCT state is tentatively assigned as the non-emissive state.

For the two-arm host **2c** in the absence of anions there are two states contributing to the absorption band around $\lambda = 377$ nm. Similarly to **1c** these are localised on the carbazole ligands, although there is no metal-based LMCT component unlike **1c**, consistent with the observed emission of **2c**. The calculations also reproduce the observed twofold increase in absorbance of **2c** compared to **1c**. The structure of

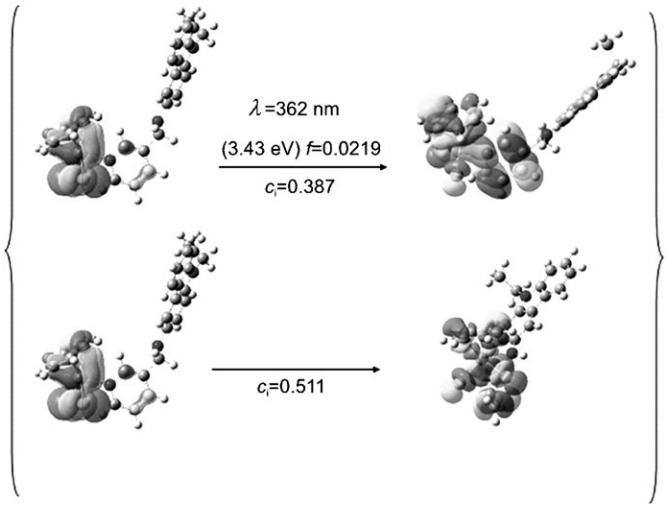


Figure 7. The first of three states giving rise to the observed $\lambda = 377$ nm (calcd $\lambda = 362$ nm) absorption in **1c**. The MLCT component allows non-radiative decay and hence no fluorescence is observed.

2c was also optimised in the presence of a Cl^- ion. The calculated geometry of the resulting complex is shown in Figure 8. The NH···Cl^- and pyridyl CH···Cl^- hydrogen bonded contacts in the theoretical structure compare well

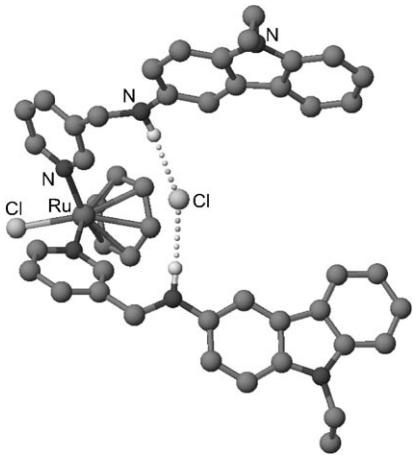


Figure 8. DFT calculated geometry for the 1:1 complex **2c**·Cl^- (CH hydrogen atoms omitted for clarity).

with the observed chemical shift changes, upon Cl^- binding in solution and with relevant crystallographic data on related compounds.[39] For the **2c**·Cl^- system, the absorption band consists mostly of carbazole localised transitions in a similar way to the case when the anion is absent, however, interestingly one strongly absorbing state in the $\lambda = 370$ nm region consists of charge transfer from a chloride p-orbital to an orbital localised over the central metal and pyridyl ligands. This provides a mechanism for the anion to quench the ILCT process, Figure 9.

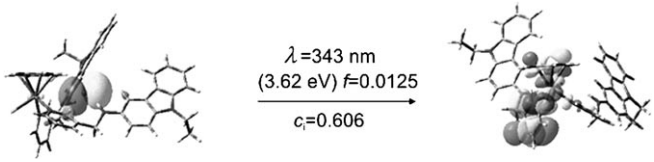


Figure 9. Charge transfer state involving Cl^- ion in **2c**·Cl^-.

Conclusion

A new series of coordination compound hosts have been synthesised. Compounds **2a** and **2b** bind a range of anions with modest selectivity for Cl^-, $H_2PO_4^-$ and acetate, forming both 1:1 and 2:1 host/guest complexes. These compounds display remarkable anion-dependent diastereotopic NMR spectra allowing for a novel means to monitor anion binding. Compound **2c** behaves differently forming 1:1 and 1:2 complexes with anions. Compound **2c** exhibits significant changes in its fluorescence upon binding coordinating anions, whereas weakly bound anions do not affect the emission. Time dependent DFT calculations suggest that absorption and hence emission in these systems involves an ILCT process that is quenched in **1c** by mixing with metal-based orbitals in an LMCT process. This mixing does not occur in **2c** but anion binding does result in quenching via a charge-transfer state. These versatile coordination compounds thus represent interesting and potentially tuneable fluorescent anion sensors.

Experimental Section

General procedure for ^{1}H NMR spectroscopic experiments: ^{1}H NMR spectroscopic titration experiments were carried out by using Varian Mercury 400 spectrometer running at 400 MHz, at room temperature. All chemical shifts are report in ppm. A specific concentration of host, typically 0.5–1.5 mM, was made up in a single NMR tube in $CDCl_3$ (0.5 mL). The anions, as their tetrabutylammonium salts, were made up to 1 mL, five times the concentration of the host, with $CDCl_3$. 10 μL aliquots of the guest were added to the NMR tube and the spectra were recorded after each addition. Results were analysed by using HypNMR 2006.[40,41]

General procedure for UV/Vis spectroscopic experiments: UV/Vis titration experiments were carried out using a UNICAM UV/Vis spectrometer (UV2–100), which is PC-controlled by means of Vision software, at room temperature. A specific concentration (as indicated in Figure captions) of host in acetonitrile (3.0 mL) was made up in a single quartz cuvette. The anions, as their tetrabutylammonium salts, were made up to 300 μL, 10 times the concentration of the host, in acetonitrile. 15 μL aliquots of the guest were added to the cuvette, with a path length of 1 cm and the spectra were recorded after each addition.

General procedure for fluorescence experiments: Fluorescence titration experiments were carried out by using a Fluoromax-3, which is PC-controlled, at room temperature. A specific concentration of host (as indicated in Figure captions) was made up in a single quartz cuvette, with a path length of 1 cm, in the acetonitrile (3.0 mL). The anions, as their tetrabutylammonium salts, were made up to 300 μL, 10 times the concentration of the host, in acetonitrile. 15 μL aliquots of the guest were added to the cuvette, the sample was excited at $\lambda = 375$ nm, and spectra were recorded after each addition.

DFT calculations: Geometry optimizations were performed by using the B3LYP functional in conjunction with the following basis: the Stuttgart–Dresden effective core potential (SDD) on the Ruthenium, the 4-31G basis on all carbon, nitrogen and hydrogen atoms, the 6-311+G(2d) basis on the chloride ions. If a guest Cl^- was present the basis was further augmented with a diffuse set of *s* and *p* functions on the peripheral hydrogen atoms. The time-dependent calculations were performed with an enlarged basis of 6-31G(d) on all atoms except ruthenium and chlorine, for which the basis was as above. Although the full conformational space was not sampled, preliminary computations were performed for each system to ensure the most sensible host–guest binding conformation. Minima were confirmed as such by using analytical frequency calculations. All computations were performed by using the Gaussian program.[42]

***N*-[(Pyridin-3-yl)methyl]benzenamine (L^1)**: Aniline (2.05 g, 21 mmol) and 3-pyridine carboxaldehyde (2.35 g, 22 mmol) were dissolved in dry 1,2-dichloroethane (250 mL), and magnesium sulfate (3.0 g, 25 mmol) was added. The solution was placed under reflux for 6 h whilst stirring. After this time the solution was filtered to remove the magnesium sulfate, and the solution concentrated under reduced pressure to yield the product as an orange oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=8.88 (d, J=1.9 Hz, 1H; Py-H), 8.56 (dd, J=4.6, 1.9 Hz, 1H; Py-H), 8.34 (s, 1H; CH), 8.14 (dt, J=7.8, 1.9 Hz, 1H; Py-H), 7.32–7.08 ppm (m, 6H; Py-H, Ar-H), ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz,): δ=157.1, 152.0, 151.4, 150.9, 134.8, 131.8, 129.2, 126.5, 123.7, 120.8, 43.5 ppm. The resulting imine was dissolved in methanol, and whilst stirring $NaBH_4$ (5.03 g, 13 mmol) was added until the solution ceased to effervesce. The solution was stirred for a further 2 h. 50:50 HCl/H_2O was added until the solution was pH 3, and then 2 M NaOH was added until the solution was pH 9. The product was extracted using dichloromethane. The organic layer was dried over $MgSO_4$, and then filtered. The solvent was evaporated under reduced pressure, and the product extracted, as a white crystalline solid and re-crystallised with dichloromethane and hexane. Yield: 3.15 g, 17 mmol, 77%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=8.53 (dd, J=5.0, 1.0 Hz, 1H; Py-H), 8.39 (d, J=1.5 Hz, 1H; Py-H), 7.71 (d, J=7.5 Hz, 1H; Py-H), 7.27 (m, 1H; Ar-H), 7.20 (t, J=8.0 Hz, 2H; Ar-H), 6.76 (t, J=7.5 Hz, 1H; Py-H), 7.64 (d, J=8.0 Hz, 2H; Ar-H), 4.36 (s, 2H; CH_2), 4.19 ppm (br s, 1H; NH); ^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz): δ=149.4, 148.9, 135.2, 129.6, 123.8, 118.3, 113.2, 46.0 ppm; MS(ES+): m/z: 185 [M^+]; elemental analysis calcd (%) for $C_{12}H_{12}N_2$: C 78.23, H 6.57, N 15.21; found: C 78.15, H 6.56, N 15.20; IR: $\tilde{\nu}$=3258 cm^{-1} (s).

4-Nitro-*N*-[(pyridine-3-yl)methyl]benzenamine (L^2): 4-Nitroaniline (13.60 g, 65 mmol) and 3-pyridine carboxaldehyde (6.93 g, 65 mmol) were dissolved in dry 1,2-dichloroethane, and magnesium sulfate (5.00 g) was added. The solution was placed under reflux for 6 h whilst stirring. After this time the solution was filtered to remove magnesium sulfate, and then concentrated under reduced pressure. The product was washed with diethyl ether, and the diethyl ether was removed under reduced pressure to yield the impure imine as dark yellow solid. ^{1}H NMR (MeOD, 400 MHz): δ=8.78 (d, J=2.4 Hz, 1H; Py-H), 8.58 (dd, J=4.8, 1.6 Hz, 1H; Py-H), 8.08 (d, J=2.0 Hz, 2H; ArH), 7.53 (dd, J=8.4, 5.6 Hz, 1H; Py-H), 7.45 (s, 1H; Py-H), 6.77 (d, J=2.0 Hz, 2H; ArH), 6.29 ppm (s, 1H; CH); MS(ES+): m/z: 228 [M^+]. The imine (7.0 g, 30.0 mmol) was dissolved in methanol, and whilst stirring $NaBH_4$ (6.0 g, 162.0 mmol) was added until the solution ceased to effervesce. The solution was stirred for a further 2 h. 50:50 HCl/H_2O was added until the solution was pH 3, and then 2 M NaOH was added until the solution was pH 9. The product was extracted using dichloromethane. The organic layer was dried over $MgSO_4$, and then filtered. The solvent was evaporated under reduced pressure, and the product re-crystallised from dichloromethane and hexane. Yield: 4.4 g, 19.1 mmol, 62%; ^{1}H NMR ($CDCl_3$, 500 MHz): δ=8.63 (s, 1H; Py-H), 8.57 (d, J=5.0 Hz, 1H; Py-H), 8.09 (dd, J=7.0, 2.0 Hz, 2H; Ar-H), 7.67 (dd, J=8.0, 2.0 Hz, 1H; Py-H), 7.30 (dd, J=8.0, 5.0 Hz, 1H; Py-H), 6.59 (dd, J=7.0, 2.0 Hz, 2H; Ar-H), 4.92 (s, 1H; NH), 4.47 ppm (d, J=6.0 Hz, 2H; CH_2); ^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz): δ=149.6, 149.3, 135.2, 126.6, 124.0, 111.72, 45.4 ppm; MS(ES+): m/z: 230 [M^+]; elemental analysis calcd (%) for $C_{12}H_{12}N_3O_2$: C 62.60, H 5.25, N 18.25; found: C 62.40, H 4.80, N 18.38; IR: $\tilde{\nu}$=3239 cm^{-1} (s).

9-Ethyl-*N*-[(pyridine-3-yl)methyl]-9*H*-carbazol-3-amine (L^3): 3-Amino-9-ethylcarbazole (9.60 g, 46 mmol) and 3-pyridinecarboxaldehyde (5.00 g, 47 mmol) were dissolved in dry 1,2-dichloroethane, and magnesium sulfate (5.00 g) was added. The solution was placed under reflux for 6 h whilst stirring. After this time the solution was filtered to remove magnesium sulfate, and then concentrated under reduced pressure to yield a brown oil. The product was washed with diethyl ether, and the brown solid impurities removed by filtration. The diethyl ether was removed under reduced pressure to yield the imine as dark yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=8.92 (d, J=1.6 Hz, 1H; Py-H), 8.53 (dd, J=4.8, 1.6 Hz, 1H; Py-H), 8.49 (s, 1H; CH=N), 8.15 (dt, J=7.7, 1.6 Hz, 1H; Ar-H), 7.97 (ddd, J=8.0, 0.4, 1.2 Hz, 1H; Ar-H), 7.91 (dd, J=2.0, 1.2 Hz, 1H; Ar-H), 7.33 (m, 2H; Ar-H), 7.11 (dt, J=7.2, 1.2 Hz, 1H; Py-H), 4.15 (q, J=7.2 Hz, 2H; CH_2), 1.26 ppm (t, J=7.2 Hz, 3H; CH_3); ^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz): δ=153.7, 153.2, 142.0, 133.5, 123.0, 122.7, 122.5, 118.9, 118.0, 107.8, 107.7, 36.7, 12.8 ppm. The imine (2.15 g, 7.18 mmol) was dissolved in methanol, and whilst stirring $NaBH_4$ (2.69 g, 71.8 mmol) was added until the solution ceased to effervesce. The solution was stirred for a further 2 h. 50:50 HCl/H_2O was added until the solution was pH 3, and then 2 M NaOH was added until the solution was pH 9. The product was extracted using dichloromethane. The organic layer was dried over $MgSO_4$, and then filtered. The solvent was evaporated under reduced pressure, and the product, re-crystallised from dichloromethane and hexane. Yield: 1.26 g, 4.18 mmol, 58%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=8.72 (d, J=2.0 Hz, 1H; Py-H), 8.56 (dd, J=5.0, 1.5 Hz, 1H; Py-H), 8.02 (d, J=7.5 Hz, 1H; Ar-H), 7.60 (d, J=7.5 Hz, 1H; Py-H), 7.46 (t, J=7.5 Hz, 1H; Py-H), 7.37 (m, 2H; Ar-H), 7.27 (m, 2H; Ar-H), 7.20 (t, J=7.5 Hz, 1H; Ar-H), 6.90 (dd, J=8.5, 2.0 Hz, 1H; Py-H), 4.44 (s, 2H; CH_2), 4.30 (q, J=7.5 Hz, 2H; CH_2), 4.05 (br s, 1H; NH), 1.40 ppm (t, J=7.5 Hz, 3H; CH_3); ^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz):149.3, 148.7, 135.4, 125.5, 123.6, 122.5, 118.1, 114.5, 109.3, 108.4, 103.8, 47.4, 37.5, 13.9 ppm; MS(ES+): m/z: 302 [M^+]; elemental analysis calcd (%) for: C 79.70, H 6.35, N 13.94; found: C 79.76, H 6.38, N 14.03.

***N*-[(Pyridin-4-yl)methyl]benzenamine (L^4)**: Aniline (5.35 g, 57 mmol) and 4-pyridine carboxaldehyde (6.2 g, 57 mmol) were dissolved in dry 1,2-dichloroethane, and magnesium sulfate (6.84 g, 57 mmol) was added. The solution was placed under reflux for 6 h. whilst stirring. The solution was filtered to remove magnesium sulfate, and then concentrated under reduced pressure to yield a yellow oil. The intermediate imine was washed with diethyl ether, and the yellow solid impurities removed by filtration. The diethyl ether was removed under reduced pressure to yield the imine as white powder (6.58 g, 36 mmol, 63%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ=8.76 (dd, J=4.5, 2.0 Hz, 2H; Py-H), 8.46 (s, 1H; CH), 7.76 (dd, J=4.5, 2.0 Hz, 2H; Py-H), 7.43 (t, J=7.5 Hz, 2H; Ar-H), 7.32–7.23 ppm (m, 3H; Ar-H); ^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz): δ=158.2, 150.84, 129.5, 127.3, 122.5, 121.2 ppm; MS(ES+): m/z: 183 [M^+]; elemental analysis calcd (%) for $C_{12}H_{10}N_2$: C 79.10, H 5.53, N 15.37; found: C 78.01, H 5.53, N 15.14. The imine (6.0 g, 33 mmol) was dissolved in methanol, and whilst stirring $NaBH_4$ (6.1 g, 165 mmol) was added until the solution ceased to effervesce. The solution was stirred for a further 2 h. 50:50 HCl/H_2O was added until the solution was pH 3, and then 2 M NaOH was added until the solution was pH 9. The product was extracted using dichloromethane. The organic layer was dried over $MgSO_4$, and then filtered. The solvent was evaporated under reduced pressure, and the product re-crystallised from dichloromethane and hexane. Yield: 4.9 g, 26.6 mmol, 81%; ^{1}H NMR ($CDCl_3$, 500 MHz): δ=8.54 (dd, J=4.5, 1.5 Hz, 2H; Py-H), 7.29 (dd, J=4.5, 1.5 Hz, 2H; Py-H), 7.17 (dd, J=7.0, 1.5 Hz, 2H; Ar-H), 6.75 (tt, J=7.5, 1.0 Hz, 1H; Ar-H), 6.58 (dd, J=9.0, 1.5 Hz, 2H; Ar-H), 4.37 ppm (s, 2H; CH_2); ^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz): δ=150.2, 129.6, 122.3, 118.2, 113.1, 47.3 ppm; MS(ES+): m/z: 185 [M^+]; elemental analysis calcd (%) for $C_{12}H_{10}N_2$: C 78.23, H 6.57, N 15.21; found: C 78.00, H 6.57, N 15.20.

***N*-[(Pyridin-2-yl)methyl]benzenamine (L^5)**: Aniline (10.7 g, 0.11 mol) and 2-pyridine carboxaldehyde (12.3 g, 0.11 mol) were dissolved in dry 1,2-dichloroethane (500 mL), and magnesium sulfate (13.2 g, 0.11 mol) was added. The solution was placed under reflux for 6 h. whilst stirring. The solution was filtered to remove the magnesium sulfate, and concentrated under reduced pressure to yield the intermediate imine product as a

yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.49 (d, J = 5.0 Hz, 1H; Ar-H), 8.46 (s, 1H; CH), 8.99 (d, J = 7.5 Hz, 1H; Py-H), 7.48 (dt, J = 7.5, 1.0 Hz, 1H; Py-H), 7.22 (t, J = 7.5 Hz, 2H; Py-H), 7.14 (d, J = 7.0 Hz, 2H; Ar-H), 7.06 ppm (m, 7.09–7.04 Hz, 2H; Ar-H); ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): δ = 151.1, 149.8, 136.6, 129.4, 126.9, 125.2, 121.9, 121.3 ppm; MS(ES+): m/z: 183 [M^+]. The imine was dissolved in methanol, and whilst stirring $NaBH_4$ (12.2 g, 0.33 mol) was added until the solution ceased to effervesce. The solution was stirred for a further 2 h. 50:50 HCl/H_2O was added until the solution was pH 3, and then 2 M NaOH was added until the solution was pH 9. The product was extracted using dichloromethane. The organic layer was dried over $MgSO_4$, and then filtered. The solvent was evaporated under reduced pressure, and the product extracted, as a white crystalline solid and recrystallised with from dichloromethane and diethylether. Yield: 6.5 g, 35 mmol, 32%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.61 (d, J = 4.5 Hz, 1H; Ar-H), 7.62 (dt, J = 8.0, 1.5 Hz, 1H; Py-H), 7.34 (d, J = 8.0 Hz, 1H; Py-H), 7.23–7.17 (m, 3H; Py-H, Ar-H), 6.76 (t, J = 7.5 Hz, 1H; Ar-H), 7.69 (d, J = 7.5 Hz, 2H; Ar-H), 4.66 (s, 1H; NH), 4.47 ppm (s, 2H; CH_2); ^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz): δ = 158.9, 137.0, 129.6, 122.4, 121.9, 117.8, 113.3, 49.5 ppm; MS(ES+): m/z: 185 [M^+]; elemental analysis calcd (%) for $C_{12}H_{12}N_2$: C 78.23, H 6.52, N 15.20; found: C 77.99, H 6.52, N 15.21.

[Ru(η^6-*p*-cymene)(*N*-{(pyridine-3-yl)methyl}benzenamine)Cl$_2$] (1a): [Ru(η^6-*p*-cymene)Cl$_2$]$_2$ (0.4 g, 0.64 mmol) and **L^1** (0.24 g, 1.3 mmol) were dissolved in toluene (100 mL), previously degassed for 1 h and left to stir at room temperature for 1 h. During this time an orange precipitate formed. The solid was collected by filtration, washed with toluene and dried in the air for 18 h (0.57 g, 1.2 mmol, 89%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.95 (s, 1H; Py-H), 8.89 (d, J = 5.6 Hz, 1H; Py-H), 7.69 (d, J = 8.0 Hz, 1H; Py-H), 7.22 (dd, J = 8.0, 5.6 Hz, 1H; Py-H), 7.15 (t, J = 8.0 Hz, 2H; Ar-H), 6.73 (t, J = 8.0 Hz, 1H; Ar-H), 6.57 (d, J = 8.0 Hz, 2H; Ar-H), 5.29 (d, J = 4.8 Hz, 2H; Ar-H), 5.03 (d, J = 4.8 Hz, 2H; Ar-H), 4.40 (brs, 1H; NH), 4.38 (s, 2H; CH_2), 2.85 (sept, J = 6.8 Hz, 1H; CH), 1.94 (s, 3H; CH_3), 1.22 ppm (d, J = 6.8 Hz, 6H; CH_3); ^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz): δ = 154.1, 153.4, 136.9, 136.5, 129.6, 124.5, 118.4, 113.4, 103.6, 97.4, 83.0, 82.4, 45.1, 30.8, 22.5, 18.3 ppm; MS(ES+): m/z: 489 [M^+]; elemental analysis calcd (%) for $C_{22}H_{26}N_2Cl_2Ru$: C 53.88, H 5.34, N 5.71; found: C 53.71, H 5.34, N 5.62; IR: $\tilde{\nu}$ = 3352 cm^{-1} (w, NH).

[Ru(η^6-*p*-cymene)(4-nitro-*N*-{(pyridin-3-yl)methyl}benzenamine)$_2$Cl][BF$_4$] (1b): [{Ru(η^6-*p*-cymene)Cl$_2$}$_2$] (1.0 g, 1.6 mmol) and **L^2** (0.8 g, 3.2 mmol) were dissolved in toluene (100 mL), previously degassed for 1 h and left to stir at room temperature for 1 h. During this time a yellow/orange precipitate formed. The solid was collected by filtration, washed with toluene and dried in the air for 18 h (1.2 g, 2.24 mmol, 68%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.76 (d, J = 6.4 Hz, 1H; Py-H), 8.74 (s, 1H; Py-H), 7.95 (d, J = 8.8 Hz, 2H; Ar-H), 7.45 (d, J = 6.4 Hz, 1H; Py-H), 7.07 (t, J = 6.4 Hz, 1H; Py-H), 6.44 (d, J = 8.8 Hz, 2H; Ar-H), 5.94 (s, 1H; NH), 5.30 (d, J = 5.6 Hz, 2H; Ar-H), 5.09 (d, J = 5.6 Hz, 2H; Ar-H), 4.15 (s, 2H; CH_2), 2.81 (sept, J = 6.8 Hz, 1H; CH), 1.61 (s, 3H; CH_3), 1.18 ppm (d, J = 6.8 Hz, 6H; CH_3); ^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz): δ = 153.8, 153.3, 152.8, 138.5, 136.8, 126.5, 124.5, 111.8 103.9, 97.3, 82.9, 82.5, 44.1, 30.9, 22.4, 18.4 ppm; MS(ES+): m/z: 535 [M^+]; elemental analysis calcd (%) for $C_{22}H_{25}N_3O_2Cl_2Ru$: C 49.35, H 4.71, N 7.85; found: C 50.39, H 4.70, N 8.92; IR: $\tilde{\nu}$ = 3238 cm^{-1} (w, NH) (persistent contamination by ≈20% **L^2**).

[Ru(η^6-*p*-cymene)(9-ethyl-*N*-{(pyridine-3-yl)methyl}-9*H*-carbazol-3-amine)Cl$_2$] (1c): [{Ru(η^6-*p*-cymene)Cl$_2$}$_2$] (0.50 g, 0.8 mmol) and **L^3** (0.50 g, 1.7 mmol) were dissolved in toluene (100 mL), previously degassed for 1 h and left to stir at room temperature for 1 h. During this time an orange precipitate formed. The solid was collected by filtration, washed with toluene and dried in the air for 18 h (0.97 g, 1.3 mmol, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.94 (s, 1H; Py-H), 8.80 (d, J = 7.6 Hz, 1H; Py-H), 7.87 (d, J = 8.0 Hz, 1H; Ar-H), 7.68 (d, J = 7.6 Hz, 1H; Py-H), 7.34 (t, J = 7.6 Hz, 1H; Py-H), 7.3–7.1 (m, 5H; Ar-H) 6.80 (d, J = 8.0 Hz, 1H; Ar-H), 5.13 (d, J = 6.0 Hz, 2H; Ar-H), 4.86 (d, J = 6.0 Hz, 2H; Ar-H), 4.39 (s, 2H; CH_2), 4.35 (brs, 1H; NH), 4.22 (q, J = 7.6 Hz, 2H; CH_2), 2.68 (sept, J = 7.0 Hz, 1H; CH), 1.74 (s, 3H; CH_3), 1.29 (t, J = 7.6 Hz, 3H; CH_3), 1.04 ppm (d, J = 7.0 Hz, 6H; CH_3); ^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz): δ = 154.5, 153.3, 140.5, 138.1, 137.1, 136.8, 129.3, 128.5, 125.9, 125.5, 124.5, 123.8, 122.5, 120.5, 118.4, 115.0, 109.7, 108.8, 103.3, 97.5, 83.2, 82.2, 46.5, 37.8, 30.8, 22.4, 18.1, 14.1 ppm; MS(ES+): m/z: 559 [M^+]; elemental analysis calcd (%) for $C_{30}H_{33}N_3Cl_2Ru$: C 59.30, H 5.47, N 6.92; found: C 59.18, H 5.61, N 6.79; IR: $\tilde{\nu}$ = 3379 cm^{-1} (w, NH).

[Ru(η^6-*p*-cymene)(*N*-{(pyridin-4-yl)methyl}benzenamine)Cl$_2$] (1d): [Ru(η^6-*p*-cymene)Cl$_2$]$_2$ (0.8 g, 1.3 mmol) and **L^4** (0.5 g, 2.7 mmol) were dissolved in toluene (100 mL), previously degassed for 1 h and left to stir at room temperature for 1 h. During this time a yellow/orange precipitate formed. The solid was collected by filtration, washed with toluene and dried in the air for 18 h (0.69 g, 1.41 mmol, 52%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.87 (d, J = 6.5 Hz, 2H; Py-H), 7.3–7.1 (m, 4H; Py-H, Ar-H), 6.73 (t, J = 8.0 Hz, 1H; Ar-H), 6.51 (d, J = 8.0 Hz, 2H; Ar-H), 5.41 (d, J = 6.0 Hz, 2H; Ar-H), 5.21 (d, J = 6.0 Hz, 2H; Ar-H), 4.49 (s, 1H; NH), 4.36 (s, 2H; CH_2), 2.97 (sept, J = 7.0 Hz, 1H; CH), 2.09 (s, 3H; CH_3), 1.29 ppm (d, J = 7.0 Hz, 6H; CH_3); ^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz): δ = 154.7, 147.3, 129.6, 129.3, 123.0, 118.3, 113.1, 103.8, 97.2, 82.9, 82.5, 46.7, 30.9, 22.5, 18.4; MS(ES+): m/z: 490 [M^+]; elemental analysis calcd (%) for $C_{22}H_{26}N_2Cl_2Ru$: C 53.88, H 5.34, N 5.71; found: C 54.43, H 5.40, N 4.99; IR: $\tilde{\nu}$ = 3315 cm^{-1} (w, NH).

[Ru(η^6-*p*-cymene)(*N*-{(pyridin-3-yl)methyl}benzenamine)$_2$Cl][BF$_4$] (2a): Compound **1a** (0.4 g, 0.8 mmol) and silver tetrafluoroborate (0.16 g, 0.8 mmol) were dissolved in 50:50 MeOH/acetone (50 mL), previously degassed for 1 h and left to stir at room temperature for 20 min. The silver(I) chloride was removed through celite and **L^1** (0.15 g, 0.8 mmol) was added to the filtrate, which was then stirred for a further 4 h. The solvent was removed under reduced pressure to yield a crude orange solid, which was re-crystallised from CH_2Cl_2 and C_6H_{14}. The orange solid was filtered and washed with C_6H_{14}, and dried in air (0.3 g, 0.4 mmol, 56%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.76 (s, 2H; Py-H), 8.38 (d, J = 5.8 Hz, 2H; Py-H), 7.54 (d, J = 7.6 Hz, 2H; Py-H), 7.0 (m, 6H; Ar-H), 6.55 (t, J = 7.6 Hz, 2H; Py-H), 6.42 (d, J = 7.6 Hz, 4H; Ar-H), 5.37 (brs, 2H; NH), 5.29 (AA′BB′, J = 6.2 Hz, 4H; Ar-H), 4.40 and 4.32 (AB, J = 17.2 Hz, 4H; CH_2), 2.28 (sept, J = 6.8 Hz, 1H; CH), 1.59 (s, 3H; CH_3), 0.83 ppm (d, J = 6.8 Hz, 6H; CH_3); ^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz): δ = 154.1, 151.2, 139.0, 138.1, 129.5, 125.1, 117.3, 112.9, 102.6, 102.4, 90.5, 81.2, 44.5, 30.9, 22.6, 17.6 ppm; MS(ES+): m/z: 639 [$M-BF_4^-$]; elemental analysis calcd (%) for $C_{34}H_{38}N_4ClRuBF_4$: C 56.25, H 5.28, N 7.72; found: C 55.86, H 5.22, N 7.63; IR: $\tilde{\nu}$ = 3421 (w, NH), 1062 cm^{-1} (s, BF_4^-).

[Ru(η^6-*p*-cymene)(4-nitro-*N*-{(pyridin-3-yl)methyl}benzenamine)$_2$Cl][BF$_4$] (2b): Compound **1b** (0.3 g, 0.6 mmol), silver tetrafluoroborate (0.2 g, 0.9 mmol) and **L^2** (0.2 g, 0.8 mmol) were dissolved in 50:50 MeOH/acetone (50 mL), previously degassed for 1 h and left to stir at room temperature for 20 min. The silver(I) chloride was removed through celite. The solvent volume was reduced under reduced pressure and the product recrystallised in the freezer from a MeOH/acetone/diethyl ether solvent mixture overnight. During this time an orange solid formed and was collected by filtration and washed with diethyl ether (0.1 g, 0.2 mmol, 33%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.84 (s, 2H; Py-H), 8.54 (d, J = 5.5 Hz, 2H; Py-H), 7.98 (d, J = 9.0 Hz, 4H; Ar-H), 7.63 (d, J = 5.5 Hz, 2H; Py-H), 7.12 (t, J = 5.5 Hz, 2H; Py-H), 6.67 (s, 2H; NH), 6.49 (d, J = 9.0 Hz, 4H; Ar-H), 5.47 (d, J = 6.0 Hz, 2H; Ar-H), 5.44 (d, J = 6.5 Hz, 2H; Ar-H), 4.57 and 4.49 (ABX, J = 7.0, 17.0 Hz, 4H; CH_2), 2.30 (sp, J = 7.0 Hz, 1H; CH), 1.56 (s, 3H; CH_3), 0.85 ppm (d, J = 7.0 Hz, 6H; CH_3); ^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz): δ = 153.7, 152.6, 151.9, 138.4, 138.1, 137.4, 126.4, 125.2, 111.6, 102.8, 102.3, 90.2, 44.2, 30.8, 22.4, 17.7 ppm; MS(ES+): m/z: 815 [M^+]; elemental analysis calcd (%) for $C_{34}H_{36}N_6O_4ClRuBF_4$: C 50.04, H 4.45, N 10.30; found: C 50.35, H 4.86, N 10.38; IR: $\tilde{\nu}$ = 3390 (w, NH), 1061 cm^{-1} (s, BF_4).

[Ru(η^6-*p*-cymene)(9-ethyl-*N*-{(pyridine-3-yl)methyl}-9*H*-carbazol-3-amine)$_2$Cl][BF$_4$] (2c): Compound **1c** (0.5 g, 0.7 mmol) and silver tetrafluoroborate (0.15 g, 0.8 mmol) were dissolved in 50:50 MeOH/acetone (50 mL), previously degassed for 1 h and left to stir at room temperature for 20 min. The silver(I) chloride was removed through celite and **L^3** (0.25 g, 0.8 mmol) was added to the filtrate, which was then stirred for a further 4 h. The solvent was removed under reduced pressure to yield a crude orange oil. The oil was washed with ethanol and re-crystallised from CH_2Cl_2 and C_6H_{14}. The green solid was filtered and washed with

C_6H_{14}, and dried in air. (0.13 g, 0.1 mmol, 19%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=8.96 (s, 2H; Py-H), 8.48 (d, J=5.5 Hz, 2H; Py-H), 7.88 (d, J=7.5 Hz, 2H; Ar-H), 7.39 (t, J=7.5 Hz, 2H; Ar-H), 7.11 (t, J=7.5 Hz, 2H; Ar-H), 7.6–6.9 (m, Py-H, 12H; Ar-H), 5.31 (AA′BB′, 4H; Ar-H), 4.54 and 4.46 (AB, J=16.5 Hz, 4H; CH_2), 4.21 (4q, J=7.0 Hz, H; CH_2), 2.13 (sept, J=6.5 Hz, 1H; CH), 1.46 (s, 3H; CH_3), 1.33 (t, J=7.0 Hz, 6H; CH_3), 0.54 ppm (d, J=6.5 Hz, 6H; CH_3); ^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz): δ=153.9, 151.3, 140.4, 140.2, 139.0, 138.2, 133.9, 125.7, 125.7, 125.1, 123.7, 122.6, 120.6, 118.3, 114.6, 109.7, 109.0, 108.5, 103.0, 102.8, 101.9, 90.6, 80.7, 45.5, 37.7, 30.6, 22.0, 17.4, 14.2 ppm; MS(ES+): m/z: 873 [M^+−BF_4]; IR: $\tilde{\nu}$=3409 (w, NH), 1060 cm^{-1} (s, BF_4).

[Ru(η^6-*p*-cymene)(*N*-{(pyridin-4-yl)methyl}benzenamine)$_2$Cl][BF$_4$] (2d): Compound **1d** (0.4 g, 0.8 mmol), silver tetrafluoroborate (0.2 g, 0.9 mmol) and **L^4** (0.2 g, 0.8 mmol) were dissolved in 50:50 MeOH/acetone (50 mL), previously degassed for 1 h and left to stir at room temperature for 20 min. The silver(I) chloride was removed through celite. The solvent volume was reduced under reduced pressure and the product was collected as an orange oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=8.85 (d, J=6.5 Hz, 4H; Py-H), 7.41 (d, J=6.5 Hz, 4H; Py-H), 7.08 (t, J=7.5 Hz, 4H; Ar-H), 6.67 (t, J=7.5 Hz, 2H; Ar-H), 6.47 (d, J=7.5 Hz, 4H; Ar-H), 5.84 (d, J=6.0 Hz, 2H; Ar-H), 5.59 (d, J=6.0 Hz, 2H; Ar-H), 4.57 (s, 2H; NH), 4.36 (d, J=2.0 Hz, 4H; CH_2), 2.55 (sept, J=7.0 Hz, 1H; CH), 1.68 (s, 3H; CH_3), 1.11 ppm (d, J=7.0 Hz, 6H; CH_3); ^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz): δ=154.1, 154.0, 147.3, 129.6, 124.7, 118.3, 113.1, 103.5, 102.0, 88.4, 82.3, 46.7, 31.0, 22.5, 17.9 ppm; MS(ES+): m/z: 638 [M^+−BF_4]. Reliable elemental analysis was not obtained because of the oily nature of the product.

[Ru(η^6-*p*-cymene)(*N*,*N*′-{(pyridin-2-yl)methyl}benzenamine)Cl]Cl (3): [{Ru(η^6-*p*-cymene)Cl_2}$_2$] (0.80 g, 1.3 mmol) and **L^5** (0.40 g, 2.2 mmol) were dissolved in toluene (100 mL), previously degassed for 1 h and left to stir at room temperature for 1 h. During this time an orange precipitate formed. The solid was collected by filtration, washed with toluene and dried in the air for 18 h (0.52 g, 1.1 mmol, 82%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ=11.50 (s, 1H; NH), 8.95 (d, J=6.5 Hz, 1H; Py-H), 8.03 (d, J=7.5 Hz, 2H; Ar-H), 7.82 (t, J=6.5 Hz, 1H; Py-H), 7.40 (t, J=6.5 Hz, 1H; Py-H), 7.39(d, J=6.5 Hz, 1H; Py-H), 7.38 (t, J=7.5 Hz, 2H; Ar-H), 7.22 (t, J=7.5 Hz, 1H; Ar-H), 6.40 (d, J=5.5 Hz, 1H; Ar-H), 5.49 (d, J=6.5 Hz, 1H; Ar-H), 5.34 (d, J=6.5 Hz, 1H; Ar-H), 4.84 (d, J=5.5 Hz, 1H; Ar-H), 4.55 (dd, J=15.0, 5.0 Hz, 1H; CH_2), 4.30 (dd, J=15.0, 10.0 Hz, 1H; CH_2) 2.80 (q, J=7.0 Hz, 1H; CH), 2.25 (s, 3H; CH_3), 1.15 (d, J=7.0 Hz, 3H; CH_3), 0.65 ppm (d, J=7.0 Hz, 3H; CH_3); ^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz): δ=162.0, 153.1, 149.3, 139.5, 129.4, 126.9, 125.1, 122.1, 121.8, 105.5, 96.4, 86.3, 85.3, 84.4, 83.4, 58.7, 30.0, 24.0, 19.2 ppm; MS(ES+): m/z: 455 [M^+−Cl]; elemental analysis calcd (%) for $C_{22}H_{24}N_2Cl_2Ru$: C 53.88, H 5.34, N 5.71, Cl, 14.46; found: C 53.52, H 5.42, N 5.69, Cl 14.19; IR: $\tilde{\nu}$=3382 cm^{-1} (w, NH).

[Ru(η^6-*p*-cymene)(*N*,*N*′-{(pyridin-2-yl)methyl}benzenamine)Cl][BPh$_4$] ([3][BPh$_4$]): [Ru(η^6-*p*-cymene)(*N*, *N*′-((pyridin-2-yl)methyl)benzenamine)Cl]Cl (0.02 g, 0.041 mmol) was dissolved in methanol, and added to a solution of $NaBPh_4$ (0.014 g, 0.041 mmol) in methanol. A yellow precipitate was formed immediately, and collected by filtration (0.026 g, 0.032 mmol, 79%); elemental analysis calcd (%) for $C_{46}H_{46}N_2BClRu$: C 71.36, H 5.99, N 3.62; found: C 71.09, H 6.00, N 3.57.

[Ru(η^6-hexamethylbenzene)(*N*-{(pyridine-3-yl)methyl}benzenamine)Cl$_2$] (4): [{Ru(η^6-C_6Me_6)Cl_2}$_2$] (0.1 g, 0.15 mmol) and **L^1** (0.049 g. 0.27 mmol) were stirred in dry toluene (20 mL) at room temperature overnight. Over this time a dark red solid precipitates from solution, and is collected by filtration. The crude product was then washed with toluene, and the pure red solid is collected by filtration (0.089 g, 0.096 mmol, 64%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=8.71 (s, 1H; Py-H), 8.62 (d, J=6.0 Hz, 1H; Py-H), 7.60 (d, J=6.0 Hz, 1H; Py-H), 7.17 (dd, J=6.0, 1.8 Hz, 1H; Py-H), 7.09 (t, J=7.5 Hz, 2H; Ar-H) 6.65 (t, J=7.5 Hz, 1H; Ar-H), 6.51 (d, J=7.5 Hz, 2H; Ar-H) 4.32 (s, 3H; NH, CH_2), 1.80 ppm (s, 18H; C_6Me_6); elemental analysis calcd (%) for $C_{24}H_{30}Cl_2N_2Ru$: C 55.60, H 5.83, N 5.40; found C 54.90, H 5.72, N 4.85.

Crystallographic data: $C_{24}H_{30}Cl_2N_2Ru$, M_r=518.47, yellow block, 0.30×0.10×0.10 mm, monoclinic, space group *Cc* (No. 9), a=15.291(4), b=18.987(5), c=8.376(2) Å, β=94.100(7)°, V=2425.6(11) Å^3, Z=4, ρ_{calcd}=1.420 g cm^{-3}, F_{000}=1064, SMART 6k, $Mo_{K\alpha}$ radiation, λ=0.71073 Å, T=120(2) K, $2\theta_{max}$=58.4°, 19681 reflections collected, 6518 unique (R_{int}=0.0599). Final GooF=0.992, $R1$=0.0380, $wR2$=0.0755, R indices based on 5580 reflections with $I>2\sigma(I)$ (refinement on F^2), 268 parameters, 2 restraints. Lorentz polarisation and absorption corrections were applied.

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