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Tuneable reversible redox of cobalt(III) carbazole complexes

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Four tridentate carbazole-based ligands, $H_{L^{HBu/H}}^{L^{HBu/H}}$ (3,6-di(*tert*-butyl)-1,8-bis[5-(3-benzyl-1,2,3-triazole)]-9*H*-carbazole), $H_{L^{HBu/HBu}}^{HBu/HBu}$ (3,6-di(*tert*-butyl)-1,8-bis[5-(3-(4-*tert*-butyl)benzyl-1,2,3-triazole)]-9*H*-carbazole), $H_{L^{H/H}}^{H/H}$ (1,8-bis[5-(3-(4-*tert*-butyl)benzyl-1,2,3-triazole)]-9*H*-carbazole), were prepared and complexed with cobalt(II) tetrafluoroborate. *In situ* air oxidation resulted in cobalt(III) complexes **1**-**4** with the general formula [Co^{III}(L)₂]BF₄·xH₂O (**1**: L = L^{IBu/H}, x = 2; **2**: L = L^{IBu/HBU}, x = 1; **3**: L = L^{H/H}, x = 0.5; **4**: L = L^{H/HBU}, x = 2). X-ray structural characterisation confirmed that the four complexes are isostructural, with two orthogonally coordinated deprotonated tridentate ligands providing an octahedral N₆-donor set to the cobalt(III) ion. ¹H NMR studies show that this structure is maintained in CDCl₃ and DMSO-*d*₆ solution. Cyclic voltammetry on **1**-**4** in MeCN showed that all of the complexes exhibit two reversible, one-electron oxidation processes (probably due to ligand oxidations), and an irreversible or quasi-reversible reduction process (probably due to reduction of CO(III) to CO(III)). As expected, the oxidations move 120-140 mV to lower potentials on adding *tert*-butyl substituents to the 3 and 6 positions of the carbazole rings (and the potentials are far less sensitive to the nature of the benzyl ring substituents).

Introduction

Transition metal complexes of carbazole-based *acyclic* ligands have many practical applications,¹ including as catalysts for Nozaki-Hiyama reactions,² and as cyanide detection agents using quenching of fluorescence (I, Figure 1).³ There are also a few examples of *macrocyclic* complexes featuring carbazole units in porphyrin-like systems,¹ with the extended aromatic system giving potentially interesting photoelectric properties,⁴, ⁵ while others feature alternating carbazole and pyridine units (IV, Figure 2).⁶

Several of these complexes have interesting redox properties: the most relevant of which, to the present study, is the *macrocyclic cobalt(II)* carbazole complex (**IV**, Figure 2). This complex exhibited two reversible one-electron redox events, at $E_m = 0.78$ and 1.05 V (vs. Ag/Ag⁺), which the authors suggested could be due to Co(II) to Co(III) oxidation and a ligand centered oxidation, respectively.⁶ However, the neutral metal-free macrocycle showed two irreversible oxidation processes at significantly higher potentials (first onset at 1.25 V), which were attributed to the two carbazole moieties being consecutively oxidized to cation radicals. A related series of

twelve *nickel(II)* complexes, NiL₂, of a family of *acyclic* diphenylamine-dipyrazolyl ligands (**II**, Figure 1) also exhibited interesting redox properties.⁷ These complexes have two quasi-reversible one-electron processes, ascribed by the authors to ligand centered oxidations, which were tuned over a wide range (700 mV) by varying the two substituents **X** and **Y** *para*- to the central amine nitrogen on each ligand (Figure 1).



Figure 1. Cu(II) and Ni(II) complexes of carbazole and diphenylamine based acyclic ligands: $[Cu^{II}(L^{EBU/H})X] I$, left,³ $[Ni^{II}(X,Y)_2] II$, right,⁷

One area of potential improvement for more efficient and industrially viable dye-sensitized solar cells (DSSCs) is the development of alternatives to the wide-spread use of I_3 /l⁻ redox electrolyte, ⁸ with considerable interest being focused on the use of cobalt based redox electrolytes.⁹⁻¹¹ A key requirement for an effective redox electrolyte is an appropriately positioned reversible redox process, with the ideal positioning of this redox process dependent on the specific dye used. Reports of effective cobalt based redox electrolytes have had processes centered near the Fc/Fc⁺ redox couple, with some examples falling slightly below (-90

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⁺Electronic Supplementary Information (ESI) available: Additional organic synthesis details, ¹H ¹³C and 2D NMR spectra, cyclic voltammograms and analysis, figures of the structures (CCDC 1510199-1510202) and CSD search fragment. See DOI: 10.1039/x0xx00000x

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Scheme 1: Synthetic route to the family of bis(triazolyl)carbazole ligands from 9*H*-carbazole. Reagents and conditions: (a) ¹BuCl, anhydrous AlCl₃, dry DCM, RT; (b) Nbromosuccinimide, silica gel, dry DCM, RT, light-free; (c) anhydrous AlCl₃, dry toluene, RT; (d) TMS-acetylene, Pd(PPh₃)₂Cl₂, Cul, dry NEt₃, reflux; (e) K₂CO₃, MeOH, reflux; (f) 4substituted benzyl bromide, NaN₃, ascorbic acid, CuSO₄-5H₂O, Na₂CO₃, DMF:H₂O (4:1).



mV)¹⁰ and others slightly above (+220 mV)¹¹ this reference couple. We have reported cobalt complexes with reversible redox in this region,¹²⁻¹⁴ but which had poor solubility and were not readily tuneable. Hence we decided to instead target cobalt complexes of readily tuneable carbazole-based tridentate ligands (Scheme 1).

Δ search of the CSD using а generic diphenylamine/carbazole N₃-bound cobalt fragment (ESI, Figure S57) returned just four structures (Figure 2).^{6, 15-17} All four complexes were of cobalt(II), but they differ in coordination numbers, ranging from 7 for III (N_7 pentagonal bipyramidal), to 6 for IV (N_4O_2 octahedral), to 5 for V (N_3Cl_2 trigonal bipyramidal), to 4 for VI (N_3 Cl flattened tetrahedral). Complexes III, IV and VI were red, with the last two stated to be high-spin Co(II), and III reported to have μ = 4.6 B.M, consistent with also being high-spin Co(II). In contrast, V was blue, with no spin state explicitly stated. Two of the four ligands were carbazole-based (IV and VI, Figure 2) and two were diphenylamine-based (III and V, Figure 2). Two of them were *macrocyclic* ligands (III and IV, Figure 2).^{6, 16} In one of the diphenylamine complexes, blue complex V, the cobalt(II) was bound through a still protonated amine group (Co-N 2.33 Å) whereas in III this moiety was deprotonated (Co-N 2.09 Å). In comparison the carbazole complexes had shorter Co-N(central) bond lengths of 1.91-1.95 Å. The Co-N(flanking) bond lengths are shorter in the two acyclic complexes, 2.05-2.08 Å, 17 than in the two macrocyclic complexes, 2.31-2.37 Å. 6 , ¹⁶ This is likely due in part to the smaller coordination numbers for the two acyclic complexes (4 and 5, versus 6 and 7 for the macrocycles). The geometrical constraints imparted by the macrocycles may also be playing a role. High spin complex IV also exhibits two significantly shorter 'axial' Co-N(carbazole) bonds (1.93 and 1.95 Å) than the four 'equatorial' bonds (2.222.35 Å). Interestingly, of these four cobalt(II) compounds, two were prepared without the use of inert atmospheres (IV and V),^{6, 15} one under a nitrogen atmosphere (III),¹⁶ and one under strict Schlenk conditions (VI).¹⁷



Figure 2. Structurally characterized cobalt complexes of carbazole and diphenylamine based ligands. Clockwise from top left: $[Co^{IL}_{J}(py)_2]BPh_4$;¹⁶ $[Co^{IL}_{J}(THF)(H_2O)]$ -THF;⁶ [(5)Co^{II}Cl];¹⁷ $[Co^{II}_{J}(Bopa-ip)Cl_2]$.¹⁵ Bond distances for the cobalt(II) coordination spheres are given in Å and rounded to 3 s.f.

Given (a) the redox processes of the *macrocyclic carbazole cobalt(II)* complex **IV** (Figure 2) fall close to the range interesting for DSSCs,⁶ (b) the series of *nickel* complexes **II** (Figure 1) show how *acyclic carbazole-like ligands* can provide redox tuneability,⁷ (c) the *paucity* of cobalt complexes of carbazole or carbazole-like ligands and the *complete lack*, to date, of bis-ligand CoL₂ or cobalt(III) complexes, it was thought that CoL₂ complexes of carbazole ligands such as that reported

by Jang and co-workers (for generating a cyanide sensing copper complex, I, Figure 1),³ may prove interesting. The synthesis and redox chemistry of the first family of such complexes is reported herein.

Results and Discussion

Synthesis of ligands

The synthetic route to the four ligands is shown in Scheme 1 and was inspired by the published synthesis³ of $HL^{tBu/H}$, but differs in the details (including the protecting group employed, and use of one-pot CuAAC), all of which are provided herein.

Because the 3,6-positions of 9*H*-carbazole are the most reactive sites,¹⁸ the first step is protection of these positions through Friedel-Crafts alkylation (step a).^{17, 19, 20} After recrystallisation from cyclohexane to remove the other alkylated products (mostly mono- and tri-alkylated), this gives clean 3,6-di-*tert*-butyl-9*H*-carbazole in moderate yield (37%, comparable to literature reports of 47%),²⁰ and is easily carried out on a tens of grams scale. It should be noted that, subsequent to the present study, an improved protocol for this step was reported by Cole and Kunz in 2016,²¹ which allowed for a similar scale (20 g) whilst vastly improving the yield (95%), by using a method published by Hou in 2006.²²

In the next step, bromination of the 1- and 8- positions is carried out using N-bromosuccinimide (NBS) and silica in DCM (step b); a method adapted from the protocol Smith reported in 1992 for the bromination of carbazoles.¹⁸ The reaction slurry is stirred in light-free conditions for several days, and affords microanalytically 1,8-dibromo-3,6-di-tert-butyl-9Hclean carbazole in excellent yields (96%). Previously this step has involved use of Br₂ (a volatile liquid and cumulative toxin) and glacial acetic acid, so avoiding the use of Br₂ reduces exposure to hazardous materials, and facilitates larger scale reactions, while still giving comparable yields (96% with NBS, cf. 99% using Br₂ and glacial AcOH).²⁰ The yield reported here is similar to that reported for the analogous NBS reaction with 3,6dimethylcarbazole (95%).17

If desired, it is then possible to remove the *tert*-butyl groups from the 3,6-positions in a reverse Friedel-Crafts reaction to give 1,8-dibromocarbazole (step c), using a method²³ adapted from Tashiro's protocols reported in 1979 for the trans-alkylation of aromatic compounds.²⁴ This method is a viable alternative to the literature route, which instead progresses through nitration, bromination, reduction of the nitro groups to amines, then removal of the amine groups (15% in 4 steps cf. 18% in 3 steps in the current study).²⁵ It also has the advantage of utilizing a precursor already prepared in large quantities for synthesis of the other ligands described herein.

The Sonogashira cross-coupling of the 1,8-dibrominated carbazoles with a protected alkyne was altered from that reported by Jang and co-workers in 2011 for the synthesis of HL^{tBu/H}, in which a 2-methyl-3-butyn-2-ol group was used.³ The alcohol protected alkyne proved difficult to isolate cleanly, and the subsequent deprotection step appears to cause some

degradation of the product. Attempts to purify the deprotected alkyne formed via this route proved unsuccessful, with a clean sample unable to be obtained, likely due to further degradation of the product during purification. This method did provide material suitable for subsequent reaction, however the obtained HL^{tBu/H} also proved difficult to purify, thus a cleaner route was desired. To this end, ethynyltrimethylsilane (TMS-acetylene) was instead employed as the protected alkyne. The two protected 1,8-dialkyne intermediates are obtainable in excellent yields (84-89%, step d), slightly higher than the 81% reported for the 2-methyl-3butyn-2-ol protected alkyne.³ The TMS protecting group is then removed through a straightforward methanolysis reaction, which gives the corresponding pair of deprotected terminal dialkynes cleanly in quantitative yields. This change to a TMS protecting group proved a real boon, greatly facilitating the clean synthesis of this family of ligands, while also improving yield for the two steps from 71% to 81-88%. For completeness we note that, concurrent with the present study, one of these two dialkynes was reported as being prepared by a similar method, although specific synthetic details were not provided in that paper.²⁶

Alternative protecting groups such as tributyl(trimethylsilylethynyl)tin have been used and can give very good yields (99% reported for the two steps),²⁷ but the reagent is both more expensive and significantly more toxic.

The TMS-protected alkyne appears stable indefinitely, but the deprotected alkynes are somewhat prone to degradation, so they were prepared from the protected alkyne as required for prompt subsequent reaction, or stored in the freezer for short periods (stable for a week or two).

The final step is *in situ* generation of the benzyl or 4-*tert*butylbenzyl azide of choice from the corresponding organic bromide and NaN₃,²⁸ then, in the same pot, a CuAAC reaction²⁹⁻³¹ with the appropriate 1,8-diethynylcarbazole to form the four ligands targeted in this work. These ligands were obtained in moderate to good yields (41-83%), although HL^{tBu/H} was obtained in lower yields than previously reported (60% cf. 81%).³ Compared to the reported synthesis, in which benzylazide was first isolated and then reacted with the alkyne, we consider that the ease of a one-pot reaction and the safety benefit of not isolating a potentially explosive organic azide are worth the slightly reduced yield.

Synthesis of cobalt complexes

Initially attempts were made to isolate the $[Co^{II}L_2]$ complexes, with a view towards potential spin crossover activity.³² However it proved difficult to isolate the cobalt(II) complexes as whilst the early yellow-orange of the reaction solutions indicate that $[Co^{II}L_2]$ species may be formed initially, they are very air-sensitive and the color continues to change, first to yellow-green and then on to the green-blue of the cobalt(III) complexes. Given the negative potentials of the Co^{III}/Co^{II} redox couple (*vide infra*), it is unsurprising that those initial attempts to isolate the cobalt(II) complexes were unsuccessful. Given the reversible redox observed, we decided to instead target

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the isolation of a family of cobalt(III) complexes and to investigate the tune-ability of the redox potentials.

With this revised goal in mind, the four cobalt(III) complexes 1-4 were synthesized by combining, initially under an inert atmosphere, $Co^{II}(H_2O)_6(BF_4)_2$ and two equivalents of the desired ligand in either acetone:methanol (1), pyridine (2 and 4) or DMF (3). For the complexations not performed in pyridine (1 and 3), an excess of triethylamine was added as a base. In order to ensure complete oxidation to cobalt(III), after a minimum of 30 minutes the reaction solutions were opened to air. In the case of 1, 3 and 4, subsequent diffusion of diethyl ether vapour into the reaction solution yielded crystals which were filtered and then dried to give $[Co^{III}(L^{tBu/H})_2]BF_4 \cdot 2H_2O(1)$, $[Co^{III}(L^{H/H})_2]BF_4 \cdot 0.5H_2O$ (3) and $Co^{III}(L^{H/tBu})_2]BF_4 \cdot 2H_2O$ (4), as blue-green solids in yields of 64, 61 and 39% respectively. For 2, the reaction was instead taken to dryness and the solid residue dissolved in acetonitrile before vapor diffusion of diethyl ether into the complex solution. The resulting bluegreen crystalline solid was filtered and dried in vacuo giving $[Co^{III}(L^{tBu/tBu})_2]BF_4 \cdot H_2O$ (2) in 63% yield.

The four cobalt(III) complexes were characterized by microanalysis, ESI-MS, ¹H, ¹³C and 2D NMR spectroscopy and X-ray crystallography. In all four cases, **1–4**, the microanalysis data matched the calculated values for $[Co^{III}(L)_2]BF_4$ ·xH₂O and the mass spectra showed a single major peak which matches the predicted isotope pattern of the expected $[Co^{III}(L)_2]^+$ fragment.

NMR spectroscopy

The ¹H NMR spectra of these diamagnetic cobalt(III) complexes all show the conspicuous absence of the amine proton signal of the carbazole, signifying deprotonation and subsequent metal coordination has occurred (Figures 3 and 4). There is no broadening or splitting of the signals of the complexes compared to the free ligand, consistent with diamagnetic cobalt(III), and indicating that the symmetry of the free ligands seen by NMR is retained in these complexes.

Comparison of the ¹H NMR spectra in CDCl₃ of the free ligand $HL^{tBu/tBu}$ and the corresponding complex **2** reveals several shifts in signal positions on deprotonation and subsequent cobalt coordination (Figure 3). Notably, the H₄ (carbazole) and H₁₅ (carbazole tert-butyl) peaks have been shifted downfield relative to the free ligand. In contrast, all other peaks have been shifted upfield, with the protons on the benzyl tert-butyl group, benzyl ring, and CH₂ linker experiencing the largest shifts. The downfield shift in the carbazole proton presumably arises due to the 3⁺ cobalt ion removing electron density from the formally anionic ligand, but it is interesting to note that the other carbazole proton, H_2 , is unshifted. The significant upfield shift of the resonances of the benzyl arm is consistent with shielding due to throughspace interactions with the carbazole moiety of the other coordinated ligand (as is observed in the solid state, vide infra). The existence of these close contacts was further investigated by 2D ROESY NMR spectroscopy in DMSO-d₆. Through-space H-H interactions are observed between the benzyl groups and carbazole groups, and between carbazole *tert*-butyl groups (*i.e.* H_{15}) and benzyl arms (Figures S48 and S49); importantly these interactions are not observed for the free ligand (Figure S56). Taken together, the 1D and 2D NMR data are consistent with the complexes having a tightly folded structure in both CDCl₃ and DMSO-*d*₆ solution.

A comparison of the four complexes with their free ligands is shown in Figures 3-4 (2 and 3) and Figures S41 - S46. Generally, the complexes show relatively similar ¹H NMR spectra, although interestingly the triazole resonances in complexes 1 and 2, which have *tert*-butyl groups attached to the carbazole moiety, are significantly downfield relative to the same resonances in complexes 3 and 4, which do not have these *tert*-butyl groups.







Figure 4. Expansion of the key region of the ¹H NMR spectra of the cobalt(III) complexes **2** and **3** and the corresponding free ligands $HL^{Bu/tBu}$ and $HL^{H/H}$ (298 K, DMSO- d_{e}). Scheme 1 shows the numbering scheme used. Stacked plots of all four complexes and their corresponding ligands are provided in the SI, S41-44.

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	$[Co^{III}(\boldsymbol{L}^{tBu/H})_2]BF_4$	$[Co'''(L^{tBu/tBu})_2]BF_4 \cdot 1.5Et_2O \\ \cdot solvent^{a}$	[Co ^Ⅲ (L^{H/H}) ₂]BF₄·0.5DMF ·0.5H₂O ^b	$[Co^{III}(\mathbf{L}^{H/tBu})_2]BF_4 \cdot 1.5Et_2O$ ·solvent ^a
Space Group	P4/n	P21/c	P2 ₁ /n	P-1
M-N _{cbz}	1.928(3)	1.916-1.921(3) [1.919]	1.924-1.929(2), 1.917-1.923(2), [1.923]	1.937-1.940(5) [1.939]
$\textbf{M-N}_{triazole}$	1.945(2)	1.936-1.949(3) [1.944]	1.950-1.957(2), 1.943-1.947(2), [1.949]	1.938-1.951(5) [1.946]
$N_{\text{triazole}}\text{-}M\text{-}N_{\text{triazole}}$	179.52(12)	177.53(13), 176.90(14) [178.72]	176.54(8), 177.17(8), 178.06(8),175.68(8) [176.86]	176.3(2), 175.35(18) [175.8]
N_{cbz} -M- N_{cbz}	180	178.61(14)	178.39(8), 179.48(8) [178.94]	177.93(19)
<i>Cis</i> -angles ^c	89.76-90.24 [90.00]	87.55-92.12 [90.01]	84.44-93.21 [90.01]	84.7-92.66 [90.06]
N_{cbz} - M - $N_{triazole}$	90.24(6)	90.09-91.30 [90.78]	90.21-91.55[90.92]	89.8-91.5[90.7]
Σ (O _h) ^c	1.92	12.07	17.95, 15.73	18.09
Cbz∠Cbz ^d	90.00	74.17	82.11, 89.07 [85.59]	81.74
Trz∠Trz ^e	20.98	16.29, 24.57 [20.43]	17.69, 13.64, 4.67, 17.34 [13.34]	17.41, 17.71 [17.56]
Cbz∠Trz ^f	14.30	8.83, 10.41, 15.41, 16.28 [12.73]	8.85, 9.13, 2.99, 14.73, 4.66, 6.95, 5.46, 11, 96 [8,09]	7.96, 9.45, 10.00, 7.94 [8.84]

Table 1 Selected bond lengths (Å) and angles (°) for the structures of the family of four [Co^{III}(L)₂]BF₄ complexes. Where a range is provided *-*, the average is presented in [*].

^{*a*} Platon-Squeeze was used to account for lattice electron density (presumably disordered solvents of crystallisation) that was unable to be modelled in a sensible way.^{33 b} The crystal structure contains two full complexes within the asymmetric unit. ^{*c*} Range of *cis* angles for the CoN₆ center(s) with the mean value in parentheses. ^{*d*} Σ (O_h), the octahedral distortion parameter, is calculated as the sum of the variances of each of the 12 cis angles from the ideal 90°: Σ (O_h) = 0° is a perfect O_h.^{34-37 d} Angle between the mean planes of the carbazole rings of a complex. ^{*e*} Angle between the mean planes of each triazole ring within a ligand. ^{*f*} Angle between the mean plane of the carbazole ring for each ligand.

Structure Descriptions

Single crystals of all four $[Co^{III}(L)_2]BF_4$ complexes were grown by diffusion of diethyl vapor into solutions of the complexes (see experimental section for details) and X-ray structure determinations carried out. The four complexes are isostructural (Figure 5, and SI Figure S58). In each complex, the cobalt(III) ion is coordinated in an N₆ octahedral fashion by two, roughly perpendicular, deprotonated tridentate $(L)^$ ligands (Figure 5). The oxidation state of the cobalt ion is clear from consideration of the sharp NMR spectra (see earlier), the charge balance, and the relatively short Co-N bond lengths (1.92-1.97 Å), all of which are consistent with cobalt(III) (Table 1). These are the first examples of cobalt(III) complexes of such ligands.

Each ligand is coordinated through the N₃ donor pocket created by the nitrogen atom of the carbazole moiety and two triazole nitrogen atoms. The ligands impose very regular ($\Sigma \leq 18^{\circ}$, Table 1) octahedral coordination geometry on the cobalt(III) ion, with all *cis*-angles close to 90° (84.4-93.2°, Table 1). The planes of the carbazole moieties of each ligand are roughly perpendicular to one another (74-90°, Table 1), as are the planes of the triazole rings.

The structures of the complexes do vary in the position of the benzyl 'arms' relative to the plane of the carbazole moiety (Figure 6). In $[Co^{III}(L^{tBu/tBu})_2]^+$, $[Co^{III}(L^{H/H})_2]^+$ and $[Co^{III}(L^{H/tBu})_2]^+$, the arms of one ligand are orientated towards the same side of the plane of the carbazole moiety, while in the other ligand the arms are pointing to opposite sides of the plane. However, in $[Co^{III}(L^{tBu/H})_2]^+$, the benzyl arms of *both* ligands are orientated

towards opposite sides of the plane of the carbazole moiety, creating a 'propeller-like' motif. The content of noncoordinated lattice solvent also varies between the structures.



Figure 5. Perspective view of the cation of $[Co^{III}(L^{H/H})_2]BF_4 \cdot 0.5DMF \cdot 0.5H_2O$. For clarity, solvent molecules, the counter anion and hydrogen atoms have been omitted. See SI, Figure S58, for figures showing the structures of the other three complexes.

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Figure 6. Comparison of benzyl arm positions found in the four cobalt(III) complexes: trans-trans propeller (left, $[Co^{III}(L^{tBu/H})_2]^*$) and cis-trans (right, $[Co^{III}(L^{tBu/tBu})_2]^*$, $[Co^{III}(\mathbf{L}^{H/H})_2]^+$ and $[Co^{III}(\mathbf{L}^{H/tBu})_2]^+)$. Electrochemistry Cyclic voltammetry was carried out on the family of four cobalt(III) complexes in MeCN versus Ag/AgNO₃. The solubility of the present set of complexes is not optimal, with concentrations employed in these cyclic voltammograms (CVs) ranging from 0.3 - 0.8 mmol L⁻¹, rather lower than the 1 mmol L⁻¹ usually employed. Nevertheless, multiple processes were readily observed in the CVs between -1.02 and 0.80 V, including two reversible redox events at positive potentials for each complex (Table 2, Figure 7). These are tentatively assigned to successive single electron oxidations [as ΔE \sim $\Delta E(Fc/Fc^{\dagger})$] of each ligand to form carbazole-based cation

return waves, was also observed and is tentatively assigned to the $\mathrm{Co}^{\mathrm{III}}/\mathrm{Co}^{\mathrm{II}}$ redox couple. Due to the proximity of the two positive potential redox events, scan rate studies were carried out on the pair of them (Figure 9 and ESI, Figures S2, S7, S10). As expected for reversible processes, 38, 39 no change was observed in the observed E_{pa} and E_{pc} values with respect to scan rate (Figure 9 and ESI, Tables S1-S4).

radicals. At negative potentials an irreversible or quasireversible reduction event (Table 2, Figure 8), with weaker

Table 2: Summary of cyclic voltammetry data for the cobalt(III) complexes, 1-4, of the four carbazole ligands.⁴

Complex ^b R = Cz substituents R ² = Bn substituents	Reduction, E _{pa} (E _{pc}) /V	Oxidation 1, E _m /V, (ΔE /mV)	Oxidation 2, E _m /V, (ΔE /mV)
(1) R = ^t Bu R ² = H	-1.02 (-0.48)	0.36 (51)	0.56 (72)
(2) $\mathbf{R} = {}^{t}\mathbf{B}\mathbf{u} \mathbf{R}^{2} = {}^{t}\mathbf{B}\mathbf{u}$	-1.00 (-0.59)	0.38 (65)	0.59 (65)
(3) $R = H$ $R^2 = H$	-0.85 (-0.76)	0.48 (76)	0.68 (115)
(4) $R = H R^2 = {}^{t}Bu$	-0.91 (-0.63)	0.52 (66)	0.72 (84)

^aData collected in MeCN (0.1 mol L⁻¹ TBAPF versus 0.01 mol L⁻¹ Ag/AgNO₃) at 100 mV s⁻¹ scan rate. The Ec/Ec⁺ redox couple occurred at $E_m = 0.08\pm0.01V$ with $\Delta E =$ 0.07 ± 0.01 V. The processes at positive potentials were examined in separate CVs to those at negative potentials. ^b See Scheme 1 for substituent positions of R and R².

mmol L^{-1}), $[Co^{III}(L^{H/H})_2]BF_4$:0.5H₂O (**3**) (red, 0.3 mmol L^{-1}) and $[Co^{III}(L^{H/HBu})_2]BF_4$:2H₂O (**4**) (black, 0.8 mmol L^{-1}) in MeCN (0.1 mol L^{-1} TBAPF versus 0.01 mol L^{-1} Ag/AgNO₃) at 100 mV s⁻¹ scan rate. The Fc/Fc⁺ redox couples occurred at E_m = 0.08±0.01V with ΔE = 0.07±0.01 V.

The first reversible redox process occurs at $E_m(\Delta E)$ of 0.36(0.05), 0.38(0.07), 0.48(0.07), 0.52(0.07) V for complexes 1 - 4, respectively. The second reversible process occurs close to the first, at $E_m(\Delta E)$ of 0.56(0.07), 0.59(0.07), 0.68(0.11), 0.72(0.08) V for 1 – 4, respectively.

Comparisons of the CVs of complex 1 with 2 and of complex 3 with 4 indicates that, as expected, the addition of a tert-butyl group to the 4-position of the benzyl 'arm', a relatively remote position, has a negligible effect on the carbazole redox processes: the two reversible redox events shift by only 0.02-0.04 V, to slightly more positive potentials. In contrast, comparisons of the CVs of 1 with 3 and of 2 with 4 reveal that the addition of the tert-butyl groups to the 3,6positions of the carbazole unsurprisingly has a much greater effect on the carbazole-based redox processes: the two reversible redox events occur at 0.12-0.14 V lower potentials, consistent with the expected inductive electron donation of these tert-butyl groups making the oxidation of the carbazole moieties easier.

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Potential (V) Figure 7. Cyclic voltammograms to positive potentials for $[Co^{III}(L^{IBu/H})_2]BF_4 \cdot 2H_2O$ (1) (pink, 0.4 mmol L^1 although not fully dissolved), $[Co^{III}(L^{IBu/HBu})_2]BF_4 \cdot H_2O$ (2) (blue, 0.4



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Figure 8. Cyclic voltammograms to negative potentials for $[Co^{III}(L^{1Bu/H})_2]BF_4\cdot 2H_2O$ (1) (pink, 0.4 mmol L⁻¹ although not fully dissolved), $[Co^{III}(L^{1Bu/HB})_2]BF_4\cdot H_2O$ (2) (blue, 0.4 mmol L⁻¹), $[Co^{III}(L^{H/H})_2]BF_4\cdot 0.5H_2O$ (3) (red, 0.3 mmol L⁻¹) and $[Co^{III}(L^{H/HB})_2]BF_4\cdot 2H_2O$ (4) (black, 0.8 mmol L⁻¹) in MeCN (0.1 mol L⁻¹ TBAPF versus 0.01 mol L⁻¹ Ag/AgNO₃) at 100 mV s⁻¹ scan rate. The Fc/Fc⁺ redox couples occurred at $E_m = 0.08\pm0.01V$ with $\Delta E = 0.07\pm0.01$ V.

The quasi-/irreversible reduction process observed for each complex occurred at $E_{pa}[E_{pc}] = -1.02[-0.48], -1.00[-0.59], -0.85[-$ 0.76], -0.91 [-0.63] for complexes 1 - 4 respectively (Table 1). Scan rate studies of these processes show that both E_{pa} and E_{pc} values shift significantly as scan rates increase (Figures 11, S4, S6, S8 and S11, Tables S1-4). The quasi-reversible processes of the 3,6-unsubstituted carbazole complexes, 3 and to a lesser extent 4, become more reversible when isolated from the positive potential redox events (Figure 10 and Figure S1 in ESI, cf. Figures S8 and S11 in ESI): whilst the E_{pc} and E_{pa} peaks of this quasi-reversible process move further apart at higher scan rates (from 25 to 400 mVs⁻¹: ΔE = 79 to 148 mV for **3** and 147 to 430 mV for 4), the E_m values remain relatively stable (-0.81 V for 3 and -0.77 V for 4; Tables S3-4). In contrast, the reduction process for each of the 3,6-di-tert-butyl substituted carbazole complexes, 1 and 2, remains irreversible (ESI Figures S3 and S5).



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Figure 9. Cyclic voltammograms of $[Co^{II}(L^{Bu/Bu})_2]BF_4$ ·H₂O (**2**) in MeCN from $0 \rightarrow +1.1 \rightarrow 0$ V versus 0.01 mol L⁻¹ Ag/AgNO₃ at scan rates 25, 50, 100, 200 and 400 mV s⁻¹.



Figure 10. Cyclic voltammograms of $[C0^{III}(L^{H/H})_2]BF_4\cdot0.5H_2O$ (**3**) in MeCN, from $0 \rightarrow -1.1 \rightarrow 0$ V versus 0.01 mol L^{-1} Ag/AgNO₃ for 100, 200 and 400 mV s⁻¹ scan rates, and $-0.5 \rightarrow -1 \rightarrow -0.5$ V for 25 and 50 mV s⁻¹ scan rates.

Conclusions

A detailed multi-step route to families of new tridentate carbazole-based ligands is reported, with four such ligands successfully prepared, and the analytically pure cobalt(III) complexes of them obtained. X-ray structural characterization of all four complexes confirmed that, as expected, the complexes are isostructural, with two ligands binding in a tridentate fashion to an octahedral cobalt(III) center. ¹H NMR

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studies indicate that this motif is maintained in solution. Cyclic voltammetry showed similar redox behaviour for all four complexes, with two reversible, single-electron oxidation events tentatively assigned to radical formation on each of the carbazole ligands. An irreversible or quasi-reversible reduction event was also observed, which was tentatively assigned as the Co(III)/Co(II) couple. The positions of the reversible redox processes were able to be tuned by up to 140 mV (Table 2): introducing electron releasing *tert*-butyl groups to the 3 and 6 positions of the carbazole dropped the redox potential down to 0.36 V versus 0.01 mol L⁻¹ Ag/AgNO₃.

This family of robust carbazole-based N₃ ligands has great potential. The resulting cobalt(III) complexes are the first of such carbazole ligands, and they exhibit reversible and tuneable redox behavior at potentials close to that of the Fc/Fc⁺ couple. In future studies the *tuneability of the redox potential* will be further probed: the use of 3,6- substituents on *the carbazole ring* that have more pronounced electron releasing properties is expected to bring the redox potentials down into the region of interest for use as redox electrolytes in DSSCs. As expected, this study confirms that the *benzyl substituents* off the triazole rings have *little effect on the redox potentials*, so these substituents will also be varied more widely, but with the aim of enhancing the *solubility* of the resulting complexes.

Experimental

General

Where applicable, MeCN, toluene and DCM were dried using a Pure Solv MD-6 Solvent Purification System, other solvents and reagents were reagent grade, unless otherwise specified, and used as received from commercial suppliers. Dry triethylamine was distilled and stored over KOH pellets. The EDTA solution used was made as follows: EDTA (29 g, 0.10 mol) stirring in aqueous ammonia solution (37%, 100 mL) was diluted to 1 L using distilled H_2O .

Elemental analyses (C, H, N and Br) were carried out by Campbell Microanalytical Laboratory at the University of Otago, with a standard absolute error of $\pm 0.3\%$. NMR spectra were collected on Varian 400-MR or 500 MHz VNMRS spectrometers at 298 K. ESI-MS spectra were collected on a Bruker MicrOTOF_o mass spectrometer at 180°C.

Electrochemistry

Electrochemical measurements were performed using an Iviumstat.XRe potentostat in MeCN freshly distilled over calcium hydride. Experiments were carried out on the family of four cobalt(III) complexes **1-4** (0.3-0.8 mmol L⁻¹, variation due to solubility) in a 0.1 mol L⁻¹ NBu₄PF₆ MeCN solution versus a 0.01 mol L⁻¹ AgNO₃/Ag reference electrode. The Fc/Fc⁺ redox couple was used as a reference check for all studies, and it occurred at $E_m = 0.08\pm0.01$ V with $\Delta E = 0.07\pm0.01$ V.

X-ray crystallography

X-Ray crystallographic data were in all cases collected on an Oxford Diffraction SuperNova diffractometer equipped with a Cryostream N₂ open-flow cooling device at 100 K using graphite monochromated Mo or Cu K α radiation and an Atlas CCD (Table 3). Scans were performed in such a way as to collect a complete set of unique reflections to a maximum resolution of 0.80 Å. Raw frame data (including data reduction, inter-frame scaling, unit cell refinement and absorption corrections) for all structures were processed using *CrysAlis Pro.*⁴⁰

Structures were solved and refined using SIR92,⁴¹ SUPERFLIP⁴², SHELXL-97⁴³ and the CRYSTALS⁴⁴ suite. Hydrogen atoms were visible in the Fourier difference maps for three complexes (not $[Co^{III}(\mathbf{L}^{H/tBu})_2]BF_4 \cdot 1.5Et_2O \cdot solvent)$, and were initially refined using restraints on bond lengths and positions, with these initial positions then used as the basis for the riding model⁴⁵ (except for the O-H hydrogen atoms). For $[\mathsf{Co}^{\text{\tiny{III}}}(\boldsymbol{L}^{\boldsymbol{H/tBu}})_2]\mathsf{BF}_4\boldsymbol{\cdot} 1.5\mathsf{Et}_2\boldsymbol{O}\boldsymbol{\cdot} \mathsf{solvent}, \quad \mathsf{hydrogen} \quad \mathsf{atoms} \quad \mathsf{were}$ inserted at calculated positions and for all complexes the C-H hydrogen atoms rode on the atoms to which they were bound, with *U*(H) = 1.2 U(attached atom). For $[Co^{III}(L^{H/H})_2]BF_4 \cdot 0.5H_2O \cdot 0.5DMF$, hydrogen atoms on the oxygen atom of the water molecule were located from the difference map and refined using restraints on bond lengths and angles. PLATON-SQUEEZE33 was used in the case of $[Co^{III}(L^{tBu/tBu})_2]BF_4 \cdot 1.5Et_2O \cdot solvent$ and $[Co^{III}(L^{H/tBu})_2]BF_4 \cdot 1.5Et_2O$ solvent, where the anion and solvent molecules listed were not excluded prior to treating the structure with SQUEEZE.

Crystals of $[Co^{III}(L^{tBu/H})_2]BF_4$ were twinned, but an appropriate twin law was found using ROTAX.⁴⁶ The BF₄ anion was disordered over two sites, both situated on a four-fold rotation axis. This disorder was modelled using two partial occupancy sites (0.75:0.25) which required restraints on bond lengths, angles, and thermal and vibrational ellipsoid parameters to reach a sensible refinement.

The structure of $[Co^{III}(L^{tBu/tBu})_2]BF_4\cdot 1.5Et_2O\cdot$ solvent had one half of an Et_2O sitting about a special position, and one *tert*butyl group twirl-disordered, which was modelled over two sites (0.65:0.35) with constraints on C-C bond length. Restraints were also applied to bonds of the solvent molecules, and the thermal and vibrational ellipsoid parameters of the solvent molecules, several *tert*-butyl groups, and the BF₄ anion. There was an additional region of electron density, appearing to correspond to disordered partial occupancy Et₂O and MeCN solvent molecules, which was unable to be sensibly modelled, so SQUEEZE was applied. The SQUEEZE result gave 26 e⁻ per complex molecule, which reasonably matches one MeCN (22 e⁻ per complex); a formula of $[Co^{III}(L^{tBu/tBu})_2]BF_4\cdot 1.5Et_2O\cdotMeCN$ would be consistent with this.

For $[Co^{III}(L^{H/H})_2]BF_4 \cdot 0.5H_2O \cdot 0.5DMF$ the thermal ellipsoids of the benzyl groups are somewhat enlarged and elongated, likely due to significant motion; unfortunately an alternative positon was not visible.

The data of $[Co^{III}(L^{H/tBu})_2]BF_4 \cdot 1.5Et_2O \cdot solvent$ are of relatively low quality, and numerous restraints were required

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to achieve a sensible result. One of the Et_2O molecules was located on a symmetry position, causing only half of it to lie in the asymmetric unit. This Et_2O (0.5:0.5) and the BF₄ anion (0.6:0.4) were both disordered over two sites. Restraints were

applied to bond lengths and angles of the solvent, BF_4 anion, *tert*-butyl groups, and some of the benzyl rings to maintain a sensible refinement. Thermal and vibrational ellipsoid

Table 3: Crystal data and structure refinement for the four cobalt(III) complexes. Note that [Co ^{III} (L ^{tBU/LBU})2]BF4· 1.5Et2O·solvent and [Co ^{III}	"(L ^{H/tBu}) ₂]BF ₄ ·1.5Et ₂ O·solvent had SQUEEZE
applied, so M, is inaccurate.	

	[Co ^{III} (L ^{tBu/H}) ₂]BF ₄	[Co ^{III} (L ^{tBu/tBu}) ₂]BF ₄ ·	[Co [™] (L^{H/H}) ₂]BF₄·	[Co ^{III} (L ^{H/tBu}) ₂]BF ₄ ·
		1.5Et ₂ O solvent	0.5H ₂ O·0.5DMF	1.5Et ₂ O·solvent
Empirical formula	C ₇₆ H ₇₆ BCoF ₄ N ₁₄	C ₉₈ H ₁₂₃ BCoF ₄ N ₁₄ O _{1.5}	C ₁₂₃ H ₉₇ B ₂ Co ₂ F ₈ N ₂₉ O ₂	C ₈₂ H ₉₁ BCoF ₄ N ₁₄ O _{1.5}
Mr	1331.27	1666.90	2304.80	1442.44
Wavelength [Å]	Cu: 1.54184	Mo: 0.71073	Mo: 0.71073	Cu: 1.54184
Crystal system	Tetragonal	Monoclinic	Monoclinic	Triclinic
Space group	P4/n	P21/c	P2 ₁ /n	P-1
a [Å]	16.32274(18)	16.6488(4)	17.3437(3)	15.7973(3)
<i>b</i> [Å]	16.32274(18)	20.3208(6)	24.7996(4)	16.5287(4)
c [Å]	13.22212(18)	28.7288(11)	26.5881(5)	18.5432(4)
α [°]	90	90	90	72.8513(19)
β [°]	90	94.014(3)	107.976(2)	74.9270(19)
γ[°]	90	90	90	67.484(2)
Volume [ų]	3522.79(5)	9695.6(4)	10877.7(2)	4214.09(9)
Z	2	4	4	2
Density (calcd) [Mg m ⁻³]	1.255	1.142	1.407	1.137
Abs. coeff.[mm ⁻¹]	2.426	0.237	0.388	2.076
F(000)	1396	3556	4760	1522
Crystal size [mm]	0.45 x 0.40 x 0.35	0.42 x 0.19 x 0.13	0.51 x 0.30 x 0.21	0.64 x 0.58 x 0.39
θ range for data collection	3.342 to 76.224	2.927 to 29.747	2.867 to 29.748	3.071 to 77.217
[°]				
Reflections collected	19255	98773	175733	83092
Indpt reflections	3681	23829	28282	17513
R(int)	0.052	0.061	0.029	0.064
Max/min transmission	1.00 / 0.63	1.00 / 0.59	1.00 / 0.83	1.00 / 0.63
Data/restraints	3664 / 94 / 237	17264 / 190 / 1114	27139 / 2 / 1501	13732 / 1114 / 979
/parameters				
Goodness-of-fit on F ²	1.0276	0.9664	0.9564	0.9790
R ₁ /wR ₂ [I>2σ(I)]	0.0619 / 0.1725	0.0870 / 0.2103	0.0582 / 0.1409	0.1173 / 0.3113
R_1/wR_2 (all data)	0.0673 / 0.1809	0.1029 / 0.2234	0.0696 / 0.1517	0.1361/0.3408
Max/Min e ⁻ density [eÅ ⁻³]	1.44 / -1.09	1.74 / -0.79	1.02 / -0.67	1.07 / -0.92

restraints were also required for all atoms. Two SQUEEZE refinements were carried out, with one applying to all solvent electron density and the other only the diffuse residual electron density. The full SQUEEZE did not lead to a significantly improved refinement, hence is not presented. The SQUEEZE results gave 78 e⁻ per complex, which was difficult to assign, although it was consistent with either three Et₂O (75 e⁻ per complex) or an Et₂O, H₂O and pyridine (77 e⁻ per complex). Despite the issues, all non-H atoms were able to be refined anisotropically, and no restraints were applied to the bonds of the carbazole/triazole parts, so the connectivity is still clear and general conclusions about bonding can be derived.

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 1510199-1510202.

Synthesis

See Scheme 1 for numbering schemes used for NMR assignments.

3,6-Di(tert-butyl)-9H-carbazole was prepared according to a literature procedure,²⁰ with the substitution of cyclohexane for the hexane recrystallisation (see SI).

1,8-dibromo-3,6-di(*tert***-butyl)**-9*H*-carbazole. To a pale orange mixture of 3,6-di(*tert*-butyl)-9*H*-carbazole (1.96 g, 7.01 mmol) and silica (6.0 g) in dry DCM (75 mL) was added *N*-bromosuccinimide (2.49 g, 14.0 mmol). The resulting dark brown mixture was stirred at RT under light-free conditions for 3 days. Filtration of the reaction mixture gave a dark grey solution, which was passed through a silica plug. Elution with DCM yielded a pink-orange solution, which was dried over MgSO₄, filtered and taken to dryness under reduced pressure to provide the title compound as a pale grey solid (2.93 g, 6.70 mmol, 96%). Analysis found: C, 55.16; H, 5.31; Br, 36.54; N, 3.21. Calc. for C₂₀H₂₃Br₂N: C, 54.94; H, 5.30; Br, 36.55; N, 3.20. ESI-MS (neg., CHCl₃/MeOH) m/z = 436.008 (calc. for

 $[C_{20}H_{22}Br_2N]^-$ 436.011). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.13 (br s, 1H, NH), 7.97 (dd, 2H, J = 1.6, 0.6 Hz, H₄) 7.63 (d, 2H, J = 1.7 Hz, H₂), 1.44 (s, 18H, H₅). IR (ATR), *inter alia*, v (cm⁻¹) = 3451, 2960, 2901, 2863, 1719, 1616, 1562, 1491, 1361, 1282, 1264, 1232, 1889, 1053, 862, 843, 729, 665, 636.

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1,8-dibromo-9H-carbazole. To a pale gold solution of 1,8dibromo-3,6-di(tert-butyl)-9H-carbazole (1.09 g, 2.49 mmol) in dry toluene (50 mL) was added anhydrous AlCl₃ (1.00 g, 7.50 mmol). The resulting dark brown reaction mixture was stirred at RT for 8.5 h. The reaction mixture became dark green within the first 30 min. Complete conversion to the desired product was indicated by t.l.c. (5:1 petroleum ether:EtOAc). The reaction mixture was washed with H_2O (2 × 50 mL) and the aqueous washes were combined and extracted into DCM. The combined organic extracts were dried over MgSO₄, filtered and taken to dryness under reduced pressure to yield a brown waxy oil (1.32 g). The crude residue was dissolved in diethyl ether (12 mL) to give an orange solution, which was concentrated to 3 mL and cooled in an ice bath to yield a pale brown precipitate. The title compound was isolated via filtration as an off-white solid (0.28 g). Treating the filtrate to the same concentration/cooling procedure provided a second crop of product (0.13 g, combined yield: 0.41 g, 50%). ESI-MS (neg., MeOH): m/z = 323.892 (calc. for $[C_{12}H_6Br_2N]^{-} 323.885$). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.36 (br s, 1H, N**H**) 7.99 (d, 2H, J = 7.8 Hz, H₄), 7.61 (dd, 2H, J = 7.8, 0.9 Hz, H₂), 7.16 (dd, 2H, J = 7.8, 7.8 Hz, H₃). 13 C NMR (101 MHz, CDCl₃): δ 137.9, 128.9, 125.0, 121.4, 120.0, 104.6. IR (ATR), inter alia, v (cm⁻¹) = 3454, 3068, 2959, 2864, 1906, 1844, 1785, 1604, 1560, 1495, 1477, 1424, 1298, 1261, 1228, 1182, 830, 755, 724, 679. R_f = 0.73 (5:1 petroleum ether:EtOAc).

3,6-di(tert-butyl)-1,8-bis[(trimethylsilyl)ethynyl]-9H-

carbazole. 1,8-dibromo-3,6-di(tert-butyl)-9H-carbazole (3.85 g, 8.80 mmol) in dry triethylamine (25 mL) was deoxygenated with argon for 20 minutes. Afterwards, [Pd(PPh₃)₂Cl₂] (0.368 g, 0.524 mmol) and Cul (0.139 g, 0.731 mmol) were added, followed by a further 5 minutes of argon bubbling. Ethynyltrimethylsilane (1.99 g, 20.3 mmol) was added, the vial capped, and the mixture heated in an 80 °C oil bath for 1 day, then left stirring overnight to cool. The mixture was diluted with petroleum ether (150 mL), filtered through celite using petroleum ether (5 \times 40 mL) to rinse, then solvents were removed in vacuo to give a caramel coloured solid (4.71 g). The solid was dissolved in minimum petroleum ether and filtered through silica (50 mL) using petroleum ether to elute. The first pale yellow fraction was collected until further elution was colourless, then the solvents removed in vacuo to give a pale yellow solid (3.68 g, 89%). Analysis found: C, 76.23; H, 8.74; N, 2.92. Calc. for C₃₀H₄₁NSi₂ (471.84 g mol⁻¹): C, 76.37; H, 8.76; N, 2.97. ESI-MS (pos., DCM/MeOH) m/z: 472.282 (calc. for $[C_{30}H_{42}NSi_2]^+ = 472.285); 494.266 \text{ (calc. for } [C_{30}H_{41}NSi_2Na]^+ =$ 494.267). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.34 (s, 1H, NH), 8.04 (d, 2H, J = 1.5 Hz, H₄), 7.60 (d, 2H, J = 1.8 Hz, H₂), 1.44 (s, 18H, H₆), 0.35 (s, 18H, H₅). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) = 142.6, 139.0, 126.8 (C₂), 123.1, 117.7 (C₄), 104.9, 101.4, 98.6, 34.7, 31.9 (C₆), 0.21 (C₅). IR (ATR), inter alia, v (cm⁻¹) = 3468,

2962, 2899, 2865, 2150, 1589, 1490, 1290, 1273, 1249, 1238, 1202, 1047, 929, 838, 759, 674, 645, 564, 460.

1,8-bis[(trimethylsilyl)ethynyl]-9H-carbazole. То suspension of 1,8-dibromo-9H-carbazole (1.46 g, 4.49 mmol), Cul (0.05 g, 0.27 mmol) and Pd(PPh₃)₂Cl₂ (0.16 g, 0.23 mmol) in dry triethylamine (23 mL) was added ethynyltrimethylsilane (1.5 mL, 10.8 mmol). The reaction mixture was deoxygenated with argon, then stirred at 75 °C under an argon atmosphere for 2 days. The resulting dark brown mixture was diluted with petroleum ether (50 mL), then filtered through celite. The celite plug was washed with petroleum ether (200 mL). The resulting yellow-orange solution was taken to dryness under reduced pressure to yield dark brown oil, which was subjected to column chromatography on silica. Elution ($R_f = 0.24$) with petroleum ether isolated the title compound as a pale yellow solid (1.35 g, 84%). Analysis found: C, 73.69; H, 7.24; N, 3.83. Calc. for C22H25NSi2: C, 73.48; H, 7.01; N, 3.89. ESI-MS (neg., MeOH): m/z = 358.139 (calc. for $[C_{22}H_{24}NSi_2]$: 358.145). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.57 (br s, 1H, NH), 8.02 (d, 2H, J = 7.8 Hz, H₄), 7.56 (dd, 2H, J = 7.5, 1.1 Hz, H₂), 7.20 (dd, 2H, J = 7.7, 7.7 Hz, H₃), 0.37 (s, 18H, H₅). IR (ATR), inter alia, v (cm⁻¹) 3460, 3060, 2958, 2149, 1598, 1497, 1409, 1580, 1298, 1260, 1251, 1226, 1162, 1004, 840, 833, 771, 740, 708, 662, 564

3,6-di(tert-butyl)-1,8-diethynyl-9H-carbazole. А suspension of 3,6-di(tert-butyl)-1,8-bis[(trimethylsilyl)ethynyl]-9H-carbazole (1.42 g, 3.01 mmol) in MeOH (60 mL) was deoxygenated with argon. K₂CO₃ (2.49 g, 18.0 mmol) was added and the resulting yellow suspension was stirred at reflux under an argon atmosphere for 30 min. The reaction mixture was diluted with H₂O (60 mL) then extracted into petroleum ether (3 × 100 mL). The combined organic extracts were dried over MgSO₄, filtered and taken to dryness under in vacuo to give the product as an off-white foam in quantitative yield. Analysis found: C, 87.77; H, 7.77; N, 4.18. Calc. for C₂₄H₂₅N: C, 88.03; H, 7.70; N, 4.28. ESI-MS (pos., MeOH): m/z = 328.208 (calc. for $[C_{24}H_{26}N]^+$ 328.206). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.45 (br s, 1H, NH), 8.08 (d, 2H, J = 1.9 Hz, H₄), 7.64 (d, 2H, J = 1.8 Hz, H₂), 3.46 (s, 2H, H₅), 1.44 (s, 18H, H₆). ¹³C NMR $(126 \text{ MHz}, \text{CDCl}_3) \delta (\text{ppm}) = 142.9, 139.3, 127.7, 123.3, 118.1,$ 104.0, 81.5, 80.6, 34.9, 32.0. IR (ATR), inter alia, v (cm⁻¹) = 3456, 3287, 2954, 2902, 2864, 2104, 1761, 1601, 1489, 1435, 1396, 1362, 1324, 1289, 1271, 1237, 1202, 919, 838, 749, 644.

1,8-diethynyl-9H-carbazole. A suspension of 1,8bis[(trimethylsilyl)ethynyl]-9H-carbazole (0.43 g, 1.5 mmol) in MeOH (25 mL) was deoxygenated with argon. K₂CO₃ (1.00 g, 7.2 mmol) was added and the resulting yellow suspension was stirred at reflux under an argon atmosphere for 30 min. The reaction mixture was diluted with H₂O (25 mL) then extracted into DCM (3 × 50 mL). The combined organic extracts were dried over MgSO₄ filtered and taken to dryness *in vacuo* to give the product as a pale pink-brown solid (0.25 g, 97%). Analysis found: C, 88.47; H, 4.32; N, 6.59. Calc. for C₁₆H₉N: C, 89.28; H, 4.21; N, 6.51. Calc. for C₁₆H₉N·0.03DCM: C, 88.40; H, 4.19; N, 6.43. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.64 (br s, 1H, NH), 8.07 (d, 2H, J = 7.9 Hz, H₄), 7.60 (dd, 2H, J = 7.6, 1.1 Hz, H₂), 7.22 (dd, 2H, J = 7.7, 7.7 Hz, H₃), 3.50 (s, 2H, H₅). ¹³C NMR (126

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MHz, CDCl₃) δ (ppm) = 140.7, 129.89, 123.3, 121.7, 119.9, 104.9, 82.3, 79.9. IR (ATR), *inter alia*, v (cm⁻¹) = 3366, 6275, 3058, 2918, 2100, 1596, 1579, 1495, 1419, 1333, 1297, 1236, 1221, 777, 742, 656, 617, 568.

HL^{tBu/H}. To a suspension of ascorbic acid (0.106 g, 0.6 mmol), CuSO₄·5H₂O (0.075 g, 0.3 mmol), Na₂CO₃ (0.212 g, 2.0 mmol) and NaN₃ (0.150 g, 2.3 mmol) in DMF/H₂O (4:1, 3 mL) was added benzyl bromide (0.27 mL, 2.3 mmol). The resulting suspension was stirred at RT for 5 min, during which time it turned yellow. To this suspension was added 3,6-di(tert-butyl)-1,8-diethynyl-9H-carbazole (0.327 g, 1.0 mmol) in DMF/H₂O (4:1, 1 mL). The resulting red-orange mixture was stirred at RT for 16 h, by which time a pale orange precipitate had formed. The reaction mixture was diluted with EDTA solution (100 mL) and stirred at RT for 1 h. An orange-brown solid was collected via filtration, washed with H₂O (200 mL) then dissolved in DCM (100 mL). The resulting dark orange solution was washed with water (100 mL), and the aqueous layer extracted into DCM (100 mL). The combined organic extracts were taken to dryness under reduced pressure to yield an orange-brown solid. Recrystallisation of the crude residue from toluene (35 mL) provided HL^{tBu/H} as a pale brown solid (0.359 g, 60%). Analysis found: C, 76.90; H, 6.78; N, 16.27. Calc. for C₃₈H₃₉N₇: C, 76.87; H, 6.62; N, 16.51. ESI-MS (pos., DCM/MeOH): m/z = 594.3336 (calc. for $C_{38}H_{40}N_7$ 594.3340). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 11.75 (s, 1H, NH) 8.10 (d, J = 1.8 Hz, 2H, H₄), 7.94 (s, 2H, H₆), 7.66 (d, J = 1.8 Hz, 2H, H₂), 7.45 - 7.36 (m, 10H, H_{9/10/11}), 5.68 (s, 4H, H₇), 1.47 (s, 18H, H₁₅). ¹³C NMR (126 MHz, $CDCl_3$) δ (ppm) = 148.2, 141.9 (C₁₂), 135.9, 135.1 (C₈), 129.3 $(C_{9/10/11})$, 128.9 $(C_{9/10/11})$, 128.3 $(C_{9/10/11})$, 124.0, 120.4 (C_2) , 119.3 (C₆), 116.3 (C₄), 112.9 (C_{4a}), 54.5 (C₇), 34.9 (C₁₄), 32.3 (C₁₅). IR (ATR), inter alia, v (cm⁻¹) = 3397, 3129, 3065, 3032, 2952, 2901, 2865, 1607, 1537, 1485, 1434, 1362, 1288, 1268, 1193, 1052, 1002, 866, 708, 692, 646.

HL^{tBu/tBu}. A mixture of ascorbic acid (209 mg, 1.19 mmol), Na₂CO₃ (186 mg, 1.75 mmol), NaN₃ (149 mg, 3.82 mmol) and 4-tert-butylbenzyl bromide (868 mg, 3.82 mmol) in DMF:H₂O (4:1, 4.5 mL) was deoxygenated with N₂ bubbling for 35 minutes. 3,6-di(tert-butyl)-1,8-diethynyl-9H-carbazole (568 mg, 1.73 mmol) and CuSO₄·5H₂O (142 mg, 0.57 mmol) were added with DMF:H₂O (4:1, 3 mL) followed by a further 5 minutes of N₂ bubbling. The orange mixture was then stirred at RT for 3 days under argon atmosphere. EDTA solution (40 mL) was added and the resulting mustard-coloured mixture vigorously stirred before adding H₂O (50 mL). The mixture was cautiously extracted with DCM (100 mL, 50 mL), then the combined DCM fractions washed with a 1:1 brine:H₂O solution (125 mL, 100 mL; brine dilution seems to help the layers to separate). The aqueous washes were back-extracted with DCM (100 mL), and then the DCM fractions combined as an orange solution. The DCM solution was dried over MgSO₄, filtered, and then solvents removed in vacuo to give the crude product as a sandy-coloured solid (1.33 g), which was stirred overnight in diethyl ether (200 mL). The suspension was filtered to give an orange filtrate and an off-white solid, which was dried further in vacuo to give microanalytically clean ligand (1.02 g. 1.44 mmol, 83%). Analysis Found: C, 77.98; H, 7.92; N, 13.76.

Calculated for $C_{46}H_{55}N_7$: C, 78.26; H, 7.85; N, 13.89. ESI-MS (pos., CHCl₃/MeOH) *m/z*: 728.4363 (calc. for $[C_{46}H_{55}N_7Na]^* =$ 728.4411). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 11.70 (s, 1H, NH), 8.10 (d, 2H, J = 1.3 Hz, H₄), 7.96 (s, 2H, H₆), 7.67 (d, 2H, J = 1.5 Hz, H₂), 7.43 (d, 4H, J = 8.3 Hz, H₁₀), 7.33 (d, 4H, J = 8.3 Hz, H₉), 5.64 (s, 4H, H₇), 1.47 (s, 18H, H₁₅), 1.32 (s, 18H, H₁₃). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 151.8 (C₁₁), 147.9, 141.7, 135.7, 131.9, 127.8, 126.0, 123.8, 120.2, 119.1, 116.3, 112.7, 54.0 (C₇), 34.7 (C₁₂), 34.6 (C₁₄), 32.1 (C₁₃), 31.3 (C₁₅).

HL^{H/H}. To a suspension of ascorbic acid (0.11 g, 0.6 mmol), CuSO₄·5H₂O (0.075 g, 0.3 mmol), Na₂CO₃ (0.21 g, 2.0 mmol) and NaN₃ (0.15 g, 2.3 mmol) in DMF/H₂O (4:1, 3 mL) was added benzyl bromide (0.27 mL, 2.3 mmol). The resulting suspension was stirred at RT for 5 min, during which time it turned yellow. To this suspension was added 1,8-diethynyl-9Hcarbazole (0.22 g, 1.0 mmol) in DMF/H₂O (4:1, 1 mL). The resulting dark yellow mixture was stirred at RT for 20 h, by which time an off-white precipitate had formed with a yellow supernatant. The reaction mixture was diluted with EDTA solution (100 mL) and stirred at RT for 1 h. An off-white solid was collected via filtration, washed with H₂O (200 mL) and dried in vacuo (0.32 g). The crude residue was subjected to column chromatography on silica. Elution ($R_f = 0.18$) with 5% EtOAc in CHCl₃/toluene (1:1) provided $HL^{H/H}$ as a white solid (0.20 g, 41%). Analysis found: C, 74.73; H, 4.79; N, 20.20. Calc. for C₃₀H₂₃N₇: C, 74.83; H, 4.81; N, 20.36. ESI-MS (pos., MeOH) m/z: 504.1886 (calc. for $[C_{30}H_{23}N_7Na]^+$ 504.1907). ¹H NMR (500 MHz, CDCl₃): δ 12.21 (br s, 1H, NH) 8.08 (d, J = 7.7 Hz, 2H, H₄), 7.91 (s, 2H, H₆), 7.61 (dd, J = 7.5, 1.1 Hz, H₂), 7.43 - 7.35 (m, W_{h/2} = 8.4 Hz, H_{9/10/11}), 7.24 (dd, J = 7.7, 7.7 Hz, 2H, H₃), 5.67 (s, 4H, H₇). ¹³C NMR (126 MHz, CDCl₃) = δ 147.8 (C₅), 137.2, 134.9 (C₈), 129.3 (C_{9/10/11}), 128.9 (C_{9/10/11}), 128.3 (C_{9/10/11}), 124.1, 122.6 (C₂), 120.2 (C₄), 119.4 (C₆), 119.1 (C₃), 113.7, 54.5 (C₇). IR (ATR), *inter alia*, v (cm⁻¹) = 3381, 3136, 3037, 2948, 1611, 1590, 1496, 1437, 1425, 1312, 1267, 1057, 1046, 774, 710, 635, 618, 591, 554.

 $\rm HL^{\rm H/tBu}.$ A mixture of NaN3 (272 mg, 4.18 mmol), ascorbic acid (338 mg, 1.92 mmol), 4-tert-butylbenzyl bromide (0.77 mL, 4.20 mmol), Na₂CO₃ (204 mg, 1.92 mmol) and CuSO₄ (160 mg, 0.64 mmol) in DMF:H₂O (4:1, 9 mL) was deoxygenated with N₂ bubbling for 35 minutes. 1,8-diethynyl-9H-carbazole (417 mg, 1.94 mmol) was added using DMF:H₂O (4:1, 1 mL) to rinse, followed by a further 10 minutes of N₂ bubbling. The N₂ flow was replaced with a septa and an argon balloon, and then the orange-brown mixture was stirred at RT for 2 days. EDTA solution (80 mL) was added and the mixture vigorously stirred before adding H₂O (100 mL). The greenish suspension was cautiously extracted with DCM (2 × 100 mL, 40 mL), then the extracts combined and washed with a dilute aqueous NaCl solution (2 \times 120 mL). The washes were back-extracted with DCM (40 mL), before combining the DCM fractions, drying them over MgSO₄, filtering, and drying in vacuo to give the crude product as a sandy-white coloured solid. The crude product was stirred in diethyl ether (120 mL) for 20 minutes then filtered to give a yellow filtrate and an off-white solid, which was dried further in vacuo (899 mg, 78%). The ligand was used without further purification. ESI-MS (pos.,

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DCM/MeOH) *m/z*: 616.307 (calc. for $[C_{38}H_{39}N_7Na]^+$ 616.316). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 12.14 (s, 1H, NH), 8.06 (d, 2H, J = 7.7 Hz, H₄), 7.92 (s, 2H, H₆), 7.62 (d, 2H, J = 7.4 Hz, H₂), 7.43 (d, 4H, J = 8.4 Hz, H₁₀), 7.32 (d, 4H, J = 8.3 Hz, H₉), 7.23 (t, 2H, J = 7.6 Hz, H₃), 5.64 (s, 4H, H₇), 1.32 (s, 18H, H₁₃). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 151.9 (C₁₁), 147.5, 137.1, 131.7, 128.0, 126.1, 123.8, 122.4, 120.0, 119.2, 118.8, 113.6, 54.0 (C₇), 34.6 (C₁₂), 31.2 (C₁₃).

[Co^{III}(L^{tBu/H})₂]BF₄·2H₂O (1). HL^{tBu/H} (30 mg, 0.050 mmol) was dissolved in acetone (5 mL) containing triethylamine (5 drops) and the solution deoxygenated with bubbling argon. $Co(H_2O)_6(BF_4)_2$ (8.5 mg, 0.025 mmol) was dissolved in MeOH (2 mL) and the solution deoxygenated with bubbling argon. The pale pink metal salt solution was added to the yellow ligand solution, causing it to darken slightly. The reaction was stirred under a nitrogen balloon for 30 minutes, then opened to the air and the dark green solution subjected to diethyl ether vapour diffusion, which resulted in dark green crystals of $[Co^{III}(L^{IBu/H})_2](BF_4)$, some of which were twinned crystals suitable for X-ray crystallography. The crystals were isolated via filtration, washed with diethyl ether, and dried in vacuo (22 mg, 64%). Analysis found: C, 66.7; H, 5.9; N, 14.1. Calculated for C₇₆H₇₆N₁₄CoBF₄·2H₂O (1367.31 g mol⁻¹): C, 66.8; H, 5.9; N, 14.3. ESI-MS (pos., MeOH): m/z = 1243.567 (calc. for $[C_{76}H_{76}N_{14}Co]^{+}$ ($[Co(L^{tBu/H})_2]^{+}$) = 1243.570). ¹H NMR (500 MHz, DMSO- d_6) δ (ppm) = 8.99 (s, 4H, H₆), 8.54 (d, 4H, J = 2 Hz, H₄), 7.83 (d, 4H, J = 2 Hz, H_2), 7.12 (dd, 4H, J = 8, 8 Hz, H_{11}), 7.00 (dd, 8H, J = 8, 8 Hz, H₁₀), 6.44 (d, 8H, J = 8 Hz, H₉), 4.90 (s, 8H, H₇), 1.52 (s, 36H, H₁₅). ¹³C NMR (126 MHz, DMSO- d_6) δ (ppm) = 144.2 (C₅), 140.8 (C_{1a}), 138.1 (C₃), 134.1 (C₈), 128.2 (C₁₀), 128.0 (C_{11}) , 127.6 (C_{4a}) , 127.2 (C_9) , 122.9 (C_6) , 118.8 (C_4) , 118.4 (C_2) , 108.6 (C1), 55.0 (C7), 34.6 (C14), 32.1 (C15). IR (ATR), inter alia, v $(cm^{-1}) = 3130$ (w), 2950 (m), 2900 (w), 2865 (w), 1588 (w), 1547 (m), 1497 (w), 1471 (m), 1455 (m), 1435 (m), 1362 (m), 1329 (w), 1274 (vs), 1229 (s), 1202 (m), 1176 (w), ~1100 - 1000 (broad, s), 1068 (s), 1052 (s), 1022 (vs), 869 (m), 860 (m), 710 (vs), 693 (s), 581 (w), 546 (w), 526 (w). A_m (MeCN, at 0.5 mmol L^{-1}) = 56 Ω^{-1} cm² mol⁻¹.

[Co^{III}(L^{tBu/tBu})₂]BF₄·H₂O (2). A solution of HL^{tBu/tBu} (169 mg, 0.239 mmol) in pyridine (50 mL) was deoxygenated with N₂ bubbling for 30 minutes. To the stirring solution was added Co(H₂O)₆(BF₄)₂ (41 mg, 0.120 mmol) under N₂ flow, followed by a further 5 minutes of N_2 bubbling. The N_2 flow was switched for a septum and argon balloon, and the red-orange solution was then stirred for 3 hours at room temperature. The red solution was then opened to air and diethyl ether (40 mL) was added before stirring the solution overnight. The solvents were removed in vacuo yielding an oily red solid and some offwhite solid. The red solid was redissolved in MeCN and the greenish-orange mixture filtered to give an off-white solid and a greenish-orange filtrate. The filtrate was then subjected to diethyl ether vapour diffusion, which yielded X-ray quality single crystals of [Co^{III}(L^{tBu/tBu})₂]BF₄·1.5Et₂O·solvent as bluegreen plates (60.5 mg, 32%). The crystals were isolated via filtration and brief air drying, followed by drying in vacuo before analysis. The filtrate was reduced in volume, and resubjected to ether vapour diffusion, leading to a second crop

of blue-green crystals (58.2 mg, 31%; 118.7 mg, 63% total). Analysis found: C, 69.99; H, 7.25; N, 12.18. Calculated for C₉₂H₁₀₈N₁₄CoBF₄·H₂O (1573.73 g mol⁻¹): C, 70.22; H, 7.05; N, 12.46. ESI-MS (pos., MeCN): m/z = 1467.8270, 1468.8313 (calc. for $[C_{92}H_{108}N_{14}Co]^+$ ($[Co(L^{tBu/tBu})_2]^+$) = 1467.8208, 1468.8240). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.49 (s, 4H, H₄), 7.94 (br. s, 4H, H₆), 7.69 (br. s, 4H, H₂), 7.05 (d, 8H, J = 8.3 Hz, H₁₀), 6.53 (d, 8H, J = 8.1 Hz, H₉), 4.84 (s, 8H, H₇), 1.59 (s, 36H, H₁₅), 1.21 (s, 36H, H₁₃). ¹H NMR (400 MHz, DMSO- d_6) δ (ppm) = 8.99 (s, 4H, H₆), 8.53 (d, 4H, J = 1.8 Hz, H₄), 7.86 (d, 4H, J = 1.8 Hz, H₂), 6.94 (d, 8H, J = 8.4 Hz, H_{10}), 6.31 (d, 8H, J = 8.4 Hz, H_9), 4.82 (s, 4H, H₇), 1.51 (s, 18H, H₁₅), 1.12 (s, 18H, H₁₃). ¹³C NMR (101 MHz, DMSO- d_6) δ (ppm) = 150.5 (C₁₁), 144.2 (C₅), 140.8 (C_{1a}), 138.6 (C₃), 131.3 (C₈), 127.6 (C_{4a}), 126.8 (C₉), 124.9 (C₁₀), 122.5 (C₆), 118.8 (C₄), 117.5 (C₂), 108.7 (C₁), 54.4 (C₇), 34.6 (C₁₄), 34.1 (C12), 32.1 (C15), 31.0 (C13). ¹³C NMR (126 MHz, CDCl3), inter alia, δ (ppm) = 151.8 (C₁₁), 130.2, 127.8 (C₉), 125.6 (C₁₀), 55.5 (C_7) , 34.5 (C_{14}) , 32.4 (C_{15}) , 31.2 (C_{13}) . IR (ATR), inter alia, v (cm⁻¹) = 3132 (w), 2954 (s), 2903 (m), 2866 (m), 1668 (w), 1614 (w), 1548 (m), 1512 (w), 1476 (s), 1441 (s), 1362 (s), 1329 (m), 1274 (vs), 1229 (vs), ~1100 - 1000 (vs, broad), 1023 (vs), 861 (m), 784 (s), 731 (w), 712 (s), 686 (m), 666 (m), 647 (m), 629 (w), 559 (m), 522 (m). $\Lambda_{\rm m}$ (MeCN) = 134 Ω^{-1} cm² mol⁻¹.

[Co^{III}(L^{H/H})₂]BF₄·0.5H₂O (3). Separately, a yellow solution of HL^{H/H} (96 mg, 0.199 mmol) in DMF (6 mL) and a bright pink solution of $Co(H_2O)_6(BF_4)_2$ (34 mg, 0.100 mmol) in DMF (2 mL) were deoxygenated with N_2 bubbling for 45 minutes. The cobalt solution was then added via syringe to the ligand solution, and the resultant amber solution stirred for a further 5 minutes under N₂. Addition of NEt₃ (0.28 mL, 2.01 mmol) caused an immediate darkening of the solution, progressing through dark brown to orange and then brown-green over 40 minutes whilst stirring under N2. After opening to air the solution slowly turned more intensely green-blue over several hours; the solution was left stirring overnight. The resultant deep blue-green solution was subjected to diethyl ether vapour diffusion, which yielded X-ray quality single crystals of $[Co^{III}(L^{H/H})_2]BF_4 \cdot 0.5H_2O \cdot 0.5DMF$ as dark blue blocks (68.4 mg, 61%). The crystals were isolated via filtration and brief air drying, followed by drying in vacuo overnight. Analysis Found: C. 64.31; H, 4.01; N, 17.74 %. Calculated for C₆₀H₄₄N₁₄CoBF₄·0.5H₂O (1115.85 g mol⁻¹): C, 64.58; H, 4.06; N, 17.57. ESI-MS (pos., MeCN): m/z = 1019.3284 (calc. for $[C_{60}H_{44}N_{14}Co]^+$ $([Co(L^{H/H})_2]^+) = 1019.3200)$. ¹H NMR (400 MHz, DMSO- d_6) δ (ppm) = 8.87 (s, 4H, H₆), 8.49 (d, 4H, J = 8.0 Hz, H₄), 7.76 (d, 4H, J = 6.9 Hz, H₂), 7.30 (t, 4H, J = 7.5 Hz, H₃), 7.12 (t, 4H, J = 7.5 Hz, H₁₁), 6.99 (t, 8H, J = 7.8 Hz, H₁₀), 6.40 (d, 8H, J = 8.0 Hz, H₉), 4.92 (s, 8H, H₇). ¹³C NMR (126 MHz, DMSO-d₆) δ (ppm) = 144.2 (C₅), 142.5 (C_{1a}), 134.4 (C₈), 128.9 (C₁₀), 128.6 (C11), 128.1 (C4a), 127.8 (C9), 123.4 (C6), 122.6 (C4), 121.6 (C2), 116.7 (C₃), 109.6 (C₁), 55.4 (C₇). IR (ATR), inter alia, v (cm⁻¹) = 3129 (w), 3032 (w), 1664 (w), 1610 (w), 1578 (w), 1551 (w), 1496 (w), 1478 (m), 1456 (w), 1420 (s), 1343 (m), 1266 (vs), 1229 (s), 1167 (w), ~1100 - 950 (vs, broad), 938 (m), 774 (vs), 746 (s), 721 (vs), 701 (vs), 626 (m), 571 (s), 518 (m), 473 (w), 461 (w), 408 (w). $\Lambda_{\rm m}$ (MeCN) = 132 Ω^{-1} cm² mol⁻¹.

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[Co^{III}(L^{H/tBu})₂]BF₄·2H₂O (4). HL^{H/tBu} (90 mg, 0.1516 mmol) was dissolved in pyridine (16 mL) with gentle heating, and then deoxygenated on a Schlenk line with successive vacuum and nitrogen cycles. Pyridine (2 mL) was degassed as above, and then $Co(H_2O)_6(BF_4)_2$ (25.3 mg, 0.0743 mmol) added under positive N₂ pressure to give a pale orange-pink solution, which was degassed with further vacuum/purge cycles; N₂ flow was left on. A transfer needle was added between the metal salt and ligand flasks, and then the cobalt solution transferred dropwise to the ligand, causing the pale yellow solution to turn orange. The orange solution was then degassed with another vacuum/N₂ cycle before being stirred for 1 day under a nitrogen balloon, before exposing the orange solution to air and subjecting it to diethyl ether vapour diffusion. This yielded X-ray quality single crystals of [Co^{III}(L^{H/tBu})₂]BF₄•1.5Et₂O·solvent as blue blocks (39 mg, 0.0287 mmol, 39%). The crystals were isolated via filtration followed by air drying, and then analysed. Found: C, 66.67; H, 5.80; N, 14.52. Calculated for $C_{76}H_{76}N_{14}Co \cdot BF_4 \cdot 2H_2O$ (1367.31 g mol⁻¹): C, 66.76; H, 5.90; N, 14.34 %. . ESI-MS (pos., MeCN): m/z = 1243.5634 (calc. for $\left[\mathsf{C}_{76}\mathsf{H}_{76}\mathsf{N}_{14}\mathsf{Co}\right]^{+}\left(\left[\mathsf{Co}(\boldsymbol{\mathsf{L}}^{\mathsf{H/tBu}})_{2}\right]^{+}\right)=1243.5704\right).\ ^{1}\mathsf{H}\ \mathsf{NMR}\ (500\ \mathsf{MHz},$ DMSO- d_6) δ (ppm) = 8.84 (s, 4H, H₆), 8.50 (d, 4H, J = 7.6 Hz, H₄), 7.73 (d, 4H, J = 7.4 Hz, H₂), 7.29 (t, 4H, J = 7.5 Hz, H₃), 6.96 (d, 8H, J = 8.4 Hz, H_{10}), 6.32 (d, 8H, J = 8.4 Hz, H_9), 4.85 (s, 8H, H_7), 1.17 (s, 36H, H $_{13}).$ ^{13}C NMR (126 MHz, DMSO- $d_6)$ δ (ppm) = 150.5 (C₁₁), 143.6 (C₅), 142.1 (C_{1a}), 130.9 (C₈), 127.6 (C_{4a}), 127.0 (C₉), 125.1 (C₁₀), 122.9 (C₆), 122.0 (C₄), 121.1 (C₂), 116.1 (C₃), 109.6 (C1), 54.6 (C7), 34.1 (C12), 31.0 (C13). IR (ATR), inter alia, v $(cm^{-1}) = 3131$ (w), 3058 (w), 2952 (m), 2902 (w), 2866 (w), 1612 (w), 1579 (w), 1552 (w), 1512 (w), 1477 (m), 1420 (s), 1349 (m), 1266 (vs), 1229 (s), 1213(m), 1167 (w), ~1100-1000 (broad, vs), 1051 (vs), 936 (w), 767 (vs), 746 (vs), 712 (m), 691 (m), 625 (w), 564 (m), 575 (s), 519 (m). $\Lambda_{\rm m}$ (MeCN) = 123 Ω^{-1} $cm^2 mol^{-1}$.

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Table of contents text:

Four structurally characterised $[Co^{III}L^{R/R'}_{2}]BF_{4}$ complexes, of four acyclic bis(triazolyl)carbazole ligands $L^{R/R'}$, all show a pair of reversible one-electron redox processes which can be tuned by variation of the carbazole substituents R.

Table of Contents graphic:

