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ARTICLE

5-Ferrocenyl-2,2'-bipyridine Ligands: synthesis, palladium(II) and copper(I) complexes, optical and electrochemical properties.

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S. Ø. Scottwell,^a K. J. Shaffer,^a C. J. McAdam,^a and J. D. Crowley.^a

Two ferrocene-appended 2,2'-bipyridine ligands, 5-ferrocenyl-2,2'-bipyridine (Fc-bipy) and 5-ferrocenyl-5'-methyl-2,2'-bipyridine (Fc-bipy-Me) metalloligands were synthesised using palladium(0) catalysed Suzuki-Miyaura cross-coupling reaction. Their coordination chemistry with palladium(II) and copper(I) ions was examined. The molecular structures of several complexes, including [Pd(Fc-bipy-Me)(Cl)₂], [Pd(Fc-bipy)(py)₂](SbF₆)₂, [Pd(Fc-bipy)(DMAP)₂](SbF₆)₂, [Pd(Fc-bipy-Me)(DMAP)₂](SbF₆)₂, and [Cu(Fc-bipy)(6,6'-dimesityl-2,2'-bipyridine)](PF₆) and [Cu(Fc-bipy-Me)(6,6'-dimesityl-2,2'-bipyridine)](PF₆) were determined using X-ray crystallography. ¹H and ¹³C NMR spectra and high resolution electrospray mass spectrometry (HR-ESMS) experiments confirmed that the majority of the complexes are stable in solution. The exceptions were [Pd(Fc-bipy)(DMAP)₂](SbF₆)₂ and [Pd(Fc-bipy-Me)(DMAP)₂](SbF₆)₂ which were found to disproportionate to give equilibrium mixtures containing [Pd(Fc-bipy)₂](SbF₆)₂ and [Pd(DMAP)₄](SbF₆)₂. The optical absorption and electrochemical properties of these complexes were compared to those of the parent ligands. The 5-ferrocenyl-2,2'-bipyridine ligands are yellow/orange in colour with the expected weak d-d transition found at ~450 nm. The absorption bands of the palladium(II) and copper(I) complexes are red-shifted relative to the free ligands and show enhanced molar absorptivity. The complexes all display strong MLCT absorptions in the visible spectrum, the palladium(II) compounds are deep purple (λ_{max} = ~540-560 nm), while the copper(I) complexes are red-brown (λ_{max} = ~470 nm). Electrochemical investigations showed that all the compounds displayed the expected chemically reversible one-electron oxidation of the ferrocenyl group. The reduction potential of the redox-active ferrocene unit was anodically shifted, relative to the free ligand, upon complexation to the metal ions. The copper(I) complexes displayed an additional reversible oxidation wave that was assigned as a Cu(II)/Cu(I) redox process.

ARTICLE

Introduction

Ferrocene has been known for over 60 years¹ and is the most ubiquitous of the metallocenes. The sustained interest in this molecule is at least in part due to the ready synthesis of ferrocene derivatives and their reversible redox properties. Ferrocene-containing systems have found applications in a wide range of areas, including catalysis,² electrochemical sensing,³ molecular recognition⁴ and electronics.⁵ Additionally, systems have been exploited to develop molecular machines⁶ and cytotoxic agents.⁷

Many of these applications take advantage of heterocyclic ferrocene compounds, particularly those containing pyridines (py).⁸ The conjugation of pyridyl units onto ferrocene has been used to develop a range of redox-active metalloligands.⁹ 2-,¹⁰ 3-,^{10j-l, 11} and 4-,^{10k, 10l, 11f, 12} substituted ferrocenyl-pyridines (Fig. 1, A-C) have been generated and their properties exhaustively explored. Surprisingly, the analogous ferrocenyl bipyridines¹³ have not received as much attention despite the wide ranging applications of the 2,2'-bipyridine (bipy) ligand architecture.¹⁴ The synthesis and coordination chemistry of the 6-ferrocenyl 2,2'-bipyridine isomer **D** has been reported by a number of authors.^{10d, 10f, 15} However, the corresponding 4- and 5-ferrocenyl 2,2'-bipyridine isomers **E** and **F** have not yet appeared in the literature. More functionalised systems featuring the 4-ferrocenyl 2,2'-bipyridine as a subunit are known.^{13p, 16} Likewise, as part of work towards developing ferrocene-based molecular machines,^{11d} we have previously reported the system **G** which contained the 5-ferrocenyl 2,2'-bipyridine subunit. In order to push forward the development of these ferrocene-containing molecular machine systems we needed to better understand the coordination chemistry and physical properties of 5-ferrocenyl 2,2'-bipyridine.

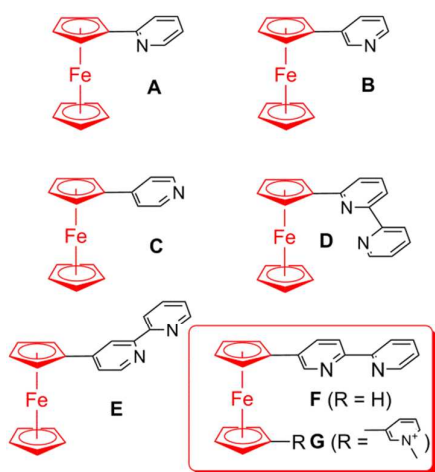


Figure 1. Isomeric ferrocenyl-pyridines (A-C) and bipyridines (D-F) and the molecular rotor (G) developed by Bosnich and co-workers.

Herein we report the synthesis of 5-ferrocenyl-2,2'-bipyridine and the structurally related 5-ferrocenyl-5'-methyl-2,2'-bipyridine metalloligands. Coordination complexes of these ligands with Pd(II) and Cu(I) ions were generated. Additionally, the electrochemical and optical absorption properties of the ligands and the corresponding complexes have been examined.

Results and Discussion

Ligand Synthesis

The two structurally related 5-ferrocenyl-2,2'-bipyridine ligands **3a-b** were generated using the Pd(0) catalysed Suzuki-Miyaura cross-coupling reaction (Scheme 1). Exploiting the microwave accelerated reaction conditions developed by Braga *et al.*,¹⁷ the commercially available ferroceneboronic acid (**1**), one of the 5-bromo-2,2'-bipyridines, either **2a** or **2b**,¹⁸ Na₂CO₃, NaOH and the [PdCl₂(1,1'-bis(diphenylphosphino)ferrocene)] catalyst were suspended in a mixture of 1,4-dioxane, dimethoxyethane and water then irradiated (300 W) for 30 minutes at 110 °C. After work-up the ligands **3a-b** were isolated as orange solids in acceptable yields (62-73%). The ligands were characterised using ¹H, ¹³C NMR, and IR spectroscopies, as well as high resolution electrospray ionisation mass spectrometry (HR-ESI-MS) and elemental analysis. Additionally, the molecular structure of the ligand **3a** was confirmed via X-ray crystallography (ESI†). X-ray quality crystals of **3a** were grown by vapour diffusion of petroleum ether into a chloroform solution of **3a**. These orthorhombic (*Pccn*) crystals diffracted weakly so efforts were made to grow better quality crystals. This resulted in a second batch of weakly diffracting monoclinic (*P2_{1/c}*) crystals of **3a**. Despite the weak diffraction from both sets of crystals the connectivity of **3a** was shown unequivocally (ESI†). The ferrocene unit adopted an eclipsed conformation and the nitrogen atoms of the 2,2'-bipyridine unit were found in the *anti*-conformation as was expected^{11d} (ESI†). The main difference in the two polymorphs is the torsion angle between the ferrocene and the attached bipyridine unit which differs between the two by 5.62° (ESI†).

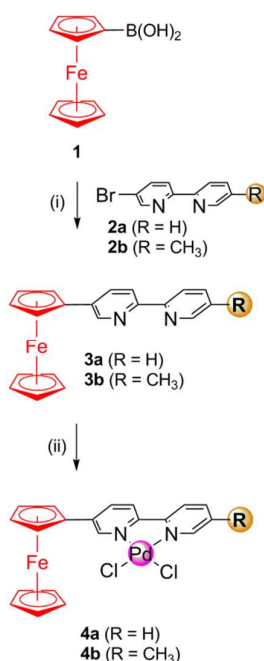
Palladium(II) Complexes

While a wide range of metal complexes of 6-ferrocenyl 2,2'-bipyridine **D** have been synthesised we initially targeted the generation of palladium(II) complexes of 5-ferrocenyl 2,2'-bipyridines **3a-b**. Palladium(II) complexes continue to be of great importance in catalysis and metallo-supramolecular chemistry and we have previously exploited Pd(II) complexes to generate reversible switching of the ferrocene-based molecular rotor **G**.^{11d}

The palladium(II) dichloride complexes **4a-b** were synthesised in excellent yields (90-97%) by stirring [PdCl₂(CH₃CN)₂] and one of the ferrocene ligands **3a** or **3b** in acetone solution at room temperature for 30 minutes (Scheme 1). Upon addition of the [PdCl₂(CH₃CN)₂] to the orange solution containing the ligand a purple coloured precipitate immediately formed, indicative of complexation. Elemental analysis and IR spectra were consistent with the formation of the expected [PdCl₂(**3a** or **3b**)] complexes **4a-b**. Surprisingly, the complexes proved exceedingly insoluble in all common organic solvents and water making further solution state characterisation difficult. Heating a suspension of **4a** to near the boiling point of *d*₆-DMSO enabled the acquisition of the ¹H NMR spectrum of the complex. This was consistent with the coordination of the palladium to the ferrocene ligand (ESI†). However, the initial purple coloured solution rapidly changes to brown and the ¹H NMR spectrum became broad suggesting that these relatively harsh conditions lead to the degradation of the complex.

The molecular structure of the complex **4b** was confirmed via X-ray crystallography (Fig. 2a). X-ray quality crystals of **4b** were grown by layering a chloroform solution of the ligand **3b** on top of an acetone solution of the $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ salt and allowing them to slowly diffuse together. As expected, the 5-ferrocenyl-5'-methyl-2,2'-bipyridine ligand was coordinated to the $\text{Pd}(\text{Cl})_2$ fragment in a square planar fashion (Fig. 2a). The Pd-N (2.027(3) and 2.024(3) Å) and Pd-Cl (2.291(1) and 2.2944(7) Å) bond lengths and angles (Figure 2a) are very similar to the average values (Pd-N 2.034 Å, Pd-Cl 2.290 Å) obtained from Cambridge Structural Database (CSD)[‡] for $[\text{Pd}(\text{bipy})\text{Cl}_2]$ complexes indicating that the 5-ferrocenyl 2,2'-bipyridine ligand is behaving like a normal bipy ligand. This is quite different to the known 6-ferrocenyl 2,2'-bipyridine system. Addition of $\text{Pd}(\text{Cl})_2$ to **D** instead generates an *ortho* palladated complex due to the close proximity of the ferrocenyl unit to the coordination pocket of the ligand.^{10d, 19}

Interestingly, the complex **4b** forms head-to-tail dimers in the extended solid state structure that appear to be stabilized by metal-metal (Pd-Pd distance = 3.3811(3) Å) and π -anion²⁰ (centroid – Cl distances range from 3.405-3.340 Å) interactions (ESI[†]).

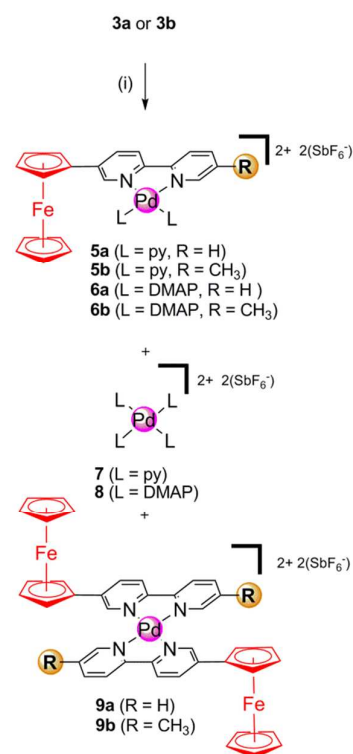


Scheme 1. Synthesis of the 5-ferrocenyl-2,2'-bipyridines **3a-b** and their corresponding palladium(II) dichloride complexes **4a-b**. (i) 1 M $\text{Na}_2\text{CO}_3(\text{aq})$, 3 M $\text{NaOH}(\text{aq})$, dioxane, DME, $[\text{Pd}(\text{dppf})\text{Cl}_2]$, MW (300 W), 110 °C, 30 mins; (ii) $[\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2]$, acetone, RT, 30 min

While palladium dichloride complexes are often used as starting materials for other palladium systems the extreme insolubility of **4a-b** preclude their use in the generation of further complexes. As complexes of the type $[\text{Pd}(\text{bipy})(\text{py})_2]^{2+}$ are often used to generate metallosupramolecular architectures we were interested in methods that would allow the synthesis of the $[\text{Pd}(\mathbf{3a} \text{ or } \mathbf{3b})(\text{py})_2]^{2+}$ complexes, **5a-b** and **6a-b**. The one-pot method²¹ shown in scheme 2 was used to generate the cationic palladium complexes **5a-b** and **6a-b** in modest isolated yields (63–77%).

Pyridine or 4-dimethylaminopyridine (DMAP) were added to a solution of $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ in acetone and stirred at room temperature for 30 minutes. AgSbF_6 was then added to abstract the chloride ligands, and the pale yellow solution was filtered to remove the precipitated AgCl . Finally an acetone solution of one of the ferrocene ligands, either **3a** or **3b**, was added

resulting in the immediate formation of a purple solution. Vapour diffusion of diethyl ether into the reaction solution generated a mixture of purple and colourless crystals. These different crystals were painstakingly physically separated in order to obtain the pure products **5a-b** and **6a-b** (purple) along with a small amount of the by-products $[\text{Pd}(\text{L} = \text{py} \text{ or } \text{DMAP})_4](\text{SbF}_6)_2$, **7** or **8** (colourless). Mass balance would require the presence of a small amount of the bis-bipy complexes **9a-b**. Related systems are known,^{21–22} but crystals of these compounds were not isolated from the reaction mixture. **9a** was generated independently in good isolated yield (ESI[†]). The generation of a similar three component mixture using a related one pot synthetic approach has been observed before in the literature.^{21a}



Scheme 2. Synthesis of the cationic palladium complexes **5a-b** and **6a-b**, **7**, **8** and **9a-b**. (i) a) $[\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2]$, py or DMAP (2 eq.), 30 mins, RT, b) AgSbF_6 (2 eq.), 30 mins, RT, c) **3a** or **3b**, 1h, RT.

X-ray quality crystals of the ferrocene complexes **5a**, **6a-b**, and the by-product **7** were obtained and the molecular structures of these species determined using crystallography (Figure b, 2c and ESI[†]). The structures of the metal cations **5a** and **6a-b** were as expected with the palladium ions coordinated to one of the ferrocenyl bipyridine ligands and two additional monodentate ligands (either py or DMAP) in a square planar arrangement.^{11d} The Pd- N_{bipy} (2.031(5) and 2.040(5) Å) and Pd- N_{py} (2.010(5) and 2.021(5) Å) bond lengths (Figure 2b) for **5a** are very similar to the distances observed in the related $[\text{Pd}(\text{G})(\text{Py})_2]^{3+}$ complex^{11d} and the average values (Pd- N_{bipy} 2.011 Å, Pd- N_{py} 2.025 Å) obtained from the CSD,[‡] for $[\text{Pd}(\text{bipy})(\text{Py})_2]^{2+}$ complexes. Somewhat unexpectedly the (Pd- N_{bipy} 2.019(3) and 2.014(2) Å, Pd- N_{DMAP} 2.022(3) and 2.017(3) Å) of the complex **6a** were very similar to those observed for **5a** despite DMAP being a more basic ligand than py. However, the Pd- N_{DMAP} bond lengths in **6b** (1.980(8) and 1.983(7)) were slightly shorter than those of **6a** and consistent with a stronger metal ligand interaction between the Pd ion and the basic DMAP ligands. As is common for bipy metal complexes a range of edge-to-face (H-centroid distance range 2.724-3.068 Å) and face-to-face (centroid-centroid distance range 3.705-3.870 Å) π - π

interactions are observed in the extended structures of **5a** and **6a-b** (ESI[†]).

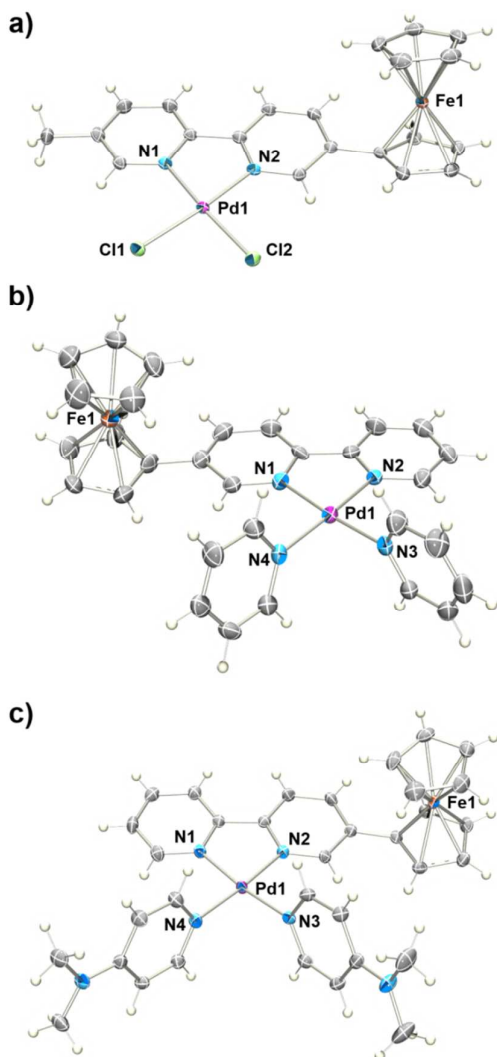


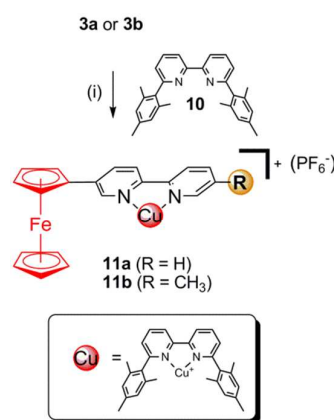
Figure 2. ORTEP diagrams showing the solid state structures of the palladium complexes a) **4b** (Selected bond lengths (Å) and angles (°): Pd1-N1: 2.024, Pd1-N2: 2.027, Pd1-Cl1: 2.294, Pd1-Cl2: 2.291, N1-Pd1-N2: 80.68, N2-Pd1-Cl2: 94.54, N1-Pd1-Cl1: 93.84, Cl1-Pd1-Cl2: 90.92), b) **5a** (Selected bond lengths (Å) and angles (°): Pd1-N1: 2.010, Pd1-N2: 2.021, Pd1-N3: 2.040, Pd1-N4: 2.031, N1-Pd1-N2: 81.09, N2-Pd1-N3: 96.13, N3-Pd1-N4: 88.00, N4-Pd1-N1: 94.87), and c) **6a** (Selected bond lengths (Å) and angles (°): Pd1-N1: 2.019, Pd1-N2: 2.014, Pd1-N3: 2.022, Pd1-N4: 2.017, N1-Pd1-N2: 81.32, N2-Pd1-N3: 94.36, N3-Pd1-N4: 89.97, N4-Pd1-N1: 94.27). The ellipsoids are shown at the 50% probability level. Solvent, counterions and hydrogen atoms are omitted for clarity.

¹H NMR and HR-ESMS spectra of the pyridine complexes **5a** and **5b** were consistent with the retention of the solid state structure when the compounds are dissolved in either acetone or acetonitrile solution (ESI[†]). Surprisingly, the spectra of the DMAP complexes **6a** and **6b** were more complicated (ESI[†]). Careful analysis of the ¹H NMR spectra of both **6a** and **6b** indicated the presence of **6a-b**, **8** and **9a-b** suggesting that the heteroleptic palladium compounds disproportionate generating an equilibrium that contains a mixture of homoleptic and heteroleptic palladium complexes (ESI[†]). HR-ES-MS spectra provided further support for this postulate with ions due to each of the components of the equilibrium observed (for example $m/z = 927.0359$ for [**5a**-SbF₆]⁺, $m/z = 831.1292$ [**8**-SbF₆]⁺, $m/z = 802.9516$ [**9a**+OH-2SbF₆]⁺). This behavior seems to be connected to the presence of the more basic DMAP ligands which seem to stabilise the homoleptic complex **8** (L = DMAP)

relative to the heteroleptic **6a-b**, generating an equilibrium mixture containing **6a-b**, **8** (L = DMAP) and **9a,b**.

Copper(I) complexes

The recently developed HETPHEN strategy has been extensively exploited to generate heteroleptic copper(I) complexes by combining sterically bulky bipyridine or phenanthroline ligands with another diimine ligand.²³ These complexes have found applications in the generation of optical materials,²⁴ metallocupramolecular architectures²⁵ and molecular machines.^{6a, 26} The 5-ferrocenyl 2,2'-bipyridine HETPHEN Cu(I) **11a-b** were synthesised using the method developed by Schmittel *et al.* (Scheme 3).²³ The 6,6'-dimesityl-2,2'-bipyridine ligand (**10**) was first added to [Cu(CH₃CN)₄]PF₆ in acetone to generate the yellow complex [Cu(**10**)(CH₃CN)₂]PF₆ *in situ*. Then one of the ferrocene-appended bipyridine ligands **3a** or **3b** was added resulting in the instantaneous formation of a deep red coloured solution, consistent with the generation of the desired complexes **11a-b**.



Scheme 3. General route for Cu(I) complexation. (i) [Cu(CH₃CN)₄]PF₆, **10**, acetone, r.t., 15 mins.

Vapour diffusion of diethyl ether into the acetone reaction mixtures resulted in the formation of X-ray quality crystals which were isolated in excellent yields (82-83%). Despite crystallising in different space groups (**11a**, monoclinic, P2₁/n, **11b**, tetragonal, I4₁/a) the structures of the two complexes were nearly identical (Fig. 3). The copper(I) ions were coordinated to **10** and one of the ferrocenyl-bipy ligands in a distorted tetrahedral coordination geometry (N1-Cu1-N2 81.88(9)° and 82.40(1)°, N3-Cu1-N4 79.46(9)° and 80.33(1)°). Analysis of related [Cu(bipy)₂]⁺ complexes in the CSD[‡] shows that the average N-Cu-N angle for these systems is 82.11° indicating that this type of tetrahedral distortion is universally observed for these copper(I) bis-bipy complexes. The Cu-N_{bipy} bond lengths of the complexes are all very similar, ranging from 2.007(3)-2.035(2) Å, and slightly shorter than the average bond distances found in the CSD for related bipy/phen Cu(I) structures of 2.045 Å. The 6,6'-dimesityl-2,2'-bipyridine ligand is wrapped around the bipy unit of the ferrocenyl ligand in the expected "pac-man-like"^{24a} orientation stabilized by π-π interactions (centroid-centroid distances 3.720-3.793 Å between the mesityl and bipyridine units (Figure)).

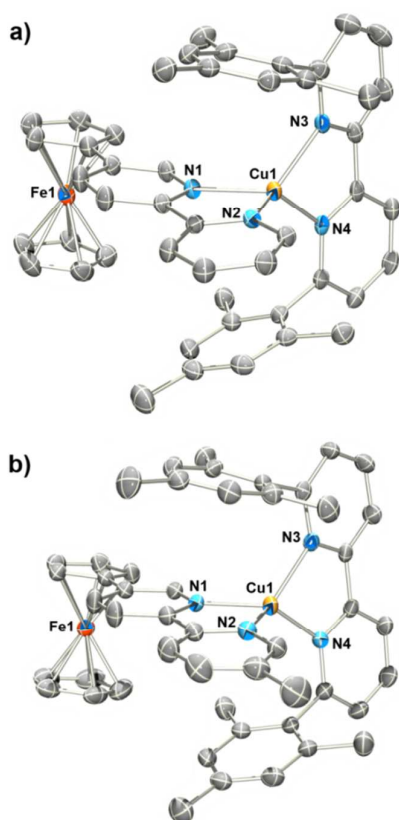


Figure 3. ORTEP diagrams of the molecular structures of a) **11a** (Selected bond lengths (Å) and angles (°): Cu1-N1: 2.033, Cu1-N2: 2.021, Cu1-N3: 2.035, Cu1-N4: 2.035, N1-Cu1-N2: 81.88, N3-Cu1-N4: 79.46, N1-Cu1-N3: 122.82, N2-Cu1-N4: 130.98), and b) **11b** (Selected bond lengths (Å) and angles (°): Cu1-N1: 2.026, Cu1-N2: 2.007, Cu1-N3: 2.027, Cu1-N4: 2.010, N1-Cu1-N2: 82.40, N3-Cu1-N4: 80.33, N1-Cu1-N3: 117.83, N2-Cu1-N4: 126.28). The ellipsoids are shown at the 50% probability level. Solvent, counterions and hydrogen atoms are omitted for clarity.

^1H NMR and HR-ESMS spectra confirmed that the complexes **11a-b** were stable in solution (ESI †). The ^1H NMR signals due to the ferrocene-appended bipyridine protons were only slightly shifted from the values observed for the “free” ligand due to competing effects (a downfield shift caused by metal complexation and upfield shifts due to π - π interactions with the mesityl units). However, due to the lower symmetry of the complexes the previously equivalent H_b and H_c protons of the mesityl units are split into two signals ($\text{H}_{n \text{ and } p}$ and $\text{H}_{m \text{ and } q}$) as one side of the mesityl substituent is in closer proximity to the ferrocene than the other once coordinated to the copper ion (ESI †). The complexes appeared to be remarkably stable as little to no fragmentation was observed under the conditions used for the mass spectrometry experiments. The isotopically resolved [**11a** or **11b** - PF_6] $^+$ ion was observed for each complex ($m/z = 795.2176$ for [**11a**- PF_6] $^+$ and $m/z = 809.2398$ for [**11b**- PF_6] $^+$) (ESI †).

Physical Properties

Electronic Absorption Spectra: UV-Vis absorption spectra of the two ligands (**3a-b**), the stable and soluble Pd(II) complexes (**5a-b** and **9a**), and the Cu(I) complexes (**11a-b**) were recorded in acetone (Fig. 4 and ESI †). The 5-ferrocenyl-2,2'-bipyridine ligands display two bands in the solvent accessible window. A relatively intense band was observed at ~ 364 nm with a weak metal-centred transition found at ~ 450 nm, 15c generating the expected yellow-orange coloured ligands. Complexation of the ligands to metal ions is accompanied by intense colour changes. The Pd(II) compounds (**5a-b** and **9a**) are all deep purple in

colour consistent with other literature examples. $^{11d, 27}$ The colour arises from a strong MLCT absorption around 540-560 nm, sitting squarely in the green/yellow section of the spectrum and tailing off into the red, resulting in the deep purple compounds. The copper(I) complexes (**11a-b**) are the expected red-brown colour, displaying intense MLCT bands at ~ 470 nm. $^{6a-c, 24}$

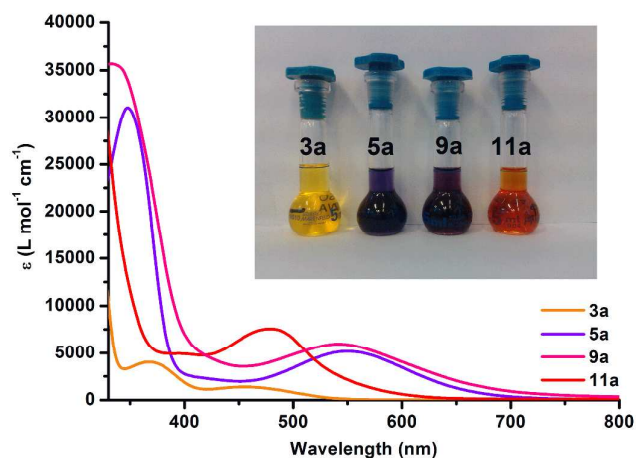


Figure 4. UV-Vis spectra of ligand **3a**, Pd(II) complexes **5a** and **9a**, and Cu(I) complex **11a** in acetone.

Electrochemistry: The electrochemistry of the ligands and complexes was investigated in acetone using a combination of cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. The results are presented in Table 1 and the voltammogram of **11b** in Figure 5. Additional figures and data for acetonitrile and dichloromethane solution experiments are given in the ESI † .

Table 1. Electrochemical data for **3a-b**, **5a**, **9a** and **11a-11b** in acetone.

Compound	E° (V) a	
	Cu $^{II/I}$	Fe $^{+/0}$
3-FcPy (B)	-	0.56
3a	-	0.57
3b	-	0.56
5a	-	0.69
5b	-	0.68
9a	-	0.67
11a	0.59	0.69
11b	0.59	0.69
[Cu(bipy(Mes) $_2$ (bipy)](BF $_4$)	0.56	-

a $\sim 1 \times 10^{-3}$ M in analyte, 0.1 M Bu $_4$ NPF $_6$, referenced to [Fc*] $^{+/0} = 0.00$ V.

All samples show the predicted one-electron chemically reversible oxidation of the ferrocenyl group. For **3a** the E° of 0.57 V for this redox couple compares well with that found for the closely related 3-ferrocenylpyridine (Fig 1, **B**; $E^\circ = 0.56$ V (acetone)). The effect on the ferrocenyl redox potential of a methyl 5'-bipy substituent (**3b**) is within the experimental error, but is observed as a subtle shift in the predicted cathodic direction.

For complexes **5a-b**, coordination of the bipy ligand to palladium gives the anticipated anodic shift of the ferrocenyl E° . The novelty of the palladium complexes makes comparison with other systems difficult, however the shift observed (120 mV) is significantly larger than that observed upon coordination of 3-ferrocenylpyridine to palladium 28 and 6-

ferrocenylbipyridine to other metal systems.^{15c, 15d} Ferrocenyl redox currents measured for **9a** are approximately double that of solutions of **5a**, consistent with the presence of the two independent metallocene units in the complex **9a**.

The complexes **11a-b** show two reversible redox processes associated with the ferrocenyl and copper components. In this class of compound there is a complex interplay between the steric demands of the HETPHEN ligands and the variations of the geometry of the Cu(II) and Cu(I) states.^{24a, 29} The E° for Cu^{II/I} is highly sensitive to this interplay and is observed over a 400 mV potential window. Nishihara and co-workers have prepared several ferrocenyl HETPHEN systems, including a 2-[2-(5-ferrocenyl)pyridyl]-4-methylpyrimidine (FcMpmPy) complex, which contains the same 5-ferrocenylpyridyl substitution as **11a/b**.^{6c} Due to intramolecular rotation, the FcMpmPy complex exists as a dynamic mixture of two structural isomers and required complex analysis to interpret the observed electrochemistry and assign the Cu^{II/I} and ferrocenyl E° s. Comparatively, both 5-ferrocenyl- and 5-ferrocenyl-5'-methyl- systems of **11a/b** are relatively simple and do not require low temperature, simulation, or spectroelectrochemical techniques to interpret. We associate the oxidations observed at E° 0.59 and 0.69 V to the Cu^{II/I} and ferrocenyl oxidations respectively from consideration of the various E° data in differing solvents (ESI), and by direct comparison with data for [Cu(bipy(Mes)₂(bipy))(BF₄)].^{24a} For the ligands **3a/b**, an irreversible bipy reduction process was observed at -2.1 V near the end of the acetone solvent window. Reduction processes for the complexes were poorly defined and not resolved; however, a quasi-reversible reduction is seen for the copper complexes **11a/b** at -1.63 V (Figure 5).

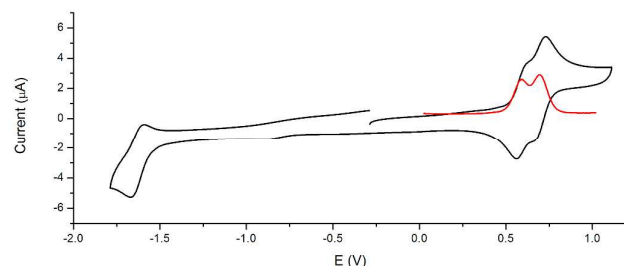


Figure 5. CV (100 mV s⁻¹, black trace) and DPV (red trace) of the Cu(I) complex **11b** (0.1 M Bu₄NPF₆, acetone, [Fc*]^{+/0}).

Conclusions

Two ferrocene-appended 2,2'-bipyridine metalloligands, 5-ferrocenyl-2,2'-bipyridine and 5-ferrocenyl-5'-methyl-2,2'-bipyridine, were synthesised using the Pd(0) catalysed Suzuki-Miyaura cross-coupling reaction. Their coordination chemistry with Pd(II) and Cu(I) ions was examined and the molecular structures of four palladium(II) and two copper(I) complexes were determined using X-ray crystallography. ¹H and ¹³C NMR spectra and HR-ESMS experiments confirmed that the majority of the complexes are stable in solution. The exceptions were the [Pd(Fc-bipy)(DMAP)₂](SbF₆)₂ complexes which were found to disproportionate to give equilibrium mixtures containing [Pd(Fc-bipy)₂](SbF₆)₂ and [Pd(DMAP)₄](SbF₆)₂. The electron absorption and electrochemical properties of these complexes were compared to those of the parent ligands. The ligands and the complexes are all highly coloured. The 5-ferrocenyl-2,2'-

bipyridine ligands are yellow/orange in colour with the expected weak d-d transition found at ~450 nm. The absorption bands of the Pd(II) and Cu(I) complexes are red-shifted relative to the free ligands and show enhanced molar absorptivity. The complexes all display strong MLCT absorptions in the visible spectrum, the Pd(II) compounds are deep purple in colour (λ_{max} = ~540-560 nm, while the copper(I) complexes are red-brown in colour (λ_{max} = ~470 nm). Electrochemical investigations showed that all the compounds displayed the expected chemically reversible one-electron oxidation of the ferrocenyl group. The reduction potential of the redox-active ferrocene unit was anodically shifted in the metal complexes compared to the ligands, as expected, and the introduction of a second redox active centre in the case of the Cu(I) complexes resulted in two separate oxidations, both of which could be assigned to their respective centres.

The result herein suggest that these and related ferrocene-bipy ligands and complexes could be exploited to develop dye-sensitized solar cells (DSSC)^{24, 30} redox-active metallosupramolecular systems and molecular machines. Efforts in these directions are underway.

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Notes and references

^a Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand. Fax: +64 3 479 7906; Tel: +64 3 479 7731; E-mail: jcrowley@chemistry.otago.ac.nz

[‡] CSD accessed via ConQuest 1.16 (current version 2014). The number of hits used for structural comparison was 45, 11, and 52 respectively for the PdCl₂, PdPy₂/PdDMAP₂, and Cu complexes.

†Electronic Supplementary Information (ESI) available: the supplementary information contains the experimental procedures, ¹H and ¹³C NMR, HR-ESI-MS, UV-Vis, electrochemical and crystallographic data. CCDC reference numbers 1000093-1000101. See DOI: 10.1039/b000000x/

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Two previously unreported 5-ferrocenyl-2,2'-bipyridine ligands were synthesised using the palladium(0) catalysed Suzuki-Miyaura cross-coupling reaction. Palladium(II) and copper(I) complexes of these ligands were synthesized. The complexes were deeply coloured. The optical and electrochemical properties of the complexes were compared to those of the “free” ligands.

