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Towards building blocks for metallosupramolecular structures: non-symmetrically-functionalised ferrocenyl compounds†

William D. J. Tremlett, [a] James D. Crowley, [b] L. James Wright [a] and Christian G. Hartinger *[a]

Metallosupramolecular architectures formed from metal ions and bridging ligands are increasing in popularity due to their range of applications and ease of self-assembly. Many are able to readily change their shape and/or function in response to an external stimulus and have the ability to encapsulate guest molecules within their internal cavities. Ferrocenyl groups (Fc) have been incorporated previously within the bridging ligands of metallosupramolecular structures due to their ideal attributes brought about by the structural and rotational flexiblity of the two cyclopentadienyl (Cp) rings coordinated to the Fe(II) centre. However, the majority of these Fc-based structures contain symmetrically substituted Cp rings. We report the synthesis and characterisation of non-symmetrically functionalised Fc-based ligands incorporating both *N*,*N*′ and NHC-donor groups chosen for their differing coordination properties. Both substituents were designed to coordinate to a single metal centre with the dissimilar coordination properties of each donor group facilitating stimulus-induced dissociation/association of one of the substituents as an opening/closing mechanism. Preliminary investigations into the coordination of these Fc-based ligands to a $[Ru(\eta^6\text{-}p\text{-cymene})]^{2+}$ moiety indicated complexation through a mixture of either a bi- or tridentate fashion, as alluded by ^{1}H NMR spectroscopy and mass spectrometry. Density functional theory (DFT) calculations revealed the Fc-based ligands adopt a *syn* conformation driven by H-bonding and π-interactions between the two Cp substituents, which facilitate coordination of both donor groups towards the metal centre.

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Introduction

Ferrocene (Fc) is perhaps one of the most resourceful organometallic molecules studied for over 70 years. Having been first reported in 1951,[1] Fc derivatives have attracted research interests in medicinal chemistry,[2–5] catalysis,[6,7] materials[8,9] and electrochemistry.[10,11] The extensive use of Fc as an organometallic building block has largely been due to its synthetic versatility and convenience, intrinsic air, heat and photochemical stability, and reversible oxidation to the cytotoxic ferrocenium cation (Fc^+).[12–17]

Incorporating Fc as part of supramolecular and metallosupramolecular architectures, in particular 1,1′-disubstituted Fc derivatives, is appealing for the design of stimulus-responsive systems, primarily due to the rotational freedom and flexibility of the cyclopentadienyl (Cp) rings about the Fe(II) centre.[18] This molecular ball-bearing character allows substituents to be brought together and/or repelled by the addition and removal of external stimuli, such as redox processes,[19,20] competing ligands[21–24] and light.[25] Numerous studies have shown the formation of molecular machines, such as switches, rotors, springs, brakes and scissors, using ferrocene-derived scaffolds that exploit these characteristics.[26–32]

Metal–ligand interactions provide a versatile method of constructing one-, two- or three-dimensional supramolecular assemblies depending on the coordination modes and bonding strengths between metal ions (M) and ligand donor groups (L). As such, careful consideration is required when designing metallosupramolecular architectures, in particular the structure and coordination properties of the ligands, to avoid improperly formed architectures. Fc-based ligands offer

[a]*School of Chemical Sciences, University of Auckland, 23 Symonds Street, Auckland 1010, New Zealand. E-mail: c.hartinger@auckland.ac.nz; Tel: +64-9923-3220*
[b]*Department of Chemistry, University of Otago, PO Box 56, Dunedin 9054, New Zealand*

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the advantage of internal rotational freedom of the Cp rings which enables them to adopt multiple conformations, whereas metal ions can form various complexes which can undergo ligand dissociation or structure reformation events that occur when exposed to an external stimulus.

In our previous work, symmetrically-functionalised ferrocenyl ligands bearing pyridyl donor groups were used to form a series of PdL-, PdL_2- and Pd_2L_4-type architectures which showed reversible disassembly and reassembly when a competing ligand was introduced and removed, respectively.[33] Herein, we have expanded these Fc-derived molecules to incorporate both *N*,*N*′ and pro-*N*-heterocyclic carbene (NHC)-donors to provide a ligand system with two dissimilar coordination sites that may be used to coordinate to a metal centre. We have carried out preliminary investigations into the complexation of these non-symmetrically substituted Fc-based ligands towards a Ru(II) centre.

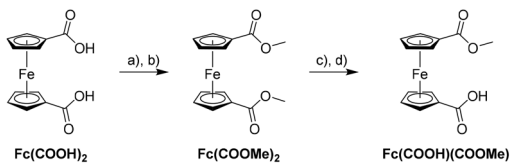
Results and discussion

The target ferrocenyl ligands were designed to incorporate different donor groups on either Cp ring, each with dissimilar metal-coordinating properties. NHCs form highly stable metal-NHC complexes,[34–46] whereas *N*,*N*′-donor groups, such as pyridyl-triazole (pytri), form more labile bonds that are susceptible to cleavage by external stimuli. Bidentate pytri-type ligands have been shown to be effective metal chelators,[23,47] and have displayed appealing photo-ejection properties when coordinated to Ru(II).[25,48]

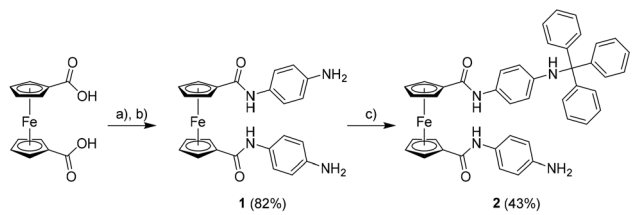
Initially, different strategies for the non-symmetric substitution of Fc were explored including the coupling of two *p*-phenylenediamine units to $Fc(COOH)_2$ to form 1,1′-bis[[(4-aminophenyl)amino]carbonyl]ferrocene (Scheme 1; **1**),[33] and subsequent protection of one arylamine unit with either *tert*-butyloxycarbonyl (Boc), fluorenylmethyloxy carbonyl (Fmoc) or triphenylmethyl (trityl) groups. Unfortunately, the protection with Boc was unsuccessful, and no Boc-containing products could be identified in the ^{1}H NMR spectrum of the crude product. Protection of one of the arylamine substituents of **1** with Fmoc was achieved, however, this molecule was susceptible to hydrolysis and the majority of the protecting group was cleaved during attempted purification by flash chromatography. Treatment of the Fc-diamine with triphenylmethyl chloride (TrCl) and *N*,*N*-diisopropylethylamine (DIPEA) produced the singly protected product in 43% yield which was isolated by flash chromatography without degradation (Scheme 1; **2**). Nevertheless, subsequent attempts to functionalise the free amino group resulted in cleavage of the trityl protecting group.

We found that the target ferrocenyl compounds could be synthesised using a modular approach in which pre-formed pytri and pro-NHC donor moieties were selectively coupled to the non-symmetrically-functionalised ferrocenyl scaffold. Asymmetry of the Fc moiety was achieved by the hydrolysis of one methyl ester group of 1,1′-bis(methoxycarbonyl)ferrocene ($Fc(COOMe)_2$) through the treatment with 1.1 equivalents of sodium hydroxide in methanol (2.8 M; Scheme 2).[49] The mono-carboxylate intermediate precipitated from solution as it formed, which prevented hydrolysis of the second methyl ester group. Acidification with concentrated hydrochloric acid produced 1-carboxy-1′-(methoxycarbonyl)ferrocene (Fc(COOH)(COOMe)) in high yield of 91%.[49,50]

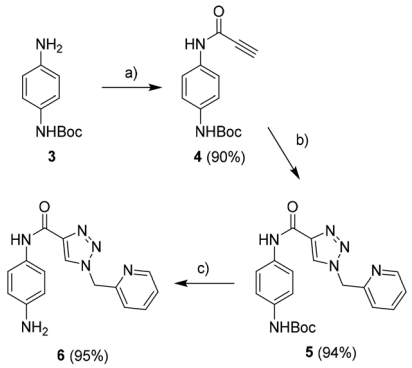
To synthesise the dissimilar donor moieties, we used *p*-phenylenediamine as a diamine with low steric hindrance around the functional groups which we could use to introduce both the *N*,*N*′-pytri and pro-NHC-donor substituents (Schemes 3 and 4). In order to form the pytri fragment, one amino group of *p*-phenylenediamine was first Boc-protected using standard



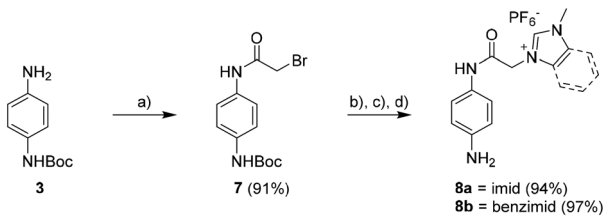
Scheme 2 Preparation of Fc(COOH)(COOMe).[49,50] Reagents and conditions: (a) $(COCl)_2$, DMF (cat.), CH_2Cl_2, rt, 3 h; (b) MeOH, rt, 1 h, 97% over two steps; (c) NaOH 2.8 M, MeOH–acetone, rt, 18 h; (d) conc. HCl, H_2O, rt, 91% over two steps.



Scheme 1 Protection of one of the two substituted Cp moieties with a trityl group. Reagents and conditions: (a) $(COCl)_2$, DMF (cat.), CH_2Cl_2, rt, 3 h; (b) *p*-phenylenediamine, Et_3N, CH_2Cl_2, rt, 18 h, 82% over two steps;[33] (c) TrCl, DIPEA, DMF–CH_2Cl_2 (1 : 40), rt, 18 h, 43%.



Scheme 3 Preparation of pytri fragment **6**. Reagents and conditions: (a) propiolic acid, DIC, CH_2Cl_2–DMF (11.5 : 1), 0 °C → rt, 24 h, 90%; (b) 2-(azidomethyl)pyridine $CuSO_4{\cdot}5H_2O$, sodium ascorbate, CH_2Cl_2–H_2O (3 : 1), rt, 18 h, 94%; (c) TFA–CH_2Cl_2 (1 : 5), rt, 2 h, 95%.



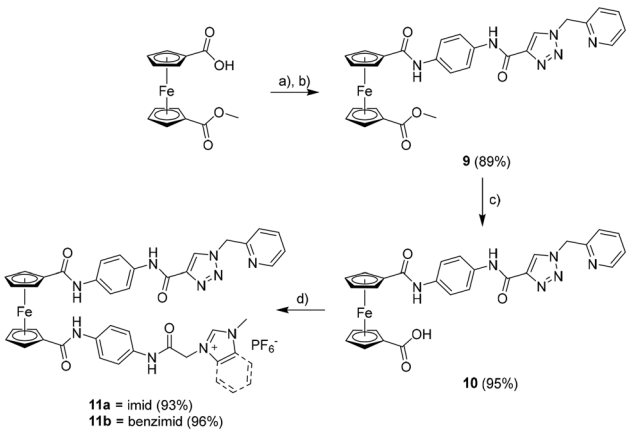
Scheme 4 Preparation of (benz)imidazolium fragments **8a** and **8b**. Reagents and conditions: (a) bromoacetic acid, DIC, CH_2Cl_2, 0 °C → rt, 18 h, 91%; (b) 1-methylimidazole or 1-methylbenzimidazole, CH_3CN, reflux, 24 h; (c) TFA–CH_2Cl_2 (1 : 5), rt, 2 h; (d) KPF_6, satd aq $NaHCO_3$, H_2O, rt 10 min, 94 or 97% over 3 steps.

protection procedures (Scheme 3; **3**).[51] Amide **4** was formed in high yield through the coupling of Boc-protected amine **3** and propiolic acid using *N*,*N*′-diisopropylcarbodiimide (DIC) as the coupling reagent (Scheme 3).[52] A copper-catalyzed azide–alkyne cycloaddition (CuAAC) reaction between amide **4** and 2-(azidomethyl)pyridine in a biphasic mixture of dichloromethane and water produced the pytri compound **5** in 95% yield (Scheme 3). The ^{1}H NMR spectrum of **5** (Fig. S1†) showed the absence of the terminal alkyne proton, previously exhibited in the ^{1}H NMR spectrum of **4** at 2.91 ppm, and the triazole proton was observed at the characteristic chemical shift of 8.30 ppm. The methylene singlet appeared at 5.71 ppm, which is considerably downfield from the corresponding signal for 2-(azidomethyl)pyridine (4.49 ppm). Standard Boc deprotection conditions using trifluoroacetic acid, with subsequent neutralisation by sodium bicarbonate and dichloromethane extraction, was employed to produce the deprotected compound **6** (Scheme 3) in high purity, as confirmed by elemental analysis. In the ^{1}H NMR spectrum of **6** (Fig. S3†), the chemical shifts observed for the phenyl protons were similar to those observed for **5**, and the two amino protons were observed as a broad singlet at 3.63 ppm. The mass spectrum confirmed the structure to be the deprotected pytri product **6** with a pseudo-molecular ion peak $[\mathbf{6} + Na]^+$ observed at *m*/*z* 317.1119 (m_{calc} 317.1121).

To form a suitable moiety containing a pro-NHC donor, mono-functionalisation of *p*-phenylenediamine with an imidazolium-derived moiety was required. Starting with the Boc-protected *p*-phenylenediamine **3**, treatment with bromoacetic acid using DIC as the coupling reagent under similar reaction conditions to those used for the synthesis of **4**, gave the alkyl bromide **7** (Scheme 4).[53] Either 1-methylimidazole or 1-methylbenzimidazole was then separately alkylated with alkyl bromide **7**, the reactions being carried out in acetonitrile heated under reflux. The imidazolium intermediate remained in solution during the reaction, whereas the benzimidazolium analogue precipitated as a white powder. Removal of the Boc protecting group from both of these compounds was easily achieved by treatment with trifluoroacetic acid (Scheme 4). However, after neutralisation the isolated products were a mixture of bromide and trifluoroacetate salts. To overcome this, the crude product was treated with excess potassium hexafluorophosphate in water at 0 °C. The more hydrophobic hexafluorophosphate salts (**8a** and **8b**) precipitated as pure products under these conditions (Scheme 4). The ^{31}P{^{1}H} and ^{19}F-{^{1}H} NMR spectra for both compounds exhibited the characteristic chemical shifts (−144.2 and −70.1 ppm, respectively) and multiplicities expected for hexafluorophosphate counterions in $(CD_3)_2SO$. The ^{1}H NMR spectra (Fig. S5 and S7†) showed the free primary aryl amine resonances at 4.93 and 4.95 ppm, respectively, each integrating to two protons. Mass spectrometry of both **8a** and **8b** showed the pseudo-molecular ion peaks attributed to $[M - PF_6]^+$ at *m*/*z* 231.1249 (m_{calc} 231.1240) and 281.1396 (m_{calc} 281.1397), respectively. The hexafluorophosphate counterion was also observed in the mass spectra in negative ionisation mode as a peak at *m*/*z* 144.9647.

To couple the pytri-containing fragment **6** to the Fc framework, the carboxylic acid group in Fc(COOH)(COOMe) was first converted to the acid chloride and then **6** was added (Scheme 5). Product **9** precipitated from the reaction mixture and was purified by flash chromatography. The ^{1}H NMR spectrum of **9** (Fig. S9†) showed the presence of two amido NH resonances at 8.94 and 8.19 ppm, compared to the sole amide peak in **6** at 8.77 ppm. The phenyl protons appeared at 6.69 to 7.73 ppm, considerably downfield from those observed for **6**. Hydrolysis of the methyl ester in **9** was achieved by treatment with sodium hydroxide in methanol (2.8 M), and after adjustment of the pH to 5 by addition of hydrochloric acid, compound **10** precipitated from solution in excellent yield (Scheme 5). The carboxylic acid proton was observed at 12.20 ppm in the ^{1}H NMR spectrum of **10** measured in $(CD_3)_2SO$ (Fig. S11†) and a pseudo-molecular ion peak at *m*/*z* 573.0928 assigned to $[\mathbf{10} + Na]^+$ (m_{calc} 573.0944) was detected in the mass spectrum.

Attachment of the second substituent on Fc proceeded by coupling the carboxylic acid group in **10** with the amino group in **8a** or **8b**. Amide bond formation was achieved using the coupling agent 1-(bis(dimethylamino)methylene)-1*H*-1,2,3-tria-



Scheme 5 Preparation of ferrocenyl compounds **11a** and **11b**. Reagents and conditions: (a) $(COCl)_2$, DMF, CH_2Cl_2, rt, 2 h; (b) **6**, Et_3N, CH_2Cl_2, rt, 18 h, 89% over two steps; (c) NaOH, MeOH–CH_2Cl_2, rt, 18 h, 95%; (d) **8a** or **8b** HATU, DIPEA, DMF, rt, 18 h, 93 or 96%.

zolo[4,5-*b*]pyridinium 3-oxide hexafluorophosphate (HATU). The products, **11a** or **11b**, respectively, were obtained in very high yields (Scheme 5). Clear indication of amide formation was the absence of signals assigned to the amino (**8a** and **8b**) and carboxylic acid (**10**) protons in the ^{1}H NMR spectra of **11a** and **11b** (Fig. S13 and S15†), as well as the detection of signals associated with the two ferrocenyl amide groups observed as overlapping signals at 9.62 ppm. Moreover, the structures were confirmed by mass spectrometry with pseudo-molecular ion peaks assigned to $[M - PF_6]^+$ ions at *m*/*z* 763.2180 (m_{calc} 763.2187) and 813.2327 (m_{calc} 813.2344) for **11a** and **11b** (Fig. S18 and S19†), respectively.

As no suitable single crystals for X-ray diffraction (XRD) analyses could be obtained, both the cations of **11a** and **11b** were examined using density functional theory (DFT) calculations to provide insight into the relative orientations of the Cp fragments and H donor/acceptor groups. A series of different conformational isomers was generated with the four amide groups having different combinations of *syn* and *anti* conformations relative to the other substituent on Fc (Fig. S23†). All structures were assumed to adopt a *syn* conformation about the Cp rings whereby each substituent is stacked on top of the other held together by intermolecular interactions. The calculations showed that the most stable conformations for both structures had an *anti* arrangement of the amide bonds adjacent to the Fc moiety and a *syn* arrangement of the other amide groups (Fig. 1 and Table S1†). Each Cp substituent was stabilised in a *syn* conformation by a combination of H-bonding between amide groups and π-interactions between the phenyl linkers. The closest distances between the carbonyl oxygen atom on one substituent and the amido proton on the other were 2.372 and 2.352 Å, and between the phenyl linkers 3.300 and 3.323 Å for **11a** and **11b**, respectively. The close spatial positioning of the pro-NHC and pyridyl-triazole donor groups indicated the two substituents of these molecules should be able to coordinate to a metal centre in an overall tridentate fashion through both donor groups (Fig. 1).

Attempts to coordinate the donor groups of either **11a** or **11b** to a Ru(*p*-cymene) moiety[54–56] resulted in complexes that are tentatively formulated as **12a** and **12b** (Scheme 6). Coordination to Ru(*p*-cymene) was explored, as the arene ligand occupies three coordination sites, allowing for the bidentate triazolyl and monodentate NHC to complete the coordination sphere about the Ru centre. The preparations were carried out in two stages, with the first step involving treatment of **11a** or **11b** with silver oxide to form the corresponding NHC-Ag intermediates. These were not isolated but used directly in subsequent transmetallation reactions with $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$.[57] In the ^{1}H NMR spectra of **12a** and **12b**, no resonances that could be assigned to the imidazolium protons, which appeared as a singlets at 8.54 and 9.08 ppm for **11a** and **11b**, respectively were observed. Six signals were observed in the ^{1}H NMR spectra of the crude products of complexes **12a** and **12b** between 9.5 and 8.0 ppm which integrated for six protons. Whereas the ^{1}H NMR spectra of the ligands in the same region integrated to seven protons. Moreover, the aromatic protons associated with the *p*-cymene ligands appeared downfield compared to the corresponding signals in $[(p\text{-cymene})RuCl_2]_2$, as a result of the new coordination environment for ruthenium. The ratio of the integrals for the *p*-cymene methyl signals and cyclopentadienyl signals confirmed the Ru(*p*-cymene) and ferrocenyl moieties were present in a 1 : 1 ratio. Further characterisation and peak assignment by 2D NMR spectroscopic methods proved unsuccessful as more than one set of signals was observed which could not be separated, and the heterodimetallic compounds could not be isolated in sufficient purity.

Although **12a** and **12b** could not be purified sufficiently to enable full characterisation, the mass spectra of crude samples (Fig. S21 and S22†) provided evidence towards the formation of both complexes with pseudo-molecular ion signals at *m*/*z* 499.1176 (m_{calc} 499.1128) and 524.1223 (m_{calc} 524.1207),

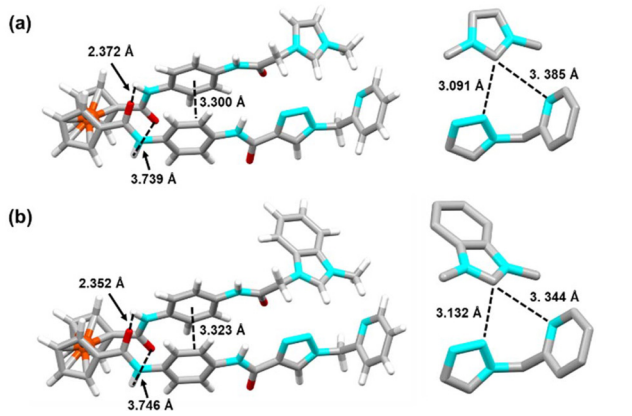
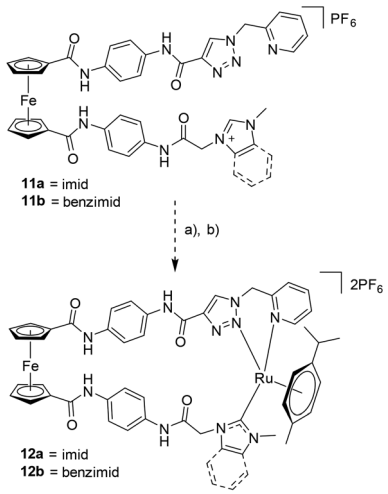


Fig. 1 DFT-calculated and energy-optimised geometries of cations of (a) **11a** and (b) **11b**.



Scheme 6 Complexation studies of ferrocenyl ligands **11a** and **11b** to Ru(cym)Cl moieties. Reagents and conditions: (a) Ag_2O, CH_3CN, 60 °C, 4 h; (b) $[(p\text{-cymene})RuCl_2]_2$, $AgPF_6$, CH_3CN, 60 °C, 18 h.

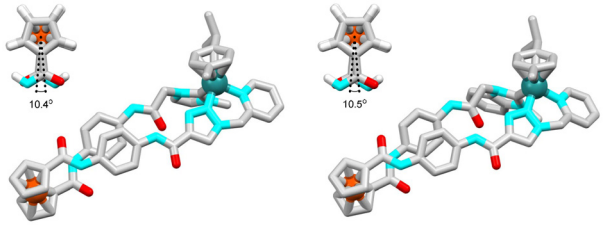


Fig. 2 DFT-calculated structures of the proposed heterobimetallic compounds incorporating a pytri and either imidazole (left) or benzimidazole (right) NHC ligands connected through a *p*-phenylenediamine linker. Hydrogen atoms have been removed for clarity.

respectively, which corresponded to the $[M - 2PF_6]^{2+}$ ion in each case. In addition, the pseudo-molecular ions $[M - PF_6]^{+}$ were observed at *m*/*z* 1143.1953 (m_{calc} 1143.1904) and 1193.2055 (m_{calc} 1193.2062), respectively. Although mass spectrometry did not provide further insight into the coordination mode of the formed complex, the detection of well-defined peaks in the ^{1}H NMR spectra suggests that one coordination species is most prominent in the crude products. However, the exact coordination mode of the ligands to the Ru centre remains elusive as the compounds could not be isolated in sufficient purity for further characterisation.

DFT calculations of the target tridentately-coordinated heterobimetallic complexes (Fig. 2) revealed the most stable conformations involved an *anti*-conformation for the two amide groups directly bound to the ferrocenyl scaffold and a *syn*-conformation for the two amide groups remote from this unit. The torsion angles of the two Cp rings were 10.4° and 10.5° for **12a** and **12b**, respectively, as shown in Fig. 2. The four amide groups appear to have a significant role in controlling the twist angles associated with the two Cp rings with H-bonding interactions present between the amide groups on the two different substituents on Fc. The DFT calculations also confirmed there was no undue strain associated with coordination of the three donor groups on the two Fc substituents towards the Ru(*p*-cymene) moiety.

Experimental

Materials and methods

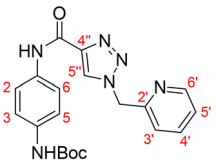
Unless otherwise stated, all reactions were carried out under a nitrogen (N_2) atmosphere using oxygen-free standard techniques. Starting materials and other reagents purchased from commercial suppliers were used without further purification. All solvents used in the reactions, except dimethyl sulfoxide, were dried through a solvent purification system under a nitrogen atmosphere (LC Technology Solutions Inc., SP-1 solvent purifier) and transferred into Schlenk flasks that were dried under vacuum and purged with N_2 prior to use. All synthesised reagents were dried under vacuum in Schlenk flasks prior to use.

Bromoacetic acid (AK Scientific, Union City, California, United States, >99%), 2-(bromomethyl)pyridine hydrobromide (AK Scientific, Union City, California, United States, 98%), *n*-butyllithium (Sigma-Aldrich, St Louis, Missouri, United States, 2 M in cyclohexane), copper(II) sulfate pentahydrate (ECP Limited, Auckland, New Zealand, 98%), di-*tert*-butyl dicarbonate (Sigma-Aldrich, St Louis, Missouri, United States, 99%), *N*,*N*′-diisopropylcarbodiimide (Sigma-Aldrich, St Louis, Missouri, United States, 99%), *N*,*N*-diisopropylethylamine (Sigma-Aldrich, St Louis, Missouri, United States, 99%), ferrocene (Sigma-Aldrich, St Louis, Missouri, United States, 98%), glacial acetic acid (Merck, Darmstadt, Germany, 100%), HATU (AK Scientific, Union City, California, United States, 99%), hydrochloric acid (Merck, Darmstadt, Germany, 37%), 1-methylbenzimidazole (Sigma-Aldrich, St Louis, Missouri, United States, 99%), 1-methylimidazole (AK Scientific, Union City, California, United States, 99%), 4,4′-methylenedianiline (AK Scientific, Union City, California, United States, 98%), oxalyl chloride (Sigma-Aldrich, St Louis, Missouri, United States, ≥99%), *p*-phenylenediamine (Sigma-Aldrich, St Louis, Missouri, United States, 98%), potassium hexafluorophosphate (Sigma-Aldrich, St Louis, Missouri, United States, ≥99.0%), propiolic acid (AK Scientific, Union City, California, United States, 97%), silver hexafluorophosphate (AK Scientific, Union City, California, United States, 98%), silver oxide (Sigma-Aldrich, St Louis, Missouri, United States, 99%), sodium L-ascorbate (Sigma-Aldrich, St Louis, Missouri, United States, ≥98%), sodium azide (Sigma-Aldrich, St Louis, Missouri, United States, ≥99%), sodium hydroxide (ECP Limited, Auckland, New Zealand, 98%), sulfuric acid (JT Baker, Radnor, Pennsylvania, United States, 98%), tetrakis(acetonitrile)palladium(II) tetrafluoroborate (Sigma-Aldrich, St Louis, Missouri, United States, 98%), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (Sigma-Aldrich, St Louis, Missouri, United States, 99%), triethylamine (Romil Pure Chemistry, Waterbeach, Cambridge, England, ≥99.5%), trifluoroacetic acid (ECP Limited, Auckland, New Zealand, 99%), and trityl chloride (Sigma-Aldrich, St Louis, Missouri, United States, 97%) were obtained from commercial sources.

NMR spectra were recorded at ambient temperature on a Bruker AVIII 400 MHz spectrometer, operating at either 399.89 or 400.13 MHz (^{1}H), 100.61 MHz (^{13}C{^{1}H} DEPTQ), 161.87 MHz (^{31}P{^{1}H}) or 375.89 MHz (^{19}F{^{1}H}). Electrospray ionisation mass spectrometry (ESI-MS) data were recorded on a Bruker Daltonics micrOTOF-QII mass spectrometer in positive or negative ionisation mode. Elemental analyses were carried out on the vario EL cube CHNOS Elemental Analyzer at the University of Auckland.

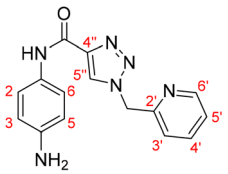
Syntheses

***tert*-Butyl-4-(*N*-1-(2-pyridinylmethyl)-1*H*-1,2,3-triazole-4-carboxamide)phenylcarbamate (5).**



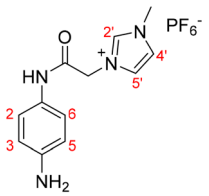
A solution of 2-(azidomethyl)pyridine (2.68 g, 20.0 mmol) in CH_2Cl_2 (50 mL) was added to a suspension of $CuSO_4{\cdot}5H_2O$ (208 mg, 0.83 mmol) and sodium ascorbate (330 mg, 1.66 mmol) in water (100 mL) followed by alkyne **4** (4.33 g, 16.6 mmol) in CH_2Cl_2 (250 mL). The resulting mixture was stirred vigorously at rt for 16 h. The reaction mixture was extracted with CH_2Cl_2 (3 × 100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by flash chromatography (hexanes/EtOAc 1 : 1 → EtOAc neat) to afford **5** (6.14 g, 94%) as a white solid. R_f 0.43 (EtOAc/hexanes 4 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (s, 1H, NHCO(C_2N_3)), 8.61 (d, 1H, ^3J = 4.9 Hz, H-6′), 8.30 (s, 1H, H-5″), 7.72 (td, 1H, ^3J = 11.6 Hz, ^3J = 2.0 Hz, H-4′), 7.61 (d, 2H, ^3J = 8.9 Hz, H-2 and H-6), 7.36 (d, 2H, ^3J = 8.8 Hz, H-3 and H-5), 7.29 (ddd, 1H, ^3J = 7.5 Hz, ^3J = 5.0 Hz, ^4J = 1.1 Hz, H-5′), 7.24 (d, 1H, ^3J = 7.9 Hz, H-3′), 6.48 (s, 1H, N*H*$CO_2C(CH_3)_3$), 5.71 (s, 2H, CH_2), 1.51 (s, 9H, $CO_2C(CH_3)_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.7 (C, NH*C*O(C_2N_3)), 153.6 (C, C-2′), 152.9 (C, *C*$O_2C(CH_3)_3$), 150.3 (CH, C-6′), 144.0 (C, C-4″), 137.6 (CH, C-4′), 135.1 (C, C-1), 132.9 (C, C-4), 126.5 (CH, C-5″), 123.9 (CH, C-5′), 122.6 (CH, C-3′), 120.8 (2 × CH, C-2 and C-6), 119.4 (2 × CH, C-3 and C-5), 80.7 (C, $CO_2C(CH_3)_3$), 56.1 (CH_2, CH_2(py)), 28.5 (3 × CH_3, $CO_2C(CH_3)_3$); MS (ESI$^+$): m/z = 417.1636 [M + Na]$^+$ (m_{calc} = 417.1646); Calcd for $C_{20}H_{22}N_6O_3$: C 60.90, H 5.62, N 21.31%. Found: C 60.88, H 5.97, N 21.40%.

***N*-(4-Aminophenyl)-1-(2-pyridinylmethyl)-1*H*-1,2,3-triazole-4-carboxamide (6).**



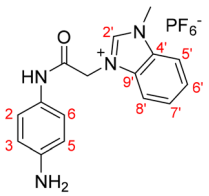
TFA (40 mL) was added to a suspension of **5** (6.14 g, 15.6 mmol) in CH_2Cl_2 (200 mL) at rt and the resulting solution was stirred for 2 h. The solvents were removed under a stream of N_2, the resultant residue suspended in saturated aqueous $NaHCO_3$ (200 mL) and the aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with brine (200 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to afford **6** (4.36 g, 95%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 1H, NHCO(C_2N_3)), 8.61 (d, 1H, ^3J = 4.1 Hz, H-6′), 8.28 (s, 1H, H-5″), 7.71 (td, 1H, ^3J = 7.7 Hz, ^3J = 1.7 Hz, H-4′), 7.47–7.43 (m, 2H, H-2 and H-6), 7.29 (ddd, 1H, ^3J = 7.5 Hz, ^3J = 5.0 Hz, ^4J = 0.9 Hz, H-5′), 7.23 (d, 1H, ^3J = 7.7 Hz, H-3′), 6.70–6.67 (m, 2H, H-3 and H-5), 5.71 (s, 2H, CH_2), 3.63 (br s, 2H, NH_2); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.6 (C, NH*C*O(C_2N_3)), 153.7 (C, C-2′), 150.2 (CH, C-6′), 144.2 (C, C-4″), 143.6 (C, C-1), 137.5 (CH, C-4′), 129.0 (C, C-4), 126.3 (CH, C-5″), 123.8 (CH, C-5′), 122.6 (CH, C-3′), 121.9 (2 × CH, C-2 and C-6), 115.6 (2 × CH, C-3 and C-5), 56.1 (CH_2, CH_2(py)); MS (ESI$^+$): m/z = 317.1119 [M + Na]$^+$ (m_{calc} = 317.1121); Calcd for $C_{15}H_{14}N_6O{\cdot}0.1CH_2Cl_2$: C 59.84, H 4.80, N 27.87%. Found: C 59.89, H 4.73, N 27.75%.

***N*-(4-Aminophenyl)-3-methyl-1*H*-imidazole-1-acetamide (8a).**



1-Methylimidazole (740 μL, 9.28 mmol) was added to a suspension of **7** (2.78 g, 8.44 mmol) in CH_3CN (120 mL). The reaction mixture was heated under reflux for 24 h and then cooled to rt and the reaction mixture concentrated *in vacuo*. The resultant oil was suspended in CH_2Cl_2 (100 mL), TFA was added (20 mL) and the resulting solution stirred for 2 h. The solvents were removed under a stream of N_2 and the residue was dissolved in water (100 mL). The solution was neutralised with saturated aqueous $NaHCO_3$ and treated with KPF_6 (6.21 g, 33.7 mmol) at 0 °C. The resulting precipitate was collected by filtration, washed with ice-cooled water (3 × 40 mL) and dried *in vacuo* to afford **8a** (2.97 g, 94%) as an off-white powder. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 10.05 (s, 1H, NHCO), 9.08 (s, 1H, H-2′), 7.71 (d, 2H, ^3J = 9.8 Hz, H-4′ and H-5′), 7.20 (d, 2H, ^3J = 8.7 Hz, H-2 and H-6), 6.52 (d, 2H, ^3J = 8.6 Hz, H-3 and H-5), 5.10 (s, 2H, CH_2), 4.93 (s, 2H, NH_2), 3.90 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2SO$): δ 162.5 (C, C═O), 145.4 (C, C-1), 137.8 (CH, C-2′), 127.2 (C, C-4), 123.9 (CH, C-4′ or C-5′), 123.0 (CH, C-4′ or C-5′), 120.9 (2 × CH, C-2 and C-6), 113.9 (2 × CH, C-3 and C-5), 51.0 (CH_2, CO*C*H_2), 35.8 (CH_3, (imid)CH_3); ^{31}P{^{1}H} NMR (162 MHz, $(CD_3)_2SO$): δ −144.2 (sep, 1P, ^1J = 711 Hz, PF_6); ^{19}F{^{1}H} NMR (376 MHz, $(CD_3)_2SO$): δ −70.1 (d, 6F, ^1J = 711 Hz, PF_6); MS (ESI$^+$): m/z = 231.1249 [M − PF_6]$^+$ (m_{calc} = 231.1240); MS (ESI$^-$): m/z = 144.9647 [PF_6]$^-$ (m_{calc} = 144.9647); Calcd for $C_{12}H_{15}N_4OPF_6{\cdot}0.4CH_3CN$: C 39.15, H 4.16, N 15.70%. Found: C 39.68, H 4.56, N 15.17%.

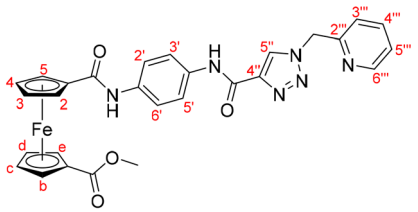
***N*-(4-Aminophenyl)-3-methyl-1*H*-benzimidazole-1-acetamide (8b).**



1-Methylbenzimidazole (1.12 g, 8.48 mmol) was added to a suspension of **7** (2.54 g, 7.71 mmol) in CH_3CN (120 mL). The reaction mixture was heated under reflux for 24 h and then cooled to rt. The resulting precipitate was collected *via* filtration, washed with EtOAc (3 × 50 mL) and air dried. The precipitate was suspended in CH_2Cl_2 (100 mL), TFA was added (20 mL) and the resulting solution stirred for 2 h. The solvents were removed under a stream of N_2 and the residue dissolved in water (100 mL). The solution was neutralised with saturated aqueous $NaHCO_3$ and treated with KPF_6 (5.67 g, 30.8 mmol) at 0 °C. The resulting precipitate was collected by filtration, washed with ice-cooled water (3 × 40 mL) and dried *in vacuo* to

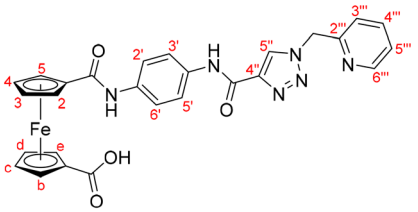
afford **8b** (3.45 g, 97%) as a white powder. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 10.20 (s, 1H, NHCO), 9.72 (s, 1H, H-2′), 8.06–8.03 (m, 1H, H-5′), 8.00–7.98 (m, 1H, H-8′), 7.72–7.70 (m, 2H, H-6′ and H-7′), 7.22 (d, 2H, ^3J = 8.5 Hz, H-2 and H-6), 6.52 (d, 2H, ^3J = 8.5 Hz, H-3 and H-5), 5.43 (s, 2H, CH_2), 4.95 (s, 2H, NH_2), 4.15 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$): δ 162.2 (C, C═O), 145.5 (C, C-1), 143.8 (CH, C-2′), 131.6 (C, C-4′ or C-9′), 131.4 (C, C-4′ or C-9′), 127.2 (C, C-4), 126.8 (CH, C-6′ or C-7′), 126.5 (CH, C-6′ or C-7′), 120.9 (2 × CH, C-2 and C-6), 113.8 (2 × CH, C-3 and C-5), 113.6 (2 × CH, C-5′ and C-8′), 48.8 (CH_2, $COCH_2$), 33.3 (CH_3, (imid)CH_3); $^{31}P\{^1H\}$ NMR (162 MHz, $(CD_3)_2SO$): δ −144.2 (sep, 1P, ^1J = 711 Hz, PF_6); $^{19}F\{^1H\}$ NMR (376 MHz, $(CD_3)_2SO$): δ −70.1 (d, 6F, ^1J = 711 Hz, PF_6); MS (ESI^+): m/z = 281.1396 $[M - PF_6]^+$ (m_{calc} = 281.1397); MS (ESI^-): m/z = 144.9647 $[PF_6]^-$ (m_{calc} = 144.9647); Calcd for $C_{16}H_{17}N_4OPF_6$: C 45.23, H 4.06, N 13.04%. Found: C 45.33, H 4.22, N 13.06%.

1-[[(*N*-1-(2-Pyridinylmethyl)-1*H*-1,2,3-triazole-4-carboxamide)-4-aminophenyl]carbonyl]-1′-(methoxycarbonyl)ferrocene (9).



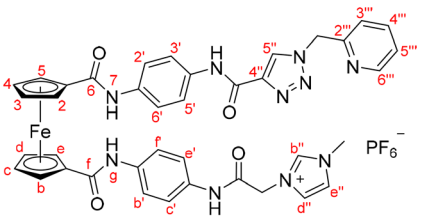
$(COCl)_2$ (1.80 mL, 21.0 mmol) was added to a suspension of Fc(COOH)(COOMe) (2.02 g, 7.01 mmol) in CH_2Cl_2 (80 mL) followed by 1–2 drops of DMF. The reaction mixture was stirred at rt for 2 h, and then concentrated *in vacuo* to afford acid chloride Fc(COCl)(COOMe) (2.14 g, quant.) as a red solid which was used without further purification. A solution of freshly prepared Fc(COCl)(COOMe) (2.14 g, 6.98 mmol) in CH_2Cl_2 (80 mL) was added dropwise to a solution of **6** (2.27 g, 7.71 mmol) and Et_3N (1.95 mL, 14.0 mmol) in CH_2Cl_2 (50 mL) at rt over 30 min. The reaction mixture was stirred for 18 h, the resulting precipitate collected by filtration and washed with ice-cooled CH_2Cl_2 (2 × 10 mL). The crude precipitate was purified by flash chromatography (CH_2Cl_2/MeOH 39 : 1 → 19 : 1) to afford **9** (3.53 g, 89%) as an orange powder. R_f 0.23 (CH_2Cl_2/MeOH 39 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.94 (s, 1H, NHCO(C_2N_3)), 8.62 (d, 1H, ^3J = 5.2 Hz, H-6‴), 8.32 (s, 1H, H-5″), 8.19 (s, 1H, N*H*CO(C_5H_4)), 7.77–7.68 (m, 5H, H-2′, H-3′, H-5′, H-6′ and H-4‴), 7.30 (ddd, 1H, ^3J = 7.8 Hz, ^3J = 4.7 Hz, ^4J = 1.6 Hz, H-5‴), 7.24 (s, 1H, H-3‴), 5.72 (s, 2H, CH_2), 4.80 (t, 2H, ^3J = 2.0 Hz, H-b and H-e), 4.64 (t, 2H, ^3J = 2.0 Hz, H-2 and H-5), 4.50 (t, 2H, ^3J = 2.0 Hz, H-c and H-d), 4.45 (t, 2H, ^3J = 2.0 Hz, H-3 and H-4), 3.84 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.7 (C, *C*OOCH$_3$) 167.8 (C, NH*C*O(C_5H_4)), 157.8 (C, NH*C*O(C_2N_3)), 153.6 (C, C-2‴), 150.3 (CH, C-6‴), 144.0 (C, C-4″), 137.6 (CH, C-4‴), 135.3 (C, C-4′), 133.6 (C, C-1′), 126.6 (CH, C-5″), 123.9 (CH, C-5‴), 122.6 (CH, C-3‴), 120.7 (4 × CH, C-2′, C-3′, C-5′ and C-6′), 79.7 (C, C-1), 79.1 (C, C-a), 72.8 (2 × CH, C-c and C-d), 72.4 (2 × CH, C-b and C-e), 71.7 (2 × CH, C-3 and C-4), 70.8 (2 × CH, C-2 and C-5), 56.1 (CH_2, CH_2(py)), 52.4 (CH_3, COO*C*H$_3$); MS (ESI^+): m/z = 565.1294 $[M + H]^+$ (m_{calc} = 565.1282); Calcd for $C_{28}H_{24}FeN_6O_4 \cdot 0.3CH_2Cl_2$: C 57.63, H 4.20, N 14.25%. Found: C 58.11, H 3.51, N 14.87%.

1-[[(*N*-1-(2-Pyridinylmethyl)-1*H*-1,2,3-triazole-4-carboxamide)-4-aminophenyl]carbonyl]-1′-(carboxy)ferrocene (10).



A solution of NaOH in MeOH (724 μL, 2.8 M) was added to a suspension of **9** (1.04 g, 1.84 mmol) in CH_2Cl_2 (150 mL) and stirred at rt for 18 h. The resulting solution was concentrated *in vacuo*, the crude residue dissolved in water (40 mL) and then acidified to pH 5 using 1 M HCl at 0 °C. The precipitate was collected by filtration, washed with ice-cooled water (3 × 20 mL) and concentrated *in vacuo* to afford **10** (960 mg, 95%) as an orange powder. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 12.20 (br s, 1H, COOH), 10.38 (s, 1H, NHCO(C_2N_3)), 9.68 (br s, 1H, N*H*CO(C_5H_4)), 8.78 (s, 1H, H-5″), 8.55 (dd, 1H, ^3J = 5.2 Hz, ^4J = 1.8 Hz, H-6‴), 7.84 (td, 1H, ^3J = 11.7 Hz, ^4J = 1.9 Hz, H-4‴), 7.77–7.66 (m, 4H, H-2′, H-3′, H-5′ and H-6′), 7.39–7.36 (m, 2H, H-3‴ and H-5‴), 5.83 (s, 2H, CH_2), 4.96 (s, 2H, H-2 and H-5), 4.69 (s, 2H, H-b and H-e), 4.45 (s, 4H, H-3, H-4, H-c and H-d); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$): δ 172.0 (C, COOH), 166.9 (C, NH*C*O(C_5H_4)), 158.0 (C, NH*C*O(C_2N_3H)), 154.5 (C, C-2‴), 149.5 (CH, C-6‴), 142.9 (C, C-4″), 137.4 (CH, C-4‴), 135.1 (C, C-1′ or C-4′), 133.9 (C, C-1′ or C-4′), 128.1 (CH, C-5″), 123.3 (CH, C-5‴), 122.2 (CH, C-3‴), 120.7 (2 × CH, C-2′, C-3′, C-5′ or C-6′), 120.6 (2 × CH, C-2′, C-3′, C-5′ or C-6′), 78.1 (2 × C, C-1 and C-a), 72.3 (2 × CH, C-3 and C-4 or C-c and C-d), 71.8 (2 × CH, C-3 and C-4 or C-c and C-d), 71.3 (2 × CH, C-e and C-b), 70.0 (2 × CH, C-2 and C-5), 54.5 (CH_2, CH_2(py)); MS (ESI^+): m/z = 573.0928 $[M + Na]^+$ (m_{calc} = 573.0944); Calcd for $C_{27}H_{22}FeN_6O_4 \cdot 0.6CH_2Cl_2$: C 55.13, H 3.89, N 13.98%. Found: C 54.85, H 4.27, N 13.76%.

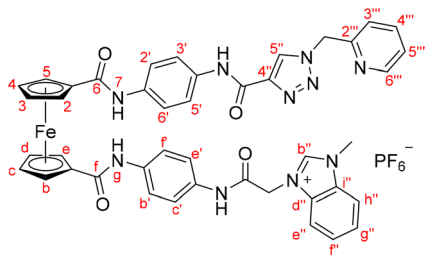
1-[[(*N*-1-(2-Pyridinylmethyl)-1*H*-1,2,3-triazole-4-carboxamide)-4-aminophenyl]carbonyl]-1′-[[(*N*-3-methyl-1*H*-imidazolium-1-acetamide)-4-aminophenyl]carbonyl]ferrocene hexafluorophosphate (11a).



HATU (296 mg, 0.78 mmol) and DIPEA (249 μL, 1.42 mmol) were added to a suspension of **10** (357 mg, 0.65 mmol) in DMF (8 mL) and the reaction mixture was stirred at rt for 10 min. Compound **8a** (323 mg, 0.97 mmol) was added and the reaction was stirred for a further 18 h. Water (20 mL) was added to

the reaction mixture, the precipitate collected by filtration, washed with water (4 × 10 mL) and dried *in vacuo* to afford **11a** (548 mg, 93%) as an orange powder. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 10.45 (s, 1H, N*H*COCH$_2$(imid)), 10.38 (s, 1H, N*H*CO(C$_2$N$_3$H)), 9.62 (s, 1H, H-7 or H-g), 9.61 (s, 1H, H-7 or H-g), 9.10 (s, 1H, H-b″), 8.79 (s, 1H, H-5″), 8.55 (d, 1H, ^{3}J = 7.8 Hz, H-6‴), 7.85 (td, 1H, ^{3}J = 11.5 Hz, ^{4}J = 1.8 Hz, H-4‴), 7.76–7.63 (m, 8H, H-d″ and H-e″ and H-2′, H-3′, H-5′, H-6′, H-b′, H-c′, H-e′ or H-f′), 7.52 (d, 2H, ^{3}J = 8.9 Hz, H-2′, H-3′, H-5′, H-6′, H-b′, H-c′, H-e′ or H-f′), 7.40–7.36 (m, 2H, H-3‴ and H-5‴), 5.84 (s, 2H, C*H*$_2$(py)), 5.19 (s, 2H, CH$_2$(imid)), 4.95 (t, 4H, ^{3}J = 2.4 Hz, H-2, H-5, H-b and H-e), 4.49 (t, 4H, ^{3}J = 2.0 Hz, H-3, H-4, H-c and H-d), 3.92 (s, 3H, CH$_3$); ^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2SO$): δ 167.8 (C, C-6 or C-f), 167.7 (C, C-6 or C-f), 163.9 (C, *C*OCH$_2$(imid)), 158.6 (C, *C*O(C$_2$N$_3$H)), 155.0 (C, C-2‴), 150.0 (CH, C-6‴), 143.4 (C, C-4″), 138.4 (CH, C-b″), 137.9 (CH, C-4‴), 135.6 (C, C-1′, C-4′, C-a′ or C-d′), 135.5 (C, C-1′, C-4′, C-a′ or C-d′), 134.5 (C, C-1′, C-4′, C-a′ or C-d′), 134.2 (C, C-1′, C-4′, C-a′ or C-d′), 128.6 (CH, C-5″), 124.4 (CH, C-3‴, C-5‴, C-e″ or C-h″), 123.9 (CH, C-3‴, C-5‴, C-e″ or C-h″), 123.5 (CH, C-3‴, C-5‴, C-e″ or C-h″), 122.7 (CH, C-3‴, C-5‴, C-e″ or C-h″), 121.5 (2 × CH, C-2′, C-3′, C-5′, C-6′, C-b′, C-c′, C-e′ or C-f′), 121.2 (2 × CH, C-2′, C-3′, C-5′, C-6′, C-b′, C-c′, C-e′ or C-f′), 121.1 (2 × CH, C-2′, C-3′, C-5′, C-6′, C-b′, C-c′, C-e′ or C-f′), 119.9 (2 × CH, C-2′, C-3′, C-5′, C-6′, C-b′, C-c′, C-e′ or C-f′), 78.6 (C, C-1 or C-a), 78.6 (C, C-1 or C-a), 72.3 (2 × CH, C-3, C-4, C-c or C-d), 72.3 (2 × CH, C-3, C-4, C-c or C-d), 70.7 (4 × CH, C-2, C-5, C-b and C-e), 55.0 (CH$_2$, CH$_2$(py)), 51.6 (CH$_2$, CH$_2$(imid)), 36.3 (CH$_3$, (imid)CH$_3$); ^{31}P{^{1}H} NMR (162 MHz, $(CD_3)_2SO$): δ −144.2 (sep, 1P, ^{1}J = 711 Hz, PF$_6$); ^{19}F{^{1}H} NMR (376 MHz, $(CD_3)_2SO$): δ −70.1 (d, 6F, ^{1}J = 711 Hz, PF$_6$); MS (ESI$^+$): m/z = 763.2180 [M − PF$_6$]$^+$ (m_{calc} = 763.2187); MS (ESI$^-$): m/z = 144.9647 [PF$_6$]$^-$ (m_{calc} = 144.9647); Calcd for $C_{39}H_{35}FeN_{10}O_4PF_6$·0.5DMF: C 51.47, H 4.11, N 15.56%. Found: C 51.78, H 4.41, N 15.50%.

1-[[(*N*-1-(2-Pyridinylmethyl)-1*H*-1,2,3-triazole-4-carboxamide)-4-aminophenyl]carbonyl]-1′-[[(*N*-3-methyl-1*H*-benzimidazolium-1-acetamide)-4-aminophenyl]carbonyl]ferrocene hexafluorophosphate (11b).



HATU (338 mg, 0.89 mmol) and DIPEA (310 μL, 1.78 mmol) were added to a suspension of **10** (407 mg, 0.74 mmol) in DMF (10 mL) and the reaction mixture was stirred at rt for 10 min. Compound **8b** (474 mg, 1.11 mmol) was added and the reaction was stirred for a further 18 h. Water (30 mL) was added to the reaction mixture, the precipitate collected by filtration, washed with water (4 × 10 mL) and dried *in vacuo* to afford **11b** (683 mg, 96%) as an orange powder. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 10.61 (s, 1H, N*H*COCH$_2$(benzimid)), 10.39 (s, 1H, N*H*CO(C$_2$N$_3$H)), 9.74 (s, 1H, H-b″), 9.63 (s, 1H, H-7 or H-g), 9.62 (s, 1H, H-7 or H-g), 8.79 (s, 1H, H-5″), 8.55 (d, 1H, ^{3}J = 4.4 Hz, H-6‴), 8.05 (br s, 2H, H-f″ and H-g″), 7.86 (td, 1H, ^{3}J = 8.1 Hz, ^{4}J = 1.9 Hz, H-4‴), 7.76–7.63 (m, 8H, H-2′, H-3′, H-5′, H-6′, H-b′, H-c′, H-e′ or H-f′ and H-e″ and H-h″), 7.54 (d, 2H, ^{3}J = 8.7 Hz, H-2′, H-3′, H-5′, H-6′, H-b′, H-c′, H-e′ or H-f′), 7.39–7.36 (m, 2H, H-3‴ and H-5‴), 5.84 (s, 2H, C*H*$_2$(py)), 5.52 (s, 2H, CH$_2$(benzimid)), 4.95 (t, 4H, ^{3}J = 1.9 Hz, H-2, H-5, H-b and H-e), 4.49 (t, 4H, ^{3}J = 1.9 Hz, H-3, H-4, H-c and H-d), 4.17 (s, 3H, CH$_3$); ^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2SO$): δ 167.3 (C, C-6 or C-f), 167.2 (C, C-6 or C-f), 163.1 (C, *C*OCH$_2$(benzimid)), 158.1 (C, *C*O(C$_2$N$_3$H)), 154.5 (C, C-2‴), 149.5 (CH, C-6‴), 143.9 (CH, C-b″), 142.9 (C, C-4″), 137.4 (CH, C-4‴), 135.2 (C, C-1′, C-4′, C-a′ or C-d′), 135.0 (C, C-1′, C-4′, C-a′ or C-d′), 134.0 (C, C-1′, C-4′, C-a′ or C-d′), 133.7 (C, C-1′, C-4′, C-a′ or C-d′), 131.7 (C, C-d″), 131.4 (C, C-i″), 128.1 (CH, C-5″), 126.7 (CH, C-e″ or C-h″), 126.5 (CH, C-e″ or C-h″), 123.4 (CH, C-5‴), 122.2 (CH, C-3‴), 121.0 (2 × CH, C-2′, C-3′, C-5′, C-6′, C-b′, C-c′, C-e′ or C-f′), 120.7 (2 × CH, C-2′, C-3′, C-5′, C-6′, C-b′, C-c′, C-e′ or C-f′), 120.6 (2 × CH, C-2′, C-3′, C-5′, C-6′, C-b′, C-c′, C-e′ or C-f′), 119.5 (2 × CH, C-2′, C-3′, C-5′, C-6′, C-b′, C-c′, C-e′ or C-f′), 113.6 (2 × CH, C-f″ and C-g″), 78.2 (C, C-1 or C-a), 78.1 (C, C-1 or C-a), 71.8 (4 × CH, C-3, C-4, C-c and C-d), 70.2 (4 × CH, C-2, C-5, C-b and C-e), 54.5 (CH$_2$, *C*H$_2$(py)), 48.9 (CH$_2$, CH$_2$(benzimid)), 33.4 (CH$_3$, (benzimid)CH$_3$); ^{31}P{^{1}H} NMR (162 MHz, $(CD_3)_2SO$): δ −144.2 (sep, 1P, ^{1}J = 711 Hz, PF$_6$); ^{19}F{^{1}H} NMR (376 MHz, $(CD_3)_2SO$): δ −70.2 (d, 6F, ^{1}J = 711 Hz, PF$_6$); MS (ESI$^+$): m/z = 813.2328 [M − PF$_6$]$^+$ (m_{calc} = 813.2344); MS (ESI$^-$): m/z = 144.9647 [PF$_6$]$^-$ (m_{calc} = 144.9647); Calcd for $C_{43}H_{37}FeN_{10}O_4PF_6$·2H$_2$O·0.65DMF: C 51.80, H 4.41, N 14.31%. Found: C 51.43, H 4.03, N 14.10%.

DFT calculations

GAUSSIAN 09W[58] was used to calculate the optimised ground state structures and frequencies for the different molecules by density functional theory (DFT) with the B3LYP-D3 hybrid exchange functional and a split basis set for C, H, N and O (6-31G(d,p)) and the transition metals iron and ruthenium (SDDAll) in vacuum. This method is the integral equation formalism variant of the polarizable continuum model (IEFPCM).[59] The EmpiricalDispersion = GD3 keyword was implemented for the empirical dispersion correction for the optimisation of the molecules.[60]

Conclusions

We have shown a synthetic route towards the formation of Fc-derived molecules incorporating both *N*,*N*′- and NHC-donor groups for metal complexation[47,55] and as precursors towards heterodimetallic supramolecular architectures. This approach was chosen as the NHC ligand would coordinate strongly to a transition metal ion, while the *N*,*N*′-pytri donor may undergo stimulus-induced cleavage from the metal centre. A convergent synthetic strategy was found to give the target compounds in

high yields. The compounds were characterised by NMR spectroscopy, ESI-MS and elemental analyses, which unambiguously confirmed the nature of the compounds as well as their purity. DFT calculations for the ferrocene derivatives with non-symmetric substituents revealed that they converge towards a *syn* conformation driven by H-bonding and π-interactions. The spatial orientation of the *N*,*N*′ and pro-NHC-donor groups relative to each other suggests potential for metal complexation. Preliminary studies on the coordination to Ru(*p*-cymene) moieties revealed successful complex formation though probably a mixture of both bi- and tridentate coordination occurred, as supported by ^{1}H NMR spectroscopic analysis. The mass spectra of the crude products for both Ru derivatives showed the singly and doubly charged $[M - PF_6]^+$ and $[M - 2PF_6]^{2+}$ ions, respectively, indicating the coordination of the ferrocenyl ligand to the Ru(*p*-cymene) moiety although the coordination mode remains elusive. The DFT-calculated structures of the heterodimetallic compounds confirmed the favourable coordination of the Ru(*p*-cymene) moiety to the ferrocenyl ligand through both the pytri and NHC donor groups without strain to the ligand or about the Ru(II) ion. Future studies will explore the coordination chemistry of these new rotationally flexible ligands with a range of metal ions and complexes.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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