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Synthesis and Characterization of Azidobipyridyl Ruthenium Complexes and Their "Click" Chemistry Derivatives

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The ligand 4-azido-2,2′-bipyridyl (**1**) has been used to prepare 1,2,3-triazole-substituted ligands through copper-catalyzed alkyne/azide cycloaddition (CuAAC or "click" chemistry) with phenylacetylene, ethynylferrocene and 2-ethynylpyridine to yield 4-(4-phenyl-1,2,3-triazol-1-yl)-2,2′-bipyridyl (**2a**), 4-(4-ferrocenyl-1,2,3-triazol-1-yl)-2,2′-bipyridyl (**2b**) and 4-[4-(pyridyl-2-yl)-1,2,3-triazol-1-yl]-2,2′-bipyridyl (**2c**). Complexes of the form [Ru(*p*-cymene)(Cl)(L)]PF_6 (**3**, L = **1**; **4a**, L = **2a**; **4b**, L = **2b**) were then prepared and characterized. We also report the synthesis of the complex of the analogous ligand 4,4′-bisazido-2,2′-bipyridyl (**1′**), [Ru(*p*-cymene)(Cl)-(**1′**)]PF_6 (**3′**). Complexes **4a** and **4b** were also prepared by an alternative route, whereby **3** undergoes CuAAC coupling with phenylacetylene and ethynylferrocene respectively. Complexes prepared with ligands that are pre-assembled or "clicked" at the metal show identical ^{1}H NMR spectra. CuAAC coupling of **3** and 2-ethynylpyridine results in the formation of the complex [Ru(*p*-cymene)(Cl)(**2c**)]PF_6 (**4c**), which contains a coordinatively vacant pyridyltriazole moiety. The reaction of [Ru(*p*-cymene)$(Cl)_2]_2$ with pre-assembled **2c** results in the formation of the dinuclear complex [{Ru(*p*-cymene)(Cl)}$_2$(**2c**)]·2PF_6 (**5**), which incorporates ruthenium atoms at both bipyridyl and pyridyltriazole binding domains. The ^{1}H NMR spectrum of the complex shows two signals for the triazole ring proton as well as duplicate signals for other protons of the bridging ligand, which indicates that **5** is produced as a mixture of diastereoisomers. The complex [{Ru(*p*-cymene)Cl}$_2$(di-4-([1-{2,2′-bipyrid-4-yl}triazol-4-yl]methyl)-ether)][PF_6]$_2$ (**7**) was also prepared through the coupling of **3** with dipropargyl ether.

Introduction

The synthesis and preparation of supramolecular architectures containing photo- and redox-active transition-metal centres has become an area of intense interest.[1–3] The strong interest in this area stems from the potential application of these materials for the modelling of energy transfer processes in biological photosynthesis, the development of new light harvesting photocatalysts and new materials for solar energy conversion. The traditional method for the preparation of such metallosupramolecular materials has relied on the preparation of bridging ligands with multiple coordination sites into which metal centres can subsequently be incorporated. This methodology suffers from key disadvantages with problems in controlling the selectivity of metal binding when, for example, heterometallic complexes are required and where the bridging ligand is nonsymmetric. Extended ligand-based approaches have also been championed in which complexes are prepared and modified at their periphery to graft a second binding domain onto the complex.[4]

A desirable convergent route to such architectures would involve the coupling of discrete preformed complexes into supramolecular complexes under mild conditions in as few steps as possible. Such an approach would require a coupling reaction that is highly efficient and high yielding and for which the required functional groups for the coupling reaction can be easily incorporated into the periphery of the metal-complex components. With such a methodology in place and a library of suitably derivatized transition-metal-complex components available, this would allow facile access to supramolecular architectures with an extraordinary diversity of structure.

A series of such candidate coupling reactions exists and falls under the umbrella term of "click" chemistry.[5,6] These reactions are highly efficient, selective and high yielding, are tolerant of a wide range of other functional groups, proceed in a variety of solvents including protic media, and require minimal work-up and product purification. The most prominent of these reactions is the copper-catalyzed alkyne/azide cycloaddition (CuAAC) to form 1,4-disubstituted-1,2,3-triazoles. The reaction has attracted enormous interest in the areas of organic synthesis, materials and polymer science[7–9] and the modification of biological macromolecules.[10,11] Alkyne and azide starting materials are also either readily commercially available or have facile routes to their synthesis. Curiously though, CuAAC only relatively

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recently began to attract significant interest from the inorganic community for use in ligand design[12–36] and for the construction of self-assembled supramolecular architectures.[37–39] This area has recently been the subject of a comprehensive review.[40]

Therefore, we have begun to explore the use of CuAAC towards such a modular approach for the construction of supramolecular architectures. A few reports have appeared on the CuAAC modification of transition-metal complexes with peripheral alkyne functionalities. Ren first demonstrated the peripheral modification of alkynyl-substituted diruthenium complexes.[41,42] More recently, Sierra and co-workers reported the formation of dinuclear complexes from alkynyl-substituted Fischer carbene complexes of pentacarbonylchromium(0) by CuAAC coupling with bis-azide spacers including bis(azidomethyl)ferrocene.[43] Similar results have been obtained with analogous pentacarbonyltungsten(0) complexes.[44] Constable et al. have demonstrated the coupling of azidosugars with alkyne-functionalized bipyridyl ligands and the preparation of their ruthenium complexes.[45]

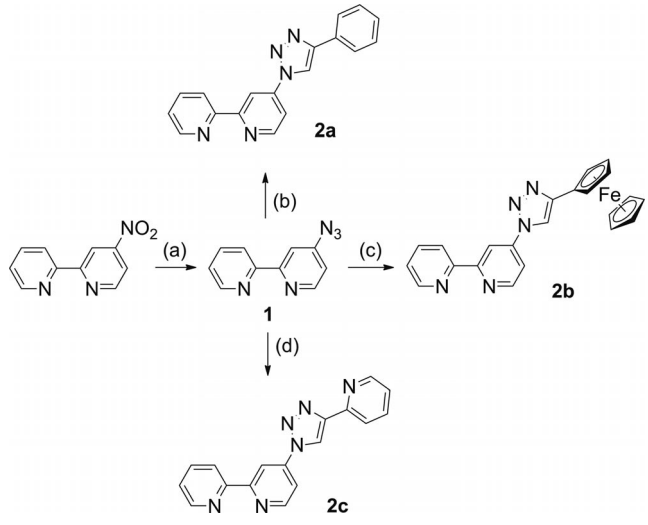
The comparable use of azido-functionalized complexes is far less developed. Azidoferrocenes have been used for the preparation of ferrocenyl triazoles, which have subsequently been used as monodentate ligands, for example.[12] Fallahpour has developed routes to azide derivatives of bipyridyl and terpyridyl[46–48] ligands and demonstrated the formation of azidoterpyridyl complexes. However, attempts to prepare their ruthenium complexes led to azide reduction to the amine under the conditions used. Whilst we were carrying out the work presented in this paper, Aukauloo and co-workers utilized an azido bipyridyl ligand to prepare a chromophore tagged ligand and its $[Ru(bpy)_2]$ complex (bpy = 2,2′-bipyridyl) and showed that there is efficient electron transfer through the triazole linker.[49] However, there remains very little in the literature regarding the CuAAC functionalization of complexes with coordinated azide-substituted ligands. Chitre et al. recently reported the synthesis of a homoleptic ruthenium(II) 4,4′-bisazido-2,2′-bipyridyl complex but were unable to affect subsequent CuAAC derivatization owing to decomposition of the complex under the reaction conditions.[50] Beyond ferrocene, the first example of CuAAC modification of an azide-functionalized complex that we are aware of was demonstrated by Constable and co-workers. Using bis(azidoterpyridyl)-iron(II), the azide-functionalized ligand, attached to the metal centre under mild conditions, can subsequently undergo CuAAC modification.[51]

Here, we present recent results on the coordination chemistry of mono- and bis(azido)bipyridyl ligands in their $[Ru(p\text{-cymene})Cl]^+$ complexes. Subsequently, we show the first example of CuAAC modification of a ruthenium complex with pendant azide functionalities. Such complexes will have applications as important synthons for the preparation of functional luminescent molecular devices and solar-cell dyes for example. Therefore, we have made some of the first steps towards the goal of the development of a general click-chemistry-based methodology for the construction of functional supramolecular architectures from alkyne- and azide-functionalized transition-metal-complex components.

Results and Discussion

The monoazido-substituted ligand 4-azido-2,2′-bipyridyl (**1**) was prepared from its nitro-substituted analogue by reaction with sodium azide in dimethylformamide (DMF) at 100 °C in a procedure modified from that reported previously by Fallahpour.[52] After purification by flash chromatography, **1** was isolated as a pale yellow solid in excellent yield. The ^{1}H NMR spectrum of **1** in [D]chloroform exhibits a total of seven resonances, typical of a 4-substituted bpy ligand. The presence of the azide group is confirmed by the observation of a peak at 2115 cm^{-1} in the infrared spectrum. 4,4′-Diazido-2,2′-bipyridyl (**1′**) was similarly prepared from 4,4′dinitro-2,2′-bipyridyl, again, in excellent yield. The ^{1}H NMR spectrum of **1′** in [D]chloroform exhibits three resonances, which reflects the symmetry of the ligand, and the presence of the azide groups is again confirmed by a peak at 2117 cm^{-1} in the infrared spectrum.

Having isolated and characterized ligands **1** and **1′**, we decided to investigate the use of these azides in CuAAC reactions. The reaction of **1** with phenylacetylene or ethynylferrocene in 1:1 water/tetrahydrofuran (THF) in the presence of copper(II) sulfate and sodium ascorbate resulted in the formation of the triazole-substituted ligands **2a** and **2b**, respectively, in moderate yields (Scheme 1). The ^{1}H NMR spectra of **2a** and **2b** show characteristic singlet resonances for the proton of the triazole ring at δ = 8.48 and 8.18 ppm, respectively. For **2b**, the resonances of the substituted cyclopentadienyl (Cp) ring of the ferrocene moiety appear at δ = 4.82 and 4.37 ppm, and the unsubstituted Cp ring gives rise to a singlet at δ = 4.12 ppm. Formation of the cycloaddition triazoles is also confirmed by the absence of the azide

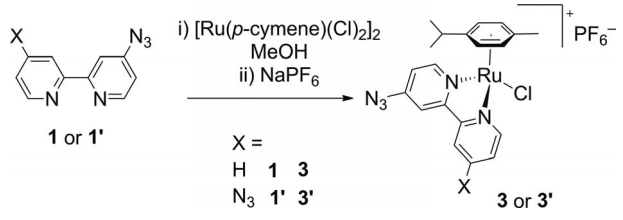


Scheme 1. Synthesis of 4-azido-2,2′-bipyridyl (**1**) and subsequent CuAAC derivatives, (a) NaN_3, DMF, 100 °C, (b) phenylacetylene, $CuSO_4$, sodium ascorbate, 1:1 THF/water, r.t., (c) ethynylferrocene, $CuSO_4$, sodium ascorbate, 1:1 THF/water, r.t., (d) 2-ethynylpyridine, $CuSO_4$, sodium ascorbate, 1:1 THF/water, r.t.

stretch in the infrared spectra of the products. The reaction with 2-ethynylpyridine resulted in the formation in good yield of the heteroditopic ligand **2c**, which has bpy and pyridyltriazole binding domains. Its ^{1}H NMR spectrum exhibits a singlet for the triazole ring proton at δ = 8.91 ppm, and a further 11 signals are evident for the protons of the bipyridyl domain and the pyridyl ring appended to the triazole. These were assigned by COSY and NOESY spectroscopy.

CuAAC coupling of **1′** with phenyl acetylene and 2-ethynylpyridine appeared to similarly result in their triazole products, however, these proved to be rather insoluble and therefore extremely difficult to characterize. The reaction of **1′** with ethynylferrocene to produce the desired bis(ferrocenyltriazolyl)bpy ligand proved unsuccessful and no product was isolable despite several attempts under various conditions. It is possible that the failure of this reaction is due to decomposition of the diazido starting material.

We then began to explore the coordination chemistry of these new ligands. [Ru(*p*-cymene)(Cl)$_2$]$_2$ was stirred with ligand **1** in methanol at room temperature, which led to a bright yellow solution and the complex [Ru(*p*-cymene)(**1**)Cl]$^+$ was subsequently isolated as its PF_6^- salt (**3**, Scheme 2). The infrared spectrum of **3** shows a characteristic peak corresponding to the azide stretch at 2124 cm^{-1}, which is shifted by 9 cm^{-1} relative to that of the non-coordinated ligand. The ^{1}H NMR spectrum of the complex contains seven resonances in the aromatic region for the bpy ligand. The signals for the nonsubstituted pyridyl ring are all deshielded on coordination as is the H-6 proton of the azide-substituted ring, which appears at δ = 9.15 ppm. The resonances for the arene protons of the cymene ligand appear at δ = 5.91 and 5.71 ppm. These signals appear as triplets rather than a pair of doublets as in the ^{1}H NMR spectrum of the precursor [Ru(*p*-cymene)(Cl)$_2$]$_2$, which shows that the symmetry of the cymene has been broken by the asymmetry of the coordinated ligand **1**. In addition, the ^{1}H NMR spectrum exhibits two closely overlapping doublets, which correspond to the methyl groups of the isopropyl group of the cymene ligand at δ = 1.04 and 1.03 ppm and shows that they are not magnetically equivalent. This is presumably due to hindered rotation of the isopropyl group and the aforementioned asymmetry of the complex is due to the presence of ligand **1**.



Scheme 2. Synthesis of ruthenium complexes of ligands **1** and **1′**.

The complex [Ru(*p*-cymene)Cl(**1′**)]PF_6 (**3′**) was prepared by an identical procedure to that for **3**. Similarly, a characteristic azide stretch is observed in the infrared spectrum at 2125 cm^{-1}. The ^{1}H NMR spectrum shows resonances for the bpy protons at δ = 9.15, 7.94 and 7.37 ppm, and the arene signals appear at δ = 5.90 and 5.69 ppm. Complexes **3** and **3′** exhibit similar features in their UV/Vis absorption spectra with intense ligand-based absorptions at around 300 nm with less intense metal-to-ligand charge transfer (MLCT) based absorptions tailing off towards 450 nm (Figure 1). A slight redshift in the absorption profile of **3′** relative to that of **3** is observed owing to the presence of the second azide moiety. A single-crystal X-ray structure was determined for the complex but unfortunately this was not of suitable quality for publication. Atomic coordinates and a plot of the molecular structure are included in the Supporting Information for the curious reader for information only. Further crystals of X-ray diffraction quality could not be obtained.

The analogous complexes of ligands **2a** and **2b** were also prepared by the same route as that for the preparation of **3** and **3′** (Scheme 3). Therefore, the addition of these ligands

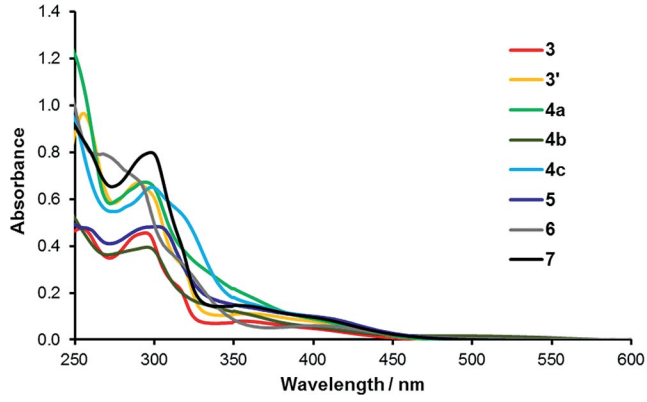
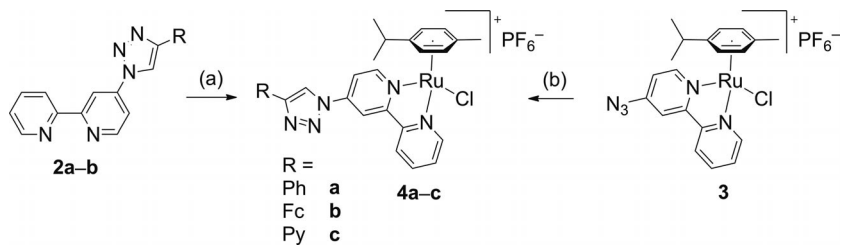


Figure 1. UV/Vis absorption spectra of complexes in acetonitrile solutions.



Scheme 3. Synthesis of complexes **4a**–**c** by reaction of [Ru(*p*-cymene)(Cl)$_2$]$_2$ with ligands **2a** and **2b** or by CuAAC coupling with phenylacetylene, ethynylferrocene or 2-ethynylpyridine, respectively: (a) i) [Ru(*p*-cymene)(Cl)$_2$]$_2$, MeOH, r.t., **2a** or **2b**. ii) $NaPF_6$. (b) Alkyne, $CuSO_{4(aq)}$, sodium ascorbate, 1:1 THF/water.

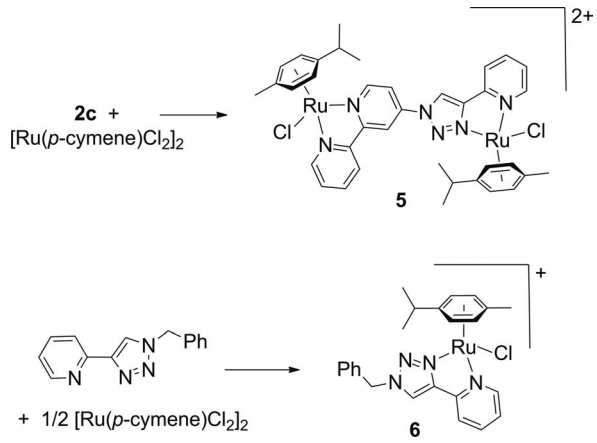
to [Ru(*p*-cymene)$(Cl)_2]_2$ led to the isolation of the complexes [Ru(*p*-cymene)(**2a**)Cl]PF_6 (**4a**) and [Ru(*p*-cymene)(**2b**)Cl]PF_6 (**4b**). Similarly to the ^{1}H NMR spectrum of **3**, the spectra of **4a** and **4b** show nonequivalence of the isopropyl methyl groups of the cymene ligand owing to the asymmetry of the chelating bpy ligands. The ^{1}H resonances for the arene protons adjacent to the isopropyl group appear as an apparent triplet, whereas the resonances for the arene protons adjacent to the methyl substituent appear as a doublet for both **4a** and **4b**. The nonequivalence of the arene CH positions adjacent to the isopropyl group in each complex is also evident in the ^{13}C NMR spectra, in which the signals appear at δ = 87.5 and 87.4 and δ = 87.6 and 87.5 ppm for these positions in **4a** and **4b**, respectively. Two ^{13}C resonances are also observable for the CH arene positions adjacent to the methyl group but with a much smaller separation (these signals are separated by only 0.04 ppm for **4a**).

The UV/Vis absorption spectrum for **4a** displays similar features to those of **3** and **3′**, whereas that of **4b** exhibits an additional absorption owing to the presence of the ferrocene moiety at ca. 492 nm and tailing off beyond 550 nm (Figure 1, Table 1).

Table 1. UV/Vis absorption data for complexes in acetonitrile solutions.

Complex	Wavelength /nm
3	297, 316, 357, 404
3′	293, 318, 363, 410
4a	297, 330, 367, 406
4b	300, 354, 409, 492
4c	302, 319, 366, 411
5	297, 305, 367, 416
6	271, 293, 314, 403
7	301, 317, 355, 413

When [Ru(*p*-cymene)$(Cl)_2]_2$ was allowed to react with an equivalent of the ditopic ligand **2c**, the dinuclear complex **5** was formed and it was isolated as its PF_6^- salt (Scheme 4). Examination of the ^{1}H NMR spectrum of the complex reveals two singlet resonances for the triazole ring proton at δ = 9.42 ppm, which are assigned because of their lack of coupling in the COSY spectrum. NMR assignments for the other ligand protons were then made by using COSY and NOESY data. Similar duplicate resonances were then found for the 3- and 6-position protons of the pyridyl ring of the bpy domain of the ligand to which the triazole ring is attached (Figure 2). A similar split may occur for the 5-position proton but the resonance is obscured through overlap with resonances of the 4-position protons of the other two pyridyl rings. The resonance for the isopropyl methine proton of the cymene ligand of the ruthenium centre occupying the pyridyl triazole domain appears as two overlapping septets and two signals are also observed for the methyl substituent. These extra signals arise because of the asymmetry of the binding domains, which renders the two ruthenium centres chiral. Hence, a total of four isomeric complexes are possible, which will result in two sets of NMR signals. The equal intensity of the signals for each pair of isomers suggests that the stereochemistry of the first ruthenium centre to coordinate to the ligand does not influence the chirality adopted at the second ruthenium centre as it coordinates to the other binding domain. Several attempts to separate and independently isolate the diastereoisomers by column chromatography or recrystallization proved unsuccessful.



Scheme 4. Preparation of the dinuclear complex [{Ru(*p*-cymene)-$Cl\}_2$(**2c**)]$^{2+}$ (**5**) and the 1-benzyl-4-(pyrid-2-yl)-1,2,3-triazole (pytz) complex [(*p*-cymene)RuCl(pytz)]$^+$ (**6**).

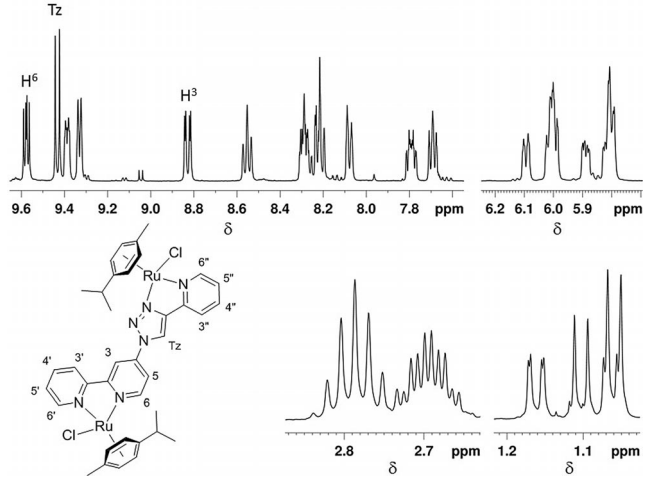


Figure 2. Selected regions of the ^{1}H NMR spectrum of **5**.

By using the ligand 1-benzyl-4-(pyrid-2-yl)-1,2,3-triazole (pytz), we also prepared the complex [Ru(*p*-cymene)-Cl(pytz)]PF_6 (**6**) as a spectroscopic model for the pytz-like domain of **5** by a route analogous to that for the preparation of **3** and **4a**–**b**. The ^{1}H NMR spectrum exhibits four resonances for the pyridyl ring at positions close to those observed for the comparable protons in **5**. However, the resonance for the triazole proton appears at δ = 8.55 ppm, shielded by 0.87 ppm relative to that of **5**. The shift in the triazole proton resonance is ascribed to the presence of the more electron-donating benzyl substituent of the pytz ligand compared to the bpy moiety that is attached to the triazole in **5**. Examination of the UV/Vis absorption spectra of the complexes **4c**, **5** and **6** reveals similar features over similar wavelength ranges to each other and those of other

complexes (Figure 1). Therefore, it was not possible to assign any particular feature of the spectrum of **5** as arising from the bpy- or pytz-like domains based on the data for the other complexes.

After fully characterizing the ruthenium cymene complex of ligand **1** and its CuAAC derivatives **2a** and **2b**, we turned our attention to the reactivity of the ligated azido ligand in **3** toward CuAAC reactions. Thus, complex **3** was shown to undergo CuAAC modification of the outer coordination sphere with phenylacetylene and ethynylferrocene as an alternative route to complexes **4a** and **4b** (Scheme 2). In each case, **3** was mixed with an equivalent of the appropriate alkyne in 1:1 THF/water in the presence of copper sulfate and sodium ascorbate. The ^{1}H NMR spectra of **4a** and **4b** derived through this alternative route are identical to those of the same complexes obtained by reaction with the preassembled triazole-containing ligands **2a** and **2b**. In contrast to these results, Chitre et al. were unable to isolate triazole derivatives from CuAAC reaction mixtures containing the complex $[Ru(\mathbf{1}')_3]^{2+}$. It is possible that the increased number of azide groups results in instability of these moieties toward decomposition.

When **3** is coupled with 2-ethynylpyridine the complex **4c** is formed (Scheme 3). The ^{1}H NMR spectrum of the isolated product shows signals characteristic of the 4-substituted bpy ligand along with broad signals for the triazole proton and the third pendant pyridyl ring. Despite treatment of the product with aqueous ammonia, the broad nature of these resonances is most likely due to the coordination and exchange of paramagnetic copper(II) left over from the CuAAC reaction mixture. On rewashing a dichloromethane solution of the product with aqueous ammonia solution to remove the remaining copper ions, the resonances for the protons of the coordinatively vacant pyridyltriazole moiety become resolved in the ^{1}H NMR spectrum (Figure 3).

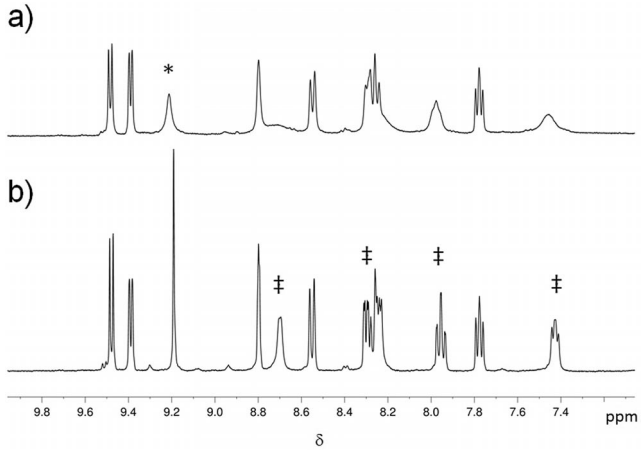
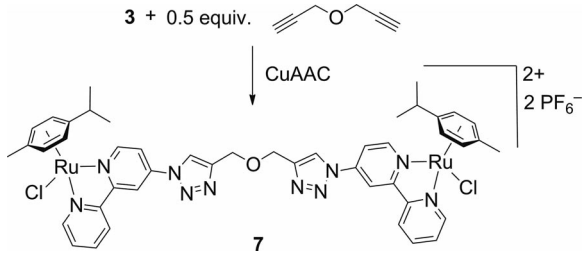


Figure 3. ^{1}H NMR spectra of **4c** a) isolated product before final ammonia wash b) after final ammonia wash.

To extend the CuAAC methodology further, we then coupled **3** with half an equivalent of the dialkyne dipropargyl ether to form the dinuclear complex **7** (Scheme 5). The ^{1}H NMR spectrum of the complex shows two signals for the triazole ring protons centred at δ = 9.29 ppm, again, likely owing to the formation of isomeric mixtures of complexes. However, the other signals in the spectrum do not appear to show this kind of duplication. Mass spectrometry data shows the detection of the dication $[\mathbf{7} - 2PF_6]^+$ (m/z = 515). These isomers were again inseparable by conventional chromatographic or recrystallization methods. The UV/Vis absorption spectrum of **7** has a very similar appearance to those of the other triazole derivatives of **3**.



Scheme 5. Preparation of dinuclear complex **7**.

The results presented here clearly show the potential for the use of CuAAC coupling at the metal centre by utilizing synthetically versatile synthons such as ruthenium(II) arene complexes. This paves the way for the site-specific inclusion of photophysically active ruthenium centres in functional heteronuclear supramolecular assemblies. Indeed, we are currently investigating the use of this methodology and complexes such as **4c** as precursors for heterodinuclear dye-sensitized solar cell pigments and will publish results in this area in due course.

Conclusions

We have successfully demonstrated the CuAAC modification of useful ruthenium cymene complexes bearing azide-functionalized bipyridyl ligands. The choice of the organometallic starting material $[Ru(p\text{-cymene})Cl_2]_2$ allows the incorporation of azide functionality into the periphery of a synthetically useful synthon for the preparation of functionally useful metal complexes under mild condition without decomposition of the azide group.

Ruthenium cymene complexes of bipyridyl ligands are extremely useful synthons for the preparation of heteroleptic luminescent complexes, sensitizing dyes for solar-cell applications and for anticancer drugs. Therefore, the strategies that we have begun to explore here may pave the way for the development of a general methodology for the CuAAC coupling of modular, functionally useful transition-metal-complex components into supramolecular architectures with applications in, for example, light-harvesting solar energy conversion and sensitized photocatalysis.

Experimental Section

General: All synthetic procedures were carried out under nitrogen. $[Ru(p\text{-cymene})(Cl)_2]_2$[53] was prepared by a literature procedure. All solvents were purchased from either Acros Organics or Aldrich

Chemicals and were used as supplied. NMR spectra were recorded with Bruker Avance 500 and AMX 400 spectrometers and mass spectrometry was performed by using a Bruker MicroQ-TOF instrument.

4-Azido-2,2′-bipyridyl (1): A mixture of 4-nitro-2,2′-bipyridyl (0.57 g, 2.8 mmol) and NaN_3 (1.50 g, 3.85 mmol) was heated in DMF (10 mL) for 3 h at 100 °C. The dimethylformamide was removed by rotary evaporation, and water (40 mL) was added. The mixture was extracted with dichloromethane (3 × 30 mL), the combined organic phase was dried with $MgSO_4$, and the solvent was removed. 4-Azido-2,2′-bipyridyl was purified by column chromatography (silica gel, dichloromethane/AcOEt, 1:1) to yield a yellow solid (0.53 g, 95%) ^{1}H NMR ($CDCl_3$): δ = 8.69 (ddd, J = 4.8, 1.8 and 0.9 Hz, 1 H, 6′-H), 8.58 (d, J = 5.4 Hz, 1 H, 6-H), 8.40 (dt, J = 7.8 and 0.9 Hz, 1 H, 4′-H), 8.15 (d, J = 2.3 Hz, 1 H, 3-H); 7.83 (td, J = 7.8 and 1.8 Hz, 1 H, 5′-H), 7.34 (ddd, J = 7.5, 4.8 and 1.2 Hz, 1 H, 3′-H), 6.94 (dd, J = 5.4 and 2.3 Hz, 1 H, 5-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 160.0, 155.2, 150.5, 149.8, 149.2, 137.1, 124.3, 121.3, 114.2, 111.2 ppm. MS (ESI): m/z = 220 [M + Na]$^+$. HRMS: calcd for $C_{10}H_7N_5Na$ [M + Na]$^+$ 220.059366; found 220.058833. IR (ATR): $\tilde{\nu}$ = 2115 cm^{-1}.

4,4′-Diazido-2,2′-bipyridyl (1′): A mixture of 4,4′-dinitro-2,2′-bipyridyl (0.10 g, 0.4 mmol) and NaN_3 (0.25 g, 3.85 mmol) was heated in dimethylformamide (10 mL) for 3 h at 100 °C. The solvent was removed by rotary evaporation, and water (40 mL) was added. The mixture was extracted with dichloromethane (3 × 30 mL), the combined organic phase was dried with $MgSO_4$, and the solvent was removed. 4,4′-Diazido-2,2′-bipyridyl was then purified by column chromatography (silica gel, dichloromethane/AcOEt, 1:1) to yield a yellow solid (0.09 g, 95%). ^{1}H NMR ($CDCl_3$): δ = 8.58 (d, J = 5.4 Hz, 2 H, 6-H), 8.14 (d, J = 2.2 Hz, 2 H, 3-H), 6.96 (dd, J = 5.4 and 2.2 Hz, 2 H, 5-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 157.3, 150.8, 150.3, 114.9, 111.8 ppm. MS (ESI): m/z = 261 [M + Na]$^+$. HRMS: calcd for. $C_{10}H_6N_8Na$ [M + Na]$^+$ 261.060765; found 261.060763. IR (ATR): $\tilde{\nu}$ = 2117 cm^{-1}.

4-(4-Phenyl-1,2,3-triazol-1-yl)-2,2′-bipyridyl (2a): 4-Azido-2,2′-bipyridyl (0.5 g, 2.54 mmol) and phenylacetylene (0.39 g, 3.80 mmol) were dissolved in THF (30 mL), and water was added (30 mL). $CuSO_4$ (1 M aqueous solution, 2.54 mL) was then added followed by freshly prepared sodium ascorbate solution (1 M aqueous solution, 5.08 mL) dropwise. The solution was allowed to stir at room temperature for 1 h. After removal of the THF under vacuum, dichloromethane (30 mL) and conc. NH_3 (15 mL) were added to the solution. The solution was allowed to stir for a further 30 min at room temperature to remove Cu^{I}. The organic phase was washed twice with water (30 mL) and once with brine (30 mL) and then dried with $MgSO_4$. The solvent was removed under vacuum, and the product was recrystallized from dichloromethane and hexane to yield a buff solid (0.58 g, 76%) ^{1}H NMR ($CDCl_3$): δ = 8.84 (d, J = 5.3 Hz, 1 H, bpy 6-H), 8.75 (d, J = 2.1 Hz, 1 H, bpy 3-H), 8.72 (d, J = 4.5 Hz, 1 H, py), 8.50 (d, J = 8.0 Hz, 1 H, py), 8.48 (s, 1 H, Tz), 7.99 [dd, J = 5.3 & 2.1 Hz, 1 H, py(tz)], 7.94 (d, J = 7.7 Hz, 2 H, Ph), 7.87 (td, J = 7.7 and 1.6 Hz, py), 7.48 (t, J = 7.7 Hz, 2 H, Ph), 7.39 (m, 2 H, Ph and py) ppm. ^{13}C NMR ($CDCl_3$): δ = 158.5, 154.8, 151.1, 149.3, 149.0, 144.1, 137.1, 129.8, 129.0, 128.8, 126.0, 124.5, 121.4, 116.9, 113.9, 110.2 ppm. MS (ESI): m/z = 322 [M + Na]$^+$. HRMS: calcd. for $C_{18}H_{13}N_5Na$ [M + Na]$^+$ 322.106317; found 322.106153.

4-(4-Ferrocenyl-1,2,3-triazol-1-yl)-2,2′-bipyridyl (2b): 4-Azido-2,2′-bipyridyl (0.10 g, 0.51 mmol) and ethynylferrocene (0.16 g, 0.76 mmol) were dissolved in THF (15 mL), and water was added (15 mL). $CuSO_4$ (1 M aqueous solution, 0.51 mL) was added followed by freshly prepared sodium ascorbate solution (1 M aqueous solution, 1.01 mL) dropwise. The solution was allowed to stir at room temperature for 1 h. After removal of the THF under vacuum, dichloromethane (30 mL) and conc. NH_3 (10 mL) were added to the solution, which was allowed to stir for a further 30 min at room. The organic phase was washed twice with water (15 mL) and once with brine (15 mL) and then dried with $MgSO_4$. The solvent was removed under vacuum, and the product was recrystallized from dichloromethane and hexane to yield an orange solid (0.087 g, 42%). ^{1}H NMR ($CDCl_3$): δ = 8.83 [d, J = 5.4 Hz, 1 H, py(tz)], 8.74 (ddd, J = 4.7, 1.7 and 0.7 Hz, 1 H, py), 8.69 [d, J = 2.0 Hz, 1 H, py(tz)], 8.51 (d, J = 7.9 Hz, 1 H, py), 8.18 (s, 1 H, Tz), 8.01 [dd, J = 5.4 and 2.1 Hz, 1 H, py(tz)], 7.89 (td, J = 7.7 and 1.7 Hz, 1 H, py), 7.40 (ddd, J = 7.6, 4.7 and 1.2 Hz, 1 H, py), 4.82 (t, J = 1.9 Hz, 2 H, C_5H_4Fe), 4.37 (t, J = 1.9 Hz, 2 H, C_5H_4Fe), 4.12 (s, 5 H, Cp) ppm. ^{13}C NMR ($CDCl_3$): δ = 158.4, 154.9, 151.1, 149.2, 148.5, 144.2, 137.2, 124.5, 121.5, 115.7, 113.9, 110.0, 74.3, 69.7, 69.1, 66.9 ppm. MS (ESI): m/z = 430 [M + Na]$^+$. HRMS: calcd. for $C_{22}H_{17}FeN_5Na$ [M + Na]$^+$ 430.072559; found 430.073052.

4-[4-(Pyridin-2-yl)-1,2,3-triazol-1-yl]-2,2′-bipyridyl (2c): 4-Azido-2,2′-bipyridyl (0.25 g, 1.27 mmol) and 2-ethynylpyridine (0.196 g, 1.90 mmol) were dissolved in THF (30 mL), and water was added (30 mL). $CuSO_4$ (1 M aqueous solution, 1.27 mL) was added followed by freshly prepared sodium ascorbate solution (1 M aqueous solution 2.54 mL) dropwise. The solution was allowed to stir at room temperature for 1 h. After removal of the THF under vacuum, dichloromethane (30 mL) and conc. NH_3 (15 mL) were added to the solution, which was allowed to stir for a further 30 min at room temperature. The organic phase was washed twice with water (30 mL) and once with brine (30 mL) and then dried with $MgSO_4$. The solvent was removed under vacuum, and the product was recrystallized from dichloromethane and hexane to yield a white solid (0.31 g, 81%). ^{1}H NMR ($CDCl_3$): δ = 8.91 (s, 1 H, Tz), 8.88 [d, J = 2.1 Hz, 1 H, bpy py(tz)], 8.85 [d, J = 5.4 Hz, 1 H, bpy py(tz)], 8.72 (ddd, J = 4.8, 1.8 and 0.8 Hz, 1 H, tz-*py*), 8.65 (ddd, J = 4.8, 1.7 and 0.8 Hz, 1 H, bpy py), 8.49 (dt, J = 8.0 and 0.8 Hz, 1 H, tz-*py*), 8.27 (dt, J = 8.0 and 0.9 Hz, 1 H, bpy py), 7.97 [dd, J = 5.4 and 2.2 Hz, 1 H, bpy py(tz)], 7.87 (td, J = 7.8 and 1.7 Hz, 1 H, tz-*py*), 7.84 (td, J = 7.8 and 1.7 Hz, 1 H, bpy py), 7.38 (ddd, J = 7.5, 4.8 and 1.2 Hz, 1 H, tz-*py*), 7.30 (ddd, J = 7.7, 4.8 and 1.2 Hz, 1 H, bpy py) ppm. ^{13}C NMR ($CDCl_3$): δ = 158.7, 154.8, 151.1, 149.7, 149.6, 149.56, 149.4, 144.1, 137.1, 137.0, 124.5, 123.4, 121.3, 120.6, 119.6, 113.8, 110.7 ppm. MS (ESI): m/z = 323 [M + Na]$^+$. HRMS: calcd. for $C_{17}H_{12}N_6Na$ [M + Na]$^+$ 323.101566; found 323.101593.

[Ru(*p*-cymene)(1)Cl]PF$_6$ (3): [Ru(*p*-cymene)(Cl)$_2$]$_2$ (0.1 g, 0.16 mmol) and **1** (0.098 g, 0.5 mmol) were suspended in methanol (30 mL) and stirred at room temperature for 12 h. The yellow solution was concentrated to 15 mL and treated with $NaPF_6$ to yield a yellow precipitate, which was collected by filtration and washed with methanol and diethyl ether to yield the desired complex as yellow crystals (0.15 g, 76%). ^{1}H NMR (CD_3CN): δ = 9.34 (ddd, J = 5.7, 1.3 and 0.7 Hz, 1 H, bpy H-6′), 9.15 (d, J = 6.3 Hz, 1 H, bpy 6-H), 8.35 (d, J = 8.1 Hz, 1 H, bpy 3′-H), 8.19 (td, J = 8.0 and 1.4 Hz, 1 H, bpy 4′-H), 7.92 (d, J = 2.5 Hz, 1 H, bpy 3-H), 7.72 (ddd, J = 7.6, 5.7 and 1.4 Hz, 1 H, bpy 5′-H), 7.37 (dd, J = 6.3 and 2.5 Hz, bpy 5-H), 5.91 (t, J = 5.7 Hz, 2 H, Cym CH-C*i*Pr), 5.71 (m, 2 H, Cym CH-CMe), 2.65 (sept, J = 7.0 Hz, *i*Pr CH), 2.21 (s, 3 H, Cym Me), 1.04 (d, J = 7.0 Hz, 3 H, *i*Pr CH_3), 1.03 (d, J = 7.0 Hz, 3 H, *i*Pr CH_3) ppm. ^{13}C NMR (CD_3CN): δ = 159.9, 159.8, 156.6, 155.3, 154.1, 140.9, 129.0, 125.0, 118.8, 115.4, 106.1, 104.6, 87.4, 85.2, 31.9, 22.2, 19.0 ppm. MS (ESI): m/z = 468.1 [M –

$PF_6]^+$. HRMS: calcd. for $C_{20}H_{21}ClN_5Ru$ $[M - PF_6]^+$ 468.052349; found 468.054448. IR (ATR): $\tilde{\nu}$ = 2124 cm^{-1}.

[Ru(*p*-cymene)(1′)Cl]PF_6 (3′): [Ru(*p*-cymene)$(Cl)_2]_2$ (0.1 g, 0.16 mmol) and **1′** (0.12 g, 0.5 mmol) were suspended in methanol (30 mL) and stirred at room temperature for 12 h. The yellow solution was concentrated to 15 mL and treated with $NaPF_6$ to yield a yellow precipitate, which was collected by filtration and washed with methanol and diethyl ether to yield the desired complex as yellow crystals (0.14 g, 66%). ^{1}H NMR (CD_3CN): δ = 9.15 (d, J = 6.4 Hz, 2 H, bpy 6-H), 7.94 (d, J = 2.4 Hz, 2 H, bpy 3-H), 7.37 (dd, J = 6.4 and 2.4 Hz, 2 H, bpy 5-H), 5.90 (d, J = 6.2 Hz, 2 H, Cym CH-C*i*Pr), 5.69 (d, J = 6.2 Hz, 2 H, Cym CH-CMe), 2.65 (sept, J = 7.0 Hz, *i*Pr CH), 2.21 (s, 3 H, Cym Me), 1.05 (d, J = 7.0 Hz, 3 H, *i*Pr CH_3) ppm. ^{13}C NMR (CD_3CN): δ = 157.0, 156.5, 154.3, 119.1, 115.7, 105.9, 104.6, 87.3, 85.0, 31.9, 22.3, 19.0 ppm. MS (ESI): m/z = 509.1 $[M - PF_6]^+$. HRMS: calcd. for $C_{20}H_{20}ClN_8Ru$ $[M - PF_6]^+$ 509.0537; found 509.0559. IR (ATR): $\tilde{\nu}$ = 2125 cm^{-1}.

[Ru(*p*-cymene)(2a)Cl]PF_6 (4a). Route A: [Ru(*p*-cymene)$(Cl)_2]_2$ (0.1 g, 0.16 mmol) and **2a** (0.15 g, 0.5 mmol) were dissolved in methanol (30 mL) and stirred at room temperature for 12 h. The yellow solution was concentrated to 15 mL and treated with $NaPF_6$ to yield a yellow precipitate, which was collected by filtration and washed with methanol and diethyl ether to yield the desired complex as yellow crystals (0.15 g, 66%).

Route B: [(4-Azido-2,2′-bipyridyl)RuCl(*p*-cymene)]PF_6 (0.1 g, 0.214 mmol) and phenylacetylene (0.033 g, 0.321 mmol) were dissolved in THF (30 mL), and water was added (30 mL). At 20 °C, $CuSO_4$ (1 M aqueous solution, 0.214 mL) was added followed by freshly prepared sodium ascorbate solution (1 M aqueous solution, 0.428 mL) dropwise. The solution was allowed to stir at room temperature for 12 h. After removal of the THF under vacuum, dichloromethane (30 mL) and conc. NH_4OH (15 mL) were added to the solution, which was allowed to stir for a further 30 min at room temperature. The organic phase was washed twice with water (30 mL) and once with brine (30 mL) and then dried with $MgSO_4$. The solvent was removed under vacuum, and the product was recrystallized from acetonitrile and ether to yield a yellow solid (0.097 g, 80%).

^{1}H NMR (CD_3CN): δ = 9.47 (d, J = 6.5 Hz, 1 H, bpy 6-H), 9.39 (d, J = 5.8 Hz, 1 H, bpy 6′-H), 8.99 (s, 1 H, Tz), 8.78 (d, J = 2.4 Hz, 1 H, bpy 3-H), 8.52 (d, J = 8.1 Hz, 1 H, bpy 3′-H), 8.27 (td, J = 7.9 and 1.3 Hz, 1 H, bpy 4′-H), 8.21 (dd, J = 6.3 and 2.4 Hz, 1 H, bpy 5-H), 8.00 (m, 2 H, *o*-Ph), 7.78 (ddd, 7.6, 5.7 and 1.3 Hz, 1 H, bpy 5′-H), 7.57 (t, J = 7.8 Hz, 2 H, *m*-Ph), 7.48 (tt, J = 7.4 and 1.2 Hz, 1 H, *p*-Ph), 5.98 (m, 2 H, Cym CH-C*i*Pr), 5.78 (d, J = 6.3 Hz, 2 H, Cym CH-CMe), 2.71 (sept, J = 7.0 Hz, 1 H, *i*Pr CH), 2.25 (s, 3 H, Cym CH_3), 1.08 (d, J = 7 Hz, *i*Pr CH_3), 1.07 (d, J = 7 Hz, *i*Pr CH_3) ppm. ^{13}C NMR (CD_3CN): δ = 157.9, 157.5, 156.7, 155.0, 149.9, 146.3, 141.0, 130.5, 130.2, 130.0, 129.2, 126.7, 125.3, 120.1, 117.7, 114.4, 106.5, 104.7, 87.5, 87.4, 85.5, 85.4, 31.8, 22.1, 18.9 ppm. MS (ESI): m/z = 570.1 $[M - PF_6]^+$. HRMS: calcd. for $C_{28}H_{27}ClN_5$ $[M - PF_6]^+$ Ru 570.099300; found 570.099993.

[Ru(*p*-cymene)(2b)Cl]PF_6 (4b). Route A: [Ru(*p*-cymene)$(Cl)_2]_2$ (0.1 g, 0.16 mmol) and **2b** (0.20 g, 0.50 mmol) were dissolved in methanol (30 mL) and stirred at room temperature for 12 h. The yellow solution was concentrated to 15 mL and treated with $NaPF_6$ to yield an orange precipitate, which was collected by filtration and washed with methanol and diethyl ether to yield the desired complex as an orange/red solid (0.21 g, 79%).

Route B: [(4-Azido-2,2′-bipyridyl)RuCl(*p*-cymene)]PF_6 (0.1 g, 0.214 mmol) and ethynylferrocene (0.067 g, 0.321 mmol) were dissolved in THF (30 mL), and water was added (30 mL). At 20 °C, $CuSO_4$ (1 M aqueous solution, 0.214 mL) was added followed by freshly prepared sodium ascorbate solution (1 M aqueous solution, 0.428 mL) dropwise. The solution was allowed to stir at room temperature for 12 h. After removal of the THF under vacuum, dichloromethane (30 mL) and conc. NH_4OH (15 mL) were added to the solution, which was allowed to stir for a further 30 min at room temperature. The organic phase was washed twice with water (30 mL) and once with brine (30 mL) and then dried with $MgSO_4$. The solvent was removed under vacuum, and the product was recrystallized from acetonitrile and ether to yield an orange/red solid. (0.10 g, 69%).

^{1}H NMR (CD_3CN): δ = 9.44 (d, J = 6.2 Hz, 1 H, bpy 6′-H), 9.38 (d, J = H = 5.5 Hz, 1 H, bpy 6-H), 8.73 (br. s, 1 H, bpy 3-H), 8.64 (s, 1 H, Tz), 8.53 (d, J = 7.9 Hz, 1 H, bpy 3′-H), 8.27 (t, J = 7.9 Hz, 1 H, bpy 4′-H), 8.17 (d, J = 5.6 Hz, 1 H, bpy 5-H), 7.77 (t, J = 6.5 Hz, 1 H, bpy 5′-H), 5.98 (t, J = 5.6 Hz, 2 H, Cym CH-C*i*Pr), 5.78 (d, J = 6.5 Hz, 2 H, Cym CH-CMe), 4.85 (s, 2 H, Fc-C_5H_4), 4.42 (s, 2 H, Fc-C_5H_4), 4.13 (s, 5 H, Cp), 2.70 (sept, J = 6.9 Hz, *i*Pr CH), 2.24 (s, 3 H, Cym Me), 1.07 (d, J = 6.9 Hz, *i*Pr CH_3), 1.07 (d, J = 6.9 Hz, *i*Pr CH_3) ppm. ^{13}C NMR (CD_3CN): δ = 157.9, 157.5, 156.8, 155.2, 149.9, 146.4, 141.1, 129.3, 125.4, 118.8, 117.6, 114.2, 106.5, 104.9, 87.6, 87.5, 85.5, 85.4, 70.8, 70.4, 68.0, 31.9, 22.3, 19.0 ppm. MS (ESI): m/z = 678.1 $[M - PF_6]^+$. HRMS: calcd. for $C_{32}H_{31}ClFeN_5Ru$ $[M - PF_6]^+$ 678.065542; found 678.068143.

[Ru(*p*-cymene)(2c)Cl]PF_6 (4c): [(4-Azido-2,2′-bipyridyl)RuCl(*p*-cymene)]PF_6 (0.1 g, 0.214 mmol) and 2-ethynylpyridine (0.033 g, 0.321 mmol) were dissolved in THF (30 mL), and water was added (30 mL). At 20 °C, $CuSO_4$ (1 M aqueous solution, 0.214 mL) was added followed by freshly prepared sodium ascorbate solution (1 M aqueous solution, 0.428 mL) dropwise. The solution was allowed to stir at room temperature for 12 h. After removal of the THF under vacuum, dichloromethane (30 mL) and conc. NH_4OH (15 mL) were added, and the mixture was allowed to stir for a further 12 h at room temperature. The organic phase was washed twice with water (30 mL) and once with brine (30 mL) and then dried with $MgSO_4$. This was repeated, and the solvent was removed under vacuum. The product was recrystallized from acetonitrile and ether to yield an orange solid (0.057 g, 47%). ^{1}H NMR (CD_3CN): δ = 9.45 (d, J = 6.4 Hz, 1 H, bpy 6-H), 9.36 (dd, J = 5.7 and 1.0 Hz, 1 H, bpy-H6′), 9.14 (s, 1 H, Tz), 8.74 (d, J = 1.9 Hz, 1 H, bpy-H3), 8.66 (s, 1 H, Py-H3), 8.50 (d, J = 7.6 Hz, 1 H, bpy-H3′), 8.28–8.16 (m, 3 H, bpy-H4′, bpy-H5 and Py-H4), 7.91 (t, J = 7.7 Hz, 1 H, Py-H5), 7.73 (td, J = 6.4 and 1.0 Hz, 1 H, bpy-H5′), 7.39 (s, 1 H, Py-H6), 5.9 (t, J = 6.3 Hz, 2 H, Cym CH-C*i*Pr), 5.76 (d, J = 6.3 Hz, 2 H, Cym CH-CMe), 2.68 (sept, J = 6.8 Hz, 1 H, *i*Pr CH), 2.16 (s, 3 H, Cym CH_3), 1.06 (d, J = 1.8 Hz, *i*Pr CH_3), 1.04 (d, J = 1.8 Hz, *i*Pr CH_3) ppm. ^{13}C NMR (CD_3CN): δ = 157.9, 157.6, 156.8, 155.0, 151.1, 150.9, 150.0, 146.3, 141.1, 138.3, 129.3, 125.5, 124.9, 122.1, 121.3, 118.1, 114.6, 106.5, 104.8, 87.6, 87.5, 85.5, 85.4, 31.9, 22.2, 19.0 ppm. MS (ESI): m/z = 571.1 $[M - PF_6]^+$. HRMS: calcd. for $C_{27}H_{26}ClN_6Ru$ $[M - PF_6]^+$ 571.094548; found 571.095033.

[{Ru(*p*-cymene)Cl}$_2$(2c)][PF_6]$_2$ (5): [$RuCl_2$(*p*-cymene)]$_2$ (0.313 g, 0.5 mmol) and 1-pyridyl-4-(2,2′-bipyridyl)-1,2,3-triazole (0.150 g, 0.5 mmol) were reacted in ethanol (50 mL) for 48 h. The solution was evaporated to dryness to afford an orange-brown solid. The orange-brown solid was dissolved in acetonitrile (3 mL), and a solution of $AgPF_6$ (0.06 g, 0.22 mmol) in acetonitrile (2 mL) was added dropwise with stirring. The reaction mixture was stirred for a further 10 min and filtered through Celite, and the solvents were evaporated to dryness to yield an orange solid (0.22 g, 88%). ^{1}H

NMR (CD_3CN): δ = 9.58 (dd, J = 5.2 and 1.6 Hz, 1 H, bpy 6-H), 9.44 (d, J = 9.6 Hz, 1 H, Tz), 9.39 (dt, J = 5.6 and 1.3 Hz, 1 H, bpy 6′-H), 9.33 (d, J = 5.4 Hz, 1 H, Py 6-H), 8.34 (dd, J = 13.2 and 2.3 Hz, 1 H, bpy 3-H), 8.56 (t, J = 7.7 Hz, bpy 3′-H), 8.25 (m, 3 H, bpy 4′-H, bpy 5-H and Py 4-H), 8.08 (d, J = 7.9 Hz, 1 H, Py 3-H), 7.80 (m, 1 H, bpy 5′-H), 7.69 (t, J = 6.6 Hz, 1 H, Py 5-H), 6.09 (d, 6.0 Hz, 1 H, cymene pytz), 6.00 (m, 3 H, cymene bpy), 5.89 (dd, J = 6.0 and 2.5 Hz, 1 H, cymene bpy), 5.81 (m, 3 H, cymene pytz), 2.78 (sept, J = 6.4 Hz, 1 H, *i*Pr CH pytz), 2.69 (m, 1 H, *i*Pr CH bpy), 2.23 (d, J = 3.6 Hz, 3 H, Cym Me bpy), 2.21 (s, 3 H, Cym Me pytz), 1.16 (dd, J = 6.4 and 1.6 Hz, 3 H, *i*Pr CH_3 pytz), 1.11 (d, 6.8 Hz, 3 H, *i*Pr CH_3 pytz), 1.07 (d, J = 7.0 Hz, 6 H, *i*Pr CH_3 bpy) ppm. ^{13}C NMR (CD_3CN): δ = 158.4, 158.0, 156.9, 156.8, 154.7, 149.0, 148.0, 148.3, 145.3, 145.2, 141.7, 141.3, 141.2, 129.7, 128.0, 125.7, 124.4, 124.3, 124.0, 118.6, 118.5, 118.3, 115.3,115.2, 107.2, 107.2, 107.0, 106.9, 105.1, 105.1, 104.0, 103.9, 87.9, 87.8, 87.6, 87.2, 87.2, 86.2, 85.8, 85.7, 85.7, 85.6, 85.6, 84.8, 32.0, 31.9, 22.5, 22.3, 22.3, 22.0, 22.0, 19.0, 18.9 ppm. MS (ESI): m/z = 421 $[M - 2PF_6]^{2+}$. HRMS: calcd. for $C_{37}H_{40}Cl_2N_6Ru_2$ $[M - 2PF_6]^{2+}$ 421.038376; found 421.040178.

[(*p*-cymene)RuCl(pytz)]PF_6 (6): $[RuCl_2(p\text{-cymene})]_2$ (0.313 g, 0.5 mmol) and 1-pyridyl-4-benzyl-1,2,3-triazole (0.223 g, 1.0 mmol) were reacted in ethanol (50 mL) for 48 h. The solution was evaporated to dryness to afford an orange-brown solid. The orange-brown solid was dissolved in acetonitrile (3 mL), and a solution of $AgPF_6$ (0.143 g, 0.564 mmol) in acetonitrile (2 mL) was added dropwise with stirring. The reaction mixture was stirred for a further 10 min and filtered through Celite, and the solvents were evaporated to dryness to yield an orange solid (0.34 g, 93%). ^1H NMR (CD_3CN): δ = 9.23 (d, J = 5.4 Hz, 1 H, Py 6-H), 8.56 (s, 1 H, Tz), 8.09 (td, J = 7.9 and 1.3 Hz, 1 H, Py 4-H), 7.92 (d, J = 7.9 Hz, 1 H, Py 3-H), 7.57 (td, J = 6.9 and 1.3, 1 H, Py 5-H), 7.46 (m, 5 H, benzyl), 6.00–5.60 (m, 6 H, Cym CH-C*i*Pr, Cym CH-Me and CH_2-benzyl), 2.63 (sept, J = 6.9 Hz, *i*Pr CH), 2.16 (s, 3 H, Cym Me), 1.09 (d, J = 6.9 Hz, *i*Pr CH_3), 0.94 (d, J = 6.9 Hz, *i*Pr CH_3) ppm. ^{13}C NMR (CD_3CN): δ = 156.3, 149.1, 147.4, 141.1, 134.8, 130.2, 129.6, 127.0, 125.8, 123.5, 106.1, 103.1, 86.5, 85.2, 85.1, 84.5, 56.9, 31.7, 22.4, 21.6, 18.7 ppm. MS (ESI): m/z = 507.1 $[M - PF_6]^+$. HRMS: calcd. for $C_{24}H_{26}ClN_4Ru$ $[M - PF_6]^+$ 507.088400; found 507.090438.

[[Ru(*p*-cymene)Cl]$_2$(di{[1-(2,2′-bipyrid-4-yl)triazol-4-yl]methyl}-ether)][PF_6]$_2$ (7): [(4-Azido-2,2′-bipyridyl)RuCl(*p*-cymene)] (0.1 g, 0.214 mmol) and dipropargyl ether (0.012 g, 0.130 mmol) were dissolved in THF (30 mL), and water was added (30 mL). At 20 °C, $CuSO_4$ (1 M aqueous solution, 0.214 mL) was added followed by freshly prepared sodium ascorbate solution (1 M aqueous solution, 0.428 mL) dropwise. The solution was allowed to stir at room temperature for 24 h. After removal of the THF under vacuum, dichloromethane (30 mL) and conc. NH_4OH (15 mL) were added to the solution, which was allowed to stir for a further 2 h at room temperature. The organic phase was washed twice with water (30 mL) and once with brine (30 mL) and then dried with $MgSO_4$. The solvent was removed under vacuum, and the product was recrystallized from acetonitrile and ether to yield a red solid (0.084 g, 60%). ^1H NMR (CD_3CN): δ = 9.47 (dd, J = 6.3 and 1.3 Hz, 2 H, bpy 6-H), 9.39 (d, J = 5.7 Hz, 2 H, bpy 6′-H), 9.30 (d, J = 5.9, 2 H, Tz), 9.14 (dd, J = 2.2 and 7.2 Hz, 2 H, bpy 3-H), 8.90 (t, J = 8.3 Hz, 2 H, bpy 3′-H), 8.37 (dt, J = 6.3 and 2.2 Hz, 2 H, bpy 5-H), 8.21 (tt, J = 7.7 and 1.3 Hz, 2 H, bpy 4′-H), 7.76 (tt, J = 6.6 and 1.3 Hz, 2 H, bpy 4′-H), 5.99 (t, J = 7.4 Hz, 4 H, Cym CH-C*i*Pr), 5.79 (d, J = 6.5 Hz, 4 H, Cym CH-CMe), 4.86 (s, 4 H, Tz-CH_2-O), 2.70 (sept, J = 6.8 Hz, 2 H, *i*Pr CH), 2.23 (s, 6 H, Cym Me), 1.07 (d, J = 2.9 Hz, *i*Pr CH_3), 1.06 (d, J = 2.9 Hz, *i*Pr CH_3) ppm. ^{13}C NMR (CD_3CN): δ = 157.9, 157.8, 156.7, 155.4, 147.7, 147.7, 146.7, 141.1, 129.2, 126.0, 123.9, 114.9, 106.5, 104.8, 87.6, 87.5, 85.6, 85.5, 64.1, 31.9, 22.3, 19.0 ppm. MS (ESI): m/z = 515.1 $[M - 2PF_6]^{2+}$. HRMS: calcd. for $C_{46}H_{48}Cl_2N_{10}ORu_2$ $[M - 2PF_6]^{2+}$ 515.0733; found 515.0781.

Supporting Information (see footnote on the first page of this article): Atomic *xyz* coordinates for the molecular structure of **3′** and NMR spectra of ligands and complexes.

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