Palladium-catalysed cross-coupling reactions of ruthenium bis-terpyridyl complexes: strategies for the incorporation and exploitation of boronic acid functionality

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The palladium catalysed Miyaura cross-coupling reactions of 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine (tpy-ϕ-Br) and 4′-bromo-2,2′:6′,2″-terpyridine (tpy-Br) with bis(neopentyl glycolato)diboron (B_2neo_2) lead to the first reported examples of boronate ester-substituted terpyridine ligands, L^1 and L^2. Ligand L^1, which incorporates a benzene ring between the terpyridine group and the boron, reacts with transition metals such as iron and ruthenium to generate complexes containing the analogous boronic acid-substituted terpyridine L^3. The heteroleptic complex $[Ru(ttpy)L^3]^{2+}$ has also been prepared by an analogous cross-coupling reaction of the bromo complex $[Ru(ttpy)(tpy\text{-}\phi\text{-}Br)]^{2+}$ with B_2neo_2 (ttpy = 4′-tolyl-2,2′:6′,2″-terpyridine). The structurally related complex $[Ru(ttpy)L^4]^{2+}$ (L^4 = terpyridine-4′-boronic acid) could not be prepared, either directly from L^2 or from $[Ru(ttpy)(tpy\text{-}Br)]^{2+}$, apparently due to competitive hydrodeboration and solvolysis. The complex $[Ru(ttpy)L^3]^{2+}$ reacts with aryl halides under standard palladium-catalysed Suzuki–Miyaura cross-coupling conditions to generate more elaborate 4′-aryl-substituted terpyridyl complexes. Cross-coupling has also been achieved by reaction of $[Ru(ttpy)(tpy\text{-}Br)]^{2+}$ with an arylboronic acid. The photophysical properties of $[Ru(ttpy)L^3]^{2+}$ are shown to be largely typical of ruthenium bis-terpyridyl complexes.

Introduction

Arylboronic acids have been the subject of considerable interest over the past decade, owing especially to their utility in organic synthesis: the metal-catalysed C–C bond forming reactions which they undergo with aryl and alkenyl halides and triflates have seen very widespread application.[1] Often referred to as the Suzuki–Miyaura reaction, this valuable cross-coupling procedure is of course a special case of the oxidative addition-transmetallation-reductive elimination sequence that is common to a wide variety of metal-catalysed coupling reactions.[2] Its attraction lies in the fact that competitive homo-coupling of the aryl halide is usually minimal.

As far as ligands for transition metals are concerned, homo-coupling procedures, especially those catalysed by $[Ni(PPh_3)_2Cl_2]$, have been used over the past decade for the preparation of a number of "back-to-back" polypyridyl ligands and their dinuclear complexes.[3,4] The coupling has been carried out both prior to metal binding and on the complexes themselves. In the latter case, the precursor to coupling is a complex which incorporates an aryl halide in one of the ligands.[4] Cross-coupling procedures, on the other hand, although applied to the synthesis of terpyridine, phenanthroline and bipyridine-based *ligands*,[5–7] have apparently not been carried out on transition metal *complexes*.

We report here our recent work on the introduction of boronic acid functionality into terpyridine ligands, both prior to and after complexation to a transition metal ion [ruthenium(II)], and the successful coupling of the resulting complexes with aryl halides under standard Suzuki–Miyaura conditions. Further incentive for the exploration of boronic acid-substituted transition metal complexes stems from the molecular recognition properties of boronic acids. In particular, arylboronic acids react reversibly with diols, catechols and amino alcohols in aqueous solution,[8] leading to potential uses as sensors for biologically significant substances such as saccharides and neurotransmitters.[9,10]

Results and discussion

Preparation of the boronic acid-substituted ligands

The conventional route to arylboronic acids involves the intermediacy of the analogous aryllithium (usually obtained by lithiation of the parent aryl bromide with n-butyllithium); this reacts rapidly with electrophilic trimethyl borate to generate the dimethyl ester of the boronic acid, which is readily hydrolysed to the acid during work-up (Scheme 1). Attempts to prepare ligand L^3 in this way from 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine (L^5) consistently failed in our hands. Use of equimolar or small excesses of butyllithium led to no net reaction, despite the immediate formation of a deep green colouration upon addition of BuLi, whilst the use of a large excess of butyllithium and borate gave an intractable dark residue from which neither starting material nor product could be extracted and identified. Use of *tert*-butyllithium proved equally unsuccessful.

An alternative method for the preparation of arylboronates appeared in 1995, namely that of Miyaura involving the palladium catalysed coupling of the aryl halide with bis(pinacolato)diboron, $(Me_4C_2O_2)B\text{–}B(Me_4C_2O_2)$.[11] The most effective catalyst here is $Pd(dppf)Cl_2$, and the presence of KOAc has been found to facilitate greatly the reaction (strong bases promote further reaction of the product with the halobenzene starting material). Application of this procedure to the bromophenyl terpyridine (L^5) proved successful for the

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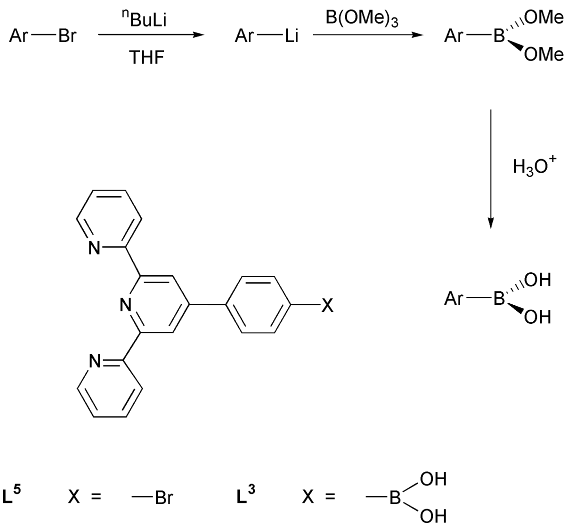


Scheme 1 The conventional synthetic pathway to arylboronic acids, which fails for 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine, L^5.

formation of L^6, the pinacolate ester of the desired ligand L^3 (Scheme 2). Nevertheless, deprotection of the resulting terpyridine boronate to generate the boronic acid (L^3) proved troublesome: as noted by others, pinacol forms a particularly stable boronate ester which is especially resistant to hydrolysis under both acidic and basic conditions.[12] The neopentyl glycolate analogues are more readily hydrolysed, and indeed the use of bis(neopentyl glycolato)diboron, under conditions otherwise identical to the pinacolate reaction, gave a boronate ester (L^1) which could now be hydrolysed readily to the boronic acid (L^3). Similarly, 4′-bromo-2,2′:6′,2″-terpyridine (tpy-Br, L^7) reacted under analogous conditions to generate L^2.

The terpyridine-boronate esters L^1 and L^2 were obtained as analytically pure colourless solids, typically in yields of about 70%, and were characterised by ^{1}H, ^{13}C and ^{11}B NMR spectroscopy. The ^{11}B shifts of 27.8 and 26.8 ppm (in CDCl$_3$) are typical of arylboronic acids and esters. Compared to the parent bromo-substituted compounds, the introduction of the boronate group leads to only a small shift to higher frequency of the ^{1}H resonances of the aromatic ring to which it is bound; the resonances of all three pyridyl groups in L^1 and the two terminal pyridyl groups in L^2 are scarcely affected. A small downfield shift of the neopentyl methylene and methyl groups, relative to bis(neopentyl glycolato)diboron, is also observed.

Complex formation

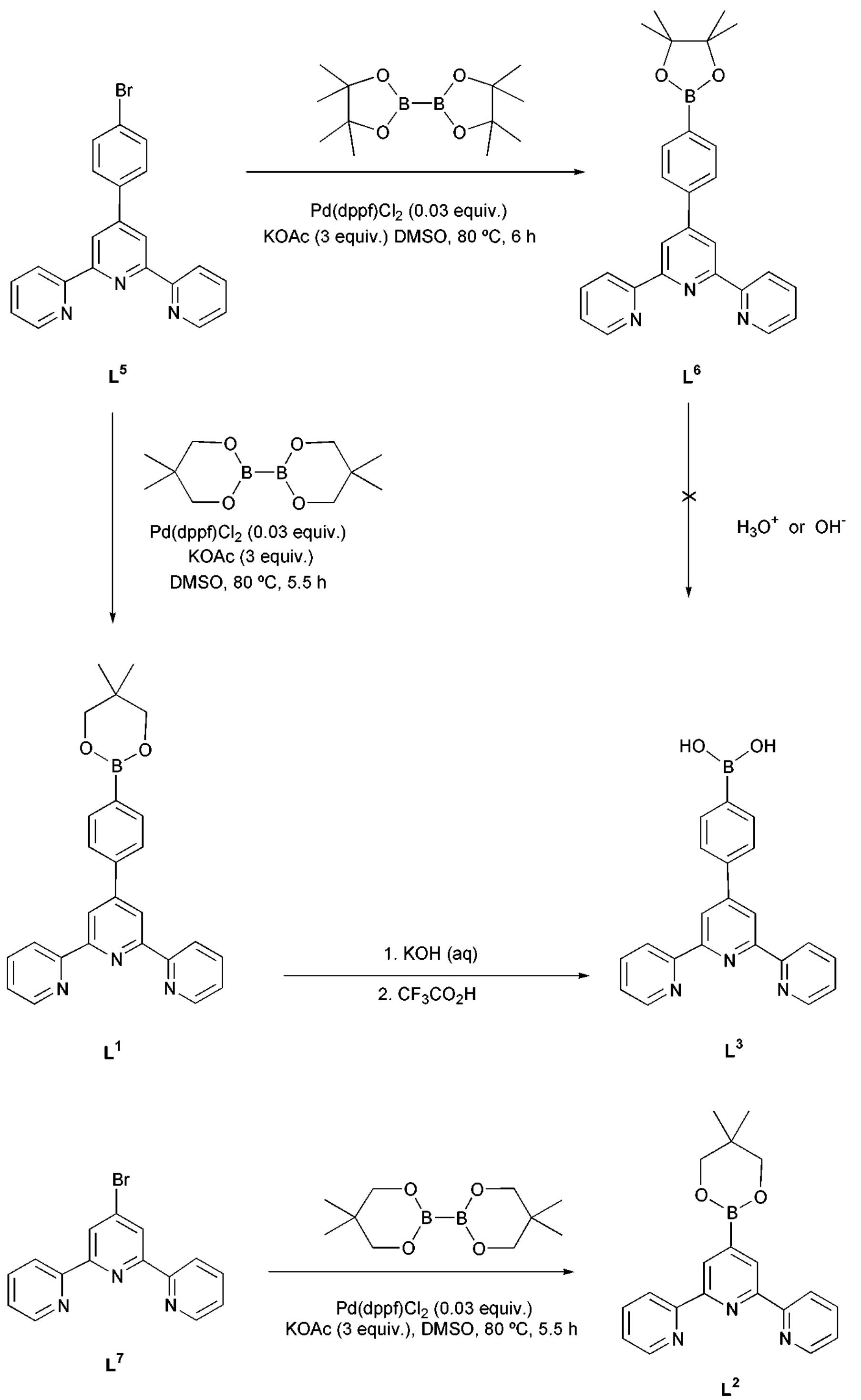
In order to assess the transition metal-binding properties of the two ligands, the preparation of complexes with ruthenium(II) was attempted. Ruthenium is an attractive metal for this purpose, as its bis-terpyridyl complexes are kinetically inert and the methodology for introducing two different terpyridines into the coordination sphere of the metal under mild conditions, to generate heteroleptic complexes, is well established.[13,14] Moreover, the photophysical properties of a number of such complexes have been studied, revealing the lowest energy excited state to be metal-to-ligand charge transfer in character but subject to efficient deactivation *via* a thermally accessible metal-centred state.[15]

Preparation of complexes from the boronate-substituted ligands. The heteroleptic complex [Ru(ttpy)L^3](PF$_6$)$_2$ was prepared using the procedure developed by Collin *et al.*, involving the silver-catalysed removal of chloride from the coordination sphere of the metal, to generate the terpyridine tris-acetone complex (Scheme 3); the weakly coordinated acetone molecules are then readily displaced by the second terpyridine under mild conditions.[14] Following anion exchange with aqueous KPF$_6$ solution, the complex was purified by chromatography on silica, using acetonitrile–water–saturated aqueous KNO$_3$ as the eluant. Under these conditions, the neopentyl glycolate group was hydrolysed such that the product finally isolated contained the boronic acid itself rather than its ester. The –B(OH)$_2$ protons appear in the ^{1}H NMR spectrum as a singlet at δ 6.31 (in CD$_3$CN). A full assignment of the ^{1}H NMR spectrum has been made on the basis of ^{1}H–^{1}H COSY (400 MHz) and NOESY (500 MHz) (details in Experimental section), the latter being particularly valuable for distinguishing between similar resonances of the two different terpyridines. The spectrum is, in fact, largely comparable to that of the closely related complex [Ru(ttpy)L^5]$^{2+}$, with similar changes in the resonances of the protons of the two terpyridines being observed upon complexation to the metal ion, compared with the free ligands. The electrospray ionisation mass spectrum shows peaks due to the mono- and bis-methyl esters of the complex, the formation of which will be favoured by the high concentration of methanol in the instrument. UV-Visible absorption and luminescence emission spectroscopic measurements are discussed in the final section below.

Although the synthesis of the homoleptic complex, [Ru(L^3)$_2$]$^{2+}$, might be expected to be straightforward (especially since potential ligand scrambling is not an issue, as it is during the preparation of heteroleptic complexes), we have found the one-step reaction of RuCl$_3$ with two equivalents of terpyridine ligand to be unreliable. Indeed, most literature reports of the preparation of such complexes have made use of the two-step procedure, involving the intermediacy of the terpyridyl ruthenium trichloride compound.[13] This intermediate is normally obtained very readily in high purity, as it precipitates from alcoholic solution during its formation from RuCl$_3$ and one equivalent of terpyridine. Use of L^1 in this way did not lead to precipitation of the expected intermediate: presumably, the presence of the boronate group augments the alcohol solubility of this compound. Spectroscopic analysis of the residue obtained upon removal of the solvent revealed only a small proportion of the desired intermediate amongst other unidentified products, and repeated attempts at recrystallisation from a range of solvents led to no significant enhancement in purity. The crude mixture was therefore reacted with a further equivalent of L^1, and the product mixture obtained subjected to anion exchange with aqueous KPF$_6$ followed by chromatography on silica, leading to a small amount of spectroscopically pure [Ru(L^1)$_2$]$^{2+}$.

The reaction of Ru(ttpy)Cl$_3$ with L^2 gave, in contrast to L^1, a complicated mixture of products, from which the analogous complex [Ru(ttpy)L^4]$^{2+}$, lacking the interposed phenyl ring, could not be isolated. Significantly, (and despite the formation of a purple colouration), no characterisable product could be isolated from the reaction of this ligand with ammonium iron(II) sulfate, which would normally be expected to give the bis-terpyridyl complex immediately.[16] Apparently, there is some instability associated with the binding of the 4′-boronic acid- or ester-appended pyridine group to transition metals (see below).

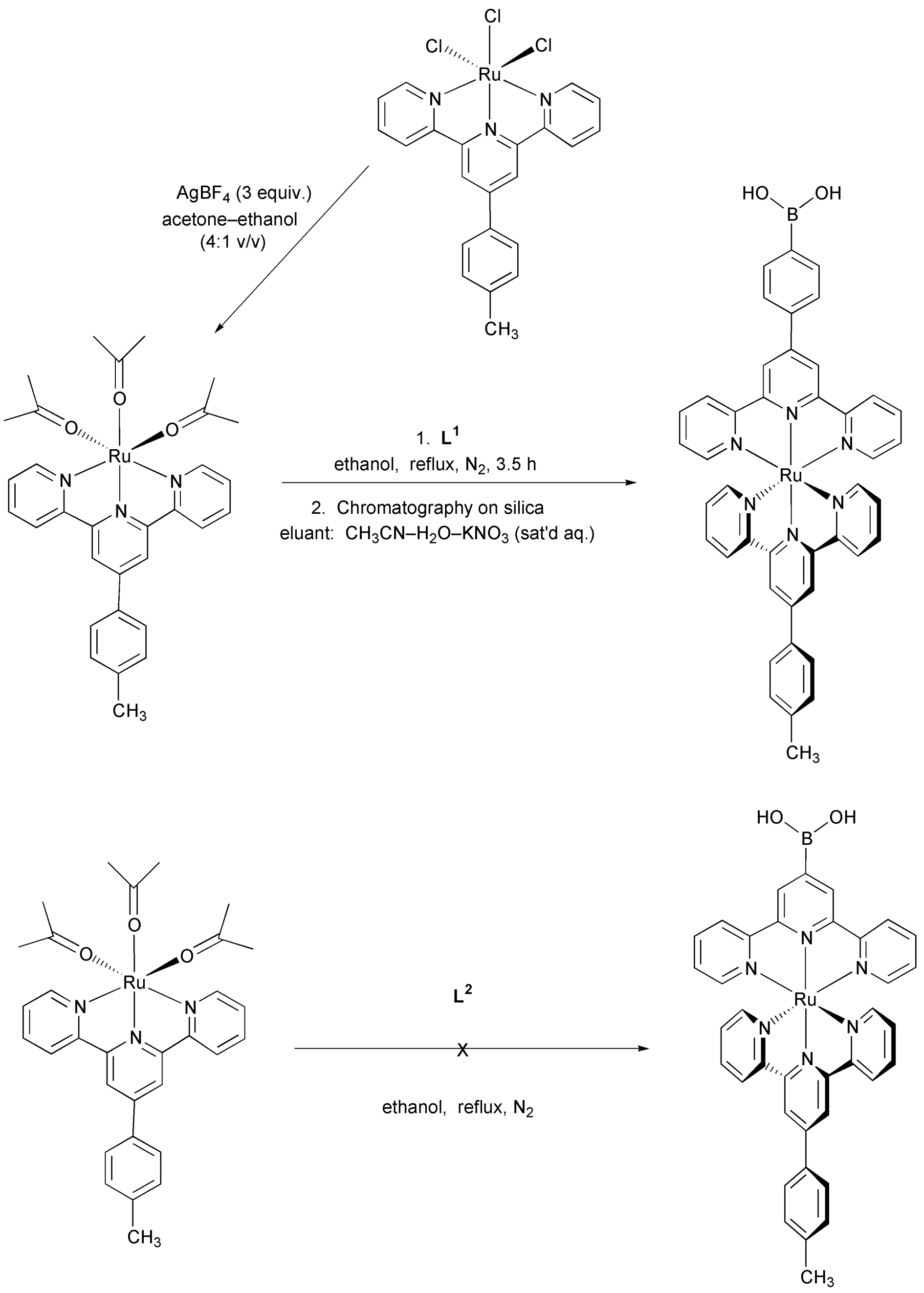
Preparation of boronate-substituted complexes from bromo-substituted complexes. That the ligands L^1 and L^2 can be prepared using the Miyaura conditions is not unexpected given the diversity of haloaromatic compounds which have been employed, including heterocycles such as 3-bromoquinoline.[11] It was less clear, however, whether boronate-substituted complexes could be prepared directly from the analogous bromo-substituted complexes: to our knowledge, there is no literature precedent for the direct formation of a boronic acid-



Scheme 2 Synthesis of the phenylboronic acid appended terpyridine, L^3 and its pinacol and neopentyl esters, L^6 and L^1. L^2 was prepared similarly. L^4 is used in the text to denote the boronic acid of ester L^2.

substituted metal complex starting from a complex incorporating a bromoaryl group.

The coupling of the bromo-substituted complex $[Ru(ttpy)L^5](PF_6)_2$ with B_2neo_2 was attempted, using the coupling conditions used for the synthesis of L^1 and L^2 {1.05 equiv. B_2neo_2, $Pd(ddpf)Cl_2$ catalyst (0.03 equiv.), KOAc as base (3 equiv.), DMSO at 80 °C for 5.5 h, Scheme 4}. There was no evidence for any reaction under these conditions: work-up led exclusively to the starting bromo complex. Use of larger quantities of reagents, together with a smaller reaction volume, longer reaction time and the presence of additional dppf, did lead to reaction (Scheme 4) but the only product isolated following chromatography was the dimerised, dimetallic complex, $[(ttpy)Ru(tpy\text{-}\phi\text{-}\phi\text{-}tpy)Ru(ttpy)](PF_6)_4$. This complex was first reported in 1993, but in that case was obtained by initial formation of the "back-to-back" *ligand* (by Ni-catalysed homocoupling of L^5), followed by complexation to two equivalents of $Ru(ttpy)Cl_3$.[17] In the present instance, a plausible explanation for its formation was that the boronate-substituted complex had indeed been formed during the reaction, but had gone on to react with the bromo-substituted starting material at a rate competitive with its rate of formation under the reaction conditions employed, by the "conventional" cross-coupling mechanism. On the other hand, a number of metal-catalysed homo-coupling reactions of bromoaryl-containing complexes have been reported, as noted in the introduction[4] (indeed complexation to a metal apparently promotes the coupling of such ligands[4a]), and so

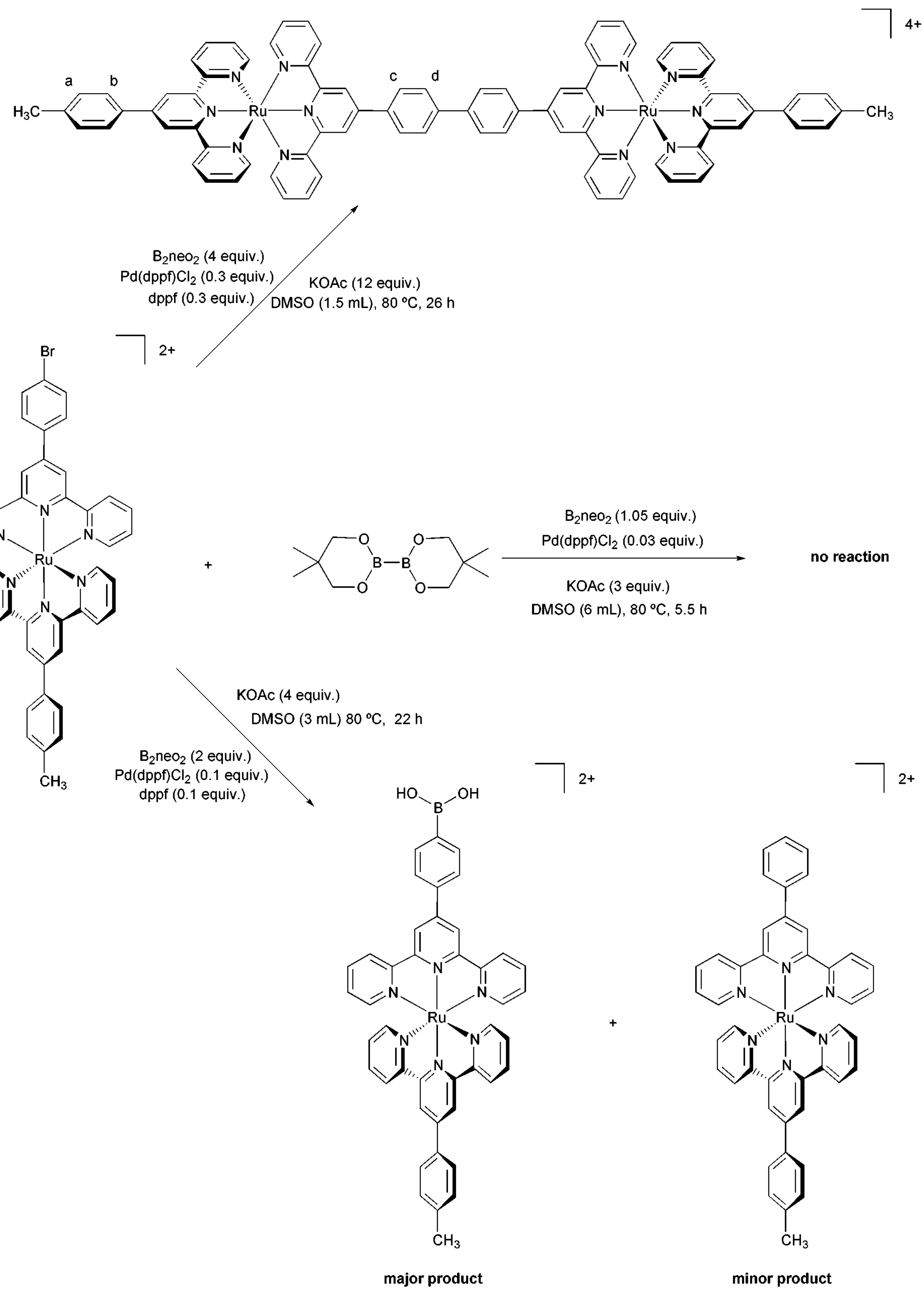


Scheme 3 Preparation of $[Ru(ttpy)L^3]^{2+}$, method A: by complexation to ligand L^1.

an alternative explanation for the formation of the dimer is simply a homo-coupling of $[Ru(ttpy)L^5]^{2+}$ catalysed by palladium. In order to assess this possibility, the reaction was repeated in the absence of B_2neo_2, but under otherwise identical conditions. Again, the product isolated was the dimer. Although this provides conclusive evidence that palladium-catalysed homo-coupling occurs, it does not rule out the formation and involvement of the boronate-substituted complex when the reaction is carried out in the presence of B_2neo_2.

The coupling reaction was therefore attempted using stoichiometry and conditions intermediate between those above. In fact, the use of two equivalents of B_2neo_2, four equivalents of base, together with the catalyst and additional free dppf ligand (0.1 equivalents of each) successfully led to the desired coupling reaction (Scheme 4). A small amount of $[Ru(ttpy)(phtpy)]^{2+}$ (phtpy = 4′-phenyl-2,2′:6′,2″-terpyridine) formed by competitive hydrodeboration was separated from the desired complex by column chromatography. Hydrolysis of the neopentyl glycolate again occurred during the work-up and purification, such that the final product was $[Ru(ttpy)L^3]^{2+}$, with identical spectroscopic signals to that prepared as outlined in the previous section. Given the low yield and presence of side-products, the other route to this complex (described above) is clearly preferable.

In light of the success of this alternative method of formation of $[Ru(ttpy)L^3]^{2+}$ directly from the bromo complex (albeit in low yield), the preparation of the hitherto elusive complex $[Ru(ttpy)L^4]^{2+}$ was attempted in the same way. The starting complex required here was $[Ru(ttpy)L^7]^{2+}$. Although not reported previously, this complex was prepared cleanly by the method described earlier involving silver-catalysed dechlorination of $Ru(ttpy)Cl_3$ in the presence of acetone and subsequent reaction with one equivalent of tpy-Br (L^7). Reaction of this complex with B_2neo_2 in DMSO in the presence of $Pd(dppf)Cl_2$ catalyst, using conditions and stoichiometries identical to those which had been successfully applied to $[Ru(ttpy)L^5]^{2+}$, led to a mixture of the starting material and one major product, as monitored by tlc. Separation by column chromatography revealed this product to be $[Ru(ttpy)(tpy\text{-}OH)]^{2+}$ (tpy-OH = 4′-hydroxy-2,2′:6′,2″-terpyridine) (Scheme 5). It is noteworthy that when not complexed

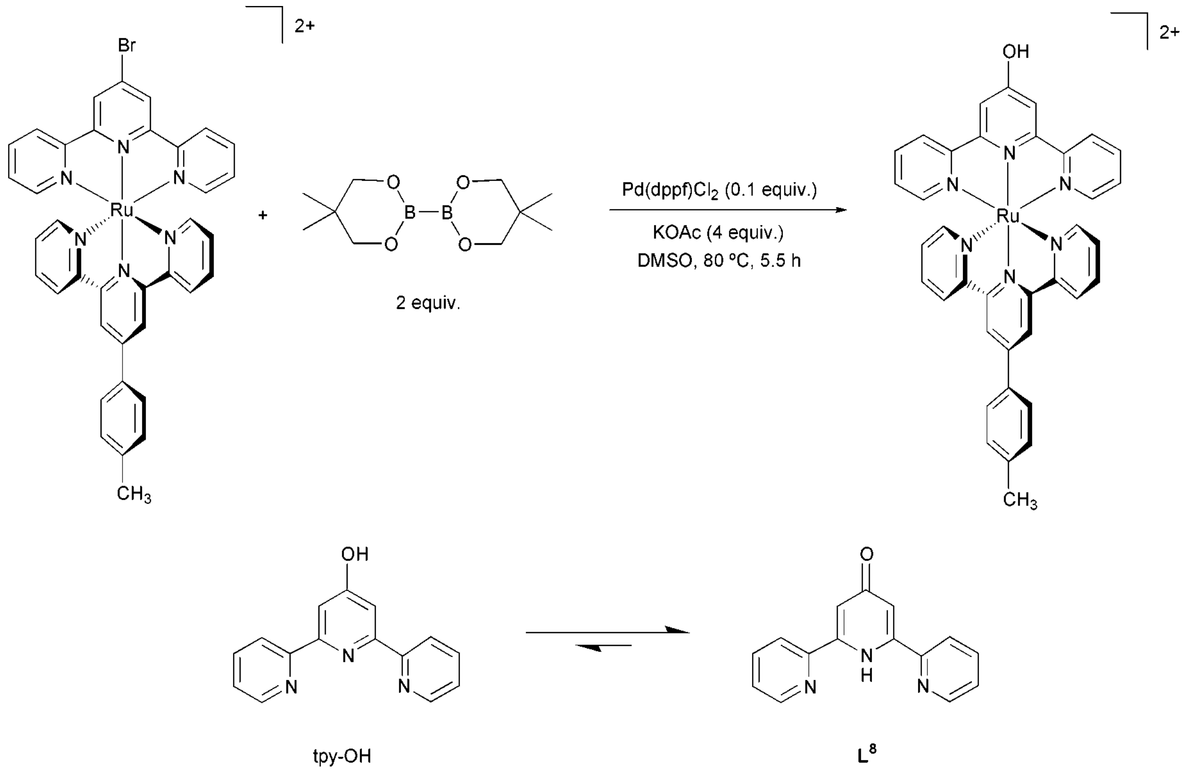


Scheme 4 Preparation of [Ru(ttpy)L^3]$^{2+}$, method B: by palladium-catalysed cross-coupling of [Ru(ttpy)L^5]$^{2+}$ with B_2neo_2.

to a metal ion, tpy-OH normally exists almost exclusively as its pyridone tautomer, L^8 [2,6-bis(2′-pyridyl)-4-pyridone]. Closely-related complexes incorporating tpy-OH have been reported previously by Constable *et al.*, but were prepared by direct reaction of L^8 with $RuCl_3$.[13a] A very small amount of [Ru(ttpy)(tpy)]$^{2+}$ was also obtained, but none of the desired complex [Ru(ttpy)L^2]$^{2+}$ nor [Ru(ttpy)L^4]$^{2+}$.

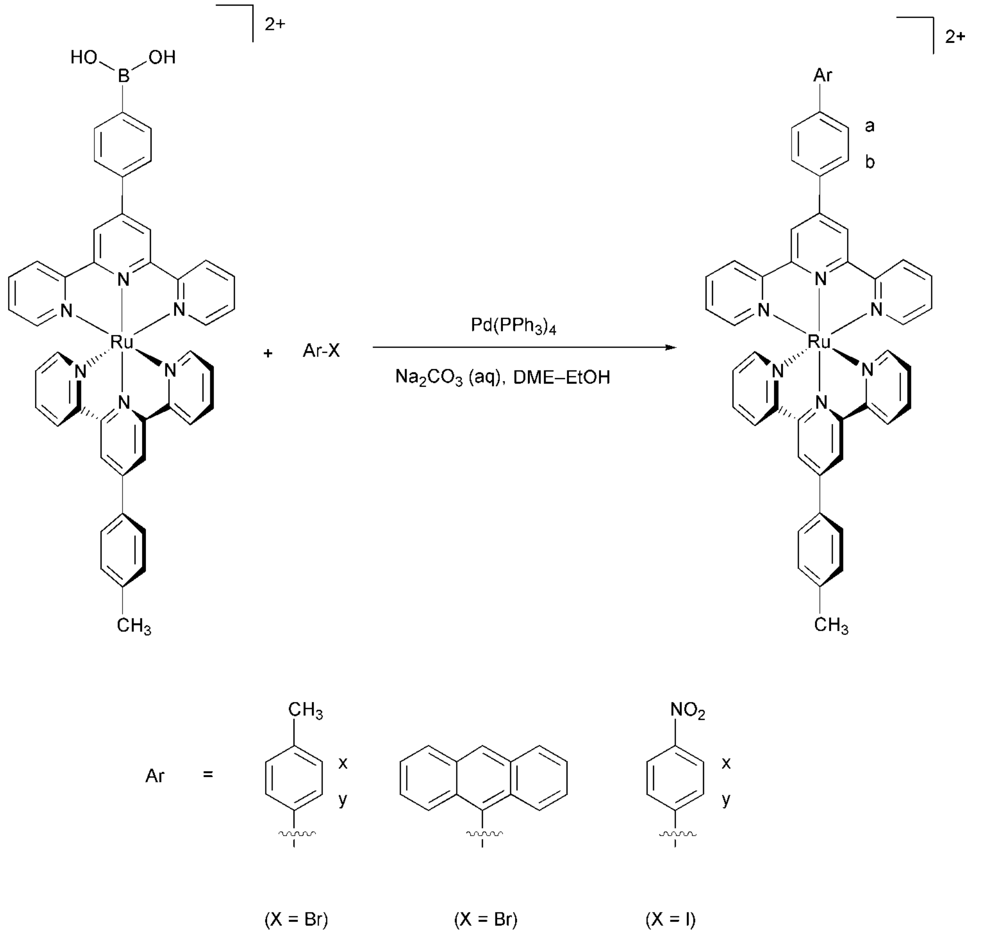
Palladium-catalysed coupling reactions of bromo- or boronic acid-substituted complexes

Coupling of the boronic acid-substituted complex with aryl halides. The palladium-catalysed cross-coupling of arylboronic acids with aryl halides has been shown to proceed under a variety of conditions: a range of catalysts, bases and solvents



Scheme 5 Attempted synthesis of [Ru(ttpy)(tpy-B(OH)$_2$)]$^{2+}$ by cross-coupling of [Ru(ttpy)L^7]$^{2+}$ with B$_2$neo$_2$.

have been employed, with varying degrees of success according to the substrates. The use of Pd(PPh$_3$)$_4$ and sodium carbonate in DME has emerged as one of the most popular and reliable combinations.[1,18] In order to explore the utility of boronic acid-appended terpyridine complexes in such coupling reactions, we investigated the reaction of [Ru(ttpy)L^3]$^{2+}$ with 4-bromotoluene. The aforementioned conditions, but with the addition of a mixture of ethanol and acetonitrile to aid in the dissolution of the complex, led cleanly to the desired coupling reaction and formation of the complex



Scheme 6 Palladium catalysed cross-coupling of [Ru(ttpy)L^3]$^{2+}$ with haloaromatics.

$[Ru(ttpy)L^9]^{2+}$ in good yield {L^9 = 4′-(4-methylbiphenyl)-2,2′:6′,2″-terpyridine} (Scheme 6).

In order to assess the generality of this method, coupling with two further haloaromatics was attempted. 1-Iodo-4-nitrobenzene reacted under comparable conditions to give $[Ru(ttpy)(tpy\text{-}\phi\text{-}\phi\text{-}NO_2)]^{2+}$. In this case, a significant amount of a second product, namely $[Ru(ttpy)(tpy\text{-}\phi\text{-}OH)]^{2+}$, was also formed, apparently by competitive hydrolytic deboronation. Such competing reactions are well documented for couplings under aqueous conditions, and may be promoted both by electron-donating and withdrawing substituents.[19a] Notably, promotion by a second row transition metal ion (Ag^+) has also been reported.[19b] In the present instance, the problem was exacerbated by the difficulty in separating the two complexes chromatographically, leading to a low yield of the desired complex.

9-Bromoanthracene coupled smoothly to the boronic acid-substituted complex, but problems of a different kind arose in this case, apparently *after* reaction. Chromatographic separation of the product gave a major fraction which, by ^1H NMR, consisted primarily of the desired product $[Ru(ttpy)(tpy\text{-}\phi\text{-}an)]^{2+}$ (an = 9-anthryl), but with some additional signals in the aromatic region. The electrospray mass spectrum confirmed the presence of this complex ($m/z = 454$, M^{2+}), but also showed a smaller second signal (with a similar isotopic distribution) at m/z 470. After storing for 40 h, the NMR spectrum of this same fraction indicated that the product had decomposed to give a complicated mixture. Given that it is well established that $[Ru(tpy)_2]^{2+}$ is able to act as a sensitiser for the T_1 state of anthracene, and also that the latter is itself quenched by dioxygen to generate singlet oxygen,[20] we suspect that the decompostion may be due to the reaction of photogenerated $^1\Delta(O_2)$ with the anthracene group of the complex to produce anthracene oxidation products. Such decomposition has indeed been reported for a related anthryl-appended complex, namely $[Ru(tpy\text{-}an)_2]^{2+}$.[20] Support for this explanation also comes from the additional signal in the mass spectrum. Thus, it is well known that the first step in the reaction of $^1\Delta(O_2)$ with anthracene itself is the [4 + 2] Diels–Alder cycloaddition of O_2 to the central ring;[21] an initial increase in the mass of the complex by 32 units is therefore to be expected, or 16 units in the doubly-charged peak in the mass spectrum, as observed.

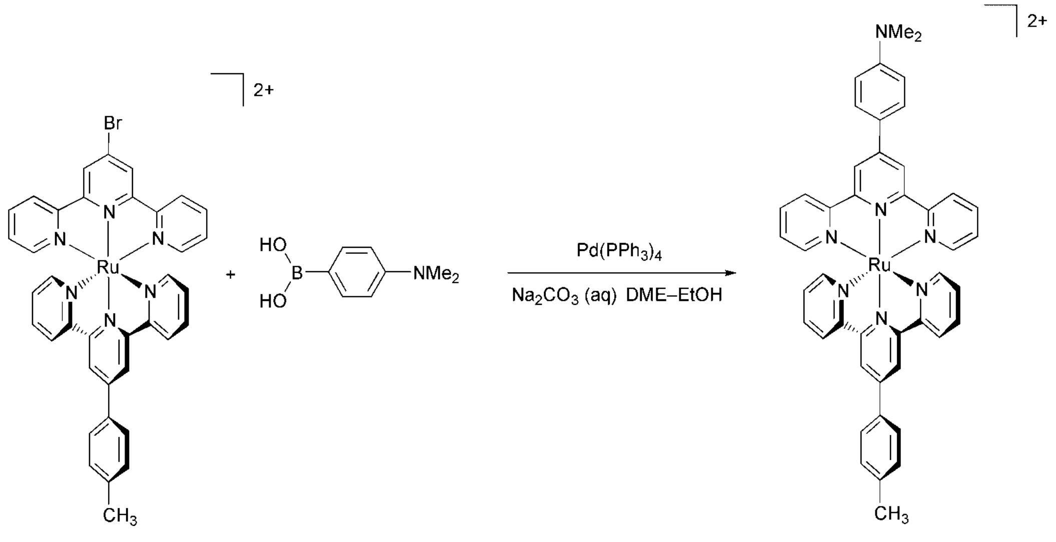
Coupling of the bromo-substituted complex with an arylboronic acid. The examples above show clearly that metal complexes incorporating boronic acid functionality are able to undergo cross-coupling reactions with haloaromatics. An alternative and perhaps more straightforward approach, however, would be to consider the coupling of a halo-substituted complex with an arylboronic acid. This possibility was tested using the complex of the bromoterpyridine ligand, $[Ru(ttpy)L^7]^{2+}$. The complex was found to couple reliably with 4-(dimethylamino)benzeneboronic acid under conditions similar to those above to give $[Ru(ttpy)(tpy\text{-}\phi\text{-}NMe_2)]^{2+}$ in high yield (Scheme 7).

The application of cross-coupling procedures to transition metal complexes of polypyridyl ligands is a largely unexplored area, with only a few isolated examples. The preparation of some heteronuclear multimetallic complexes has been achieved by cross-coupling of ruthenium(II) and osmium(II) complexes containing bromo- and ethynyl-substituted 1,10-phenanthroline as ligands,[22] and ruthenium(II) complexes of tributyltin-substituted bipyridines have been reported to undergo Stille couplings with bromoaromatics.[23] Obviously, the complexes above could equally have been prepared by prior formation of the appropriate 4′-aryl-substituted terpyridine ligand, followed by reaction with $Ru(ttpy)Cl_3$, in a more "classical" way. Nevertheless, the successful application of the coupling reactions is attractive, auguring well for the use of $[Ru(ttpy)L^3]^{2+}$ or $[Ru(ttpy)L^7]^{2+}$ as versatile synthons in the preparation of new terpyridyl complexes incorporating more exotic pendent groups including those with functionality which might normally inhibit or interfere with the complexation step.

Photophysical properties

The new complex $[Ru(ttpy)L^3]^{2+}$ displays electronic excited state properties which are typical of bis(terpyridyl)-ruthenium(II) complexes. The UV-visible absorption spectrum (Fig. 1) displays very intense absorption bands in the UV region attributable to ligand-centred (^{1}LC) transitions, and a broad intense band in the visible region (λ_{max} = 490 nm in alcohol or acetonitrile solution) due to metal-to-ligand charge transfer (^{1}MLCT) transitions. Upon excitation into the LC or ^{1}MLCT bands, the complex displays very weak and short-lived luminescence at room temperature (λ_{max} = 646 nm). At lower temperatures (Fig. 2), the emission becomes much more intense, blue-shifted (λ_{max} = 628 nm at 77 K) and longer lived (τ = 11 μs at 77 K). These observations are fully consistent with the well-documented behaviour of complexes based on $[Ru(ttpy)_2]^{2+}$ carrying 4′-aryl substituents.[15] The strong, long-lived luminescence characteristic of a ^{3}MLCT level is largely quenched at all but low temperatures owing to the presence of a thermally accessible metal-centred state, through which deactivation of the emissive state may occur.

As noted above, arylboronic acids are under investigation



Scheme 7 Palladium catalysed cross-coupling of $[Ru(ttpy)L^7]^{2+}$ with 4-(dimethylamino)benzeneboronic acid.

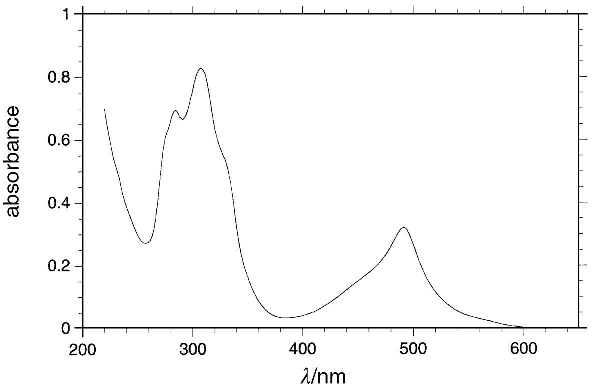


Fig. 1 UV-visible absorption spectrum of [Ru(ttpy)L^3]$(PF_6)_2$ in EtOH–MeOH (1 : 4 v/v) solution at 295 K.

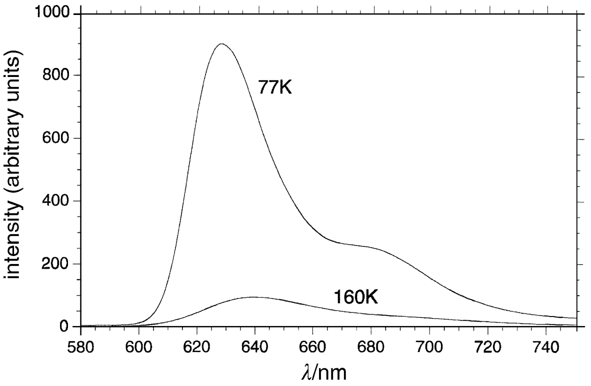


Fig. 2 Emission spectra of [Ru(ttpy)L^3]$(PF_6)_2$ in EtOH–MeOH (1 : 4 v/v) solution at 160 and 77 K; λ_{ex} = 490 nm; excitation and emission bandpass = 7.5 nm.

as sensors for saccharides and other bioactive molecules containing diols, catechols or aminoalcohols. Reversible formation of a boronate ester may occur with such substrates in aqueous solution, and signalling may be achieved through its effect on the light absorption (λ_{max}, ε, circular dichroism) or emission (λ_{max}, I) properties of chromophoric aryl groups.[9] This is often an indirect effect, in the sense that it is the pK_a associated with the $-B(OR)_2 \rightleftharpoons [-B(OR)_2(OH)]^-$ equilibrium that is perturbed (the observed optical property being a function of the coordination at boron). Thus, if a chromophoric boronic acid compound is to be useful, it must, in the first instance, be able to respond to changes in p(OH). Being a photoactive compound containing a boronic acid group, the complex [Ru(ttpy)L^3]$^{2+}$ was of interest in this respect. However, measurement of the UV-visible absorbance spectra over a range of pH values from 2 to 12 revealed no significant changes in the wavelengths of the MLCT or LC absorption maxima, and only minor and poorly reproducible changes in the absorbance values. The emission spectrum was equally insensitive to changes in pH. Clearly then, boronate anion formation has very little effect on the charge-transfer excited states in this complex, making it a poor candidate for further investigation as a sensor. That the compound is indeed able to form a complex with glucose is, however, clear from the electrospray mass spectrum run in the presence of α-D-glucose, which shows well-defined signals corresponding to glucose adducts (data in Experimental section).

The other ruthenium(II) complexes described here for the first time also displayed ground- and excited-state properties which were typical of [Ru(ttpy)$_2$]$^{2+}$ and its derivatives (data for individual complexes are included in the Experimental section). The longest lifetime was observed for the dimethylamino complex, [Ru(ttpy)(tpy-ϕ-NMe$_2$)]$^{2+}$, (τ = 16 μs at 77 K compared to 11 μs for [Ru(ttpy)$_2$]$^{2+}$); it is interesting to note that the analogous methoxy-substituted complex also displays an augmented lifetime (τ = 13 μs at 77 K).[24] The complexes incorporating *para*-substituted biphenyl substituents in the 4′ position, namely [Ru(ttpy)(tpy-ϕ-ϕ-CH$_3$)]$^{2+}$ and [Ru(ttpy)(tpy-ϕ-ϕ-NO$_2$)]$^{2+}$, also emitted strongly at 77 K (λ_{max} = 642 and 638 nm, τ = 11 and 13 μs, respectively), consistent with recent work on 4′-biphenyl-2,2′:6′,2″-terpyridine and its ruthenium(II) complexes.[25]

Summary

Terpyridines are versatile and important ligands for a wide variety of transition metal ions. Bis(terpyridyl)ruthenium(II) complexes, in particular, have seen use in a diverse range of applications (for example, as photosensitisers, as sensors and as components in molecular assemblies for generating charge-separated states). New routes to such ligands and their ruthenium complexes are therefore of considerable interest. We have shown that boronic acid functionality can be introduced into 4′-arylterpyridine ligands using the palladium-catalysed reaction of the bromo-substituted ligand with bis(pinacolato)- or bis(neopentyl glycolato)diboron. This reaction also proceeds when the ligand is itself already bound to a ruthenium(II) ion. The resulting ruthenium complex undergoes palladium-catalysed cross-coupling reactions with aryl halides to generate complexes with "extended" terpyridines; alternatively, a ruthenium(II) complex of 4-bromoterpyridine can be coupled with an arylboronic acid. These procedures may provide access to complexes not readily accessible by other means, and should allow the facile, divergent syntheses of new complexes from the bromo- and boronic acid-substituted compounds.

Experimental

General

2,6-Bis(2′-pyridyl)-4-pyridone was prepared by base-catalysed condensation of acetone with ethylpicolinate followed by ring closure with ammonium acetate, as described by Constable and Ward.[3] Subsequent conversion to 4′-bromo-2,2′:6′,2″-terpyridine (L^5) was accomplished by heating in POBr$_3$ at 110 °C for 5 h; spectroscopic data for the product was consistent with that described previously for this compound obtained using a different route.[26] 4′-(4-Bromophenyl)-2,2′ : 6′, 2″-terpyridine (L^5) was prepared according to the one-pot procedure of Spahni and Calzaferri,[27] and separated from the isomeric by-product, 6′-(4-bromophenyl)-2,2′:4′,2″-terpyridine, as previously reported.[28] Tetrakis(triphenylphosphine)-palladium(0) was obtained by hydrazine reduction of PdCl$_2$ in DMSO in the presence of triphenylphosphine.[29] [1,1′-Bis(diphenylphosphino)ferrocene] palladium dichloride, Pd(dppf)Cl$_2$, was prepared by reaction of dppf with Pd(CH$_3$CN)$_2$Cl$_2$.[30] Other reagents were used as supplied from commercial sources. DMSO was dried over molecular sieves for at least 24 h before use and dimethoxyethane was dried over sodium wire. Acetonitrile for reactions and for chromatography was HPLC grade. Chromatography was carried out on silica gel (60, 40–63μ, Fluorochem) except where stated otherwise. Proton and ^{13}C NMR spectra were recorded on Varian spectrometers: a Mercury-200 (200 and 50.3 MHz respectively), Unity-300 (300 and 75.5 MHz), a 400 MHz (400 and 100.6 MHz) or 500 MHz instrument (500 and 125.9 MHz). Proton spectra were referenced to residual protio solvent resonances (^{1}H spectra: CHCl$_3$ = 7.27; CD$_2$HCN = 1.94; CD$_3$SOCD$_2$H = 2.50; CD$_3$COCD$_2$H = 2.05 ppm); ^{13}C spectra were referenced to solvent carbon resonance (CHCl$_3$ = 77.0; CD$_3$CN = 1.3; CD$_3$COCD$_3$ = 29.8 ppm). ^{11}B spectra were recorded on the Varian Unity-300 operating at 96.2 MHz. ^{1}H–^{1}H COSY, NOESY and ^{1}H–^{13}C HETCOR spectra were recorded on the 400 or 500 MHz instruments. Electrospray mass spectra were measured on a VG Platform

II instrument. UV-Visible absorbance spectra were recorded with a Bio-Tek Instruments Uvikon-XS spectrometer using quartz cuvettes of 1 cm pathlength. Steady-state emission spectra were recorded using an Instruments S.A. Fluromax, or a Perkin-Elmer LS 50B using 1 cm pathlength degassing cuvettes. Samples for time-resolved measurements were excited at 532 nm using the frequency-doubled output of a Nd : YAG laser; the luminescence was detected with a Hamamatsu R928 photomultiplier tube and recorded using a digital storage oscilloscope. An Oxford Instruments variable temperature liquid nitrogen cryostat (DN1704) was used for low temperature measurements, using laboratory-built degassing cuvettes.

Synthetic details

4′-(4-Pinacolatoboronphenyl)-2,2′:6′,2″-terpyridine (L^6). A Schlenk tube was charged with Pd(dppf)Cl_2 (32 mg, 3.87×10^{-5} mol, 0.03 equiv.), KOAc (379 mg, 3.86 mmol, 3 equiv.) and bis(pinacolato)diboron (B_2pin_2 344 mg, 1.35 mmol, 1.05 equiv.) and flushed with nitrogen. DMSO (5 mL, stored over molecular sieves and degassed thoroughly with nitrogen before use) and 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine (L^5, 500 mg, 1.29 mmol) were then added. The mixture was stirred at 80 °C for 6 h under nitrogen. Toluene (50 mL) was added to the product and the toluene–DMSO mixture washed with water (3 × 100 mL) to remove the DMSO from the toluene layer. The aqueous layer was purple at this stage, presumably due to complexation of some terpyridine to iron released on decomposition of the catalyst. The toluene layer was dried over $MgSO_4$ and the solvent removed by rotary evaporation to give a white solid (yield 235 mg, 0.54 mmol, 42%). The product had to be stored under nitrogen to avoid rapid pink coloration due to the high affinity of this terpyridine ligand for iron in the atmosphere. ^1H NMR (300 MHz, $CDCl_3$): δ 8.76 (s, 2H, $H^{3'}$), 8.75 (dm, 2H, J 4.8, 0.9, H^6), 8.66 (d, 2H, J 7.8, H^3), 7.98 (d, 2H, J 8.4, H^{phenyl}), 7.93 (d, 2H, J 8.4, H^{phenyl}), 7.86 (td, 2H, J 7.8, 1.5, H^4), 7.34 (ddd, 2H, J 7.5, 6.3, 1.2 Hz, H^5), 1.39 (s, 12H, CH_3). $^{11}B\{^1H\}$ NMR (96.2 MHz, $CDCl_3$): δ 31.6. EI-MS: *m*/*z* 435 (M^+, 100), 420 ($[M - CH_3]^+$, 9), 349 (18), 336 (51%).

4′-{4-(Neopentyl glycolatoboron)phenyl}-2,2′:6′,2″-terpyridine (L^1). A Schlenk tube was charged with Pd(dppf)Cl_2 (30 mg, 3.6×10^{-5} mol, 0.03 equiv.), KOAc (353 mg, 3.6 mmol, 3 equiv.) and bis(neopentyl glycolato)diboron (B_2neo_2, 285 mg, 1.26 mmol, 1.05 equiv) and flushed with nitrogen. DMSO (12 mL, dried over molecular sieves and degassed with N_2 before use) and 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine (L^5, 466 mg, 1.2 mmol) were then added. After stirring at 80 °C under nitrogen for 5.5 h, the reaction mixture was diluted with toluene (80 mL) and the resulting solution washed with water (4 × 100 mL). The toluene layer was dried over $MgSO_4$ and the solvent removed by rotary evaporation. In some preparations of this compound, the crude product was contaminated with small amounts of B_2neo_2 and required further purification *via* dissolution in 10 mL CH_2Cl_2, addition of MeOH (10 mL) and then removal of CH_2Cl_2 leading to precipitation of the product as a white solid (yield 384 mg, 0.91 mmol, 76%). ^1H NMR (400 MHz, $CDCl_3$) (assigned using ^1H–^1H COSY): δ 8.77 (s, 2H, H^3), 8.75 (d, 2H, J 4.8 $H^{6'}$), 8.68 (d, 2H, J 7.8, $H^{3'}$), 7.94 (d, 4H, J 2.4, phenyls), 7.89 (td, 2H, J 8.1, J 2.1, $H^{4'}$), 7.36 (ddd, 2H, J 7.5, 4.8, 0.9 Hz, $H^{5'}$), 3.82 (s, 4H, neo CH_2), 1.07 (s, 6H, neo CH_3). ^{13}C and ^1H–^{13}C HETCOR (500 MHz, $CDCl_3$): δ 156.2 (C), 155.9 (C), 150.3 (C), 149.1 (CH, H at δ 8.75), 140.3 (C), 136.8 (CH, H at δ 7.90), 134.4 (CH, H at δ 7.94), 126.4 (CH, H at δ 7.94), 123.8 (CH, H at δ 7.36), 121.4 (CH, H at δ 8.68), 118.9 (CH, H at δ 8.77), 72.3 (CH, neo CH_2), 31.9 (C, neo), 21.9 (CH, neo CH_3). $^{11}B\{^1H\}$ NMR (96.2 MHz, $CDCl_3$): δ 27.8. EI-MS: *m*/*z* 421 (M^+, 100), 335 (20), 307 (6), 257 (10%). Elemental analysis for $C_{26}H_{24}N_3BO_2$: calc. C 74.12, H 5.74, N 10.02; found C 74.05, H 5.68, N 9.46%.

4′-(Neopentyl glycolatoboron)-2,2′:6′,2″-terpyridine (L^2). A Schlenk tube was charged with Pd(dppf)Cl_2 (39 mg, 4.8×10^{-5} mol, 0.03 equiv.), KOAc (472 mg, 4.8 mmol, 3 equiv.) and bis(neopentyl glycolato)diboron (380 mg, 1.68 mmol, 1.05 equiv.) and flushed with nitrogen. DMSO (10 mL, dried over molecular sieves and degassed with N_2 before use) and 4′-bromoterpyridine (L^7, 500 mg, 1.6 mmol) were then added. The mixture was stirred at 80 °C for 5.5 h under nitrogen and then diluted with toluene (100 mL) and the organic solution washed with water (4 × 100 mL). The toluene layer was dried over $MgSO_4$ and the solvent removed by rotary evaporation (yield 385 mg, 1.1 mmol, 69%). ^1H NMR (400 MHz, $CDCl_3$) (assigned using ^1H–^1H COSY): δ 8.81 (s, 2H, $H^{3'}$), 8.73 (d, 2H, J 4.2, H^6), 8.63 (d, 2H, J 7.5, H^3), 7.86 (td, 2H, J 7.8, 2.1, H^4), 7.33 (t, 2H, J 4.8 Hz, H^5), 3.83 (s, 4H, neo CH_2), 1.05 (s, 6H, neo CH_3). ^{13}C and ^1H–^{13}C HETCOR (400 MHz, $CDCl_3$): δ 156.6 (C), 154.6 (C), 149.1 (CH, H at δ 8.73), 136.7 (CH, H at δ 7.86), 125.6 (CH, H at δ 8.81), 123.5 (CH, H at δ 7.33), 121.1 (CH, H at δ 8.63), 72.3 (CH, neo CH_2), 31.9 (C, neo), 21.9 (CH, neo CH_3). $^{11}B\{^1H\}$ NMR (96.2 MHz, $CDCl_3$): δ 26.8. EI-MS: *m*/*z* 345 (M^+, 100), 330 ($[M - CH_3]^+$, 59), 260 (54), 233 (61%). Elemental analysis for $C_{20}H_{20}N_3BO_2$: calc. C 69.59, H 5.84, N 12.17; found C 68.13, H 5.81, N 11.54%.

[Ru(ttpy)L^3]$(PF_6)_2$. *Method A*. See Scheme 3. The method used is based on literature methodology for synthesising other $[Ru(ttpy)(tpy\text{-}X)]^{2+}$ complexes.[31] A suspension of Ru(ttpy)Cl_3[31] (162 mg, 3.05×10^{-4} mol) in a mixture of acetone and absolute ethanol (128 and 32 mL, respectively) was heated at 75 °C in the presence of $AgBF_4$ (178 mg, 9.16×10^{-4} mol, 3 equiv.) for 3 h under nitrogen. The solution became brown and the precipitate of AgCl that formed was removed by filtration through Celite. Ethanol (30 mL) was added to the filtrate and the acetone was removed by rotary evaporation without heating. More absolute ethanol was added to give a total volume of 100 mL, followed by L^1 (128 mg, 3.05×10^{-4} mol, 1 equiv.). The solution was heated under nitrogen at reflux for 3.5 h in the dark and the solvent then removed by rotary evaporation. (Note that use of L^6 instead of L^1 and work-up as below leads to the same final product.) The orange residue was dissolved in the minimum volume of acetonitrile and the solution added dropwise to a saturated aqueous solution of KPF_6. The resulting precipitate was washed with water and purified by chromatography on a silica column (30 cm by 4 cm), gradient elution from CH_3CN to 89.8% CH_3CN–10% H_2O–0.2% KNO_3 (sat'd aq.), ($R_f = 0.5$ in 89.9% CH_3CN–10% H_2O–0.1% KNO_3). After a second anion exchange with KPF_6 as above, the product was isolated as a red solid (yield 175 mg, 1.65×10^{-4} mol, 54%). ^1H NMR (500 MHz, CD_3CN) (assigned using ^1H–^1H COSY 400 MHz and NOESY 500 MHz): δ 9.03 (s, 2H, $H^{3'}$ ttpy), 8.97 (s, 2H, $H^{3'}$ boronic-tpy), 8.64 (m, 4H, H^3 both terpys), 8.21 (d, 2H, J 8.4, H^2 phenyl of ttpy), 8.13 [m, 6H, H^2 $(HO)_2B$-phenyl and H^3 phenyl of ttpy], 7.94 (t, 4H, J 7.8, H^4 both terpys), 7.59 [d, 2H, J 8.1 Hz, H^3 $(HO)_2B$-phenyl], 7.43 (m, 4H, H^6 both terpys), 7.18 (m, 4H, H^5 both terpys), 6.31 [s, 2H, $B(OH)_2$], 2.54 (s, 3H, tolyl CH_3). ^{13}C (400 MHz, CD_3CN) and ^1H–^{13}C HETCOR (500 MHz, CD_3CN): δ 159.2 (C), 156.5 (C), 156.3 (C), 153.4 (CH, H at δ 7.43), 139.0 (CH, H at δ 7.94), 136.2 (CH, H at δ 8.13), 131.3 (CH, H at δ 7.59), 128.6 and 128.4 (one is CH, H at δ 8.13), 128.4 (CH, H at δ 7.18), 127.9 (C), 125.5 (CH, H at δ 8.64), 122.7 (CH, H at δ 9.03), 122.3 (CH, H at δ 9.00), 21.4 (tolyl CH_3). ES-MS from MeOH: *m*/*z* 950 {$[(MeOBOMe)PF_6]^+$ adduct, 5}, 936 {$[(MeOBOH)PF_6]^+$ adduct, 3}, (403 ($[MeOBOMe]^{2+}$ adduct, 100), 396

([MeOBOH]$^{2+}$ adduct, 28%]. ES-MS in the presence of *ca.* 0.15 M α-D-glucose: *m*/*z* 460 ([glucose]$^{2+}$ adduct, 26), 395 ([MeOBOH]$^{2+}$ adduct, 46), 219 ([glucose + K]$^{+}$, 100), 203 ([glucose + Na]$^{+}$, 78%). UV-Vis λ_{max}/nm (ε/M^{-1} cm^{-1}) (CH_3CN): 490 (10 670), 310 (27 480), 285 (27 790). Emission (λ_{ex} = 490 nm, 293 K, H_2O): λ_{max} = 650 nm. Absorbance and emission spectra in alcohol solution are given in Fig. 1 and 2.

[Ru(ttpy)L^5](PF$_6$)$_2$. This complex was prepared in the same way as [Ru(ttpy)L^3](PF$_6$)$_2$, from Ru(ttpy)Cl$_3$ (314 mg, 5.91 × 10^{-4}) mol) and L^5 in place of L^3. In this case, the product (as its PF$_6{}^-$ salt) eluted in neat CH_3CN and was obtained as a red solid after removal of the solvent (306 mg, 2.78 × 10^{-4} mol, 47%). ^{1}H NMR (500 MHz, CD_3CN) (assigned using ^{1}H–^{1}H NOESY): δ 9.00 (s, 2H, H$^{3'}$ one terpy only), 8.99 (s, 2H, H$^{3'}$ one terpy only), 8.64 (d, 4H, *J* 8.0, H^3 both terpys), 8.12 (dd, 4H, *J* 8.6, 2.3, H^2 phenyl both terpys), 7.94 (m, 6H, H^4 and probably H^3 4-Br-phenyl-tpy), 7.58 (d, 2H, *J* 8.1, H^3 ttpy), 7.43 (t, 4H, *J* 6.4 Hz, H^6 both terpys), 7.18 (m, 4H, H^5 both terpys), 2.54 (s, 3H, tolyl CH_3). ^{13}C and ^{1}H–^{13}C HETCOR (500 MHz, CD_3CN): δ 159.1 (C), 159.0 (C), 156.4 (C), 156.2 (C), 153.3 (CH, H at δ 7.43), 149.2 (C), 147.8 (C), 141.9 (C), 138.9 (CH, H at δ 7.94), 136.9 (C), 134.8 (C), 133.6 (CH, H at δ 7.94), 131.1 (CH, H at δ 7.58), 130.5 (CH, H at δ 8.12), 128.5,† 128.4,† 128.3,† 125.4 (CH, H at δ 8.64), 125.4 (CH, H at δ 8.64), 122.3 (CH, H at δ 9.00 or 8.99), 122.2 (CH, H at δ 9.00 or 8.99), 21.3 (tolyl CH_3). ES-MS: *m*/*z* 957 ([MPF$_6$]$^+$, 3), 405, 407 ([M]$^{2+}$, 55%).

[Ru(ttpy)L^3](PF$_6$)$_2$. *Method B.* See Scheme 4. The compounds B$_2$neo$_2$ (68 mg, 2.99 × 10^{-4} mol, 2 equiv.), PdCl$_2$(dppf) (12 mg, 1.50 × 10^{-5} mol, 0.1 equiv.), KOAc (59 mg, 5.99 × 10^{-4} mol, 4 equiv.) and dppf (8 mg, 1.50 × 10^{-5} mol, 0.1 equiv.), were added to [Ru(ttpy)L^5](PF$_6$)$_2$ (165 mg, 1.50 × 10^{-4} mol) in a small Schlenk tube under nitrogen. DMSO (3 mL, dried over molecular sieves and degassed with nitrogen prior to use) was added with a syringe and the reaction heated at 80 °C under nitrogen. After 22 h, TLC (on silica with 0.2% KNO_3–10% H_2O–89.8% CH_3CN as eluant) showed that the starting material had been partially converted to product. The reaction mixture was then subjected to anion exchange with KPF_6 and chromatographed on silica leading, after further anion exchange, to the pure product as a red solid with spectroscopic characterisation as above (yield 9 mg, 8.43 × 10^{-6} mol, 6%). It was noted that some faster-moving fractions contained [Ru(ttpy)(4′-phenyl-terpy)](PF$_6$)$_2$ due to loss of the boronic acid group; ES-MS: *m*/*z* 878 ([MPF$_6$]$^+$) and 366 [M^{2+}]. Other work in our laboratory has shown that boronic acid substituents are lost rapidly in the presence of iridium(III).

[(ttpy)Ru(tpy-ϕ-ϕ-tpy)Ru(ttpy)](PF$_6$)$_4$. The dinuclear complex was obtained upon heating the following reagents in DMSO (1.5 mL) at 80 °C under nitrogen for 25 h: B$_2$neo$_2$ (134 mg, 5.95 × 10^{-4} mol, 4 equiv.), PdCl$_2$(dppf) (37 mg, 4.46 × 10^{-5} mol, 0.3 equiv.), KOAc (175 mg, 1.78 × 10^{-3} mol, 12 equiv.), dppf (25 mg, 4.46 × 10^{-5} mol, 0.3 equiv.) and [Ru(ttpy)L^5](PF$_6$)$_2$ (164 mg, 1.49 × 10^{-4} mol). (Note: a control reaction without the B$_2$neo$_2$ led to the formation of the same product, showing that the product may form by palladium-catalysed homo-coupling of the bromo complex.) After reaction, the mixture was subjected to anion exchange with KPF_6 and chromatographed on silica with CH_3CN–H_2O–KNO_3 (aq), as above; (R_f = 0.25 in 89.8% CH_3CN–10% H_2O–0.2% KNO_3). After further anion exchange with KPF_6, the product was obtained as a red solid (yield 18 mg, 8.81 × 10^{-6} mol, 6%).^{1}H NMR (200 MHz, [^{2}H$_6$]DMSO) as lit.[17] ^{1}H NMR (500 MHz, CD_3CN) (assigned using ^{1}H–^{1}H NOESY): δ 9.12 (s, 4H, H$^{3'}$, bridging terpy), 9.02 (s, 4H, H$^{3'}$, ttpy), 8.70 (d, 4H, *J* 8.6, H^3 bridging terpy), 8.69 (d, 4H, *J* 8.8, H^3 on ttpy), 8.43 (d, 4H, *J* 8.4, H^c or H^d), 8.25 (d, 4H, *J* 8.4, H^c or H^d), 8.13 (d, 4H, *J* 8.0, H^b), 7.98 (m, 8H, H^4, both terpys), 7.60 (d, 4H, *J* 8.0, H^a), 7.47 (d, 8H, *J* 5.6, H^6), 7.21 (t, 8H, *J* 7.2 Hz, H^5), 2.55 (s, tolyl CH_3). ES-MS: *m*/*z* 878 ([M + 2PF$_6$]$^{2+}$, 4), 536 ([MPF$_6$]$^{3+}$, 18), 366 ([M]$^{4+}$, 100%). UV-Vis λ_{max}/nm (CH_3CN): 495, 311, 286; [0.1 M KNO_3 (aq)]: 495, 330 (br), 277. Emission [λ_{ex} = 495 nm, 0.1 M KNO_3 (aq)]: λ_{max} = 650 nm.

Cross-coupling reaction of [Ru(ttpy)L^3]$^{2+}$ with 4-bromotoluene. A solution of 4-bromotoluene (36 mg, 2.14 × 10^{-4} mol, 2 equiv.) in 1,2-dimethoxyethane (DME, 0.5 mL) was added to a suspension of Pd(PPh$_3$)$_4$ (7.4 mg, 6.41 × 10^{-6} mol, 0.06 equiv. in the same solvent (0.5 mL). The mixture was stirred for 10 min while degassing with N_2. To this solution was added [Ru(ttpy)L^3](PF$_6$)$_2$ (114 mg, 1.07 × 10^{-4} mol, in 2 mL DME and 2 mL EtOH) and then aqueous sodium carbonate (2 M, 160 μL, 3 equiv.). The solution was heated to reflux under N_2 for 1.5 h, after which a further 1 mL of CH_3CN was added. Reflux was continued for 6 h under N_2. The reaction mixture was subjected to anion exchange with KPF_6 solution, and then chromatographed on silica using acetonitrile–acetone (1 : 1) as the eluant. The first main band which eluted gave the required product upon removal of the solvent (yield 74 mg, 6.65 × 10^{-5} mol, 62%). ^{1}H NMR (500 MHz, CD_3CN) (assigned using ^{1}H–^{1}H COSY and NOESY): δ 9.06 (s, 2H, H$^{3'}$ Me-ϕ-ϕ-tpy), 9.00 (s, 2H, H$^{3'}$ ttpy), 8.66 (dd, 4H, *J* 7.8, 5.0 Hz, H^3 both terpys), 8.30 (d, 2H, *J* 8.6, H^b), 8.12 (d, 2H, *J* 8.2, H^2 phenyl of ttpy), 8.02 (d, 2H, *J* 8.6, H^a), 7.94 (m, 4H, H^4 both terpys), 7.75 (d, 2H, *J* 8.2, H^y), 7.68 (d, 2H, *J* 8.0, H^3 phenyl of ttpy), 7.44 (d, 4H, *J* 5.4, H^6 both terpys), 7.39 (d, 2H, *J* 8.0, H^x), 7.18 (t, 4H, *J* 6.2 Hz, H^5 both terpys), 2.54 (s, 3H, tolyl CH_3), 2.44 (s, 3H, CH_3 Me-ϕ-ϕ-tpy). ^{13}C and ^{1}H–^{13}C HETCOR (500 MHz, CD_3CN): δ 159.2 (C), 156.4 (C), 156.4 (C), 153.4 (H at δ 7.44), 153.4 (H at δ 7.44), 149.3 (C), 148.7 (C), 143.7 (C), 142.0 (C), 139.3 (C), 139.0 (H at δ 7.94), 137.6 (C), 136.3 (C), 134.9 (C), 131.2 (H at δ 7.68), 130.7 (H at δ 7.39), 129.2 (probably H at δ 8.30), 128.7 (probably H at δ 8.02), 128.6 (probably H at δ 8.12), 128.4 (probably H at δ 7.18), 127.9 (probably H at δ 7.75), 125.5 (H at δ 8.66), 122.3 (Hs at δ 9.00 and 9.06), 21.4 (H at δ 2.54), 21.2 (H at δ 2.44). ES-MS: *m*/*z* 968 ([MPF$_6$]$^+$, 5), 411 ([M]$^{2+}$, 100%). UV-Vis λ_{max}/nm (CH_3CN): 492, 330 (sh), 311, 284; [KNO_3 (aq)]: 507, 344, 325, 290. Emission [λ_{ex} = 507 nm, 293 K, KNO_3 (aq)]: λ_{max} = 672 nm.

Cross-coupling reaction of [Ru(ttpy)L^3]$^{2+}$ with 1-iodo-4-nitrobenzene. A solution of 1-iodo-4-nitrobenzene (41 mg, 1.65 × 10^{-4} mol, 2 equiv.) in DME (0.6 mL) was added to a suspension of Pd(PPh$_3$)$_4$ (8 mg, 6.92 × 10^{-6} mol, 0.08 equiv.) in the same volume of DME. The mixture was degassed with N_2 for 5 min. [Ru(ttpy)L^3](PF$_6$)$_2$ (88 mg, 8.24 × 10^{-5} mol, 1 equiv.) in solution in a mixture of CH_3CN (2 mL), DME (3 mL) and EtOH (2 mL) was then added, followed by 2M Na_2CO_3 (aq) (124 μL, 3 equiv.). The mixture was degassed for a further 5 min and then heated at reflux (85 °C) for 5 h under N_2, after which TLC on silica (0.2% KNO_3–10% H_2O–89.8% CH_3CN) revealed the complete consumption of the starting material. After anion exchange with KPF_6, the crude product was chromatographed on silica with acetonitrile–acetone (1 : 1) as the initial eluant, the polarity being increased with water–KNO_3 (aq). The product eluted at 10% H_2O–0.1% KNO_3 but TLC of this fraction showed the presence of a second compound of similar R_f. ES-MS indicated that the desired [Ru(ttpy)(tpy-ϕ-ϕ-NO$_2$)]$^{2+}$ had been obtained along

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† Not clear which is which but two cross-peaks with hydrogen atoms at δ 8.12 and 7.18.

with a significant amount of [Ru(ttpy)(tpy-ϕ-OH)]$^{2+}$. Chromatography was repeated using a superior grade of silica (ICN Biomedicals, 32–63, 60 Å) and CH_3CN as the principal eluant rather than a mixture of acetonitrile and acetone. The polarity of the eluant was increased as before and the fractions subjected to anion exchange with KPF_6. Although, again, the bulk of the product eluted as a mixture, a small amount of [Ru(ttpy)(tpy-ϕ-ϕ-NO_2)]$^{2+}$ was obtained free of the second complex (yield 6 mg, 6%); spectroscopic data was consistent with that for the product obtained from reaction of Ru(ttpy)Cl_3 with the *ligand* tpy-ϕ-ϕ-NO_2.[32] ^1H NMR (500 MHz, d^6-acetone) (assigned using ^1H–^1H NOESY): δ 9.41 (s, 2H, H$^{3'}$, NO_2-ϕ-ϕ-tpy), 9.31 (s, 2H, H$^{3'}$, ttpy), 8.95 (two overlapping d, 4H, *J* 9, H^3 both terpys), 8.43 (d, 2H, *J* 8.5, H^b), 8.32 (d, 2H, *J* 8.5, H^x), 8.15 (d, 2H, *J* 8.5, H^2 phenyl ttpy), 8.10 (d, 2H, *J* 8.5, H^a), 8.07 (d, 2H, *J* 8.5, H^y), 7.99 (two overlapping m, 4H, apparent *J* 7.5, H^4 both terpys), 7.72 (two overlapping m, 4H, apparent *J* 5, H^6 both terpys), 7.46 (d, 2H, *J* 8.5, H^3 phenyl ttpy), 7.24 (two overlapping m, apparent *J* 6.5 Hz, H^5 both terpys), 2.42 (s, 3H, CH_3). ES-MS: *m/z* 999 ([MPF_6]$^+$, 3), 426 ([M]$^{2+}$, 100%). UV-Vis (CH_3CN) λ_{max}/nm: 492, 328 (sh), 311, 285 (sh).

[Ru(ttpy)(L^7)](PF_6)$_2$. This complex was prepared in the same way as [Ru(ttpy)L^3](PF_6)$_2$ (method A, above) from Ru(ttpy)Cl_3 (321 mg, 6.05×10^{-4} mol, 1 equiv.) but using ligand L^7 (189 mg, 6.05×10^{-4} mol) in place of L^3. At the end of the reaction in ethanol, a precipitate formed rapidly which was collected by centrifugation and washed once with ethanol. The ^1H NMR of the solid, after anion exchange with KPF_6, showed a good level of purity of the desired product. Nevertheless, further purification was carried out by chromatography under the conditions described above followed by anion exchange of the eluted fractions, leading to the desired complex as a red–brown solid (yield 329 mg, 3.21×10^{-4} mol, 53%). ^1H NMR (500 MHz, CD_3CN) (assigned using ^1H–^1H COSY and NOESY): δ 8.98 (s, 4H, H$^{3'}$ both terpys), 8.63 (d, 2H, *J* 8.0, H^3 one terpy only), 8.49 (d, 2H, *J* 7.8, H^3 one terpy only), 8.10 (d, 2H, *J* 8.4, H^2 phenyl), 7.94 (td, 4H, *J* 7.9, 1.4, H^4 both terpys), 7.57 (d, 2H, *J* 8.0, H^3 phenyl), 7.45 (dd, 2H, *J* 5.4, 0.8, H^6 one terpy only), 7.37 (dd, 2H, *J* 5.4, 0.8 Hz, H^6 one terpy only), 7.18 (m, 4H, H^5 both terpys), 2.53 (s, 3H, tolyl CH_3). ^{13}C and ^1H–^{13}C HETCOR (500 MHz, CD_3CN): δ 158.4 (C), 157.3 (C), 156.5 (C), 155.5 (C), 152.8 (C), 148.9 (CH, Hs at δ 7.45 and 7.37), 141.4 (C), 138.4 (C), 134.1 (CH, H at δ 7.94), 130.6 (C), 128.1 (C), 127.9 (C), 127.6 (C), 127.0 (CH, H at δ 7.57), 125.1 (CH, H at δ 7.18), 124.8 (CH, H at δ 8.10 and 7.18), 123.6‡ (CH, H at δ 8.98), 121.7 (CH, Hs at δ 8.63 and 8.49), 20.7 (tolyl CH_3). ES-MS: *m/z* 882 ([MPF_6]$^+$, 11), 367 ([M]$^{2+}$, 100%). UV-Vis λ_{max}/nm (CH_3CN): 486, 308, 283, 275; [KNO_3 (aq)]: 485, 307, 282, 274. Emission [λ_{ex} = 485 nm, 293 K, KNO_3 (aq)]: λ_{max} = 650 nm.

Reaction of [Ru(ttpy)L^7](PF_6)$_2$ with B_2neo_2, leading to [Ru(ttpy)(tpy-OH)]$^{2+}$. Dry, degassed DMSO (3 mL) was added to a mixture of [Ru(ttpy)L^7](PF_6)$_2$ (126 mg, 1.23×10^{-4} mol), B_2neo_2 (55 mg, 2.46×10^{-4} mol, 2 equiv.), $PdCl_2$(dppf) (10.1 mg, 1.23×10^{-5} mol, 0.1 equiv.) and KOAc (48 mg, 4.91×10^{-4} mol, 4 equiv.) in a small Schlenk tube under nitrogen, and the mixture heated at 80 °C. After 3 h, dppf (7 mg, 1.23×10^{-5} mol, 0.1 equiv.) was added, and heating continued for a further 2.5 h. After anion exchange with KPF_6, the residue was chromatographed on silica, initial eluant acetonitrile–acetone (1 : 1), and polarity increased with H_2O and KNO_3 (aq). The fractions containing a pure product eluted with 0.4–0.8% KNO_3 and 12% H_2O in CH_3CN–Me_2CO (1 : 1) and were subjected to further anion exchange with KPF_6. The product was identified by NMR and MS as [Ru(ttpy)(tpy-OH)](PF_6)$_2$ (yield 20 mg, 2.08×10^{-5} mol, 17%). ^1H NMR (500 MHz, CD_3CN) (assigned using ^1H–^1H COSY): δ 8.96 (s, 2H, H$^{3'}$ ttpy), 8.62 (d, 2H, *J* 8.0, H^3 ttpy), 8.40 (d, 2H, *J* 8.4, H^3 HO-tpy), 8.22 (s, 2H, H$^{3'}$, HO-tpy), 8.09 (d, 2H, *J* 8.0, H^2 phenyl), 7.90 (two overlapping m, 4H, apparent *J* 8.4, H^4 both terpys), 7.57 (d, 2H, *J* 7.8, H^3 phenyl), 7.45 (d, 2H, *J* 5.0, H^6 one terpy), 7.36 (d, 2H, *J* 5.4 Hz, H^6 one terpy), 7.15 (two overlapping m, 4H, H^5 both terpys), 2.53 (s, 3H, tolyl CH_3). ES-MS: *m/z* 672 ([M]$^+$, 12), 336 ([M]$^{2+}$, 100%). UV-Vis λ_{max}/nm (CH_3CN): 490, 303, 284, 273 sh; [in KNO_3 (aq)]: 498, 304, 280. Emission (λ_{ex} = 498 nm, 293 K, KNO_3 (aq)]: λ_{max} = 651 nm.

Cross-coupling reaction of [Ru(ttpy)L^7](PF_6)$_2$ with 4′-(dimethylamino)benzeneboronic acid. A solution of [Ru(ttpy)L^7](PF_6)$_2$ (196 mg, 1.94×10^{-4} mol, 1 equiv.) in DMSO (7 mL) was added to $Pd(PPh_3)_4$ (13 mg, 1.15×10^{-5} mol, 0.06 equiv.) in the same solvent (1 mL) in a small Schlenk tube under nitrogen. The mixture was stirred for 10 min while degassing with N_2. A suspension of 4-(dimethylamino)benzeneboronic acid (63 mg, 3.82×10^{-4} mol, 2 equiv.) in DMSO (3 mL) was added to the solution, followed by 2 M Na_2CO_3 (aq) (288 μL, 3 equiv.). The mixture was degassed further before heating at 85 °C for 18 h under N_2. TLC after 18 h showed that the starting complex had been completely consumed. It should be noted that under different reaction conditions (DME–CH_3CN–EtOH as the solvent system and reaction time of 6 h) only partial conversion to product occurred. The reaction mixture was diluted with CH_3CN and added dropwise to a saturated KPF_6 (aq) solution. The precipitate which initially formed was washed with water and found to be the spectroscopically pure product (yield 126 mg, 1.18×10^{-4} mol, 61%). A further 56 mg of crude product subsequently precipitated, which could be purified chromatographically on silica using CH_3CN–acetone, H_2O and KNO_3 as the eluants. ^1H NMR (500 MHz, d^6-acetone) (assigned using ^1H–^1H NOESY): δ 9.38 (s, 2H, H$^{3'}$ ttpy or Me_2N-ϕ-tpy), 9.30 (s, 2H, H$^{3'}$ ttpy or Me_2N-ϕ-tpy), 9.00 (dd, 4H, *J* 7.8, 5.3, H^3 both terpys) 8.22 (m, 4H, H^2 on phenyl both terpys), 8.05 (tdd, 4H, *J* 9.0, 3.5, 1.3, H^4 both terpys), 7.81 (d, 2H, *J* 5.0, H^6 either ttpy or Me_2N-ϕ-tpy), 7.74 (d, 2H, *J* 4.8, H^6 either ttpy or Me_2N-ϕ-tpy), 7.54 (d, 2H, *J* 8.0, H^3 on phenyl ttpy), 7.30 (m, 4H, H^5, both terpys), 7.01 (d, 2H, *J* 9.0 Hz, H^3 on phenyl Me_2N-ϕ-tpy), 3.13 [s, 6H, $(CH_3)_2N$], 2.49 (s, 3H, ttpy CH_3). ^{13}C NMR (500 MHz, d^6-acetone): δ 159.74, 159.58, 156.81, 156.19, 153.45, 153.19, 149.53, 148.85, 141.69, 138.95, 134.67, 131.14, 131.04, 129.42, 128.58, 128.44, 125.42, 125.41, 123.62, 121.98, 120.31, 113.24, 40.23 [$(CH_3)_2N$], 21.34 (ttpy CH_3). ES-MS: *m/z* 388 ([M]$^{2+}$, 100%). UV-Vis λ_{max}/nm (CH_3CN): 501, 310, 286 (sh) nm. Emission (λ_{ex} = 498 nm, 293 K, CH_3CN): λ_{max} = 659 nm.

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