DOI: 10.1002/asia.200900485

Alkylations of N^4-(4-Pyridyl)-3,5-di(2-pyridyl)-1,2,4-triazole: First Observation of Room-Temperature Rearrangement of an N^4-Substituted Triazole to the N^1 Analogue

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Abstract: Attempts to use alkylation to introduce a positive charge at the nitrogen atom of the 4-pyridyl ring in the bis(bidentate) triazole ligand N^4-(4-pyridyl)-3,5-di(2-pyridyl)-1,2,4-triazole (pydpt) were made to ascertain what effect a strongly electron-withdrawing group would have on the magnetic properties of any subsequent iron(II) complexes. Alkylation of pydpt under relatively mild conditions led in some cases to unexpected rearrangement products. Specifically, when benzyl bromide is used as the alkylating agent, and the reaction is carried out in refluxing acetonitrile, the N^4 substituent moves to the N^1 position. However, when the same reaction is performed in dichloromethane at room temperature, the rearrangement does not occur and the desired product containing an alkylated N^4 substituent is obtained. Heating a pure sample of N^4-Bzpydpt·Br to reflux in MeCN resulted in clean conversion to N^1-Bzpydpt·Br. This is consistent with N^4-Bzpydpt·Br being the kinetic product whereas N^1-Bzpydpt·Br is the thermodynamic product. When methyl iodide is used as the alkylating agent, the N^4 to N^1 rearrangement occurs even at room temperature, and at reflux pydpt is doubly alkylated. The observation of the lowest reported temperatures for an N^4 to N^1 rearrangement is due to this particular rearrangement involving nucleophilic aromatic substitution: a possible mechanism for this transformation is suggested.

Keywords: alkylation · iron · N ligands · structure elucidation · triazoles

Introduction

Our primary interest in N^4-substituted 3,5-di(2-pyridyl)-1,2,4-triazoles stems from the observation of spin-crossover (SCO) transitions in iron(II) complexes when these ligands are incorporated into the coordination sphere.[1–3] Amongst other possible variations, the general route to N^4-substituted 3,5-di(2-pyridyl)-1,2,4-triazoles (Rdpt) developed in this group provides access to Rdpt with almost any substituent at the N^4 position.[4] We have used a range of such Rdpt ligands to prepare families of iron(II) complexes (Figure 1).[3,5] The electron-donating and -withdrawing ability of the N^4 substituent is an obvious feature to vary as this should alter the nature of the triazole ring and hence change the ligand-field strength of the resulting ligand. To

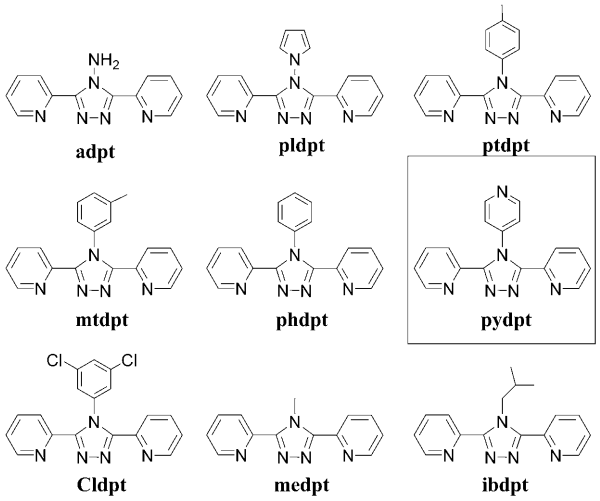

Figure 1. N^4-substituted-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole ligands (Rdpt) used in this and previous studies. The ligand in the box is pydpt, which was employed in this study.

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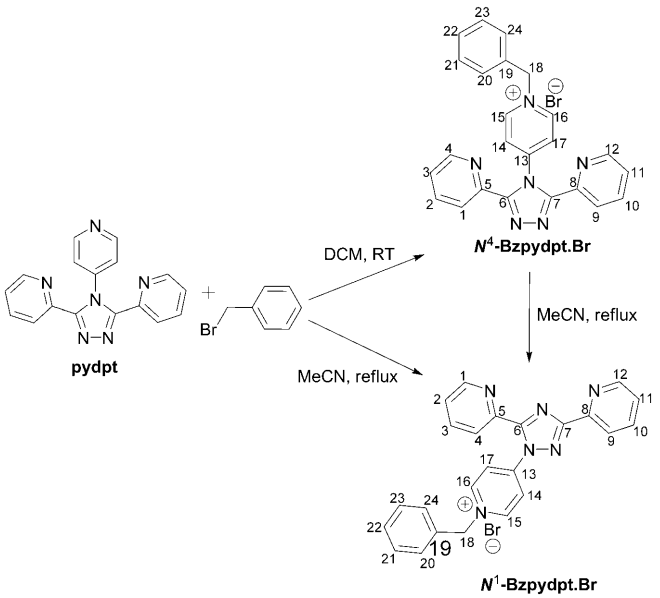
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.200900485.

date, the N^4 substitutents employed in Rdpt ligands from which iron(II) complexes have been prepared have included amino, pyrrolyl, phenyl, tolyl, 4-pyridyl, 3,5-dichlorophenyl, isobutyl, and methyl (Figure 1).[1–3,5] Although there are both electron-donating and -withdrawing substituents in this selection, we have observed that the differences in the iron(II) complexes of these Rdpt ligands are not always as substantial as were hoped for. What is missing from this family is a highly electron-withdrawing N^4 substituent. One way of producing a very electron-withdrawing substituent is to introduce a positive charge on the N^4 substituent. Ligands with a positive charge have been utilized by other research groups to prepare iron(II) complexes. Of most interest here is the work initiated by Constable and co-workers, in which terpyridine ligands with a pendant 4-pyridyl group were alkylated with a variety of alkylating agents, and the resulting positively charged ligands were successfully complexed.[6–8] Since our pydpt ligand contains a 4-pyridyl group as the N^4 substituent, in principle an analogous alkylation would be a convenient route to an Rdpt ligand with the desired positive charge. In turn, this should allow us to investigate how such a strongly electron-withdrawing group affects the magnetic behavior of the subsequently prepared iron(II) complexes.



Scheme 1. Observed products of alkylations of pydpt with 10 equivalents of benzyl bromide; subsequent conversion of N^4-Bzpydpt·Br into N^1-Bzpydpt·Br.

Results and Discussion

Preparation of Compounds

The alkylating agent chosen for the initial experiments was benzyl bromide. A similar procedure to that employed by Constable and co-workers to alkylate terpyridine ligands was followed:[7] pydpt was dissolved in acetonitrile, 10 equivalents of benzyl bromide was added, and the solution was heated at reflux for 3 hours. When the solution was cooled to room temperature, a white solid precipitated. Filtering and drying in vacuo resulted in a sample that gave microanalytical data that is consistent with that expected for the desired benzylated ligand with a bromide counter anion, N^4-(4-benzylpyridinium)-3,5-di(2-pyridyl)-1,2,4-triazole bromide (N^4-Bzpydpt·Br), in 39% yield. However, the reduced symmetry evident from the ^{1}H NMR spectrum indicated that the N^4 substituent had shifted to the N^1 position, giving N^1-(4-benzylpyridinium)-3,5-di(2-pyridyl)-1,2,4-triazole bromide (N^1-Bzpydpt·Br), in which the two 2-pyridyl rings are not equivalent (Scheme 1).

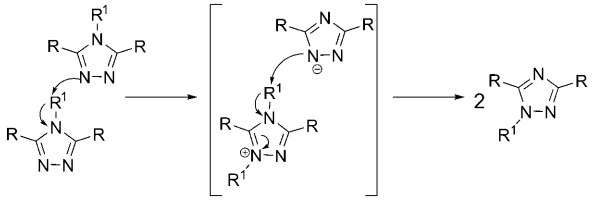
The reaction product was crystallized as the BF_4 salt by allowing an aqueous solution of it and excess aqueous ammonium tetrafluoroborate to stand at room temperature. Single-crystal X-ray structure determination of the resulting large colorless blocks confirmed them to be N^1-Bzpydpt·BF_4 (Figure 3, see below). Subsequent cooling of the aqueous solution to 4°C gave a bulk, analytically pure, crystalline sample in an overall yield of 99%.

Although this rearrangement was interesting, the N^4-substituted compound N^4-Bzpydpt·Br was still required for complexation studies. As reaction at 81°C (b.p. of MeCN) gave N^1-Bzpydpt·Br, the reaction was instead carried out at room temperature in the hope of avoiding the rearrangement. These Rdpt ligands are highly soluble in chlorinated solvents, so the reaction was attempted in dichloromethane (DCM; Scheme 1). An excess (10 equivalents) of benzyl bromide was added to a solution of pydpt in DCM to afford a white precipitate. Elemental analysis of the white powder after drying in vacuo gave data consistent with the pure benzylated product Bzpydpt·Br (80% yield). The ^{1}H NMR spectrum showed only one set of signals for the two 2-pyridyl rings; thus, the substituent had remained at the N^4 position and the desired product N^4-Bzpydpt·Br was obtained. When this room-temperature reaction is carried out in MeCN rather than DCM the same outcome is observed, but the reaction is slower and the desired product does not precipitate directly from the reaction solution, so the workup is less convenient. The solubility of the N^4-substituted variant differs from that of the N^1-substituted variant. This difference was particularly noticeable during the conversion of the bromide salt into the tetrafluoroborate salt, as the N^4-substituted product precipitated immediately (in 64% yield; see below for X-ray structure determination; Figure 4) and did not require cooling to 4°C as was required for the N^1-substituted product.

Heating N^4-Bzpydpt·Br, obtained from the room-temperature alkylation in DCM, to reflux in acetonitrile yields the rearranged product N^1-Bzpydpt·Br. This clean conversion indicates that N^4-Bzpydpt·Br is the kinetic product, whereas N^1-Bzpydpt·Br is the thermodynamic product of monoalkylation of pydpt.

Such rearrangements in 1,2,4-triazoles are not unprecedented; there are reports of similar rearrangements in which the N^4 substituents used were either alkyl or allyl.[9,10] However, in all of the systems studied to date the reactions re-

quired high temperatures, typically above 300 °C, and most were carried out in sealed glass tubes. The lowest temperature reported prior to the present study is 150 °C (and not in a sealed tube) for 4-phenacyl-1,2,4-triazole.[10] In that case the accepted mechanism involves two S_N2 type reactions (Scheme 2). The first reaction involves the formation of the



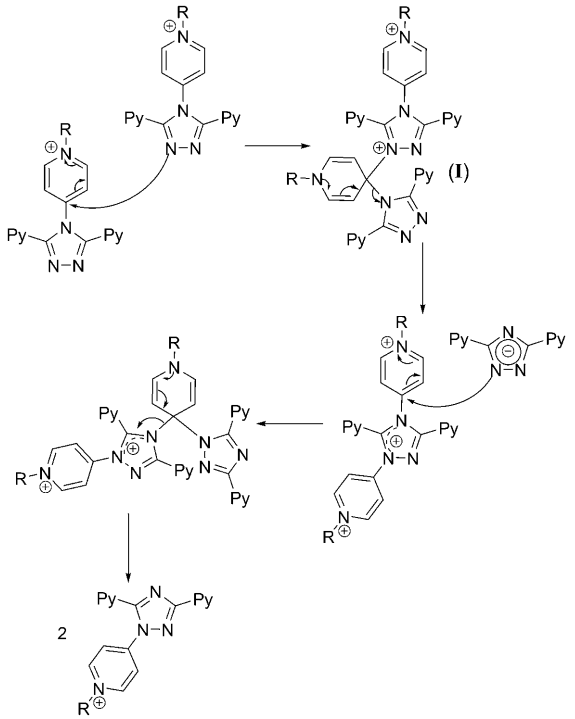
Scheme 2. The accepted mechanism of N^4 to N^1 rearrangement in 4-substituted-1,2,4-triazoles.

intermediate ion pair (triazolium/triazolate) in which a second *N* substituent attaches to the N^1 position of what becomes a triazolium cation, and the resulting triazolate anion has lost all *N* substituents. The second nucleophilic attack occurs between the resulting ions whereby the N^1 atom of the triazolate anion attacks the N^4 substituent on the triazolium cation to give the N^1-substituted 1,2,4-triazole products.

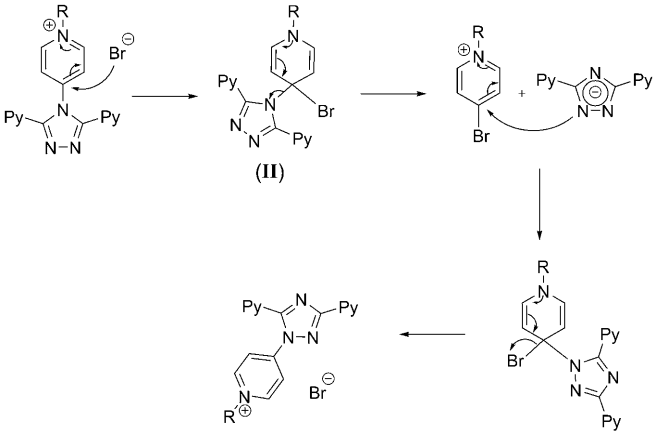
In our system, the mechanism, rather than being S_N2 like, would most likely be an aromatic nucleophilic substitution reaction (Schemes 3 and 4). Instead of R = alkyl or allyl, in our case R is a highly electron-withdrawing, positively charged, benzylated (and hence activated towards nucleophilic substitution) 4-pyridyl ring. This highly polarized N^4 substituent will be more susceptible to nucleophilic attack at C^4, thus significantly lowering the energy barrier towards rearrangement and leading to the low rearrangement temperature we observed (refluxing MeCN, 81 °C). Consistent with this view, heating the unalkylated, R = 4-pyridyl, starting material pydpt at reflux in MeCN, or even at 150 °C in 1-methyl-2-pyrrolidinone, gave no rearranged product. Unchanged starting material was recovered in both cases along with partial decomposition products in the case of the 150 °C reaction. Thus, it is the benzylation of the 4-pyridyl substituent that activates the system towards the observed N^4 to N^1 rearrangement.

Two plausible mechanisms, both of which involve nucleophilic attack at the C^4 position of the 4-pyridyl ring, are proposed for the rearrangement (Schemes 3 and 4). The first is similar to the previous triazole rearrangement reactions in that the N^1 nitrogen atom of a second triazole species acts as the nucleophile; therefore, the rearrangement might proceed as shown in Scheme 3.

This mechanism would involve a relatively bulky nucleophile that would generate a sterically demanding intermediate **I** (Scheme 3). Alternatively, the nucleophile might be a bromide anion, for which the reaction would proceed in a similar fashion (Scheme 4), only this time the intermediate **II** would be less sterically cumbersome. Such mechanisms are not unprecedented; in 2001, Castagnoli Jr and co-workers proposed a similar mechanism for the rearrangement of some indazolyl derivatives.[11]



Scheme 3. Postulated mechanism for the observed N^4 to N^1 rearrangement (in which the nucleophile is a second triazole species) when alkylation is carried out with a) R = benzyl in refluxing acetonitrile and b) R = methyl at room temperature.



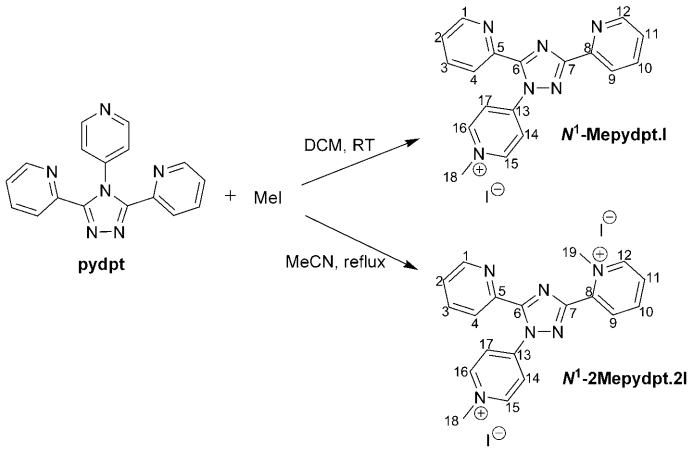
Scheme 4. Proposed mechanism for the N^4 to N^1 rearrangement if the nucleophile is a bromide ion.

Unlike the first postulated mechanism, the second is anion-dependent, so we carried out an initial test of this dependency. As stated above, when N^4-Bzpydpt·Br is heated at reflux in MeCN, the result is complete conversion into the thermodynamic product N^1-Bzpydpt·Br. To test whether a second triazole species (Scheme 3) or a bromide ion

(Scheme 4) acts as the nucleophile, we prepared N^4-Bzpydpt·BPh_4 because the tetraphenylborate anion cannot act as a nucleophile. It was isolated in 88% yield by the addition of an aqueous solution of $NaBPh_4$ to an aqueous solution of N^4-Bzpydpt·Br followed by filtration of N^4-Bzpydpt·BPh_4, which formed as a fine white precipitate immediately on mixing. Trace amounts of bromide (0.5%) present in this sample were removed through recrystallization by vapor diffusion of diethyl ether into an acetone solution of the sample, as the second mechanism would be catalytic in bromide. The result was a white crystalline sample in which no bromide was detectable (<0.3%). Heating N^4-Bzpydpt·BPh_4 (25 mg) at reflux in MeCN (10 mL) for 3 h (the same time and volume of MeCN as was used for the rearrangement of N^4-Bzpydpt·Br to N^1-Bzpydpt·Br) resulted in the formation of a yellow solid that was subsequently identified by ^{1}H NMR spectroscopy as the rearrangement product N^1-Bzpydpt·BPh_4. Although we cannot rule out the mechanism shown in Scheme 4, as undetectable traces of bromide could still be present, this result lends support to our suggestion that the mechanism shown in Scheme 3 is the one that is operational in this case.

Following on from this intriguing study into the benzylated derivatives, we decided to attempt the alkylations with methyl iodide. The less sterically bulky methyl group, and more reactive iodide, were chosen to ascertain whether the resulting, less bulky, ligand would more readily bind iron(II) (see below).

The methyl iodide alkylation reactions gave quite different results to the benzyl bromide reactions. Using the same protocols as above (DCM at room temperature and MeCN at reflux), we again obtained alkylated products (Scheme 5). However, even when pydpt was stirred at room temperature in DCM with excess MeI (10 equivalents), the rearranged product N^1-Mepydpt·I was isolated in good yield (69%) and characterized by ^{1}H NMR spectroscopy, microanalysis, mass spectrometry, and X-ray crystallography (Figure 5, see below).



Scheme 5. Observed products of alkylations of pydpt with 10 equivalents of methyl iodide.

In contrast to this result, the reaction using benzyl bromide (to prepare N^4-Bzpydpt·Br) did not result in rearrangement at room temperature in DCM. To ascertain whether the iodide anion facilitated the observed methylation and rearrangement of pydpt to N^1-Mepydpt·I in DCM at room temperature, the benzylation of pydpt with benzyl bromide in the presence of 10 mol% nBu$_4$NI was attempted at room temperature in DCM. The alkylation proceeded smoothly to give N^4-Bzpydpt$^+$ (as it did in the absence of I^-). No trace of N^1-Bzpydpt$^+$ was observed. This result indicates that the rearrangement is not anion-dependent and hence that the mechanism shown in Scheme 4 is not operational in this case.

Remarkably, when the methylation of pydpt was carried out in refluxing MeCN, and the intense orange reaction solution was subjected to vapor diffusion of diethyl ether, the product was identified as the doubly alkylated N^1-2Mepydpt·2I and was obtained in 60% yield. While the 4-pyridyl nitrogen atom is the most susceptible to alkylation, there are multiple sites for the second alkylation to occur. The first alkylation and rearrangement results in the two 2-pyridyl groups no longer having equivalent chemical environments; therefore, either of these groups can be alkylated, and two of the triazole nitrogen atoms are also in principle available for alkylation. The site of the second alkylation is clearly revealed by the X-ray structure determination (Figure 6, see below).

X-ray Crystallography

Single platelike crystals of pydpt were grown by the slow evaporation of a solution in dichloromethane. The X-ray crystal structure determination is included here to provide comparisons to the alkylated derivatives. The compound crystallized in the orthorhombic space group *Pbca* and contains one molecule in the asymmetric unit (Figure 2). Analysis of the 2-pyridyltriazole mean-plane angles reveals a relatively planar structure [mean-plane angle range = 6.5(3)–21.9(5)°], but the 4-pyridyl moiety is closer to a right-angled orientation with respect to the central triazole ring [mean-plane angle = 72.3(6)°].

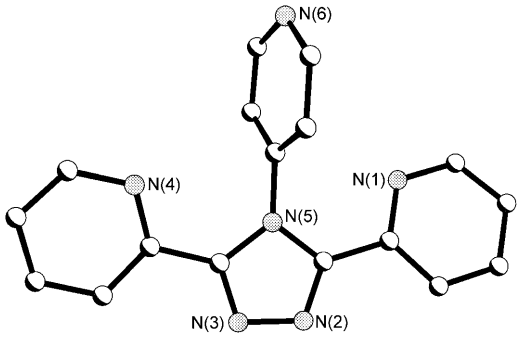


Figure 2. Perspective view of pydpt. Hydrogen atoms omitted for clarity.

Single crystals of N^1-Bzpydpt·BF_4 were grown by the slow evaporation of an aqueous solution, and the X-ray crystal structure was determined. The compound crystallized in the triclinic space group $P\bar{1}$ and contained one molecule in the asymmetric unit (Figure 3). The connectivity of the compound is in full agreement with the deduction made on the basis of the ^{1}H NMR data; that is, the benzylated 4-pyridyl group is located on the N^1 atom rather than the desired N^4 position. There is an interstitial water molecule that forms two hydrogen bonds to tetrafluoroborate counteranions [O(1)···F(4) = 2.756(4) Å, O(1)–H(1X)···F(4) = 131°, and O(1)···F(3)^i = 3.003(4) Å, O(1)–H(1Y)···F(3)^i = 132°], and a strong interaction occurs between the positively charged benzylated 4-pyridyl ring and the tetrafluoroborate counteranion [F(1)···N(6) = 2.939(1) Å and F(1)···centroid = 2.956(1) Å]. The dihedral angles formed between the mean planes of the 2-pyridyl rings and the triazole ring are 21° and 12° for the rings of N(1) and N(4), respectively, so this portion of the compound is relatively planar. However, the N^1-4-pyridyl ring is significantly twisted relative to the triazole ring (41°), albeit not as much as the N^4-4-pyridyl was in the starting material pydpt (72°).

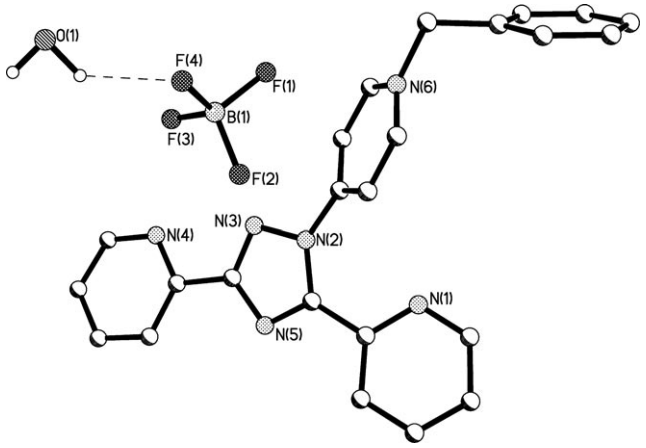


Figure 3. Perspective view of the asymmetric unit of N^1-Bzpydpt·BF_4. Hydrogen atoms other than those on the interstitial water molecule omitted for clarity.

Single crystals of N^4-Bzpydpt·BF_4 were obtained by recrystallization from hot water/methanol (10:1), and the X-ray crystal structure was determined (Figure 4). The asymmetric unit contained two independent molecules of the desired product N^4-Bzpydpt·BF_4 and no molecules of solvation. The connectivity of the two independent molecules is consistent with that predicted from the ^{1}H NMR spectrum, since the benzylated 4-pyridyl substituent is connected at the N^4 nitrogen atom. The di(2-pyridyl)triazole portion of these two molecules is relatively flat [range of mean plane angles = 1.43–13.31°], while the mean planes of the benzylated 4-pyridyl ring and the attached triazole ring are at near right angles (80° and 89°). The rings are much less coplanar than in N^1-Bzpydpt·BF_4, in which the substituent, albeit N^1-bound, is twisted by only 41° relative to the attached triazole. Both of the BF_4^- counterions are involved in anion···π interactions with the triazole rings of the cationic components, and one of the BF_4^- counterions has twirl disorder [F(23)···centroid($_{triazole}$N(2)) = 3.123(2) Å, F(4)···centroid($_{triazole}$N(22)) = 3.293(7) Å, and F(7)···centroid($_{triazole}$N(22)) = 3.065(7) Å]. The F···triazole interaction clearly is not strong enough to constrain the BF_4^-, as one of the disordered fluorine atoms is involved in the aforementioned interactions [F(4) and F(7)].

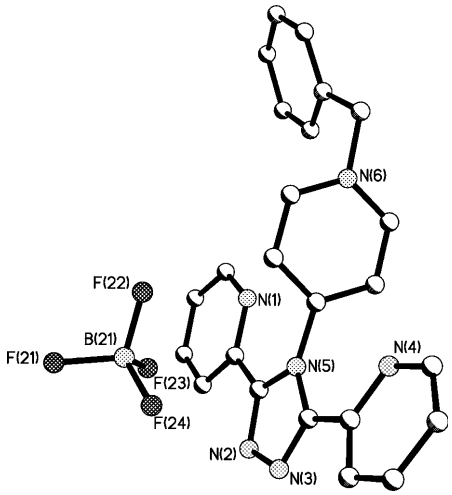


Figure 4. Perspective view of N^4-Bzpydpt·BF_4. Only one of the two independent molecules within the asymmetric unit is shown. Hydrogen atoms omitted for clarity.

Single crystals of N^1-Mepydpt·I were obtained as colorless rods by the vapor diffusion of *tert*-butylmethyl ether into a solution of N^1-Mepydpt·I in DMSO. The compound crystallized in the chiral, orthorhombic space group $P2_12_12_1$, which contained one molecule in the asymmetric unit (Figure 5). The crystal structure confirmed the connectivity predicted from the NMR studies with the methylated 4-pyridyl group located at the N^1 position. The crystal structure contains no solvent or disorder. The iodide counteranion has short contacts to the positively charged 4-pyridyl nitrogen atoms on

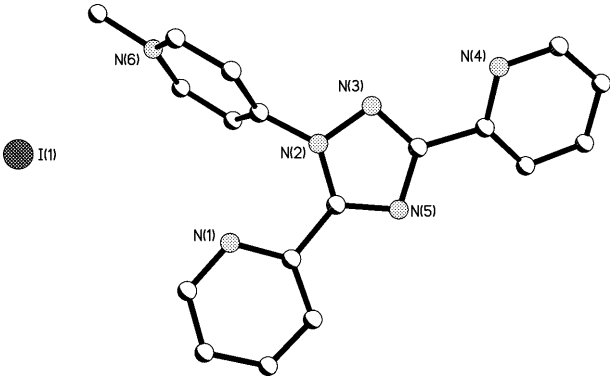


Figure 5. Perspective view of the asymmetric unit of N^1-Mepydpt·I. Hydrogen atoms omitted for clarity.

adjacent molecules in the unit cell [I(1)···N(6) = 3.636(6) Å and I(1)···N(6)′ = 3.735(6) Å], thus facilitating the linking of molecules. The angles between pyridyl and triazole rings are similar to those seen in N^1-Bzpydpt·BF_4 with a mean-plane angle range of 8.49(4)–24.09(3). The pyridinium ring is closer to a right-angled orientation to the triazole ring with a mean-plane angle of 67.41(2), similar to that of the starting material pydpt.

Single orange platelike crystals of N^1-2Mepydpt·2I were grown by diffusion of diethyl ether vapor into the acetonitrile reaction solution. The compound crystallized in the monoclinic space group $P2_1/n$ containing one molecule in the asymmetric unit. The compound is clearly doubly alkylated with the second methylation having occurred at one of the two 2-pyridyl rings (Figure 6). The mean-plane angles

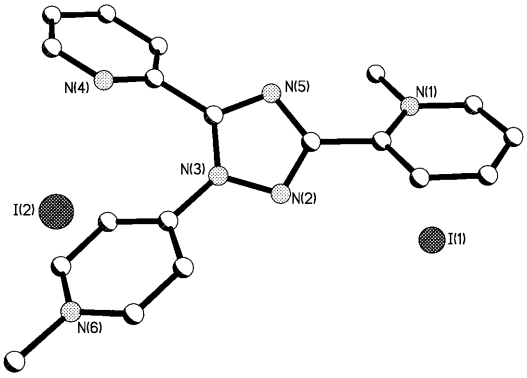


Figure 6. Perspective view of the asymmetric unit of doubly alkylated N^1-2Mepydpt·2I. Hydrogen atoms omitted for clarity.

formed between the triazole and pendant 2-pyridyl rings [28.8(2)° to 38.5(2)°] are further from planar than in the previous structures. However, with an angle of just 29.9(3)° the methylated 4-pyridyl ring makes the smallest angle to the triazole ring of all four of the structures presented here. Again, there are short contacts between the positively charged, alkylated, nitrogen atoms and the iodide counteranions [N(1)···I(1) = 3.636(9) Å and N(6)···I(2) = 3.811(9) Å].

Complexation Studies

Having successfully attached the highly electron-withdrawing, positively charged substituent to the triazole ring at both the N^4 (N^4-Bzpydpt·BF_4) and N^1 (N^1-Bzpydpt·BF_4) positions, we attempted to prepare iron(II) complexes of these benzylated ligands. Unlike typical Rdpt ligands,[2,12] there are two very different binding modes possible for N^1-Bzpydpt·BF_4 (Figure 7). In one mode, a bidentate binding pocket is formed by an N^2 atom of the triazole and the nitrogen atom of a 2-pyridyl ring (Figure 7a), and a second potential bidentate binding pocket is formed "out the back" by an N^4 atom of the triazole and the nitrogen atom of the other 2-pyridyl ring. The second, quite different binding mode involves a terdentate binding pocket, formed by the

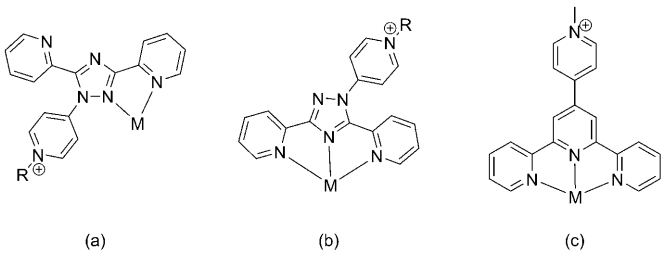


Figure 7. a, b) Potential binding modes of N^1-Rpydpt·X. c) The observed binding mode of the analogous alkylated terpyridyl ligand.[6,7]

two 2-pyridyl nitrogen atoms and the N^4 triazole nitrogen atom (Figure 7b). This second binding mode bears some resemblance to that seen for similarly alkylated terpyridyl moieties (Figure 7c) complexed with iron(II),[6,7] however this binding mode is anticipated to be less favorable than it is for terpy, since rather than having a central six-membered heterocycle, it involves a five-membered heterocycle.[13]

Initially, the complexations were carried out in the same way as for the dinuclear bis and mononuclear tris Fe^{II} complexes of Rdpt reported earlier.[3,5] However, when excess iron(II) tetrafluoroborate was added to either N^1-Bzpydpt·BF_4 or N^4-Bzpydpt·BF_4 in acetonitrile, unlike in the case of the other Rdpt ligand reactions with iron(II), there was no color change, and vapor diffusion of diethyl ether into the solution or evaporation of the solvent yielded only white precipitates or, in the case of N^1-Bzpydpt·BF_4, colorless crystals, which were found to uncomplexed ligands. This observation indicates that in introducing a highly electron-withdrawing positive charge to the N^1 or N^4 substituent there has been such a dramatic reduction in the electron-donating ability of the nitrogen atoms that typically bind to the metal ions that they no longer coordinate readily. Because the ligand reactivity was so severely reduced, we attempted the complexation reaction at reflux in acetonitrile with N^1-Bzpydpt·BF_4 (but not N^4-Bzpydpt·BF_4 as it would likely rearrange). Despite the elevated temperature, there was no observed color change (this is not required, as a high-spin complex could be white/colorless; however, there is usually some small change in the color of the reaction solution upon complexation), and the slow evaporation of the acetonitrile reaction solution gave large colorless blocks coated in brown oil. The large blocks were again found to be the noncoordinated ligand N^1-Bzpydpt·BF_4. The identity of the brown oil could not be established. Similarly, we have been unable to isolate any iron(II) complexes to date with the less bulky methyl groups attached to the ligand in N^1-Mepydpt·I. We cannot rule out that such complexes can be formed, but it is clear that, totally unlike the alkylated terpyridines, the alkylated Rdpt compounds are at best reluctant ligands for Fe^{II}.

Conclusions

Alkylation of pydpt utilizing excess benzyl bromide or methyl iodide in either refluxing acetonitrile or at room temperature in dichloromethane gave some unexpected alkylated products. The expected product N^4-Bzpydpt·Br was obtained from a reaction using excess benzyl bromide in DCM at room temperature. However, in refluxing acetonitrile, the N^4 to N^1 rearrangement product N^1-Bzpydpt·Br resulted. This rearrangement occurred at the lowest temperature seen until now: the previous minimum was 150 °C.

Heating a pure sample of N^4-Bzpydpt·Br to reflux in MeCN resulted in clean conversion into N^1-Bzpydpt·Br. This result is consistent with N^1-Bzpydpt·Br being the thermodynamic product and N^4-Bzpydpt·Br being the kinetic product.

Unlike in previously reported systems, the rearrangement in our system, which features an alkylated 4-pyridyl substituent, is believed to proceed by means of nucleophilic aromatic substitution rather than by S_N2 like reactions. Hence, the positively charged aromatic substituent facilitates the aromatic nucleophilic substitution reaction, leading to the lower rearrangement temperature observed. A test reaction using a bulky nonnucleophilic anion in place of bromide (N^4-Bzpydpt·BPh_4) still gave the rearrangement product N^1-Bzpydpt·BPh_4, indicating that it is probably the triazole species that acts as the nucleophile (not the bromide anion, although this cannot be ruled out as only catalytic/trace amounts of bromide are required). However, a full investigation of the details of the mechanism of this rearrangement is beyond the scope of the present study. Rather it is anticipated that this report will stimulate such studies by appropriate organic mechanistic experts.

Using methyl iodide in place of benzyl bromide, we were able to further reduce the rearrangement temperature to room temperature to form N^1-Mepydpt·I in DCM. In contrast, alkylation but no rearrangement was observed when pydpt was treated with benzyl bromide at room temperature in DCM. Hence, we repeated the benzylation reaction in the presence of 10 mol% iodide. Again, only N^4-Bzpydpt$^+$ was obtained, indicating that the rearrangement is not anion-dependent.

Finally, in carrying out the methylation reaction in refluxing MeCN, we observed another unexpected product, the doubly alkylated dication, which was obtained as the iodide salt N^1-2Mepydpt·2I.

In the course of this study, we were able to isolate the desired product N^4-Bzpydpt·X with a benzyl group attached to the 4-pyridyl nitrogen atom, but the presence of the associated highly electron-withdrawing positive charge appeared to render the ligand unreactive as no iron(II) complexes have been obtained to date. While not yet giving the hoped for results with Fe^{II}, this study does show just how much the choice of N^4 substituent can influence the properties of the resulting ligands and has also revealed the lowest N^4 to N^1 rearrangement temperatures seen to date.

Experimental Section

General: The ligand 4-(4-pyridyl)-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole (pydpt) was prepared as described earlier.[4] $Fe(BF_4)_2{\cdot}6H_2O$, benzyl bromide, and methyl iodide (stabilized) were purchased from commercial sources and used as received. All solvents were laboratory reagent grade except for methanol and acetonitrile. Methanol was dried by freshly distilling over magnesium and iodine before use. Acetonitrile was dried by freshly distilling over calcium hydride before use. Elemental analyses were carried out by the Campbell Microanalytical Laboratory at the University of Otago. Infrared spectra were recorded over the range 4000–400 cm^{-1} with a Perkin–Elmer Spectrum NBX FT-IR spectrophotometer as a potassium bromide pellet or a nujol mull. ESI mass spectra were recorded on a Bruker MicrOTOF$_Q$ spectrometer by Mr Ian Stewart. ^1H and ^{13}C NMR spectra were recorded on either a Varian INOVA-500, a Varian INOVA-300, a Varian 400-MR, or a Varian 500 MHz VNMRS spectrometer at 25 °C. X-ray data (Table S1, Supporting Information) were collected on a Bruker APEX II area detector diffractometer at the University of Otago using graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects, and semi-empirical absorption corrections (SCALE) were applied. The structures were solved by direct methods (SHELXS-97) and refined against all F^2 data (SHELXL-97).[14] Hydrogen atoms were inserted at calculated positions and rode on the atoms to which they were attached and all non-hydrogen atoms were made anisotropic. The SQUEEZE routine in PLATON was required to remove a poorly behaved 0.5 occupancy methanol molecule and a 0.5 occupancy water molecule in $N^{1\cdot}$-2Mepydpt·2I.[15] CCDC 748521 (pydpt), CCDC 748522 (N^4-Bzpydpt·BF_4), CCDC 748523 (N^1-Bzpydpt·BF_4), CCDC 748524 ($N^{1\cdot}$-Mepydpt·I), and CCDC 748525 ($N^{1\cdot}$-2Mepydpt·2I) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

N^1-(4-Benzylpyridinium)-3,5-di(2-pyridyl)-1,2,4-triazole bromide (N^1-Bzpydpt·Br): To a solution of pydpt (100 mg, 0.33 mmol) in acetonitrile (50 mL), benzyl bromide (280 mg, 0.4 mL, 1.65 mmol) was added. The resulting colorless solution was heated at reflux for 3 h, cooled to room temperature, and filtered to give N^1-Bzpydpt·Br as a white powder (60 mg, 39%). Anal. calcd. for $C_{24}H_{19}N_6Br{\cdot}{}^1/_2H_2O$ (480.35 g mol^{-1}): C 60.01, H 4.20, N 17.50, Br 16.63; found: C 59.99, H 4.23, N 17.53, Br 16.59%. ^1H NMR (400 MHz, [D$_6$]DMSO, reference DMSO at δ = 2.50 ppm): δ_H = 5.90 (s, 2H, H^{18}), 7.51–7.41 (m, 4H, H^{21}, H^{22}, H^{23} and H^{11}), 7.58–7.53 (m, 2H, H^{20} and H^{24}), 7.62 (ddd, J = 7.9, 5.0, 1.1 Hz, 1H, H^2), 8.01 (td, J = 7.8, 1.8 Hz, 1H, H^3), 8.12 (td, J = 7.8, 1.7 Hz, 1H, H^{10}), 8.24 (m, 2H, H^4 and H^9), 8.33 (d, J = 7.1 Hz, 2H, H^{14} and H^{17}), 8.47 (d, J = 4.7 Hz, 1H, H^1), 8.74 (d, J = 4.6 Hz, 1H, H^{12}), 9.30 ppm (d, J = 7.2 Hz, 2H, H^{15} and H^{16}). ^{13}C NMR (101 MHz, [D$_6$]DMSO, reference DMSO at δ = 39.52 ppm): δ_C = 162.4 (C^6), 155.7 (C^7), 151.1 (C^{13}), 150.5 (C^{12}), 149.5 (C^1), 148.3 (C^5), 146.6 ($C^{15/16}$), 146.1 (C^8), 138.7 (C^{10}), 137.9 (C^3), 134.5 (C^{19}), 129.9–129.4 (C^{20-24}), 126.8 (C^2), 125.7 (C^{11}), 125.3(C^9), 123.5 ($C^{14/17}$), 122.9(C^4), 63.5 ppm (C^{18}). IR (KBr): $\tilde{\nu}$ = 3425, 3109, 3030, 1632, 1586, 1522, 1511, 1496, 1468, 1447, 1423, 1390, 1353, 1280, 1250, 1215, 1154, 1087, 1044, 1008, 996, 827, 803, 795, 765, 742, 725, 701, 623, 608, 592, 479 cm^{-1}.

N^1-(4-Benzylpyridinium)-3,5-di(2-pyridyl)-1,2,4-triazole tetrafluoroborate (N^1-Bzpydpt·BF_4): To a colorless solution of N^2-(4-benzylpyridinium)-3,5-di(2-pyridyl)-1,2,4-triazole bromide (N^1-Bzpydpt·Br) (50 mg, 0.1 mmol) in water (5 mL) was added an aqueous solution (5 mL) of ammonium tetrafluoroborate (50 mg, 0.4 mmol). The solution was allowed to stand at room temperature to produce a few large, blocklike, crystals, which were removed for X-ray structure determination. The remainder of the solution was placed in the refrigerator (4 °C) overnight to yield 50 mg (99%) of N^1-Bzpydpt·BF_4 as a colorless crystalline solid. Anal. calcd. for $C_{24}H_{19}N_6BF_4$ (478.25 g mol^{-1}): C 60.27, H 4.00, N 17.57; found: C 60.33, H 4.06, N 17.66%. ^1H NMR (300 MHz, [D$_6$]DMSO, reference DMSO at δ = 2.50 ppm): δ_H = 5.90 (s, 2H, H^{18}), 7.46–7.50 (m, 4H, H^{21}, H^{23}, H^2 and H^{11}), 7.55–7.60 (m, 2H, H^{20} and H^{24}), 7.65 (d, 1H, H^{22}), 8.04 (td, 1H, H^3), 8.15 (td, 1H, H^{10}), 8.24 (d, 2H, H^9), 8.28 (d, 1H, H^4), 8.35 (d, 2H, H^{14}

and H^{17}), 8.49 (dd, 1H, H^1), 8.77 (dd, 1H, H^{12}), 9.28 ppm (d, 2H, H^{15} and H^{16}).

N^4-(4-Benzylpyridinium)-3,5-di(2-pyridyl)-1,2,4-triazole bromide (N^4-Bzpydpt·Br): To a solution of pydpt (50 mg, 0.16 mmol) in dichloromethane (20 mL) was added benzyl bromide (140 mg, 0.2 mL, 0.825 mmol). The resulting colorless solution was stirred for 3 h, over which time a white precipitate formed (60 mg, 80%). Anal. calcd. for $C_{24}H_{19}N_6Br·H_2O$ (489.37 g mol^{-1}): C 58.90, H 4.33, N 17.17, Br 16.33; found: C 58.82, H 4.61, N 16.92, Br 16.11%. ^{1}H NMR (300 MHz, [D$_6$]DMSO, reference DMSO at $\delta = 2.50$ ppm): $\delta_H = 5.97$ (s, 2H, H^{18}), 7.43–7.58 (m, 7H, H^{20-24}, H^2 and H^{11}), 8.02 (td, 2H, H^3 and H^{10}), 8.15 (dd, 2H, H^4 and H^9), 8.30 (dd, 2H, H^1 and H^{12}), 8.41 (d, 2H, H^{14} and H^{17}), 9.32 ppm (d, 2H, H^{15} and H^{16}). ^{13}C NMR (100 MHz, [D$_6$]DMSO, reference DMSO at $\delta = 39.52$ ppm): $\delta_C = 155.7$ ($C^{6/7}$), 153.7 (C^{13}), 149.5 ($C^{5/8}$), 148.8 ($C^{1/12}$), 146.5 ($C^{15/16}$), 138.0 ($C^{4/9}$), 129.8 (BzC), 129.4 (BzC), 128.5 ($C^{14/17}$), 125.5 ($C^{2/11}$), 125.3 (BzC), 124.2 ($C^{3/10}$), 63.5 ppm (C^{18}). IR (KBr): $\tilde{\nu} = 3419$, 3038, 2979, 2918, 1636, 1595, 1585, 1526, 1508, 1460, 1447, 1432, 1204, 1175, 1163, 1151, 1087, 1046, 995, 989, 873, 844, 792, 744, 723, 714, 686, 637, 620, 606, 475 cm^{-1}.

N^4-(4-Benzylpyridinium)-3,5-di(2-pyridyl)-1,2,4-triazole tetrafluoroborate (N^4-Bzpydpt·BF$_4$): To a colorless solution of N^4-(4-benzylpyridinium)-3,5-di(2-pyridyl)-1,2,4-triazole bromide (N^4-Bzpydpt·Br) (50 mg, 0.1 mmol) in water (5 mL) was added an aqueous solution (5 mL) of ammonium tetrafluoroborate (50 mg, 0.4 mmol). A white crystalline solid (35 mg, 69%) was formed immediately. Anal. calcd. for $C_{24}H_{19}N_6BF_4$ (478.25 g mol^{-1}): C 60.27, H 4.00, N 17.57; found: C 60.47, H 4.02, N 17.80%. (300 MHz, [D$_6$]DMSO, reference DMSO at $\delta = 2.50$ ppm): $\delta_H = 5.96$ (s, 2H, H^{18}), 7.43–7.55 (m, 7H, H^{20-24}, H^2 and H^{11}), 8.02 (td, 2H, H^3 and H^{10}), 8.11 (d, 2H, H^4 and H^9), 8.30 (d, 2H, H^1 and H^{12}), 8.41 (d, 2H, H^{14} and H^{17}), 9.31 ppm (d, 2H, H^{15} and H^{16}). Recrystallizing the white crystalline solid from a hot solvent mixture of water/methanol (10:1) gave single crystals suitable for X-ray diffraction studies.

N^4-(4-Benzylpyridinium)-3,5-di(2-pyridyl)-1,2,4-triazole tetraphenylborate (N^4-Bzpydpt·BPh$_4$): To a colorless solution of N^4-(4-benzylpyridinium)-3,5-di(2-pyridyl)-1,2,4-triazole bromide (N^4-Bzpydpt·Br) (40 mg, 0.08 mmol) in water (10 mL) was added an aqueous solution (5 mL) of ammonium tetraphenylborate (55 mg, 1.6 mmol). Immediately, a very fine white solid was formed (50 mg, 88%). Anal. calcd. for $C_{24}H_{19}N_6B(C_6H_5)_4·H_2O$ (728.70 g mol^{-1}): C 79.12, H 5.67, N 11.53; found: C 79.40, H 5.45, N 11.49, Br 0.5%. ^{1}H NMR (500 MHz, [D$_6$]DMSO, reference DMSO at $\delta = 2.50$ ppm): $\delta_H = 5.96$ (s, 2H, H^{18}), 6.78 (t, 4H, BPh$_4$-*H*), 6.91 (t, 8H, BPh$_4$-*H*), 7.16–7.19 (m, 8H, BPh$_4$-*H*), 7.44–7.55 (m, 7H, H^{20-24}, H^2 and H^{11}), 8.03 (td, 2H, H^3 and H^{10}), 8.11 (d, 2H, H^4 and H^9), 8.29 (d, 2H, H^1 and H^{12}), 8.40 (d, 2H, H^{14} and H^{17}), 9.30 ppm (d, 2H, H^{15} and H^{16}). To remove the trace amount of bromine present, a small sample of the fine white solid (25 mg) was dissolved in acetone and subjected to vapor diffusion of diethyl ether. The result was a fine white crystalline solid (10 mg) in which there was no detectable amount of bromine (<0.3%). ^{1}H NMR data were consistent with those of N^4-Bzpydpt·BPh$_4$.

N^1-(4-Benzylpyridinium)-3,5-di(2-pyridyl)-1,2,4-triazole tetraphenylborate (N^1-Bzpydpt·BPh$_4$): A colorless solution of the fine white solid of N^4-Bzpydpt·BPh$_4$ (25 mg, not recrystallized) in 10 mL MeCN was heated at reflux for 3 h. Removal of solvent in vacuo resulted in a pale yellow oil, which became solid upon drying in vacuo. ^{1}H NMR (400 MHz, [D$_6$]DMSO, reference DMSO at $\delta = 2.50$ ppm): $\delta_H = 5.90$ (s, 2H, H^{18}), 6.78 (t, 4H, BPh$_4$-*H*), 6.89 (t, 8H, BPh$_4$-*H*), 7.16–7.19 (m, 8H, BPh$_4$-*H*), 7.46–7.49 (m, 4H, H^{21}, H^{23}, H^2 and H^{11}), 7.55–7.60 (m, 2H, H^{20} and H^{24}), 7.66 (d, 1H, H^{22}), 8.04 (td, 1H, H^3), 8.15 (td, 1H, H^{10}), 8.23 (d, 2H, H^9), 8.29 (d, 1H, H^4), 8.35 (d, 2H, H^{14} and H^{17}), 8.49 (dd, 1H, H^1), 8.77 (dd, 1H, H^{12}), 9.28 ppm (d, 2H, H^{15} and H^{16}). When 5 mg of the fine white crystals from the acetone/diethyl ether recrystallization of N^4-Bzpydpt·BPh$_4$ was heated at reflux in 5 mL MeCN and the solvent was removed, the result was similar: a pale yellow solid was obtained which give a near identical ^{1}H NMR spectrum.

N^1-(4-Methylpyridinium)-3,5-di(2-pyridyl)-1,2,4-triazole iodide (N^1-Mepydpt·I): To a solution of pydpt (94 mg, 0.31 mmol) in dichloromethane (10 mL) was added methyl iodide (0.2 mL, stabilized MeI, 3.2 mmol). The resulting clear yellow solution was stirred for 1 h, during which time the yellow color become more intense. The darker yellow solution was then stirred for a further 48 h, over which time a bright yellow precipitate formed (95 mg, 69%). Anal. calcd. for $C_{18}H_{15}N_6I$ (442.26 g mol^{-1}): C 48.88, H 3.42, N 19.00, I 28.69; found: C 48.79, H 3.54, N 19.05, I 29.02%. ^{1}H NMR (400 MHz, [D$_6$]DMSO, reference DMSO at $\delta = 2.50$ ppm): $\delta_H = 4.39$ (s,3H, H^{18}), 7.56 (ddd, $J = 7.6$, 4.7, 0.9 Hz, 1H, H^2), 7.62 (ddd, $J = 7.6$, 4.8, 0.9 Hz, 1H, H^{11}), 8.02 (td, $J = 7.7$, 1.7 Hz, 1H, H^3), 8.13 (td, $J = 7.7$, 1.6 Hz, 1H, H^{10}), 8.31–8.24 (m, 4H, H^{14},H^{17},H^4,H^9), 8.49 (d, $J = 4.8$ Hz, 1H, H^{12}), 8.74 (d, $J = 4.7$ Hz, 1H, H^1), 9.06 ppm (d, $J = 7.1$ Hz, 2H, H^{15} and H^{16}). ^{13}C NMR (101 MHz, [D$_6$]DMSO, reference DMSO at $\delta = 39.52$ ppm): $\delta_C = 162.4$ (C^6), 155.5 (C^7), 150.6(C^{13}), 150.5 (C^1), 149.5 (C^{12}), 148.3(C^5), 147.4 ($C^{15/16}$), 146.1 (C^8), 138.7 (C^{10}), 137.9 (C^3), 126.7 (C^{11}), 125.7 (C^2), 125.3 (C^9), 122.9 (C^4 and $C^{14/17}$), 48.3 ppm (C^{18}). IR (KBr): $\tilde{\nu} = 3004$, 1630, 1583, 1518, 1458, 1431, 1281, 1247, 1205, 1186, 1170, 1094, 995, 841, 795, 740, 719, 628, 599 cm^{-1}. ESIMS (pos.): *m*/*z* 315.132 [N^1-Mepydpt]$^+$.

N^1-(4-Methylpyridinium)-3-(2-methylpyridinium)-5-(2-pyridyl)-1,2,4-triazole diiodide ($N^{1'}$-2Mepydpt·2I): To a solution of pydpt (105 mg, 0.35 mmol) in acetonitrile (20 mL) was added methyl iodide (0.2 mL, stabilized MeI, 3.2 mmol). The resulting clear yellow solution was heated at reflux for 1 h, during which time the clear yellow solution become intense orange. The orange solution was heated with stirring for a further 6 h, over which time a small amount of bright yellow precipitate formed. The reaction mixture was cooled to −4 °C and the resulting precipitate of $N^{1'}$-2Mepydpt·2I was filtered (92 mg, 60%). Anal. calcd. for $C_{19}H_{18}N_6I_2$ (584.20 g mol^{-1}): C 39.06, H 3.11, N 14.39; found: C 38.90, H 3.19, N 14.25%. ^{1}H NMR (400 MHz, [D$_6$]DMSO, reference DMSO at $\delta = 2.50$ ppm): $\delta_H = 4.44$ (s, 3H, H^{19}), 4.74 (s, 3H, H^{18}), 7.69 (ddd, $J = 7.7$, 4.8, 1.1 Hz, 1H, H^2), 8.18 (td, $J = 7.8$, 1.7 Hz, 1H, H^3), 8.36–8.27 (m, 2H, H^4 and H^{11}), 8.42 (d, $J = 8.2$ Hz, 2H, H^{14} and H^{17}), 8.53 (ddd, $J = 4.8$, 1.6, 0.9 Hz, 1H, H^1), 8.83–8.79 (m, 2H, H^9 and H^{10}) 9.16 (d, $J = 8.2$ Hz, 2H, H^{15} and H^{16}), 9.28 ppm (d, 1H, H^{12}). ^{13}C NMR (101 MHz, [D$_6$]DMSO, reference DMSO at $\delta = 39.52$ ppm): $\delta_C = 156.0$, 155.5, 150.1, 149.7, 149.3, 147.8, 146.5, 145.2, 143.3, 138.9, 129.8, 129.0, 127.3, 125.6, 123.5, 49.6, 48.6 ppm. IR (KBr): $\tilde{\nu} = 3039$, 1640, 1625, 1579, 1517, 1467, 1444, 1397, 1382, 1358, 1289, 1219, 1180, 1143, 1086, 1045, 1010, 855, 814, 779, 751, 729, 720, 696, 686, 609, 535, 514, 435, 406 cm^{-1}. ESIMS (pos.): *m*/*z* 165.077 [$N^{1'}$-2Mepydpt]$^{2+}$.

Acknowledgements

This work was supported by the University of Otago and the Marsden Fund. We thank the Tertiary Education Commission (New Zealand) for the award of a Bright Futures Top Achiever Doctoral scholarship to J.A.K., the MacDiarmid Institute for Advanced Materials and Nanotechnology (J.A.K. and S.B.), and the referees for helpful comments.

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Received: September 22, 2009
Revised: December 17, 2009
Published online: March 12, 2010

