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Bipyridine Based Exoditopic Ligands : Synthesis and Structural Analysis of Homobinuclear Ruthenium Complexes

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Abstract: The synthesis of new macrocyclic ligands based on 2,2'-bipyridine unites interconnected at the 4 and 4' positions by alkyl chains was achieved. Homobinuclear Ru^{II} complexes were formed and the solid state structure of one of the diastereoisomers was investigated by X-ray analysis.
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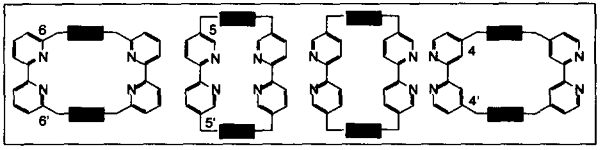
Due to the availability of numerous oxidation states as well as coordination geometry for transition metals, the design and preparation of coordination polymers, based on the bridging of metal centres by organic spacers, have attracted much attention over the past years.[1] For the formation of coordination polymers, the choice of the metal as well as the design of the ligand are essential. In order to allow the bridging between metallic centres by the ligands to take place, the organic connector must possess coordination sites oriented outwardly (exo-ligands). Based on these requirements, one may use a macrocyclic structure to impose a restricted conformational space, as well as to control both the distance and the localisation of coordination sites. We have previously reported exo-ligands based on mercaptocalix[4]arenes[2], calix[4]arene[3a] and tetraarylporphyrin[3b] bearing bidentate catechol units and macrocyclic frameworks containing bipyridine units.[4] Other exo-ligands based on bipyridine units have also been reported.[5] The chelating ability of the 2,2'-bipyridine unit towards transition metals has been widely used.[6] The design of macrocyclic frameworks containing two of these chelates may be based on their interconnection by two bridges. The orientation of the coordination sites within the framework of the ligand results from the connection position on the 2,2'-bipyridine units. Whereas the connection at the 6 and 6' positions leads exclusively to endo-ligands in which the coordination sites are convergently oriented towards the interior of the macrocycle, the use of the 5 and 5' positions affords ligands which may act either as endo- or exo-ligands. Finally, the interconnection at the 4 and 4' positions leads exclusively to exo-ligands (scheme 1). Although, many bipyridine containing endo-ligands have been reported[6], only few examples of exo-ligands based on the interconnection at the 4 and 4' positions have been published.[4]



Scheme 1

In our early design of the ligand **1** the interconnection of the 2,2'-bipyridine units at the 4 and 4' positions

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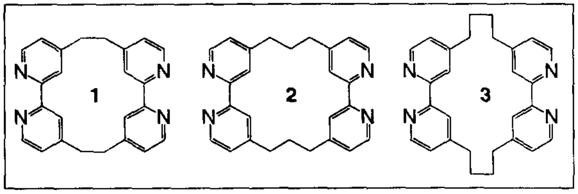
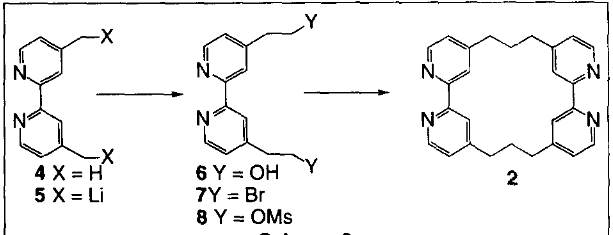
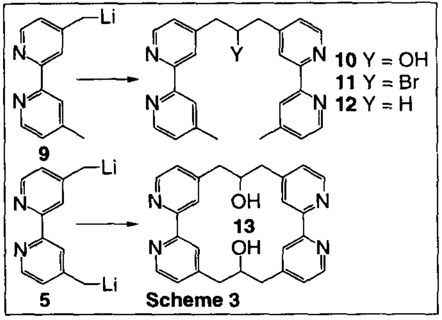
was achieved by two ethylene chains.[4b] In the solid state, X-ray studies of both the free ligand **1** and its binuclear ruthenium complex revealed that whereas the free ligand adopts an "oblong-shape" conformation, for the separated diastereoisomer of the exo-homobinuclear $\mathrm{Ru^{II}}$ complex, the ligand adopts a "roof-shape" type conformation. In order to remove some of the strain imposed by the ethylene chains and thus favour a linear conformation, we have designed and prepared exo-ligands **2** and **3** resulting from the interconnection of two 2,2'-bipyridine units by two propylene and butylene chains respectively. In the present contribution, we describe the synthesis of both ligands as well as their corresponding homobinuclear $\mathrm{Ru^{II}}$ complexes.



The common starting material for the synthesis of both **2** and **3** was the 4,4'-dimethyl-2,2'-bipyridine **4**, prepared by Raney Ni coupling of 4-picoline.[7] The synthesis of **2** was first attempted by nucleophilic displacement of bromides on **7** by the lithium derivative **5** (scheme 2). The dibromo **7**, a rather unstable molecule which must be used rapidly after its generation, was first prepared (50 %) by HBr (48%) treatment of **6**. The latter was obtained by condensing the lithium derivative **5**, generated from **4** by LDA at 0° C in dry THF, with *para*-formaldehyde (20 %).[8] In order to avoid the formation of **7** under acidic conditions, another route, based on the mesylation of **6** affording the compound **8** (78 %) and subsequent treatment of the latter with LiBr in acetone (95 %), was followed. Unfortunately, the condensation, under high dilution conditions, of **7** with the lithium derivative **5** in THF failed. The synthesis of compound **2** was attempted using another strategy based on the preparation of the linear analogues **12** which was prepared from the bromo derivative **11**, obtained by bromination of **10**, by treatment with $LiAlH_4$.[9] Unfortunately, by condensing **5** with methyl formate, no trace of the compound **13** could be detected. Even, the stepwise strategy consisting in condensing the compound **10**, prepared by the reaction of the monolithium derivative **5** with methyl formate (20 %), with 3 eq. of LDA followed by further addition of methyl formate failed (scheme 3). Finally, again using the strategy followed for the preparation of the linear compound **12**,[10] the desired compound **2** could be obtained by a double capping process resulting from the reaction of **5** with CH_2Br_2 in THF and under high dilution (1 %).[11]

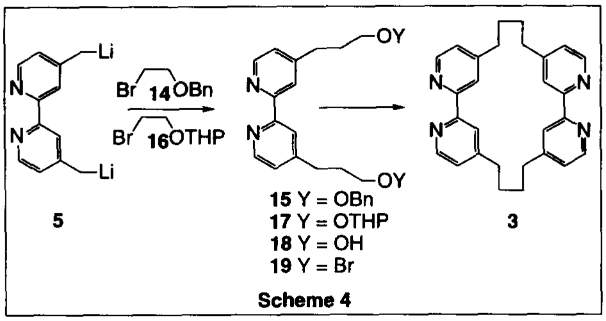


Scheme 2



Scheme 3

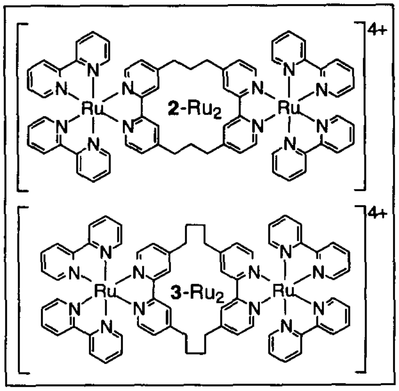
The synthesis of **3** was achieved, in a stepwise fashion, by condensing **5** with **19** (scheme 4). For the preparation of the latter, two different protective groups were used. In a first attempt, the benzyl protected diol **15** was prepared upon condensation in THF of the lithium compound **5** with the mono bromo compound **14**. The latter was obtained, in four steps, by bromination of the corresponding alcohol, prepared by DIBAL opening of the cyclic acetal formed between ethylene glycol and benzaldehyde.[12] Unfortunately the purification of **15** appeared to be rather tedious. Although, **19** could be directly obtained by



Scheme 4

treatment of **15** with BBr_3 in CH_2Cl_2, we were unable to purify it. For that reason, **19** was prepared using another protective group. Treatment of **5** by **16**, prepared by reaction of 1-bromoethanol with DHP[13], gave the protected diol **17** in 54 % yield. Deprotection of the latter afforded the diol **18** (76 %) which was transformed into **19** (84 %) by 48 % HBr in the presence of few drops of conc. H_2SO_4. The desired macrocycle **3**[11] was obtained in 5 % yield by condensation, under high dilution, of the dilithium derivative **5** with the dibromo **19** in THF at rt.

The homobinuclear Ru(II) complexes **2**-Ru_24PF_6 and **3**-Ru_24PF_6 were prepared as orange solids in almost quantitative yield by reacting **2** and **3** respectively with 2 eq. of $Ru(bipy)_2Cl_2$[14] in degased butanol/water mixture. Precipitation of the PF_6^-salts[15] from an aqueous solution afforded the pure complexes as a mixture of diastereoisomers, as expected for octahedral metal complexes bearing three bidentate ligands. Although for the binuclear Ru^{II} complexes formed with the ligand **1**, both the ^1H and ^{13}C NMR studies revealed the presence of different signals for the diastereoisomers[4b], the diastereomeric differentiation dropped gradually by increasing the length of the spacer within the ligand and consequently the distance between the chiral centres. Indeed, for **2**-Ru_2 complexes the signals appeared to be slightly different, whereas for **3**-Ru_2 almost no differentiation could be observed by NMR at 300 MHz.



In the case of **3**-Ru_24PF_6 complexes, suitable monocrystals could be obtained from a acetone/ether mixture. The X-ray analysis[16] revealed the presence of the meso (Δ,Λ) stereoisomer (figure 1). Both Ru(II) centres are hexacoordinated with an almost octahedral geometry. The Ru-N distances ranging from 2.04 to 2.09 Å are similar to those observed for the well-known $Ru(bipy)_3(PF_6)_2$ complex.[17] Within the complex, the two Ru cations are distant by 13.1 Å. In marked contrast with **1**-Ru_24PF_6 complexes[4b] and as expected from the design, the ligand **3** adopts a zig-zag type conformation (figure 1 right) in which the chelating nitrogen centres of both bipyridine units are located in almost the same plane. Rather unexpectedly though, among the four PF_6^- present, two of them are located close to the centre of the complex above and bellow the main plane.

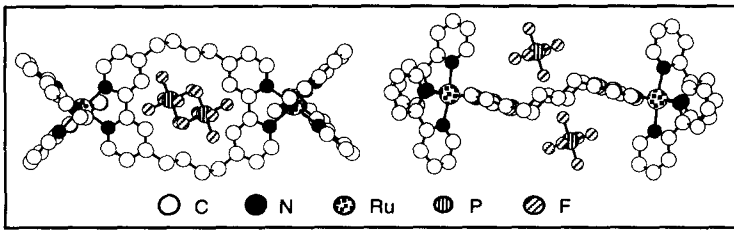


Figure 1: X-ray analysis of 3-Ru_24PF_6 complex. Top (left) and lateral (right) views. For the sake of clarity, hydrogen atoms are not presented

In summary, the synthesis of new macrocyclic exo-ligands based on 2,2'-bipyridine units interconnected at the 4 and 4' positions by propylene and butylene chains was achieved. For both compounds **2** and **3**, their ability to form discrete exobinuclear complexes was demonstrated by the formation of exo-homobinuclear Ru^{II} complexes. In the case of 3-Ru$_2$4PF6 complexes, one of the diastereoisomers was isolated by fractional crystallisation and its solid state structure was elucidated by an X-ray study. The formation of coordination polymers using both ligands **2** and **3** and transition metals with tetrahedral or square planar geometry of coordination is currently under investigation.

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11. Both compounds were also characterised by high resolution mass spectrometry. Selected NMR (δ(ppm)) data: **2**: ^{1}H (CDCl$_3$, 300 MHz, 25 °C): 2.35 (m, 4H, CH$_2$); 2.84 (m, 8H, CH$_2$); 6.87 (dd, 5.0 Hz, 1.6 Hz, 4H, CH$_{pyr}$(5,5')); 7.75 (d, 1.6 Hz, 4H, CH$_{pyr}$(3,3')); 8.25 (d, 5.0 Hz, 4H, CH$_{pyr}$(6,6')); ^{13}C (CDCl$_3$, 75 MHz, 25 °C): 27.85 (CH$_2$); 35.40 (CH$_2$); 122.81, (C$_{pyr}$(3,3')); 123.98 (C$_{pyr}$(5,5')); 148.89 (C$_{pyr}$(6,6')); 150.93 (C$_{pyr}$(4,4')); 155.58 (C$_{pyr}$(2,2')); **3**: ^{1}H (CDCl$_3$, 300 MHz, 25 °C): 1.65 (m, 8H, CH$_2$); 2.65 (br.s, 8H, CH$_2$); 7.04 (dd, 5.0 Hz, 1.7 Hz, 4H, CH$_{pyr}$(5,5')); 7.51 (dd, 1.6 Hz, 0.7 Hz, 4H, CH$_{pyr}$(3,3')); 8.49 (dd, 4.9Hz, 0.7Hz, 4H, CH$_{pyr}$(6,6')); ^{13}C (CDCl$_3$, 75 MHz, 25 °C): 27.57 (CH$_2$); 34.22 (CH$_2$); 120.66, (C$_{pyr}$(3,3')); 124.33 (C$_{pyr}$(5,5')); 148.97 (C$_{pyr}$(6,6')); 151.47 (C$_{pyr}$(4,4')); 156.17 (C$_{pyr}$(2,2')).
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15. Both complexes were also characterised by high resolution mass spectrometry (FAB mode). Selected NMR (δ(ppm)) data: **2-**Ru$_2$, 4PF$_6^-$: ^{1}H (CDCl$_3$, 300 MHz, 25 °C): 2.26 (m, 4H, CH$_2$(b)); 2.67 (m, 8H, CH$_2$(a)); 7.36 (d, 5.9 Hz, 4H, CH$_{pyr}$(5)); 7.42-7.48 (m, 8H, CH$_{pyr}$(5')); 7.68 (d, 5.9 Hz, 4H, CH$_{pyr}$(6)); 7.73 (d, 5.3 Hz, 4H, CH$_{pyr}$(6')); 7.81 (d, 5.3 Hz, 4H, CH$_{pyr}$(6')); 8.04-8.11 (m, 8H, CH$_{pyr}$(4')); 8.26 (s, 4H, CH$_{pyr}$(3)); 8.51 (d, 8.3 Hz, 8H, CH$_{pyr}$(3')); ^{13}C (CD$_3$CN, 75 MHz, 25 °C): 29.39 (CH$_2$(b)); 32.56 (CH$_2$(a)); 125.23 (C$_{pyr}$(3')); 125.70 (C$_{pyr}$(3)); 128.58 (C$_{pyr}$(5')); 128.71 (C$_{pyr}$(5)); 138.70 (C$_{pyr}$(4')); 152.36, 152.57, 152.78 (C$_{pyr}$(6), C$_{pyr}$(6')); 153.98 (C$_{pyr}$(4)); 158.00, 158.08 (C$_{pyr}$(2), C$_{pyr}$(2')); **3-**Ru$_2$, 4PF$_6^-$: ^{1}H (CDCl$_3$, 300 MHz, 25 °C): 1.78 (m, 8H, CH$_2$); 2.92 (br.s, 8H, CH$_2$); 7.24 (br.d, 4H, CH$_{pyr}$(5)); 7.36 (m, 8H, CH$_{pyr}$(5')); 7.55 (d, 5.8 Hz, 4H, CH$_{pyr}$(6)); 7.69 (m, 8H, CH$_{pyr}$(6')); 8.02 (m, 8H, CH$_{pyr}$(4')); 8.48 (br.d, 12H, CH$_{pyr}$(3'), CH$_{pyr}$(3)); ^{13}C (CD$_3$CN, 75 MHz, 25 °C): 28.98 (CH$_2$); 34.81 (CH$_2$); 125.18 (C$_{pyr}$(3')); 128.44, 128.51, 128.96 (C$_{pyr}$(3), C$_{pyr}$(5'), C$_{pyr}$(5)); 138.68 (C$_{pyr}$(4')); 151.73 (C$_{pyr}$(6)); 152.44, 152.60 (C$_{pyr}$(6')); 155.25 (C$_{pyr}$(4)); 157.75, 158.02, 158.09 (C$_{pyr}$(2), C$_{pyr}$(2')).
16. *X-ray data for* ***3-Ru$_2$ complex*** C$_{68}$H$_{60}$N$_{12}$Ru$_2$•4PF$_6$•CH$_3$OH, M = 1859.4, monoclinic, a = 9.960(3), b = 29.196(10), c = 13.553(4) Å, β = 100.39(2)°, U = 3876.5 Å^3, space group P2$_1$/c Z = 2, Dc = 1.593 gcm^{-3}, μ(Cu-Kα) = 49.947 cm^{-1}. Crystal dimensions 0.40x0.35x0.30 mm. Data were measured at 173K on a Philips PW1100 diffractometer with graphite monochromated Cu-Kα radiation. The structure was solved by direct methods and refined anisotropically using absorption corrected data to give R = 0.093, Rw = 0.126 for 2981 independent observed reflections [$|F_o| > 3\sigma(|F_o|$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
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