

# Novel anion binding selectivity trends exhibited by new dinuclear rhenium(i), ruthenium(ii) and osmium(ii) bipyridyl cleft-type receptors

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**Novel dinuclear rhenium(i), ruthenium(ii) and osmium(ii) bipyridyl cleft-type receptor systems exhibit remarkable selectivity for dihydrogenphosphate over halide anions dictated by the nature of the bridging linkage and the transition-metal Lewis-acidic centre.**

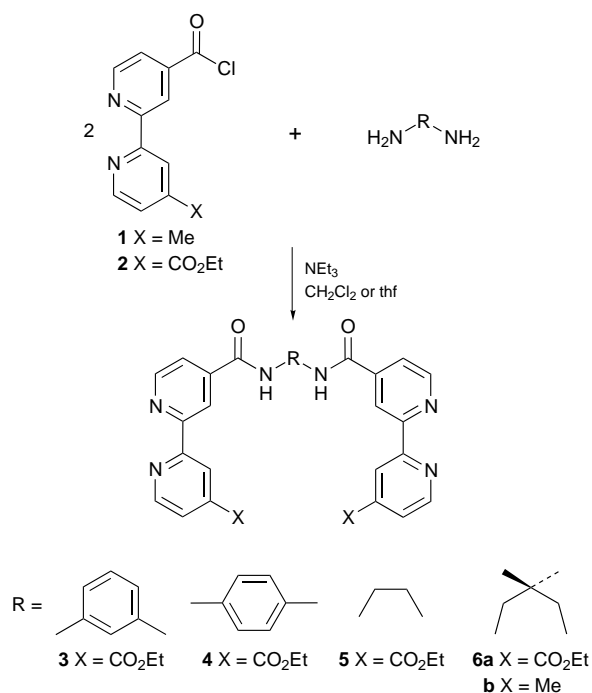
Anions are of crucial importance in many essential chemical and biochemical processes and therefore their binding and recognition is presently the subject of intensive research.<sup>1</sup> To date, a number of research groups have designed and synthesised anion binding reagents that use either favourable hydrogen-bonding interactions alone,<sup>2,3</sup> or hydrogen-bonding interactions in conjunction with electrostatic forces<sup>4–6</sup> to coordinate and, in some instances, sense anions. Examples of the latter which have been particularly successful in this respect are amide containing cobaltocenium<sup>7,8</sup> and ruthenium(ii) polypyridyl molecules.<sup>9–11</sup> In an effort to enhance selective anion recognition through the design of new cooperative polymetallic Lewis-acidic systems, we report here the synthesis of novel dinuclear transition-metal bipyridyl, cleft-type receptors whose remarkable selectivity for the dihydrogenphosphate anion over halide anions is profoundly influenced by the nature of the bridging linkage, and the electronic character of the transition-metal Lewis-acidic centre.

The reaction of 4-carboxy-4'-methyl-2,2'-bipyridine<sup>12</sup> or 4-carboxyl-4'-ethoxycarbonyl-2,2'-bipyridine<sup>13</sup> with thionyl chloride afforded the acid chlorides **1** and **2** respectively in quantitative yields. The condensation of 2 equiv. of **1** or **2** with

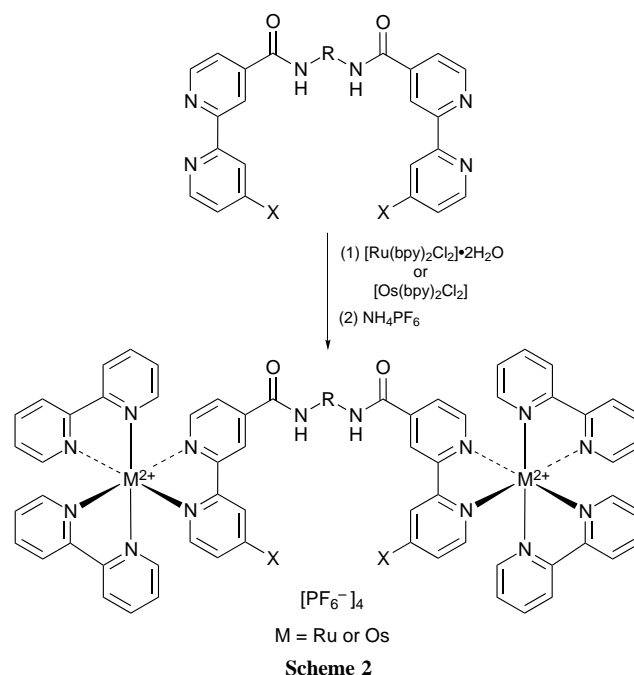
1 equiv. of diamine in dichloromethane solution afforded the new 'cleft'-type bipyridyl (bpy) ligands **3–6** in excellent yields (Scheme 1). The free ligands were chelated to the positively charged  $[M(\text{bpy})_2]^{2+}$  fragment ( $M = \text{Ru}, \text{Os}$ ) unit by reaction with either 2 equiv. of *cis*- $[\text{Ru}(\text{bpy})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ <sup>14</sup> or *cis*- $[\text{Os}(\text{bpy})_2\text{Cl}_2]$ <sup>15</sup> in ethanol–water–acetic acid. The mixed ruthenium–osmium receptor, Ru–**6b**–Os, was prepared by reaction of ligand **6b** with 1 equiv. of *cis*- $[\text{Ru}(\text{bpy})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ , followed by 1 equiv. of *cis*- $[\text{Os}(\text{bpy})_2\text{Cl}_2]$ . The crude products were purified by column chromatography on Sephadex LH-20 and converted to the hexafluorophosphate salts with an excess of aqueous  $\text{NH}_4\text{PF}_6$  (Scheme 2). The rhenium(i) receptor, Re–**6b**–Re, was prepared by reaction of the free ligand **6b** with 2 equiv. of  $[\text{Re}(\text{CO})_5\text{Br}]$  in thf and purified by recrystallisation from acetone–diethyl ether (Scheme 3).<sup>‡</sup>

Proton NMR titration experiments with  $\text{Cl}^-$  and  $\text{H}_2\text{PO}_4^-$  anions were carried out in  $(\text{CD}_3)_2\text{SO}$  solution and revealed significant downfield shifts in the receptors' amide and 3,3'-bpy protons. For example, the amide protons of Ru–**6b**–Ru were perturbed by 0.93 ppm and the 3,3'-bpy protons by 0.84 ppm after the addition of an excess of tetrabutylammonium dihydrogenphosphate. In all cases the resulting titration curves (for example, Fig. 1) suggest complexes with a 1 : 1 receptor : anion stoichiometry are formed in solution. Stability constants were calculated from the titration data using the EQNMR computer program<sup>16</sup> and the values are presented in Table 1.<sup>§</sup>

Clearly the nature of the bridging linkage has a dramatic influence on the anion binding strength and selectivity these dinuclear cleft-type receptors display. Of particular note is the

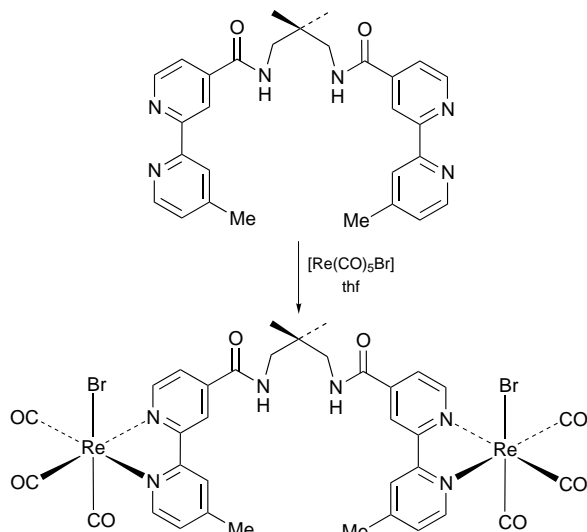


Scheme 1



Scheme 2

remarkable increase in the magnitude of stability constant of  $\text{H}_2\text{PO}_4^-$  that results from simply altering the linkage from *m*-phenylene Ru-3-Ru ( $K = 55 \text{ m}^{-1}$ ) to *p*-phenylene Ru-4-Ru ( $K = 4320 \text{ m}^{-1}$ ), with the halide stability constant values remaining virtually unchanged. In addition, whereas the ethyl-bridged receptor Ru-5-Ru forms an extremely weak complex



Scheme 3

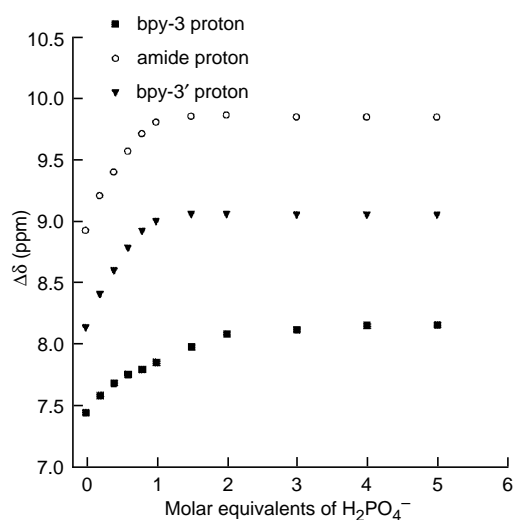


Fig. 1  $^1\text{H}$  NMR titration curve of Ru-6b-Ru with  $\text{NBu}_4\text{H}_2\text{PO}_4$  in  $(\text{CD}_3)_2\text{SO}$

Table 1 Stability constant data for dinuclear cleft-anion receptors in  $(\text{CD}_3)_2\text{SO}$

Receptor	$K(\text{Cl}^-)^{a,b}/\text{m}^{-1}$	$K(\text{Br}^-)^{a,b}/\text{m}^{-1}$	$K(\text{H}_2\text{PO}_4^-)^{a,b}/\text{m}^{-1}$
Ru-3-Ru	25	45	55
Ru-4-Ru	55	40	4320
Ru-5-Ru	70	60	10
Ru-6a-Ru	245	170	19700
Re-6b-Re	120	— <sup>c</sup>	1820
Ru-6b-Ru	310	220	15480
Ru-6b-Os	440	— <sup>c</sup>	22150
Os-6b-Os	825	— <sup>c</sup>	>30000

<sup>a</sup> Average for amide and bpy protons. <sup>b</sup> Errors estimated to be < 10%. <sup>c</sup> Not calculated.

with  $\text{H}_2\text{PO}_4^-$  and is  $\text{Cl}^-$  selective, the 2,2'-dimethyl-1,3-propane-bridged analogue, Ru-6a-Ru forms an extremely strong and selective complex with  $\text{H}_2\text{PO}_4^-$ . Comparing Ru-6a-Ru and Ru-6b-Ru, it is also of interest to note there is a significant 4'-bipyridyl substituent effect, with  $\text{H}_2\text{PO}_4^-$  anions favouring the ester containing receptor and chloride the methyl containing one.

Table 1 also demonstrates that the nature of the bipyridyl-coordinated transition-metal centre strikingly dictates the strength and degree of anion recognition selectivity. With both  $\text{H}_2\text{PO}_4^-$  and  $\text{Cl}^-$  anionic guest species the stability constants increase in magnitude in the order Re-6b-Re < Ru-6b-Ru < Ru-6b-Os < Os-6b-Os. From electrostatic considerations it is perhaps not surprising the neutral bis-rhenium(i) receptor forms the relatively weaker anion complexes. However, what is unexpected is the dramatic increase in magnitude of stability constant for the osmium-containing receptors, especially in respect to  $\text{H}_2\text{PO}_4^-$  complexation. This observation suggests the  $(\text{bpy})_2\text{Os}^{2+}$  moiety is a particularly efficient Lewis-acidic centre to incorporate into this new cleft-type class of transition-metal bipyridyl amide anion receptor.

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### Footnotes

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‡ All new compounds were fully characterised by elemental analysis,  $^1\text{H}$  and  $^{13}\text{C}$  NMR and FABMS.

¶ The addition of chloride or dihydrogenphosphate anions to  $(\text{CD}_3)_2\text{SO}$  solutions of  $[\text{M}(\text{bpy})_3][\text{PF}_6]_2$  ( $\text{M} = \text{Ru}, \text{Os}$ ) had no effect on the  $^1\text{H}$  NMR spectrum. The metal-free bipyridyl ligands exhibited extremely weak and insignificant interactions with both chloride and dihydrogenphosphate anions in  $(\text{CD}_3)_2\text{SO}$ .

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