**Metal-based Polypyridyl Ligands: Catalysis, Redox Behavior and Supramolecular Assemblies**

Neutral tris(pyridyl) ligands of the general type [Y(Py)3] (Py = 2-pyridyl, Y = CR, COR, CH, N, P, P=O, As; **A** Fig. 1), have emerged as a new important family of ligands with interesting coordination characteristics, as shown by a large number of studies in the past few years and developing applications in catalysis. However, most of these systems are based on relatively simple pyridine ligands with no elaboration or functionalization of their framework. It is been only relatively recently, however, that attention has turned to ligands containing the heavier Group 13 and 14 atoms at the bridgehead. This change from a non-metallic to a more metallic atom in particular opens up the possibility of redox activity and variable oxidation states at the bridgehead.

In this program, we have developed a synthetic methodology to prepare new tris(2-pyridyl) aluminate ligands [RAl(2-py′)3] (**B**, Fig 1) in multigram scale containing different bridgehead groups (R’) and substituted (R) or non-substituted 2-pyridyl groups (2-py′) and studied the structure-reactivity relationship of such compounds. Although neither the bridgehead group (R’) nor remote ring Me-groups appear to have any steric or electronic impact on metal coordination, the introduction of Me groups into the pyridyl substituent at the 6-position has a marked effect on the ability of the ligands to form sandwich arrangements of the type [{RAl(2-py′)3}2M. We have also developed a convenient synthetic methodology, using a set of ligand exchange reactions in which the lithium precursors [RAl(2-py´)3Li] react with M(II)-halides (MX2) or cyclopentadienide reagents (MCp2), to access different heterometallic complexes. From these studies, we have found that the electronic and steric properties of the ligand can be easily tuned though the introduction of groups at the 6 position of the pyridyl ring (R = CH3, CF3, and Br). The introduction of such groups greatly affects the coordination properties of the ligand and can be potentially used for the stabilisation of unusual metal oxidation states. These studies also show that, unlike other main group metal bridged tris-pyridyl ligand systems (such as the SnII variant [Sn(2-py)3]-), the presence of Al provides a redox-stable ligand set. This is best illustrated by the stabilisation of Sm2+ in the sandwich compound [{EtAl(2-py)3}2Sm], a very rare example of this type of sandwich structure containing this metal in the II-oxidation state.



**Fig. 1**. The framework found in the family of tris(2-pyridyl) ligands (**A**), the tris(2-pyridyl)aluminate family of ligands (**B**), and the sandwich compound [{EtAl(2-py)3}2Sm] (**C**).

Although the introduction of electron-withdrawing groups such as CF3 and Br into the 6-positions of the pyridyl ring completely blocks the coordination behaviour of the ligand, this steric effect can potentially be turned to an advantage in the stabilization of unusual AlIII complexes. An example of the effects of this is seen in the stabilization of terminal Al-OH groups in a new class of stable heteroleptic aluminium 2-py/OH complexes (**C**, Fig 1). Facile incorporation of alcohols into heteroleptic 2-py ligand arrangements can also be accomplished. This opens up a new avenue for extensive elaboration of the steric and donor character of these ligands and the introduction of chirality (in the form of chiral alkoxide ligands, see below).

In the course of the project we have explored other unknown facets of pyridyl aluminate ligands, such as the ability of tris(pyridyl) aluminates to act as ‘soft’ pyridyl transfer reagents, allowing the direct synthesis of (MePy)3Sn–Sn(MePy)3, a Janus-Head pyridyl ligand system featuring a Sn-Sn bond, by reaction with SnCl2 in a one-pot reaction. The synthesis avoids the use of highly unstable or poorly defined SnIV hexa-halides and it is the first demonstration of the ability of tris(2-pyridyl) aluminate anions to act as 2-pyridyl transfer reagents in combination with oxidation of metal centres.

**Tris-Pyridyl aluminates in catalysis: Preparation of chiral pyridyl ligands and chiral complexes**

The most recent studies have now indicated the surprising conclusion that epoxidation reaction of alkenes may involve 2-py ligand displacement, in a short induction period, to form the active catalyst which contains an Al-(-O)-FeIII fragment. Thus the catalytic reaction with O2 can be seen as resulting from a synergy of the two metal components, the combined oxophilicity on one hand and the flexibility of oxidation state on the other. We have found that the controlled O2-oxidation of the Sm(II) sandwich compound [{EtAl(2-py)3}2Sm] gives the Sm(III)/Al(III) compound [{EtAl(2-py)3}{EtAl(2-py)2O}Sm]2, containing the novel multifunctional dianionic ligand [EtAl(2-py)2O]2-(**1**, Figure 2). The formation of this O-bridged Al-O-Sm arrangement is potentially relevant to the catalytic epoxidation of styrene with dry air using heterobimetallic sandwich compounds. In this context the new complex [{EtAl(2-py)3}{EtAl(2-py)2O}Sm]2 can be regarded as a potential model intermediate in this type of reaction by which molecular O2 is transferred into active O atoms prior to reaction with the alkene.



**Fig 2**. Heterobimetallic Sm(III)/Al(III) compound [{EtAl(2-py)3}{EtAl(2-py)2O}Sm]2 (**1**) and chiral pyridyl aluminates (**2** and **3**).

The development of asymmetric oxidation catalysts requires incorporating chirality at the *tris*-pyridyl ligands. Since chiral bridgehead or ring substituents are in close proximity to the Al/M active metal centres, both are likely to have an effect on chiral transmission to a pro-chiral alkene substrate such as terminal alkenes of the type RCH=CH2. We have explored two obvious ways to introduce chirality within the tris-pyridyl ligands: substitution of the bridgehead position (R’) with a chiral substituent or substitution of the 2-py´ units with chiral groups at the pyridyl ring (R). We have introduced chirality through the bridgehead atom of the trispyridyl ligand (*i.e.* introduction of a sec-butyl group). Although the synthesis of the ligand is in low yield and a racemic mixture is obtained, heterometallic complexes (*i.e.* Ca/Al and Mn/Al) incorporating the ligand can be prepared.

Regarding the introduction of chiral substituents at the 6-position of the pyridyl ring, we have shown that the presence of groups at the 6- position of the 2-py substituents (*i.e*., adjacent to the N-atom) has a large effect on the coordination ability of the resulting [RAl(2-py´)3]- anions. In the case of the 6-Me substituted ligand [EtAl(6-Me-2py)3] *cannot* form a sandwich compound with Fe owing to steric congestion. At the same time, if the chiral ring substituent is too remote, then it is unlikely to have an effect on the enantioselectivity of epoxidation. We circumvent these difficulties by introducing chirality through a novel methodology in the form of a chiral alkoxide. In this manner, the first examples of chiral pyridyl aluminates can be prepared by selective replacement of one or two the pyridyl groups under mild conditions and without racemization (**2** and **3**, Figure 2). The generalization of this methodology and its selectivity in building heteroleptic systems is demonstrated by the introduction of other functionalities (*i.e.* carboxylic acids) in the aluminate framework, thus showing its potential for extensive elaboration of the steric and donor character of these ligands.