Highly selective epoxidation of styrene using a transition metal–aluminium(III) complex containing the $[MeAl(2\text{-}py)_3]^-$ anion (2-py = 2-pyridyl)†

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The reactions of $[MeAl(2\text{-}py)_3Li\cdot thf]$ (1) with $FeCl_2$ or Cp_2Mn in toluene–thf give simple access to the Group 13–transition metal heterometallic complexes $[\{MeAl(2\text{-}py)_3\}_2M]$ [M = Fe (2), Mn (3)]; complex 2 has been shown to be a highly selective styrene epoxidation catalyst in air.

In the past two decades there has been considerable interest in tris-pyridyl ligands of the general type shown in Fig. 1.[1] Interest in these and in related tris-pyrazolylborates and -methanes[2] has focused on their broad applications in coordination, organometallic and bioinorganic chemistry as well as in homogeneous catalysis. One potential difference between the tris-pyridyl and tris-pyrazolyl ligands is the better σ-donor and π-acceptor properties of pyridine,[1] which should lead to differences in coordination properties. Modification of the bridgehead groups/atoms (Y) provides a further potential means by which metal coordination properties of tris-pyridyl ligands can be tailored, both geometrically and electronically. To date, the vast majority of studies of ligands of this type have involved those containing non-metallic bridgeheads, commonly Y = CX (X = H, OH, OR, NH_2), N, P and P=O.[1] Our interest in this area has focused on the incorporation of p-block metals as the bridgehead.[3] Such species normally have larger bite angles than their non-metallic counterparts and can have variable oxidation states and potential electrochemical activity at the bridgehead. The coordination of such ligands to metal centres also provides a simple approach to heterometallic compounds. We report here the successful application of this approach in the synthesis of the Al(III)–transition metal complexes $[\{MeAl(2\text{-}py)_3\}_2Fe]$ (**2**) and $[\{MeAl(2\text{-}py)_3\}_2Mn]$ (**3**) using the $[MeAl(2\text{-}py)_3]^-$ anion, a ligand which combines the features of negative charge found in tris-pyrazolylborate ligands with the different donor characteristics of pyridyl counterparts. The potential of these heterometallic species as homogeneous catalysts is illustrated by the selective epoxidation of styrene by **2** in air.

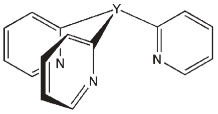
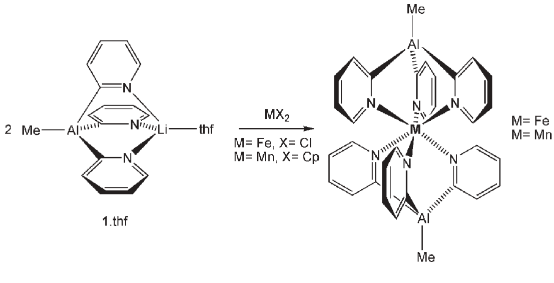


Fig. 1 Structural arrangement found in tris-pyridyl ligands (*e.g.*, Y = HC, P, N).

We recently reported the first potential source of a Group 13 tris-pyridyl ligand $[MeAl(2\text{-}py)_3]^-$.[4] Preliminary studies revealed, however, that as a consequence of the polarity of the C–Al bond one facet of the behaviour of this anion is its ability to function as a thermally-stable source of $[2\text{-}py]^-$, reaction of the $[MeAl(2\text{-}py)_3]^-$ ion with CuCl giving $[\{Cu(2\text{-}py)\}_3]_\infty$.[4] Surprisingly, the reactions of $[\{MeAl(2\text{-}py)_3Li\cdot thf]$ (**1**) with $FeCl_2$ or Cp_2Mn (1 : 1 or 1 : 2 equivalents) follow a completely different course, the products being the heterometallic compounds $[\{MeAl(2\text{-}py)_3\}_2Fe]$ (**2**) and $[\{MeAl(2\text{-}py)_3\}_2Mn]$ (**3**) in which transfer of the $[MeAl(2\text{-}py)_3]^-$ anion intact to the Fe(II) and Mn(II) centres has occurred (Scheme 1) (ESI†,§). The different outcome of the reaction involving Cu(I) presumably results from the preference for a linear ligand coordination geometry in $[\{Cu(2\text{-}py)\}_3]_\infty$. The ^1H NMR spectrum of **2** indicates the presence of at least one paramagnetic species in solution (200–300 K). Magnetic measurements of solid **2** confirm that the complex is paramagnetic at room temperature.[5] Only charge-transfer transitions can be observed in the UV/visible spectrum of **2** in thf. Two of these absorptions [27 322 (ε = *ca.* 8 000 $mol^{-1}\ dm^3\ cm^{-1}$) and 23 175 (ε = *ca.* 17 100 $mol^{-1}\ dm^3\ cm^{-1}$)] have similar energies and extinction coefficients to those found previously in the solution spectra of $[\{Y(2\text{-}py)_3\}_2Fe]^{2+}$ (Y = CH, P=O).[6a] However, unlike the latter an extremely intense, low-energy transition [19 627 cm^{-1} (ε = *ca.* 26 000 $mol^{-1}\ dm^3\ cm^{-1}$)] is also found for **2**, which is responsible for the deep-red colour of the complex.[7] Cyclic voltammetry of **2** shows the



Scheme 1

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† Electronic supplementary information (ESI) available: §synthetic details and characterisation data for complexes **2** and **3**; ¶details of the catalytic reaction and kinetic plot for the epoxidation of styrene at 80 °C. See http://www.rsc.org/suppdata/cc/b4/b413488e/

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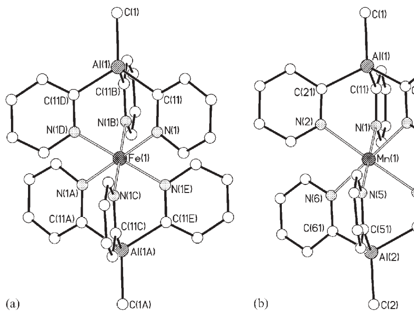
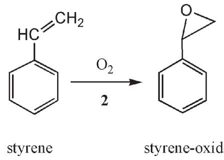


Fig. 2 (a) Structure of the Fe(II) complex **2**, of crystallographic $\bar{3}$ symmetry. Selected bond lengths (Å) and angles (°): Fe(1)–N(1) 2.054(3), Al(1)–C(1) 1.969(3), Al(1)–C(11) 1.969(3), C(11)–N(1) 1.369(4), Al(1)···Fe(1) 3.334(7), intra-ligand N···N mean 3.01, C(11)–Al(1)–C(11B) 101.8(1), C(1)–Al(1)–C(11) 116.3(1), C(11)–N(1)–Fe(1) 123.3(2), N(1)–Fe(1)–N(1A) 180.0, N(1)–Fe(1)–N(1B) 94.2(1), N(1)–Fe(1)–N(1C) 85.8(1). Symmetry: A $2 - x, -y, 2 - z$; B $1 - y, -1 + (x - y), z$; C $1 + y, 1 - (x - y), 2 - z$. (b) Structure of the Mn(II) complex **3**: Mn(1)–N(1) 2.305(3), Mn(1)–N(2) 2.300(3), Mn(1)–N(3) 2.296(3), Mn(1)–N(4) 2.295(4), Mn(1)–N(5) 2.300(3), Mn(1)–N(6) 2.291(3), Al(1,2)–C(1,2) mean 1.983(5), Al(1,2)–C(11–61) 2.010(4)–2.014(3), Mn(1)···Al(1,2) mean 3.493, intra-ligand N···N mean 3.28, Cα–Al–Cα 103.5(2)–104.7(2), N–Mn(1)–N 88.2(2)–179.6(3). H atoms and the molecule of thf in the lattice of **3** have been omitted for clarity.

presence of a quasi-reversible Fe(III)/Fe(II) couple of $E_{1/2} = -0.08$ V together with an irreversible Fe(II)/Fe(I) couple at –1.13 V (relative to Ag/Ag$^+$).[6b]

The low-temperature X-ray crystallographic studies of **2** (Fig. 2a) and **3**·thf (Fig. 2b)‡ show that both complexes have similar structural arrangements in which octahedral Fe(II) and Mn(II) ions are coordinated by two [MeAl(2-py)$_3$]$^-$ anions. Bis-coordinated transition metal complexes of this type are common for tris-pyridyl ligands containing non-metallic (C, N and P) bridgeheads, and the Fe(II) cations [{N(2-py)$_3$}$_2$Fe]$^{2+}$, [{HOC(2-py)$_3$}$_2$Fe]$^{2+}$ and [{O=P(2-py)$_3$}$_2$Fe]$^{2+}$ have been characterised previously.[6a,8] However, **2** and **3** are the first examples of such bis-coordinated complexes containing metallic bridgeheads and are the first examples of neutral bis-coordinated complexes containing any type of tris-pyridyl ligand. The neutrality of **2** and **3** makes them comparable with classical tris-pyrazolylborate complexes,[9] such as the Fe(II) complex [{HB(pz)$_3$}$_2$Fe].[6a] Although the Cα–Al–Cα angles within the [MeAl(2-py)$_3$]$^-$ anions of **3** [103.5(2)–104.7(2)°] are similar to those found in the Li$^+$ precursor **1** [103.8(1)–104.4(1)°],[4] there is a noticeable compression of the bridgehead angle in **2** [101.8(1)°]. This difference is explained by the shortness of the Fe–N bonds in **2** [2.054(3) Å][6,9] compared to the much longer Mn–N bond distances in **3** [2.291(3)–2.305(3) Å]. The bond lengths in both complexes are, however, consistent with the presence of high-spin Fe(II) and Mn(II) ions.



Scheme 2

Although a large number of catalytic systems based on a range of transition metals have been reported for the oxidation of alkenes, these have normally required expensive oxidants in the reactions (such as H_2O_2 and TBHP).[10] These systems are commonly not environmentally friendly, are not selective and require high reactor pressures.[11] Preliminary studies of the use of **2** as a homogeneous catalyst for the industrially important epoxidation of styrene (Scheme 2) were undertaken at various temperatures (Table 1) (ESI†,¶). Most significant is the selective formation of styrene oxide in this reaction under extremely mild conditions using only air as the oxidant. For example, although the conversion of styrene into styrene oxide is only 45.7% at 65 °C in 1 h, the product is generated almost exclusively under these conditions and little 1,2-diol is formed. In addition, no polymers and no benzaldehyde are generated at this temperature. To the best of our knowledge, **2** is one of the most selective epoxidation catalysts for styrene yet observed, in the absence of an added oxidant.[12,13] For example, the most selective catalyst of this type previously reported for the epoxidation of styrene gave a 45% conversion to products with a selectivity of 65% styrene oxide (*i.e.*, well below the selectivity of **2** in this reaction).[12] At this stage, the mechanism of the reaction is not known. However, previous studies suggest that it could involve the initial formation of a binuclear μ_2-O bridged Fe(III) complex as the active species.[6a,9a]

In summary, we have shown that the [MeAl(2-py)$_3$]$^-$ anion can be readily transferred on to transition metal centres, the compounds **2** and **3** being the first bis-coordinated complexes involving a metallic scorpionate ligand of this type. The observed selectivity of the epoxidation reaction of styrene is particularly worthy of note and provides future promise of the potentially broader applications of these readily accessible bimetallic main group–transition metal complexes in catalysis.

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Table 1 Reaction conditions, conversions and product distributions for the reactions of styrene with dry air in the presence of **2**. All reactions were undertaken at a pressure of 45 bar under an inert atmosphere

				Product selectivity			
Experiment No.	Temp./°C	Time/h	Conv. (%)	Epoxide	Diols	Polymers	Benzaldehyde
1	65 °C	1	45.7	96.5	3.2	—	—
		4	84.3	86.5	13.5	—	—
2	65 °C	1	46.3	97.1	2.8	—	—
		4	85.0	85.5	14.5	—	—
3	80 °C	1	65.7	89.5	5.1	5.3	—
		4	88.5	63.1	15.6	21.2	—
4	100 °C	0.5	72.0	39.0	14.5	18.8	27.6
		4	99.6	—	32.3	27.5	40.3

Colleges, Cambridge (Fellowship for A. D. H.), B.P. (R.R.), Clare College, Cambridge (Denman Baynes Fellowship, R. A. L.) St. Catharine's College, Cambridge (Fellowship for A. D. W.), the States of Guernsey and the Domestic and Millennium Fund (R. A. K.), and the Cambridge European Trust (F. G.) for financial support. We also thank Dr. J. Davies for collecting X-ray data on complexes **2** and **3**.

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Notes and references

‡ Crystal data for **2**: $C_{32}H_{30}Al_2FeN_6$, M= 608.43, rhombohedral, space group $R\bar{3}$, Z = 3, a = b = 10.2291(5), c = 33.6643(18) Å, V = 3050.5(3) Å, μ(Mo–Kα) = 0.438 mm^{-1}, T = 180(2) K. Data were collected on a Nonius KappaCCD diffractometer. Of a total of 5072 reflections collected, 670 were independent (R_{int} = 0.072). The structure was solved by direct methods and refined by full-matrix least squares on F^2 (G. M. Sheldrick, SHELX-97, Göttingen, 1997). Application of the SQUEEZE programme in PLATON (version 1.07: A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7) removed unassigned residual electron density due to disordered solvent. Final $R1$ = 0.042 [$I > 2\sigma(I)$] and $wR2$ = 0.113 (all data). CCDC 249604. Crystal data for **3**·thf; $C_{36}H_{38}Al_2MnN_6O$, M = 679.62, monoclinic, space group Cc, Z = 4, a = 9.2658(19), b = 24.167(5), c = 15.877(3) Å, V = 3553.1(12) Å, μ(Mo–Kα) = 0.458 mm^{-1}, T = 180(2) K. Data were collected on a Nonius KappaCCD diffractometer. Of a total of 9511 reflections collected, 4469 were independent (R_{int} = 0.067). The structure was solved by direct methods and refined by full-matrix least squares on F^2 (G. M. Sheldrick, SHELX-97, Göttingen, 1997). Four residual maxima in the final difference Fourier (*ca.* 2–3 eÅ^{-3}) could not be explained. Repeated data collection failed to resolve this problem that was attributed to co-crystallisation of small amounts of an unidentified material. The most satisfactory refinement was obtained by arbitrarily assigning metal atoms of 10% occupancy to the four sites of residual electron density. Final $R1$ = 0.069 [$I > 2\sigma(I)$] and $wR2$ = 0.179 (all data). CCDC 249605. See http://www.rsc.org/suppdata/cc/b4/b413488e/ for crystallographic data in .cif or other electronic format.

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