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Nucleophilic attack at pyridine nitrogen and its use to access a novel mono-anionic ligand for iron-based ethylene polymerisation catalysts†

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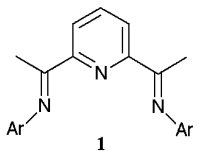
Addition of MeLi to bis(imino)pyridines results in an unprecedented nucleophilic attack at pyridine nitrogen to afford novel mono-anionic [N,N,N] ligands: their treatment with $FeCl_3$, followed by MAO activation, affords highly active ethylene polymerisation catalysts.

Some of the most significant recent advances in olefin polymerisation catalysis have been found where unsaturated nitrogen donor groups, especially imines, are incorporated into a bidentate or tridentate ligand frame.[1] Most notable have been α-diimine (Ni, Pd),[2] bis(imino)pyridine (Fe, Co)[3] and salicylaldimine (Ti,[4] Ni[5]) ligand systems. However, the precise role of such ligands in the active catalysts is still not well understood. They differ from other categories of ligands in that they possess a number of potentially reactive sites, including the nitrogen and carbon centres of the imino unit,[6,7] and their adjacent functionalities. For example, in the case of bis(imino)-pyridines (**1**) deprotonation of the ketimine methyl group by a



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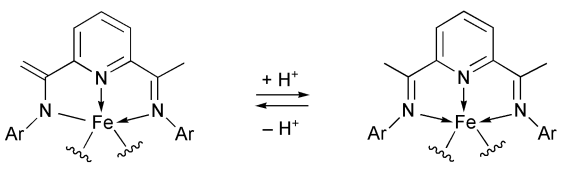
non-nucleophilic base such as lithium diisopropylamide (LDA) can be exploited to prepare modified bis(imino)pyridine ligands,[8] while nucleophilic attack at the 2 and 3 positions of the pyridine ring has been observed in an active vanadium catalyst system.[9] Additionally, we have shown that Me_3Al can attack the imine carbon to give a monoanionic imino-amide ligand.[10] These unsaturated ligands are also known to undergo ready one-electron reduction reactions.[11]

In the case of iron catalysts bearing bis(imino)pyridine ligands we have found no evidence for the ligand being modified at the metal centre due to the action of methylaluminoxane (MAO). Indeed, the ligand can be recovered in high yield after acid work-up of polymerization mixtures.[3] While this seems to rule out any C–C bond formation, it does not eliminate the possibility of *in situ* deprotonation of the ketimine methyl group to afford a monoanionic ligand that would be re-protonated upon work-up as shown in Scheme 1. Partly for this reason, and partly with a view to providing a useful handle by ^{2}H NMR spectroscopy for studying the paramagnetic pre-



Scheme 1

† Electronic supplementary information (ESI) available: further characterisation data for **2a**–**5a**. See http://www.rsc.org/suppdata/cc/b2/b203805f/

cursors and active species, we decided to prepare d_6-bis(imino-)pyridines in which the two ketimine methyl groups are deuterated.[12] We considered that replacing the protons at this position by deuterons would result in a system that is more robust towards deprotonation by basic reagents such as MeLi. In earlier studies we had found that Bu^{n}Li reacts with per-protio bis(imino)pyridines to give deep blue products which, upon treatment with $FeCl_3$ and MAO, afford highly active ethylene polymerization catalysts.[13] Attempts to identify the product(s) of alkyllithium addition to bis(imino)pyridines had proved unsuccessful; these reactions invariably gave a variety of products which were evident by NMR spectroscopy. Here, we describe the reaction of d_6-bis(imino)pyridines with MeLi to afford novel [N,N,N] ligands arising from nucleophilic attack at pyridine nitrogen. To our knowledge, such a reaction is without precedent. Subsequent treatment of the lithium salts of these ligands with $FeCl_3$ gave highly active iron catalysts for ethylene polymerisation.

The d_6-derivatives of **1** were prepared by heating the ligand precursor, 2,6-diacetylpyridine, to reflux in D_2O–ethanol-d_1 for a prolonged period (> 24 h). Deuteration of the backbone position is achieved to > 90% saturation, presumably *via* enamine intermediates. Condensation between the d_6-precursor and excess aniline in ethanol-d_1 completes the synthesis to give a family of [{(2,6-$R_2C_6H_3$)N=C(CD_3)}$_2C_5H_3N$] ligands (R = Pr^i, **2**; R = Et, **3**; R = Me, **4**) and the mesityl derivative [{(2,4,6-$Me_3C_6H_2$)N=C(CD_3)}$_2C_5H_3N$] (**5**). As anticipated, EI mass spectra of **2**–**5** display molecular ions up to six mass units higher than for their protio-analogues. The addition of 1–2 equivalents of MeLi to a slurry of **2** in Et_2O at −78 °C produces a deep-blue solution whose colour persists upon warming to room temperature. Dark blue crystals of air-sensitive **2a** were obtained in 60% yield as the sole product after work-up. Integration of the ^{1}H NMR spectrum of **2a** in benzene-d_6 revealed that a single methyl group had been added to **2**. Also observed in the spectrum were signals arising from two sets of methine protons, four sets of isopropyl methyl hydrogens, and a symmetric AX_2 pattern due to the pyridine protons (δ 6.91 (2H), 5.41 (1H), $^3J_{HH'}$ 7.3 Hz) that have moved markedly upfield with respect to the pyridine protons of **2**. Evidently the added methyl has destroyed the planar symmetry of the pyridine ring in **2** yet preserved the overall C_s symmetry of the molecule. These data are consistent with addition of the methyl group to either the 1-N or 4-*para*-C positions of the pyridine ring. Dark-blue crystals of **3a**–**5a**, with spectroscopic properties analogous to those of **2a**, could be likewise obtained from **3**–**5**, respectively. Given that no coupling is observed between the added methyl and the protons of the pyridine ring, it is reasonable to conclude that MeLi has attacked at the pyridine nitrogen (Scheme 2). N-methylation was unequivocally confirmed by a single-crystal X-ray diffraction experiment and the structure of **2a** is shown in Fig. 1.‡

The molecule possesses approximate, non-crystallographic C_s symmetry about the C1–N1–Li vector and therefore the solution structure is preserved in the solid-state. The central nitrogen (N1) is directly bonded to three carbon centres and the bond lengths and bond angles are consistent with a fully

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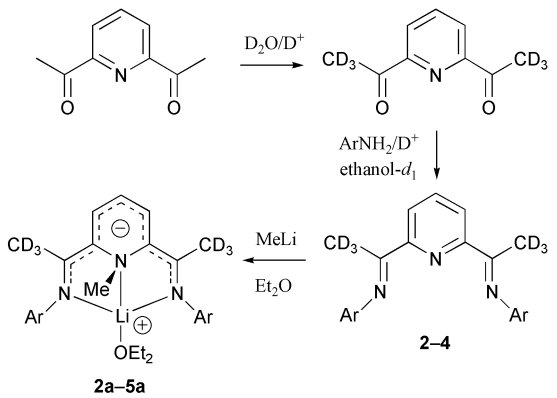
saturated nitrogen centre. While N1 no longer participates in a planar aromatic heterocycle, the C–C bond lengths within the pyridine ring (1.38–1.40 Å) indicate extensive delocalization. The C–C linkages between the ring and the imine arms (C3–C21, C4–C7 = 1.431(4), 1.427(4) Å) are both significantly short, whereas the C=N distances between the *ipso*-carbon and the imine nitrogen are long (C21–N2, C7–N3 = 1.319(2), 1.322(3) Å) compared to the equivalent distances in the carbocyclic analogues [1,3-(2,6-$Pr^i_2C_6H_3N$=C(Me))$_2C_6H_3$].[14] Evidently, delocalization extends beyond the ring to each of the imine arms, and the formal negative charge associated with the structure is apparently distributed over nine centres. Consistent with this hypothesis is the observed symmetric coordination geometry around the lithium nucleus. The unsaturated nitrogen donors of **2a** are separated from the lithium centre by an average distance of 2.16 Å, whereas the Li–N1 distance, formally a lone pair interaction, is 2.029(5) Å. Coordination around the Li atom is completed by a single, disordered Et_2O molecule.

This highly selective nucleophilic attack at pyridine nitrogen is believed to arise from a combination of favourable circumstances: (i) di-*ortho* substitution of the aryl ring that effectively shields the imino-carbon from nucleophilic attack, (ii) deuterium substitution at the ketimine position disfavouring proton (or more precisely, deuteron) abstraction§ and (iii) chelation of MeLi by the pyridine and imino nitrogen donors places the MeLi in a favourable position for methyl migration to the pyridine nitrogen (Scheme 3). Taken together, these factors combine to direct MeLi towards the pyridine nitrogen in a fashion analogous to the 1,4-Michael addition of nucleophiles to α,β-unsaturated electrophiles. Whereas a similar 1,5- or



Scheme 2

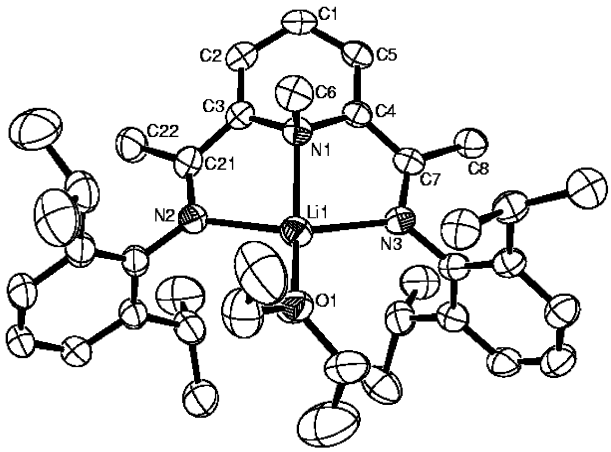
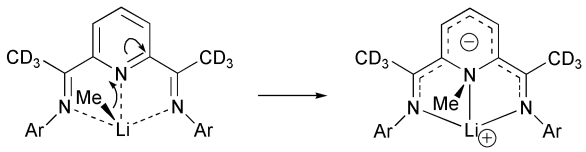


Fig. 1 ORTEP representation and numbering scheme for **2a**. Selected interatomic distances () and angles (°): N1–C3 1.457(3), N1–C4 1.455(3), N1–C6 1.485(3), N1–Li 2.029(5), C3–C2 1.377(4), C1–C2 1.394(4), N1–C3 1.457(3), C1–C5 1.395(4), C5–C4 1.382(4), C3–C21 1.431(4), C4–C7 1.427(4), N2–C21 1.319(4), N2–Li 2.163(5), N3–C7 1.322(3), N3–Li 2.156(5); C2–C1–C5 117.1(3), C3–N1–C6 110.8(2), C4–C7–N3 118.8(2), C5–C4–C7 126.1(3).



Scheme 3

1,4-conjugate addition may potentially occur at the *para*- or *meta*-carbons of the pyridine ring, pre-coordination of lithium by the nitrogen donors of **2** is likely to be responsible for the observed N-methylation (Scheme 3).[15]

In support of our earlier observation, that highly active iron-based ethylene polymerization catalysts are obtained upon treatment of bis(imino)pyridine/Bu^nLi mixtures with $FeCl_3$, addition of **2a** to $FeCl_3$, followed by activation with MAO, afforded an ethylene polymerisation catalyst of comparable activity to the bis(imino)pyridine iron systems.[3] Significantly, the bis(imino)pyridine **2** is isolated in good recovered yield after work-up, indicating that the methyl group has undergone a 'reverse' migration, most likely in this case to the iron centre. The possibility of forming *in situ* iron alkyl species using this novel methylated ligand is attractive and the subject of on-going investigations.

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Notes and references

‡ *Crystal data* for **2a**: $C_{38}H_{56}LiN_3O$, M = 577.80, monoclinic, $P2_1/c$, a = 12.9736(10), b = 13.9491(10), c = 19.6901(14) Å, β = 96.189(4)°, V = 3542.5(5) Å^3, T = 173(2) K, Z = 4, μ(Mo-Kα) = 0.06 mm^{-1}. 13102 reflections measured, 4251 unique (R_{int} = 0.076). Refinement on all F^2, final R_1 = 0.059 (for 3340 reflections with $I > 2\sigma(I)$), wR_2 = 0.154 (for all data). CCDC reference number 184284. See http://www.rsc.org/suppdata/cc/b2/b203805f/ for crystallographic data in CIF or other electronic format.

§ In independent studies, Gambarotta and coworkers have isolated a related pyridine-methylated species from the reaction of per-protio bis(imino)pyridine with MeLi (personal communication).

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