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Bis(imino)pyridine cobalt alkyl complexes and their reactivity towards ethylene: a model system for β-hydrogen chain transfer†

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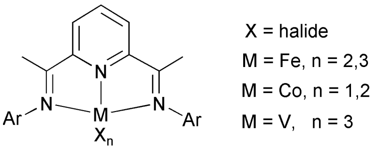
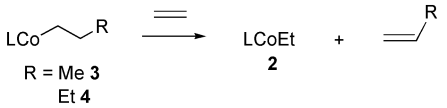
Bis(imino)pyridine cobalt(I) *n*-alkyl complexes react with ethylene by β-hydrogen transfer, allowing direct study of a termination step commonly encountered in polymerisation and oligomerisation catalysis.

In recent years bis(imino)pyridine (L) ligands have been found to afford some of the most highly active ethylene polymerisation catalysts when attached to metals such as Fe,[1] Co[1] and V[2] (Scheme 1). Difficulties encountered in synthesising iron alkyl derivatives, the surprising inertness of heavier metal (Ru, Rh) derivatives,[3] and the paramagnetism accompanying the V system[2] has made detailed study of the reactivity of long-chain metal alkyls in LMR species problematic. In the cobalt case, however, diamagnetic alkyl complexes are isolable,[4] thus offering a unique opportunity to gain insight into the steric and electronic influences of bis(imino)pyridine ligands on the reactivity of their associated metal alkyls.



Scheme 1

Although LCoR (R = *n*-propyl, *n*-butyl) species are not active for ethylene polymerisation, here we show that they react with ethylene to give LCoEt along with formation of α-olefin *via* the *olefin displacement* process shown in eqn. 1. This cobalt-mediated reaction provides a useful model for the commonly encountered β-H chain transfer process found in many polymerisation systems and bears special relevance to catalyst systems supported by bis(imino)pyridine ligands.



(1)

There are two principal mechanistic pathways for β-H transfer, one involving β-H elimination and formation of an intermediate metal hydride species (path A, Scheme 2), the other direct β-H transfer to monomer (path B). Distinguishing between these two pathways has proved challenging and, to date, few systems have proved amenable to direct experimental investigation.§ Here we describe our synthetic and mechanistic studies on the bis(imino)pyridine cobalt system and the insight it has afforded into the β-H transfer reaction.

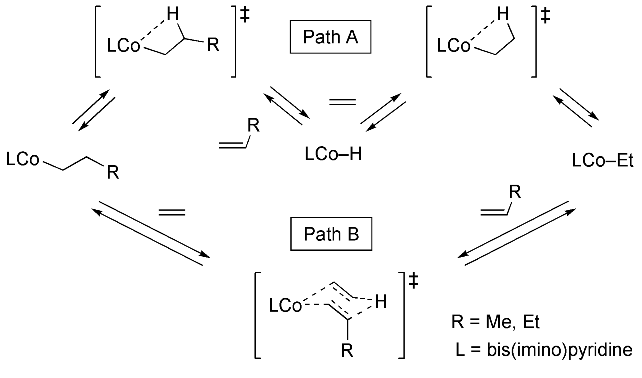
The cobalt(I) ethyl, *n*-propyl and *n*-butyl complexes **2**–**4** were prepared by treatment of LCoCl$_2$ (**1**) with slightly more than two equivalents of RMgX. They are diamagnetic square planar complexes, with distinctive high field resonances attributable to the ketimine methyl groups[5] (δ −1.33 to −1.35 **2**–**4**) and the β-hydrogens of the alkyl chain (δ −1.18 **2**, −0.73 **3**, −0.85 **4**). Since the one-bond ^{1}H–^{13}C coupling constants for **2** and **3** were in the range expected for non-agostic alkyl groups (123–125 Hz), and no appreciable change occurred in the chemical shift of the β-hydrogens in **4** on cooling a sample in d$_8$-toluene to 193 K, nor upon addition of a donor solvent such as THF or diethyl ether, it was concluded that the high field shifts for the β-hydrogens do not arise as a consequence of β-agostic interactions and, therefore, may reasonably be attributed to ring current effects.

Treatment of **3** or **4** with ethylene leads to loss of CH_2=CHR (R = Me, Et) and formation of **2**.¶ The reaction can be conveniently followed by NMR spectroscopy which reveals a first order dependence of the reaction rate on [LCoCH$_2$CH$_2$R] ($t_{1/2}$ 40 min for **3**, 179 min for **4** at 294 K), and a zeroth order dependence on [C$_2$H$_4$]. C–H bond-breaking in the transition state for the rate determining step is established by a primary kinetic isotope effect (k_H/k_D) of 3.32(0.04).‖

The reaction rate is sensitive to the length of the *n*-alkyl chain. At 294 K, β-H transfer for the *n*-propyl derivative **3** proceeds 4.5 times faster than for the *n*-butyl derivative **4**, due, it is presumed, to increased steric congestion in the transition state for the *n*-butyl species. In order to obtain more insight into the nature of the transition state, the reaction of **4** with ethylene was followed over the temperature range 283–315 K. Clean transformations are observed in each case, affording linear plots of ln({[LCo^{n}Bu]$_0$ − [LCo^{n}Bu]}/[LCo^{n}Bu]$_0$) *vs.* time. From an Eyring plot (Fig. 1), the activation parameters $\Delta H^{\ddagger}$ = 103(4) kJ mol^{-1} and $\Delta S^{\ddagger}$ = 26(13) J mol^{-1} K^{-1} were obtained.

The positive entropy of activation, along with the independence of the reaction rate on ethylene pressure, are more consistent with path A, since the involvement of ethylene in the transition state for path B would be anticipated to afford a first order dependence on [C$_2$H$_4$] and a *negative* entropy of activation (more order in the transition state for the concerted process).**

Two other pieces of evidence also point towards the mechanism proceeding by β-H transfer to metal (path A): (i) the exchange reaction between cobalt(I) *n*-butyl **4** with propene proceeds at the same rate as for the reaction of **4** with ethylene.†† If the concerted path B was followed, then it would be expected that incorporation of propene into the transition



Scheme 2 Pathways for β-hydrogen transfer.

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† Electronic supplementary information (ESI) available: experimental details for compounds **2**–**4**, kinetic analysis, and sample NMR spectra. See http://www.rsc.org/suppdata/cc/b2/b207794a/

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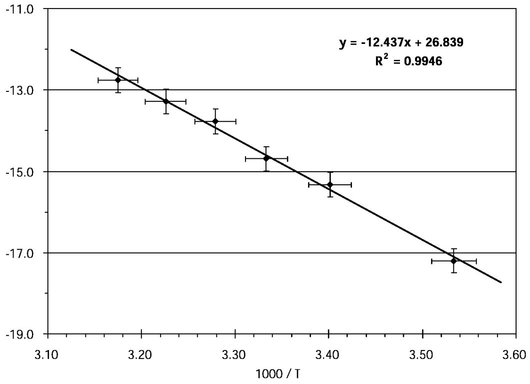

Fig. 1 Eyring plot for the reaction of the bis(imino)pyridyl cobalt(I) *n*-butyl **4** with ethylene.

state would lead to a significant increase in steric congestion and thereby reduce the rate of the reaction, whereas the transition state for path A does not involve the incoming monomer;‡‡ (ii) reaction of the cobalt(I) methyl derivative, LCoMe,[4] with hydrogen gives a diamagnetic product, presumed to be the hydrido species LCoH, with concomitant production of methane. It has not proved possible to isolate this product, but when treated *in situ* with ethylene, the cobalt(I) ethyl complex **2** is obtained.

Taken together, these observations strongly indicate that β-H chain transfer in this cobalt system proceeds *via* a step-wise mechanism involving a cobalt-hydride intermediate rather than a concerted process involving direct β-H transfer to monomer.

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Notes and references

§ A study of [{PhP(CH$_2$SiMe$_2$NSiMe$_2$CH$_2$)$_2$PPh}Ta(C$_2$H$_4$)Et] showed that both the ethyl and ethylene groups are in equilibrium with free ethylene. Mechanistic investigations by NMR spectroscopy led to the conclusion that the transfer of the β-hydrogen occurred directly between the ethyl and ethylene moieties without formation of a Ta-H intermediate.[6] In the cobalt system, [(C$_5$H$_5$)Co(C$_2$H$_4$)Et], the degenerate equilibrium between the two stereoisomers was proposed to proceed *via* intermediate [(C$_5$H$_5$)Co(C$_2$H$_4$)$_2$H],[7] while DFT calculations on Ni(α-diimine) ethylene polymerisation catalysts indicate that chain termination occurs *via* β-H transfer and a Ni-H intermediate.[8]

¶ In the absence of olefin **2**–**4** decompose to as yet unidentified diamagnetic species. The only volatile product isolable from this process is alkane, most likely arising *via* a ligand cyclometallation reaction. The decomposition is suppressed in the presence of ethers and samples of **2** can be kept for several weeks in the presence of 1-hexene without decomposition. These observations imply that olefin coordinates weakly to the alkyl species **2–4** thus preventing this decomposition pathway from occurring (though in no case have olefin adducts proved detectable by NMR spectroscopy).

‖ The deuterium kinetic isotope effect was determined by following the reaction of LCoCD$_2$CD$_2$CD$_2$CD$_3$ **4**-*d*$_9$ with C$_2$D$_4$; it is necessary for both substrates to be fully deuterated since H/D scrambling arising from exchange between deuterio isotopomers of LCoEt and C$_2$H$_4$ is much faster than the reaction of **4**-*d*$_9$ with C$_2$H$_4$.

** For path B to be independent of ethylene concentration, the transition state would either have to be accessed *via* a reaction intermediate formed in a pre-equilibrium in which ethylene is weakly coordinated to the metal centre, or possess a 'late' transition state with product-like character. If the latter were the case then the transition state would involve a significant degree of C–H bond formation, and thus a much smaller kinetic isotope effect would be anticipated.

†† The reaction rates are the same within error over the first half-life of the reaction; however, after the first half-life the propylene reaction shows a more complicated rate law dependence.

‡‡ On the available evidence it is not possible to rule out the Co-alkyl and Co-hydride intermediates containing coordinated olefin. Indeed, **2** is found to be more stable in the presence of 1-hexene, suggesting that this is the case for Co-alkyl species, and therefore also likely on steric grounds for the Co-hydride species. However, the independence of the rate on ethylene concentration indicates that the rate limiting step does not involve association of ethylene.

1 (*a*) G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, G. A. Solan, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1998, 849; (*b*) B. L. Small, M. Brookhart and A. M. A Bennett, *J. Am. Chem. Soc.*, 1998, **120**, 4049; (*c*) G. J. P. Britovsek, M. Bruce, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. Mastroianni, S. J. McTavish, C. Redshaw, G. A. Solan, S. Strömberg, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 1999, **121**, 8728.
2 D. Reardon, F. Conan, S. Gambarotta, G. Yap and Q. Y. Yang, *J. Am. Chem. Soc.*, 1999, **121**, 9318.
3 E. L. Dias, M. Brookhart and P. S. White, *Organometallics*, 1999, **19**, 4995.
4 (*a*) M. J. Humphries, G. K. B. Clentsmith, V. C. Gibson and K. P. Tellmann, *Abstracts of Papers*, 222nd ACS National Meeting, Chicago, IL, USA, August 26–30, 2001. AN 2001:637421; (*b*) V. C. Gibson, M. J. Humphries, K. P. Tellmann, D. F. Wass, A. J. P. White and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 2001, 2252; (*c*) T. M. Kooistra, Q. Knijnenburg, J. M. M. Smits, A. D. Horton, P. H. M. Budzelaar and A. W. Gal, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 4719.
5 Similar high-field chemical shifts have previously been observed in α-diimine complexes of nickel: M. Svodoba and H. tom Dieck, *J. Organomet. Chem.*, 1980, **191**, 321; H. tom Dieck, M. Svodoba and T. Greiser, *Z. Naturforschung*, 1981, **36b**, 823.
6 M. D. Fryzuk, S. A. Johnson and S. J. Rettig, *J. Am. Chem. Soc.*, 2001, **123**, 1602.
7 M. Brookhart, D. M. Lincoln, M. A. Bennett and S. Pelling, *J. Am. Chem. Soc.*, 1990, **112**, 2691.
8 L. Deng, P. Margl and T. Ziegler, *J. Am. Chem. Soc.*, 1997, **119**, 1094.