EXAFS Studies of the Activation of Homogeneous Nickel Catalysts for Propene Dimerisation by Aluminium Reagents

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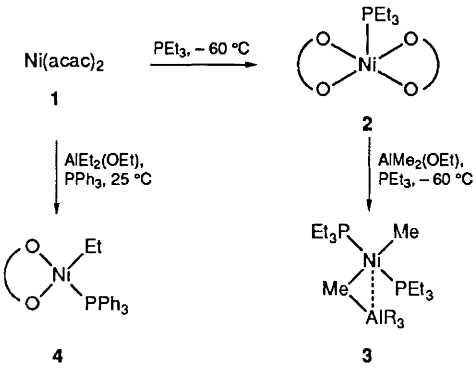
Ni K-edge EXAFS studies on propene dimerisation catalysts, formed by the interaction of solutions of $NiCl_2(PEt_3)_2$ with $Al_2Me_3Cl_3$ and $AlEt_3$ at −40 °C, indicate a first coordination sphere of C and P atoms; Ni··Al shells at *ca.* 2.97 Å suggest Ni–C–Al interactions which probably stabilise the nickel centre.

Despite substantial efforts, the role of Lewis acids in the activation of nickel complexes towards the dimerisation of alkenes remains unclear.[1] We were thus led to start an EXAFS study of the activation process; although this technique has had little application in the field of homogeneous catalysis,[2,3] its pivotal role now in heterogeneous catalysis and metalloenzymes indicated that it was appropriate to the nickel problem.[4] We now report Ni K-edge EXAFS results which probe the local structure of the major species present during the activation and operation of active propene dimerisation catalysts.

To test the whole approach, model reactions were carried out as illustrated in Scheme 1. The Ni K-edge EXAFS-obtained† structural information is summarised in Table 1. Precision on Ni··X distances is considered to be 1.5%[9] and precisions on coordination numbers are *ca.* 0.3. Cleavage of the Ni–Ni interactions in trimeric $Ni(acac)_2$ **1** occurs on the addition of PEt_3 in diethyl ether at −60 °C, forming a paramagnetic 5-coordinate adduct **2** (Ni–O 2.01 Å, and Ni–P 2.42 Å). Subsequent reaction with $AlMe_2(OEt)$ at that temperature is a route to the isolation of $Ni(Me)_2(PEt_3)_2$.[10] Indeed the EXAFS analysis of this solution did indicate a coordination sphere of 2 C atoms (Ni–C 1.91 Å) and 2 P atoms (Ni–P 2.12 Å). However, in addition there was a clear peak in the Fourier transform that fitted best for 1 Al atom with an Ni··Al distance of 2.97 Å; attempts to model this shell with C or Ni atoms yielded unrealistic parameters. So this indicates adduct formation in solution at this temperature, with a possible structure indicated as **3**. The sum of the Ni and Al covalent radii is 2.4 Å, substantially less than the observed distance, so a Ni–C–Al interaction seems the more plausible means of deriving this well-ordered shell. Following the preparation for the complex $Ni(Et)(acac)(PPh_3)$ **4** in toluene (an intermediate step in the alkylation of the nickel centre) afforded a solution which yielded structural parameters similar to those derived in the crystal,[11] *viz.* Ni–O 1.88, Ni–C 1.97 and Ni–P 2.13 Å; in addition the Ni··C distance to the first non-adjacent carbons of the chelate ring could also be detected at room temperature (2.82 Å). These experiments showed that stepwise alkylation could be monitored *in situ* and provide reliable structural information about the nickel coordination sphere.



Scheme 1 Hacac = pentane-2,4-dione

The Ni K-edge EXAFS data of the brown solutions formed from the activation of $NiCl_2(PEt_3)_2$ by $Al_2Me_3Cl_3$ and $AlEt_3$ in *p*-fluorotoluene at −40 °C are presented in Fig. 1. Solutions treated with propene afforded product distributions (determined by GC–MS) of 4 : 2 : 1 C_6 : C_9 : C_{12} oligomers, with the C_6 fraction containing predominantly 2,3-dimethylbutenes, 4-methylpent-1-ene and 2-methylpent-2-ene (consistent with previously reported data[12]). Attempted activation by $ZnEt_2$ resulted in incomplete formation of face-centred cubic nickel

Table 1 Ni K-edge EXAFS results for the model reactions (Scheme 1)

Sample	N^a	R/Å	A/Å$^{2\,b}$
$Ni(acac)_2$–PEt_3 in Et_2O at −60°C	4.2 O	2.01	0.010
	1.2 P	2.42	0.008
	3.6 C	2.88	0.015
$Ni(acac)_2$–PEt_3–$AlMe_2(OEt)$ in Et_2O at −60 °C	2.2 C	1.91	0.005
	1.9 P	2.12	0.012
	0.9 Al	2.97	0.015

[a] Coordination number. [b] Debye-Waller factor $A = 2\sigma^2$, σ = mean square internuclear separation.

Table 2 Ni K-edge EXAFS results from the three spectra recorded at −40 °C in *p*-fluorotoluene

Sample	N^a	R/Å	A/Å$^{2\,b}$
$NiCl_2(PEt_3)_2$–$Al_2Cl_3Me_3$	2.7 C	1.91	0.010
	2.0 P	2.21	0.012
	1.1 Al	2.96	0.009
	2.0 Cl	4.38	0.011
$NiCl_2(PEt_3)_2$–$AlEt_3$	2.2 C	1.93	0.012
	2.1 P	2.20	0.010
	1.5 Al	2.98	0.009
	2.2 Cl	4.40	0.021
$NiCl_2(PEt_3)_2$–$AlEt_3$–C_3H_6	2.0 C	1.86	0.007
	2.0 P	2.15	0.013
	2.2 Al	2.93	0.011

[a] Coordination number. [b] Debye-Waller factor $A = 2\sigma^2$, σ = mean square internuclear separation.

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† X-Ray absorption spectra were recorded on Station 7.1 of the Synchrotron Radiation Source at the Daresbury Laboratory using an Si(111) order-sorting monochromator. Data were either acquired in transmission mode, or in fluorescence using a single Tl/NaI scintillation counter with a Co foil filter. Room temperature samples were made up in a nitrogen glove box and spectra recorded using sealed Al cells with Mylar windows. Cold solutions of the $AlMe_2(OEt)$, $Al_2Me_3Cl_3$ and $AlEt_3$ treated samples were made up using standard inert-atmosphere techniques under Ar and transferred *via* cannula into a similar cell attached to a Dewar flask filled with an acetone slush bath. Data reduction was carried out using PAXAS,[5] with the spherical wave analysis performed using EXCURVE.[6] The statistical validity of shells was assessed by published means.[7] The numbers of independent parameters used in these fits are within the guideline:

$$N_{pts} = 2(k_{max} - k_{min})(R_{max} - R_{min})/\pi \text{ (Ref. 8).}$$

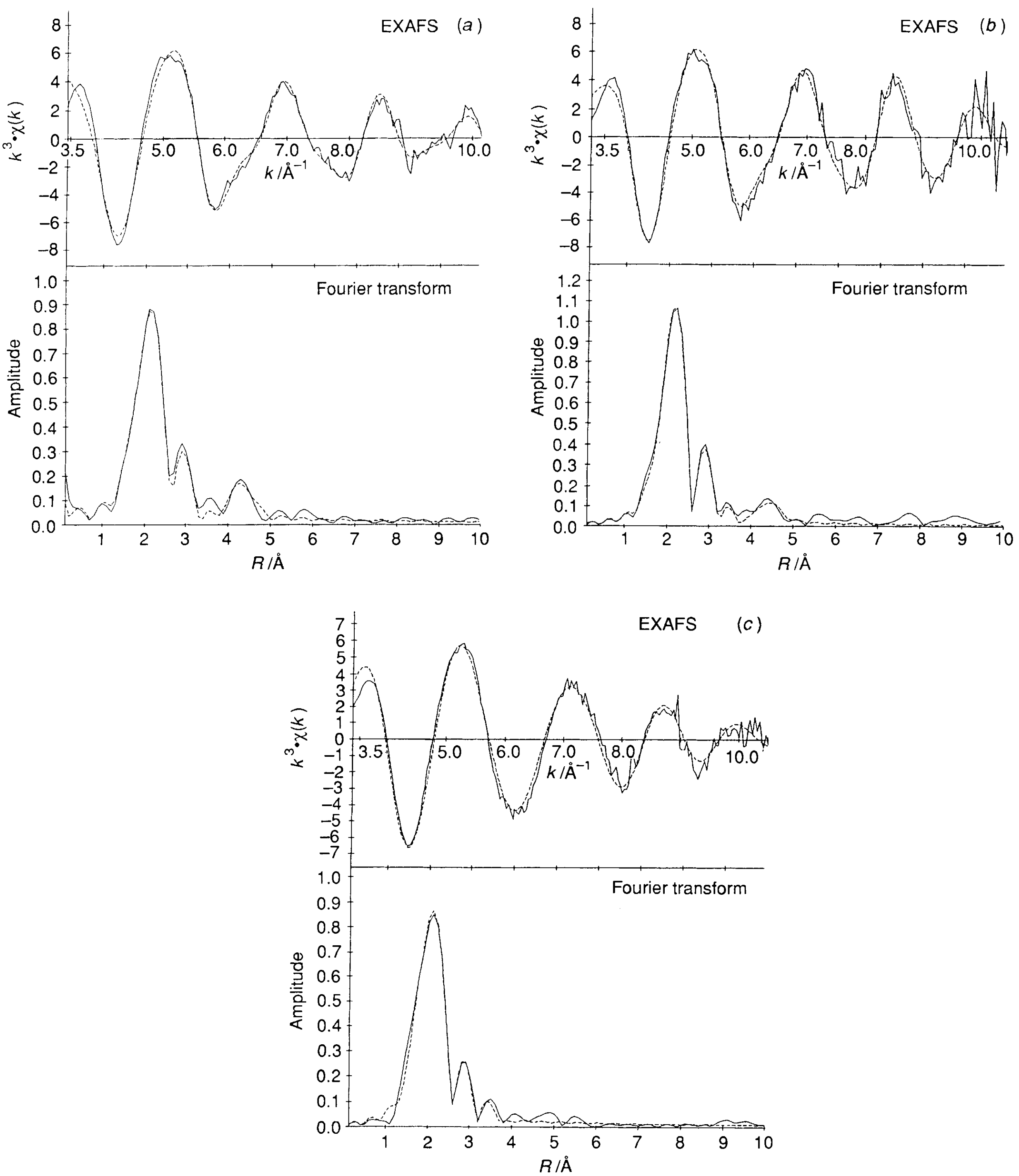
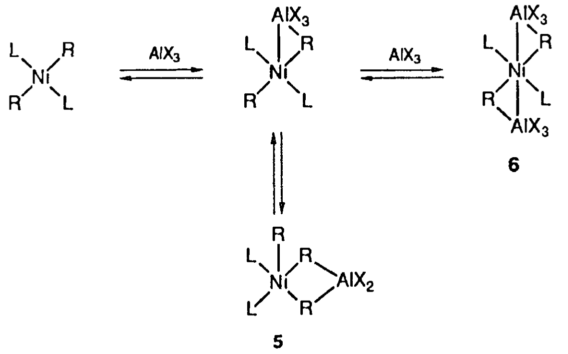


Fig. 1 The Ni K-edge k^3-weighted EXAFS data and Fourier transforms, phase-shift corrected for carbon, of (*a*) the $NiCl_2(PEt_3)_2$–$Al_2Me_3Cl_3$ (25 mmol dm^{-3} Ni; Ni : Al = 1 : 10) reaction products in *p*-fluorotoluene at −40 °C, (*b*) $NiCl_2(PEt_3)_2$–$AlEt_3$ (25 mmol dm^{-3} Ni; Ni : Al = 1 : 10) at −40 °C and (*c*) solution (*b*) after exposure to propene. (—) Experiment and (- - - -) spherical wave theory. *R*-factors and E_0 values (*a*) R = 15.3%; E_0 = 15.1 eV, (*b*) R = 19.5%; E_0 = 15.4 eV and (*c*) R = 17.9%; E_0 = 18.3 eV.

particles, as evidenced by the first four shells in that structure (Ni–Ni 2.45, 3.42, 4.14 and 4.87 Å). Little activity was observed for propene dimerisation from this solution.

The analysis of the Ni K-edge EXAFS data of the $Al_2Me_3Cl_3$-activated system [Fig. 1(*a*)] showed a first coordination shell of 2.7 C atoms (1.91 Å) and 2.0 P atoms (2.21 Å) (Table 2). In addition there were two more distant shells evident in the Fourier transform; the first of these was best modelled by 1.1 Al (Ni··Al 2.96 Å), with the second due to *ca.* 2 Cls (Ni··Cl 4.38 Å). This indicates a mean structure like **5**, similar at nickel to that proposed for the product of the reaction of $Ni(bipy)Me_2$ (bipy = 2,2′-bipyridine) and $AlMe_3$.[13] Assuming the terminal Al–Cl and bridging Al–C distances in Al_2X_6 (X = Cl and Me) and a planar bridge, the Ni–C–Al and Cl–Al–Cl bond angles can be estimated as 95 and 118° respectively. The four-membered ring is considered crucial to provide a rigid enough framework for the Cl shell to be identified.

Parallel experiments using $AlEt_3$ produced the EXAFS data in Fig. 1(*b*). This refined fit indicated a first coordination



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Scheme 2

sphere of 2.2 C (1.93 Å) and 2.1 P (2.20 Å) and higher Ni··Al coordination number (1.5) (Table 2). The variation in Ni–C and Ni··Al coordination numbers is on the borderline of being statistically significant, but this variation could be accommodated with the equilibrium system shown in Scheme 2, in which there is a larger proportion of species **6** than **5** with the $AlEt_3$ promoter. The $^{31}P\{^1H\}$ NMR spectrum of the $Al_2Cl_3Me_3$ system at −40 °C contains nine resonances for coordinated PEt_3, indicating the existence of several species and isomers. Addition of propene to the $AlEt_3$ system causes a change in the EXAFS pattern [Fig. 1(*c*), Table 2], in which the removal of the Ni··Cl shell is apparent. So the concentrations of species like **5** have been substantially reduced. A reduction in the mean Ni–C bond length to 1.86 Å is also observed (Table 2), possibly indicating a change in the mode of coordination on the addition of propene.

It is therefore suggested that the Ni··Al interaction may be one stabilising factor for the Ni^{II} organometallics, perhaps retarding β-hydride or reductive elimination to afford metal. The lower Lewis acidity of $ZnEt_2$ may prevent any Ni··Zn interaction from competing with elimination processes. We note also that an Ni–C–Al interaction has been invoked in the catalytic mechanism of alkene oligomerisation by Ni(norbornene)$_3$–$AlBu_3$[14] and does indeed seem to be present once propene is added. The complexity and highly air-sensitive nature of these systems makes them extremely difficult to study using standard techniques; this study offers the first direct structural parameters for Ni–C–Al interactions in solution.

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