

## *In Situ* NMR and EXAFS Studies of the Homogeneous Alkene Oligomerisation Catalyst $\text{Ni}(\text{cod})_2\text{-Ph}_2\text{PCH}_2\text{C}(\text{CF}_3)_2\text{OH}$

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NMR and extended X-ray absorption fine structure (EXAFS) studies indicate that the nickel coordination sphere of the highly active alkene oligomerisation catalyst formed on addition of  $\text{Ph}_2\text{PCH}_2\text{C}(\text{CF}_3)_2\text{OH}$  to  $\text{Ni}(\text{cod})_2$  (cod = cycloocta-1,5-diene) is  $\text{Ni}\{\text{Ph}_2\text{PCH}_2\text{C}(\text{CF}_3)_2\text{O}\}\text{H}\{\text{Ph}_2\text{PCH}_2\text{C}(\text{CH}_3)_2\text{OH}\}$ .

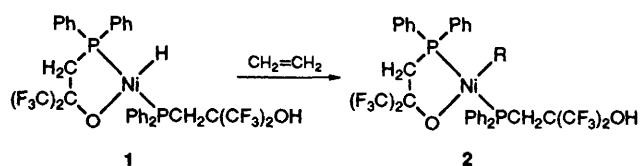
Homogeneous nickel catalysts are widely used in the oligomerisation of short chain alkenes to longer chain products. One example of this is the conversion of ethene to  $\alpha$ -olefins ( $\text{C}_6\text{-C}_{20}$ ) during the Shell higher olefins process (SHOP). The mechanism for catalysis is often discussed in terms of the initial formation and repeated regeneration of a nickel hydride intermediate.<sup>1,2</sup> A number of organometallic nickel hydrides have been isolated<sup>3,4</sup> but little direct evidence exists for their presence in active catalyst solutions.

Keim *et al.* reported that a model of the SHOP catalyst, formed by the addition of the bidentate ligand  $\text{Ph}_2\text{PCH}_2\text{C}(\text{CF}_3)_2\text{OH}$  to  $\text{Ni}(\text{cod})_2$ , contained a triplet in the  $^1\text{H}$  NMR at  $\delta -23.8$ ,<sup>5</sup> which is consistent with the formation of a nickel hydride. This signal was reportedly lost on reaction with ethene, with peaks generated in the regions expected for alkyl formation. Both a hydride and alkyl species were isolated from the system, but only on the addition of  $\text{PCy}_3$  (Cy = cyclohexyl) to stabilise the active complexes (which kills the

catalyst) and the structure of the *in situ* hydride has not been further probed.

Our  $^1\text{H}$  NMR observations showed that although the hydride signal was formed in a 1:1 solution of  $\text{Ni}(\text{cod})_2$  and  $\text{Ph}_2\text{PCH}_2\text{C}(\text{CF}_3)_2\text{OH}$ , a larger proportion of unreacted  $\text{Ni}(\text{cod})_2$  remained, and the intensity of the hydride could be maximised by addition of a 2:1 excess of phosphine (which also removed all of the  $\text{Ni}(\text{cod})_2$ ). Fig. 1(a) shows the  $^{31}\text{P}$  NMR of a 1:2 solution of  $\text{Ni}(\text{cod})_2$  and  $\text{Ph}_2\text{PCH}_2\text{C}(\text{CF}_3)_2\text{OH}$  in  $[\text{D}_8]\text{toluene}$ , prepared under an inert and anhydrous atmosphere, recorded at  $-40^\circ\text{C}$ , after being allowed to react at  $10^\circ\text{C}$  for 10 min. The minor couplings on the two doublet of doublets (*ca.* 72 Hz) are identical to those of the hydride triplet in the  $^1\text{H}$  NMR and could be removed by selectively decoupling at the hydride resonance frequency. The coupling is similar to those in a range of *trans* square planar  $(\text{PR}_3)_2\text{NiHX}$  complexes (*e.g.* R =  $\text{Pr}^i$ , Cy, X =  $\text{Cl}^-$ ,  $\text{BH}_4^-$ ), which give rise to hydride triplets in their  $^1\text{H}$  NMR around  $\delta -20$ , with *cis* P-H couplings of approximately 70 Hz.<sup>6</sup>

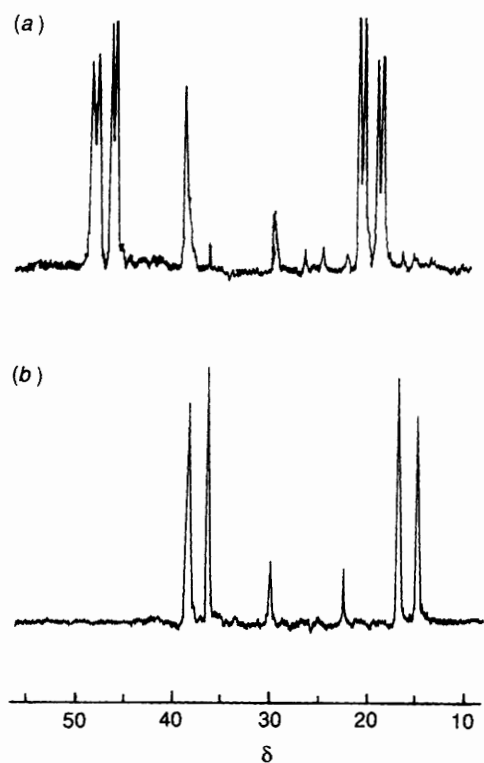
The major coupling (273 Hz) is consistent with a *trans* coupling between two inequivalent phosphines.<sup>7</sup> The inequivalence and the 25 ppm chemical shift difference between the two signals can be explained by the presence of two binding forms of the ligand, monodentate and bidentate, giving rise to structure 1. The downfield signal would then be the bidentate



**Table 1** EXAFS derived structural parameters for the catalyst at various stages of formation

| Solution   | Shell | CN <sup>a</sup> | d(Ni-X)/Å   | 2σ <sup>2</sup> /Å <sup>2</sup> | R <sup>b</sup> (%) | d(X-ray)/Å              |
|--|-------|-----------------|-------------|---------------------------------|--------------------|-------------------------|
| (i) Ni(cod) <sub>2</sub> -toluene  | C     | 9               | 2.08        | 0.016                           | 23.7               | 2.12 (av) <sup>c</sup>  |
|  | C     | 7               | 2.92        | 0.020                           |                    | 2.98 (av) <sup>c</sup>  |
| (ii) Ni(cod) <sub>2</sub> -Ph <sub>2</sub> PCH <sub>2</sub> C(CF <sub>3</sub> ) <sub>2</sub> OH-toluene -40 °C         | O     | 1               | 1.91        | 0.007                           | 28.1               | 1.87 <sup>d</sup>       |
|  | P     | 2               | 2.16        | 0.022                           |                    | 2.14, 2.18 <sup>d</sup> |
|  | C     | 3               | 2.84        | 0.018                           |                    |                         |
| (iii) Ni(cod) <sub>2</sub> -Ph <sub>2</sub> PCH <sub>2</sub> C(CF <sub>3</sub> ) <sub>2</sub> OH-alkene-toluene -40 °C | C(O)  | 2               | 2.00 (1.97) | 0.012                           | 24.2               |                         |
|  | P     | 2               | 2.18        | 0.019                           |                    |                         |
|  | C     | 4               | 2.86        | 0.022                           |                    |                         |
| (iv) Ni(cod) <sub>2</sub> -Ph <sub>2</sub> PCH <sub>2</sub> C(CF <sub>3</sub> ) <sub>2</sub> OH-alkene-toluene 20 °C   | O     | 1               | 1.88        | 0.006                           | 22.8               |                         |
|  | P     | 2               | 2.18        | 0.016                           |                    |                         |
|  | C     | 4               | 2.83        | 0.022                           |                    |                         |

<sup>a</sup> Estimated error in coordination numbers  $\approx \pm 20\%$ . <sup>b</sup> R factors defined as  $(\int |\chi_T - \chi_E| k^3 dk / \int |\chi_E| k^3 dk) \times 100\%$ . <sup>c</sup> Average distances from Ni(cod)<sub>2</sub> X-ray crystal structure.<sup>11</sup> <sup>d</sup> Distances compared with X-ray crystal structure of {Ph<sub>2</sub>PCH<sub>2</sub>C(CF<sub>3</sub>)<sub>2</sub>O}NiH(PCy<sub>3</sub>).<sup>5</sup>



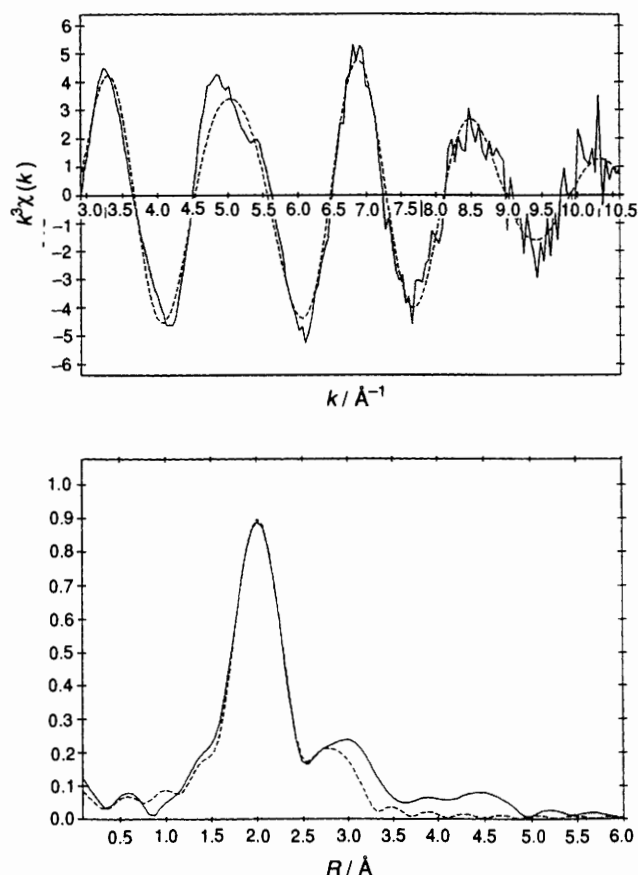
**Fig. 1** <sup>31</sup>P NMR of Ni(cod)<sub>2</sub>-Ph<sub>2</sub>PCH<sub>2</sub>C(CF<sub>3</sub>)<sub>2</sub>OH in [2H<sub>8</sub>]toluene at -40 °C; (a) before reaction with ethene; (b) after reaction with ethene at 10 °C

form, with a 25 ppm coordination shift resulting from the formation of a five-membered ring.<sup>8</sup>

The resonance at δ 30 is due to some phosphine oxide impurity in the ligand. The other major peak at δ 40 has not been assigned although it could possibly be an intermediate in the formation of the hydride.

Fig. 1(b) shows the <sup>31</sup>P NMR of a 1 : 2 solution of Ni(cod)<sub>2</sub> and Ph<sub>2</sub>PCH<sub>2</sub>C(CF<sub>3</sub>)<sub>2</sub>OH in toluene which was reacted with ethene at 10 °C for 10 min before cooling to -40 °C to record the spectrum. The hydride coupling was no longer present but the *trans* P-P coupling was retained, suggesting alkyl species **2** had been formed. The phosphine oxide is again present but the other major impurity resonance in Fig. 1(a) is lost.

The nickel coordination sphere has also been studied by EXAFS spectroscopy. The nickel K-adsorption edges were recorded for the following solutions: (i) Ni(cod)<sub>2</sub> in toluene ([Ni] = 50 mmol) at -10 °C; (ii) Ni(cod)<sub>2</sub>-Ph<sub>2</sub>PCH<sub>2</sub>C(CF<sub>3</sub>)<sub>2</sub>OH in toluene ([Ni] = 50 mmol, [P] = 100 mmol) at -40 °C, which had first been reacted at 10 °C for 10 min; (iii) Ni(cod)<sub>2</sub>-Ph<sub>2</sub>PCH<sub>2</sub>C(CF<sub>3</sub>)<sub>2</sub>OH-excess propene, in



**Fig. 2** Background subtracted  $k^3$ -weighted EXAFS spectrum and Fourier transform for Ni(cod)<sub>2</sub>-Ph<sub>2</sub>PCH<sub>2</sub>C(CF<sub>3</sub>)<sub>2</sub>OH-alkene in toluene at -40 °C: (—) experimental; (---) theoretical

toluene ([Ni] = 50 mmol, [P] = 100 mmol) at -40 °C, which had been reacted at 10 °C for 10 min and (iv) solution (iii) allowed to warm to 20 °C.

The background subtracted spectra were obtained using the program PAXAS.<sup>9</sup> Fitting of the  $k^3$ -weighted EXAFS spectra was performed in EXCURV92.<sup>10</sup> Fig. 2 shows the background subtracted  $k^3$ -weighted EXAFS and Fourier transform, together with the theoretical fit, for solution (iii). Table 1 contains the resulting structural parameters for the best fits to the EXAFS data, for all four solutions.

The EXAFS derived distances for Ni(cod)<sub>2</sub> show some inconsistency with the X-ray crystallography data<sup>11</sup> even allowing for experimental error ( $\pm 0.02$ – $0.03$  Å). This may be explained by the spread of distances in the X-ray data (2.11–2.14 and 2.94–3.00 Å), with the EXAFS distances

tending towards the closer backscatterers. The EXAFS derived coordination numbers for the catalyst in the absence of alkene are consistent with structure **1**. The Ni–O and Ni–P distances are compared with the X-ray data for  $[\{\text{Ph}_2\text{PCH}_2\text{C}(\text{CF}_3)_2\text{O}\}\text{NiH}(\text{PCy}_3)]^5$  and give good agreement.

After reaction with propene the EXAFS at  $-40^\circ\text{C}$  could best be fitted by having a shell of two carbons at 2 Å. As nearly as good a fit could be achieved by having a shell of two oxygens at a similar distance. Two separate shells of oxygen and carbon could not be differentiated satisfactorily owing to high correlations between the two shells caused by the similarity of the backscatterers. However, the increase in coordination and the bond distances are consistent with alkyl formation as in structure **2**. The EXAFS in the presence of propene at  $20^\circ\text{C}$  shows the shell of two phosphorus atoms is still present. It also suggests that the substrate alkene has mostly been consumed and the hydride **1** has been reformed by  $\beta$ -hydride elimination.

Hence, both NMR and EXAFS confirm the coordination sphere of the hydride as **1** and that 2 molecules of phosphine remain bound on reaction with alkene at low temperature and atmospheric pressure. However, catalytic efficiency is greatest with a 1 : 1 mixture of phosphine to  $\text{Ni}(\text{cod})_2$ .<sup>12</sup> This suggests that species **1** and **2** are in equilibrium with the active form, which has only one ligand coordinated. Therefore, phosphine dissociation is required to allow catalysis, in accord with earlier kinetic evidence on a related system.<sup>13</sup>

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