Extended X-ray absorption fine structure (EXAFS) characterisation of dilute palladium homogeneous catalysts†

Steven G. Fiddy,*[ab] John Evans,*[a] Mark A. Newton,[a] Thomas Neisius,[b] Robert P. Tooze[c] and Richard Oldman[c]

[a] Department of Chemistry, The University of Southampton, Highfield, Southampton, UK SO17 1BJ.
 E-mail: je@soton.ac.uk
[b] ESRF, PO Box 220, Grenoble Cedex, F-38043, France. E-mail: fiddy@esrf.fr
[c] ICI-Synetix, PO Box 1, Belasis Ave, Billingham, UK TS23 1BL

Highly dilute EXAFS characterisation for the elucidation of species involved in Heck chemistry is demonstrated; the major "monomer" species of Herrmann's acetate-bridged phosphapalladadacycle is characterised and species present during the course of a 50 ppm [Pd] Pd(OAc)$_2$/PBu$^t_3$ catalysed Heck reaction are presented.

The development and design of homogeneous metal catalysts has recently shown that to provide high activity, an extremely low level of catalyst is often required. Prominent examples of this are the Synetix titanium based catalysts for polyester production.[1] However, it has proven extremely difficult to characterise any of the solution species present at the very low catalyst concentrations used. Further, the presence of monomer–dimer equilibria can complicate structural characterisation at high concentrations. Due to the ultra dilute nature of many catalysts, frontline structural techniques such as NMR and vibrational spectrocopy can be of limited utility. Until recently, the utilisation of EXAFS for catalytic studies has been limited by time and detection constraints to samples where the concentration of the absorber atom is > *ca.* 1000 ppm. The advent of third generation synchrotron sources and beamlines providing very high X-ray brilliance such as ID26 at the European Synchrotron Radiation Facility (ESRF) potentially permit these dilution limits to be overcome.[2] To date, few articles have been published making full use of the capability to study ultra-dilute samples[3] and *none* characterising catalytic systems. Here, we present recent results describing the characterisation of transition metal catalyst species at low concentrations, matching those used in industrial situations.

The Heck reaction was chosen for study for this technique as it has been shown that dimeric structures often exist in Heck reaction solutions at higher catalyst concentrations,[4] and, for certain catalysts, it has been observed that the turnover rate increases with dilution, a classic sign that there is an equilibrium between the active monomers and the less active oligomers.[5]

Two different Heck palladium catalysts are presented in this report, the acetato-phosphapalladadacycle (1a) and a palladium acetate/tri(*tert*-butyl) phosphine (PBu$^t_3$) (1 : 3) catalyst. Both of these catalysts have already been shown to be highly active for the Heck, Suzuki, Stille and amination reactions and work with the less expensive aryl bromides and chlorides.[6] However, there is still much debate as to the mechanism by which these catalysts proceed, with few reports to date on the mechanism of the Pd(OAc)$_2$/PBu$^t_3$ system in the Heck reaction.

For the preformed palladacyle catalyst, experiments were conducted to identify the major "monomer" species present at industrially relevant dilutions. Fig. 1 shows the Pd K-edge EXAFS spectra obtained from the Herrmann acetatopalladacycle[7] (Scheme 1a) diluted in a solution of *N*-methyl pyrrolidinone (NMP). Spectrum (a) was obtained from a transmission
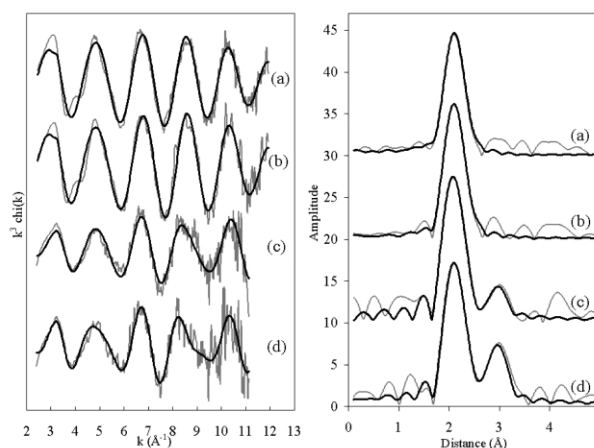
Fig. 1 The Pd K-edge EXAFS of **1a** diluted in NMP showing the data for (a) 5000 ppm, (b) 500 ppm, (c) 150 ppm and (d) 50 ppm. All spectra collected on ID26 except (a), recorded on station 9.2, SRS, Daresbury.

XAS experiment collected on Station 9.2 at the Daresbury laboratories. Spectra (b)–(e) were recorded on ID26 at the ESRF in fluorescence mode‡. The Pd K-edge EXAFS derived structural parameters are summarised in Table 1.

Firstly, good quality EXAFS data can be collected on concentrations of greater than or equal to 50 ppm. Secondly, and very importantly, no obvious features were observed during the experiments themselves or the consquential EXAFS analysis that indicated the decomposition of the palladacycle to palladium metal due to the high X-ray beam intensities. Thirdly, and most interestingly from a catalytic viewpoint, significant changes can be observed in the EXAFS/Fourier transform as the dilution is increased. It has already been shown that, in its solid state, the palladacycle forms a dimer complex with the presence of two acetate bridges (Species **1a**).[7] In solution, however, it is proposed that the bound acetate ligands enter into monomer/dimer equilibria with solvent molecules possibly involved (Species **1b**).[7] The major change observed during the measurements occurred between the concentrations of 500 ppm and 150 ppm, with a significant change in the EXAFS envelope and the growth of a new feature at *ca.* 3 Å in the Fourier transform. This is proposed to relate to the increase in the fraction of monomer species, with the 50 ppm dilution EXAFS best fitted to a model containing only 1 carbon at 2.07 Å and 1 phosphorus at 2.32 Å, with an additional shell of light backscatterers (C or O) at 2.99 Å. A very important point to note is that the fitting of palladium to model the features observed at 3 Å did not produce a
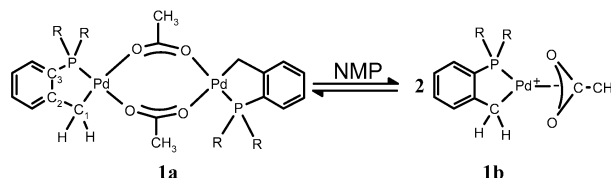
Scheme 1 Monomer/dimer equilibria for Herrmann acetatopalladacycle.

Table 1 Structural and statistical parameters derived from analysis of the EXAFS spectra shown in Fig. 1

Conc (ppm)	Scatterer	CN	R [Å]	$2\sigma^2$ [Å^2]	R [%]
5000	C	1.1(3)	2.04(2)	0.002(2)	28.7
	O	1.8(4)	2.18(2)	0.028(13)	
	P	0.9(1)	2.251(8)	0.006(2)	
500	C	1.0(2)	2.02(2)	0.005(3)	30.2
	O	1.9(5)	2.18(2)	0.012(6)	
	P	1.0(2)	2.243(9)	0.002(3)	
150	C	1.0(2)	2.067(9)	0.011(2)	41.4
	P	1.0(2)	2.31(1)	0.006(4)	
	C	1.6(5)	2.98(2)	0.003(2)	
50	C	1.0(2)	2.08(1)	0.009(2)	42.7
	P	1.0(2)	2.32(2)	0.005(4)	
	C	2.9(6)	2.99(2)	0.002(2)	

CN = coordination number, R = bond length and $2\sigma^2$ = Debye Waller factor. Note true errors in bond length are about 2%; those for the coordination numbers are *ca.* 15%.

successful fit to the data, clearly demonstrating that the new peak in the Fourier transform is *not* due to colloidal Pd. Only light backscatterers such as O or C produce a significant improvement; distances and angles are consistent with the phenyl carbons of the cyclopalladated five-membered ring (Pd–C_1–C_2 96°), as observed for **1a**. Another feature worthy of note is that fitting oxygens to model any bridged acetate groups (2 O at 2.13 Å) or NMP interactions lead only to high Debye–Waller factors and no significant reduction in the *R*-factor, suggesting the bridging acetate form (**1a**) is a minor species and NMP interactions are minimal at the 50 ppm dilution level. Therefore, a proposed form for the major monomer species in NMP is shown (species **1b**).

Fig. 2 shows the EXAFS collected at specific temperatures and times during the course of the $Pd(OAc)_2/PBu^t_3$ catalysed Heck reaction.§

When all reagents are charged together at room temperature, the EXAFS can be best fitted to a 1st coordination sphere of 4 oxygens at 2.02(1) Å. This is in good agreement with the crystal structure of palladium acetate (Pd–O distances 1.973–2.014 Å),[8] suggesting that at 295 K, there is no change in palladium environment. However, as the solution reaches 353 K, a change in the EXAFS envelope occurs with a reduction in amplitude and shape. EXAFS analysis suggests a two shell model of 1.3 oxygens at 1.99(5) Å and 1.3 phosphorus at 2.30(4) Å. An explanation for this is an equilibrium between the initial palladium precursor and the palladium(0) bisphosphine species,
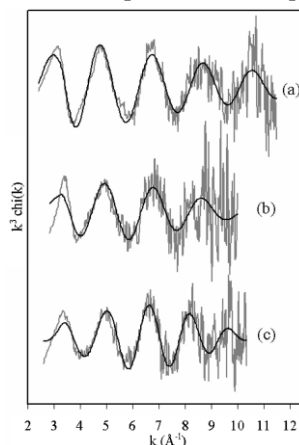

Fig. 2 Pd K edge k^3-weighted EXAFS derived from a $Pd(OAc)_2/PBu^t_3$ catalyst: (a) at room temperature, (b) at 353 K and (c) after 4 minutes at 393 K. Grey and black lines indicate experimental and theoretical fits derived from spherical wave analysis in EXCURV98[11]†. Each spectrum is an average of 6 accumulations, with each accumulation taking *ca.* 30 minutes.

$Pd(PBu^t_3)_2$, which is well known and fully characterised.[9] Also worthy of note is the absence of any features that could be associated with bromine, an indication that oxidative addition of the bromoacetophenone has *not* yet occurred. On further heating (393 K for 4 min – no product formation by GC†), the EXAFS envelope again changes significantly with the best fit of two phosphorus at 2.28(2) Å and one bromine at 2.51(2) Å. Attempts to fit an extra shell of C or O resulted in no improvement in the fit; the *R*-factor decreased by only 1%. Therefore, although there may be the presence of a light element, no definite analysis can be concluded about it. However, the EXAFS data now shows that oxidative addition of the activated bromobenzene has occurred. Finally, as the reaction proceeds, very little change in the EXAFS occurs. The best fit to the final state (not shown), recorded after 1 hour of reaction (~ 100% completion by GC†) is a two shell model of 2 phosphorus at 2.27(2) Å and 1 bromine at 2.49(2) Å. However, the fit appears more complete suggesting that the presence of lighter scatterers is minimal and therefore, the final species is hypothesised to be $[(PBu^t_3)_2Pd(H)(Br)]$ or similar. An analogous species $[(PEt_3)_2Pd(H)(Cl)]$ is already known to exist.[10] Interestingly, throughout the entire catalytic reaction, the presence of two bromines (suggesting bridging bromines) is not observed indicating that, at this dilution level, relatively inactive dimeric species are not formed to any great degree.

In conclusion, it has been demonstrated that analysable quality EXAFS that can yield important structural information concerning Pd species involved in Heck chemistry can be collected at dilute and industrially relevant concentrations with a current dilution limit of 50 ppm. It is envisaged that this approach can be applied to other homogeneous metal catalyst systems and will provide a methodology to bridge the gap between the characterisation of catalysts in academic and industrial situations.

Notes and references

‡ Dilute EXAFS was collected using a solid state 13-element Ge detector, tuned to the Pd Kα fluorescence peak. An average of 2 scans was required for 500 ppm with 50 ppm requiring 10 scans, with a scan time of 25 min.
§ The reaction chosen for the study involves the coupling of 4-bromoaceto-phenone with butyl acrylate. The [Pd] was 50 ppm (0.5 mM) and the catalyst to reagent ratio was 1 : 2000. Tributylamine was used as base, with NMP as the reaction solvent. The reaction was conducted *ex situ* and was injected into a sample cell. All measurements were conducted at standard room temperature and pressure with data collection regimes based on previous reaction profile studies (See ESI†).

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