

In situ investigation of the oxidative addition in homogeneous Pd catalysts by synchronised time resolved UV-Vis/EXAFS†

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Simultaneous structuro-kinetic information obtained *via* time resolved stopped-flow/UV-Vis spectroscopy/dispersive EXAFS (EDE) experiments elucidated a two-step process for the addition of iodobenzene to [(Ph₃P)₂Pd(dba)].

The versatility of palladium catalysis has been widely explored, particularly in C–C and C–X bond formation processes,¹ and has found several industrial applications in recent years.² Many of the reactions initiate with the oxidative addition of an aryl halide to a palladium(0) precursor, and this has been often implicated as the rate-determining step of the catalytic cycle. Numerous techniques have been applied to elucidate structural and kinetics details of the reaction, including: DFT calculations,³ EXAFS,⁴ cyclic voltammetry, NMR, UV-Vis and IR spectroscopies⁵ and X-ray crystallography.⁶ These are often employed independently, so that data extrapolation is necessary to gain complementary information. To date, NMR spectroscopy is the only single method that offers simultaneous structuro-kinetic information in real time; however, its inherent timescale restricts its use for the observation of transient reaction intermediates, which are detectable only if they have a significant lifetime (typically tens of seconds).

A combination of complementary spectroscopic techniques is increasingly applied to X-ray sources for the elucidation of catalytic mechanisms under *operando* conditions because they provide a much better understanding of the process as a whole. Assemblies such as EDE/FT-IR and EDE/Raman/UV-Vis have already proven to be very powerful in the study of heterogeneous catalysts.⁷

In the present communication we will describe the use of synchronised, thermostated stopped-flow/multi-wavelength UV-Vis spectroscopy/EDE‡ to examine a prototypical oxidative addition reaction of iodobenzene to [(PPh₃)₂Pd(dba)] (**1**) in a homogeneous solution.⁸ The experiment combines UV-Vis spectroscopy with the unique structural information offered by EXAFS spectroscopy, which is particularly powerful for resolving the spatial environment of a particular atom of interest (in this case, palladium). More importantly, both techniques can be synchronised at the millisecond timescale. To the best of our knowledge, the oxidative addition reactions of Pd(0) complexes

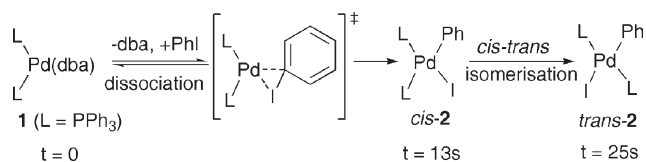
have never been investigated dynamically under *operando* conditions. Only in two instances has a similar set-up been applied: the study of copper catalysis, and an electron transfer reaction between iridium and cobalt.⁹ Herein, we will demonstrate that this multi-technique approach not only has the advantage of gaining correlated and complementary structural, electronic and kinetic information, but also of proving the reliability of the experiment by the cross-checking of spectroscopies. This last aspect is of prime importance when working at high-flux third generation sources, where X-ray induced local heating or sample degradation can seriously undermine the reliability of the conclusions drawn.^{7,9b}

By using this approach, the intimate steps involved in the oxidative addition of iodobenzene to complex **1** were delineated, including the participation of the transient intermediate *cis*-[(PPh₃)₂PdPhI] (**2**) prior to its isomerisation to the thermodynamically more stable *trans*-isomer (Scheme 1). While these results have been previously presumed¹⁰ and predicted by theoretical calculations,³ this is the first time the formation of these species have been observed *in situ*.¹¹

In a typical reaction, complex **1** was generated by mixing Pd(dba)₂ and two molar equivalents of PPh₃ in a solution of toluene (dba = dibenzylideneacetone). The oxidative addition reaction was initiated within the cuvette of a stopped-flow apparatus by injecting a solution of iodobenzene in toluene at 40 °C (40 mM of Pd after mixing). The fate of the palladium complex was monitored from the moment of mixing (*t* = 0 s).

Fig. 1 shows the temporal dependence of two unique UV-Vis absorption bands of complex **1** at 491 and 432 nm, the bands disappearing sequentially over the course of the experiment (within 13 and 25 s, respectively). Simultaneously, corresponding changes in the Pd K-edge XANES were also recorded.† The results show that synchronised time resolved EDE spectra performed at X-ray energies around the Pd K-edge (24 350 eV) can be clearly correlated to the UV-Vis changes, thus obtaining direct and complementary structural information in real time.

To facilitate EDE study, higher Pd concentrations than those normally used for catalytic reactions were employed. Nonetheless,



Scheme 1 Timescales of the oxidative addition and subsequent isomerisation.

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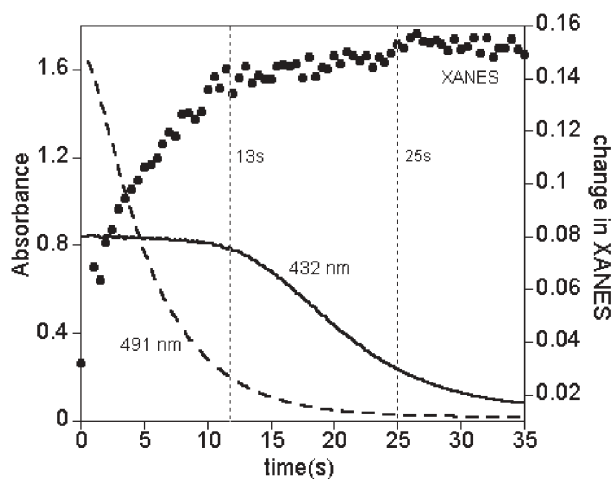


Fig. 1 Real time variation of UV-Vis spectral bands (432 and 491 nm) and the corresponding XANES feature as 10 equivalents of PhI are added to the toluene solution of $[(\text{PPh}_3)_2\text{Pd}(\text{dba})]$ (40 mM).

UV-Vis spectroscopy showed no evidence of mechanistic variation within the range of 500 μM to 40 mM. Therefore, we are confident that, in this case, the mechanistic conclusions drawn at 40 mM [Pd] may be extended to the catalytic regime. However, it is important to note that, although the palladium complexes did not undergo any beam damage, the reaction was accelerated by a factor of two in the presence of X-rays—verified by UV-Vis spectroscopy conducted with and without the application of the high-energy beams.[†]

The doubling of the observed rate constant corresponds to a mild local heating effect due to the X-rays. Compared with the damage observed for a Cu system,^{9b} the stability of the Pd sample towards X-rays may arise from the intrinsic characteristics of the Pd system, from the use of toluene as solvent (it does not undergo radiolysis), the absence of ligands that may be involved in radical parasitic reactions (*e.g.* chlorine), or from the lower flux received on the sample due to the specific experimental conditions (absorption edge considered, polychromator type, undulator gaps, attenuators used, beam operational mode, among others).

The apparent changes of the XANES and the posterior EXAFS analysis indicate that the oxidative addition process of PhI onto $[(\text{PPh}_3)_2\text{Pd}(0)(\text{dba})]$ (**1**) takes place within 25 s, yielding $[(\text{PPh}_3)_2\text{Pd}(\text{II})(\text{PhI})]$ (**2**) as the end product, after which no more significant changes were observed on the EXAFS spectra.[†] Structural parameters obtained with the best fit for the molecular models of **1** and **2** are given in Table 1. The fitting was verified to

Table 1 Structural parameters obtained from EXAFS analysis for the models $[(\text{PPh}_3)_2\text{Pd}(\text{dba})]$ (**1**) and $[(\text{PPh}_3)_2\text{PdPhI}]$ (**2**)

Model	Ab-Sc pair ^a	$d^b/\text{\AA}$	$\sigma^{2c}/\text{\AA}^2$	$\Delta E_0^d/\text{eV}$	R^e
1	Pd-C	2.19(2)	0.001(3)	2(1)	0.04
	Pd-P	2.33(1)	0.008(3)	—	—
2	Pd-P	2.32(2)	0.005(3)	-4(3)	0.04
	Pd-C	2.10(9)	0.008(3)	—	—
	Pd-I	2.68(2)	0.005(1)	—	—

^a Ab-Sc pair = absorbent and scattering pair. ^b d = bond length. ^c σ^2 = Debye-Waller factor. ^d ΔE = inner potential correction. ^e R = goodness of fit parameter in FEFF code. [†] $\Delta k = 3\text{--}13 \text{ \AA}^{-1}$, $\Delta r = 1\text{--}3 \text{ \AA}$; k^1 and k^2 .

be consistent in both k^1 - and k^2 -weighting. Other models considered, such as triangular $[(\text{PPh}_3)_2\text{Pd}]_3$, *trans*- $[(\text{PPh}_3)_2\text{PdI}]_2$ or bimolecular $[(\text{PPh}_3)_2\text{PdI}]_2$, did not fit well with the experimental spectra.[†]

This reaction takes place gradually and there is no evidence for a significant existence of intermediate species containing only one phosphine ligand, or bimolecular compounds, or any type of palladium cluster,¹³ as postulated in some instances; yet the formation of these compounds cannot be completely ruled out, because of the averaging nature of the EXAFS technique.^{6,10}

Fig. 2 shows four EXAFS spectra (in k - and r -space) obtained at different intervals of the reaction. At time 13 s, just before the start of the second step of the reaction (see Fig. 1), $[(\text{PPh}_3)_2\text{Pd}(\text{dba})]$ has started reacting (87%) in favour of $[(\text{PPh}_3)_2\text{PdPhI}]$.[†] Clearly, at time 25 s the phenyl iodide addition is complete and the EXAFS spectra is equivalent to the end product. The good quality of the data obtained for the $[(\text{PPh}_3)_2\text{Pd}(\text{dba})]$ compound in 3.8 s (19 spectra of 200 ms each) is noticeable. However, the quality of the data worsens as phenyl iodide is added. This is due to the considerable X-ray scattering

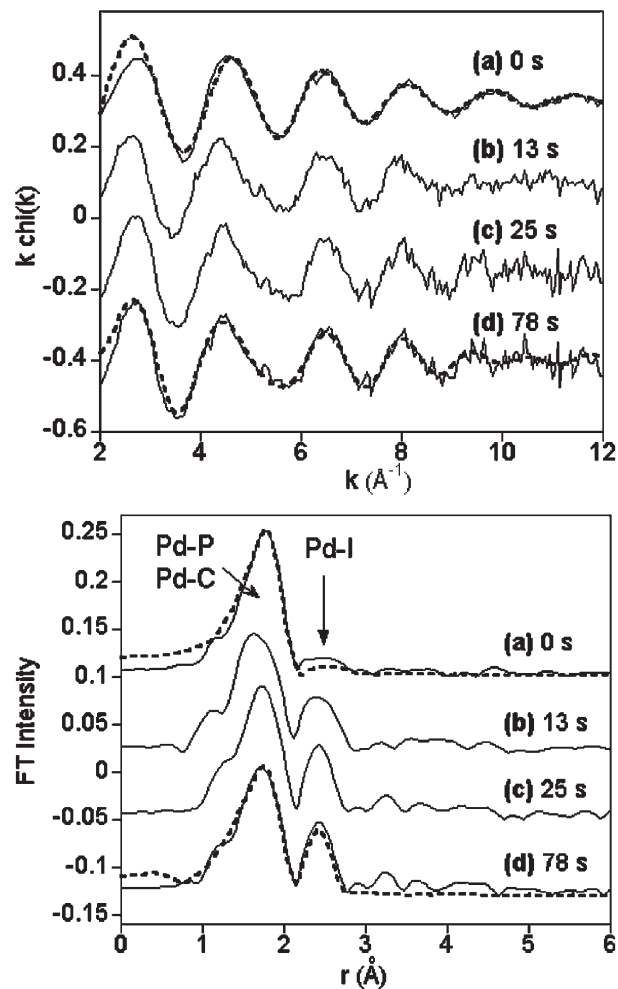


Fig. 2 EXAFS of Pd K-edge, in k - and r -space, of $[(\text{PPh}_3)_2\text{Pd}(\text{dba})]$ (40 mM) + 10 equivalents PhI taken *in situ* at different stages of the reaction: (a) time 0 s ($[(\text{PPh}_3)_2\text{Pd}(\text{dba})]$), (b) time 13 s, (c) time 25 s, (d) time 78 s ($[(\text{PPh}_3)_2\text{PdPhI}]$). For clarity purposes spectra (a) is 3.8 s worth of data, (b) 1 s, (c) 1 s and (d) 10 s. The dotted lines are the fits for models **1** and **2**

associated with the addition of a large excess of iodide in the transmission EXAFS experiment.

Thus, we verify the reaction mechanism as being composed of two steps: a concerted oxidative addition of the PhI onto $[(PPh_3)_2Pd(dba)]$ in a *cis* configuration, followed by *cis-trans* isomerisation. The oxidative addition process is distinguished indirectly from the UV-Vis spectrum as the loss of the dba ligand, and directly from the EXAFS analysis by the concomitant addition of phenyl iodide on the Pd centre, as well as by the shift in the XANES region indicating a change in the oxidation state of the palladium. The isomerisation is detectable in the UV-Vis spectrum as the loss of a band due to the phosphine ligand reorganisation and agrees, qualitatively, with the formation of a compound with higher symmetry, *i.e.* from C_s (*cis*-isomer) to C_{2h} (*trans*-isomer).

Simultaneous with describing the mechanism from a structural point of view, both techniques permit assessment of the kinetics of the conversion. Preliminary results show that at 40 °C the oxidative addition step follows a pseudo-first order rate with a global rate constant of $k_{app} = 83 \times 10^{-3} M^{-1} s^{-1}$ in the absence of the X-rays and of $k_{app} = 170 \times 10^{-3} M^{-1} s^{-1}$ in their presence.[†] This is substantially slower than reactions conducted in THF or DMF at 20 °C, previously recorded by Amatore *et al.*¹⁴ Reasons for this deviation could be due to the higher concentration of the palladium complex, which prohibits the formation of the more reactive (dba-dissociated) complex, or the use of the non-polar toluene, which can hamper the attainment of a polar transition state. On the other hand, the isomerisation appears to be a much more complex process under these conditions. The observation of a non-steady state concentration of *cis-2* also implies that the oxidative addition step is much more facile than the isomerisation process under these conditions.

This report clearly demonstrates the viability, as well as the potential, of a synchronised multi-technique and *operando* approach for the unambiguous structuro-kinetic study of the dynamic behaviour of homogeneous catalysts, especially on fast timescales. It also underlines the care that must be taken to obtain meaningful results in such cases, especially with high-flux/brilliance third generation synchrotron sources.

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Notes and references

‡ Solutions of $[(PPh_3)_2Pd(dba)]$ were prepared *ex situ* by mixing $Pd(dba)_2$ with 2 equivalents of PPh_3 in dry toluene using a Schlenk line. The stopped-flow used was a SFM-3 Bio-Logic device equipped with isolast o-rings, which are thermally resistant, compatible with all solvents and are connected to a Huber ministat ccl variable temperature bath. Cuvettes (10 × 1.5 mm) with vitreous carbon and quartz windows were used. The UV-Vis spectra were recorded on a multi-wavelength J&M TIDAS spectrometer. EDE measurements on ID24 were performed using a Si(3 1 1) crystal in the Bragg configuration. The reaction of **1** with PhI was followed over 78 seconds, with a time resolution of 500.9 ms. A FRLoN (fast readout low noise) CCD camera working in kinetic mode was used for the detection.

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