



	Experiment title: The application of bromine EXAFS to the characterisation of ultra-dilute homogeneous palladium catalysts in C-C coupling reactions	Experiment number: CH1586
Beamline: ID26	Date of experiment: from: 19/11/03 to: 25/11/03	Date of report: 26/04/04
Shifts:	Local contact(s): Dr. Olga Safonova	<i>Received at ESRF:</i>
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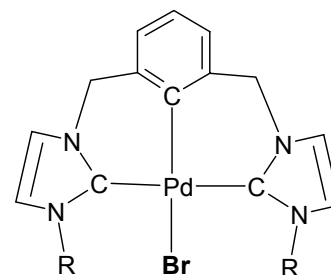
Report:

The main aim of this proposal was to apply the technique of ultra-dilute XAS at the Br K-edge to investigate the role of the halide during the Heck and Suzuki reactions and to provide complementary data to the Pd K-edge EXAFS collected during previous ID26 beamtimes. However, as it transpired, a new type of pincer carbene catalysts was investigated in particular during this beamtime as it had been shown by catalytic testing conducted in Southampton that this particular catalyst showed superior catalytic ability and was able to work with the more available chlorobenzene reactant. Therefore, it was decided that this beamtime would be used to study this catalyst in the Heck reaction at both the Br and Pd K-edges so that we had complimentary data for this work. We are very grateful to Olga Safonova for allowing us to do this by coming to the ESRF and changing the energy from Br to Pd on the weekend.

Due to the fact that both the Br and Pd edges were to be recorded for this reaction, a different methodology was used in comparison to the previous beamtimes. The catalytic reaction was set up off-line in the chemistry laboratory of ID26 under a flow of inert gas. At certain temperature/time intervals, 2mL of mixture was removed from the total volume and quenched rapidly using liquid nitrogen to stop the procedure of the reaction. Once the solution reached ambient room temperature, it was transferred to a sample vial under an inert gas and wrapped in parafilm to maintain the exclusion of air. Finally, each vial was stored in the fridge until needed. When characterisation of the sample was to be carried out, the solution was removed from the vial and injected into a simple solution cell (with the ability to allow fluorescence measurements) and placed in the beam for analysis. The two advantages of this method over the previous experiments was that the same solution could be used for both the Pd and Br edges providing consistency between the two edges measured and the solution could then be taken away for further analysis by GC to provide information regarding product formation (i.e. yield) at that point in the reaction. It was also the first time to our knowledge that the Br K-edge had been studied under such catalytic conditions and the data obtained were of a high quality. Using ID26 and a silicon photodiode, a concentration level of 50ppm was clearly achievable and it is proposed that even lower levels can be reached if future experiments permit.

The catalytic solution studied in most detail was the reaction of phenyl triflate with butyl acrylate. The mixture also contained a GC standard (for yield studies at a later date), tributylamine as a base and *N*-methyl pyrrolidinone (NMP) as an inert solvent for the mixture. The catalyst used is shown (1) and has shown excellent results for the catalysis of chlorobenzene in the Heck reaction.

Three representative spectra showing both the Br and Pd K-edges are shown.



Catalyst (1); R = [2,6-(diisopropyl)phenyl]

Figure 1: The EXAFS and associated Fourier transform from the (1) Pd K-edge and (2) Br K-edge of the intermediate species observed at (a) room temp, (b) 360mins at 140°C and (c) 720mins at 140°C.

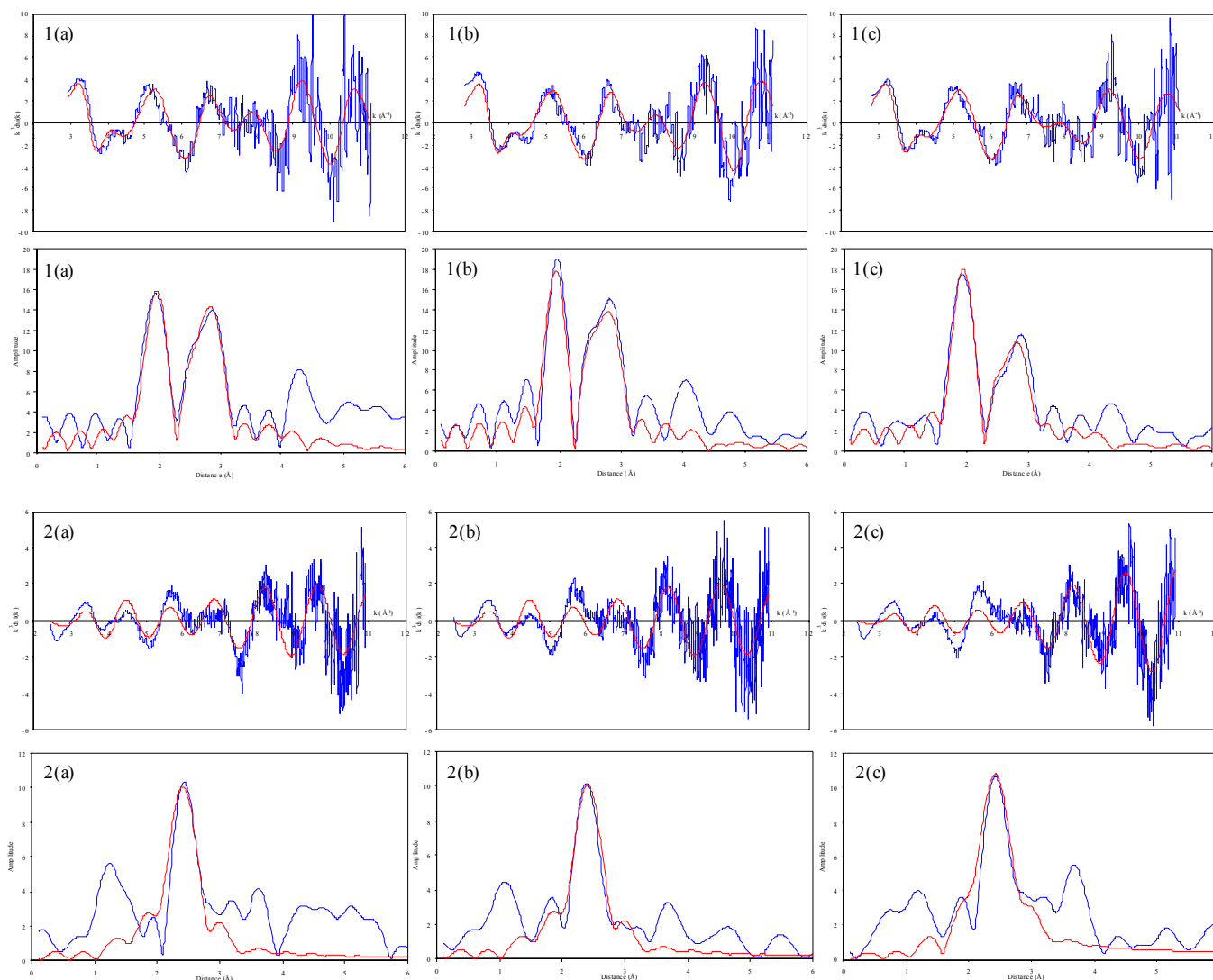


Table 1a: Structural / statistical parameters derived from analysis of the Pd K-edge EXAFS spectra shown in Fig. 1.

	Coord. Number	Type of Atom	Distance (Å)	$2\sigma^2$ (Å ²)	R(%)
Room Temp	3	Carbon	1.998	0.011	60.5
	1	Bromine	2.513	0.013	
	4	Nitrogen	2.954	0.005	
	2	Carbon	2.954	0.005	
360mins at 140°C	3	Carbon	2.011	0.008	54.9
	1	Bromine	2.504	0.015	
	4	Nitrogen	2.952	0.015	
	2	Carbon	2.952	0.015	
720mins at 140°C	3	Carbon	2.009	0.007	53.1
	1	Bromine	2.510	0.014	
	4	Nitrogen	2.961	0.015	
	2	Carbon	2.961	0.015	

Table 1b: Structural / statistical parameters derived from analysis of the Br K-edge EXAFS spectra shown in Fig. 1.

	Coord. Number	Type of Atom	Distance (Å)	$2\sigma^2$ (Å ²)	R(%)
Room Temp	1	Palladium	2.486	0.013	73.9
360mins at 140°C	1	Palladium	2.474	0.011	75.6
720mins at 140°C	0.8	Palladium	2.492	0.005	67.2

Table 1 and Figure 1 show the results concerning the coordination sphere of the Pd and Br for the three cases shown. The results all look very similar suggesting that there was very little change during the course of this reaction. This is interesting and possibly suggests three things (a) there was little or no reaction between the phenyl triflate and the butyl acrylate, (b) the coordination environment of the palladium changes very little and the catalyst works by some other means than loss of the bromine as the initial stage or (c) the amount of catalyst actually involved in the catalytic reaction i.e. the active catalyst is significantly lower than the concentration of catalyst that was under investigation (i.e. 0.5mM or 50ppm Pd). GC characterisation of the solutions unfortunately suggests that there is a low yield of the product formed suggesting that there was little or no reaction between the substrates. However, even though the yield was low (15%), there was a yield suggesting that at least some percentage of the catalyst in solution is working. Therefore, if possible, it would be very valuable and interesting to investigate these catalysts at even lower levels to define the species that is active in catalysis. With the excellent Br K-edge data collected during this beamtime for these samples, it is envisaged that there should be few problems investigated even lower levels (1-10ppm) at least at the Br K-edge. Consequently, at these lower catalyst concentration, the amount of active catalyst involved in the catalytic reaction would be significantly higher thereby minimising “inactive” species and allowing a clearer picture of the true active catalyst. Another very important piece of information arising from this data is the lack of any Pd-Pd distances. This is vitally important as it has been hypothesised by other researchers in the field of carbene catalysts that the carbene catalysts is first reduced to a Pd(0) species before being converted into small palladium clusters. In this study, we observe no evidence of Pd clustering and it therefore provides further evidence to justify our hypothesis that the active species is the palladium carbene not palladium clusters. However, it does show in a very significant way that these catalysts are stable up to 140°C for at least 12 hours and from other results not shown, 36 hours.

Also due to the ability to recorded EXAFS at both the Br K-edge and Pd K-edge for the same sample, a novel extraction and analysis protocol was used that allowed the simultaneous analysis of both edges for the same model providing a complete method to analysis and characterise these catalysts and also provide a methodology to compare the analysis of the Pd K-edge only, providing us with great insight into whether the models that are being fitted to the Pd K-edge (especially for pure Pd catalysts with no other Br or other EXAFS analysible edges involved) provides a true and honest reflection of the catalyst structure.

Table 2 and Figure 2 show the results concerning the coordination sphere of the Pd and Br for the analysis of the catalysts in NMP only at room temperature. The main connecting strand between the two edges is the Pd-Br bond and during the modelling, this has been set during the analysis to be refined to the same distance for both the Pd and Br K-edge analysis.

Figure 2: The dual-edge refinement data of the pincer carbene catalyst (1) diluted in NMP at room temp: (a) Pd K-edge EXAFS, (b) Pd K-edge Fourier transform, (c) Br K-edge EXAFS and (d) Br K-edge Fourier transform.

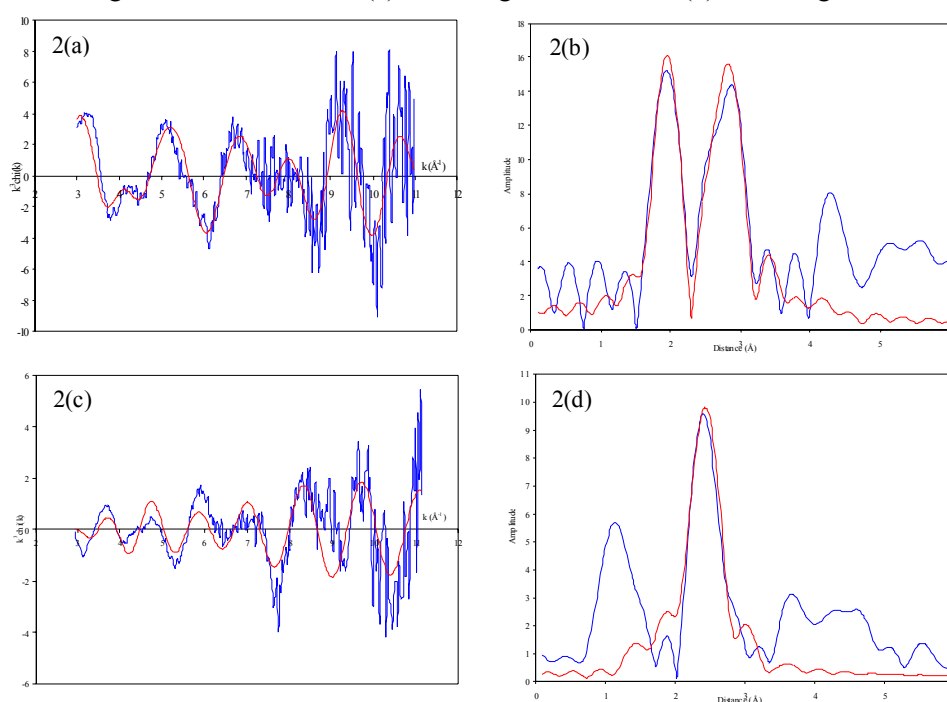


Table 2: Structural and statistical parameters derived from analysis of the EXAFS spectra shown in Fig. 2.

	Coord. Number	Type of Atom	Distance (Å)	$2\sigma^2$ (Å ²)	R(%)
Pd K-edge	3	Carbon	1.997	0.009	66.9%
	1	Bromine	2.502	0.015	
	4	Nitrogen	2.952	0.003	
	2	Carbon	2.952	0.003	
Br K-edge	1	Palladium	2.502	0.014	

As can be clearly seen, the addition of the Br EXAFS to the simultaneous analysis makes only a small difference to the analysis suggesting that the Pd model fitted provides a true reflection of the catalyst structure. Continuation of this dual edge analysis is well underway for the other sampling regimes and will give us a much clearer understanding of the intermediates involved during catalysis. Other work currently in progress for this data includes the improvement of the model for the Br K-edge to attempt to fit either the carbene ligands (i.e. either the carbene carbons or the nitrogens in the carbene ring) and/or the ligands attached to the carbenes to discover of those helps to improve the fit.

In summary, we have demonstrated that the application of bromine EXAFS to the characterisation of ultra-dilute homogeneous palladium catalysts is an important and valuable tool. It can provide a unique method to investigate the structure of these catalysts working under real industrially relevant conditions allowing us to gain insight into the fundamental information of how these systems work. However, with the combination of the Pd K-edge EXAFS and the ability to analyse the data in a simultaneous manner, it provides an even more powerful tool for the understanding of these catalysts. We have also shown very clearly that Br K-edge EXAFS on a 50ppm sample is totally feasible and it is our feeling that significantly lower concentrations can be attained at the Br K-edge. This is very important and will potentially provide an even clearer understanding of the chemistry involved because of the increase in the amount of true active catalyst present in the catalytic mixture.