Structural Characterisation of Solution Species Implicated in the Rhodium-catalysed Carbonylation of Methanol by Rh K-edge X-ray Absorption Spectroscopy

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Rhodium K-edge extended X-ray absorption fine structure (EXAFS) analysis has shown that $[\{Rh(COMe)I_3(CO)\}_2]^{2-}$ exists in tetrahydrofuran solution at −20 °C, but fragments above 0 °C to $[Rh(COMe)I_3(CO)(solv)]^-$; when solv = MeOH, the solution structure shows a substantial *trans* influence (0.2 Å) on the Rh–I bond *trans* to the Rh–COMe group.

The catalytic carbonylation of methanol is a well established industrial process in which the organometallic core of the reaction sequence is based on the chemistry of $[RhI_2(CO)_2]^-$ **1**.[1] More recent kinetic and spectroscopic studies have identified the primary reaction as the oxidative addition of iodomethane to form $[Rh(Me)I_3(CO)_2]^-$ **2**, which is then followed by a rapid methyl migration step.[2] The resulting acyl complex has been identified as a dimeric species $[\{Rh(COMe)I_3(CO)\}_2]^{2-}$ **3** in the crystal.[3] In this communication we show that extended X-ray absorption fine structure (EXAFS) analysis of the Rh K-edge spectra of these solutions provide good structural data for the rhodium species present; using the rapid-scanning Quick EXAFS technique,[4] the solvation of **3** can be monitored at low temperatures.

Fig. 1 shows the results of the curve-fitting analyses of the EXAFS data for solutions of **1**, **3** and $[Rh(COMe)I_3(CO)(solv)]^-$ **4** in methanol at room temperature.* The most interesting feature is the data obtained for the solution of the dimeric acyl complex **3**. These were very similar to interatomic distances derived from the crystal-structure determination of the pyridine complex of the monomeric anion in $[AsPh_4][Rh(COMe)(NC_5H_5)I_3]{\cdot}C_6H_5Me$ **6**.[8] In that structure a strong *trans* influence was shown by the acetyl group, causing a 0.2 Å increase in the Rh–I bond length over that of the mutually *trans* bonds; this was again clear in the solution derived from **3** and thus supports the stereochemistry given as **4** in Fig. 1, which is that shown for the pyridine adduct. Although some evidence was found for an Rh–O bond to the methanol of *ca.* 2.2 Å, this was of doubtful statistical significance in the fitting procedure. The *in situ* reaction of MeI with $[RhI_2(CO)_2]^-$ **1** in methanol gave very similar results. The formulation of **4** was suggested by Mann and co-workers[8] from NMR studies.

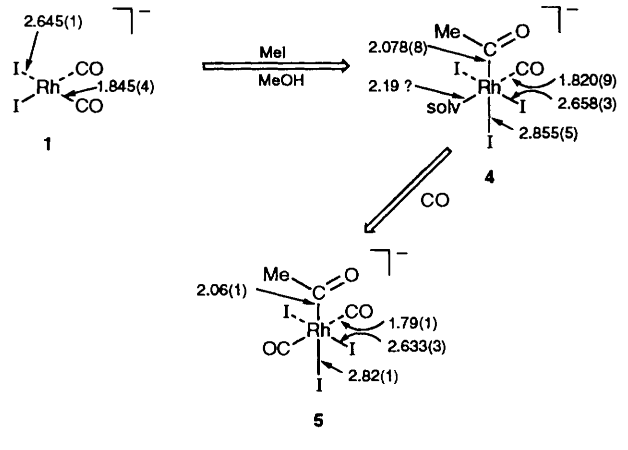

Fig. 1 Results of the Rh K-edge EXAFS data analysis of solutions of **1**, **3** giving **4**, and **5** in methanol solution (30 mmol dm^{-3}); distances in Å

Quick EXAFS[9] scans of the reaction of the dimeric anion **3** with CO in tetrahydrofuran (thf) solution were performed with alternating forward and backward scans over a 500 eV range each taking 2 min. Data from these runs could be analysed to k = 12 Å^{-1}. The calculated fit for these data at −20 °C is shown in Fig. 2(*a*), and compared also with data for **3** itself truncated to k = 12 Å^{-1} [Fig. 2(*b*)]. Refinement of solution data afforded the following parameters: 0.8(1) Rh–CO [Rh–C 1.92(1) Å, Rh···O 2.98(3) Å, Rh–C–O maintained at 180°], 2.3(1) shorter Rh–I [2.669(7) Å] and 0.75(6) long Rh–I bonds [2.98(3) Å]. A restricted number of shells could be sustained due to the smaller k range and the lower signal/noise ratio of the *in situ* Quick EXAFS data, but the similarity of the spectra and Fourier transforms as shown in Fig. 2, and the results of the curve fitting suggests the predominant species at −20 °C in thf is the starting material. However, after 10 min at 0 °C, reaction did become evident, with the spectra now more closely matching that of $[Rh(COMe)I_3(CO)_2]^-$ **5** (Fig. 3). Analysis indicated an increase in the mean Rh–CO co-ordination number of 1.3(1), and a reduction in the long Rh–I distance [Rh–I 2.91(1) Å]. It can be concluded that the solution now contains a mixture of the mono- and di-carbonyl monomeric anions **4** and **5**.

These results show that analysable EXAFS data of organometallics in solution can be acquired with fluorescence detection in a rapid-scanning operation (500 eV in 2 min). They also provide structural confirmation of the solution species related to methanol carbonylation, and the *trans* influence of the

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* Conventional scanning X-ray absorption spectra were recorded over a 16 Å^{-1} k range on Station 9.2 at the Synchrotron Radiation Source (SRS) at the Daresbury Laboratory operating at 2 GeV (*ca.* 3.20 × 10^{-10} J) in transmission mode; Quick EXAFS data were recorded over a 12 Å^{-1} k range with fluorescence detection with a Camberra 13-element solid-state detector on Station 9.3. The EXAFS analysis used background subtraction and curved-wave analysis procedures as previously described.[4] Global errors in distance determination have been estimated as 1.5%[5] and for co-ordination numbers 10–30%.[6] Multiple scattering methods were employed for the M–C–O shells.[7] The Rh···O distances and Rh–C–O angles for the metal carbonyls were, respectively, estimated as: **1**, 2.961(2) Å and 177(3)°; **4**, 3.012(4) Å and 179(1)°; **5**, 3.022(4) Å and 175(1)°.

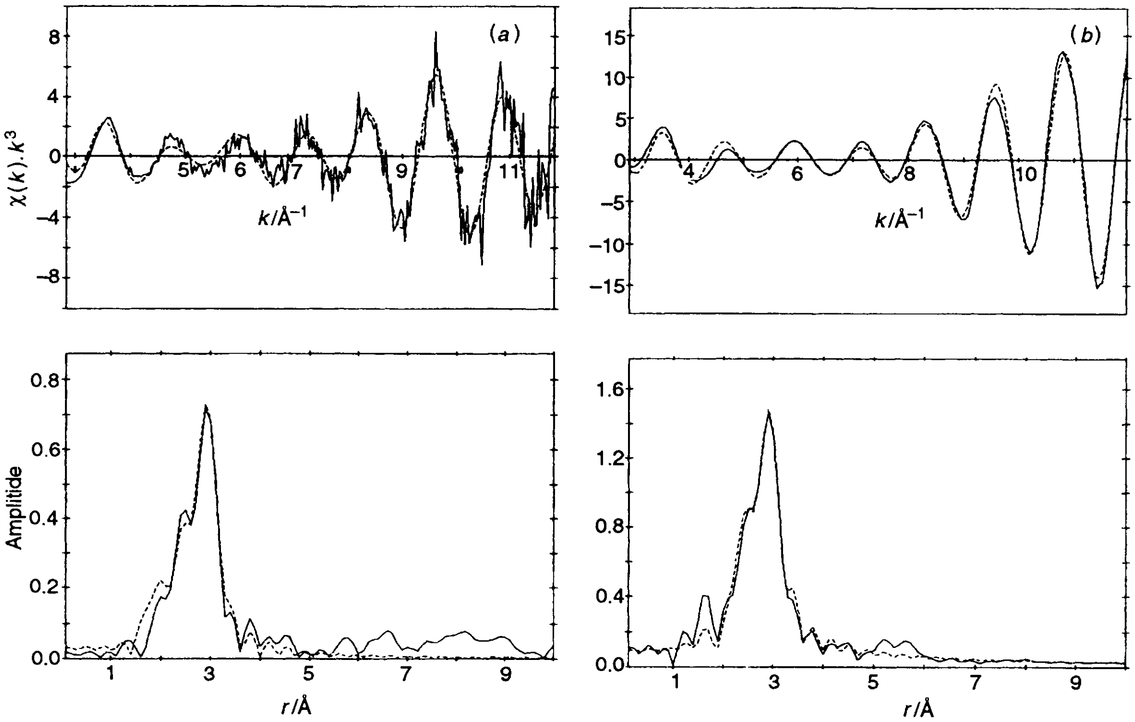

Fig. 2 Comparison of the EXAFS and Fourier transforms (——, experimental; – – – –, spherical wave theory) of (*a*) the solution of $[PPh_4]_2[\{RhI_3(COMe)(CO)\}_2]$ **3** under CO and in thf solution at −20 °C, an average of five 2 min-long spectra after 10 min reaction time, with (*b*) that of **3** as the solid cooled by liquid nitrogen with data truncated to the same *k* range (12 Å^{-1})

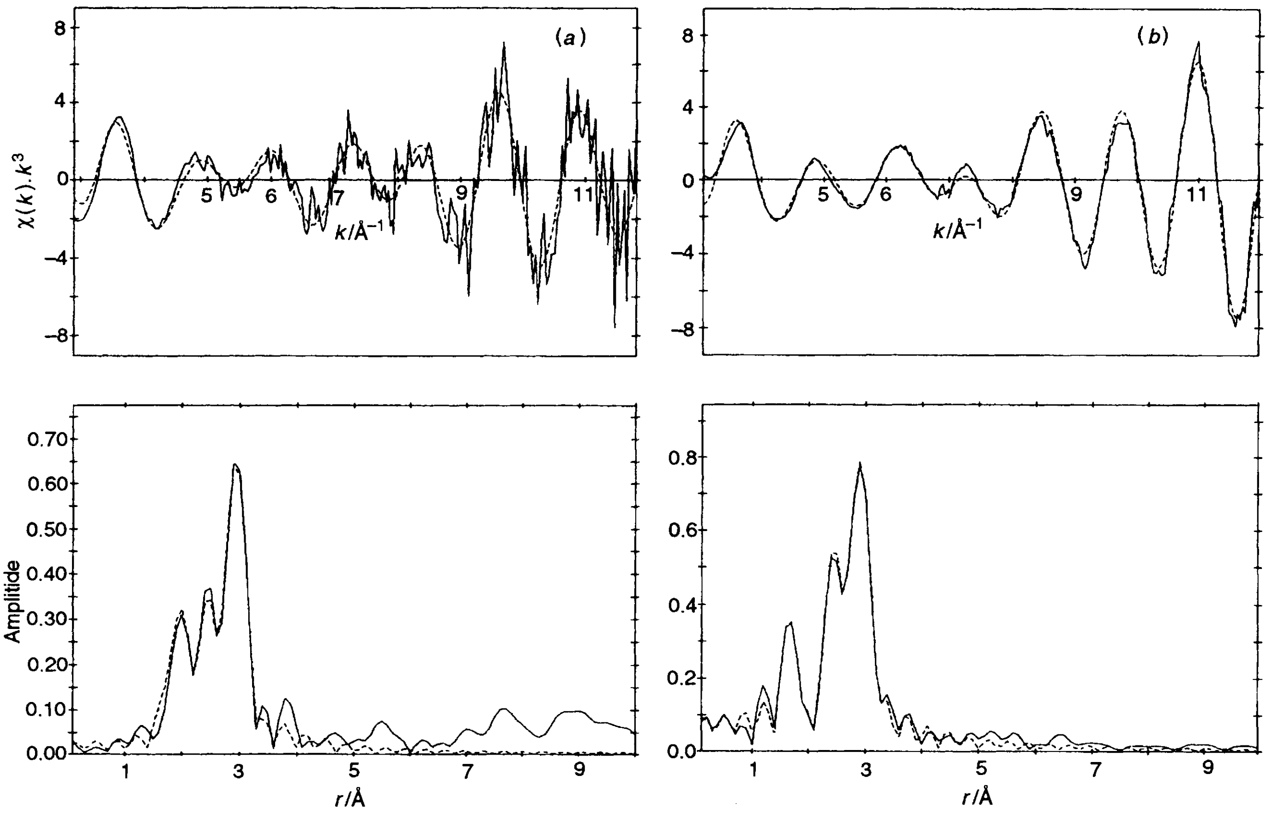

Fig. 3 Comparison of the EXAFS and Fourier transforms (——, experimental; – – – –, spherical wave theory) of (*a*) the solution of $[PPh_4]_2[\{RhI_3(COMe)(CO)\}_2]$ **3** under CO and in thf solution at 0 °C, an average of five 2 min-long spectra after 10 min reaction time, with (*b*) that of **5** in frozen methanol solution with liquid-nitrogen cooling, and data truncated to the same *k* range (12 Å^{-1})

acetyl group in the solvated acyl complex **4**. We also have demonstrated that the dimeric complex **3** can exist in low-temperature solutions in co-ordinating solvents, prior to the bridge-cleavage reactions.

Acknowledgements

We thank BP Chemicals and the University of Southampton for support, Dr D. J. Gulliver and Dr J. W. Couves for helpful discussions, and the Head of the Daresbury Laboratory for use of the SRS and other facilities.

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Received 25*th July* 1995; *Communication* 5/04930J