Insight into the mechanism of decarbonylation of methanol by ruthenium complexes; a deuterium labelling study

ESI

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1 NMR spectra

![NMR Spectrum](image)

**Figure S1** ¹H NMR (400 MHz; toluene-d₈) of [RuH₂(CO)(PPh₃)]
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1.2 Mixture [RuHD(CO)(PPh$_3$)$_3$] (major species) and [RuH$_2$(CO)(PPh$_3$)$_3$] (minor species)

Figure S3 $^1$H NMR (400 MHz; toluene-$d_8$) of [RuHD(CO)(PPh$_3$)$_3$] (2 isomers) and [RuH$_2$(CO)(PPh$_3$)$_3$] (minor species).
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Potential $[\text{RuD}_2(\text{CO})(\text{PPh}_3)_3]$
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(experiment used for determining the KIE)
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1.7 Time and temperature dependent NMR studies with NaOCD$_3$

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1.8 Time and temperature dependent NMR studies with NaOCH₃

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Identification of $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$

Figure S27 $^1$H NMR (300 MHz; toluene-$d_8$); Identification of $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ by performing the reaction under Ar.
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1.10 Identification of $[\text{RuH}_2(\text{PPh}_3)_4]$
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Evidence for $o$-D incorporation into coordinated PPh$_3$

Figure S31 $^1$H NMR (400 MHz; toluene-$d_8$); aromatic region of [RuH$_2$(CO)(PPh$_3$)$_3$]. The integration of the Ru-H signals was set at 1.0 for each
The formation of [RuH₄P₃'] the reaction of [RuHClP₃] and CD₃OD/Na requires that H/D exchange occurs into the aromatic rings of the coordinated phosphines, as previously observed by Halpern and co-workers. Some evidence that this is occurring is discussed in the main paper with signals being observed in the ¹H NMR spectrum corresponding to deuteration in the ortho positions of both Pₐ and Pₕ, broadening of the ³¹P NMR signals and evidence for incorporation of D into PPh₃ and Ph₃PO from the ³¹P NMR spectra (β-shifted resonances. In order to try to obtain quantitative data on the extent of incorporation, we have analysed the aromatic region of the ¹H NMR spectra of the final products obtained from the reaction of [RuHClP₃] with MeOH/Na and with CD₃OD/Na. For the reaction using MeOH (Figure S31), the ortho and meta protons from Pₐ and Pₕ give well separated signals, whilst the para protons resonate in the same place. The o and m protons do not overlap with signals from PPh₃ or Ph₃PO, although the p protons do.

Looking at the two resonances from the o protons, in [RuH₂(CO)P₃], the resonances at δ 7.26 and 7.4 correspond to 6 (Pₐ) and 12 Pₕ protons as expected. When the same product is made from CD₃OD/Na (Figure S32), the integrations correspond to 2.2 and 4.3 protons showing that very substantial D has been incorporated into the o-positions. (11 - 12 D per molecule). Further qualitative evidence for incorporation of D into the o positions of the phenyl rings comes from the fine structure of the resonances from the m protons on Pₕ, which is absent from the related resonance in Figures S31 and arises from Hₘ-Dₗ coupling. The incorporation of D into the ortho positions is far in excess of the 4 that would be required to give 4 non-deuterated hydrides. We conclude that fast H-D exchange occurs with the solvent in some intermediates along with loss of HD/H₂ or that D can be incorporated directly into the ligand from the solvent.
This H/D exchange must occur during the conversion of [RuHClP₃] to [RuH₂P’₄] but the final product of this first step certainly only contains Ru-H. This is best seen from the hydride resonances of [RuH₂(N₂)P₃], which very clearly shows the H-H coupling of the dihydride with no enhancement of the low frequency peaks. The [RuH₂P₄] hydride resonance is second order (AA’MM’XX’) and is identical whether the reaction is carried out in CH₃OH or CD₃OD. [RuHP₄] would be expected to show a first order resonance approaching a doublet of quartets.

3 Hydride composition for the final product from reaction of [RuHClP₃] with Na/CD₃OD

Figure S 31 shows the integrated phenyl region of a final product [RuH₂(CO)P₃] obtained using [RuHClP₃] and Na/CH₃OH with each hydride signal set to have an integrated intensity of 1.0. Figure S32 is from a similar final product when using Na/CD₃OD once again with the equal intensity hydride resonances set at 1.0 These hydride resonances, which are shown in Figure S3 arise from the two isomers of [RuHD(CO)P’₃] together with some [RuH₂(CO)P’₃].

We then analyse the integrations of the meta H atoms on the phenyl rings since they are distinct, free from interference by OPPh₃ and should not have experienced any H/D exchange. For the non-deuterated sample (Figure S31) the m resonances from Pₐ and Pₐ integrate as 12.36 and 6.56 corresponding to 12 and 6 protons respectively. The similar integration for the deuterated sample (Figure S32) gives Pₐ 24.81 and Pₐ 12.86, almost exactly double what is seen for the undeuterated sample. This means that there is on average 1 H and 1 D on each ruthenium and hence that the amount of [RuH₂(CO)P’₃] and of [RuD₂(CO)P’₃] must be the same.

By integrating the individual peaks for each hydride signal in Figure S3, it is possible to work out the ratio of the two isomers of [RuHD(CO)P’₃] (each 1.27) to [RuH₂(CO)P’₃] (1). Since [RuD₂(CO)P’₃] must also be present in the same amount as [RuH₂(CO)P’₃]. We can simulate the observed integrations if the proportions of [RuH₂(CO)P’₂] : [RuHD(CO)P’₃] (each isomer) : [RuD₂(CO)P’₃] is 0.22 : 0.28 : 0.28 : 0.22.