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

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In memory of Roberto Sánchez-Delgado a good scientist and great friend.

In the reaction of $[RuHClP_3]$ (P = PPh_3) with NaOMe in methanol, the product is $[RuH_2(CO)P_3]$. Short reaction times show that the final product is formed through $[RuH_4P_3]$ as the major intermediate. Using $NaOCD_3$ in CD_3OD, the first formed product is $[RuH_4P'_3]$ (P' is PPh_3 partially deuterated in the *ortho* positions of the aromatic rings). Further reaction leads to a mixture of $[RuH_nD_{2-n}(CO)P_3]$ (n = 0, 22 %; n = 1, 2 isomers each 28 %; n = 2, 22 %). Mechanistic aspects of both steps of the reaction are explored and, together with previously published calculations, they provide definitive mechanisms for both dehydrogenation and decarbonylation in these interesting systems.

Introduction

As part of our studies on the production of hydrogen from alcohols[1-5] and the related decarbonylation[4, 6, 7] of alcohols catalysed by $[RuH_4P_3]$ (P = PPh_3)‡ and related complexes, we have recently reported some DFT calculations on the mechanism of alcohol decarbonylation to give $[RuH_2(CO)P_3]$,[7] especially when using methanol as the substrate. A series of routes was investigated and kinetic isotope effects (k_H/k_D) calculated for each of them. We then wished to compare these kinetic isotope effects with experimental values. We originally expected to do this by carrying out reactions using a mixture of CH_3OH and CD_3OD, but complications arose because of H/D exchange. In the end we obtained the experimental value using mixtures of $^{13}CH_3OH$ and CD_3OD.[7] Even then, our anticipated use of ^1H NMR spectroscopy of the hydrido signals was complicated by isotope shifts and D broadening so we used ^{13}C NMR of the carbonyl resonance for the quantitative analysis. Some unexpected observations of the H/D labelling pattern of the products suggested that the mechanism might not be exactly as we expected so we investigated these reactions further.

Experimental

All manipulations and reactions were carried out under Ar or N_2 gas when not specified (dried through a Cr(II)/silica packed glass column) using different techniques including a standard Schlenk vacuum line and a glove box. Solvents were degassed prior to use and dried when required.

$RuCl_3{\cdot}3H_2O$ was purchased from Alfa Aesar. All solvents were purchased from Sigma-Aldrich. Toluene was dried using a Braun Solvent Purification System. Methanol was dried and degassed by distillation from magnesium methoxide under nitrogen. $[RuCl_2(PPh_3)_3]$[8], $[RuHCl(PPh_3)_3]$[9-11], $[RuH_4(PPh_3)_3]$[12, 13] and $[RuH_2(PPh_3)_4]$[13] were prepared by published procedures and all observations and NMR data were in accordance with those reported in the literature, except for $[RuH_2(PPh_3)_4]$ where no NMR data were available. $[RuH_2(CO)(PPh_3)_3]$ was prepared by an adaptation of a literature method.[6] Sodium methoxide was prepared by reacting sodium metal (supplied by Lancaster Synthesis in mineral oil; the small pieces were washed with hexane) with degassed CH_3OH, CD_3OD or $^{13}CH_3OH$. Triethylamine was purchased from Fischer Scientific and degassed before use. All gases were purchased from BOC gases. All solvents and deuterated solvents, which were not previously dried, were only degassed prior to use.

NMR spectra were recorded on Bruker Avance II 400 and 500 MHz spectrometers (^1H NMR at 400 MHz and ^{13}C NMR at 100 MHz or ^1H NMR at 500 MHz and ^{13}C NMR at 125 MHz respectively) at room temperature.

^1H NMR solvent residual signals: CD_2Cl_2 set at 5.32 ppm; toluene-d_8 at 2.08 ppm; THF-d_8 at 1.72 ppm. $^{13}C\{^1H\}$ NMR solvent signals: CD_2Cl_2 set at 53.84 ppm; toluene-d_8 at 20.43 ppm; THF-d_8 at 25.31 ppm.[14]

Synthesis of known complexes for comparative NMR data

$[RuH_2(CO)P_3]$ (P = PPh_3) was prepared by an adaptation of a literature method.[6] Sodium methoxide was prepared by reacting sodium metal (0.02 g, 0.87 mmol) with CH_3OH (0.4 mL, 9.8 mmol), under an inert atmosphere of dinitrogen and the formed solution was subsequently added to a suspension of $[RuHClP_3]$ (0.015 g, 0.016 mmol) in toluene (3 mL). After refluxing the reaction mixture for 1 hour at 100 °C, the resulting

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orange solution was cooled to room temperature and evaporated to dryness. The recovered solid was washed once with dry, degassed methanol in order to remove the methoxide and dried *in vacuo*. The collected yellow solid was analysed *via* NMR spectroscopy (toluene-d_8). The ^{1}H and ^{31}P{^{1}H} spectral data are identical to those described in the literature.[15]

^{1}H NMR (400 MHz; toluene-d_8): δ = -6.5 ppm (tdd, $J_{Ha\text{-}Pa\ (cis)}$ = 30.8 Hz; $J_{Ha\text{-}Pb\ (cis)}$ = 15.2 Hz; $J_{Ha\text{-}Hb}$ = 6.4 Hz), -8.4 (dtd, $J_{Hb\text{-}Pb\ (trans)}$ = 74.2 Hz; $J_{Hb\text{-}Pa\ (cis)}$ = 28.6 Hz; $J_{Ha\text{-}Hb}$ = 6.4 Hz). **^{31}P{^{1}H}** (400 MHz; toluene-d_8): δ = 57.4 (d, 2P, $J_{P\text{-}P}$ = 17.7, mutually *trans* P), 45.3 (t, 1P, $J_{P\text{-}P}$ = 17.7, unique P) ppm.

[RuH$_2$(N$_2$)P$_3$] The dinitrogen compound was identified by comparing the NMR spectra collected when the reaction was carried out under N_2 (see time and temperature dependent experiments) and under Ar (current experiment). The disappearance of two hydrido signals in the ^{1}H NMR spectrum of the experiment described below is attributable to the missing dinitrogen compound under the current reaction conditions. [RuHClP$_3$] (0.03 g, 0.032 mmol) was suspended in toluene (2 mL) and reacted with NaOCD$_3$, obtained by reaction of sodium metal (0.01 g, 0.43 mmol) with CD$_3$OD (0.2 mL, 4.9 mmol), at RT for 5 min under Ar. The reaction was stopped as soon as the mixture turned from purple to red/orange and the flask placed in a cold bath (dry ice/acetone). The mixture was then reduced to dryness affording an orange solid which was subsequently washed with CD$_3$OD, filtered using a cannula filtration and dried again under vacuum. The collected solid was analysed by NMR spectroscopy and the resonances missing from these spectra when compared with the spectra of a sample obtained from an identical reaction performed under N_2 were assigned to [RuH$_2$(N$_2$)P$_3$]. The ^{1}H NMR data were in agreement with those reported in the literature.[16, 17]

^{1}H NMR (400 MHz; toluene-d_8): δ = -8.6 (dtd, 1H, $J_{Hb\text{-}Pb\ (trans)}$ = 76 Hz; $J_{Hb\text{-}Pa\ (cis)}$ = 30 Hz; $J_{Ha\text{-}Hb}$ = 6 Hz), -12.8 (tdd, 1H, $J_{Ha\text{-}Pa}$ = 27; $J_{Ha\text{-}Pb}$ = 14 Hz) ppm. **^{31}P{^{1}H}** (400 MHz; toluene-d_8): δ = 56.3 (d, 2P, $J_{P\text{-}P}$ = 16.4 Hz), 43.9 (t, 1P, $J_{P\text{-}P}$ = 16.4 Hz) ppm.

[RuH$_2$(PPh$_3$)$_4$] was synthesised under argon according to literature procedure.[13]

^{1}H NMR (400 MHz, toluene-d_8): δ = -10.2 ppm (m, 2H, AA' signal, AA'MM'X$_2$ spin system, see Fig 3 and ESI Figure S29). **^{31}P{^{1}H} NMR** (400 MHz, toluene-d_8): δ = 49.14 (t, 2P, $J_{P\text{-}P}$ = 13.8 Hz), 41 (t, 2P, $J_{P\text{-}P}$ = 11.9 Hz) ppm.

Reaction of [RuHClP$_3$] with labelled methoxide

As above for the preparation of [RuH$_2$(CO)P$_3$] except that the methoxide was obtained by reacting sodium (0.01 g, 0.43 mmol) with CD$_3$OD, ^{13}CH$_3$OH or a mixture (1:1) of CH$_3$OH and CD$_3$OD (0.2 mL, 4.94 mmol). The recovered yellow solid was washed once with dry and degassed appropriately labelled methanol (not for ^{13}CH$_3$OH), in order to remove the methoxide, filtered, dried *in vacuo* and analysed by NMR spectroscopy (toluene-d_8; see Figure 1).

CD$_3$OD:

^{1}H NMR (400 MHz; toluene-d_8): δ = -6.58 (td, 1H, $J_{H\text{-}Pb}$ = 15.11 and $J_{H\text{-}Pa}$ = 30.9 Hz, H *trans* to CO), -8.41 (dt, 1H, $J_{H\text{-}Pb}$ = 28.78 and $J_{H\text{-}Pa}$ = 73.9 Hz, H *cis* to CO) ppm. [RuH$_2$(CO)P$_3$] is also present. **^{31}P{^{1}H} NMR** (400 MHz, toluene-d_8): δ = 57.1 (br, 4P, mutually *trans* P), 44.8 (br, 2P, unique P) ppm. **^{2}H{^{1}H} NMR** (500 MHz, CH_2Cl_2): 7.7, 7.30, 7.2 ppm (^{2}H, phenyl, *ortho*). A full analysis of the products from this reaction is provided in the ESI, Sections 2 and 3.

^{13}CH$_3$OH

^{1}H NMR (400 MHz; toluene-d_8): δ = -6.5 ppm (tddd, $^{2}J_{Ha\text{-}C}$ = 18.7 Hz, H$_a$ *trans* to CO), -8.4 (dtt, $J_{Hb\text{-}C}$ = $J_{H\text{-}H}$ = 6.4 Hz, H$_b$ *cis* to CO) ppm. **^{31}P{^{1}H}** (400 MHz; toluene-d_8): δ = 57.4 (dd, 2P, $J_{P\text{-}P}$ = 17.5 and $J_{P\text{-}C}$ = 7.5 Hz, P$_a$), 45.3 (td, 1P, $J_{P\text{-}P}$ = 17.5 and $J_{P\text{-}C}$ = 9 Hz, P$_b$) ppm. **^{13}C{^{1}H} NMR** (400 MHz, toluene-d_8)**:** δ = 207.3 (dt, $J_{C\text{-}Pa}$ = 7.5, J_{Pb} = 9 Hz, *C*O), 140.4 (vt, $J_{CP+CP'}$ = 40.8 Hz, $C_{ipso,}$ mutually *trans* phosphines), 138.6 (d, $J_{C\text{-}P}$ = 28.4 Hz, C_{ipso} unique phosphine), 134.4-133.9 (m, Ar), 128.2 (s, Ar), 127.3-127.1 (m, Ar) ppm.

Time and temperature dependent NMR studies with NaOCD$_3$

A solution of CD$_3$OD (0.4 mL, 9.8 mmol) containing sodium metal (0.02 g, 0.87 mmol) to form the methoxide, was added to a suspension of [RuHClP$_3$] (0.06 g, 0.065 mmol) in toluene-d_8 (3 mL). The experiment was performed using a ramping temperature (20 min at RT, heated under reflux to 55 °C for 40 min and subsequently to 100 °C for 30 min) with continuously sampling at each ramping temperature step with immediate cooling to room temperature and collection of the NMR spectrum.

Three intermediates were identified *via* ^{1}H NMR: [RuH$_4$P$_3$], [RuH$_2$(N$_2$)P$_3$] and [RuH$_2$P$_4$]. The ^{1}H spectral data of [RuH$_4$P$_3$][12] and [RuH$_2$(N$_2$)P$_3$][16, 17] were identical to those described in the literature. Spectral data of [RuH$_2$P$_4$] were as described above. An experiment using identical conditions but under argon gave the same products without [RuH$_2$(N$_2$)P$_3$].

Time and temperature dependent NMR studies with NaOCH$_3$

A solution of CH$_3$OH (0.4 mL, 9.8 mmol) containing sodium metal (0.02 g, 0.87 mmol) to form the methoxide, was added to a suspension of [RuHClP$_3$] (0.06 g, 0.065 mmol) in toluene-d_8 (3 mL). The experiment was performed using a ramping temperature (15 min at RT, heated under reflux to 55 °C for 30 min and subsequently to 100 °C for 30 min) with continuously sampling at each ramping temperature step with immediate cooling to room temperature and collection of the NMR spectrum.

Results

Our initial observations of the hydride resonance of [RuH$_n$(D)$_{2-n}$(CO)P$_3$] obtained from reactions under N_2 of [RuHClP$_3$] in toluene with labelled or unlabelled NaOMe,

formed by dissolving sodium in CH_3OH. CD_3OD, $^{13}CH_3OH$ or a 1:1 mixture of CH_3OH/CD_3OD, are shown in Figure 1.

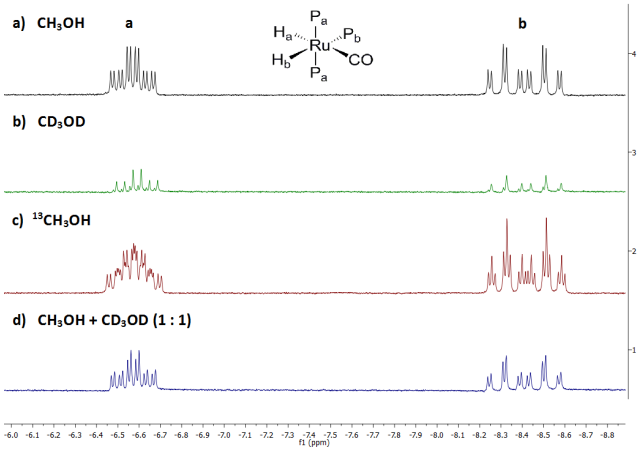


Fig. 1 Hydride region of ^1H NMR spectrum of the Ru final species arising by reaction at 100 °C of [$RuHClP_3$] in **a)** CH_3OH, **b)** CD_3OD, **c)** $^{13}CH_3OH$ or **d)** a 1:1 mixture of CH_3OH/CD_3OD each containing dissolved sodium to form the methoxide.

Using CH_3OH, the hydride resonances are as expected: δ −6.5 ppm (ddt, $J_{Ha\text{-}Pa}$ = 30.8 Hz, *cis*; $J_{Ha\text{-}Pb}$ = 15.2 Hz, *cis*; $J_{Ha\text{-}Hb}$ = 6.4 Hz, H_a) and δ -8.4 ppm ($J_{Hb\text{-}Pb}$ =74.2 Hz, *trans*; $J_{Hb\text{-}Pa}$ = 28.6 Hz, *cis*; $J_{Ha\text{-}Hb}$ = 6.4 Hz, H_b) (Figure 1a).

When the reaction was performed using only CD_3OD, ^1H NMR studies showed both isomers of [$RuHD(CO)P'_3$] (P' is PPh_3 partially deuterated in the *ortho* positions of the aromatic rings, see later) were obtained in equal proportions together with a small amount of [$RuH_2(CO)P'_3$] (Figure 1b). We note that there is a small D isotope shift in each case so that each resonance of the hydride signal of the two isomers of [$RuHD(CO)P'_3$] is coincident with the low frequency signal of each H-H doublet in the spectrum of [$RuH_2(CO)P'_3$]. Integration of individual peaks in the multiplets against the *meta*-protons of the aromatic rings (ESI Section 3) shows that there is the equivalent of 1 H and 1 D in the hydridic positions and so there must be equal amounts of [$RuH_2(CO)P'_3$] and [$RuD_2(CO)P'_3$]. Integration of the individual peaks within the hydride resonances (ESI Section 3) shows that this mixture is made up of [$RuH_2(CO)P'_3$] (22 %) the two isomers of [$RuHD(CO)P'_3$] (each 28 %) and [$RuD_2(CO)P'_3$] (22 %). Unfortunately, we did not observe Ru-D resonances in the ^2H NMR spectrum (Figure S5), despite observing D in the ortho positions of the phenyl rings (see below). This may be because the resonances will be very weak (1/12 of the intensity of the resonances from the *o*-D atoms) not superimposed and extensively broadened.

When using $^{13}CH_3OH$ coupling to ^{13}CO splits each line of the hydride resonances into a further doublet. Since $J_{Hb\text{-}C} = J_{H\text{-}H}$ the different resonances in the multiplet from H_b all appear as triplets (Figure 1c).

Finally, a 1:1 mixture of CH_3OH/CD_3OD gives a mixture of [$RuH_2(CO)P'_3$] and both isomers of [$RuHD(CO)P'_3$] (Figure 1d).

The $^{31}P\{^1H\}$ NMR spectrum of [$RuH_2(CO)P'_3$] (Figure 2a) gives a sharp doublet (δ 57.4, P_a, $J_{P\text{-}P}$ = 17.7 Hz) and triplet (45.3 P_b). These are broadened significantly if deuterium is present (Figure 2b) and split by ^{13}C from ^{13}CO (Figure 2c). The solution obtained from the reaction using $NaOMe/NaOCD_3$ shows sharp resonances from [$RuH_2(CO)P'_3$] superimposed on broad resonances from the isomers of [$RuHD(CO)P'_3$] (both isomers, Figure 2d). There is a slight D isotope shift to lower field for each resonance in solutions where CD_3OD has been used.

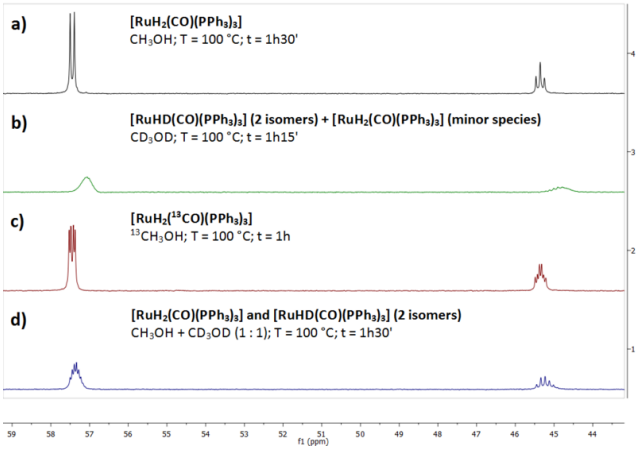


Fig. 2 $^{31}P\{^1H\}$ NMR spectra of the Ru final species arising by reaction at 100 °C of [$RuHClP_3$] (in toluene) in **a)** CH_3OH, **b)** CD_3OD, **c)** $^{13}CH_3OH$ or **d)** a 1:1 mixture of CH_3OH/CD_3OD each containing dissolved sodium to form the methoxide.

In order to try to explain the products from the reaction using only CD_3OD, further studies were carried out over shorter reaction times and at lower temperatures.

An experiment was carried out in toluene-d_8 under N_2 with slow heating to 100 °C, sampling the solution after various time intervals. The samples were cooled and analysed by ^1H NMR spectroscopy (Figure 3). The initially formed [$RuH_4P'_3$], [$RuH_2(N_2)P'_3$] and [$RuH_2P'_4$] (Figure 3a) all transformed into the mixture of [$RuH_nD_{2-n}(CO)P'_3$] (n = 0-2) once the temperature reached 100 °C together with small amounts of unidentified species giving doublets at δ -6.7, -7.5 and -8.6 ppm (Figure 3c).

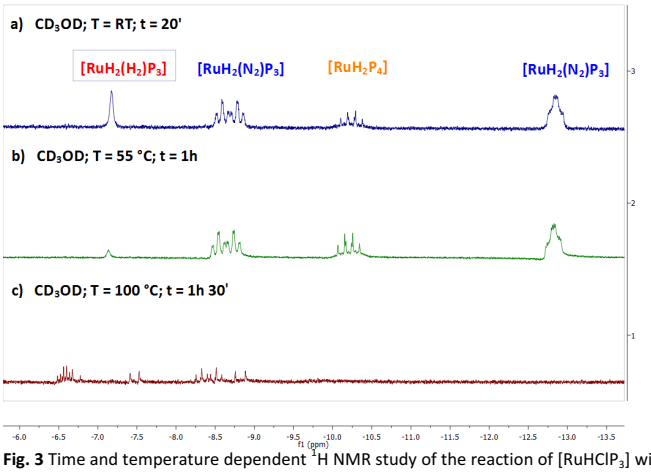
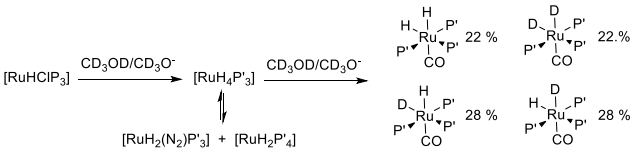


Fig. 3 Time and temperature dependent ^1H NMR study of the reaction of [$RuHClP_3$] with $NaOCD_3$: hydride region of the reaction mixture.

A similar experiment (15 min at RT, heated to 55 °C for 30 min, and to 100 °C for 30 min) was conducted in the presence of $NaOCH_3$ (obtained by reaction of sodium metal with CH_3OH),

with the only difference being that the first two ramping temperature steps were shortened in an attempt to observe the formation of similar intermediates (ESI Section 1.8), based on the evidence that formation of $[RuH_2(CO)(PPh_3)_3]$ already occurs at RT in the presence of non-deuterated methoxide. The first two ^1H NMR spectra collected after 15 min (RT) and 45 min (55 °C) exhibited the same resonances observed when using CD_3OD along with those corresponding to $[RuH_2(CO)(PPh_3)_3]$. Based on the intensity of the signals from the intermediates, it is evident that the decarbonylation reaction is much faster when no ^2H is involved, but the hydride signals of the intermediates are the same.

Summarising, the key observations are: after short reaction times, the first formed species from $[RuHClP_3]$ with $NaOCD_3$ is $RuH_4P'_3$ with all the hydrides apparently being H. This is in equilibrium with $[RuH_2P'_4]$ and, when under nitrogen, with $[RuH_2(N_2)P'_3]$. The same complexes are also formed when using $NaOCH_3$ but $[RuH_2(CO)P_3]$ is also formed. Over longer times and at higher temperatures, all the intermediates transform into $[RuH_2(CO)P_3]$ from NaOMe or a mixture of $[RuH_nD_{2-n}(CO)P'_3]$ (n = 0-2) with the H/D ratio in the hydrides being 1 and in the ratios shown in Scheme 1.

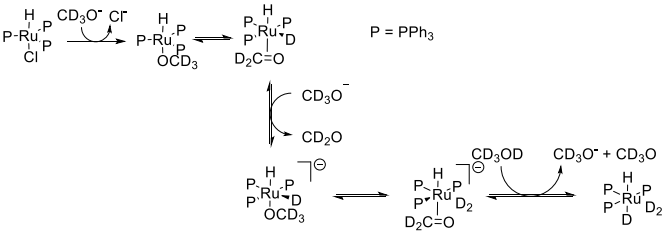


Sch. 1 Labelling of products obtained in the two steps of the reaction of $[RuHClP_3]$ with CD_3OD/CD_3O^-. P' is PPh_3 with significant incorporation of D into the *o*-positions of the aromatic rings.

In a previous study[6] some of us have presented IR evidence for formaldehyde and formyl intermediates during the reaction of $[RuHClP_3]$ with $NaOCH_3$, but we have not observed these complexes during this NMR study.

Discussion

The most surprising observation in this study is that the major species formed on reaction of $[RuHClP_3]$ with Na/CX_3OX at room temperature is $[RuH_4P'_3]$ and that the hydride, not deuteride, is formed even when X = D.



Sch. 2 Proposed mechanism for the formation of $[RuHD_3P_3]$ from $[RuHClP_3]$ and $NaOCD_3$ in the presence of CD_3OD.

A plausible mechanism for the formation of the tetrahydrido species is shown in Scheme 2. However, this mechanism shows that the product should have 3 D atoms distributed amongst the hydrido and dihydrogen ligands, which are known to be exchanging, whereas the observed product appears to have none. The only source of H in the system is PPh_3 so we propose that there is fast exchange between the hydrido/dihydrogen ligands and the *ortho* H atoms on PPh_3.

Linn and Halpern, in a paper concerning the coordination chemistry of ruthenium polyhydrides in catalytic hydrogenation of ketones and arenes and related kinetic studies, described that, when a solution of $[RuH_2D_2(PPh_3)_3]$ in THF (prepared by reaction of $[RuH_2(N_2)(PPh_3)_3]$ with D_2) was heated to 30 °C, intramolecular exchange with the *ortho* phenyl hydrogens was observed by ^2H NMR studies.[16] In a complementary work, Gusev et al. reported that complex $[RuH_4P_3]$ in toluene-d_8 under a D_2 atmosphere undergoes isotopic substitution of the hydride ligands and incorporation of deuterium into the *ortho* positions of the phenyl rings of the PPh_3 ligands (^1H NMR evidence).[12] These two studies support our hypothesis that the H atoms in $[RuH_4P'_3]$ formed from $[RuHClP_3]$ and $NaOCD_3$ come from the *ortho* positions of the phenyl rings. ^2H NMR studies of a dried and CD_3OD washed final product ($[RuHClP_3]/Na/CD_3OD$, 1.25 h, 100 °C) confirm the presence of D in the aromatic region of the NMR spectrum. (Figure 4a). The resonances at δ 7.30 and 7.24 ppm may be attributable to D in the *ortho* positions of the phenyl rings of the phosphine ligands of P_a and P_b respectively of $[RuHX(CO)P_3]$ (X = H or D) whilst the resonance at δ 7.7 is from D in the *ortho* positions of the phenyl rings in Ph_3PO. Furthermore, the small amounts of PPh_3 and Ph_3PO present in the product of a similar reaction give ^{31}P resonances (Figure 4b) which show a signal in the position expected for unlabelled compounds along with several resonances at lower frequency (unresolved for Ph_3PO) attributable to compounds bearing different numbers of *ortho*-D atoms, which give rise to isotope shifts of the P resonance. We note that, in $[RuHD_3P_3]$ there are 18 *ortho* H atoms so under fast Ru-H/*ortho*-H exchange conditions the equilibrium composition should have 3/22 = 13.6 % D atoms on the Ru. The hydride resonances of $[RuH_nD_{2-n}(N_2)P'_3]$ (P' is PPh_3 containing significant D in the *ortho* positions of the rings) clearly shows H-H coupling with no enhancement of the lower field signals of each doublet suggesting that all the hydrides in $[RuH_4P'_3]$ are H not D. Integration of the *ortho* relative to the *meta* protons In the mixture of $[RuHX(CO)P'_3]$ (X = H or D) suggest 11-12 D atoms are incorporated per complex molecule, much more than the expected 3. This observation is discussed in more detail in the ESI Section 2, but means that more than enough H atoms have been exchanged to account for the 4 hydrides observed. The incorporation of D into the *ortho* positions of the aromatic rings also accounts for the broadening of the ^{31}P resonances shown in Figures 2b and d. $[RuH_2YP'_3]$ (Y = N_2 or P') will form by displacement of H_2 by Y, as previously reported.[16, 17]

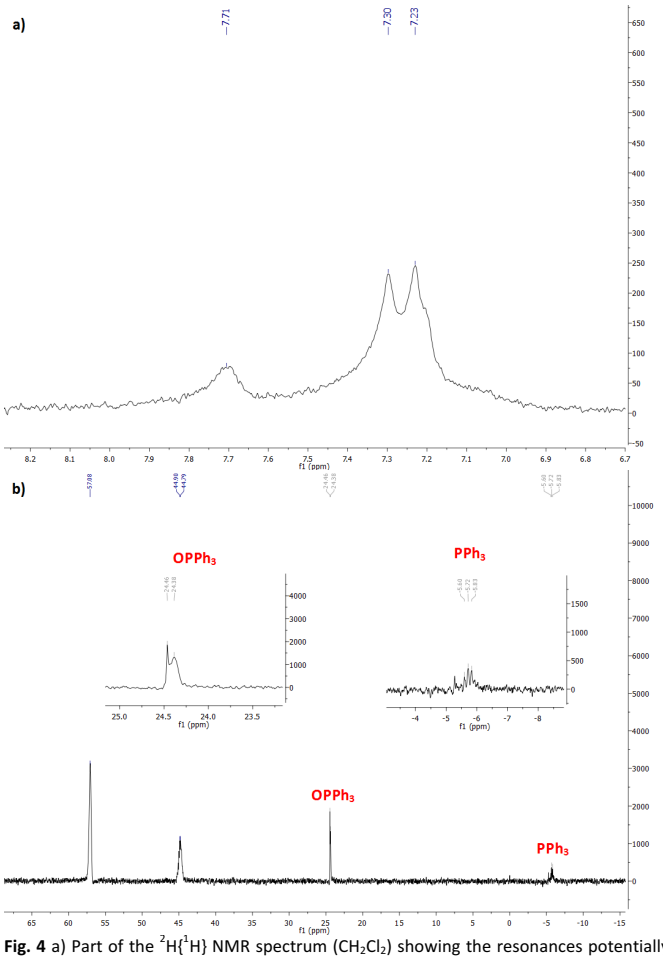


Fig. 4 a) Part of the $^{2}H\{^{1}H\}$ NMR spectrum (CH_2Cl_2) showing the resonances potentially attributable to ^{2}H in the *ortho* positions of the phenyl rings of the phosphine ligands of complex [RuHD(CO)P_3] (two isomers), [RuH_2(CO)P_3] and [RuD_2(CO)P'_3] (δ 7.2 and 7.3) and of Ph_3PO (δ 7.7 ppm); b) ^{31}P NMR spectrum of the products from reaction of [$RuHClP_3$] with $NaOCD_3$. Inset are the expanded resonances from Ph_3PO and PPh_3

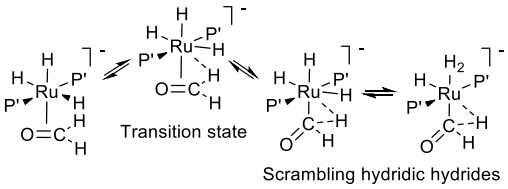
Having established that the first complex to be formed in the reaction of [$RuHClP_3$] with Na/MeOH is [RuH_4P_3], we then looked at the mechanism for the formation of [RuH_2(CO)P_3] from this complex and Na/MeOH. The key observation is that, when using $NaOCD_3$ and [$RuH_4P'_3$], the major products are a mixture of [RuH_nD_{2-n}(CO)P_3] (n = 0, 22 %, n = 1, two isomers, each 28 % and n = 2, 22 %). With the H:D ratio in the hydrides being 1:1.

We have recently reported DFT calculations aimed at understanding the mechanism of transformation of [RuH_4P_3] into [RuH_2(CO)P_3] by decarbonylation of methanol.[7] In that paper we also reported the experimental isotope effect isotope effect (k_H/k_D = 4) for the reaction of [$RuHClP_3$] with Na/MeOH/CD_3OD. At that time, we were unaware of the involvement of [RuH_4P_3] in this reaction and assumed that [$RuHClP_3$] reacted to give [RuH(OMe)P_3] and hence initiated neutral mechanism **E** of that paper, which has a computed k_H/k_D of 1.63.[7] However, given the presence of [RuH_4P_3] and the basic nature of the medium, it is probably that the first step in the decarbonylation reaction is attack of methoxide onto the ruthenium centre, replacing H_2 to give [RuH_2(OMe)P_3]$^-$ and hence leading into the anionic mechanism **G** of our theoretical paper, partially reproduced in Scheme 3 and more fully in Scheme 4. This mechanism has the lowest activation energy of all the mechanisms evaluated by DFT calculations and k_H/k_D = 1.88.[7] A mechanism such as **G** is also supported by our experimental studies on the dehydrogenation of 2-propanol catalysed by [RuH_4P_3] under basic conditions, in which we isolated intermediate, [RuH_3P_3]$^-$,[2] consistent with the cycle being initiated by attack of alkoxide to give anionic intermediates.

The products from the reaction using CD_3OD/Na have an H/D ratio among the hydrides = 1. Since the second step of the reaction starts with [$RuH_4P'_3$] containing 4 hydridic/H_2 H atoms and since 4 D are removed from CD_3OD in forming the CO ligand, it is tempting to think that these 8 H/D atoms scramble to give 1H and 1D on the metal together with 3 molecules of hydrogen with an overall H/D ratio also of 1. However, this is not possible because the first step of the reaction leads to displacement specifically of H_2 by CD_3O^- and this H_2 will be lost because the reaction is carried out under reflux. In addition, most of the reactions are carried out under N_2 where H_2 in [$RuH_4P'_3$] is replaced by N_2 or PPh_3 and again will be lost.

A possible explanation of the overall 1:1 ratio of H/D in the product mixture of [RuH_nD_{2-n}(CO)P'_3] (n = 0-2), of the equivalent amounts of [RuH_2(CO)P'_3] and [RuD_2(CO)P'_3] as well as of the equivalent amounts of the two isomers of [RuHD(CO)P'_3] and of the enhanced amounts of the two isomers of [RuHD(CO)P'_3] is shown in Scheme 4, which is based on Mechanism **G** of our previous theoretical paper.[7] In this scheme, D transfers from the CD_3OD derived ligands directly to coordinated H or D are shown so as to reduce the number of intermediates in the figure, but calculations show that they occur *via* transfer to the metal and then assembly of D_2 or HD.[7]

The key to this mechanism is that the H/D atom that is *trans* to the formyl group in the formyl complex remains *trans* to the carbon-based ligand throughout the transformation of the latter into CO by a series of β-D transfer reactions. We define the mutually *trans* H and the C based ligand as axial with the other ligands being in the equatorial plane until the fluxional 5 coordinate [RuH_nD_{2-n}(CO)P'_2] is formed. All assembly of H_nD_{2-n} (n = 0-2) also occurs in the equatorial plane. Furthermore, it requires that the hydrides and one deuteride can exchange in the formaldehyde complex, [$RuH_2D(OCD_2)P_2$. This is a reasonable proposition since the rate determining step is the reorganisation of formaldehyde in this complex (Scheme 3) so it will have a long lifetime. The transition state for this rate determining step involves an agostic interaction[18] of one of the D atoms of coordinated formaldehyde, which might facilitate exchange of the positions of H and D through the formation of coordinated HD. These suggestions are also shown in Scheme 3.

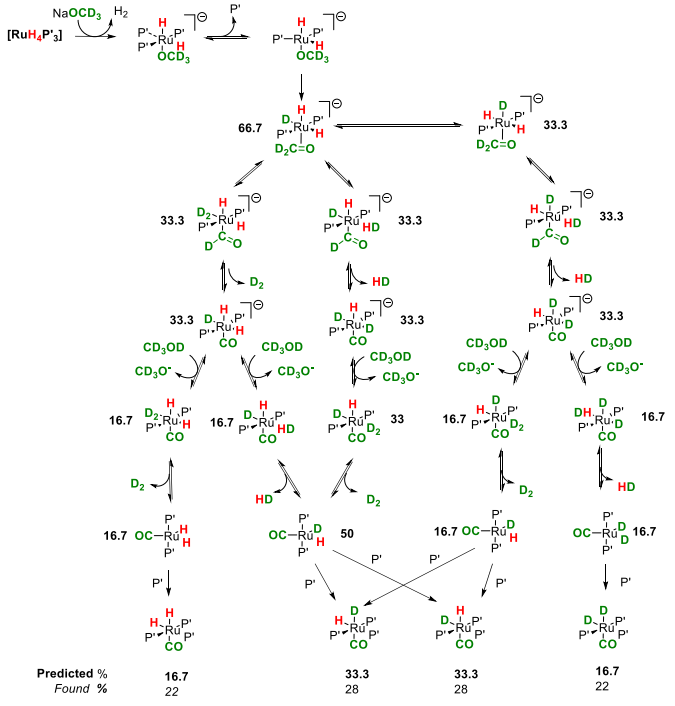


Sch. 3 Rate determining step of mechanism **G** from our theoretical paper[7] together with a possible mechanism for scrambling H/D in the formyl complex shown in Scheme 2.

Calculations suggest that the dehydrogenation and decarbonylation reactions from pathway **G** of our theoretical

paper[7] proceed *via* intermediates involving two coordinated phosphines and this seems to be required to explain the formation of the two isomers of [RuHD(CO)P'$_3$], which will form in equal amounts by coordination of P' to the fluxional 5 coordinate [RuHD(CO)P'$_2$].

In the mechanism shown in Scheme 3, [RuH$_2$D(CD$_2$=O)P'$_2$] formed from β–D transfer in [RuH$_2$(OCD$_3$)P'$_2$] can have various positions of the H and D, with those in the equatorial plane being able to be protonated by CD$_3$OD. Scheme 4 shows how these various intermediates formed lead to the observed isomers of [RuH$_n$D$_{2-n}$(CO)P'$_3$]. The numbers shown in bold in Scheme 4 indicate the percentage of each intermediate that would be formed if no isotope effects operate during this part of the reaction. The predicted percentages of each product are: [RuH$_2$(CO)P'$_3$] and [RuD$_2$(CO)P'$_3$] (each 16.7 %). [RuHD(CO)P'$_3$] (each isomer 33.3 %). These values compare quite well with the experimentally determined values of 22 % and 28 % respectively, shown in italics in Scheme 4. The small deviations are probably due to experimental error in the integration of the individual peaks in the hydride signals of the ^{1}H NMR spectrum. Indeed, if only the largest peaks in the hydride signals are used for the analysis (better signal to noise ratio), the observed ratios are 20:30, closer to the predicted values. It is unlikely that the differences between the observed and calculated values arise because of small isotope effects in the assembly of D$_2$ or HD in the equatorial plane of the relevant intermediates because these processes have been calculated to have essentially zero activation energy.[7]



Sch. 4 Proposed mechanism for the formation of [RuH$_2$(CO)P'$_3$], [RuHD(CO)P'$_3$] (2 isomers) and [RuH$_2$(CO)P'$_3$] from reaction of [RuH$_4$P'$_3$] with Na/CD$_3$OD. The numbers beside each intermediate represent the theoretical percentage of each isotopomer of that intermediate. The numbers at the bottom represent the predicted percentage of each isotopomer of the final product compared with the actual percentages observed using ^{1}H NMR spectroscopy.

Conclusions

The decarbonylation of methanol by [RuHClP$_3$] under mild basic conditions proceeds first to [RuH$_4$P$_3$] which is in equilibrium with [RuH$_2$P$_4$] and when under nitrogen with [RuH$_2$(N$_2$)P$_3$]. This result shows that alcohol dehydrogenation is favoured over decarbonylation at least under mild conditions and confirms that the rate determining step of methanol dehydrogenation is loss of H$_2$ from [RuH$_4$P$_3$].[2] When this reaction is carried out using CD$_3$O$^-$/CD$_3$OD, the key intermediate is [RuH$_4$P'$_3$] where P' is PPh$_3$ with deuterium incorporated into several of the *ortho* positions of the aromatic rings. At higher temperatures, [RuH$_2$(CO)P$_3$] is formed in CH$_3$OH/MeO$^-$, whilst in CD$_3$OD/CD$_3$O$^-$ the products are [RuH$_n$D$_{2-n}$(CO)P$_3$] (n = 0, 22 %; n = 1, 2 isomers each 28 %; n = 2, 22 %). These products confirm that the decarbonylation occurs through the anionic intermediate *mer*-[RuH$_2$(OMe)P$_3$]$^-$ It is proposed that there is free exchange of all the Ru-H/D in the formaldehyde intermediate, [RuH$_2$D(CD$_2$=O)P'$_2$] which is present before the rate determining step but that H or D *trans* to the carbon based ligand does not participate in exchange reactions in subsequent intermediates of the reaction

Acknowledgements

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Notes and references

‡ [RuH$_4$(PPh$_3$)$_3$] is known to be [RuH$_2$(H$_2$)(PPh$_3$)$_3$] with the coordinated hydrido and dihydrogen ligands exchanging fast on the NMR timescale.[19] We use the condensed form to avoid confusion when referring to partially D-labelled analogues.

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