Electronic Supplementary Material (ESI) for Dalton Transactions.

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

ESI

Contents

1 NMR spectra

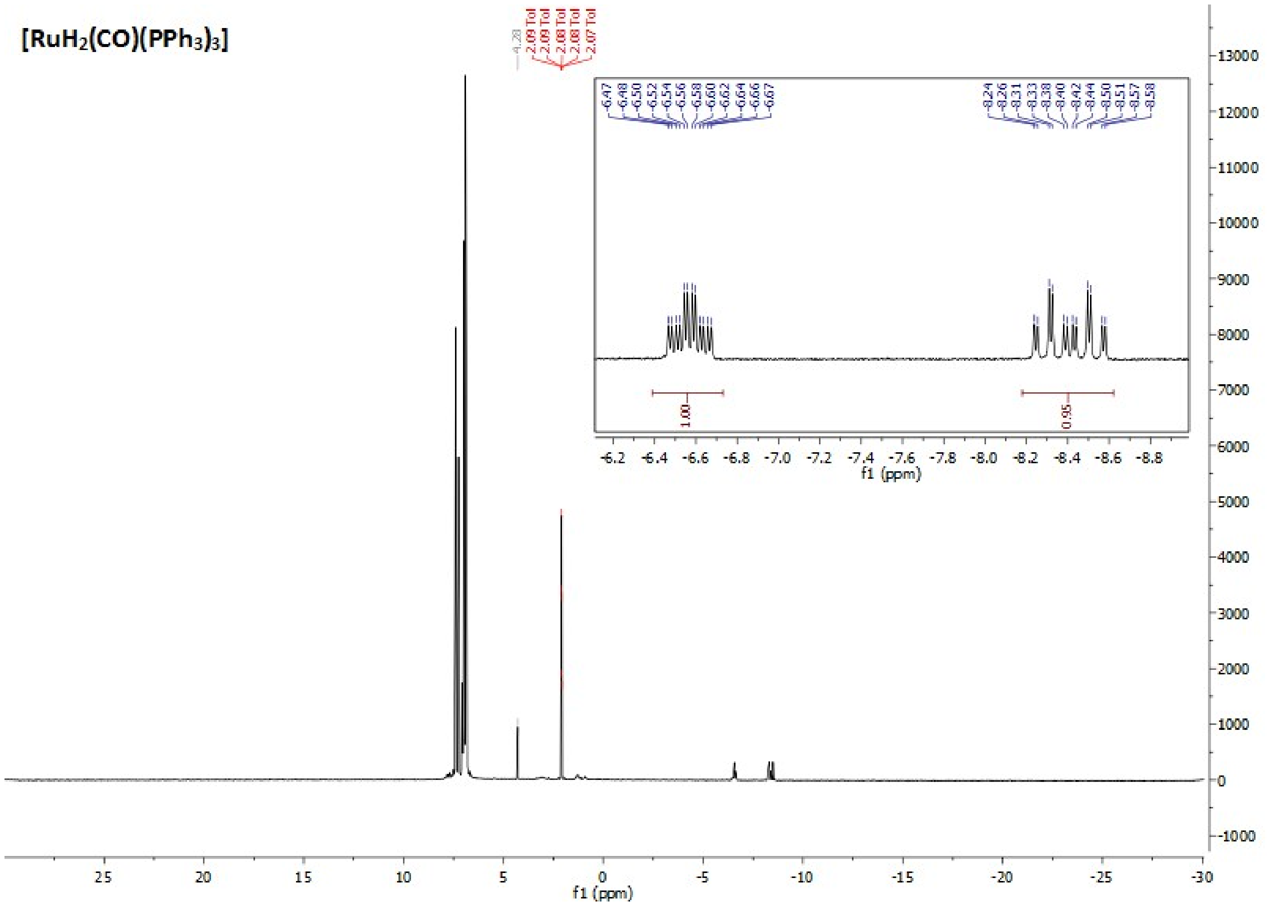

Figure S1 ^1H NMR (400 MHz; toluene-d_8) of $[RuH_2(CO)(PPh_3)_3]$

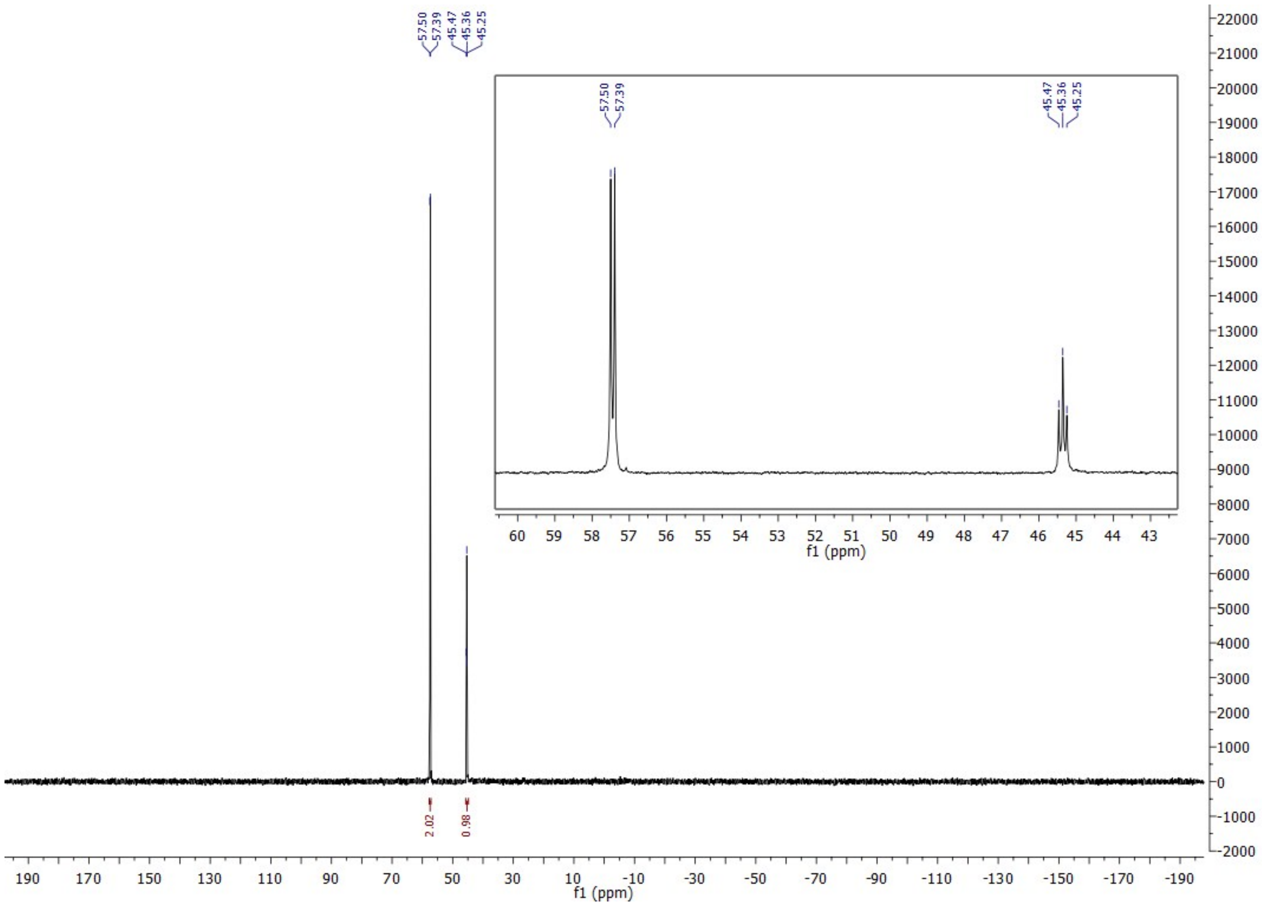

Figure S2 $^{31}P\{^1H\}$ NMR (400 MHz; toluene-*d*$_8$) of $[RuH_2(CO)(PPh_3)_3]$

1.2 Mixture [RuHD(CO)(PPh$_3$)$_3$] (major species) and [RuH$_2$(CO)(PPh$_3$)$_3$] (minor species)

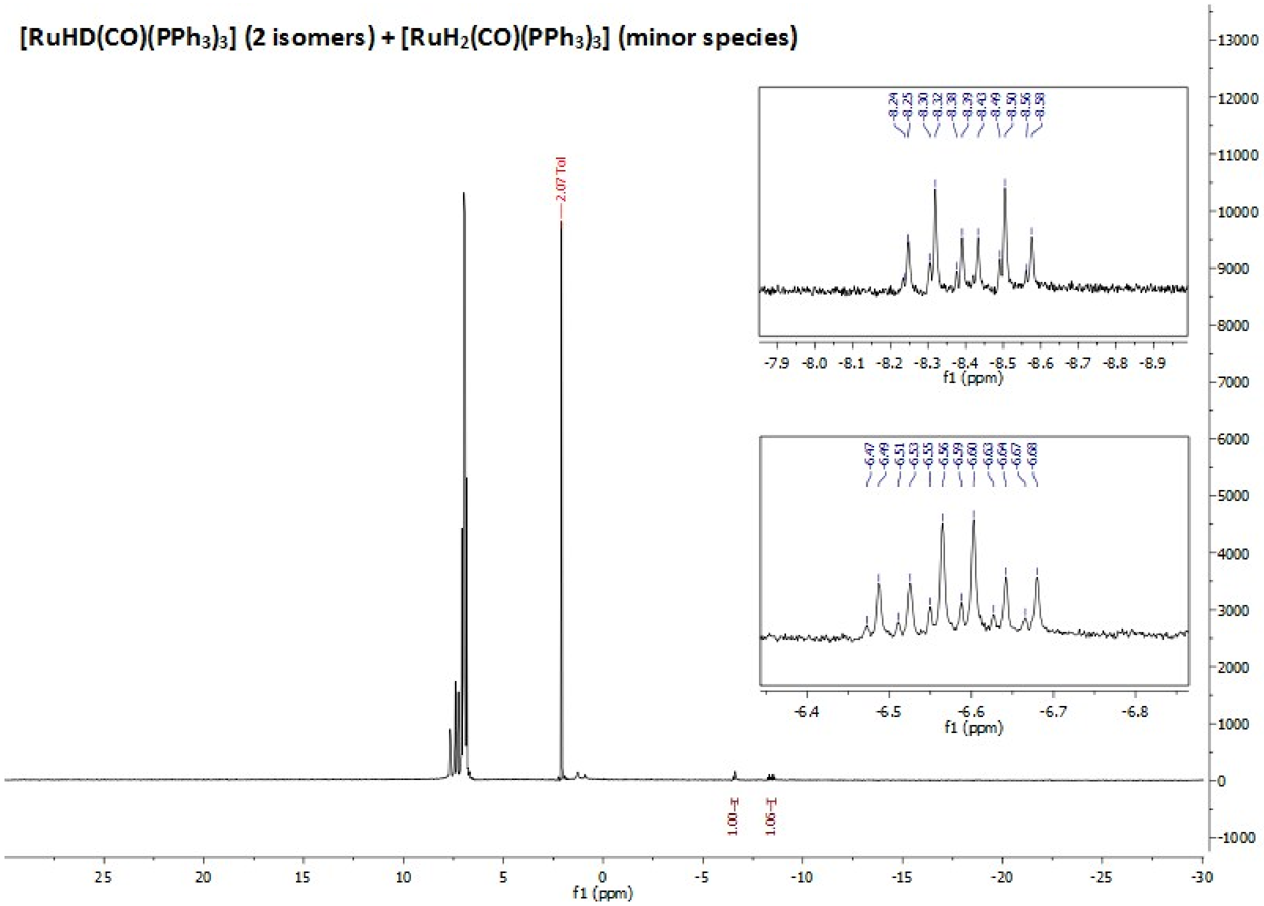

Figure S3 ^{1}H NMR (400 MHz; toluene-d_8) of [RuHD(CO)(PPh$_3$)$_3$] (2 isomers) and [RuH$_2$(CO)(PPh$_3$)$_3$] (minor species).

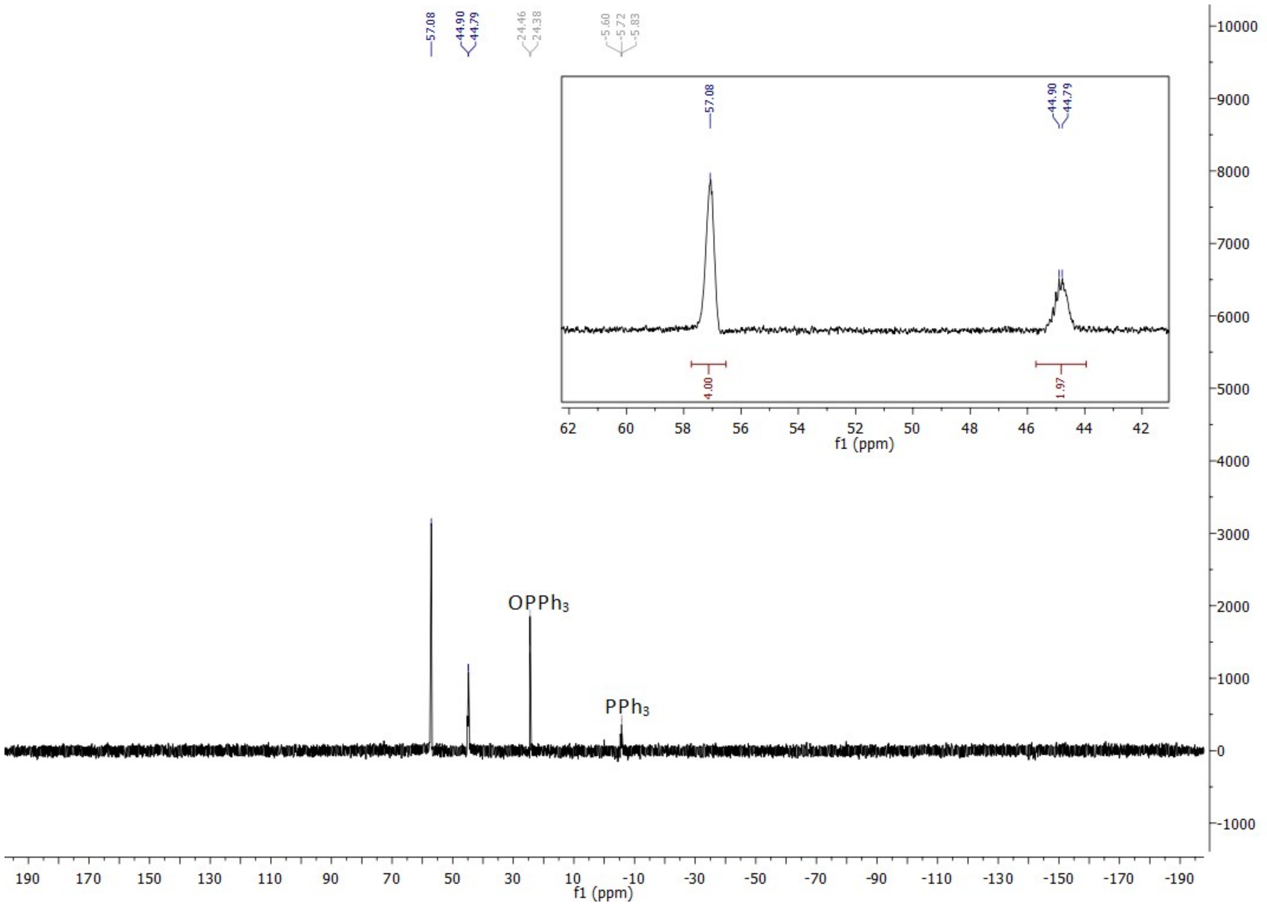

Figure S4 $^{31}P\{^{1}H\}$ NMR (400 MHz; toluene-*d_8*) of [$RuHD(CO)(PPh_3)_3$] (2 isomers) and [$RuH_2(CO)(PPh_3)_3$](minor species).

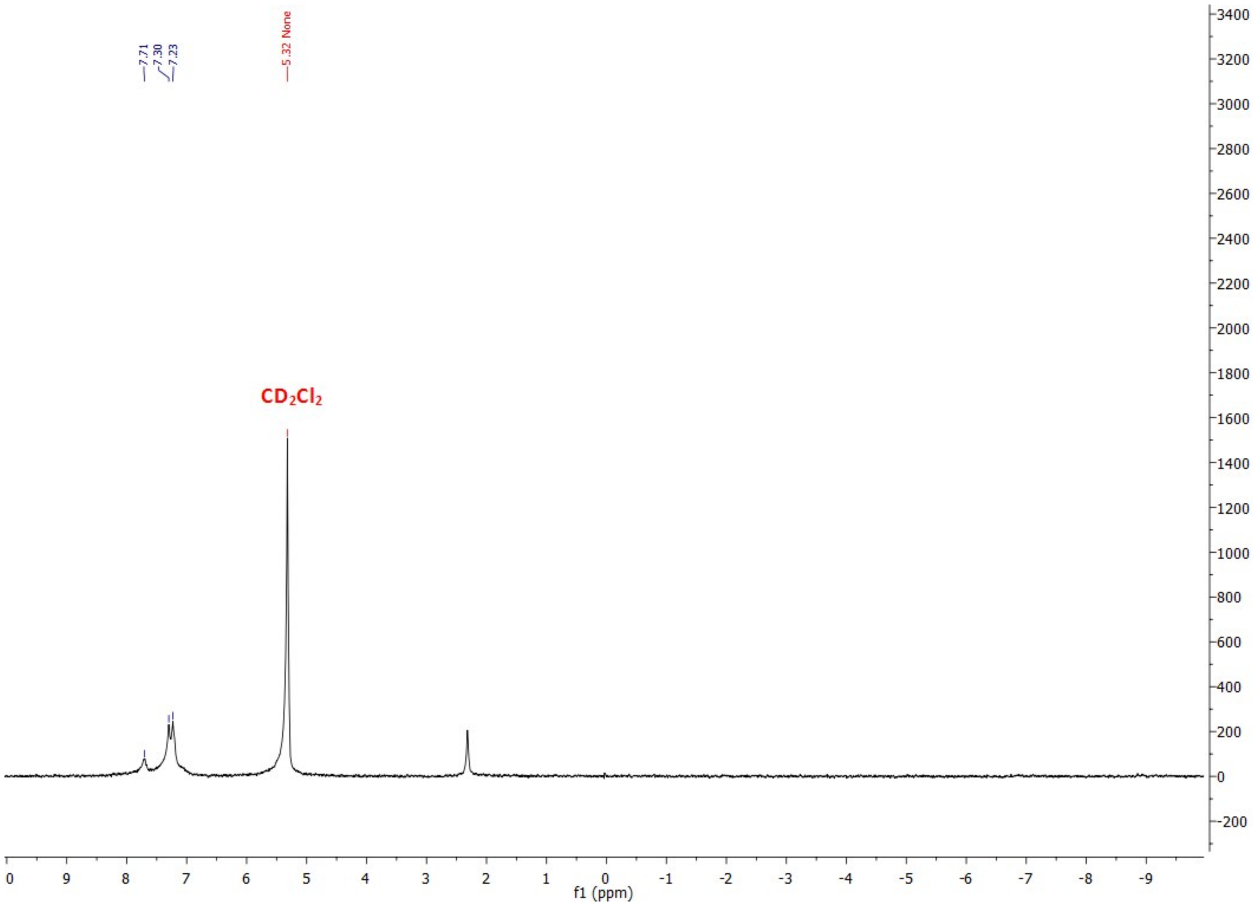

Figure S5 $^2H\{^1H\}$ NMR (500 MHz; CH_2Cl_2) of $[RuHD(CO)(PPh_3)_3]$ (2 isomers) and $[RuH_2(CO)(PPh_3)_3]$ (minor species).

1.3 Potential [$RuD_2(CO)(PPh_3)_3$]

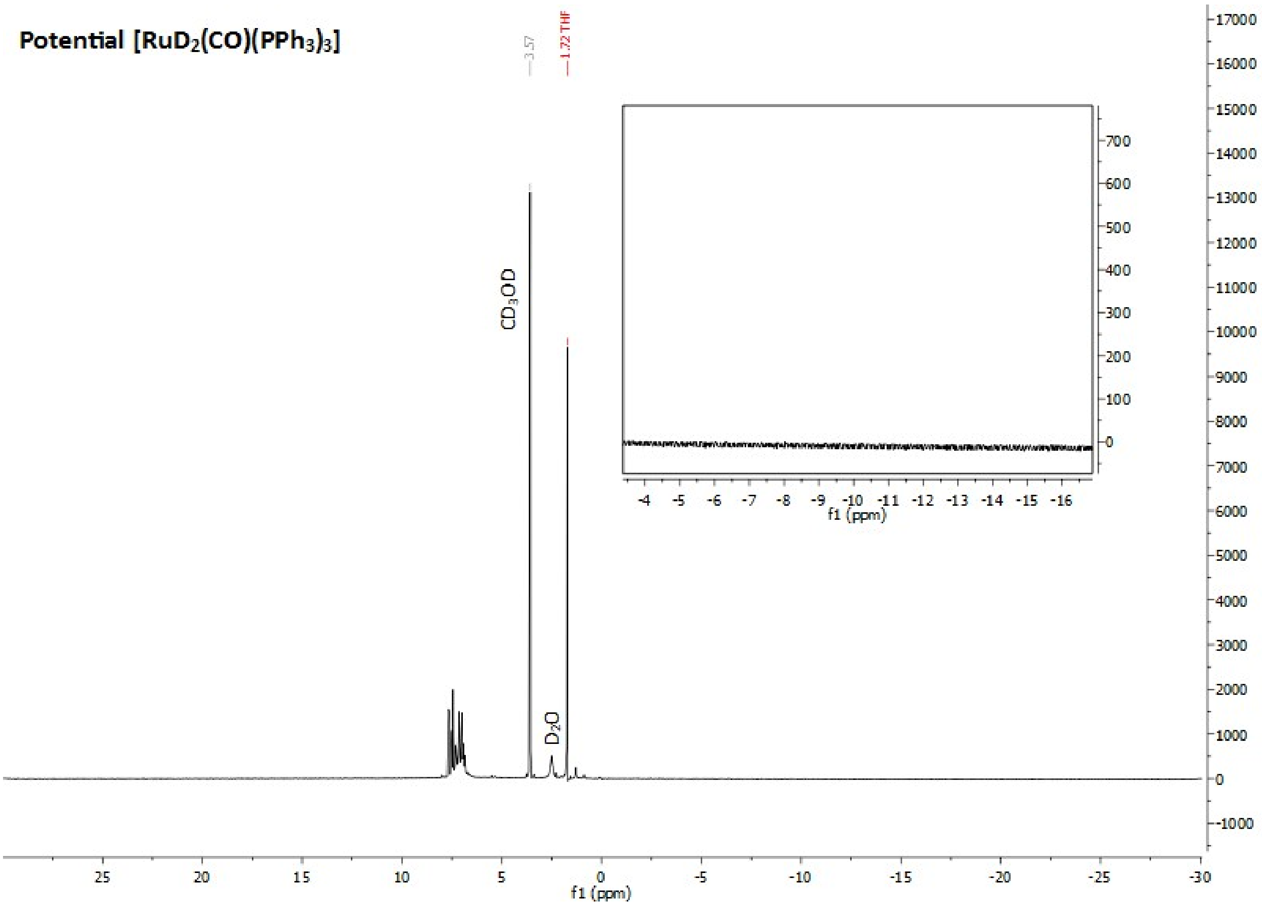

Figure S6 ^{1}H NMR (400 MHz; THF-d_8) of [$RuD_2(CO)(PPh_3)_3$]

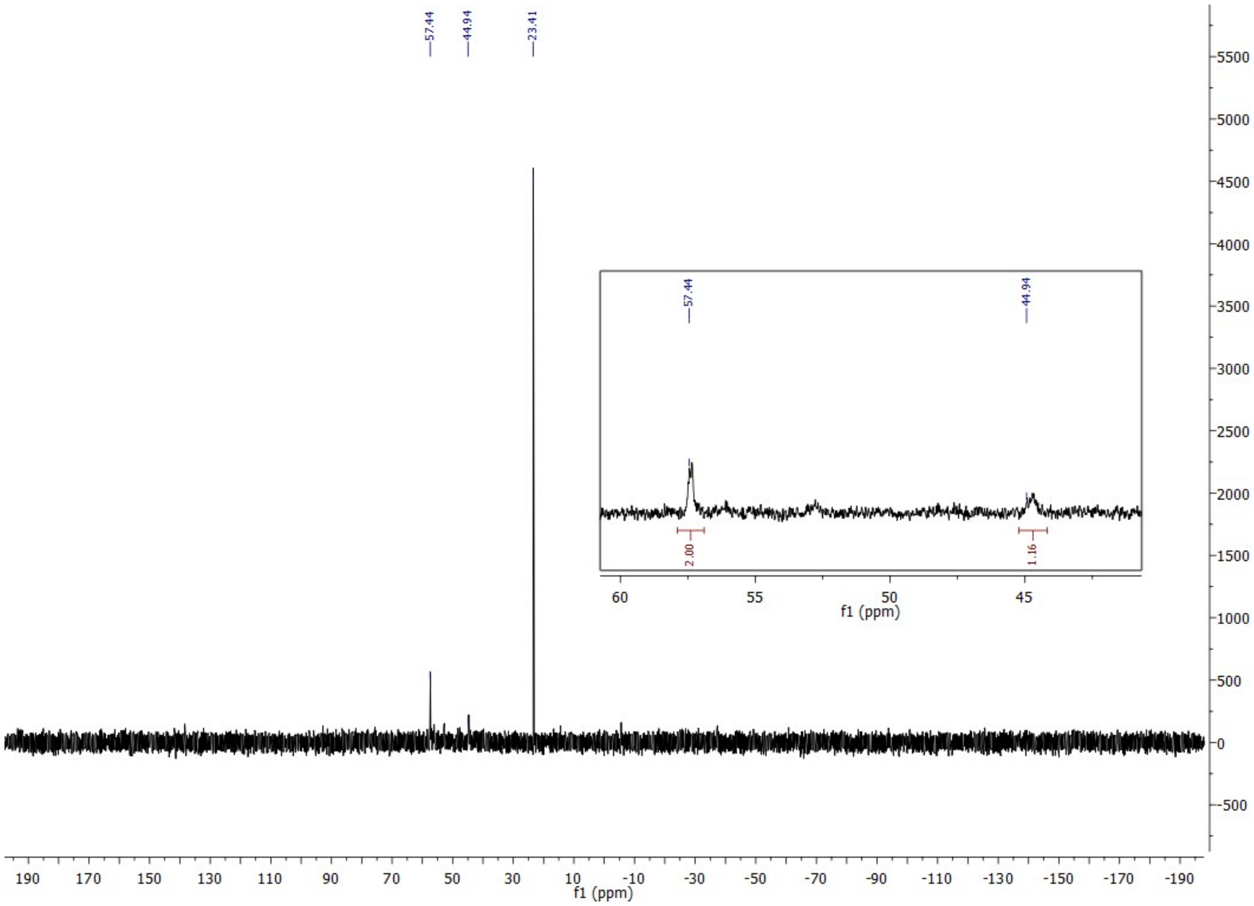

Figure S7 $^{31}P\{^1H\}$ NMR (400 MHz; THF-d_8) of $[RuD_2(CO)(PPh_3)_3]$

1.4 [$RuH_2(^{13}CO)(PPh_3)_3$] (experiment used for determining the KIE)

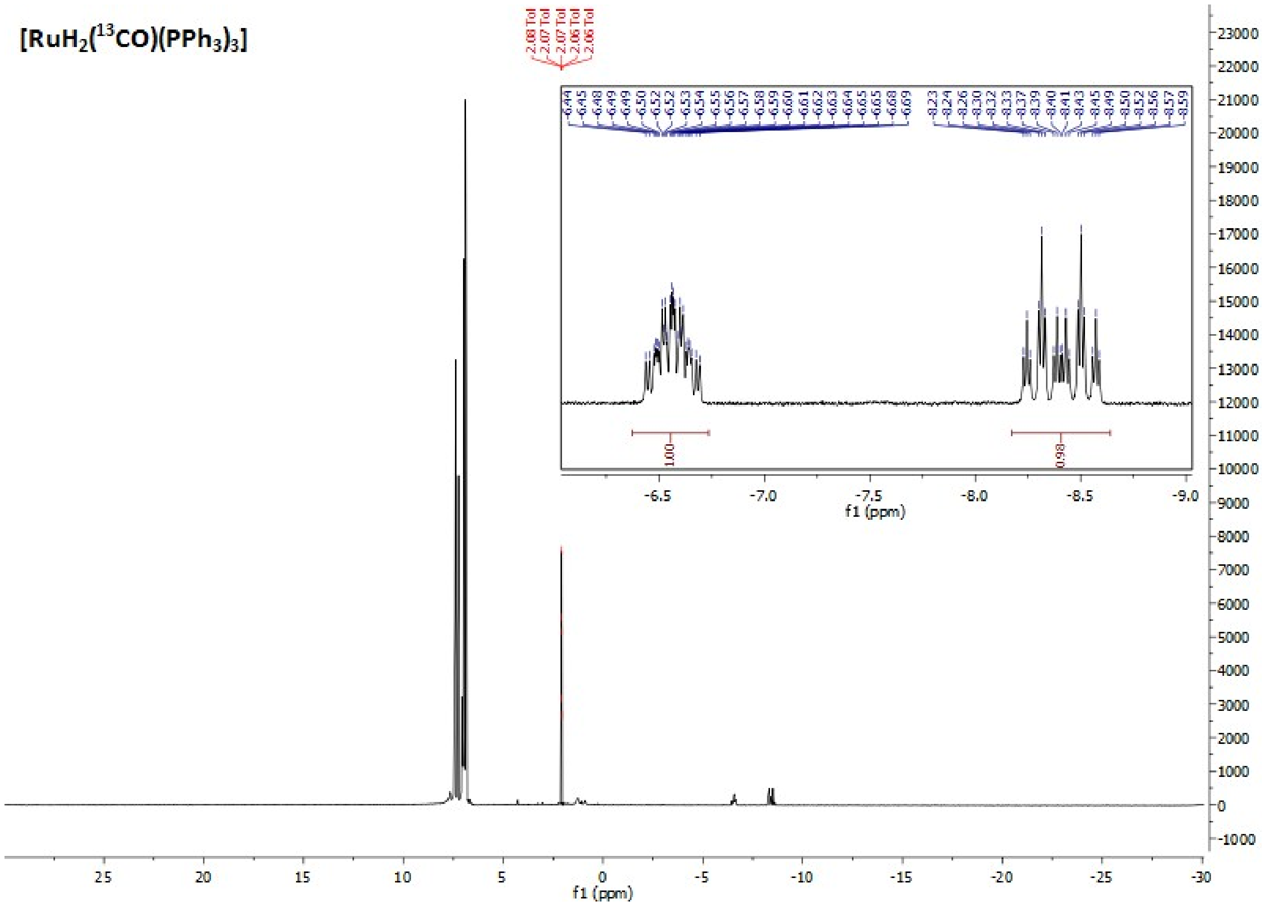

Figure S8 ^1H NMR (400 MHz; toluene-d_8) of [$RuH_2(^{13}CO)(PPh_3)_3$]

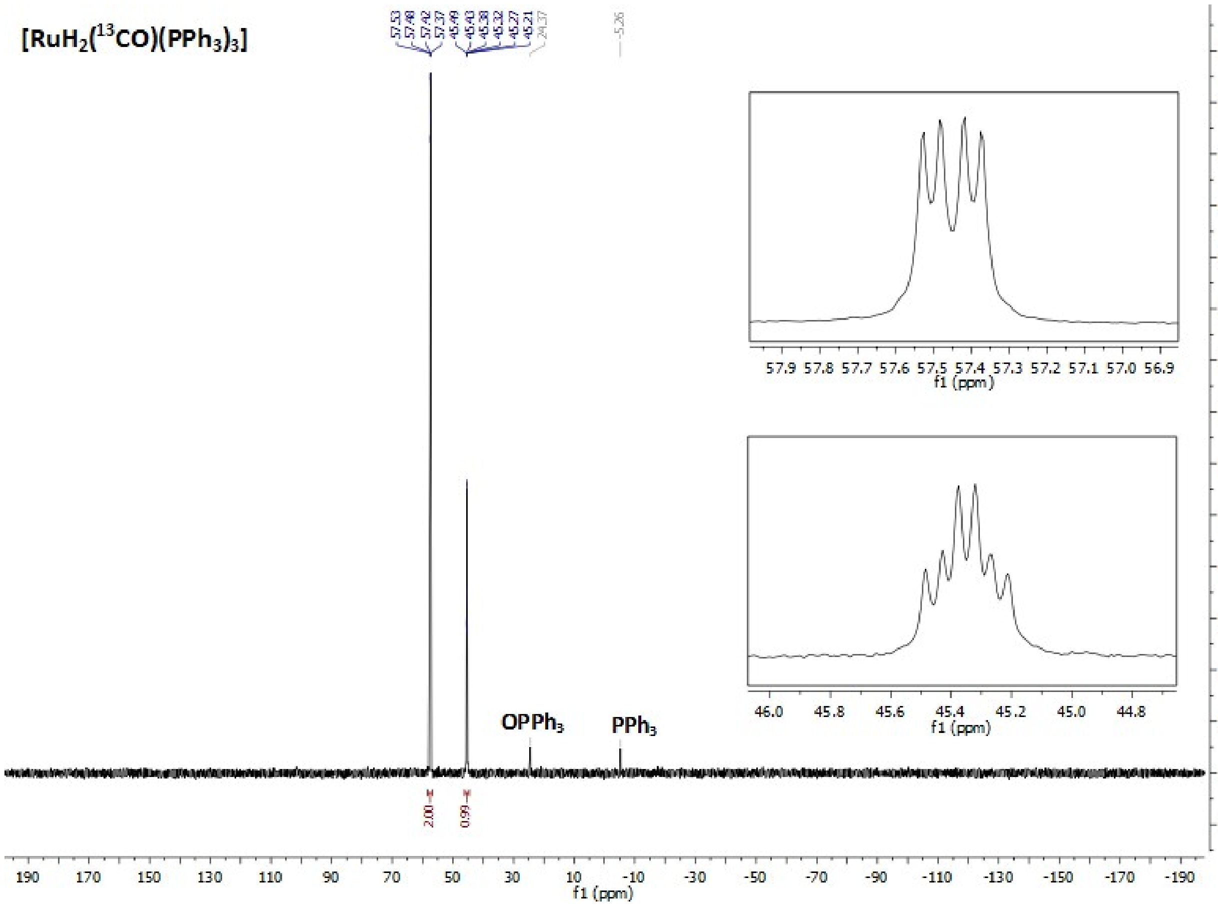

Figure S9 $^{31}P\{^{1}H\}$ NMR (400 MHz; toluene-d_8) of [RuH$_2$(^{13}CO)(PPh$_3$)$_3$]

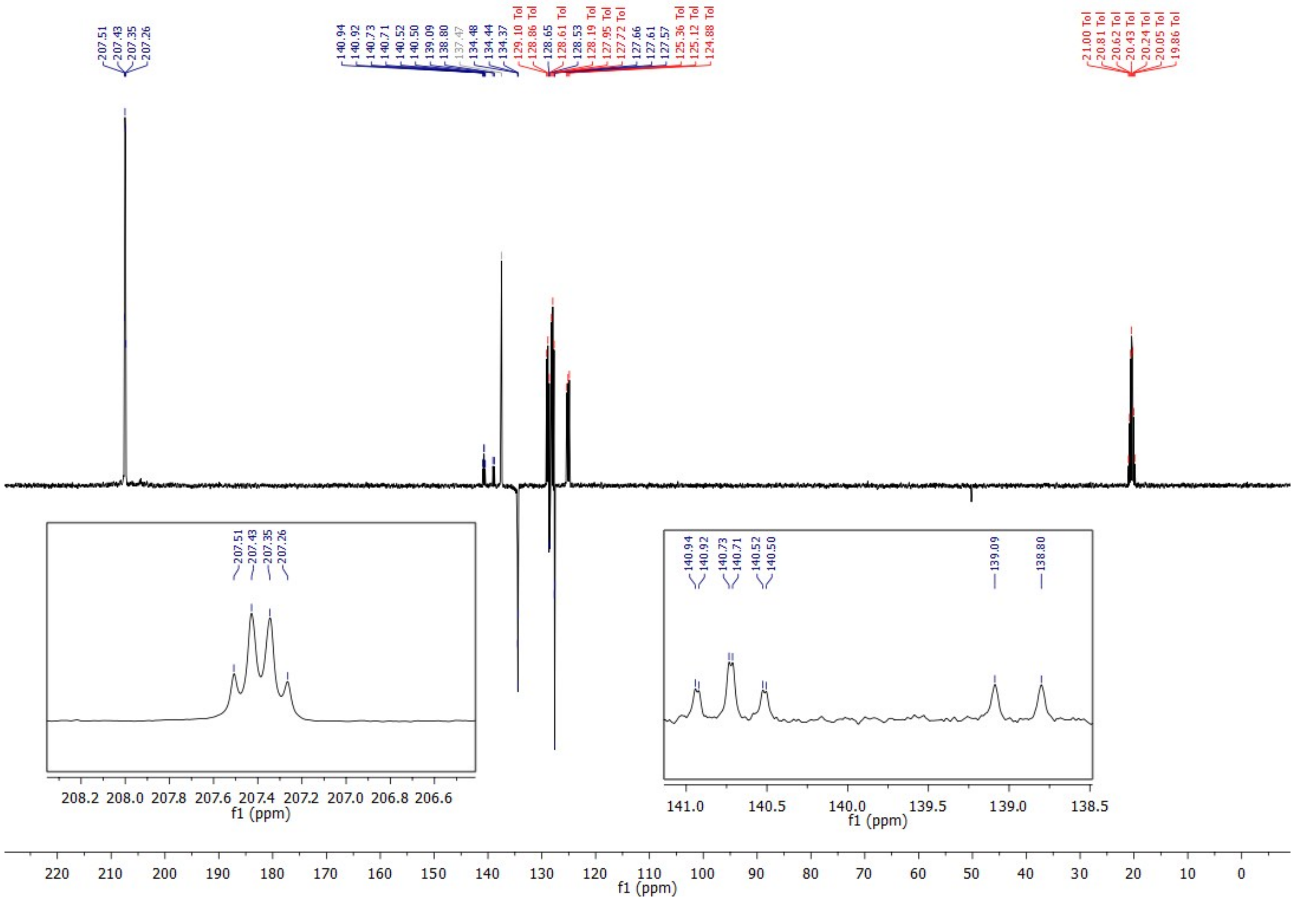

Figure S10 $^{13}C\{^{1}H\}$ NMR (400 MHz; toluene-d_8) of [$RuH_2(^{13}CO)(PPh_3)_3$]

1.5 Mixture of [$RuH_2(^{13}CO)(PPh_3)_3$] and [$RuHD(CO)(PPh_3)_3$] (experiment used for determining the KIE)

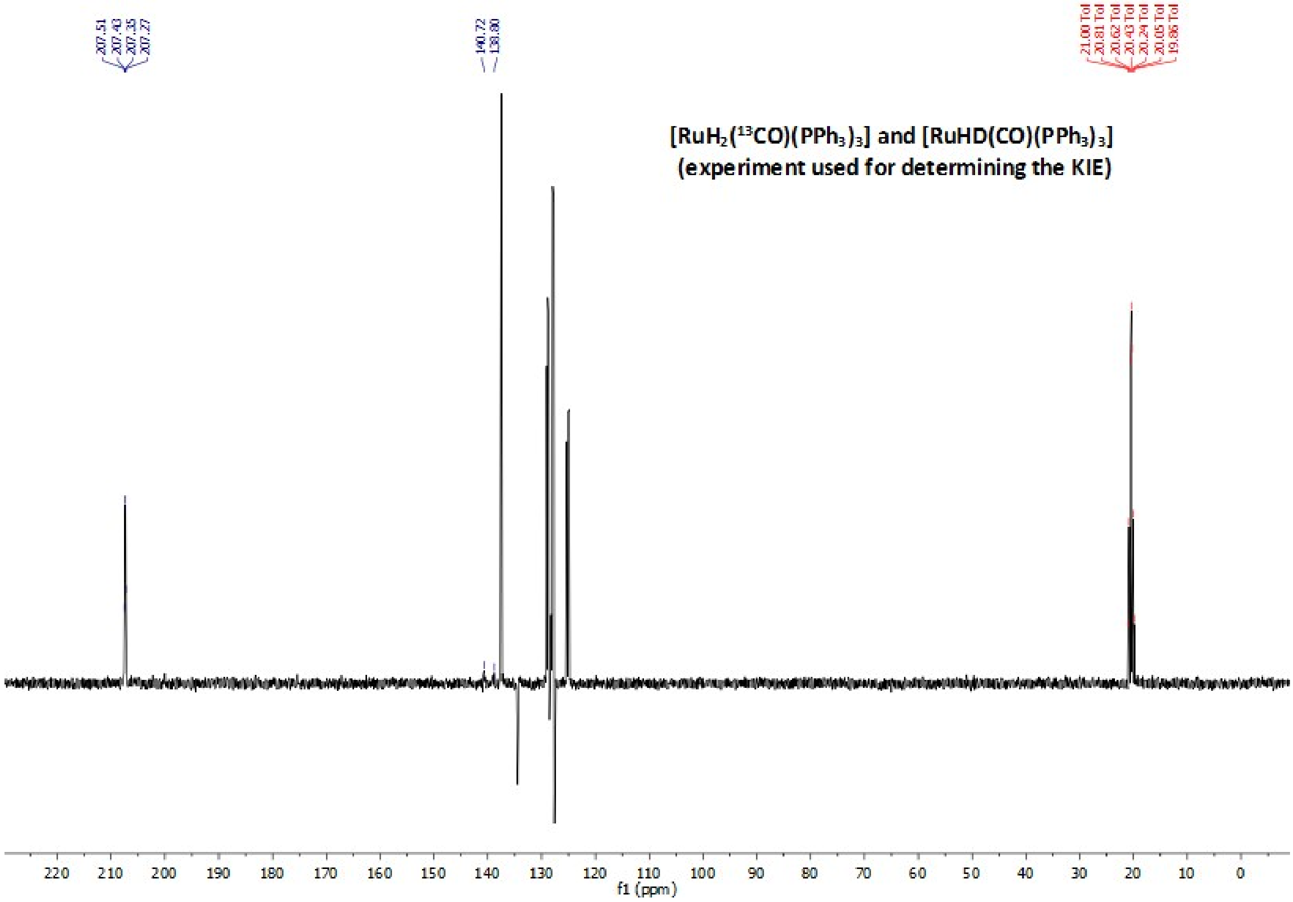

Figure S11 $^{13}C\{^1H\}$ NMR (400 MHz; toluene-d_8) of [$RuH_2(^{13}CO)(PPh_3)_3$] and [$RuHD(CO)(PPh_3)_3$]

1.6 Mixture of [$RuH_2(CO)(PPh_3)_3$] and [$RuHD(CO)(PPh_3)_3$]

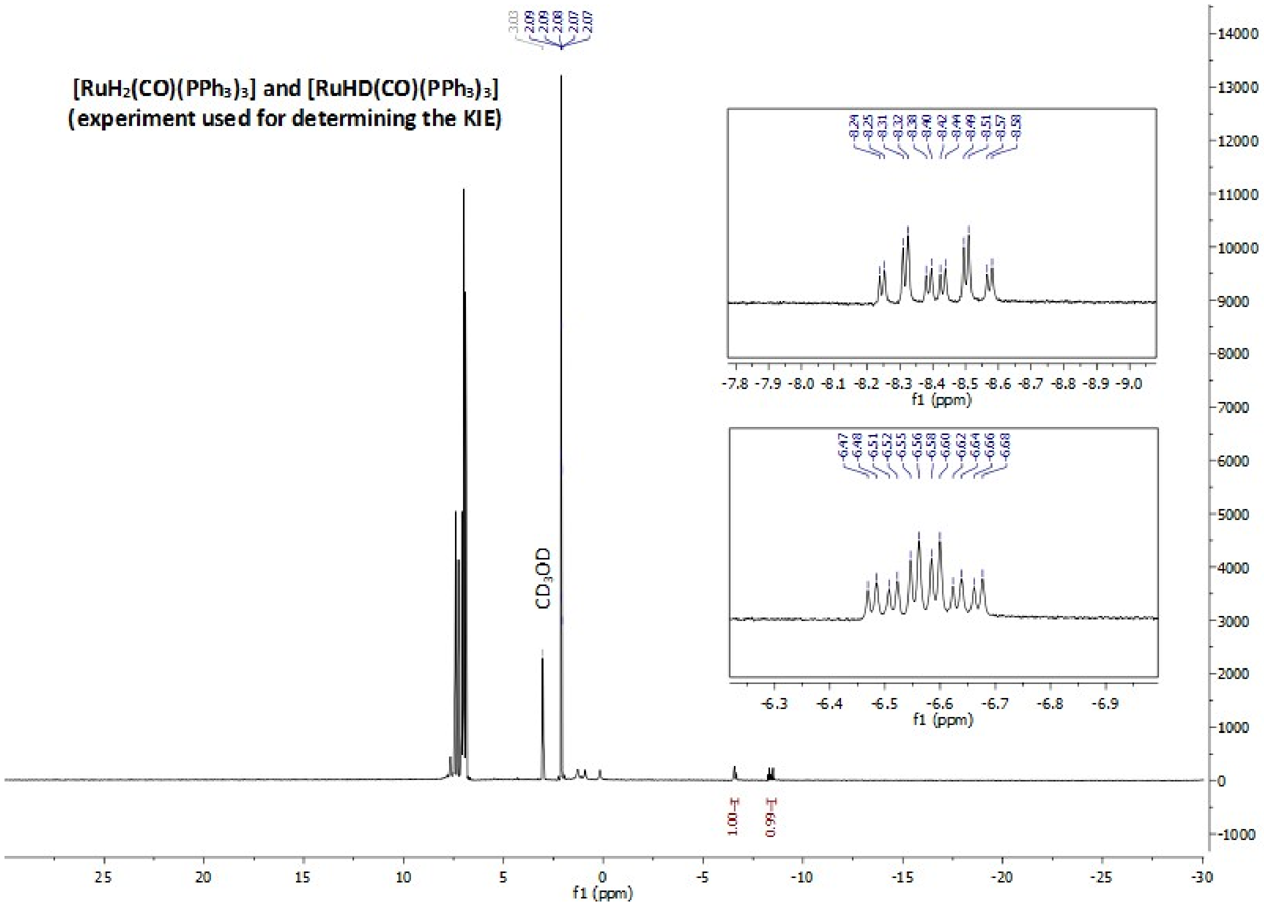

Figure S12 ^{1}H NMR (400 MHz; toluene-d_8) of $[RuH_2(CO)(PPh_3)_3]$ and $[RuHD(CO)(PPh_3)_3]$

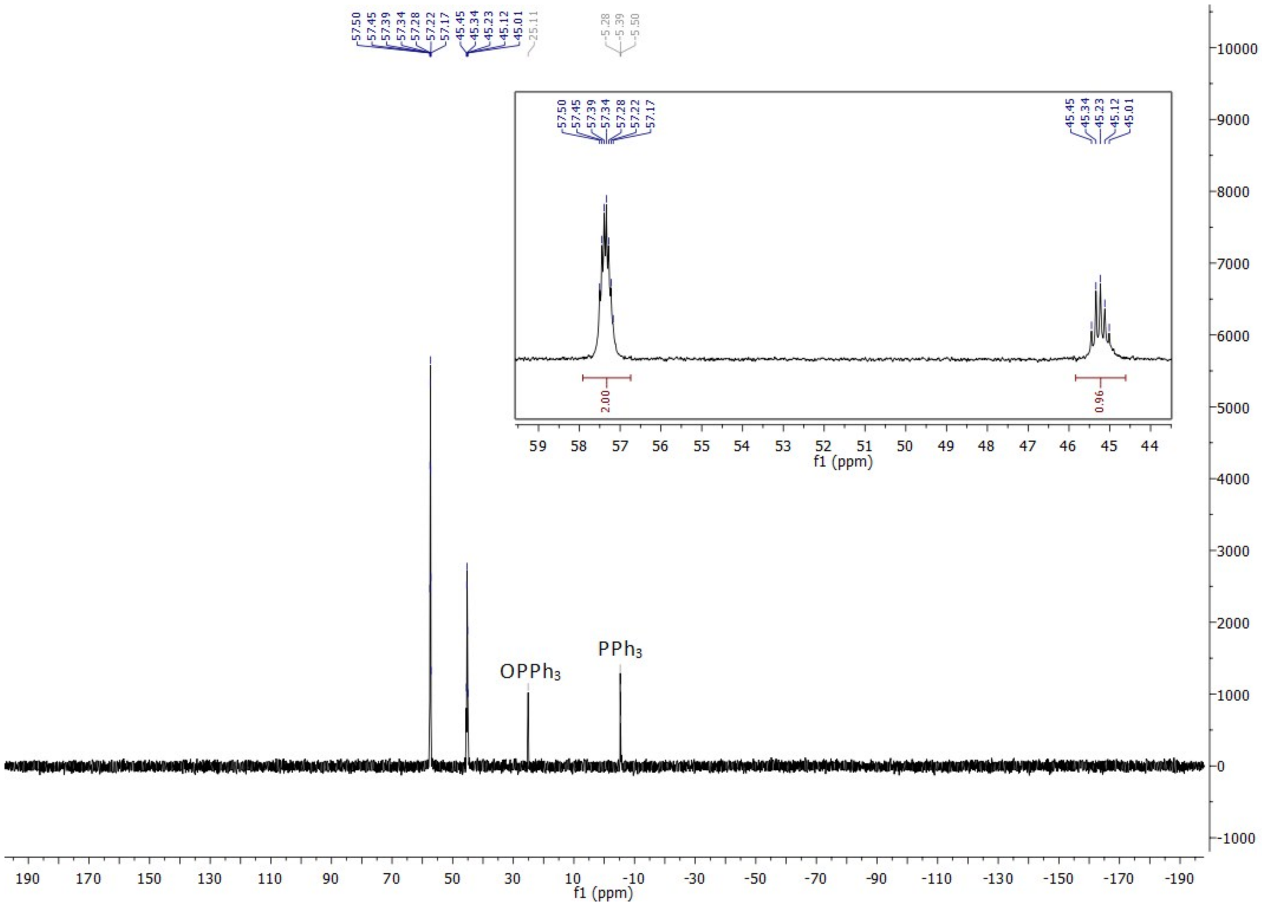

Figure S13 $^{31}P\{^1H\}$ NMR (400 MHz; toluene-d_8) of $[RuH_2(CO)(PPh_3)_3]$ and $[RuHD(CO)(PPh_3)_3]$

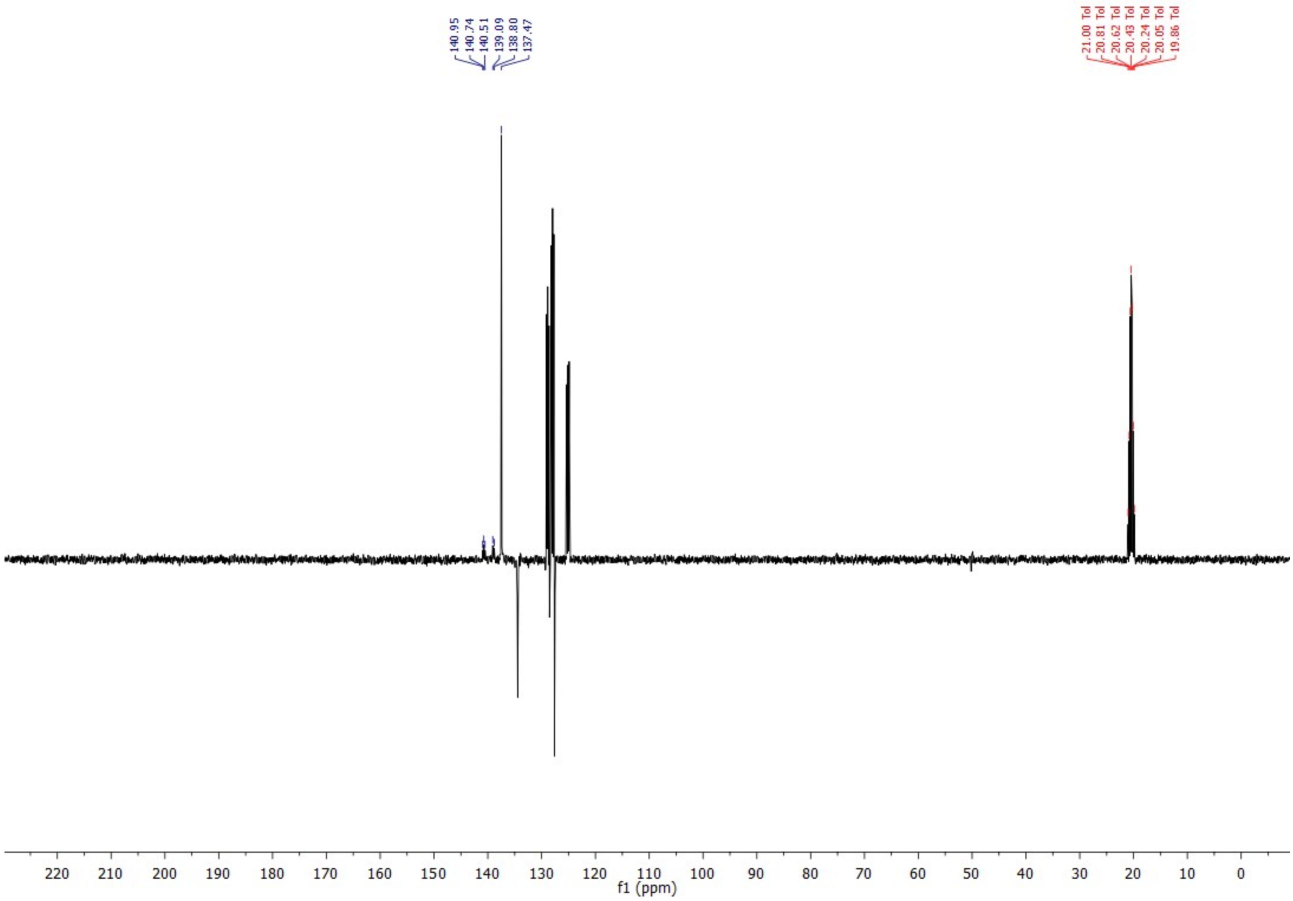

Figure S14 $^{13}C\{^1H\}$ NMR (400 MHz; toluene-d_8) of $[RuH_2(CO)(PPh_3)_3]$ and $[RuHD(CO)(PPh_3)_3]$

1.7 Time and temperature dependent NMR studies with $NaOCD_3$

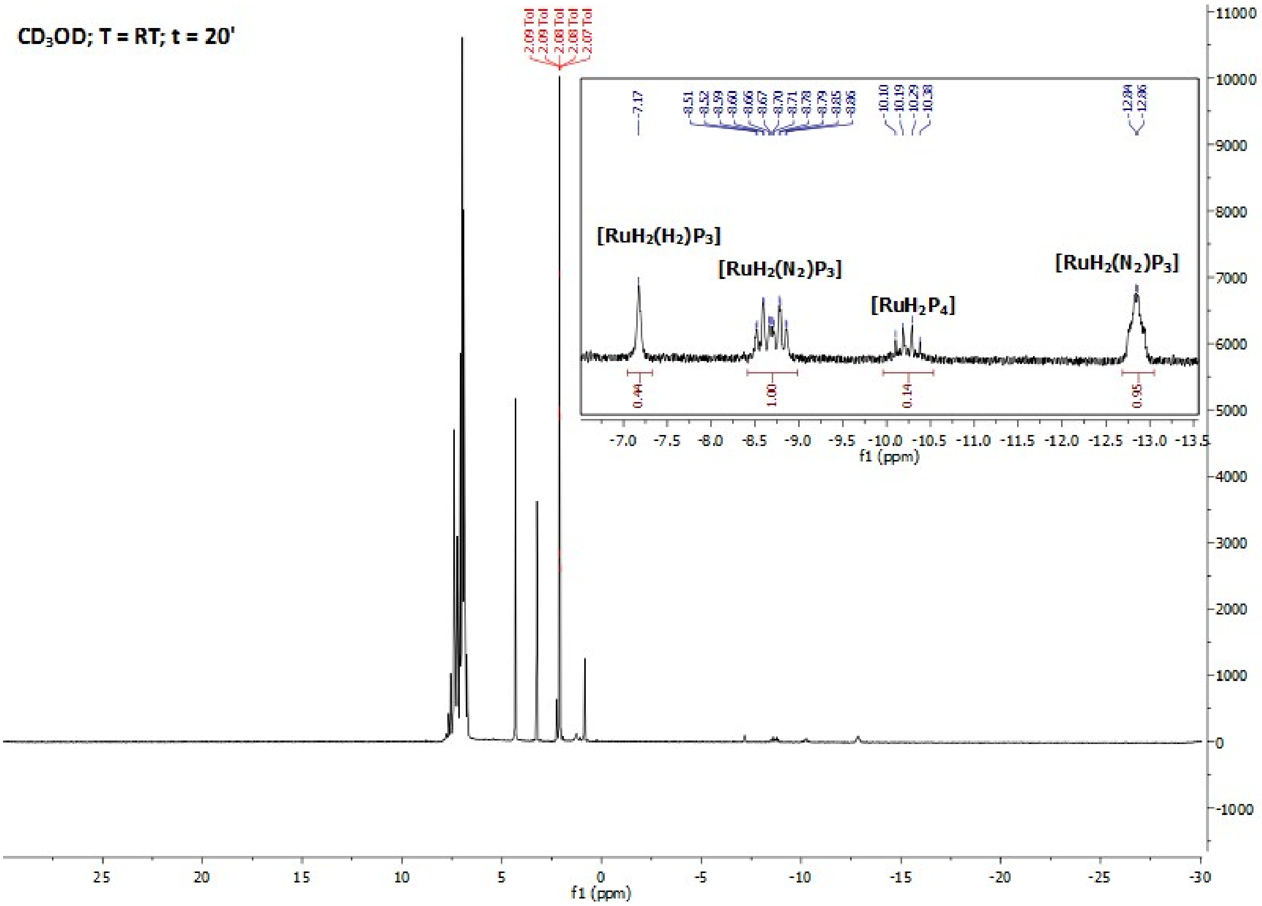

Figure S15 ^1H NMR (400 MHz; toluene-d_8); First step: 20 min at RT

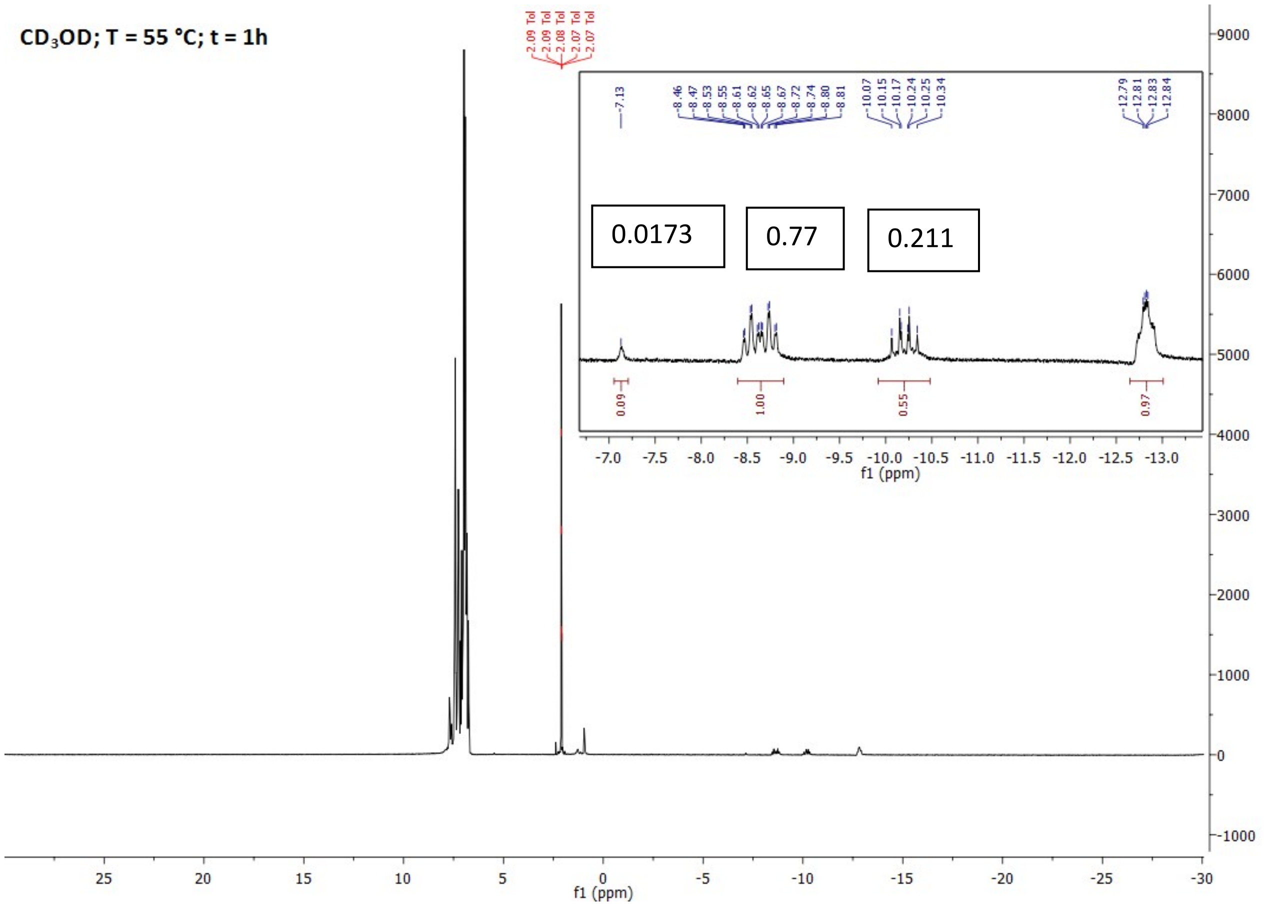

Figure S16 ^{1}H NMR (400 MHz; toluene-d_8); Second step: 40 min at 55 °C.

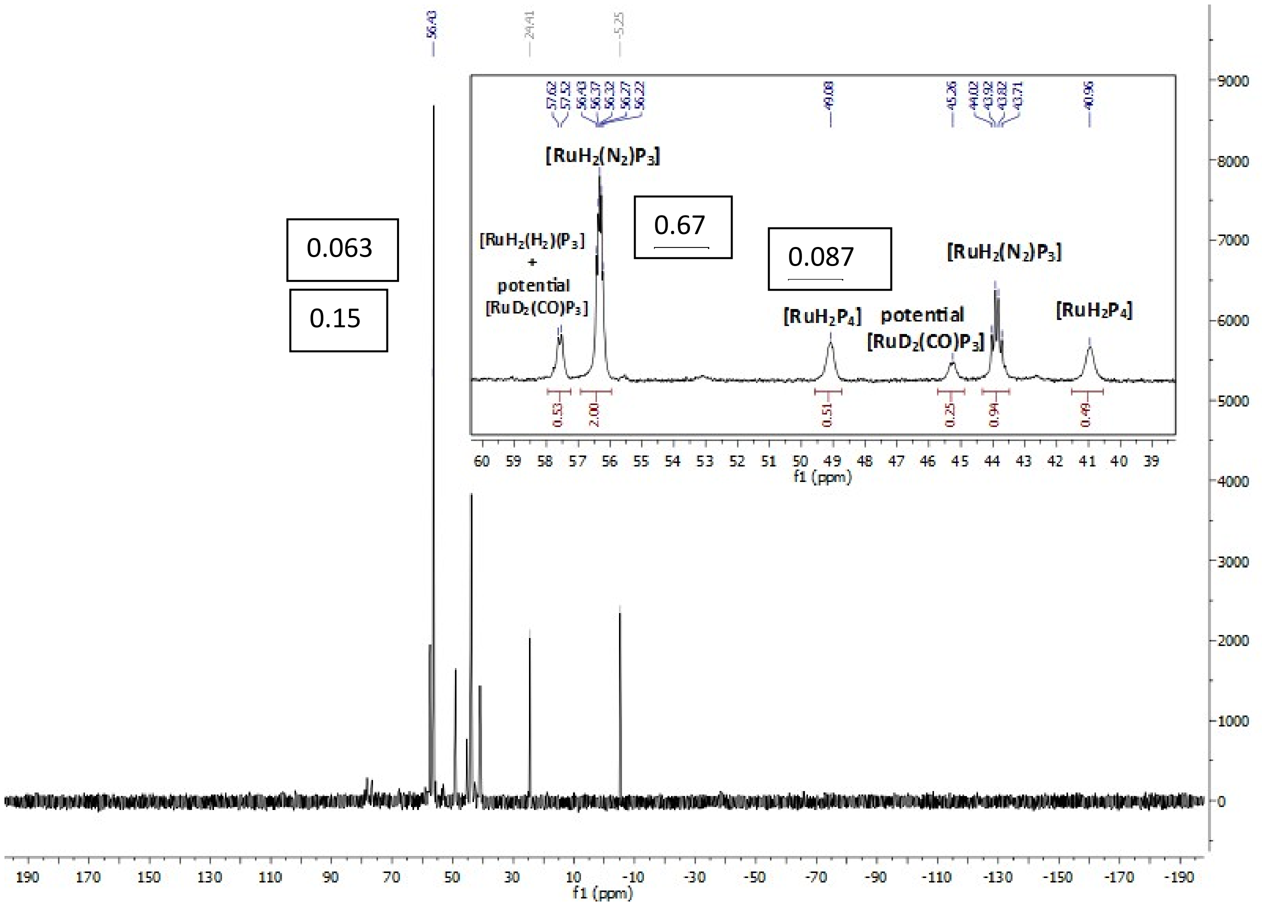

Figure S17 ^{31}P{^{1}H} NMR (400 MHz; toluene-d_8); Second step: 40 min at 55 °C.

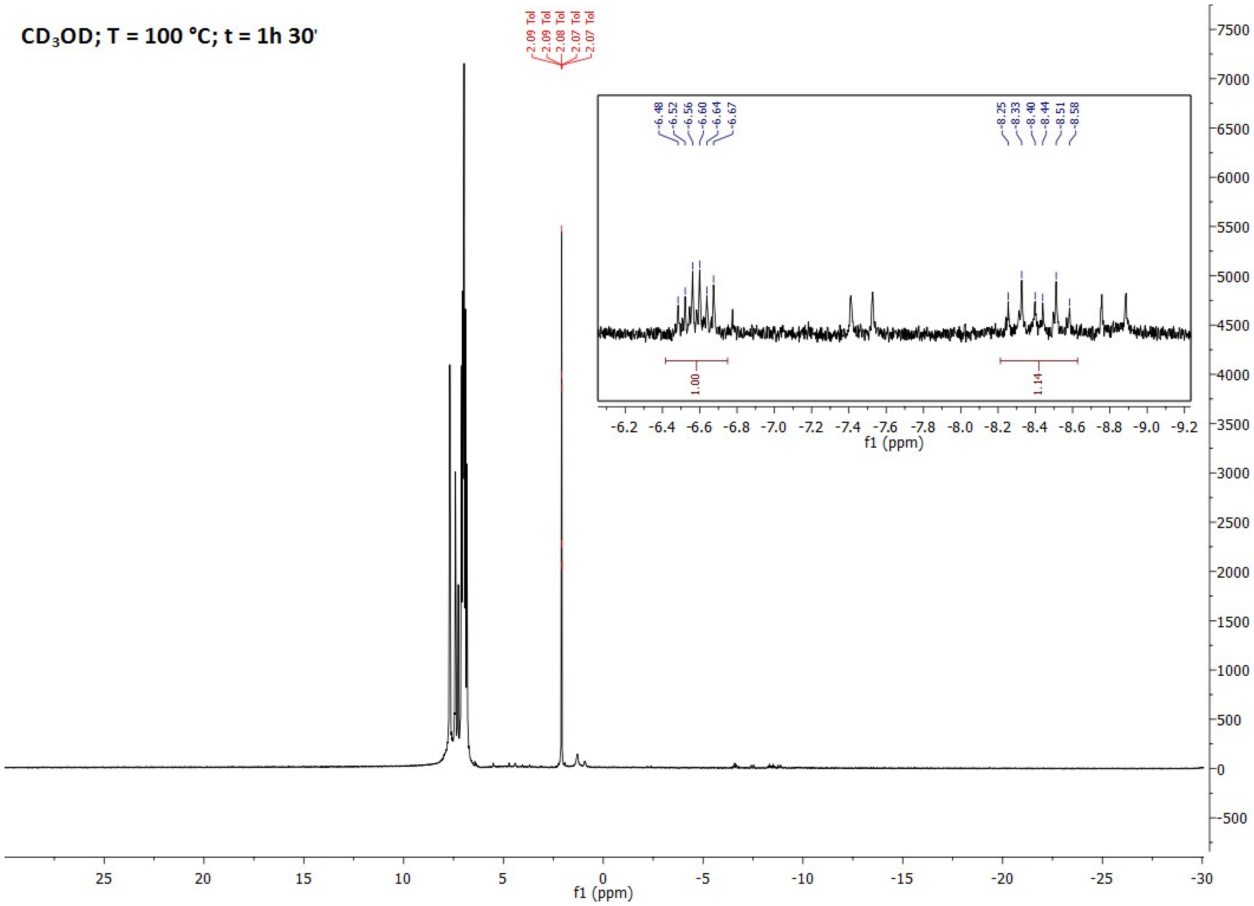

Figure S18 ^{1}H NMR (400 MHz; toluene-d_8); Third step: 30 min at 100 °C.

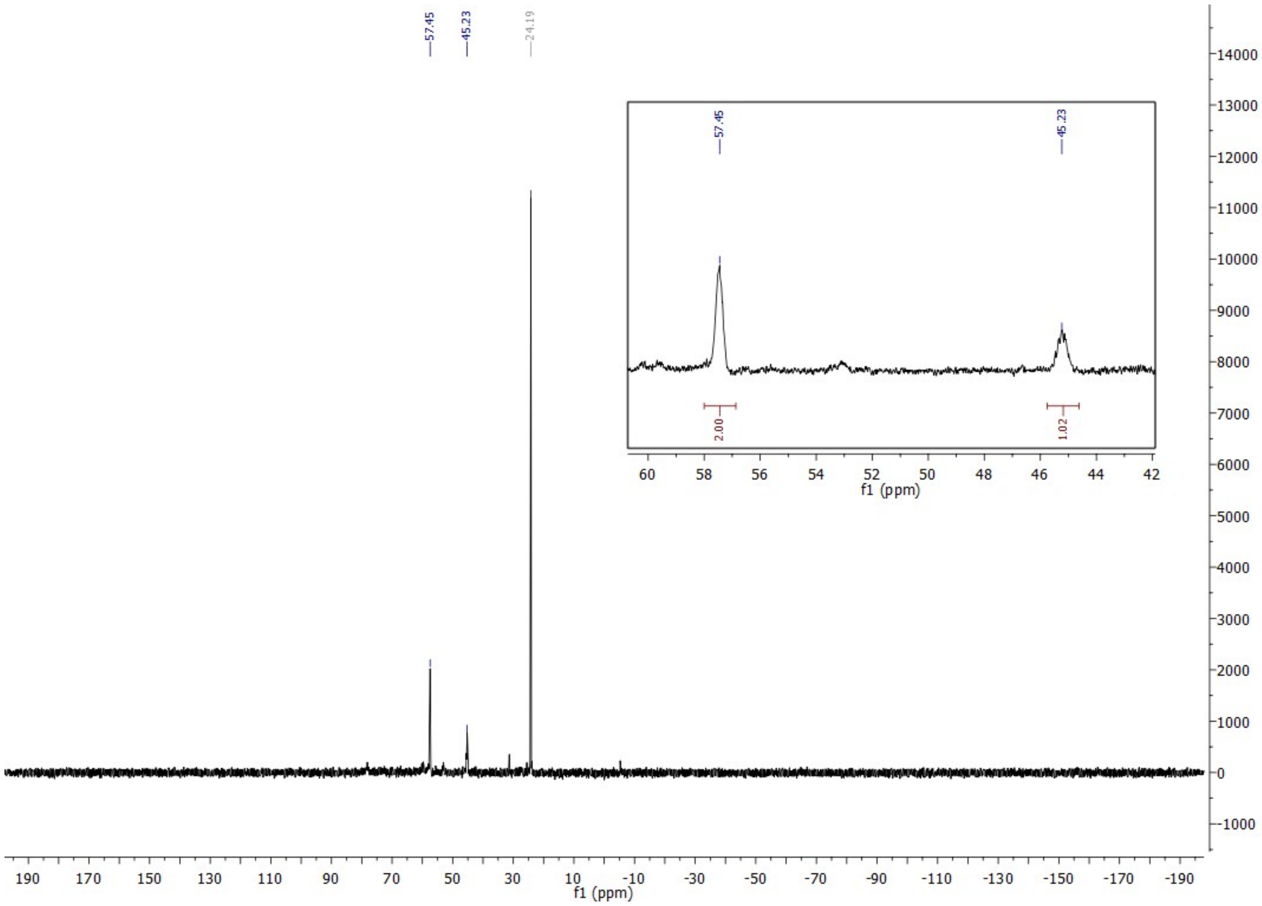

Figure S19 $^{31}P\{^1H\}$ NMR (400 MHz; toluene-d_8); Third step: 30 min at 100 °C.

1.8 Time and temperature dependent NMR studies with $NaOCH_3$

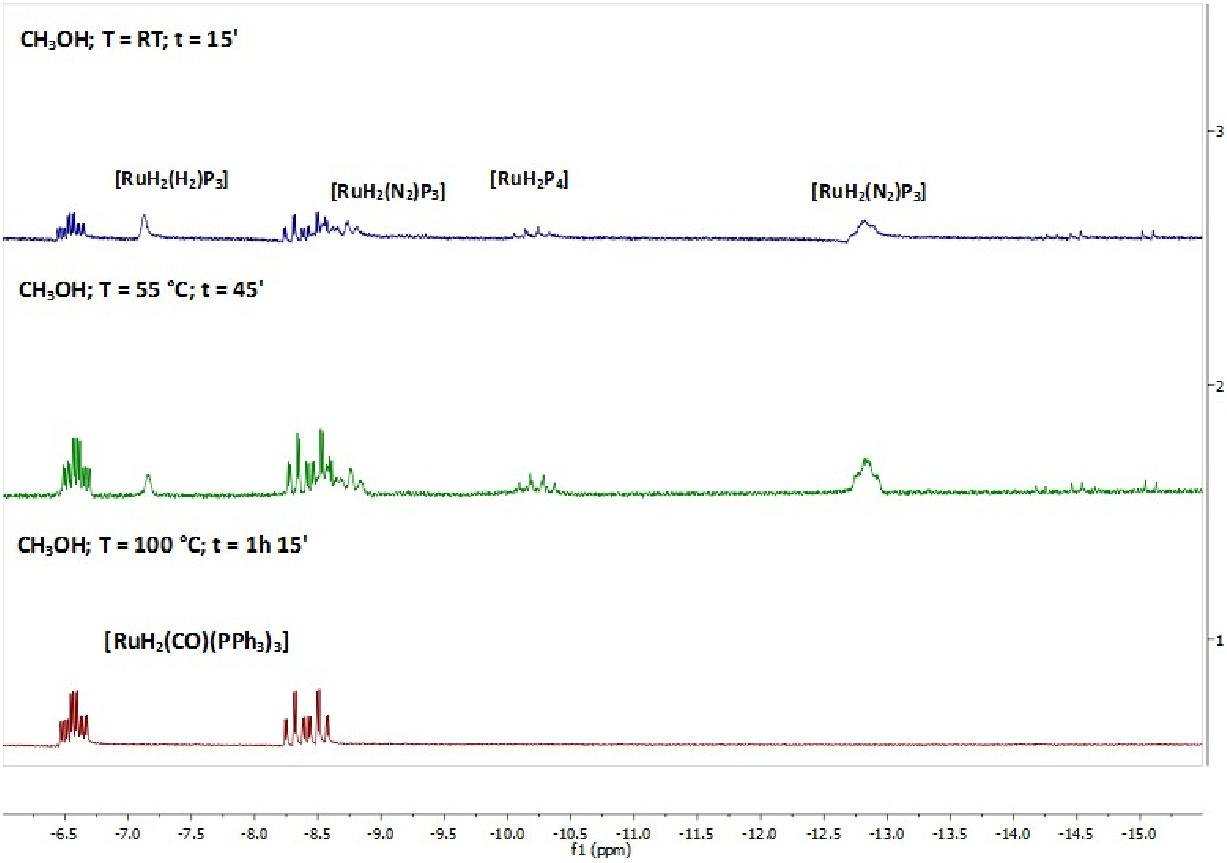

Figure S20 ^1H NMR (400 MHz; toluene-d_8). Time and temperature dependent ^1H NMR study of [$RuHClP_3$] with $NaOCH_3$: hydride region of the reaction mixture.

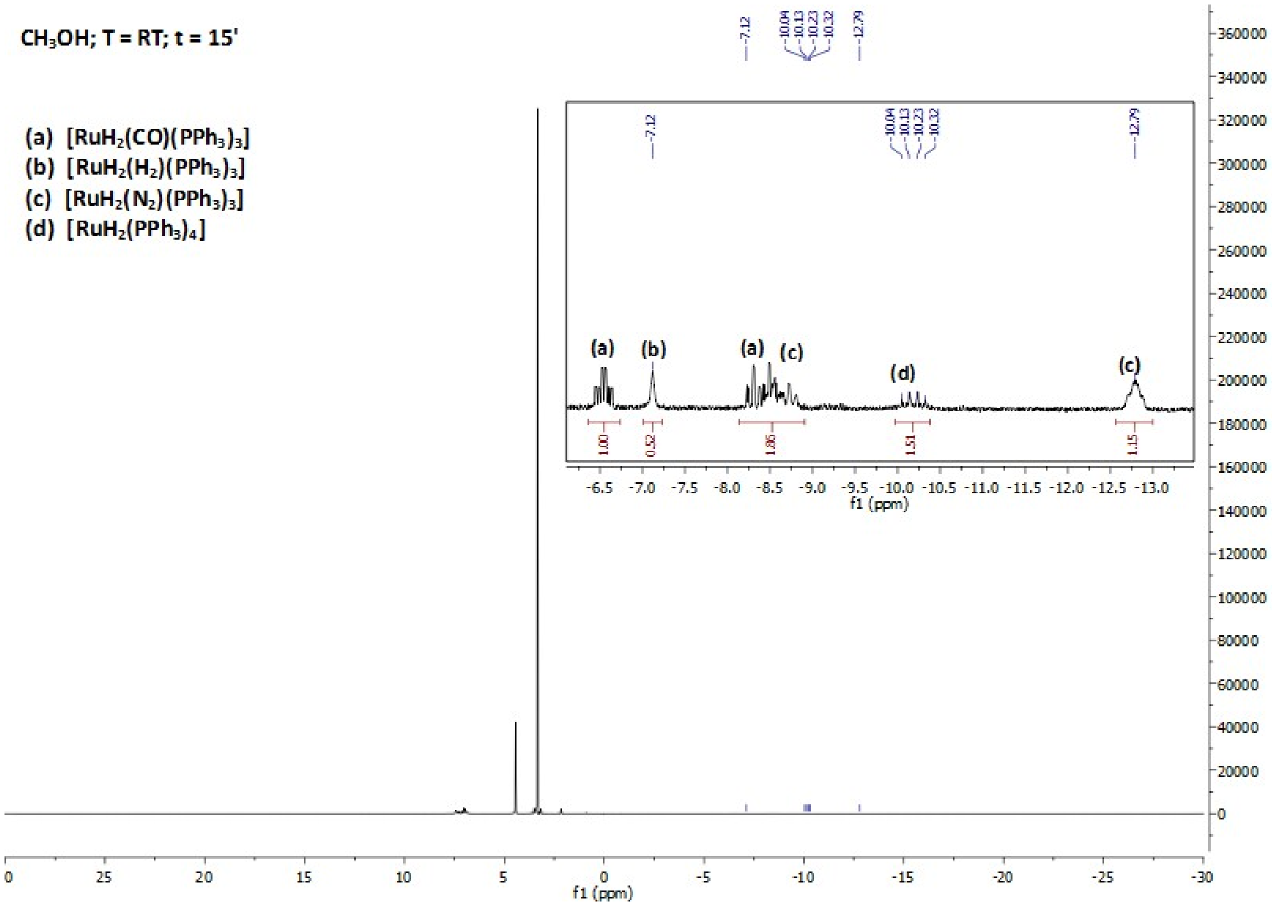

Figure S21 ^{1}H NMR (400 MHz; toluene-d_8); First step: 15 min at RT.

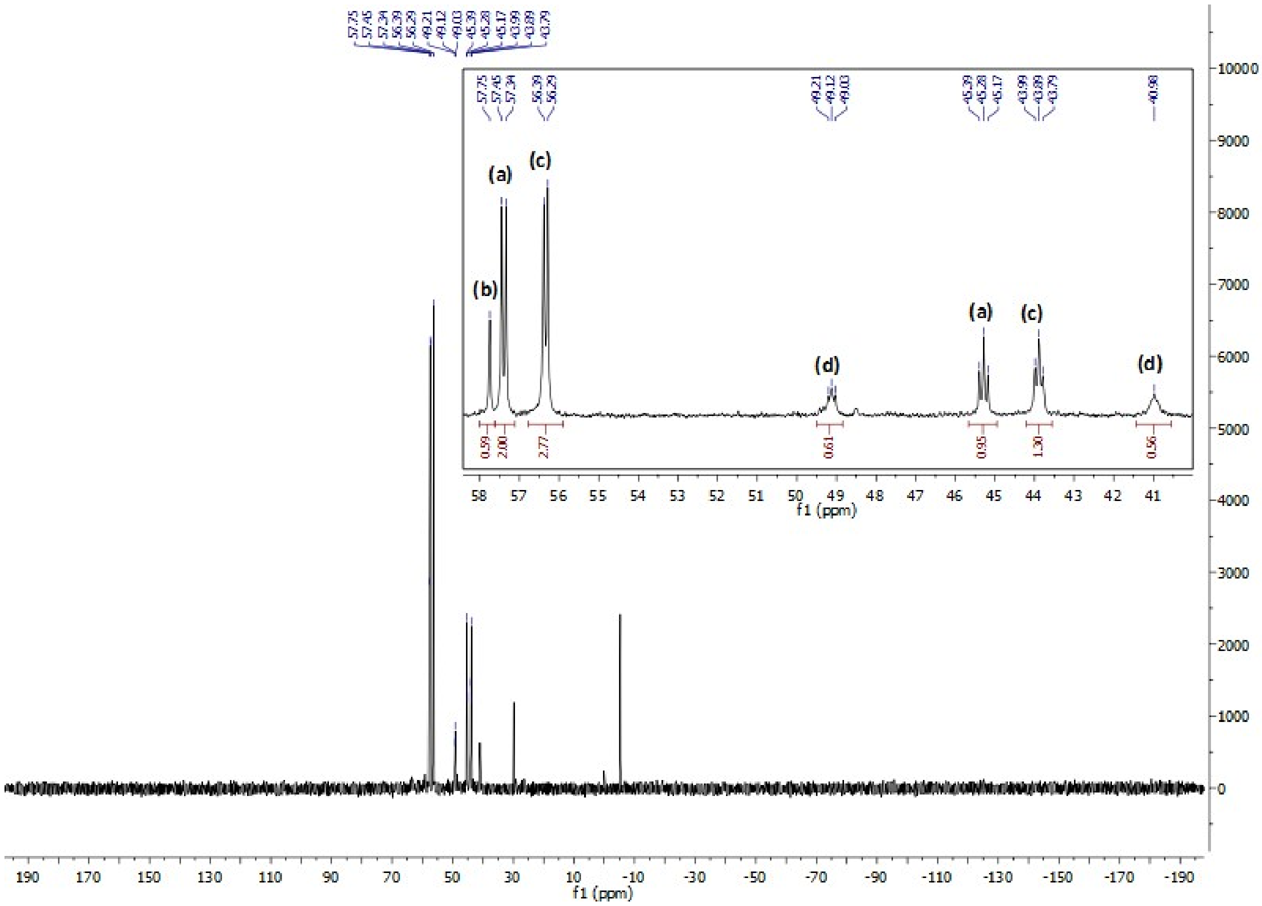

Figure S22 $^{31}P\{^{1}H\}$ NMR (400 MHz; toluene-d_8); First step: 15 min at RT.

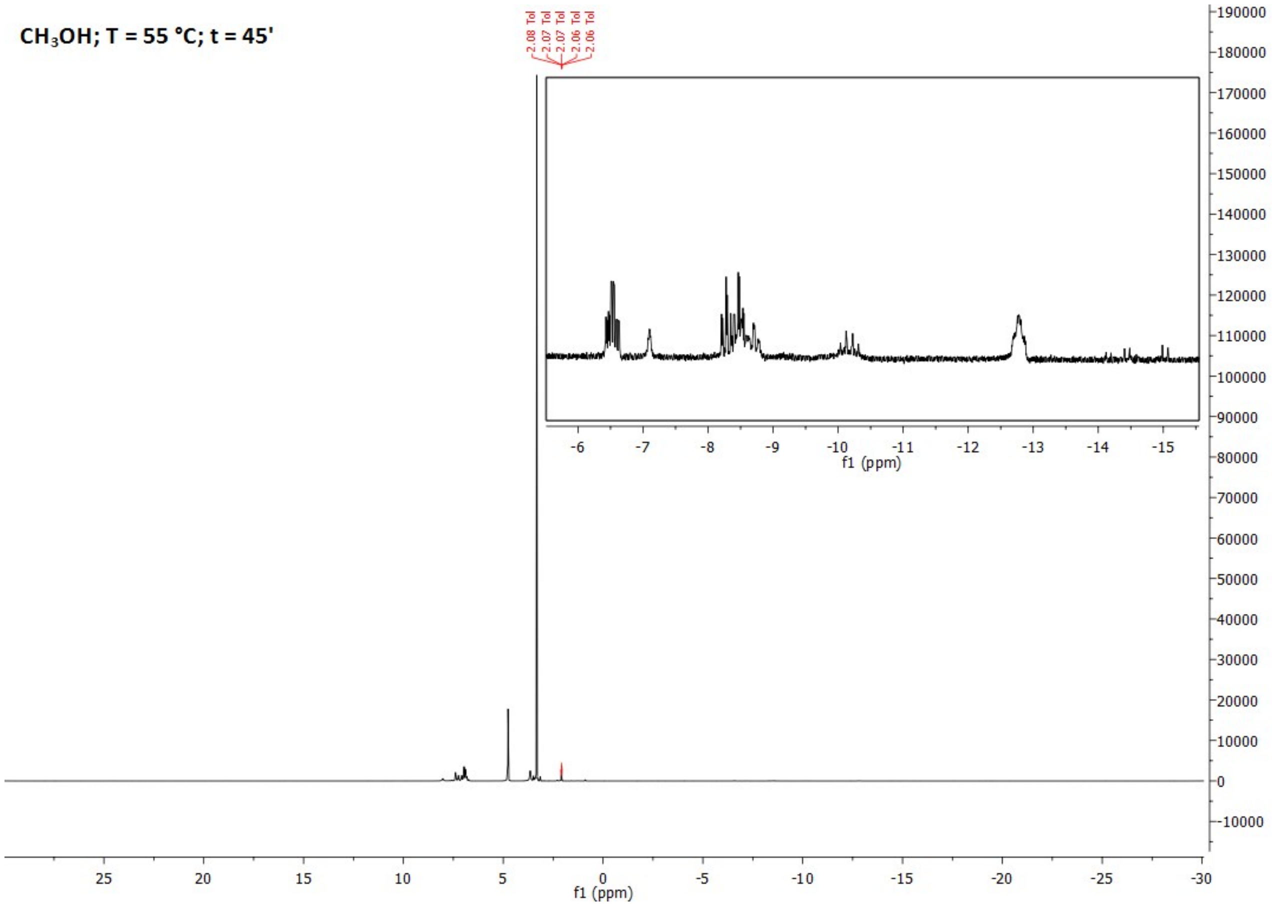

Figure S23 ^{1}H NMR (400 MHz; toluene-d_8); Second step: 30 min at 55 °C.

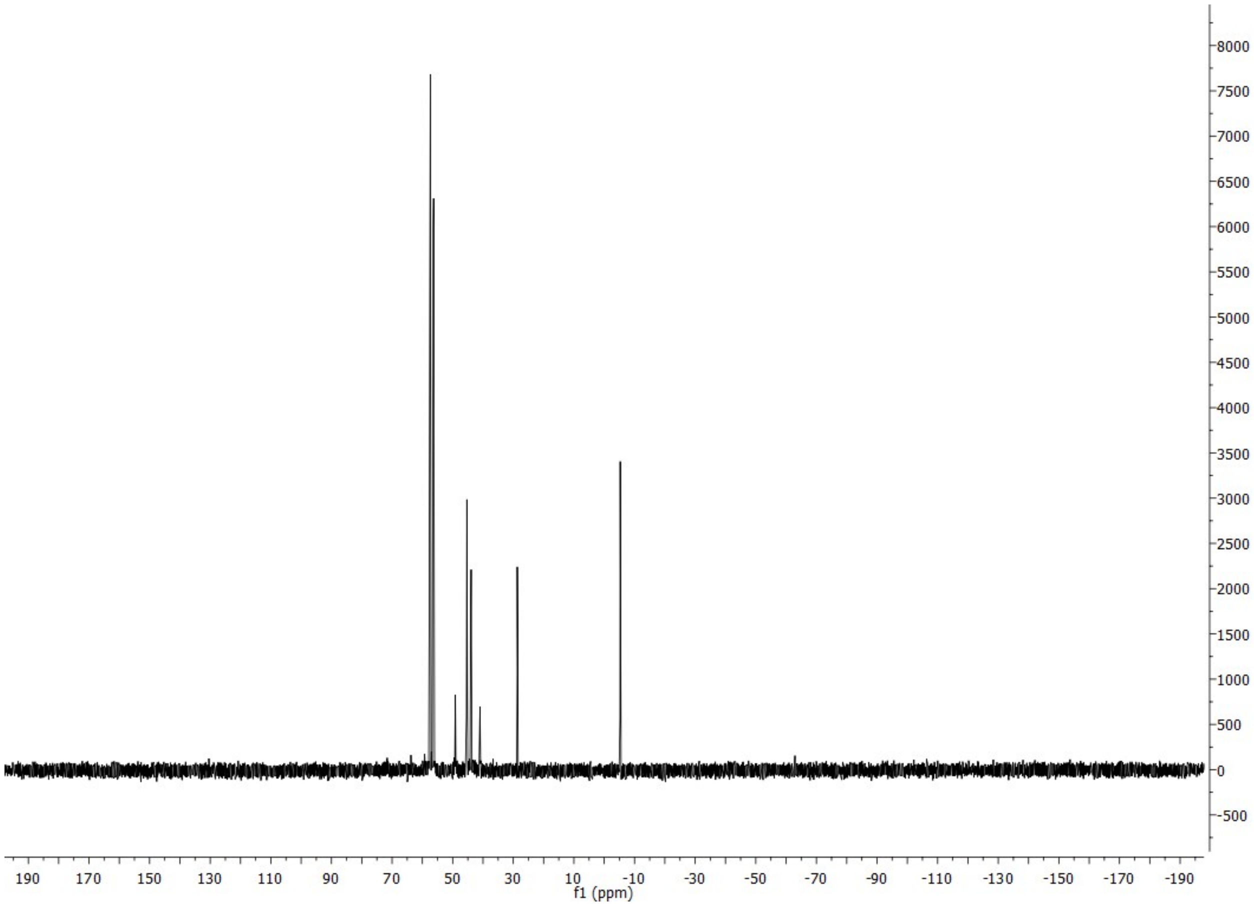

Figure S24 $^{31}P\{^{1}H\}$ NMR (400 MHz; toluene-d_8); Second step: 30 min at 55 °C.

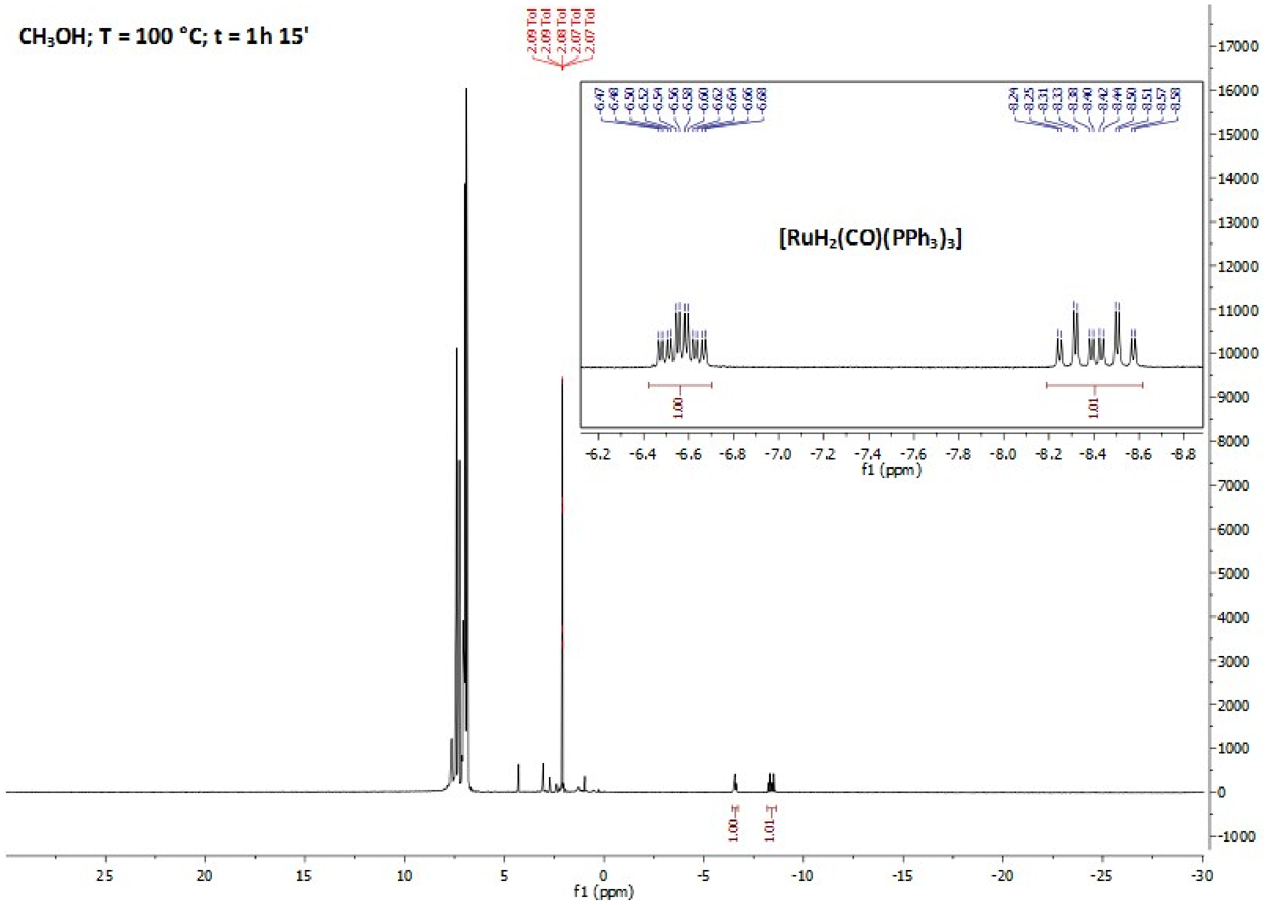

Figure S25 ^{1}H NMR (400 MHz; toluene-d_8); Third step: 30 min at 100 °C.

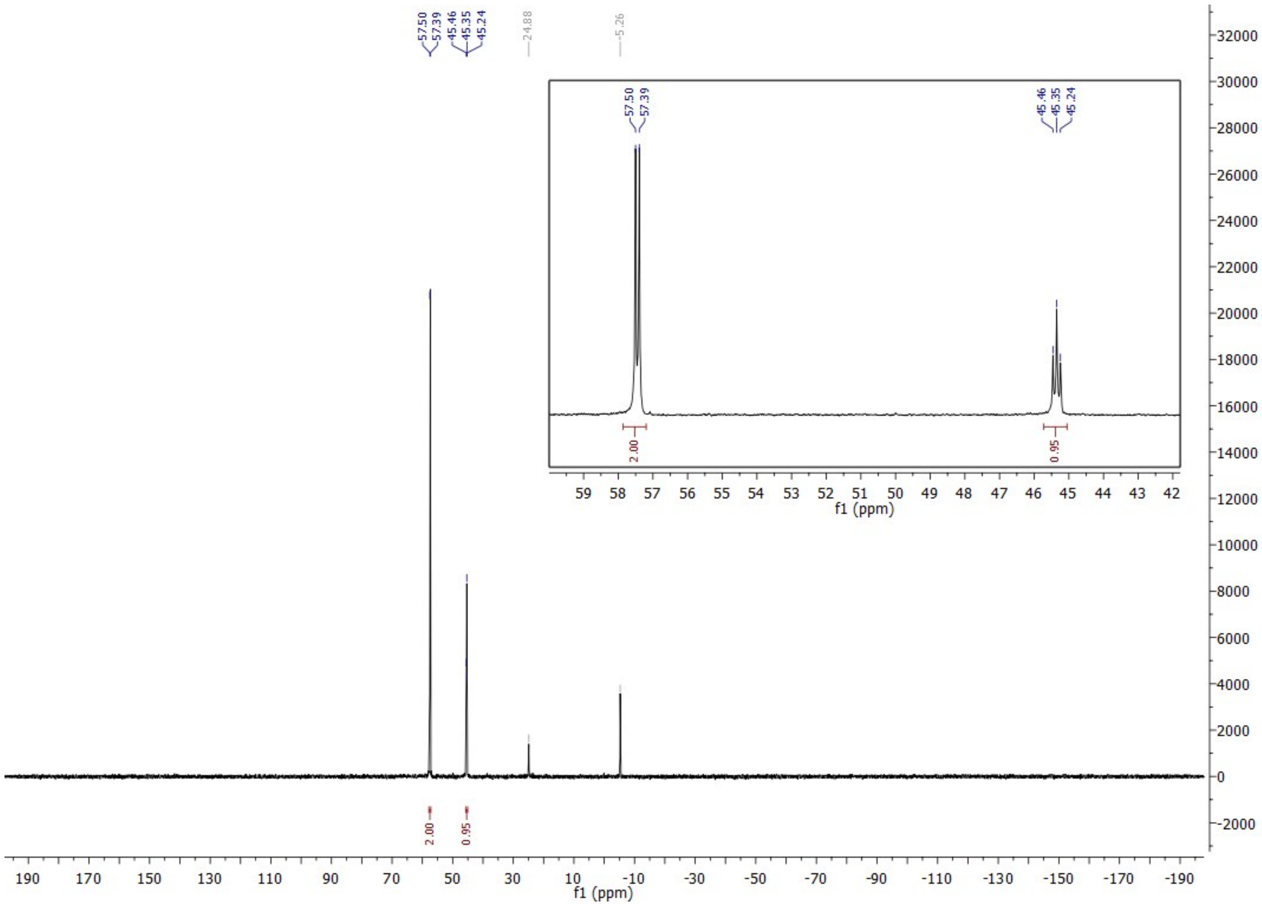

Figure S26 $^{31}P\{^1H\}$ NMR (400 MHz; toluene-d_8); Third step: 30 min at 100 °C.

1.9 Identification of $[RuH_2(N_2)(PPh_3)_3]$

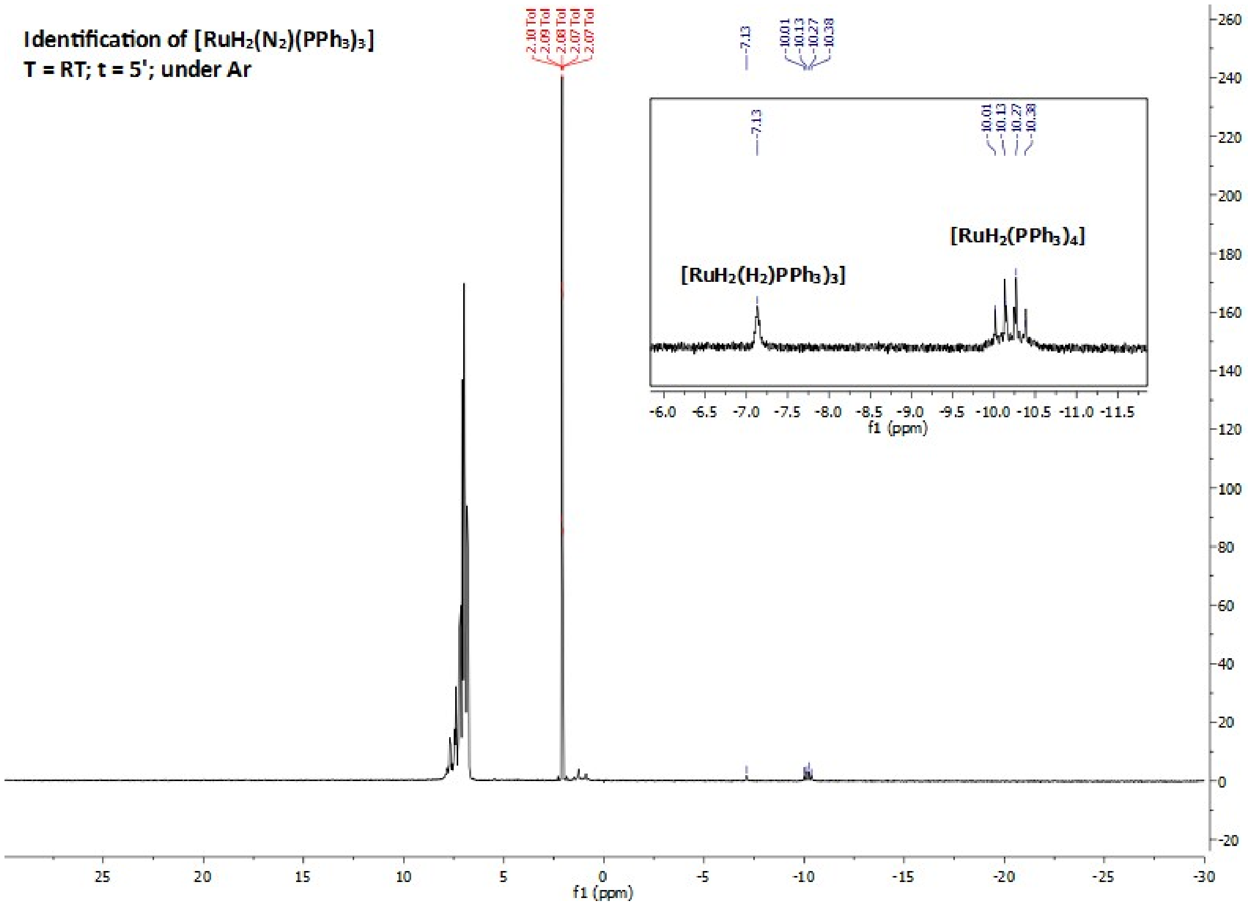

Figure S27 ^1H NMR (300 MHz; toluene-d_8); Identification of $[RuH_2(N_2)(PPh_3)_3]$ by performing the reaction under Ar.

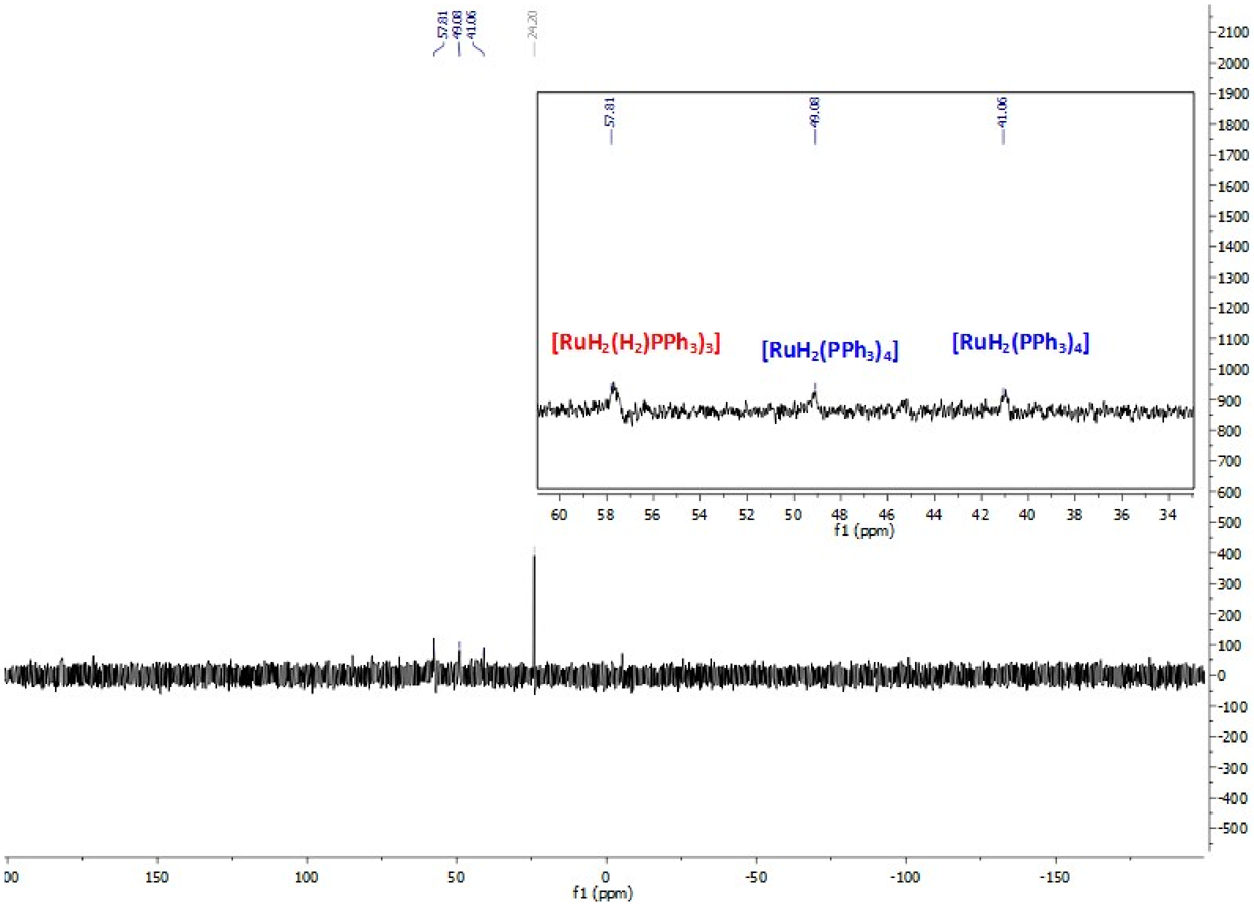

Figure S28 $^{31}P\{^1H\}$ NMR (300 MHz; toluene-d_8); Identification of [RuH$_2$(N$_2$)(PPh$_3$)$_3$] by performing the reaction under Ar.

1.10 Identification of [$RuH_2(PPh_3)_4$]

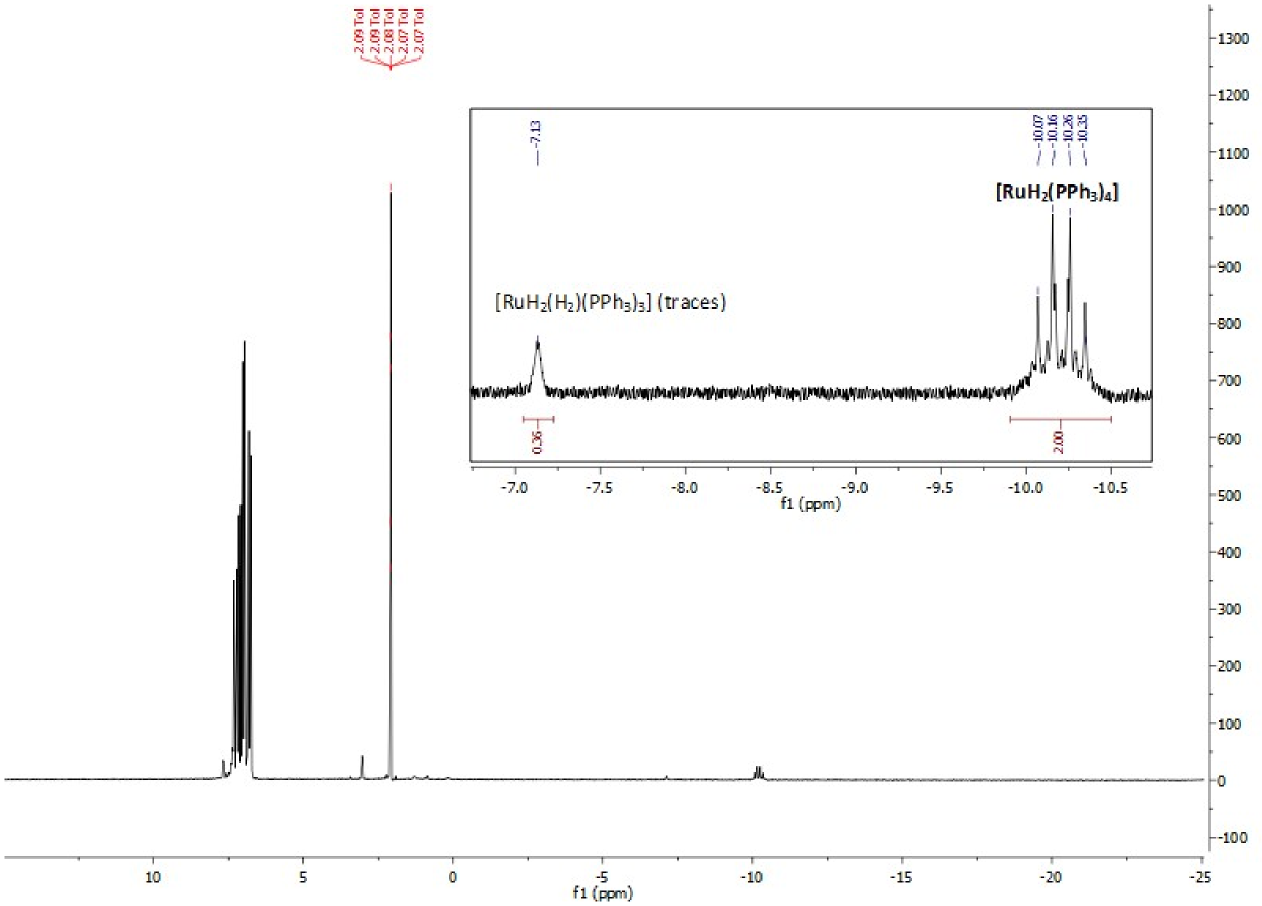

Figure S29 ^1H NMR (400 MHz; toluene-d_8) of [$RuH_2(PPh_3)_4$]

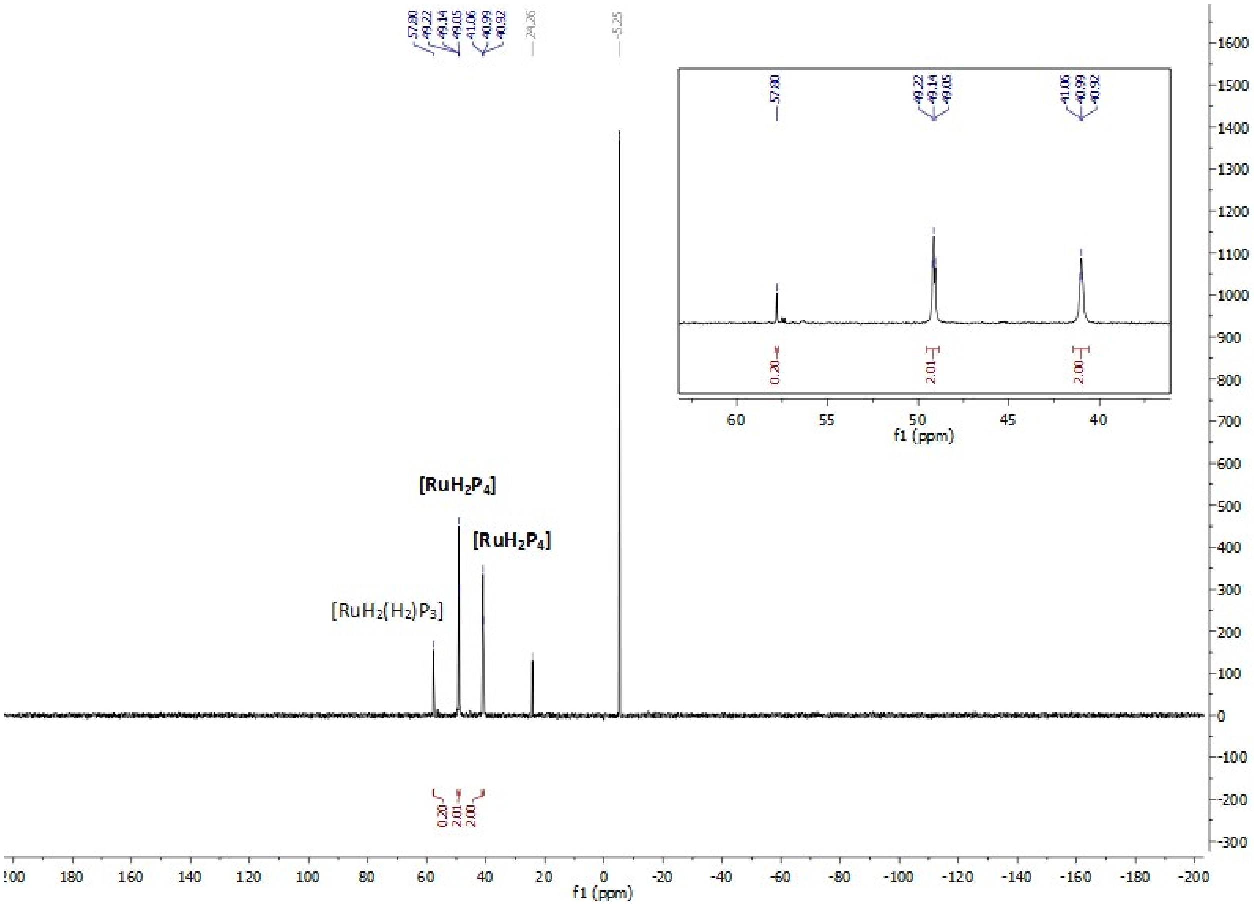

Figure S30 ^{31}P{^{1}H} NMR (400 MHz; toluene-d_8) of [RuH$_2$(PPh$_3$)$_4$]

2 Evidence for *o*-D incorporation into coordinated PPh_3

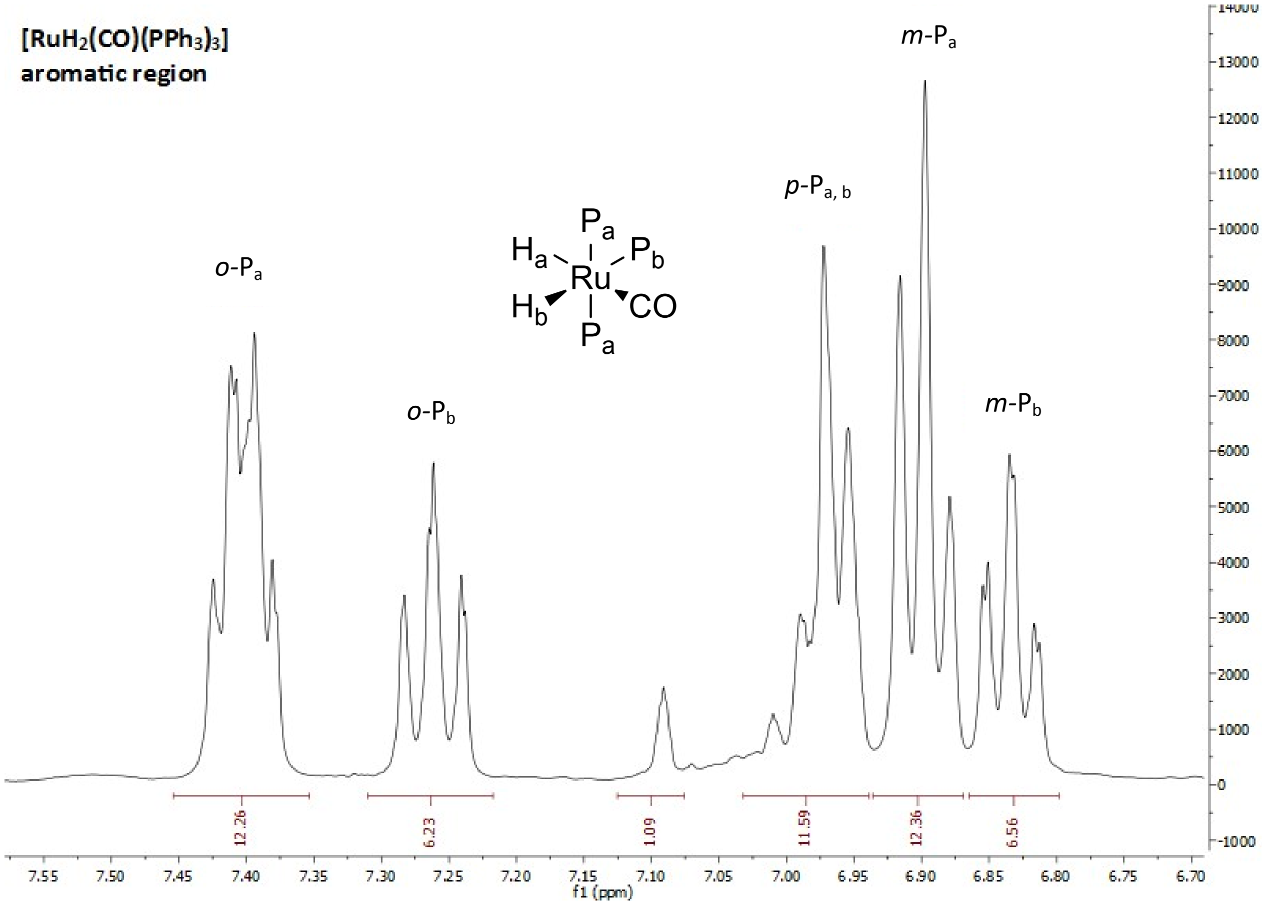

Figure S31 ^1H NMR (400 MHz; toluene-d_8); aromatic region of $[RuH_2(CO)(PPh_3)_3]$. The integration of the Ru-H signals was set at 1.0 for each

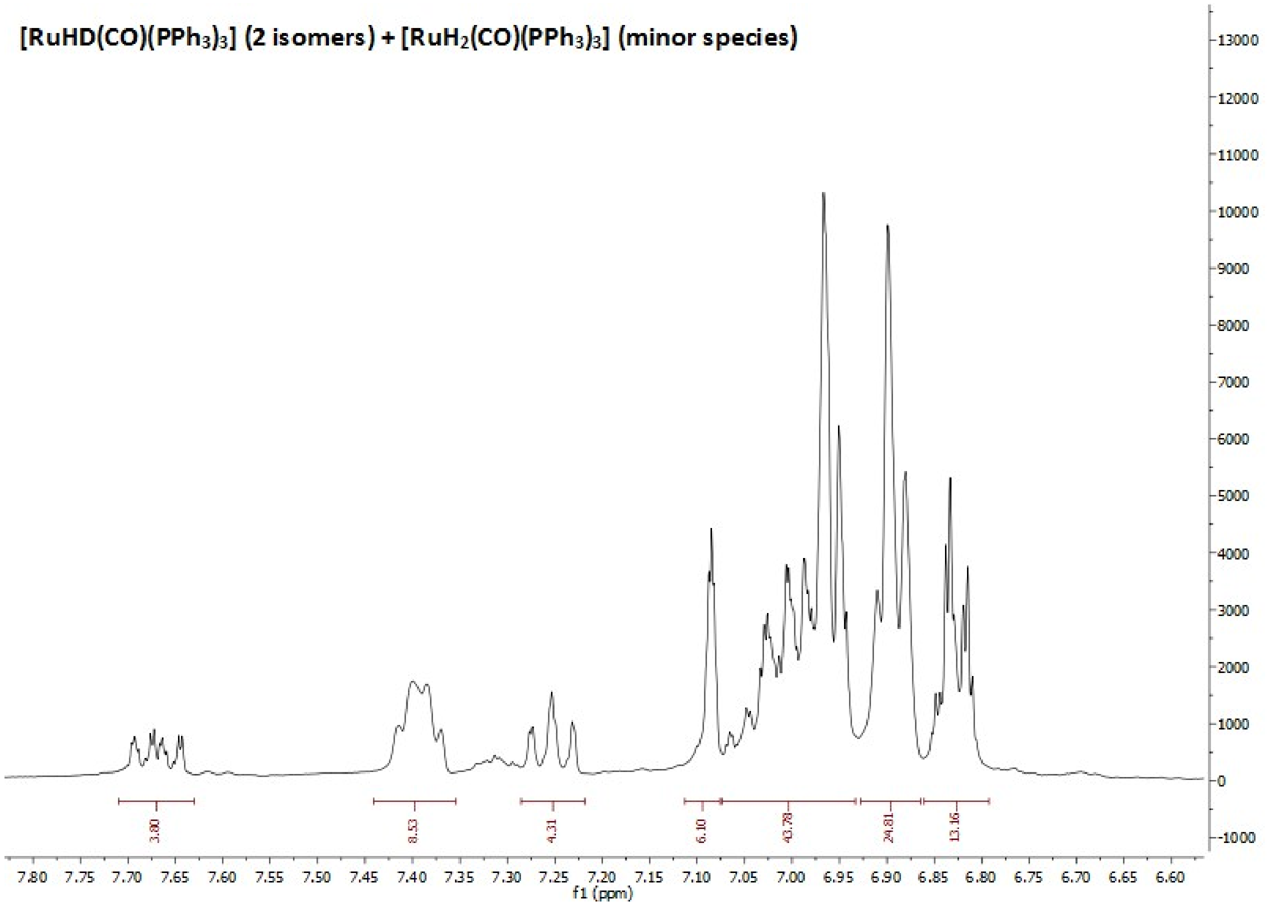

Figure S32 ^{1}H NMR (400 MHz; toluene-d_8); aromatic region of [RuHD(CO)(PPh$_3$)$_3$] (2 isomers) and [RuH$_2$(CO)(PPh$_3$)$_3$] (minor species). The Ru-H resonances were of the same intensity, which was set at 1.

The formation of [RuH$_4$P'$_3$] the reaction of [RuHClP$_3$] and CD$_3$OD/Na requires that H/D exchange occurs inti 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 ^{2}H NMR spectrum corresponding to deuteration in the *ortho* positions of both P$_a$ and P$_b$, broadening of the ^{31}P NMR signals and evidence for incorporation of D into PPh$_3$ and Ph$_3$PO from the ^{31}P 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 ^{1}H NMR spectra of the final products obtained from the reaction of [RuHClP$_3$] with MeOH/Na and with CD$_3$OD/Na. For the reaction using MeOH (Figure S31), the *ortho* and *meta* protons from P$_a$ and P$_b$ give well separated signals, whilst the *para* protons resonate in the same place. The *o* and *m* protons do not overlap with signals from PPh$_3$ or Ph$_3$PO, although the *p* protons do.

Looking at the two resonances from the *o* protons, in [RuH$_2$(CO)P$_3$], the resonances at δ 7.26 and 7.4 correspond to 6 (P$_b$) and 12 P$_a$) protons as expected. When the same product is made from CD$_3$OD/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 P$_b$, which is absent from the related resonance in Figures S31 and arises from H$_m$-D$_o$ 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/H$_2$ or that D can be incorporated directly into the ligand from the solvent.

This H/D exchange must occur during the conversion of [$RuHClP_3$] to [$RuH_4P'_4$] but the final product of this first step certainly only contains Ru-H. This is best seen from the hydride resonances of [$RuH_2(N_2)P_3$], which very clearly shows the H-H coupling of the dihydride with no enhancement of the low frequency peaks. The [RuH_2P_4] hydride resonance is second order (AA'MM'XX') and is identical whether the reaction is carried out in CH_3OH or CD_3OD. [$RuHDP_4$] would be expected to show a first order resonance approaching a doublet of quartets.

3 Hydride composition for the final product from reaction of [$RuHClP_3$] with Na/CD_3OD

Figure S 31 shows the integrated phenyl region of a final product [$RuH_2(CO)P_3$] obtained using [$RuHClP_3$] and Na/CH_3OH with each hydride signal set to have an integrated intensity of 1.0. Figure S32 is from a similar final product when using Na/CD_3OD 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 [$RuH_2(CO)P'_3$].

We then analyse the integrations of the *meta* H atoms on the phenyl rings since they are distinct, free from interference by $OPPh_3$ and should not have experienced any H/D exchange. For the non-deuterated sample (Figure S31) the *m* resonances from P_a and P_b integrate as 12.36 and 6.56 corresponding to 12 and 6 protons respectively. The similar integration for the deuterated sample (Figure S32) gives P_a 24.81 and P_b 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 [$RuH_2(CO)P'_3$] and of [$RuD_2(CO)P'_3$] 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 [$RuH_2(CO)P'_3$] (1). Since [$RuD_2(CO)P'_3$] must also be present in the same amount as [$RuH_2(CO)P'_3$]. We can simulate the observed integrations if the proportions of [$RuH_2(CO)P'_2$] : [$RuHD(CO)P'_3$] (each isomer) : [$RuD_2(CO)P'_3$] is 0.22: 0.28 : 0.28 : 0.22.