Formic Acid Selective Dehydrogenation Catalysed by Ruthenium Complexes bearing the Tripodal Ligands Triphos and NP_3

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Electronic Supplementary Information (ESI)

1. General Methods and Materials

Formic acid and *N,N*-Dimethyloctylamine were distilled in vacuum prior to use and stored under nitrogen. The formic acid to amine ratio was determined by ^{1}H NMR spectroscopy on a BrukerAvance 400 spectrometer. $Ru(acac)_3$ and HCO_2H/NEt_3 (5:2) mixture were purchased from commercial suppliers and used without further purification. Deuterated solvents for NMR measurements were purchased from commercial suppliers and stored onto activated 4A molecular sieves under N_2 before use. The variable temperature ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance 400 spectrometer (operating at 400.13, 100.61, and 161.98 MHz, respectively). Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^{1}H) or the deuterated solvent multiplet (^{13}C). $^{31}P\{^{1}H\}$ NMR were referenced to 85% H_3PO_4, with the downfield shift taken as positive.

2. Catalytic Tests

All catalytic experiments were carried out under an inert nitrogen atmosphere either in a flask heated by oil bath or in glass reactor thermostated by an external heating circuit, and repeated at least twice to check for reproducibility. The vessel was connected to a reflux condenser, which was connected to a set up of two manual burettes to measure the amounts of gas generated. The mixture of gas produced during the catalytic runs at 80 °C was analyzed by FTIR-ATR Shimadzu

IRAffinity-1 with a gas cell (path length 10 cm).

In the case of experiments run at 40 ºC (using the mixture HCO_2H/NEt_3 5:2), the automatic burette setup previously described in the literature was used.[1] The gas analysis was obtained by GC measurements on a gas chromatograph HP 6890N (permanent gases: Carboxen 1000, TCD, external calibration; amines: HP Plot Q, 30 m, FID) and a hydrogen sensor (Hach Ultra Analytics GmbH) was used for analysis of hydrogen. Typically, a ratio of hydrogen and carbon dioxide of 1:1 (±5%) was detected.

Typical procedure for the FA dehydrogenation tests at 80 °C. A solution of $HCO_2H/OctNMe_2$ (11:10, 2.73 mL, density at 25 °C = 0.894 mg mL^{-1}) was pre-warmed to 80 ºC in a three-necked round bottomed flask with a thermostated oil bath. The flask was purged with nitrogen before the starting reaction by addition of the solid catalyst. The development of gas was monitored by reading the values on the gas burette.

Typical procedure for recycling experiments at 80 °C. As soon as the gas volume evolution reached the theoretical value expected for 100% HCO_2H conversion, the apparatus was flushed with nitrogen to remove any traces of hydrogen and carbon dioxide. The remaining reaction mixture containing the catalyst and the amine, kept at 80 ºC, is reutilized as such for the following run by addition of neat HCO_2H (0.49 mL, 12.9 mmol) through a syringe.

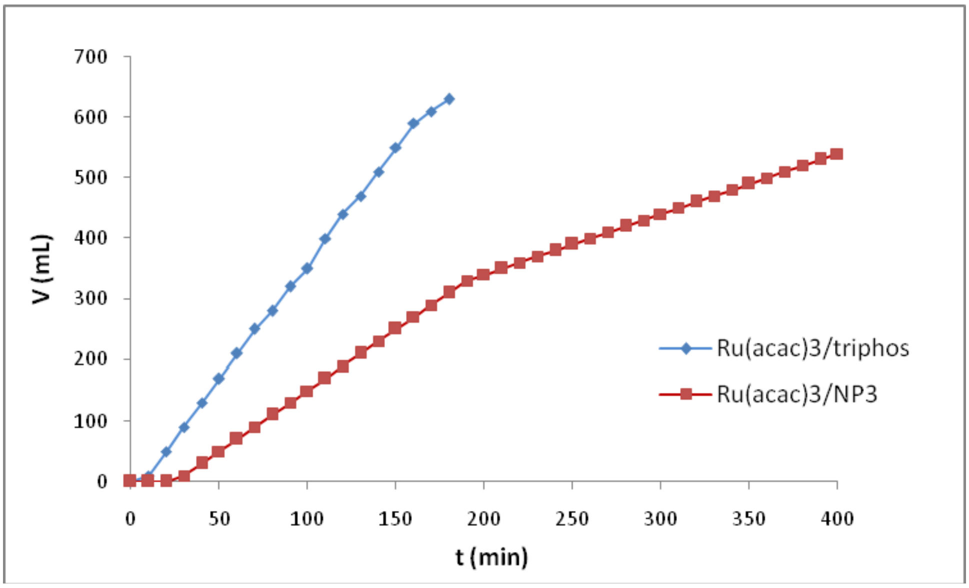

Figure S1. Reaction profiles of catalytic runs using the *in situ* procedures **i** and **ii**. Reaction conditions: Ru(acac)$_3$,12.9 µmol; ligand 12.9 µmol; $HCO_2H/OctNMe_2$ (11:10), 2.73 ml; FA:

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[1] A. Boddien, H. Junge, B. Loges and M. Beller, *ChemSusChem*, 2008, **1**, 751.

catalyst = 1000; 80 °C. Gas measured via manual gas burette and analyzed via FT-IR spectroscopy.

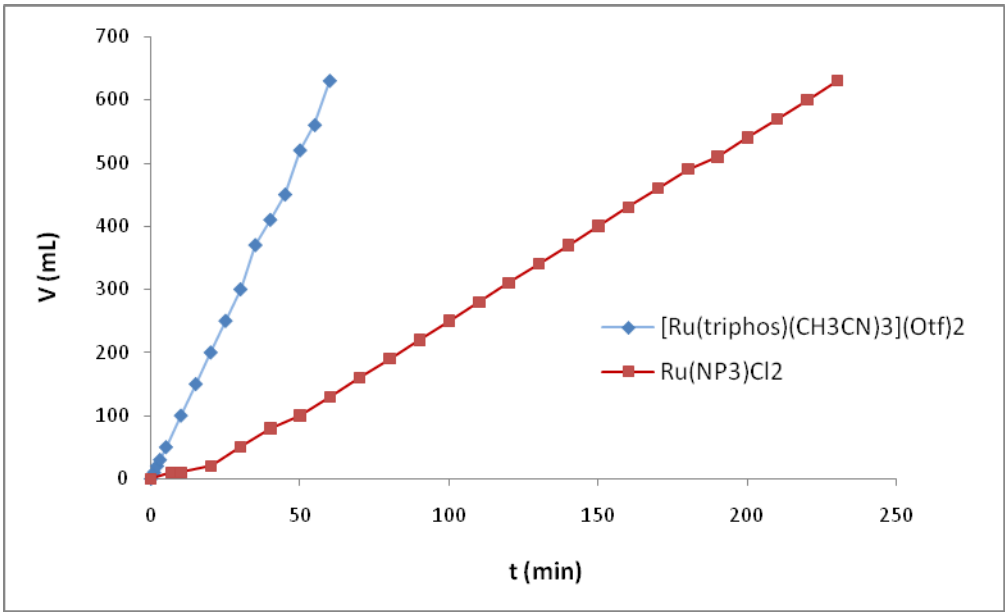


Figure S2. Reaction profiles of catalytic runs using complexes **1** and **2**. Reaction conditions: preformed catalyst 12.9 µmol; $HCO_2H/OctNMe_2$ (11:10), 2.73 ml; FA: catalyst = 1000; 80 °C. Gas measured via manual gas burette and analyzed via FT-IR spectroscopy.

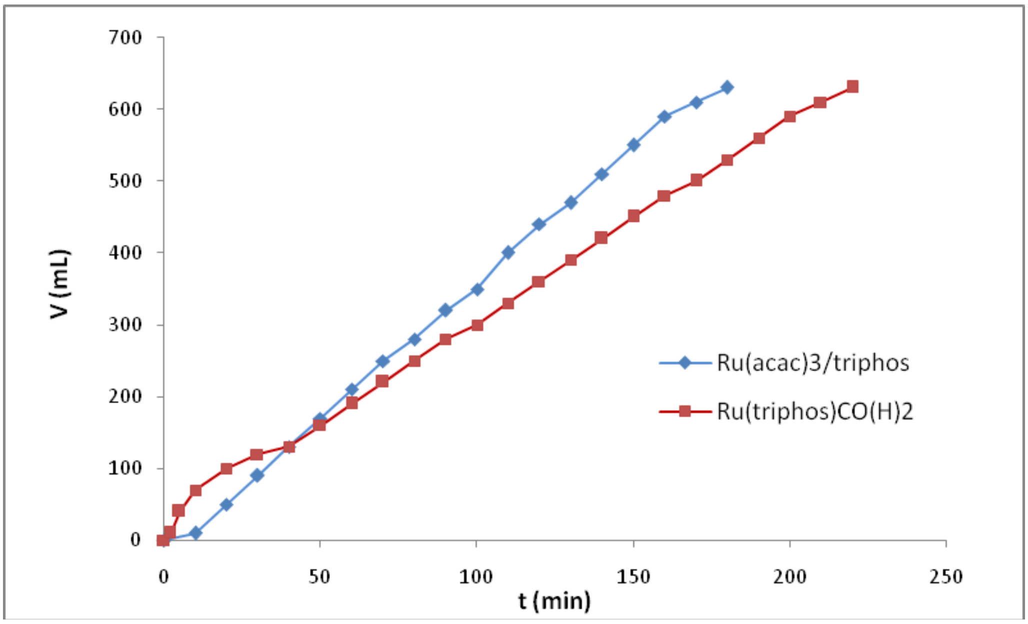


Figure S3. Reaction profiles of catalytic runs using the *in situ* procedures **i** and complex **3**. Reaction conditions: $Ru(acac)_3$, 12.9 µmol; ligand 12.9 µmol; preformed catalyst 12.9 µmol; $HCO_2H/OctNMe_2$ (11:10), 2.73 ml; FA: catalyst = 1000; 80 °C. Gas measured via manual gas burette and analyzed via FT-IR spectroscopy.

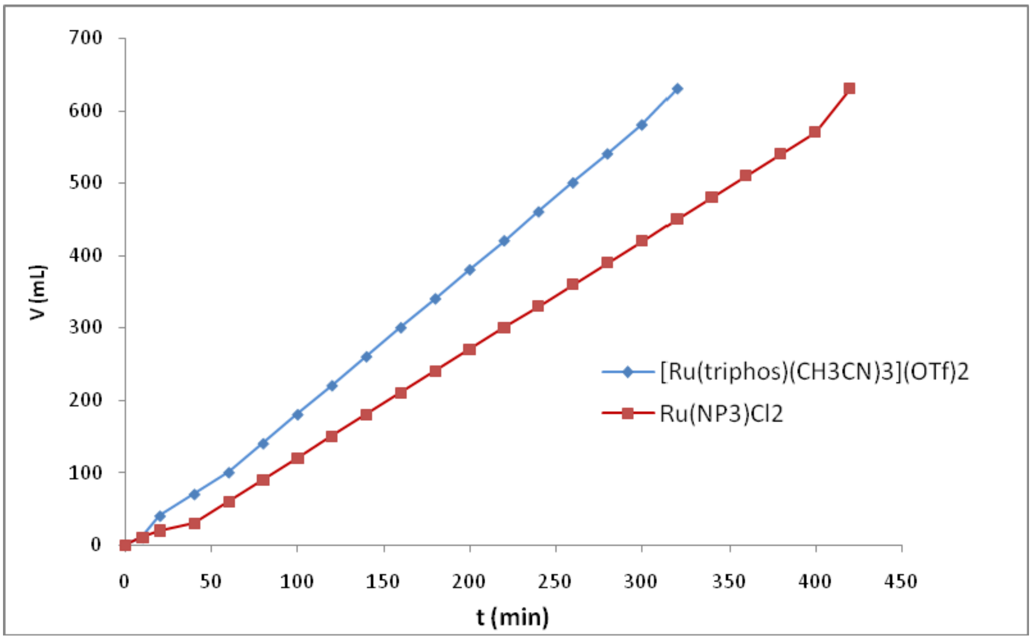


Figure S4. Reaction profiles of catalytic runs using complexes **1** and **2**. Reaction conditions: preformed catalyst 1.29 µmol; $HCO_2H/OctNMe_2$ (11:10), 2.73 ml; FA : catalyst = 10000; 80 °C. Gas measured via manual gas burette and analyzed via FT-IR spectroscopy.

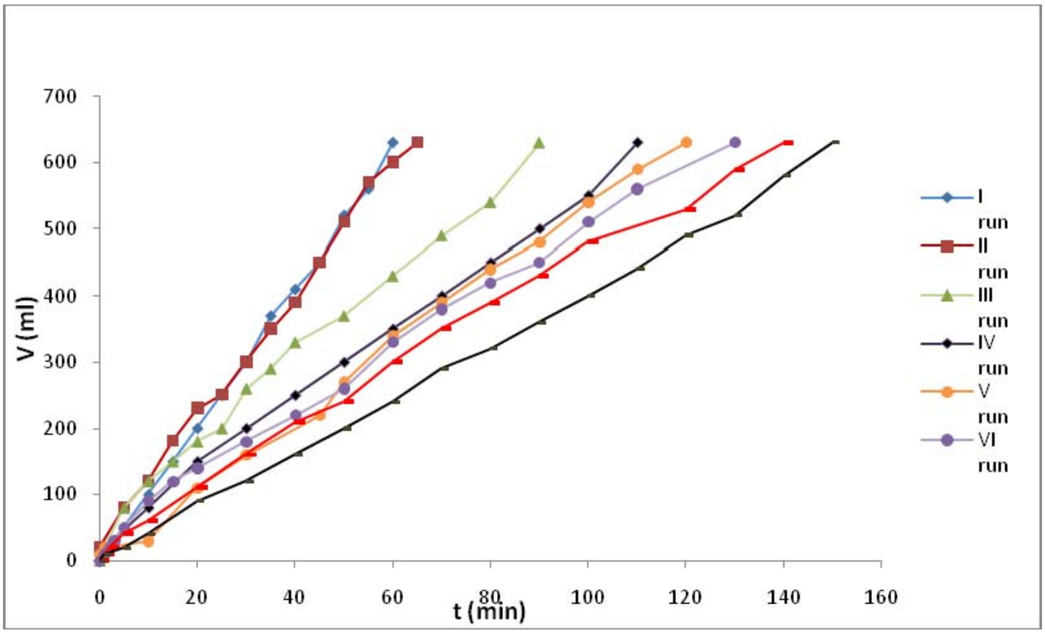


Figure S5. Reaction profiles of catalytic runs using complex **1** in the recycling experiment. Reaction conditions: preformed catalyst 12.9 µmol; $HCO_2H/OctNMe_2$ (11:10), 2.73 ml; FA: catalyst = 1000; 80 °C. Gas measured via manual gas burette and analyzed via FT-IR spectroscopy. 0.49 ml of formic acid were added to the reaction vessel after the first run.

3. Variable temperature NMR experiments

Typically, the NMR tube samples were prepared at 233 K (acetone-liquid nitrogen bath) under nitrogen by dissolving 20 mg of the Ru complex in 0.7 mL of deuterated solvent. One equiv of HCO_2NHEt_3 was then syringed into the cold tube, which was then inserted into the NMR probehead pre-cooled at 233 K. Subsequently, the probe was warmed slowly to room temperature in steps of 20 K each, and new sets of $^{31}P\{^1H\}$ and ^1H NMR data were collected at each step.

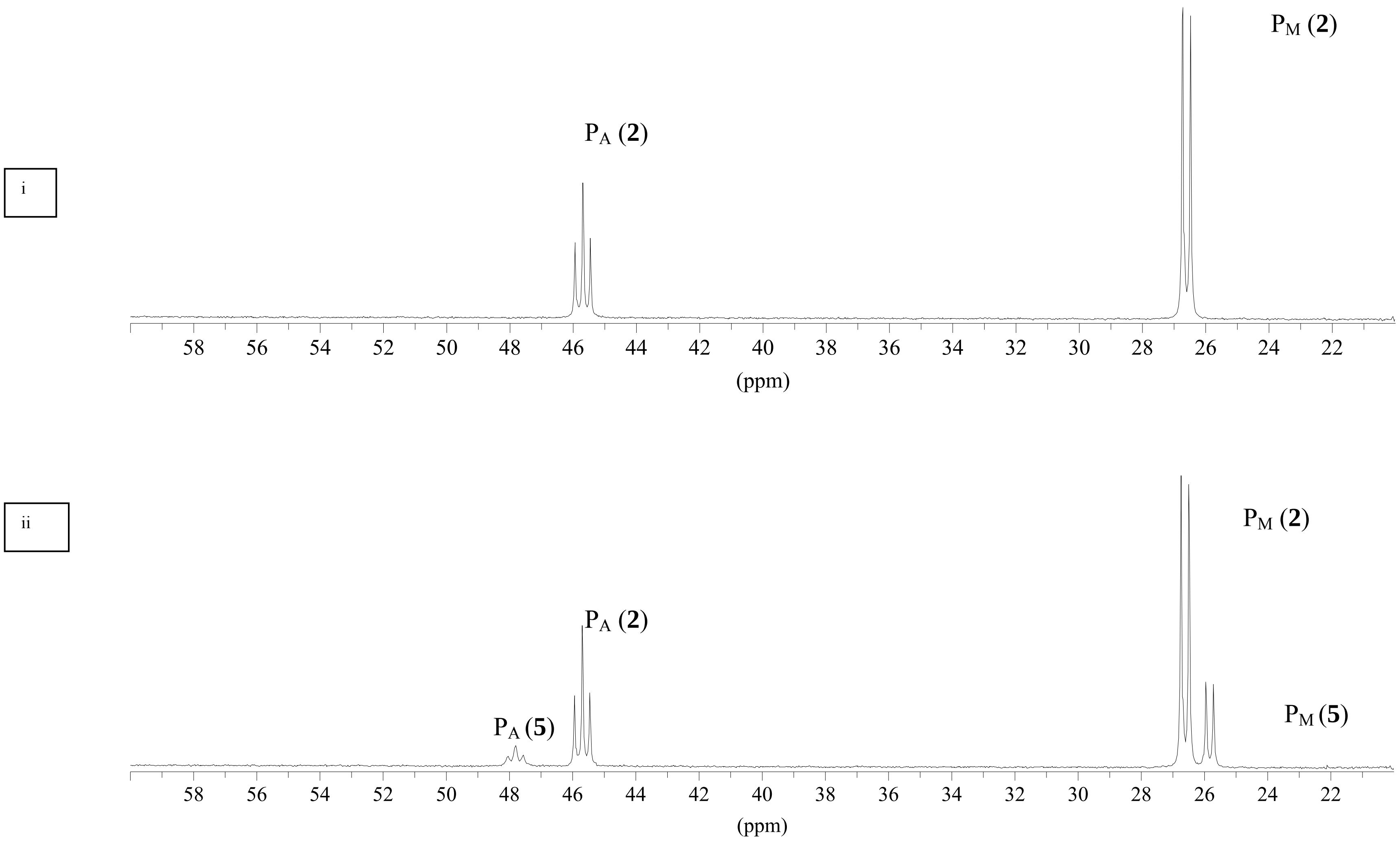
In the case of **2**, another equiv of HCO_2NHEt_3 was added at step (viii), and subsequently 5 equiv neat HCO_2H were added at step (xi), keeping the NMR tube at 233 K (acetone-liquid nitrogen bath). The sequence of spectra is shown below.

In the case of **1**, two different experiments were run, namely adding 1 or 2 equiv of HCO_2NHEt_3 together with 1 equiv of neat HCO_2H to the complex in acetone-d_6, keeping the NMR tube at 233 K (acetone-liquid nitrogen bath).

Finally a series of $^{31}P\{^1H\}$ and ^1H NMR experiments were also run for **1’** and **2** with the azeotrope HCO_2H/NEt_3 (5:2) instead of formate then formic acid, using a 5:1 ratio to the complexes at different temperatures, using the same heating sequence as for the experiments mentioned above.

The NMR spectra were collected in the temperature range 233-293 K in the case of **2** (CD_2Cl_2) or 213-313K in the case of **1** (acetone-d_6).

Figure S6. Variable temperature $^{31}P\{^{1}H\}$ NMR spectra of the reaction between **2** and HCO_2NHEt_3. All the octahedral Ru(NP_3) complexes exhibit a first order AM_2 spin system. i) **2**, 233 K; ii) **2** + 1 equiv. HCO_2NHEt_3, 233 K; iii) as ii, 253 K; (iv) as ii, 273 K; v) as ii, 283 K; vi) as ii, 293 K; vii) as ii, 273 K; viii) as ii, 233 K; ix) as ii, 213 K; x) addition of 1 equiv. HCO_2NHEt_3, 233 K; xi) as x, 293 K; xii) as x, 233 K; xiii) addition of 5 equiv. HCO_2H, 233 K; xiv) as xiii, 293 K.



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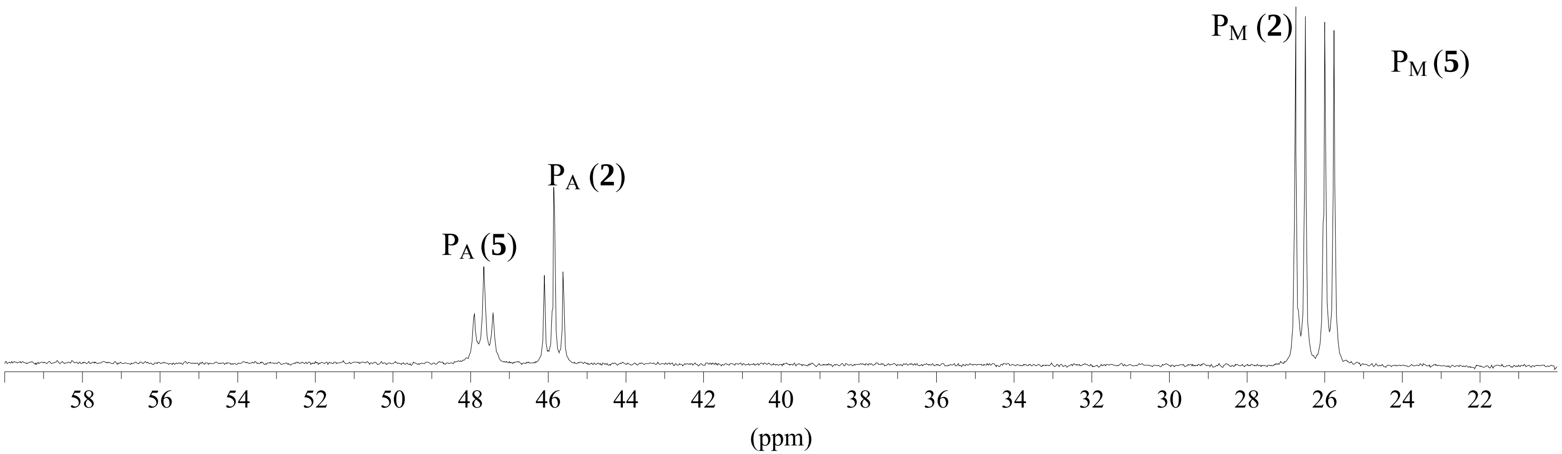
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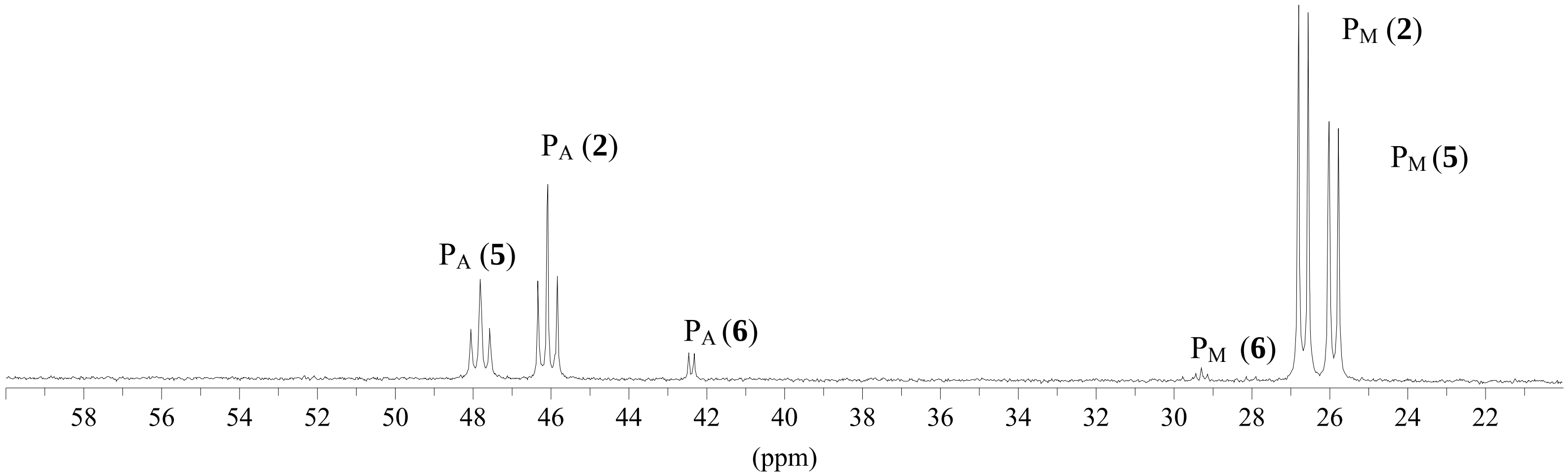
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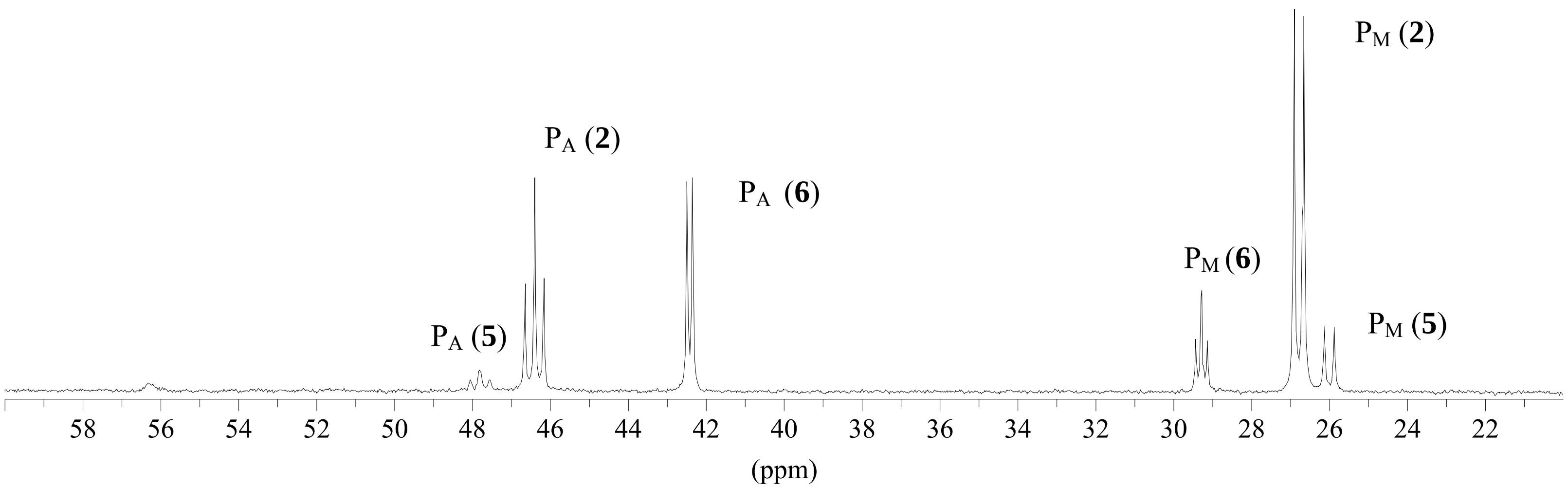
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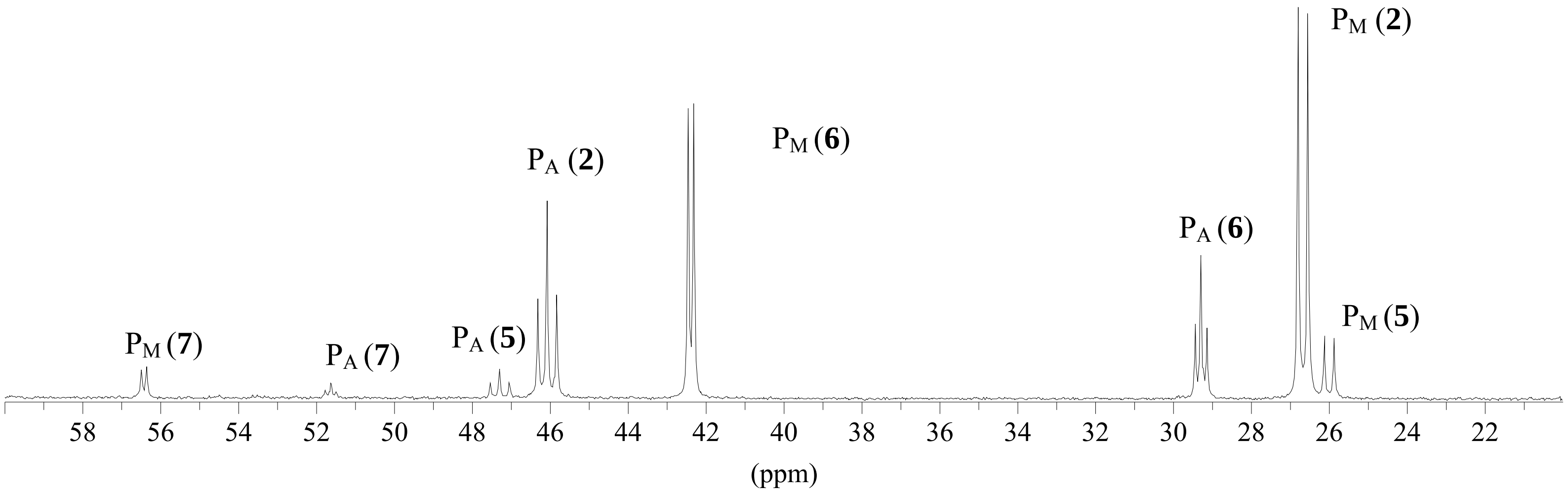
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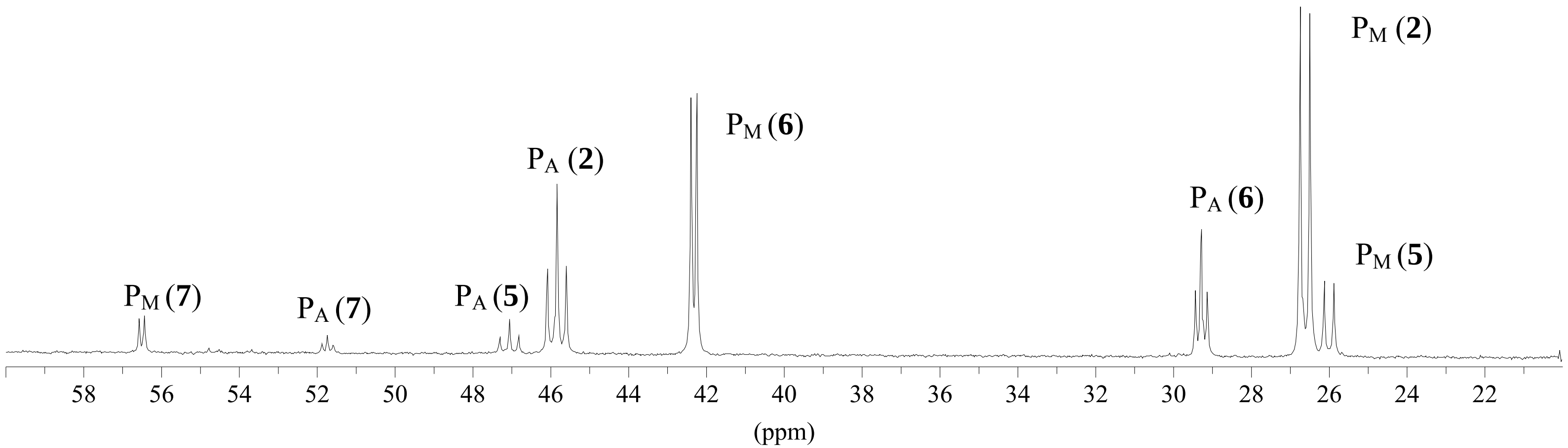
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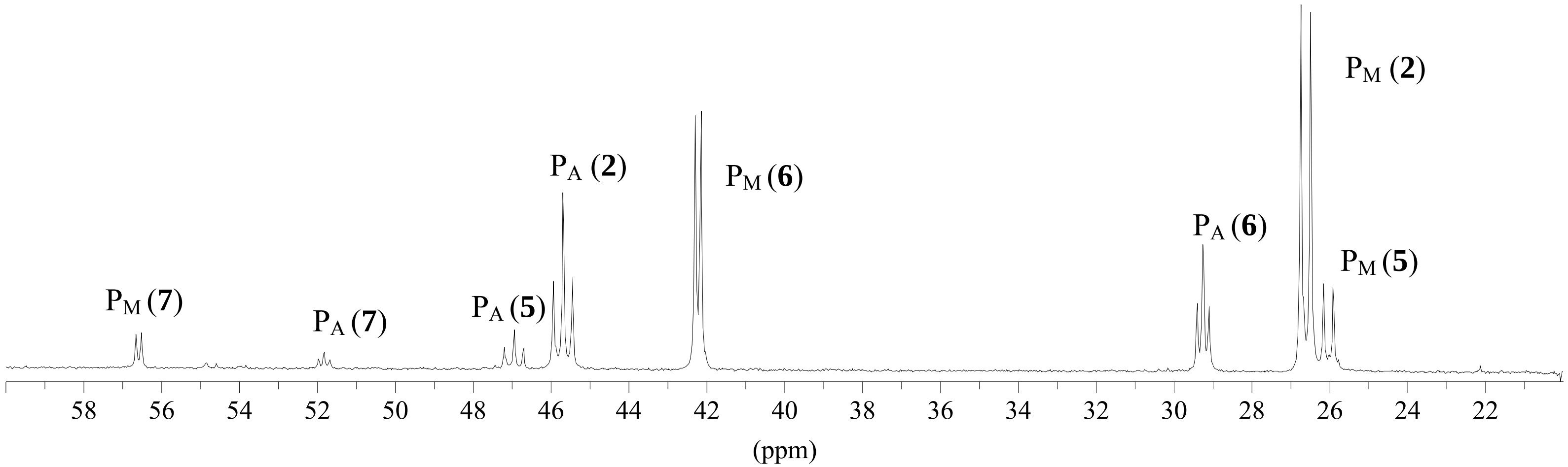
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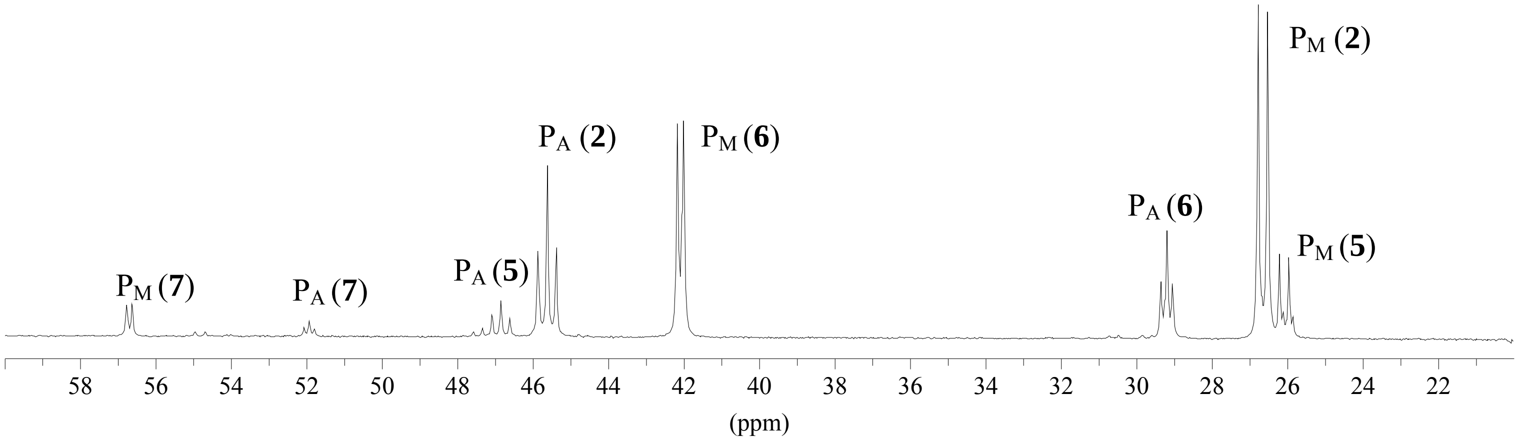
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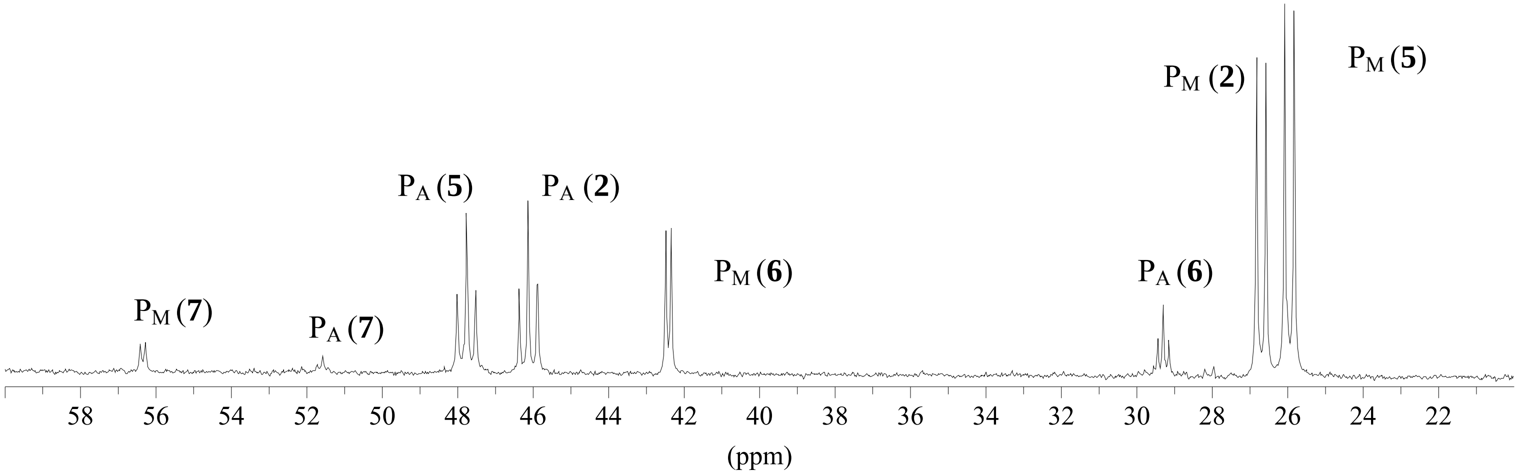
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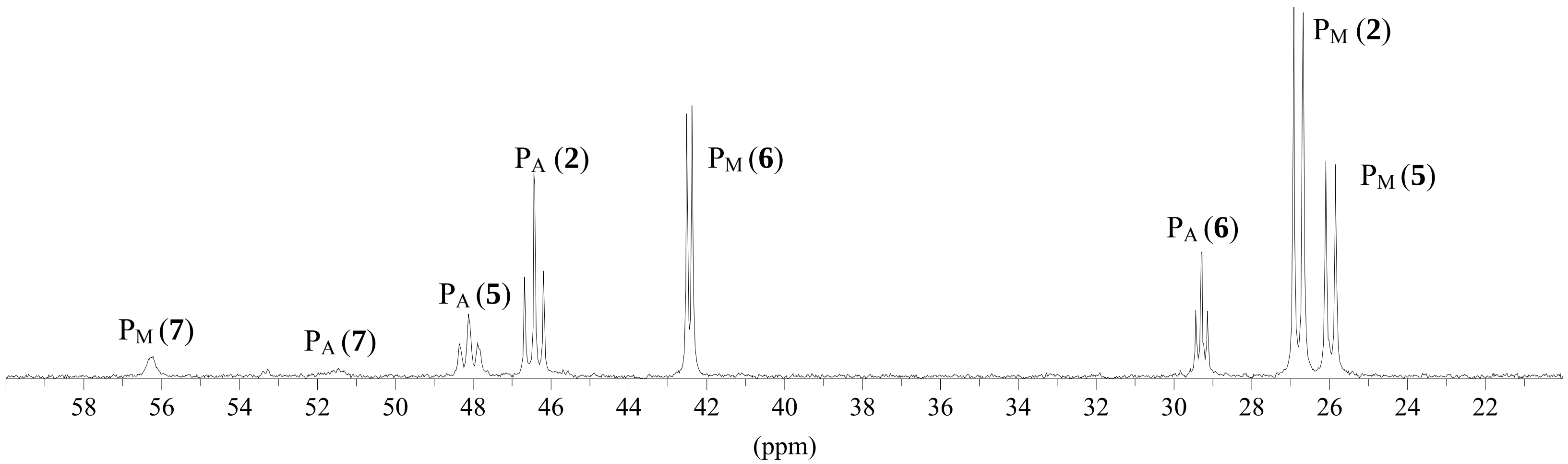
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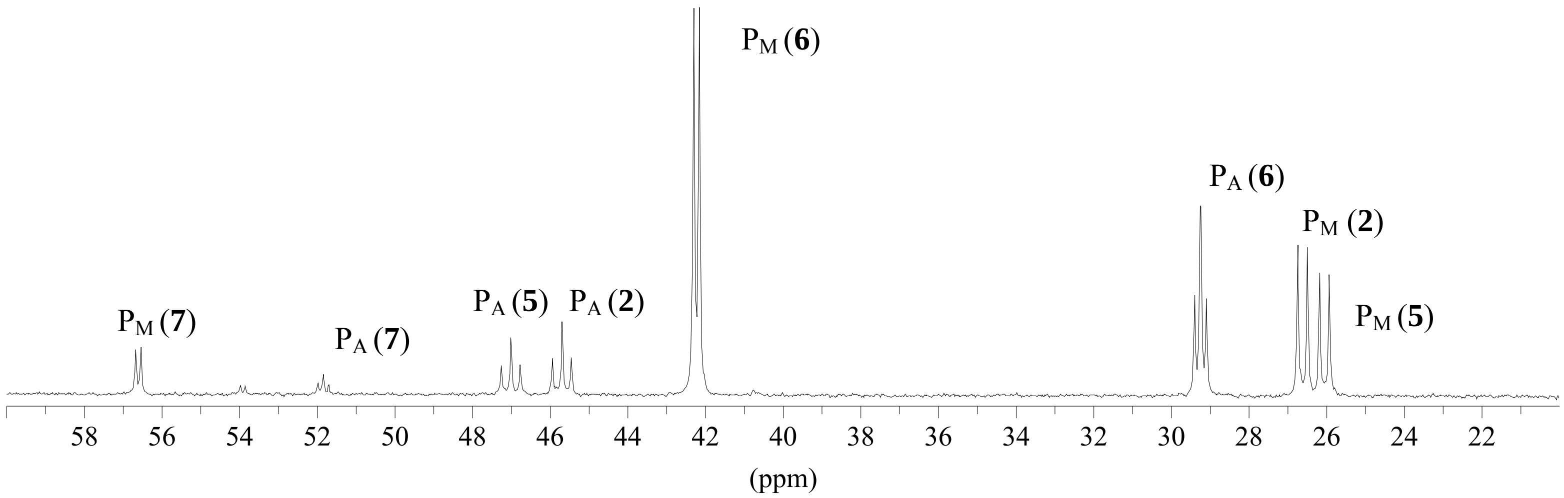
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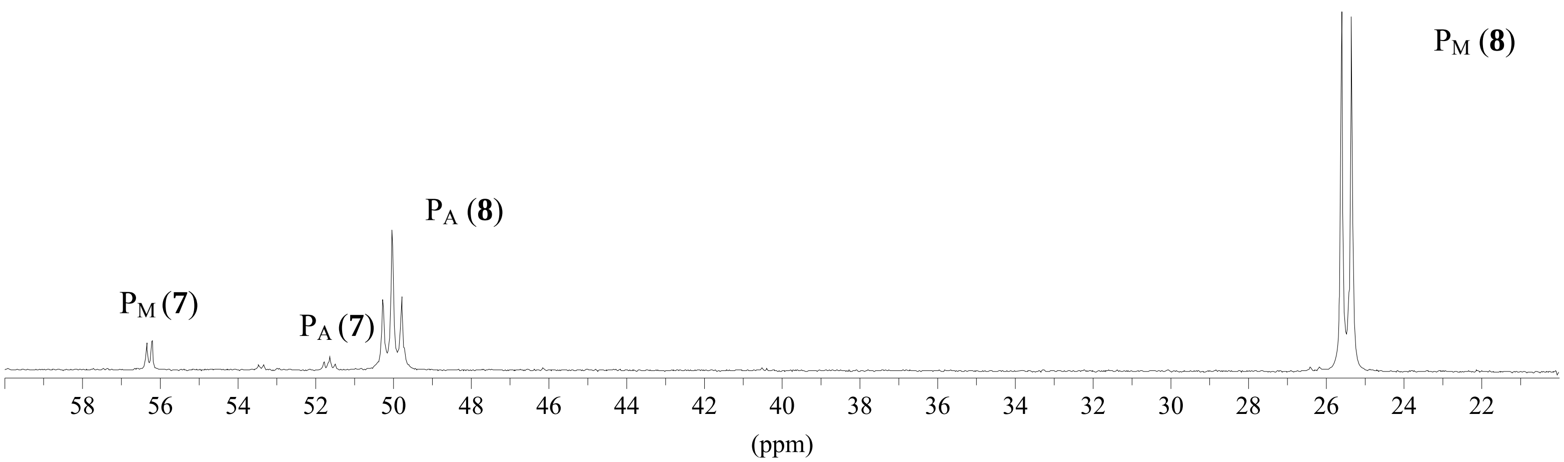
xiii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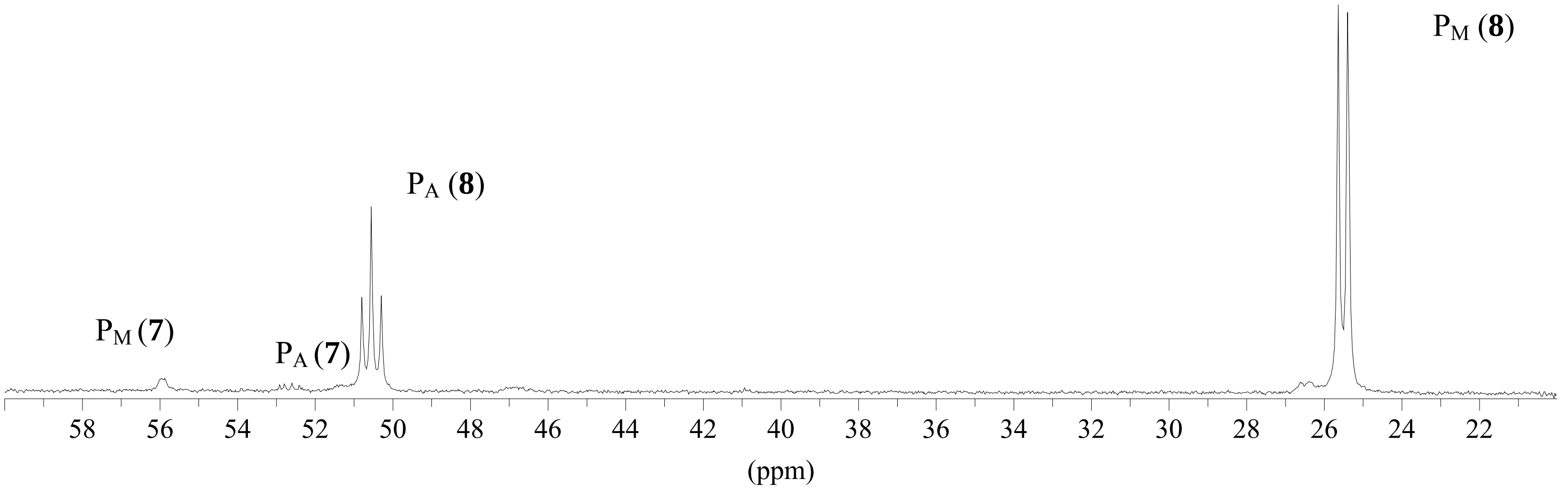
xiv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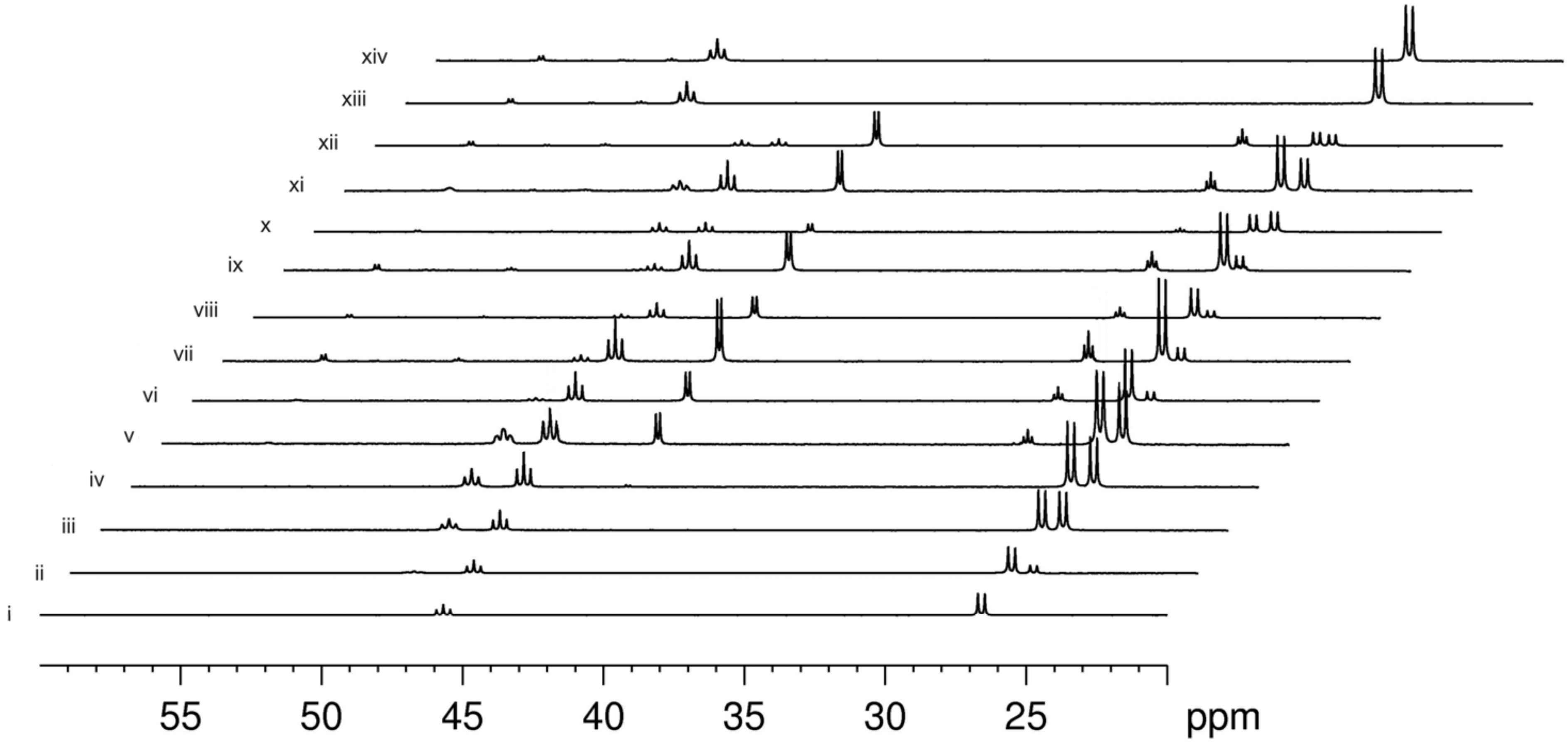

Figure S7. Variable temperature $^{31}P\{^{1}H\}$ NMR spectra of the reaction between **2** and HCO_2NHEt_3, overlay view of the experiment. i) **2**, 233 K; ii) **2** + 1 equiv. HCO_2NHEt_3, 233 K; iii) as ii, 253 K; (iv) as ii, 273 K; v) as ii, 283 K; vi) as ii, 293 K; vii) as ii, 273 K; viii) as ii, 233 K; ix) as ii, 213 K; x) addition of 1 equiv. HCO_2NHEt_3, 233 K; xi) as x, 293 K; xii) as x, 233 K; xiii) addition of 5 equiv. HCO_2H, 233 K; xiv) as xiii, 293 K.

Isolation of [Ru(κ^3-triphos)(CO)(H)$_2$] (3) from the reaction of 1' and sodium formate in methanol

To a solution of **1'** (70 mg, 6.10 x 10^{-2} mmol) in MeOH (10 mL), HCOONa (42 mg, 6.0 x 10^{-1} mmol) was added under nitrogen in a Schlenk-type round bottom flask and heated to reflux conditions for 2 h. A yellow microcrystalline precipitate formed and was filtered, washed with cold MeOH and dried under vacuum. Yield 10%. ^{31}P{^{1}H} and ^{1}H NMR data were found to be coincident with literature values.[2]

Reaction of [Ru(κ^3-triphos)(MeCN)$_3$](PF$_6$)$_2$ (1') with CO (1 atm)

A solution of **1'** (20 mg, 1,176 x 10^{-2} mmol) was dissolved in 0.6 mL of acetone-*d*$_6$ under nitrogen into a screw-cap NMR tube. The tube was placed in a ice bath and CO (1 atm) was bubbled into the solution for 15 min. The tube was then allowed to warm up to room temperature and a set of ^{31}P{^{1}H} and ^{1}H NMR spectra were collected. The initial ^{31}P{^{1}H} singlet at 27.0 ppm due to **1'** disappeared leaving two AM$_2$ sets of signals composed (**I**) of a doublet at 23.8 ppm ($^2J_{PP}$ = 40 Hz) and a triplet at 2.0 ppm and (**II**) of a triplet at 19.2 ppm ($^2J_{PP}$ = 32 Hz) and a doublet at 4.2 ppm, in *ca*. 8:1 ratio. In the corresponding ^{1}H NMR spectrum both signals of coordinated (2.49 ppm) and free MeCN (2.18 ppm) were visible. The tube was removed from the NMR probehead and warmed to 40 °C in a water bath for 2h, after which another set of NMR spectra were collected. In the ^{31}P{^{1}H} spectrum it could be observed that the ratio **I**:**II** changed to *ca*. 1:10, while no other sets of signals appeared. In parallel the ^{1}H NMR signal due to free MeCN increased in intensity while the signal due to Ru-coordinated MeCN decreased.

On the basis of these observations and literature data,[3] we attribute the signals due to **I** to [Ru(κ^3-triphos)(MeCN)$_2$(CO)]$^{2+}$ and those due to **II** to [Ru(κ^3-triphos)(MeCN)(CO)$_2$]$^{2+}$.

At this point HCO$_2$NHEt$_3$ (1 equiv) was added to the mixture at room temperature. It was possible to observe complete disappearance of the signals due to **I,** the presence of **II** and formation of two new AM$_2$ species, (**III**) characterised by a triplet at 24.8 ppm ($^2J_{PP}$ = 34 Hz) and a doublet at 0.2 ppm, and (**IV**) showing a doublet at 18.3 ppm ($^2J_{PP}$ = 36 Hz) and a triplet at 8.5 ppm. In the corresponding ^{1}H NMR spectrum, signals due to coordinated formate (8.28 ppm) and a weak high field doublet of triplets centred at -6.2 (dt, $^2J_{HP(trans)}$ = 81, $^2J_{HP(cis)}$ 15 Hz, RuH) were present.

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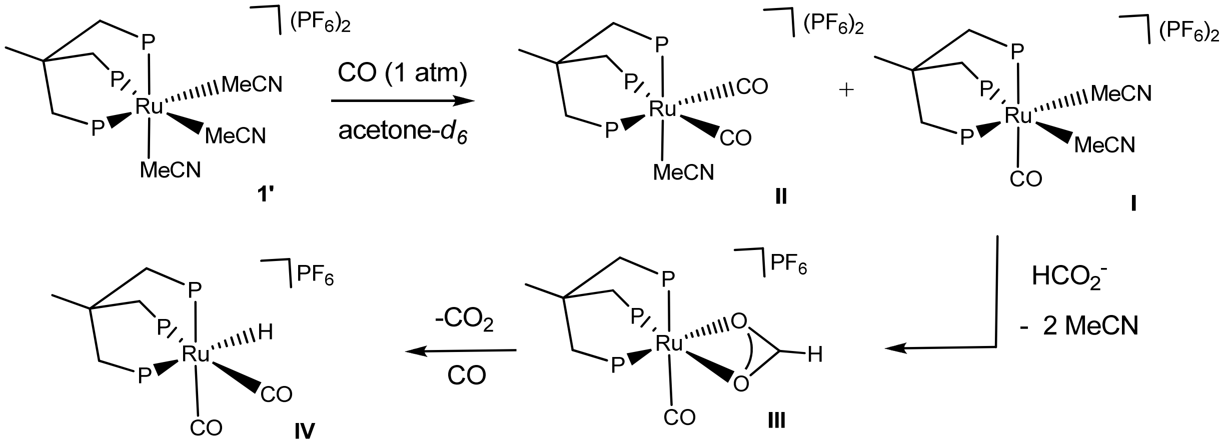
[2] V. I. Bakhmutov, E. V. Bakhmutov, N. V. Belkova, C. Bianchini, L. M. Epstein, D.Masi, M. Peruzzini, E. S. Shubina, E. V. Vorontsov and F. Zanobini, *Can. J. Chem*., 2001, **79**, 479.

[3] L. F. Rhodes, C. Sorato, L. M. Venanzi and F. Bachechi, *Inorg. Chem*., 1988, **27**, 604; D. Michos, X.-L. Luo and R. H. Crabtree, *Inorg. Chem.* 1992, **31**, 4245.

Finally, neat HCOOH (1 equiv) was added at room temperature, apparently causing no further changes. The solution was dried under vacuum. The FT-IR spectrum of the solid in nujol mull showed the presence of ν_{CO} stretching bands at 2103, 2078 and 2043 cm^{-1}.

Thus, we propose the attribution of the signals due to **III** to $[Ru(\kappa^3\text{-triphos})(\eta^2\text{-OOCH})(CO)]^+$ and of the signals due to **IV** to $[Ru(\kappa^3\text{-triphos})(H)(CO)_2]^+$. The proposed reaction pathway can be visualised in Scheme S1 below.



Scheme S1