

Electronic Supplementary Information

Ruthenium Catalyzed Hydrogen Production from Formaldehyde-Water Solution

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Materials and Methods

Chemicals. All experiments were carried out using the chemicals of higher purity purchased from Sigma Aldrich, TCI and Alfa Aesar unless otherwise specified. Ru(II)-arene complexes were synthesized according to previous reports using, Ru(II)-arene precursors, [$\{\eta^6\text{-C}_{10}\text{H}_{14}\}\text{RuCl}_2\}_2$].^{S1}

Instrumentation. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra are recorded at 298 K using D₂O or CDCl₃ as the solvent on a Bruker Avance 400 spectrometer. Tetramethylsilane (TMS) is used as an external standard and the chemical shifts in ppm are reported relative to the centre of the singlet at 7.26 ppm for CDCl₃ and 4.75 ppm for D₂O in ¹H NMR, and to the centre of the triplet at 77.0 ppm for CDCl₃ in ¹³C NMR. Suitable single crystals of complex **[Ru]-1A** and **[Ru]-3** subjected to single-crystal X-ray structural studies using Bruker APEX SMART D8 Venture CCD diffractometer and Agilent Technologies Supernova CCD system respectively. Coupling constant (*J*) values are reported in hertz (Hz), and the splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); br. (broad). ESI (positive mode), and high-resolution mass spectra (HRMS) are recorded on a micro TF-Q II mass spectrometer. The GC-TCD analyses are performed on a Shimadzu GC-2014 system using a shin carbon-ST packed column.

TON and TOF calculation:

TON calculations are performed using formula-

$$\text{TON} = \eta(\text{gas produced in mmol}) / \eta(\text{catalyst used})$$

for TOF calculation-

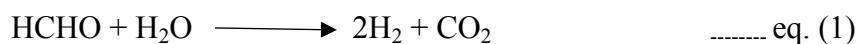
$$\text{TOF} = \text{TON} / \text{time (h)}$$

e.g. for the bulk reaction the total gas produced was 1580 mL (64.5 mmol) from 60 mmol of formaldehyde over 0.005 mmol of catalyst.

$$\text{TON} = 64.5/0.005$$

So, the calculated TON of the reaction is 12905.

Recyclability experiment: Initially, aq. formaldehyde (1.5 mol L⁻¹, 1.07 mL), **[Ru]-1** precursors [$\{(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2\}_2$] (13 μmol), and ligand (**L6**) (26 μmol) are mixed in two necked test-tube equipped with a condenser and water displacement setup. The reaction mixture is stirred at 95 °C on an oil bath. For subsequent catalytic run 1.5 mmol of formaldehyde added in each cycle and release of gas was monitored by water displacement process. Equivalence of gas calculated using the eq. (1)



So, 1 equivalent of formaldehyde produced the 3 equivalent of gas.

Mercury poisoning experiment. A two-neck test tube equipped with a condenser was charged with ruthenium-*p*-cymene dimer (**[Ru]-1**, 0.013 mmol), ligand (**L6**, 0.026 mmol), aqueous formaldehyde (13.55 mmol) and Hg(0) (250 mg). The resulting content was stirred at room temperature for 2 h followed by heating at 95 °C, and the reaction progress was monitored.

Single-crystal X-ray diffraction studies: X-ray suitable single crystals of **[Ru]-3** and **[Ru]-1A** are grown by diffusion of diethyl ether into methanol solution of complexes. Solid state structure of **[Ru]-3** is obtained using a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer while the **[Ru]-1A** is collected using a Bruker APEX SMART D8 Venture CCD diffractometer. Data were collected at 293(2) K using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The strategy for the data collection is evaluated using the CrysAlisPro CCD software. The data are collected using the standard ‘phi-omega’ scans techniques, and are scaled and reduced using CrysAlisPro RED software. The structures are solved by direct methods using SHELXS-97 and SHELXS-2014, and refined using full matrix least-squares with SHELXL-97 and SHELXS-2014, refining on F².^{S2} The positions of all the atoms are obtained by direct methods. All non-hydrogen atoms are refined anisotropically. The remaining hydrogen atoms are placed in geometrically constrained positions, and refined with isotropic temperature factors, generally 1.2 U_{eq} of their parent atoms. The crystal and refinement data are summarized in Tables S1 and Table

S4 for **[Ru]-1A** and **[Ru]-3** respectively. Selected bond lengths and bond angles are summarized in Tables S2-S3 and Table S5-S6 for **[Ru]-1A** and **[Ru]-3** respectively. CCDC deposition numbers of the complex **[Ru]-3** and **[Ru]-1A** is 1994921 and 1994922 respectively. These data are freely available at www.ccdc.cam.ac.uk (or can be procured from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

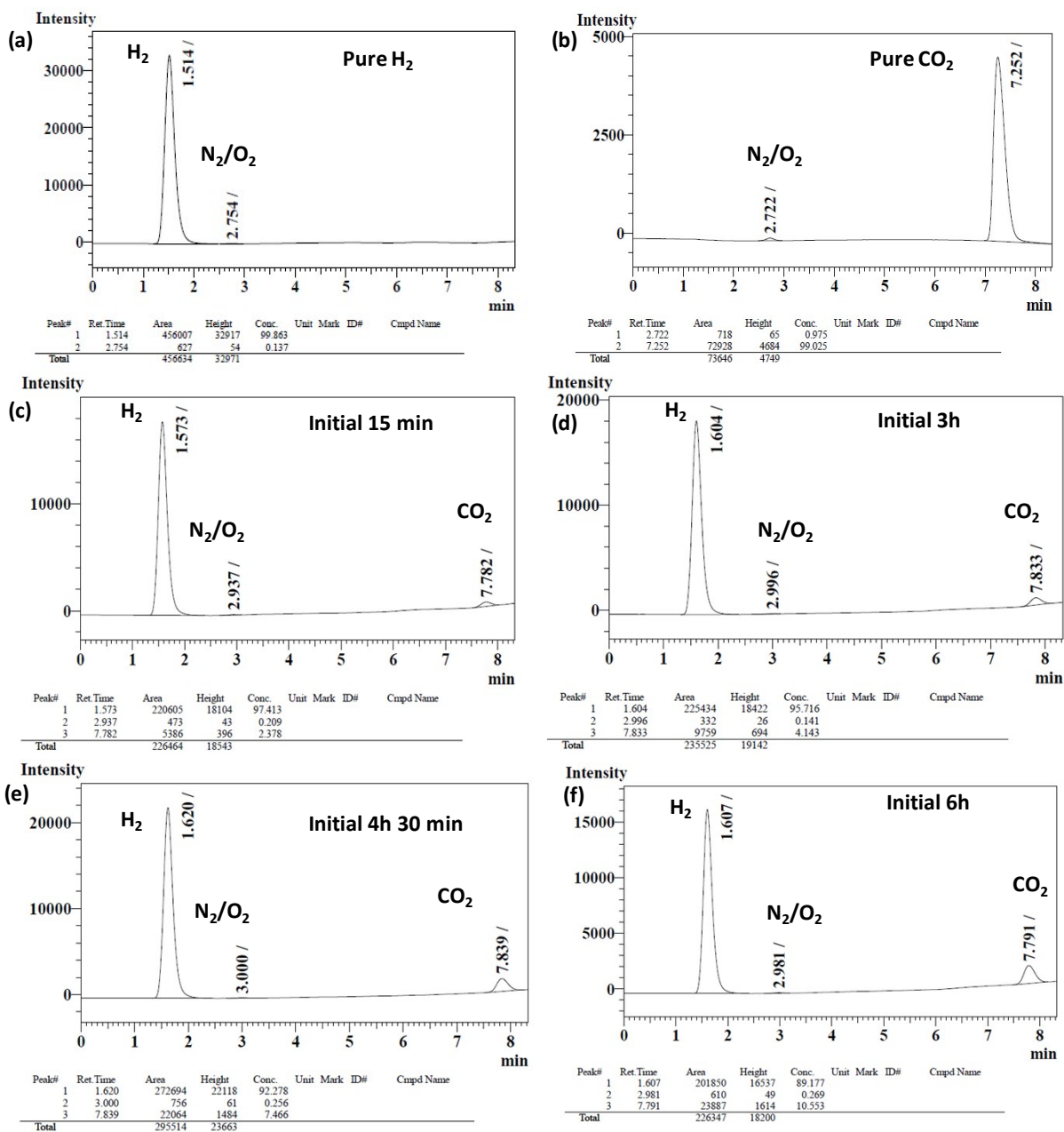


Fig. S1 GC- TCD of (a) H₂ gas (Pure sample) (b) CO₂ gas (Pure sample) and (c-f) gas evolved from aqueous formaldehyde at different time interval of the catalytic reaction. (Reaction condition: aq. formaldehyde (13.55 mmol, 1.07 mL), catalyst [Ru]-1 (13 μmol) and ligand L6 (26 μmol) at 95 °C) (Analyses performed using Argon as carrier gas)

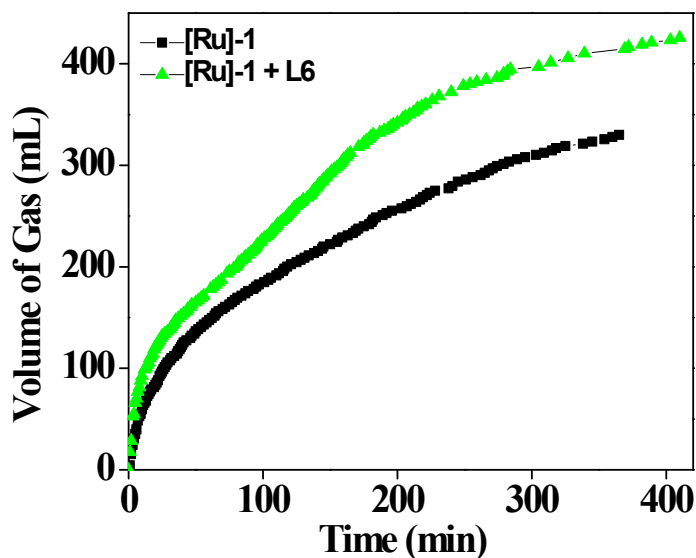


Fig. S2 Initial time course for hydrogen production from aqueous formaldehyde. (Reaction condition: aq. formaldehyde (13.55 mol L^{-1} , 1.07 mL), catalyst **[Ru]-1** ($13 \text{ }\mu\text{mol}$) and ligand **L6** ($26 \text{ }\mu\text{mol}$) at $95 \text{ }^\circ\text{C}$).

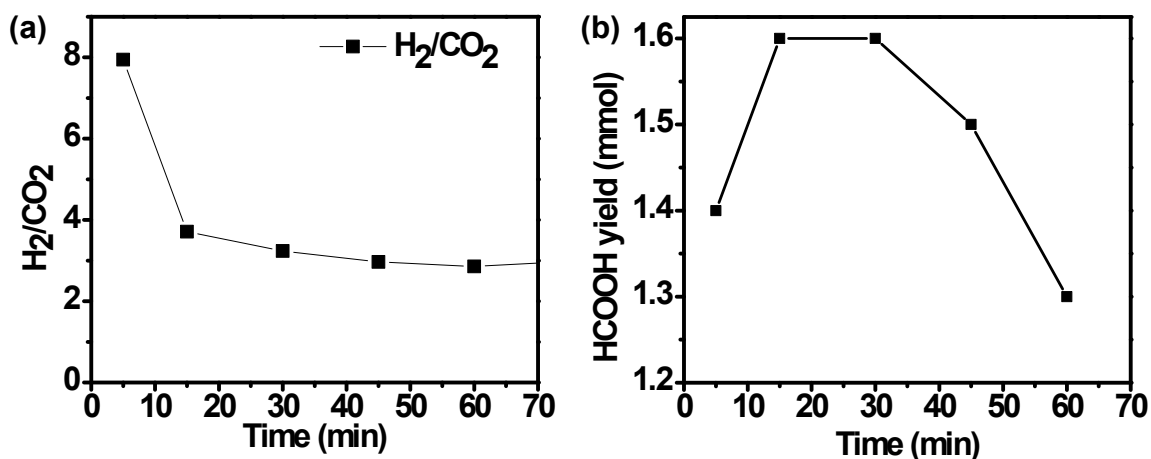


Fig. S3 (c) The H_2/CO_2 ratios in the produced gas mixture and (d) ^1H NMR yield of HCOOH during the catalytic dehydrogenation of aqueous formaldehyde in the initial 1 h of the reaction. (Reaction condition: aq. formaldehyde (13.55 mol L^{-1} , 1.07 mL), catalyst **[Ru]-1** ($13 \text{ }\mu\text{mol}$) and ligand **L6** ($26 \text{ }\mu\text{mol}$), at $95 \text{ }^\circ\text{C}$. HCOOH yield was determined using dioxane as an internal standard).

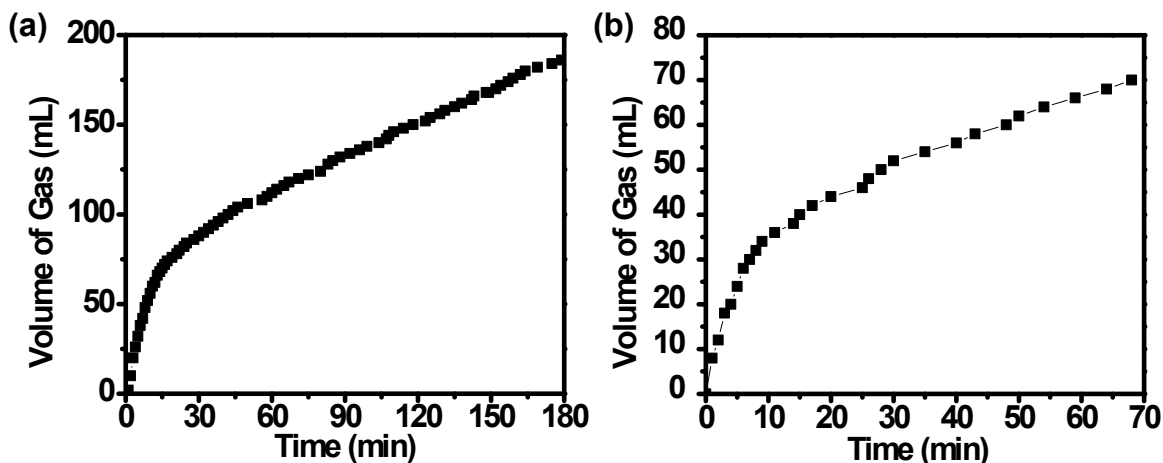


Fig. S4 Time course for hydrogen production from formic acid (a) 13.55 mol L⁻¹, 1.07 mL and (b) 1.5 mol L⁻¹, 1.07 mL over catalyst **[Ru]-1** (13 μmol) in the presence of ligand **L6** (26 μmol) at 95 °C.

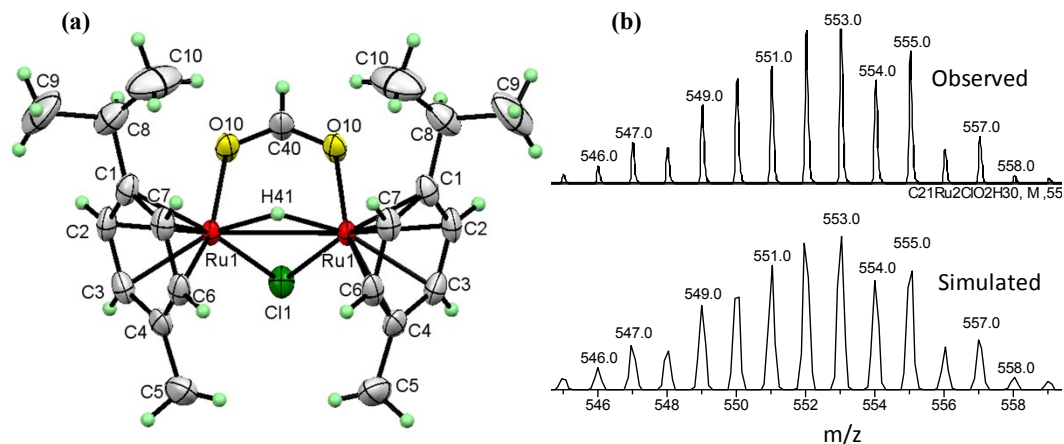


Fig. S5 (a) X-ray crystal structures of the complex **[Ru]-1A** (with 30% ellipsoid probability and counter anion PF₆⁻ is omitted for the sake of clarity) and (b) ESI-MS of the complex **[Ru]-1A**.

Table S1 Crystal structure refinement data for **[Ru]-1A**

	[Ru]-1A
empirical formula	C ₂₁ H ₃₀ ClO ₂ Ru ₂ F ₆ P
formula wt	697.01
colour	Red
crystal system	Monoclinic
space group	<i>P</i> 21/m
<i>T</i> (K)	273(2)
λ (Å), radiation	0.71073, Mo K α
<i>a</i> (Å)	8.8368(7)
<i>b</i> (Å)	13.7394(9)
<i>c</i> (Å)	10.8131(7)
α (°)	90.00
β (°)	92.992(2)
γ (°)	90.00
<i>V</i> (Å ³)	1311.05(16)
<i>Z</i>	2
$\rho_{calcd.}$ (g/cm ³)	1.766
<i>F</i> (000)	692
no. of data collected / unique data	30441 / 3351 [R(int) = 0.0411]
data / restraints / parameters	3351 / 0 / 166
final R indices [I>2sigma(I)]	R1 = 0.0356, wR2 = 0.0981
R indices (all data)	R1 = 0.0441, wR2 = 0.1123
goodness of fit	0.951

Table S2 Selected bond lengths for complexes [Ru]-1A	
Bond Length(Å)	[Ru]-1A
Ru1 Ru1	2.8393(5)
Ru1 O10	2.095(3)
Ru1 C1	2.172(4)
Ru1 C2	2.191(4)
Ru1 C3	2.197(4)
Ru1 C4	2.198(4)
Ru1 C6	2.168(4)
Ru1 C7	2.156(4)
Ru1 Cl1	2.3948(11)
Ru1 H41	1.72(3)
Ru1 C _t	1.666
Ru1 C _{avg}	2.180
C1 C2	1.420(6)
C2 C3	1.374(6)
C3 C4	1.421(6)
C4 C5	1.500(7)
C4 C6	1.402(7)
C6 C7	1.412(6)
C7 C1	1.410(5)
C8 C1	1.520(7)
C8 C9	1.500(10)
C8 C10	1.506(11)
C40 O10	1.250(3)

Table S3 Selected bond Angles for complexes [Ru]-1A	
Bond Angles (deg)	[Ru]-1A
O10-Ru1-C1	90.69(14)
O10-Ru1-C2	92.28(14)
O10-Ru1-C3	118.03(15)
O10-Ru1-C4	155.60(15)
O10-Ru1-C6	155.76(17)
O10-Ru1-C7	117.70(15)
O10-Ru1-Cl1	84.97(10)
O10-Ru1-H41	88(2)
C1-Ru1-Cl1	162.72(12)
C2-Ru1-Cl1	125.34(12)
C3-Ru1-Cl1	99.60(13)
C4-Ru1-Cl1	95.55(13)
C6-Ru1- Cl1	118.40(13)
C7-Ru1- Cl1	154.96(12)
H41-Ru1-Cl1	87.5(17)
C1-Ru1-H41	109.0(17)
C2-Ru1- H41	147.0(17)
C3-Ru1- H41	154(2)
C4-Ru1- H41	117(2)
C6-Ru1- H41	87(2)
C7-Ru1- H41	83.1(17)
Ru1- Cl1- Ru1	72.71(4)
Ct- Ru1- O10	127.79
Ct- Ru1- H41	120.83
Ct- Ru1- Cl1	133.68

Table S4 Crystal structure refinement data for [Ru]-3	
	[Ru]-3
empirical formula	C ₁₆ H ₂₂ Cl ₂ N ₄ Ru
formula wt	442.35
colour	Yellow
crystal size (mm)	0.33 x 0.26 x 0.23
crystal system	Monoclinic
space group	<i>P</i> -21/n
<i>T</i> (K)	293(2)
λ (Å), radiation	0.71073, Mo K α
<i>a</i> (Å)	9.3770(11)
<i>b</i> (Å)	17.874(3)
<i>c</i> (Å)	12.9381(19)
α (°)	90.00
β (°)	96.762(12)
γ (°)	90.00
<i>V</i> (Å ³)	2153.5(5)
<i>Z</i>	4
$\rho_{calcd.}$ (g/cm ³)	1.364
<i>F</i> (000)	896
no. of data collected / unique data	20974 / 3671 [R(int) = 0.448]
data / restraints / parameters	3671 / 0 / 211
final R indices [I>2sigma(I)]	R1 = 0.1085, wR2 = 0.2792
R indices (all data)	R1 = 0.2192, wR2 = 0.3496
goodness of fit	0.789

Table S5 Selected bond lengths for complexes [Ru]-3	
Bond Length(Å)	[Ru]-3
Ru1 N1	2.098(12)
Ru1 N3	2.125(14)
Ru1 Cl1	2.416(4)
Ru1 C2	2.186(17)
Ru1 C3	2.117(16)
Ru1 C4	2.126(16)
Ru1 C5	2.224(19)
Ru1 C6	2.186(16)
Ru1 C7	2.176(14)
Ru1 C _t	1.648
Ru1 C _{avg}	1.411
N1 C11	1.315(18)
N1 C13	1.407(19)
N2 C11	1.363(18)
N2 C12	1.27(2)
N3 C14	1.23(2)
N3 C16	1.36(2)
N4 C14	1.30(2)
N4 C15	1.30(2)
C1 C2	1.47(2)
C2 C3	1.46(3)
C3 C4	1.36(2)
C4 C5	1.43(3)
C5 C6	1.38(2)
C6 C7	1.47(2)
C7 C2	1.37(2)
C5 C8	1.60(3)
C8 C10	1.51(4)

C9 C8	1.37(4)
C12 C13	1.33(2)
C15 C16	1.37(2)

Table S6 Selected bond Angles for complexes [Ru]-3	
Bond Angles (deg)	[Ru]-3
N1-Ru1-N3	83.9(5)
N1-Ru1-Cl1	87.5(4)
N3-Ru1-Cl1	87.0(4)
N1-Ru1-C _t	128.31
N3-Ru1-C _t	128.07
Cl1-Ru1-C _t	127.46
C2-Ru1-Cl1	139.1(7)
C3-Ru1-Cl1	102.2(6)
C4-Ru1-Cl1	87.5(5)
C5-Ru1-Cl1	99.9(6)
C6-Ru1-Cl1	133.1(6)
C7-Ru1-Cl1	168.7(5)
C2-Ru1-N1	132.0(7)
C3-Ru1-N1	169.3(6)
C4-Ru1-N1	140.6(8)
C5-Ru1-N1	104.8(7)
C6-Ru1-N1	90.1(6)
C7-Ru1-N1	100.0(5)
C2-Ru1-N3	87.5(7)
C3-Ru1-N3	101.0(7)
C4-Ru1-N3	134.8(8)
C5-Ru1-N3	169.0(6)
C6-Ru1-N3	139.2(7)
C7-Ru1-N3	102.2(6)

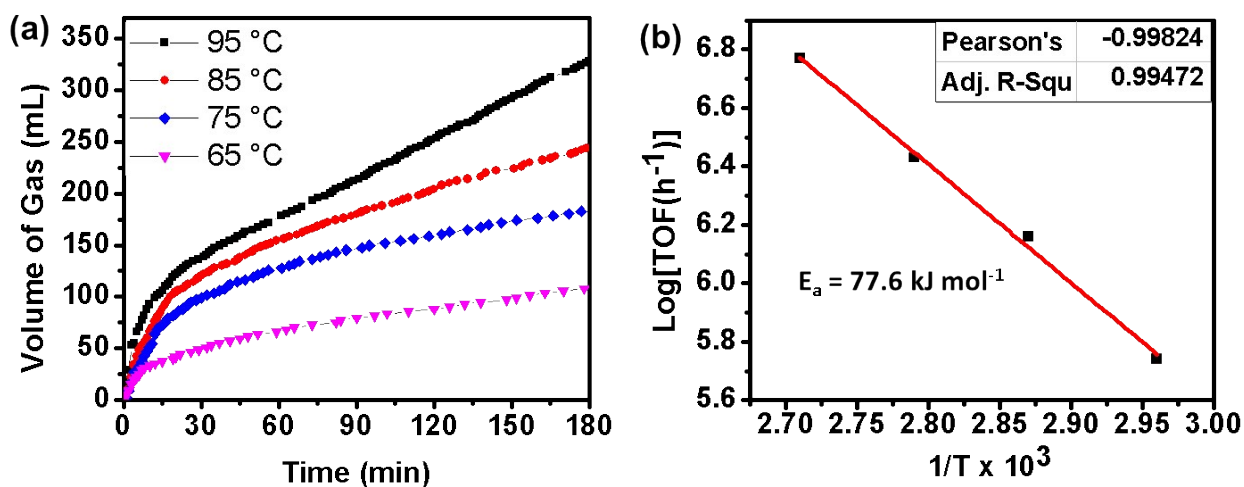


Fig. S6 (a) Temperature dependent hydrogen production from aqueous formaldehyde and (b) the corresponding Arrhenius plot of initial TOF values (initial 10 min). (Reaction condition: aq. formaldehyde (13.55 mol L⁻¹, 1.07 mL), catalyst **[Ru]-1** (13 μmol) and ligand **L6** (26 μmol) at 95 °C).

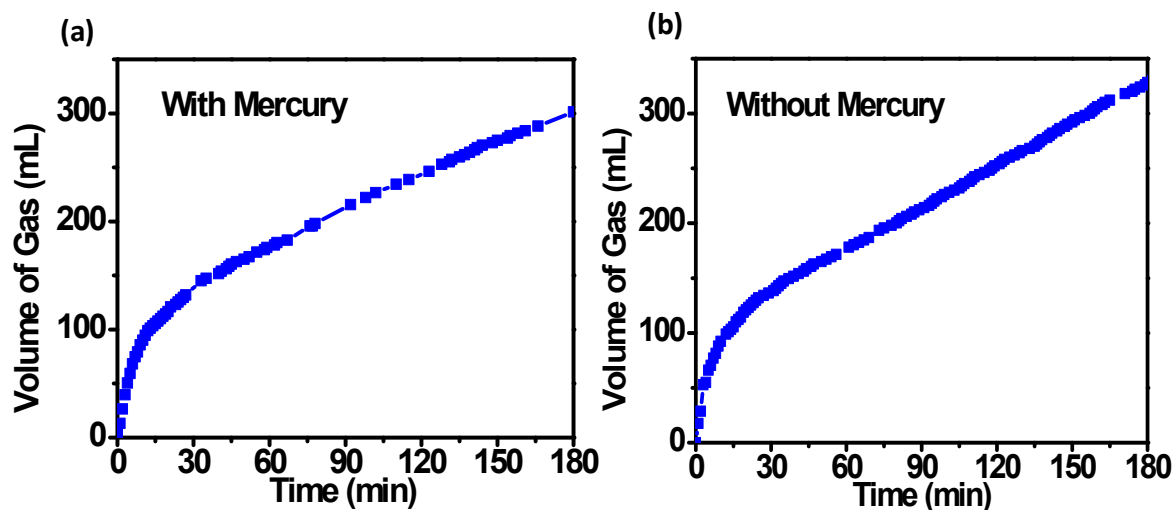


Fig. S7 Mercury poisoning test for the catalytic reaction for hydrogen production from aqueous formaldehyde (13.55 mol L⁻¹, 1.07 mL) over the catalyst **[Ru]-1** (13 μmol) in the presence of ligand **L6** (26 μmol) at 95 °C (with/without added Hg).

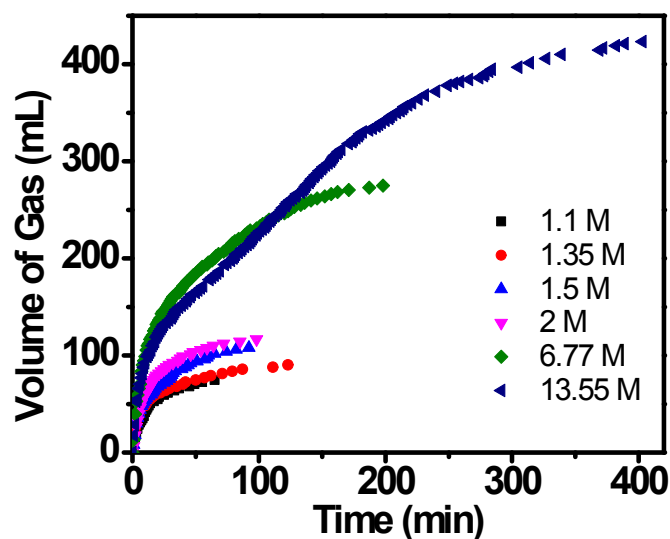


Fig. S8 Hydrogen production from varying concentration of aqueous formaldehyde (1.1–13.55 mol L⁻¹) over the catalyst **[Ru]-1** (13 μmol) and ligand **L6** (26 μmol) at 95 °C.

Table S7 Hydrogen production from varying concentration of formaldehyde

Entry	Formaldehyde (mol L ⁻¹)	Time (min)	Evolved gas (mL)	Conv. (%)	Equivalents of evolved gas
1.	1.1	65 min	75	93	2.8
2.	1.35	125 min	90.2	91	2.7
3.	1.5	92 min	108	98	2.9
4.	2	200 min	114.4	78	2.3
5.	6.75	200 min	268.2	54	1.6
6.	13.55	350 min	427.4	43	1.3

Reaction conditions: aqueous formaldehyde (1.07 mL), catalyst **[Ru]-1** (13 μmol), ligand **L6** (26 μmol) at 95 °C.

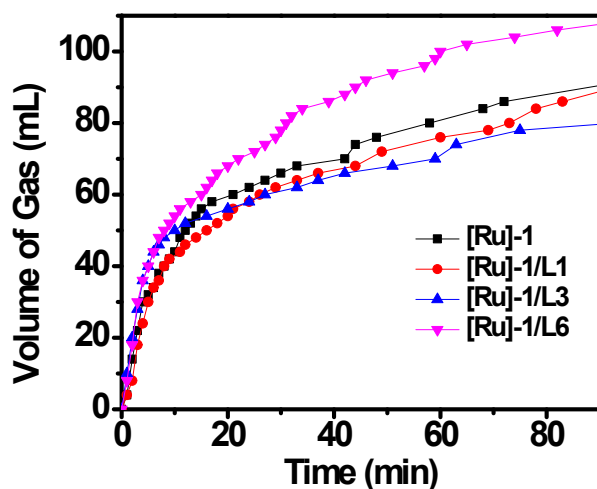


Fig. S9 Time course plot for hydrogen production from aqueous formaldehyde. (Reaction condition: aq. formaldehyde (1.5 mol L⁻¹, 1.07 mL), catalyst **[Ru]-1** (13 μmol) and ligands **L1**, **L3** and **L6** (26 μmol) at 95 °C).

Entry	Cat./ligand	Evolved Gas (equiv.)	TOF (h ⁻¹) ^[b]
1	Ru	2.46	415
2	Ru/L1	2.42	406
3	Ru/L3	2.17	471
4	Ru/L6	2.94	509

[a] Reaction was performed with aqueous formaldehyde (1.5 mol L⁻¹, 1.07 mL), catalyst **[Ru]-1** (13 μmol), ligands **L1**, **L3** and **L6** (26 μmol) in 90 min at 95 °C. [b] Average TOF for initial 10 min.

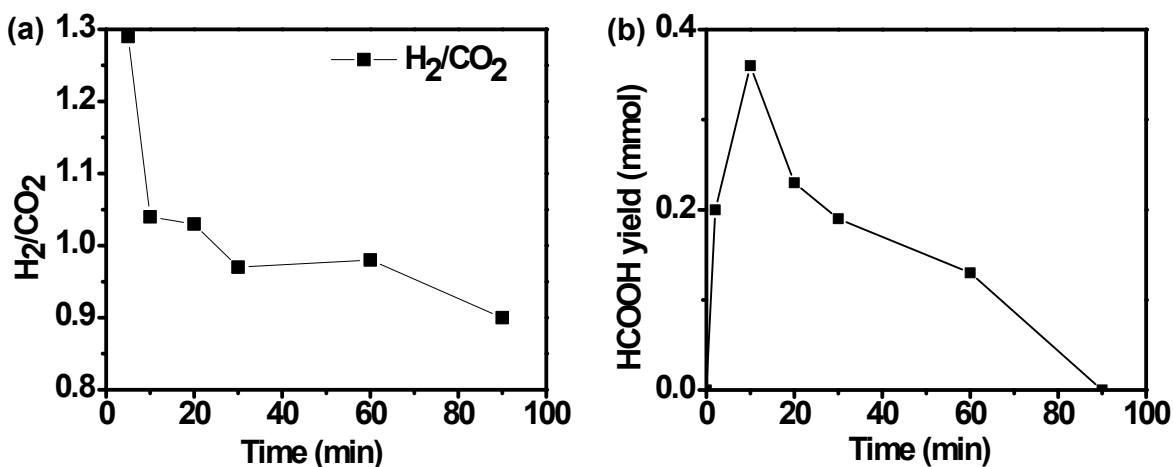


Fig. S10 (a) The H₂/CO₂ ratios in the produced gas mixture and (b) ¹H NMR yield of HCOOH during the catalytic dehydrogenation of aqueous formaldehyde in the initial 1 h of the reaction. (Reaction condition: aq. formaldehyde (1.5 mol L⁻¹, 1.07 mL), catalyst [Ru]-1 (13 μmol) and ligand L6 (26 μmol), at 95 °C. HCOOH yield was determined using dioxane as an internal standard).

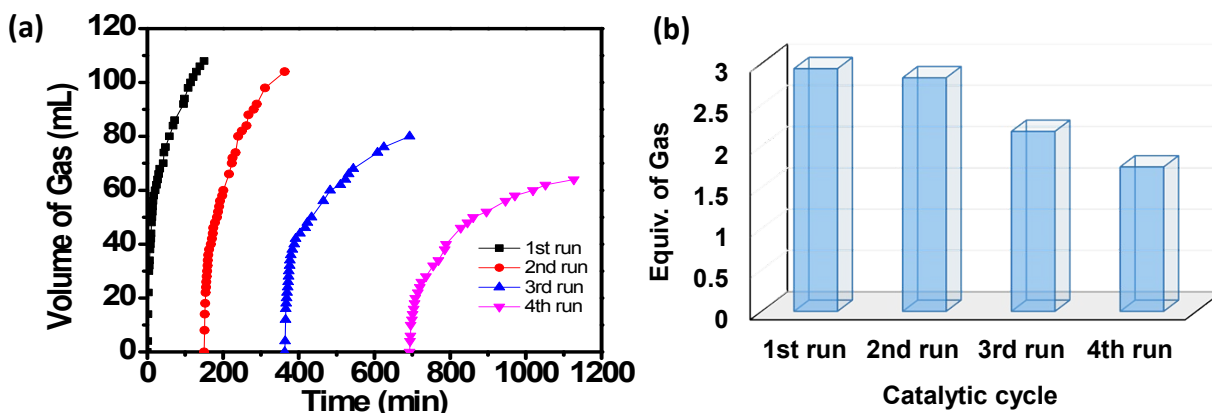


Fig. S11 Long term stability and recyclability experiment for hydrogen production from aqueous formaldehyde over complex [Ru]-1. (Reaction condition: aq. formaldehyde (1.5 mol L⁻¹, 1.07 mL), catalyst [Ru]-1 (13 μmol) and ligands L6 (26 μmol) at 95 °C; 1.5 mmol of formaldehyde added in each cycle).

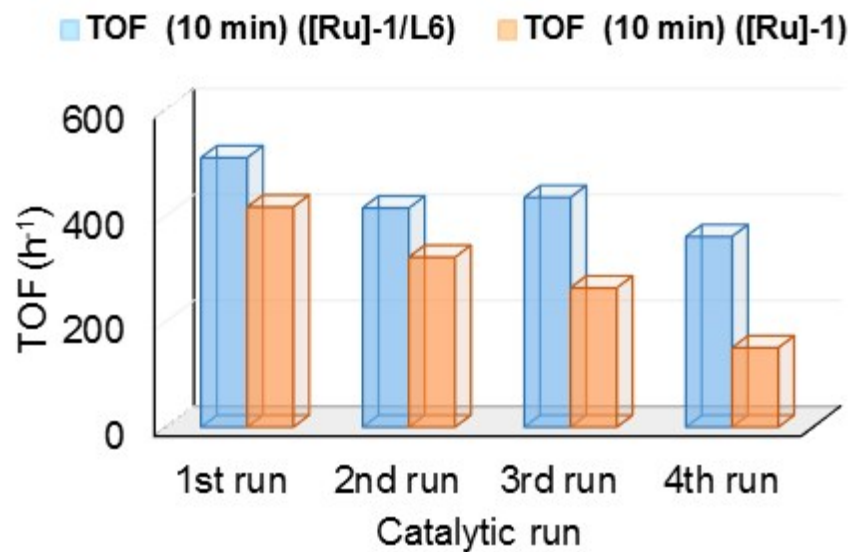
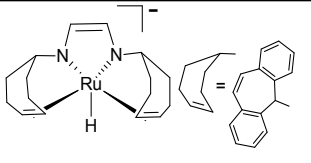
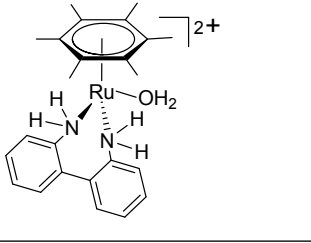
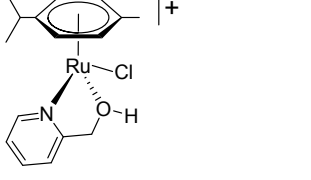
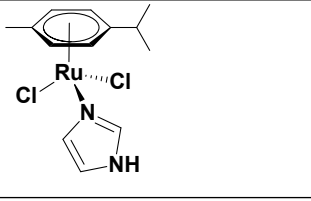


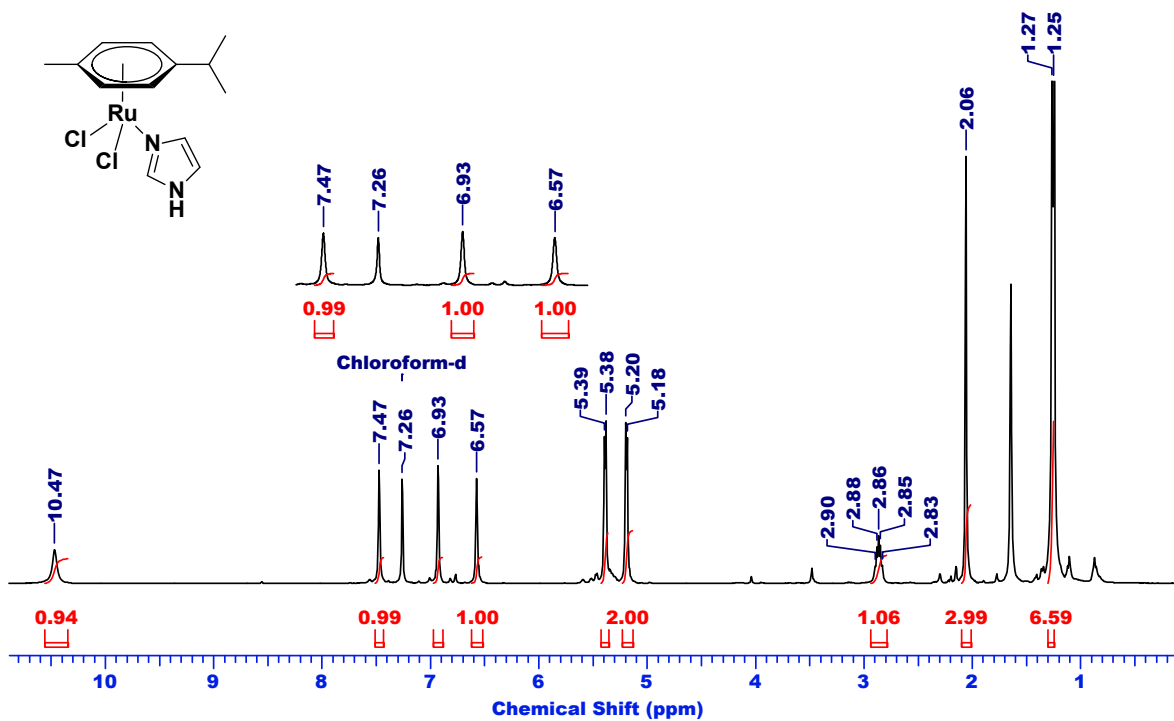
Fig. S12 TOF comparison graph for hydrogen production from aqueous formaldehyde over **[Ru]-1/L6** and **[Ru]-1**. (Reaction condition: aq. formaldehyde (1.5 mol L⁻¹, 1.07 mL), catalyst **[Ru]-1** (13 μmol) and ligands **L6** (26 μmol) at 95 °C).

Table S9. Comparative chart for catalytic formaldehyde dehydrogenation over various homogeneous complexes

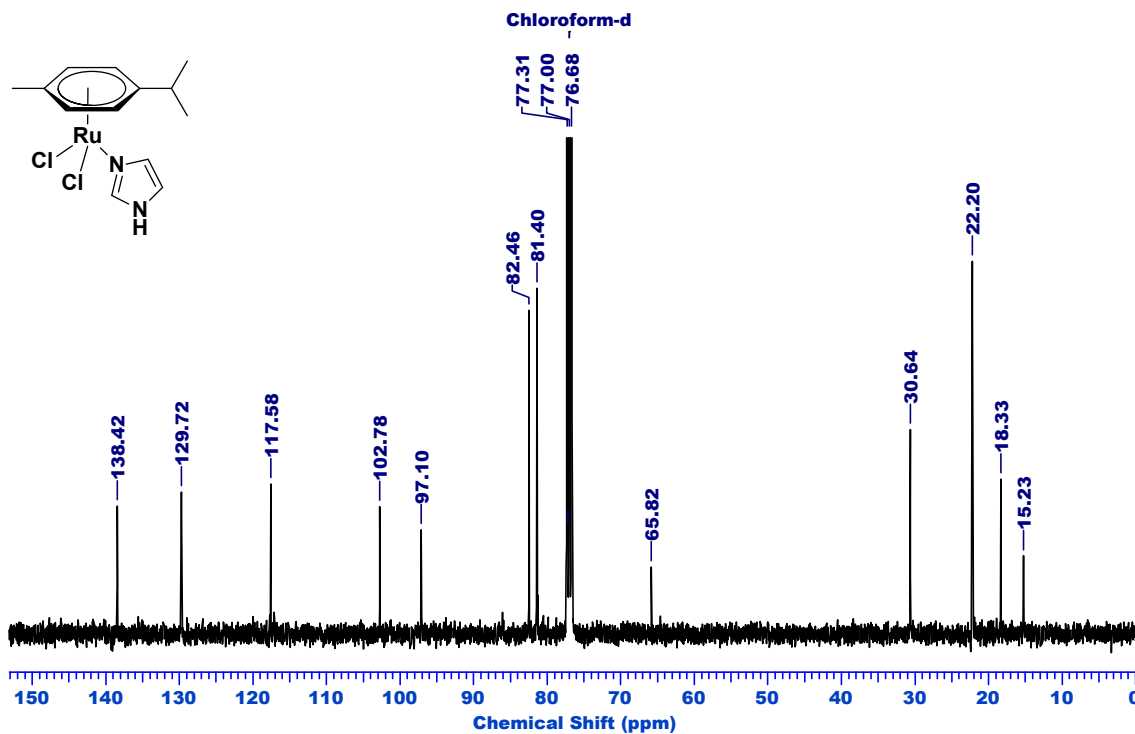
S. No.	Catalyst	Base	T (°C)	TON	TOF (h ⁻¹)	Reference
1.		-	95	700	3142 ^a	S3
2.		-	60	511	3.6 ^b	S4
3.		NaOH	reflux	178	8.9 ^b	S5

4.		KOH	60	1787	>20000 ^a	S6
5.		-	95	24000	8300 ^c	S7
6.		-	90	1838	1072 ^d	S8
7.		-	95	12905	5715 ^d	Our work
^a initial, ^b average, ^c 5 min, ^d 10 min						

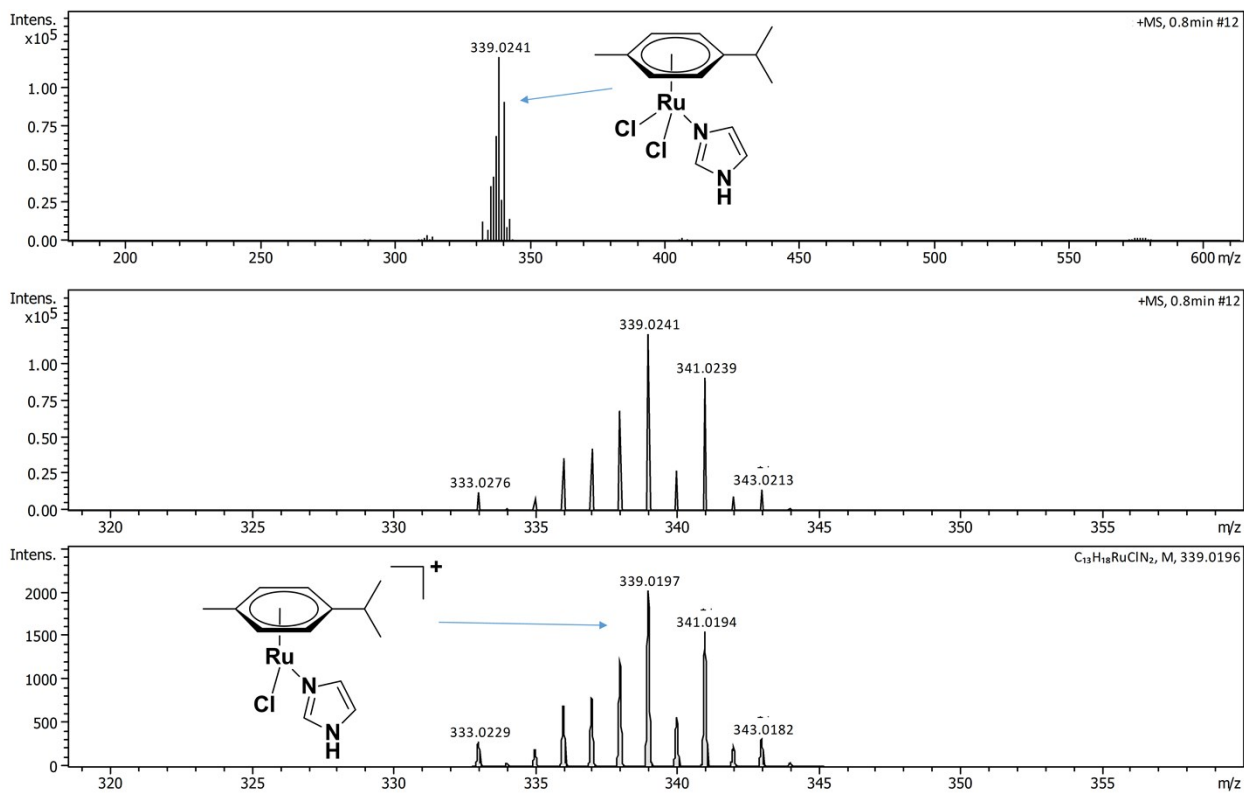
Spectral data for synthesized complexes



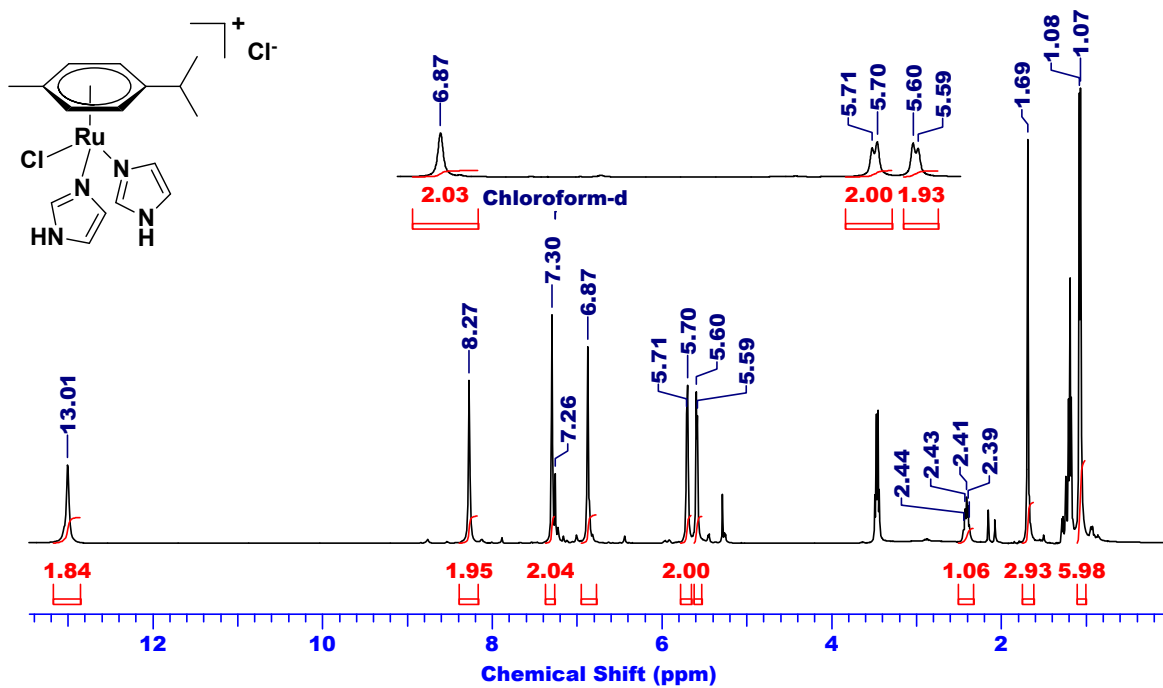
¹H NMR spectra of complex [Ru]-2



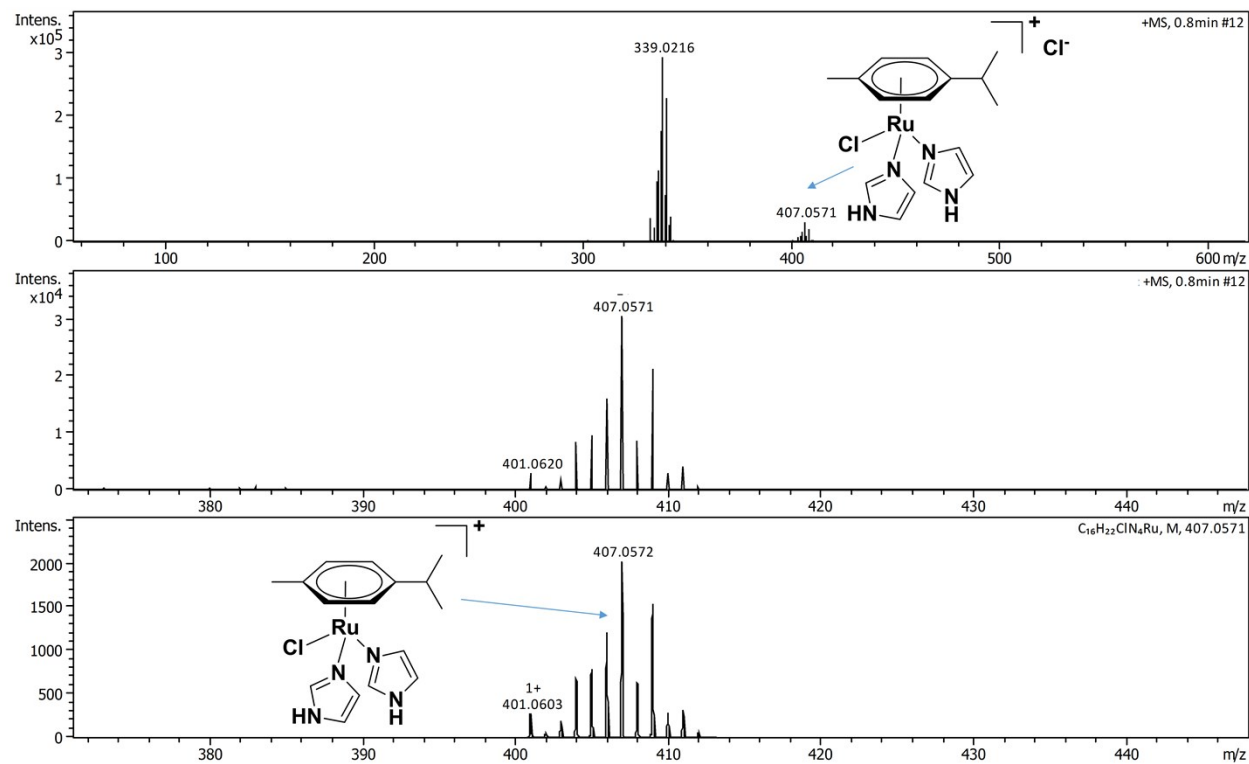
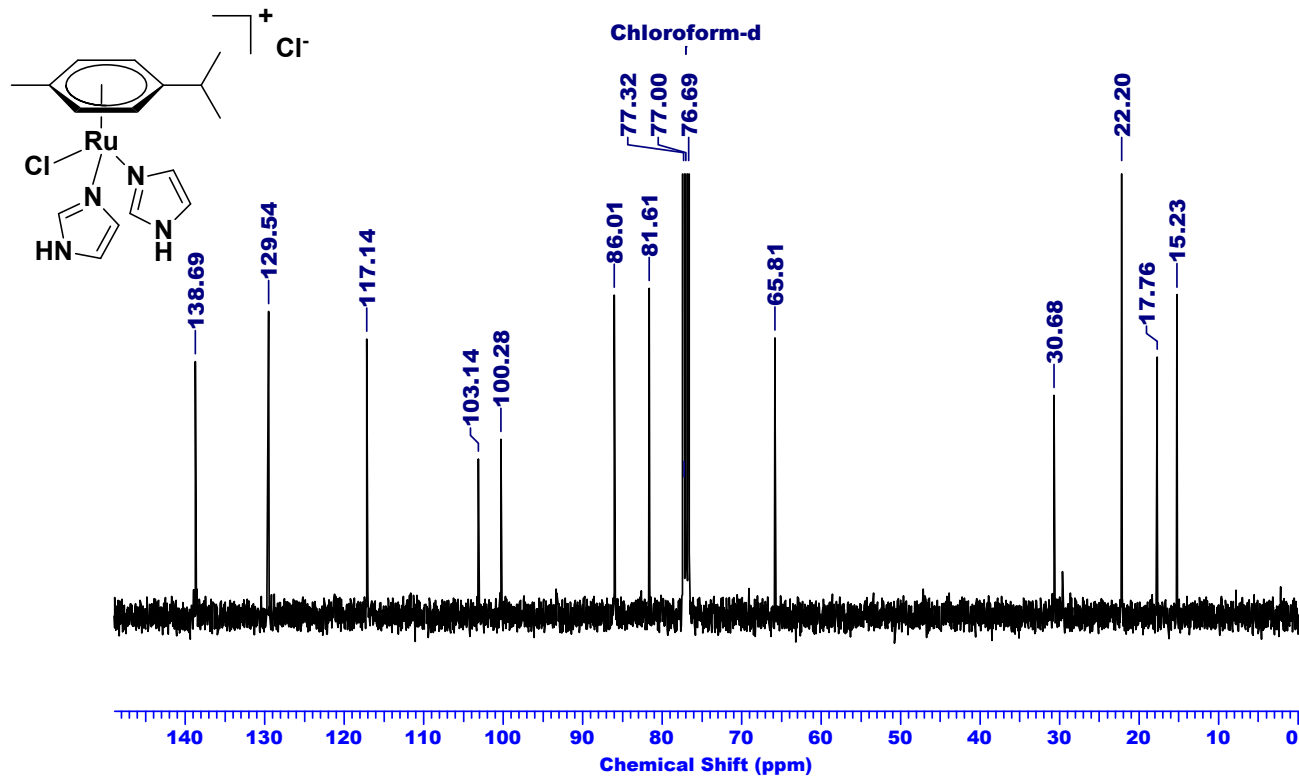
¹³C NMR spectra of complex [Ru]-2

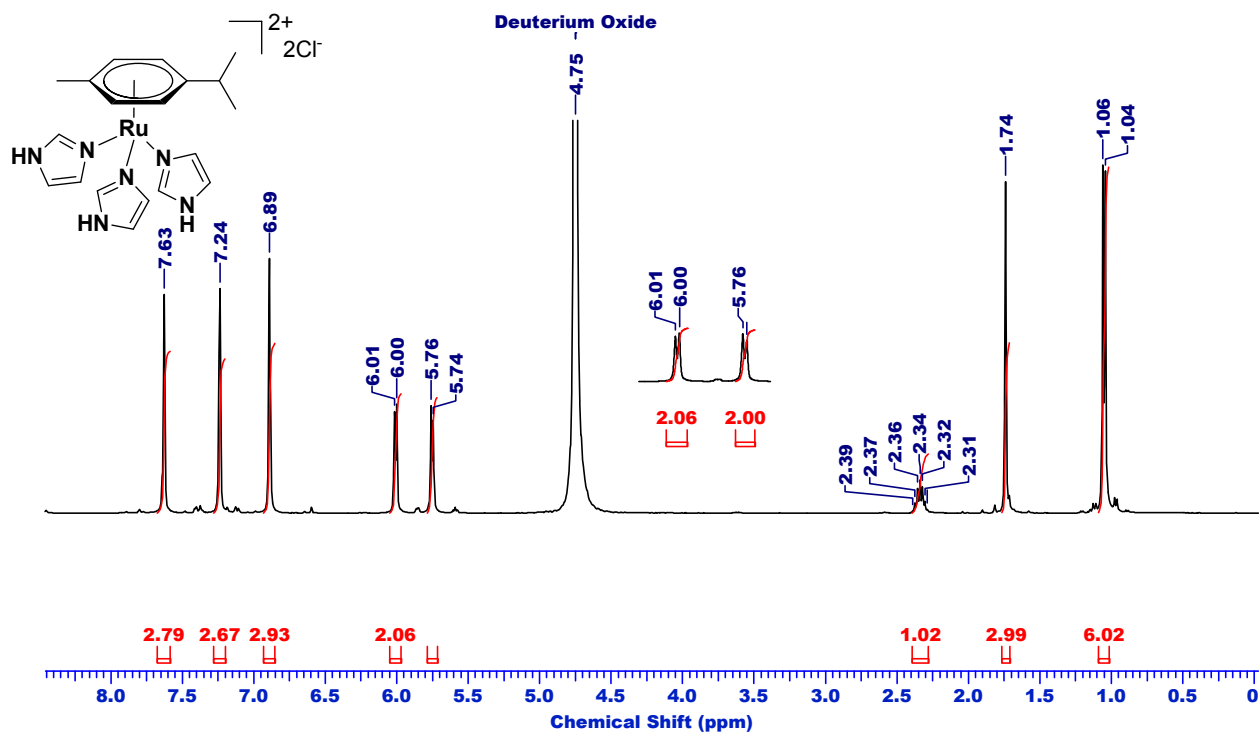


ESI-MS spectra of complex [Ru]-2

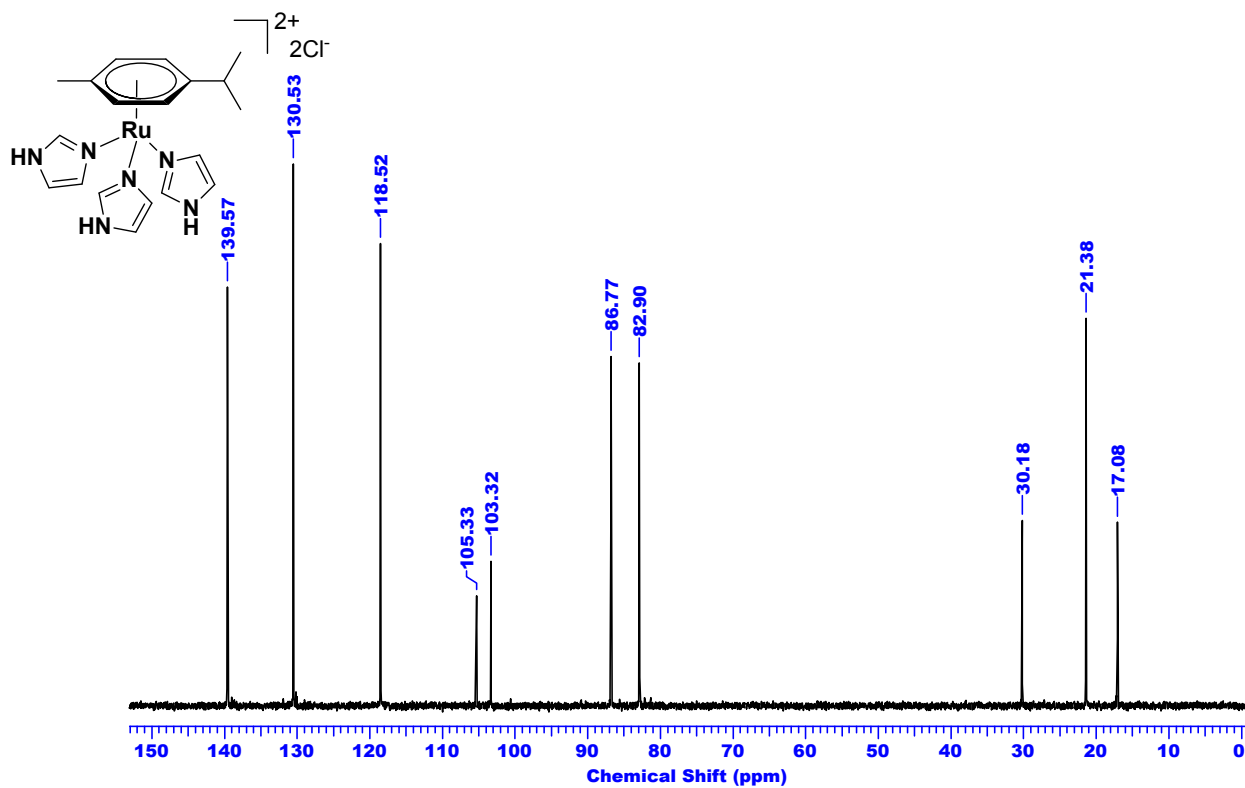


1H NMR spectra of complex [Ru]-3

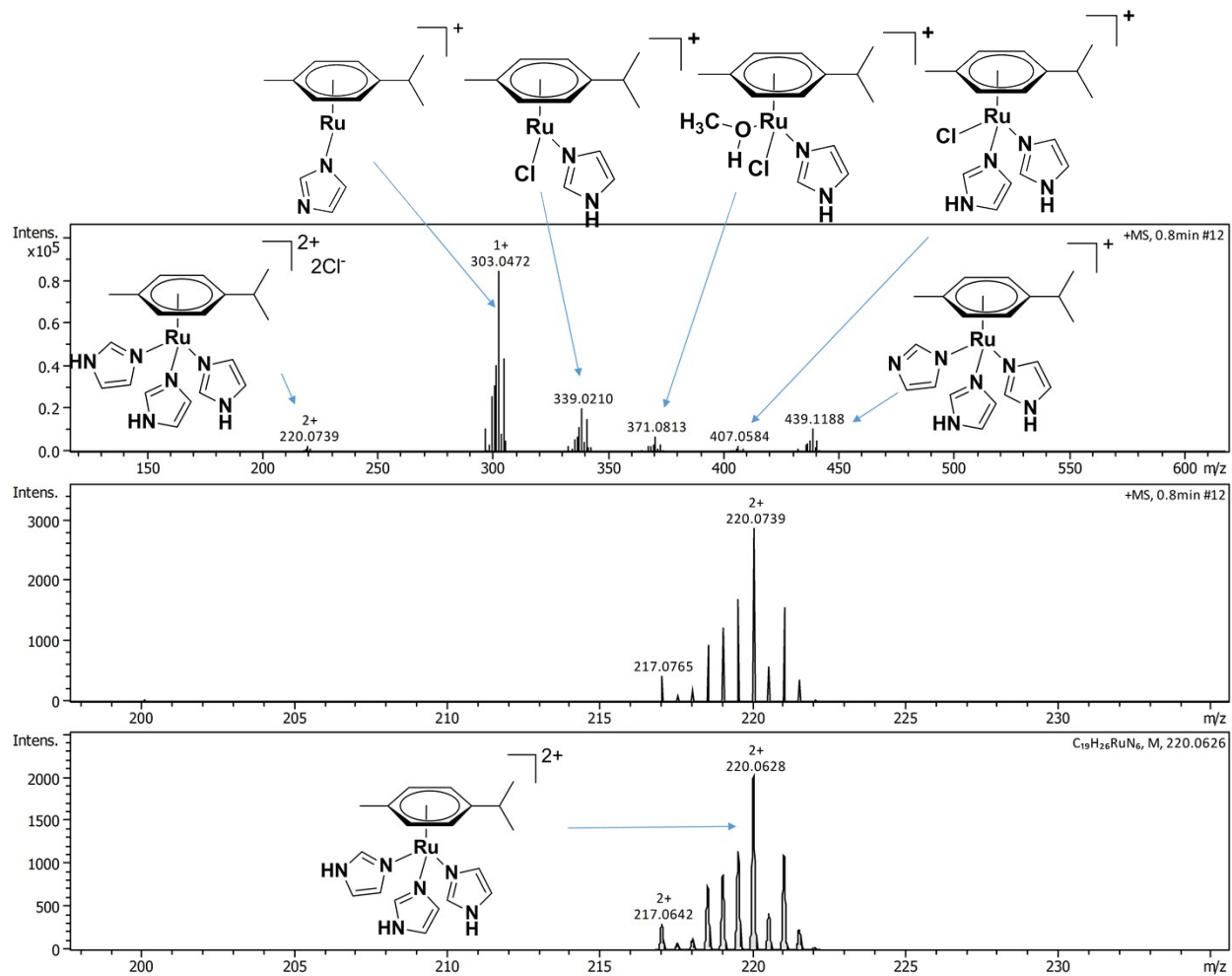




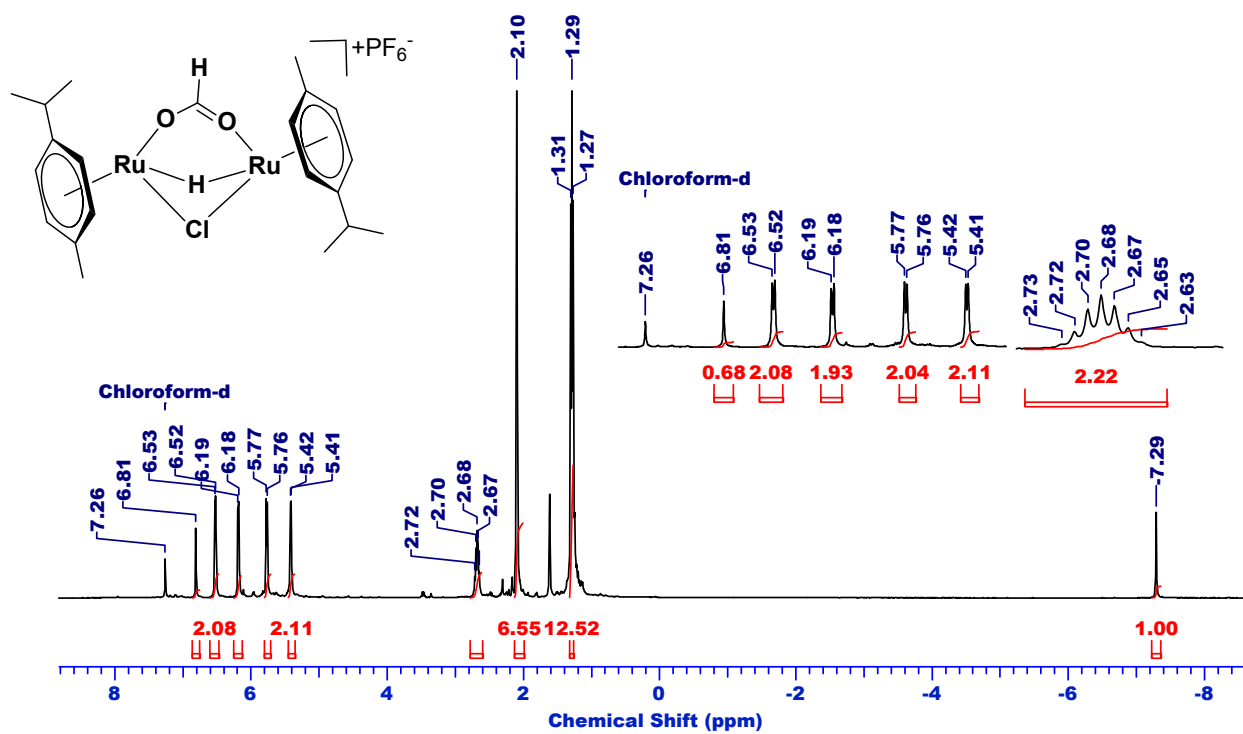
¹H NMR spectra of complex [Ru]-4



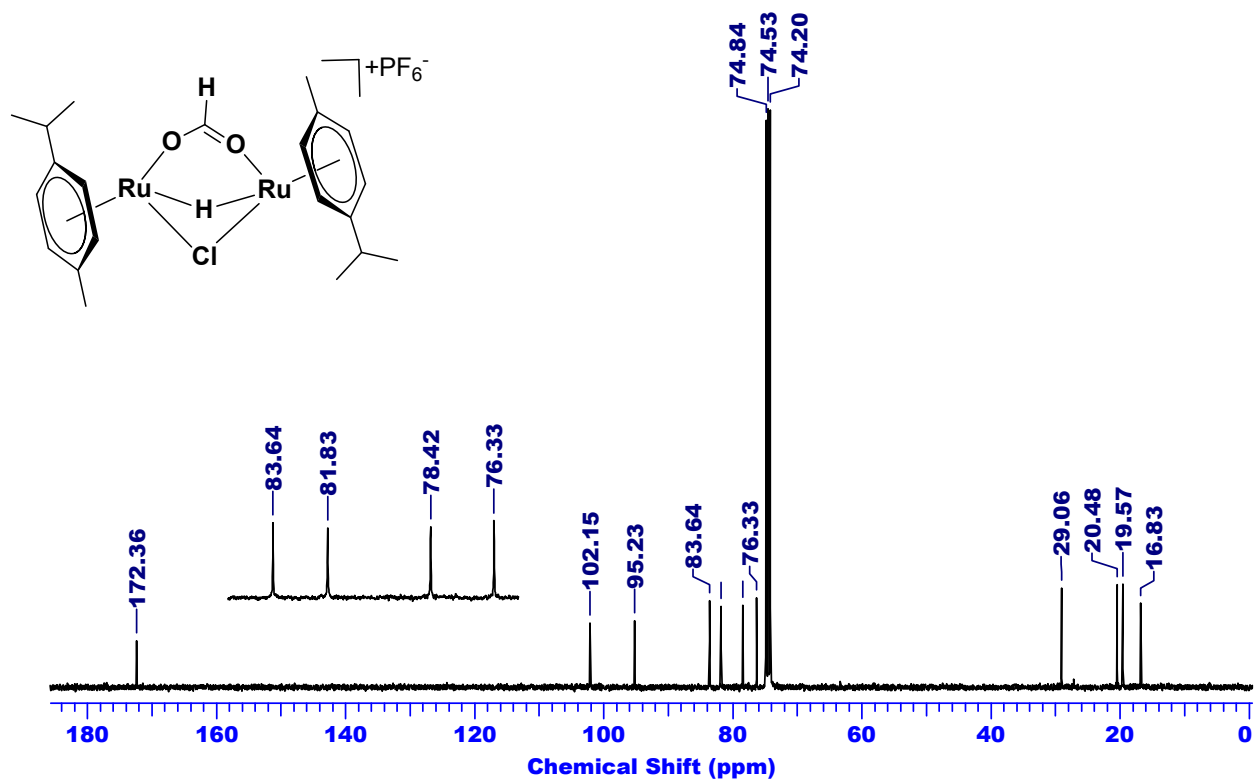
¹³C NMR spectra of complex [Ru]-4



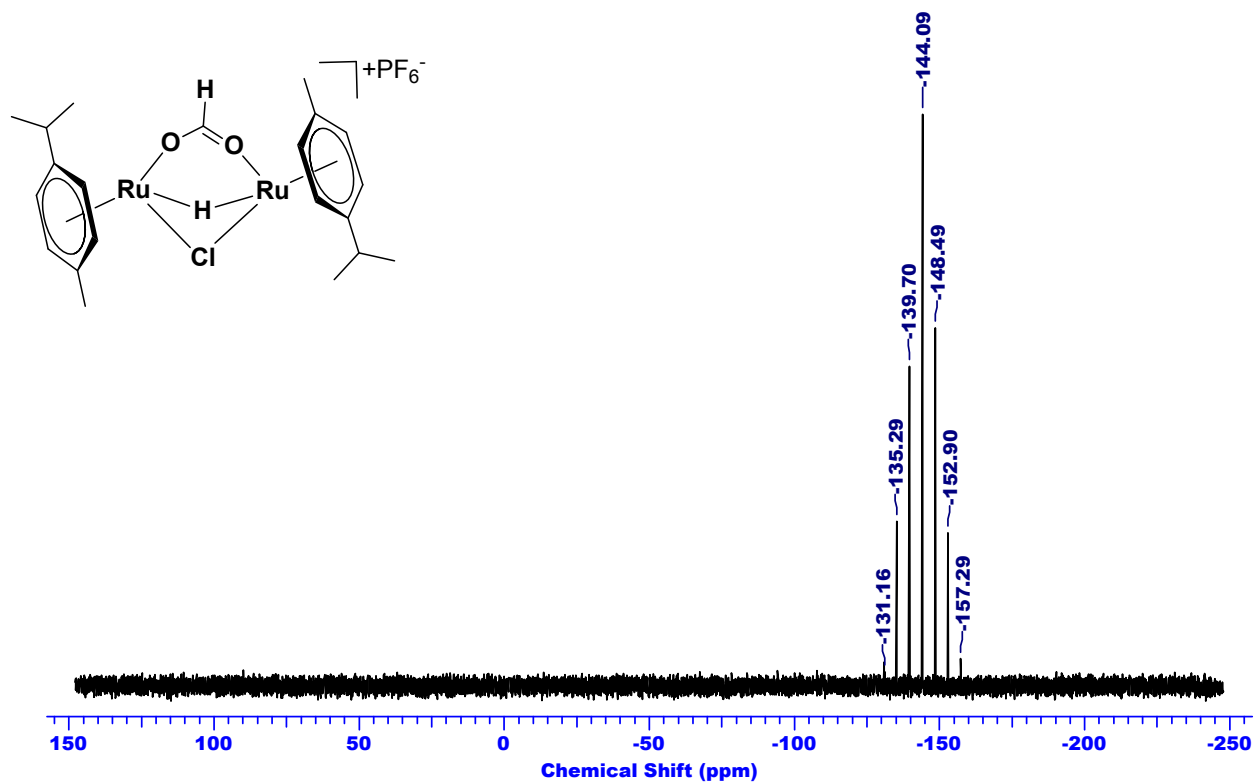
ESI-MS spectra of complex [Ru]-4



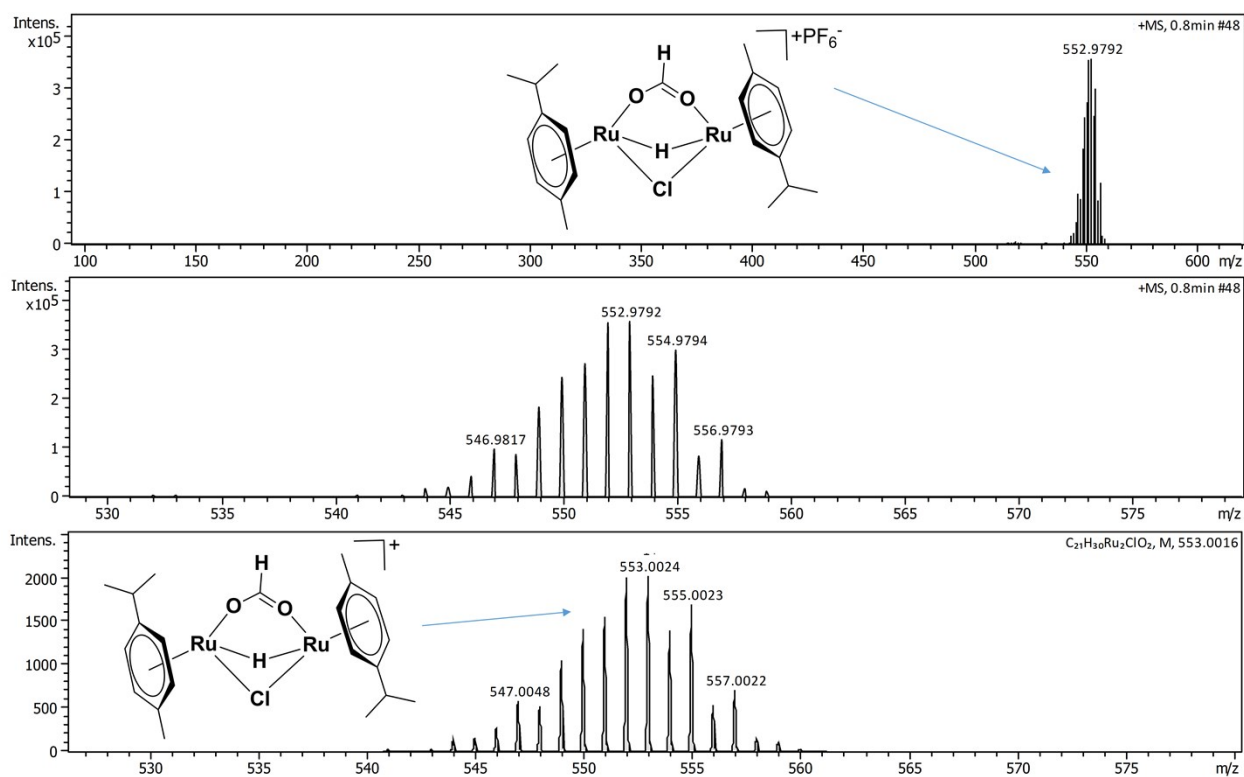
¹H NMR spectra of complex [Ru]-1A



¹³C NMR spectra of complex [Ru]-1A



^{31}P NMR spectra of complex [Ru]-1A



ESI-MS spectra of complex [Ru]-1A

References

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