Electronic Supplementary Information

Eugenol isomerization promoted by arene-ruthenium(II) complexes in aqueous media: influence of the pH on the catalytic activity

Beatriz Lastra-Barreira, Alba E. Díaz-Álvarez, Lucía Menéndez-Rodríguez, Pascale Crochet*

Laboratorio de Compuestos Organometálicos y Catálisis (Unidad Asociada al CSIC), Departamento de Química Orgánica e Inorgánica - IUQOEM, Universidad de Oviedo, C/ Julián Clavería 8, E-33006 Oviedo, Spain. Fax: (+34)-985 10 34 46, e-mail: crochetpascale@uniovi.es

1. General methods. Organic solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification, with the exception of compounds $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)(L)]$ (L = $P(OMe)_3$ (**1a**), $P(OEt)_3$ (**1b**), $P(O^iPr)_3$ (**1c**), $P(OPh)_3$ (**1d**), PPh_3 (**1e**))[1] and $[RuCl_2(\eta^6\text{-}p\text{-cymene})(L)]$ (L = $P(OMe)_3$ (**2a**), $P(OEt)_3$ (**2b**), $P(O^iPr)_3$ (**2c**), $P(OPh)_3$ (**2d**), PPh_3 (**2e**)),[1,2] which were prepared by following the methods reported in the literature. GC measurements were made on an Hewlett-Packard HP6890 equipment using a Supelco Beta-Dex™ 120 column (30 m length, 250 μm diameter). GC/MSD measurements were performed with an Agilent 6890N equipment coupled to a 5973 mass detector (70 eV electron impact ionization) using a HP-1MS column. Flash chromatography was performed using Merck silica gel 60 (230-400 mesh). $^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker DPX-300 or Bruker AV-400 instruments.

2. General procedure for the catalytic isomerization of allylbenzenes. In all cases, the product resulting from the C=C bond migration was the only compound generated. The identity of the isolated products was assessed by comparison of their NMR spectroscopic data

with those reported in the literature and their fragmentation in GC/MSD. The C=C bond stereochemistry was confirmed by ^{1}H NMR.

Isomerization of allylbenzenes without additives: Under a nitrogen atmosphere, the appropriate ruthenium catalyst precursor (0.04 mmol, 1 mol%), 1 mL of the indicated solvent (water or ethanol) and eugenol (0.616 mL, 4 mmol) were introduced into a teflon-cap sealed tube. Then, the mixture was heated at 80ºC, and the yield and selectivity of the process were monitored by GC analyses of aliquots. Similar procedures have been employed to perform the isomerization of 1,2-dimethoxy-4-allylbenzene, safrole, 2-allylphenol and allylbenzene.

Isomerization of allylbenzenes in the presence of NaOH or H_2SO_4 (pH = 4.8, 5.2, 7.2, 8.5, 10.2 or 12.9): Different aqueous solutions of NaOH or H_2SO_4 were prepared and their pH was determined with a WTW Microprocessor pHmeter equipped with a SenTix50T electrode. Catalytic experiments were carried out following a similar procedure than that described above, using these acidic or basic solutions, instead of water, as solvent. The following catalytic experiments have been performed: (*i*) The isomerization of eugenol promoted by [$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}$] (**1b**) at pH = 4.8, 5.2, 7.2, 8.5, 10.2 and 12.9; (*ii*) The isomerization of 1,2-dimethoxy-4-allylbenzene, safrole, 2-allylphenol and allylbenzene promoted by [$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}$] (**1b**) at pH = 12.9; (*iii*) The isomerization of eugenol promoted by [$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)(PR_3)$] (PR_3 = $P(OMe)_3$ (**1a**), $P(O^iPr)_3$ (**1c**), $P(OPh)_3$ (**1d**), PPh_3 (**1e**)) at pH = 4.8 and 12.9. (*iv*) The isomerization of eugenol promoted by [$RuCl_2(\eta^6$-*p*-cymene)(PR_3)] (PR_3 = $P(OMe)_3$ (**2a**), $P(OEt)_3$ (**2b**), $P(O^iPr)_3$ (**2c**), $P(OPh)_3$ (**2d**), PPh_3 (**2e**)) at pH = 4.8, 7.2 and 12.9.

Isomerization of eugenol in the absence of metallic precursor: Under a nitrogen atmosphere, 1 mL of aqueous solution of NaOH (pH = 12.9) or H_2SO_4 (pH = 4.8) and eugenol (0.616 mL, 4 mmol) were introduced into a teflon-cap sealed tube. Then, the mixture was heated at 80ºC for 48 h. Eugenol remained unchanged after this time (no products detected by GC analyses).

Isomerization of eugenol in the presence of HCl or NaCl: Under a nitrogen atmosphere, ruthenium catalyst [$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}$] (**1b**) (19.1 mg, 0.04 mmol, 1 mol%), 960 μL of water, 40 μL of aqueous HCl 1M or NaCl 1 M and eugenol (0.616 mL, 4 mmol) were introduced into a teflon-cap sealed tube. Then, the mixture was heated at 80ºC, and the yield and selectivity of the process were monitored by GC analyses of aliquots.

Isomerization of eugenol in the presence of $AgNO_3$: Under a nitrogen atmosphere and in the dark, ruthenium catalyst [$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}$] (**1b**) (19.1 mg, 0.04 mmol, 1 mol%), 920 μL of water, 80 μL of aqueous $AgNO_3$ 0.5 M and eugenol (0.616 mL, 4 mmol) were introduced into a teflon-cap sealed tube. Then, the mixture was heated at 80ºC, and the yield and selectivity of the process were monitored by GC analyses of aliquots.

3. Purification and characterization of the final products. Products were extracted from the crude reaction medium with diethyl ether and purified by column chromatography over SiO_2, using a mixture of hexanes/Et_2O as eluent.

NMR data of isoeugenol:

NMR ^{1}H, $CDCl_3$, δ: *trans*-isomer: 6.89-6.84 (m, 3 H, ArH), 6.35 (d, 1 H, $^3J_{HH}$ = 15.7, CH=), 6.10 (dq, 1 H, $^3J_{HH}$ = 15.7, $^3J_{HH}$ = 6.4, =C*H*Me), 5.79 (broad s, 1 H, OH), 3.89 (s, 3 H, OMe), 1.89 (d, 3 H, $^3J_{HH}$ = 6.4, Me); *cis*-isomer: 6.98-6.89 (m, 3 H, ArH), 6.39 (d, 1 H, $^3J_{HH}$ = 11.7, CH=), 5.72 (dq, 1 H, $^3J_{HH}$ = 11.7, $^3J_{HH}$ = 6.9, =C*H*Me), 3.88 (s, 3 H, OMe), 1.94 (d, 3 H, $^3J_{HH}$ = 6.9, Me), OH resonance not observed.

NMR ^{13}C{^{1}H}, $CDCl_3$, δ: *trans*-isomer: 146.7 and 144.8 (both s, OC_{arom}), 130.8 (s, CH=), 130.7 (s, C_{arom}), 123.4 (s, =*C*HMe), 119.3 (s, CH_{arom}), 114.5 (s, CH_{arom}), 108.0 (s, CH_{arom}), 55.8 (s, OMe), 18.3 (s, Me).

NMR data of 1,2-dimethoxy-4-(1-1-propenyl)benzene:

NMR ^{1}H, $CDCl_3$, δ: *trans*-isomer: 6.88-6.75 (m, 3 H, ArH), 6.32 (d, 1 H, $^3J_{HH}$ = 15.6, CH=), 6.08 (dq, 1 H, $^3J_{HH}$ = 15.6, $^3J_{HH}$ = 6.3, =C*H*Me), 3.85 and 3.83 (both s, 3 H each, OMe), 1.85 (d, 3 H, $^3J_{HH}$ = 6.3, Me); *cis*-isomer: 6.88-6.75 (m, 3 H, ArH), 6.59 (d, 1 H, $^3J_{HH}$ = 11.3, CH=), 5.70 (dq, 1 H, $^3J_{HH}$ = 11.3, $^3J_{HH}$ = 6.9, =C*H*Me), 3.84 and 3.83 (both s, 3 H each, OMe), 1.91 (d, 3 H, $^3J_{HH}$ = 6.9, Me).

NMR ^{13}C{^{1}H}, $CDCl_3$, δ: *trans*-isomer: 149.0 and 148.2 (both s, OC_{arom}), 131.1 (s, C_{arom}), 130.7 (s, CH=), 123.6 (s, =*C*HMe), 118.7 (s, CH_{arom}), 111.2 (s, CH_{arom}), 108.5 (s, CH_{arom}), 55.8 and 55.7 (both s, OMe), 18.3 (s, Me).

NMR data of isosafrole:

NMR ^{1}H, $CDCl_3$, δ: *trans*-isomer: 6.95 (s, 1 H, ArH), 6.80 (s, 2 H, ArH), 6.37 (dq, 1 H, $^3J_{HH}$ = 15.6, $^4J_{HH}$ = 1.5, CH=), 6.12 (dq, 1 H, $^3J_{HH}$ = 15.6, $^3J_{HH}$ = 6.5, =C*H*Me), 5.97 (s, 2 H, CH_2), 1.91 (dd, 3 H, $^3J_{HH}$ = 6.5, $^4J_{HH}$ = 1.5, Me); *cis*-isomer: 6.95-6.75 (s, 3 H, ArH), 6.42 (dq, 1 H,

$^{3}J_{HH}$ = 11.2, $^{4}J_{HH}$ = 1.5, CH=), 6.00 (s, 2 H, CH_2), 5.76 (dq, 1 H, $^{3}J_{HH}$ = 11.2, $^{3}J_{HH}$ = 6.9, =C*H*Me), 1.94 (dd, 3 H, $^{3}J_{HH}$ = 6.9, $^{4}J_{HH}$ = 1.5, Me).

NMR $^{13}C\{^{1}H\}$, $CDCl_3$, δ: *trans*-isomer: 148.0 and 146.6 (both s, OC_{arom}), 132.6 (s, C_{arom}), 130.7 (s, CH=), 123.8 (s, =*C*HMe), 120.1 (s, CH_{arom}), 108.2 (s, CH_{arom}), 105.4 (s, CH_{arom}), 100.9 (s, CH_2), 18.3 (s, Me).

NMR data of 2-(1-propenyl)phenol:

NMR ^{1}H, $CDCl_3$, δ: *trans*-isomer: 7.42-6.81 (m, 4 H, ArH), 6.77 (dq, 1 H, $^{3}J_{HH}$ = 15.9, $^{4}J_{HH}$ = 1.8, CH=), 6.28 (dq, 1 H, $^{3}J_{HH}$ = 15.9, $^{3}J_{HH}$ = 6.6, =C*H*Me), 1.95 (dd, 3 H, $^{3}J_{HH}$ = 6.6, $^{4}J_{HH}$ = 1.8, Me), resonance of OH group not observed; *cis*-isomer: 7.25-6.81 (m, 4 H, ArH), 6.48 (dd, 1 H, $^{3}J_{HH}$ = 11.1, $^{4}J_{HH}$ = 1.8, CH=), 6.04 (dq, 1 H, $^{3}J_{HH}$ = 10.9, $^{3}J_{HH}$ = 6.9, =C*H*Me), 1.80 (dd, 3 H, $^{3}J_{HH}$ = 6.9, $^{4}J_{HH}$ = 1.8, Me), resonance of OH group not observed.

NMR $^{13}C\{^{1}H\}$, $CDCl_3$, δ: *trans*-isomer: 152.9 (s, OC_{arom}), 128.4 (s, CH_{arom}), 128.2 (s, =*C*HMe), 127.7 (s, CH_{arom}), 125.9 (s, =CH), 121.4 and 116.4 (both s, CH_{arom}), 19.4 (s, Me); *cis*-isomer: 152.7 (s, OC_{arom}), 130.8 (s, C_{arom}), 130.0 (s, CH_{arom}), 128.0 (s, =*C*HMe), 125.5 (s, CH_{arom}), 125.4 (s, =CH), 121.0 and 115.9 (both s, CH_{arom}), 14.7 (s, Me)

NMR data of 1-propenylbenzene:

NMR ^{1}H, $CDCl_3$, δ: *trans*-isomer: 7.60-7.41 (m, 5 H, ArH), 6.66 (dq, 1 H, $^{3}J_{HH}$ = 15.9, $^{4}J_{HH}$ = 1.3, CH=), 6.47 (dq, 1 H, $^{3}J_{HH}$ = 15.9, $^{3}J_{HH}$ = 6.6, =C*H*Me), 2.12 (dd, 3 H, $^{3}J_{HH}$ = 6.6, $^{4}J_{HH}$ = 1.3, Me); *cis*-isomer: 7.60-7.20 (m, 5 H, ArH), 6.71 (dq, 1 H, $^{3}J_{HH}$ = 11.4, $^{4}J_{HH}$ = 1.6, CH=), 6.03 (dq, 1 H, $^{3}J_{HH}$ = 11.4, $^{3}J_{HH}$ = 7.0, =C*H*Me), 2.15 (dd, 3 H, $^{3}J_{HH}$ = 7.0, $^{4}J_{HH}$ = 1.6, Me).

NMR $^{13}C\{^{1}H\}$, $CDCl_3$, δ: *trans*-isomer: 138.2 (s, C_{ipso}), 131.4 (s, CH=), 128.7 (s, CH_{meta}), 127.0 (s, CH_{para}), 126.1 (s, CH_{ortho}), 125.8 (s, =*C*HMe), 18.7 (s, Me).

4. Catalytic activity of the complexes [$RuCl_2(\eta^6$-*p*-cymene)(PR_3)] (2a-e) in water.

Table S1. Isomerization of eugenol into isoeugenol catalyzed by complexes [$RuCl_2(\eta^6$-p-cymene)(L)] (**2a-e**) in water.[a]

Catalyst [L]	Time	Yield (%)[b]	*trans*:*cis*[b]
2a [$P(OMe)_3$]	2 h	> 99	98:2
2b [$P(OEt)_3$]	3.5 h	> 99	97:3
2c [$P(O^iPr)_3$]	5.5 h	> 99	95:4
2d [$P(OPh)_3$]	23 h	85	88:12
2e [PPh_3]	7 h	> 99	94:6

[a] Reactions carried out at 80ºC using 4 mmol of eugenol, 1 mol% of Ru and 1 mL of water. pH = 7.2. [b] Determined by GC analyses.

5. Influence of the pH on the catalytic activity of 1a-e

Table S2. Isomerization of eugenol into isoeugenol catalyzed by complexes [$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH$)(L)] (**1a-e**) in presence of NaOH or H_2SO_4.[a]

Catalyst [L]	pH	Time	Yield (%)[b]	*trans*:*cis*[b]
1a [$P(OMe)_3$]	4.8	5 min	> 99	97:3
1a [$P(OMe)_3$]	12.9	5 min	> 99	97:3
1b [$P(OEt)_3$]	4.8	10 min	> 99	98:2
1b [$P(OEt)_3$]	12.9	5 min	> 99	98:2
1c [$P(O^iPr)_3$]	4.8	10 min	> 99	96:4
1c [$P(O^iPr)_3$]	12.9	10 min	> 99	97:3
1d [$P(OPh)_3$]	4.8	7 h	95	89:11
1d [$P(OPh)_3$]	12.9	7 h	98	90:10
1e [PPh_3]	4.8	40 min	> 99	95:5
1e [PPh_3]	12.9	25 min	> 99	96:4
none[c]	4.8	48 h	0	-
none[c]	12.9	48 h	0	-

[a] Reactions carried out at 80ºC using 4 mmol of eugenol, 1 mol% of Ru, 1 mL of water and appropriate quantity of NaOH or H_2SO_4 to reach the pH indicated. [b] Determined by GC analyses. [c] Experiments carried out in absence of metallic precursor.

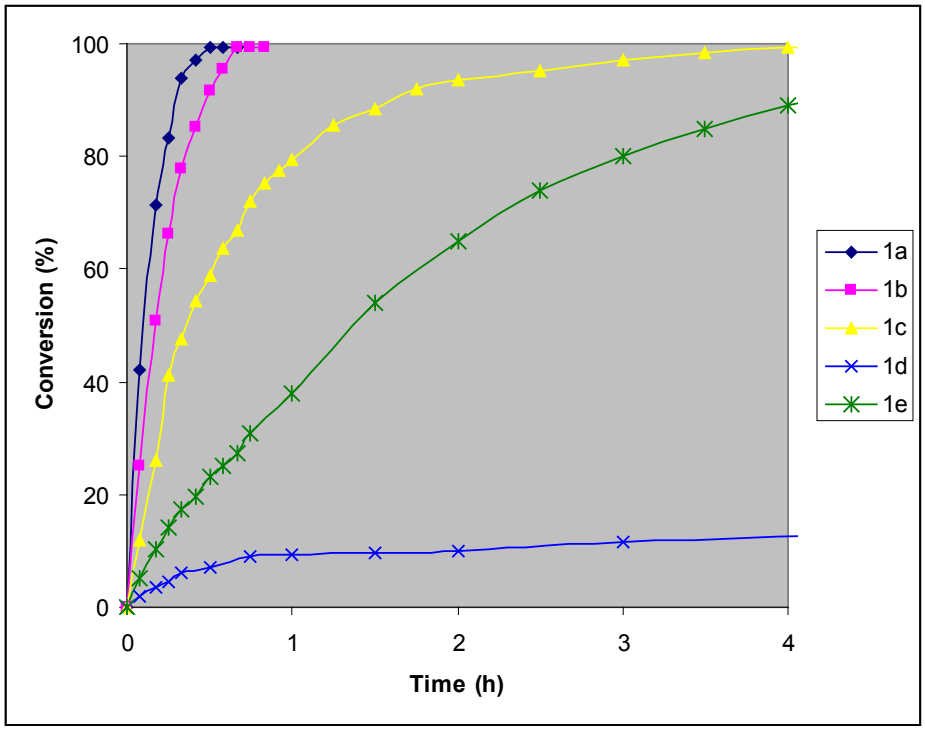
6. Influence of the pH on the catalytic activity of 2a-e

Table S3. Isomerization of eugenol into isoeugenol catalyzed by complexes [$RuCl_2(\eta^6$-*p*-cymene)(L)] (**2a-e**) in presence of NaOH or H_2SO_4.[a]

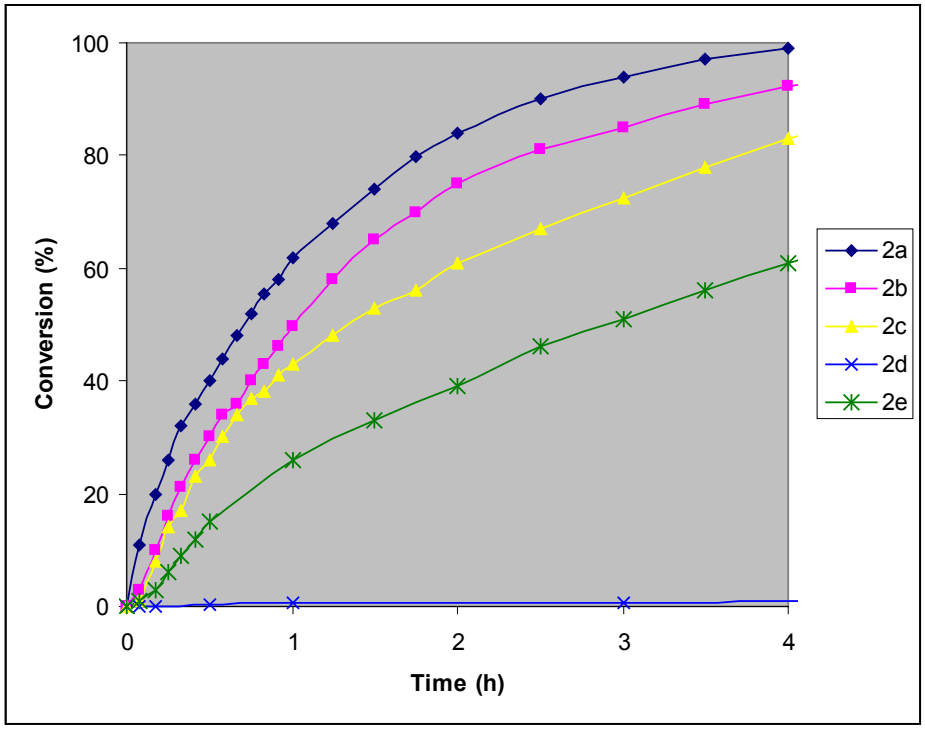
Catalyst [L]	pH	Time	Yield (%)[b]	*trans*:*cis*[b]
2a [$P(OMe)_3$]	4.8	50 min	> 99	97:3
2a [$P(OMe)_3$]	12.9	55 min	> 99	96:4
2b [$P(OEt)_3$]	4.8	1.75 h	> 99	98:2
2b [$P(OEt)_3$]	12.9	1.5 h	> 99	97:3
2c [$P(O^iPr)_3$]	4.8	2.5 h	> 99	97:3
2c [$P(O^iPr)_3$]	12.9	2.5 h	> 99	97:3
2d [$P(OPh)_3$]	4.8	10 h	> 99	90:10
2d [$P(OPh)_3$]	12.9	10 h	> 99	90:10
2e [PPh_3]	4.8	3 h	> 99	95:5
2e [PPh_3]	12.9	3.5 h	> 99	94:6

[a] Reactions carried out at 80ºC using 4 mmol of eugenol, 1 mol% of Ru, 1 mL of water and appropriate quantity of NaOH or H_2SO_4 to reach the pH indicated. [b] Determined by GC analyses.

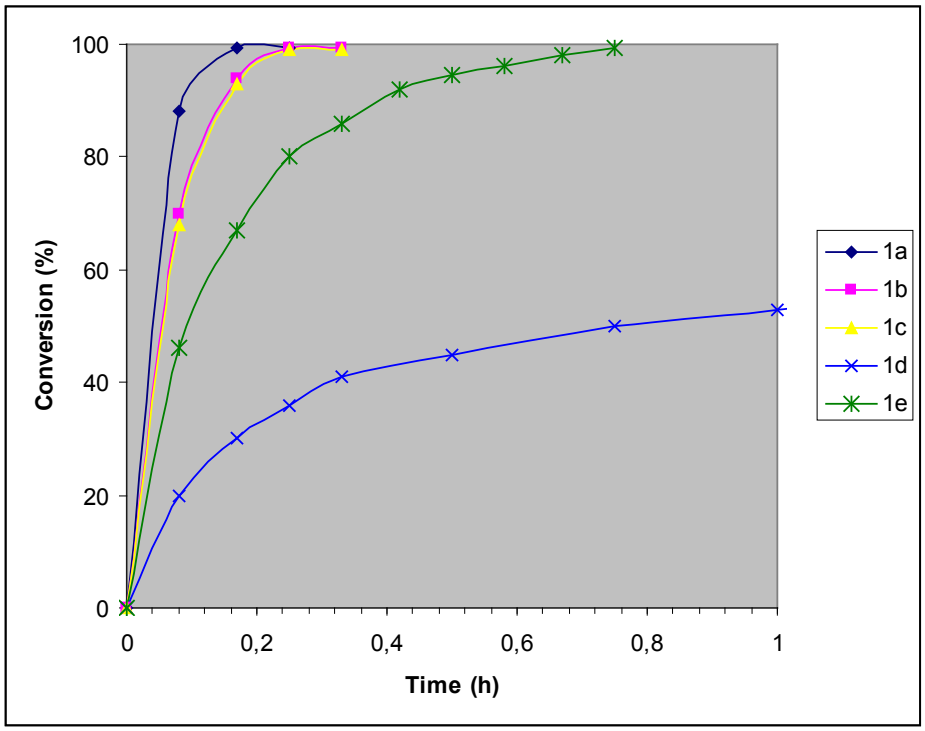
7. Conversion of eugenol vs time.



Graphic S1: Results corresponding to the catalytic experiments presented in the Table 1 of the manuscript. Only the first 4 hours are represented for clarity.



Graphic S2: Results corresponding to the catalytic experiments presented in the Table 2 of the manuscript. Only the first 4 hours are represented for clarity.



Graphic S3: Results corresponding to the catalytic experiments presented in the Table 3 of the manuscript. Only the first hour is represented for clarity.

8. Reactivity of $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}]$ (1b) towards acid and base.

Reactivity of $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}]$ (1b) towards H_2SO_4.

In a 5 mL-volumetric flask, 40 mg of complex $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}]$ (**1b**) were dissolved in D_2O. Six NMR tubes were then charged with 0.6 mL of this solution and 0, 5 or 10 µL of aqueous H_2SO_4 1 M (*i.e.* 0, 0.5 or 1 equivalents of H_2SO_4 per ruthenium) or 20, 40 or 80 µL of aqueous H_2SO_4 2.5 M were added (*i.e.* 5, 10 or 20 equivalents of H_2SO_4 per ruthenium). In each case, both $^{31}P\{^1H\}$ and ^1H NMR spectra reflected the presence of two species, the dichloro precursor $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}]$ (**1b**) and the mono-aquo derivative $[RuCl(D_2O)(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}][Cl]$ (**1b'**), in different proportion:

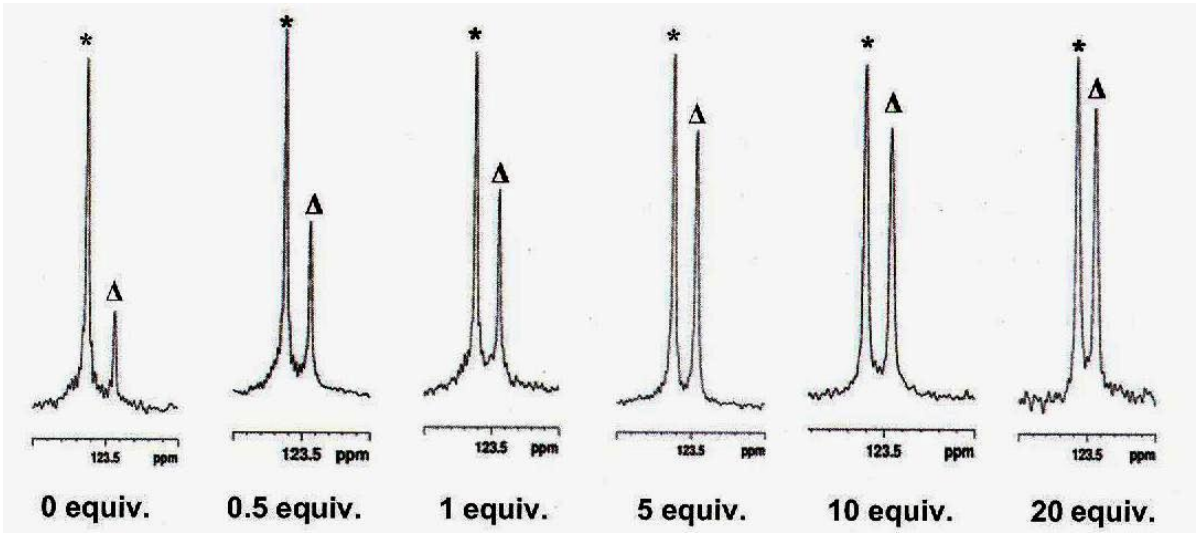


Figure S1. $^{31}P\{^1H\}$ NMR spectra of complex **1b** in presence of different amounts of H_2SO_4 (0, 0.5, 1, 5, 10 or 20 equivalent per Ru). Spectra recorded in D_2O on a Bruker AV-400 apparatus. Resonances attributed to $[RuCl_2(\eta^6\text{-}C_6H_5OCH\text{-}CH_2OH)\{P(OEt)_3\}]$ (**1b**) and $[RuCl(D_2O)(\eta^6\text{-}C_6H_5OCH\text{-}CH_2OH)\{P(OEt)_3\}][Cl]$ (**1b'**) are labelled with ∗ and Δ, respectively.

The formation of the bis-aquo complex $[Ru(D_2O)_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}][Cl]_2$ could be discarded because the new product generated does not present plane of symmetry as reflected by the inequivalence of the two ortho and the two meta hydrogen atom of the $C_6H_5OCH_2CH_2OH$ fragment in the ^1H NMR spectra:

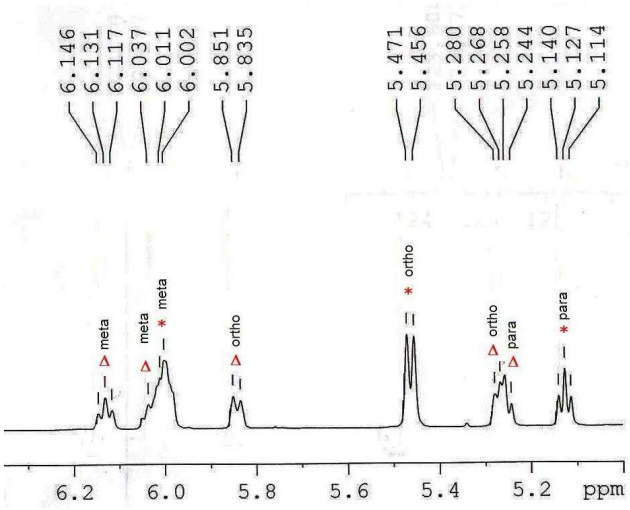


Figure S2. Details of the ^{1}H NMR spectra of **1b** in D_2O with 5 equivalents of H_2SO_4 per ruthenium. Signals due to $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}]$ (**1b**) and $[RuCl(H_2O)(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}][Cl]$ (**1b'**) are indicated with ∗ and Δ, respectively. Signal attribution has been confirmed by ^{1}H-^{1}H NMR correlation spectroscopy (cosy).

Reactivity of $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}]$ (1b) towards NaOH.

In a 5 mL-volumetric flask, 40 mg of complex $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}]$ (**1b**) were dissolved in D_2O. Six NMR tubes were then charged with 0.6 mL of this solution and 0, 5, 10, 15, 20 or 40 µL of aqueous NaOH 0.5 M (*i.e.* 0, 0.25, 0.5, 0.75, 1 or 2 equivalents of NaOH per ruthenium). In the presence of NaOH, the ^{1}H NMR spectra exhibit signals of free phenoxyethanol (in the range of 6.9-7.4 ppm for the phenyl ring) and different signals corresponding to η^6-coordinated $C_6H_5OCH_2CH_2OH$ (in the range 5.0-6.1 for the η^6-phenyl fragment):

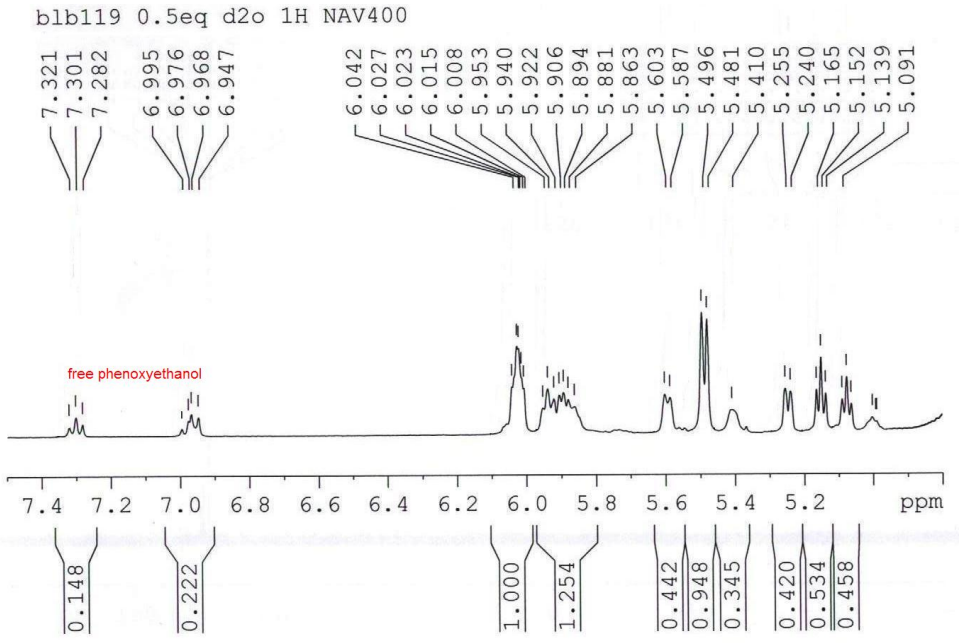


Figure S3. Details of the ^{1}H NMR spectra of **1b** in D_2O with 0.5 equivalents of NaOH per ruthenium.

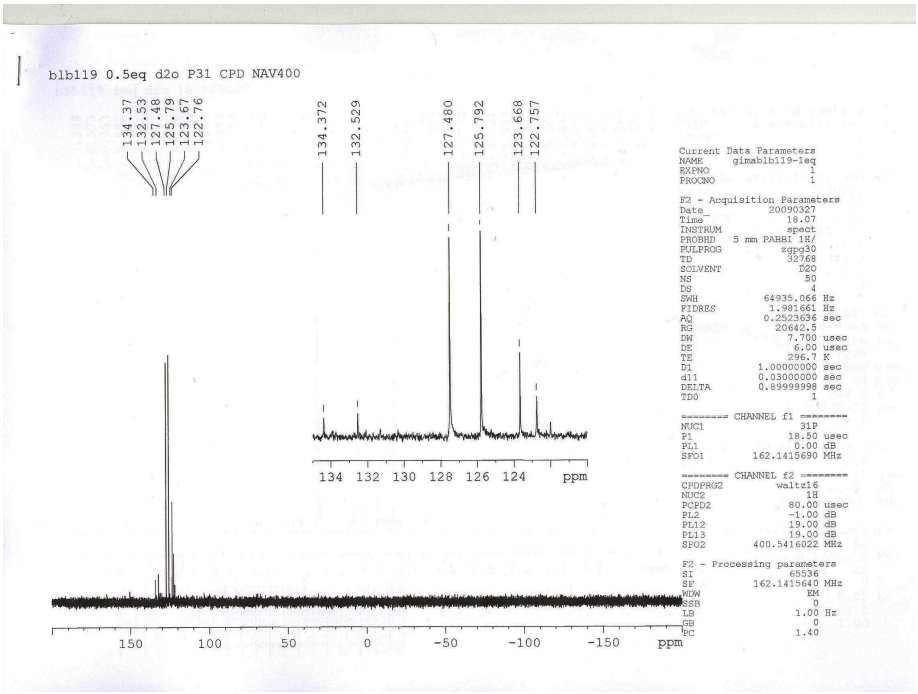


Figure S4. $^{31}P\{^{1}H\}$ NMR spectra of **1b** in D_2O with 0.5 equivalents of NaOH per ruthenium.

9. Reactivity of [$RuCl_2(\eta^6$-*p*-cymene){$P(OMe)_3$}] towards base.

First of all, the ^{1}H NMR of complex [$RuCl_2(\eta^6$-*p*-cymene){$P(OMe)_3$}] was measured in D_2O. Like observed with phenoxyethanol derivatives, in aqueous solution an equilibrium between the aquo- and the chloro-complexes, [$RuCl_2(\eta^6$-*p*-cymene){$P(OMe)_3$}] and [$RuCl(H_2O)(\eta^6$-*p*-cymene){$P(OMe)_3$}][Cl], was observed:

^{1}H NMR for [$RuCl_2(\eta^6$-*p*-cymene){$P(OMe)_3$}] in D_2O, δ: 5.72 (d, 2 H, $^{3}J_{HH}$ = 5.8 Hz, CH of cymene), 5.59 (d, 2 H, $^{3}J_{HH}$ = 5.8 Hz, CH of cymene), 3.66 (d, 9 H, $^{3}J_{PH}$ = 12.0 Hz, $P(OMe)_3$), 2.62 (m, 1 H, C*H*Me_2), 2.00 (s, 3 H, Me), ≈ 1.2 (signal overlapped by those of the other species). $^{31}P\{^{1}H\}$ NMR, d: 119.7 (s) ppm.

^{1}H NMR for [$RuCl(H_2O)(\eta^6$-*p*-cymene){$P(OMe)_3$}][Cl] in D_2O, δ: 5.92 (d, 1 H, $^{3}J_{HH}$ = 5.9 Hz, CH of cymene), 5.81 (broad s, 2 H, CH of cymene), 5.60 (d, 1 H, $^{3}J_{HH}$ = 5.9 Hz, CH of

cymene), 3.70 (d, 9 H, $^{3}J_{PH}$ = 12.3 Hz, $P(OMe)_3$), 2.62 (m, 1 H, C*H*Me_2), 2.01 (s, 3 H, Me), ≈ 1.2 (signal overlapped by those of the other species). $^{31}P\{^{1}H\}$ NMR, d: 119.4 (s) ppm.

When NaOH was added to the medium, a new derivative **A** was formed:

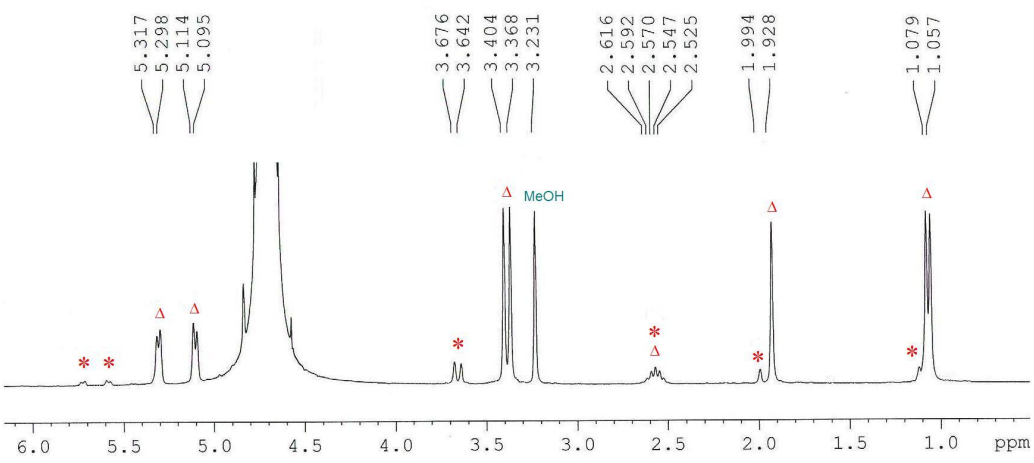


Figure S5. ^{1}H NMR spectra of $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{P(OMe)_3\}]$ in D_2O with 1 equivalent of NaOH. Complexes $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{P(OMe)_3\}]$ and A are indicated with ∗ and Δ, respectively.

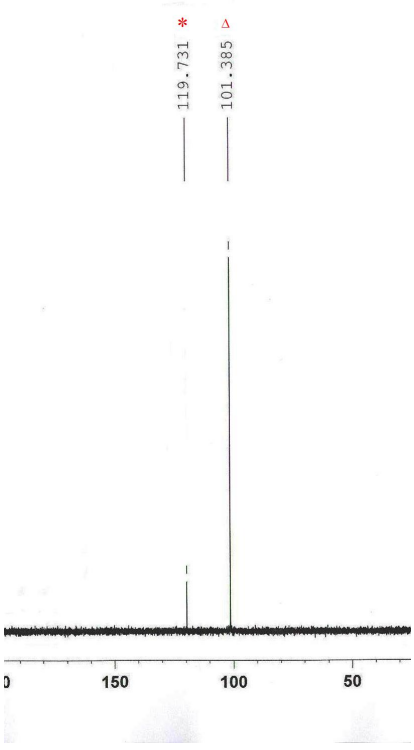


Figure S6. $^{31}P\{^{1}H\}$ NMR spectra of $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{P(OMe)_3\}]$ in D_2O with 1 equivalent of NaOH. Complexes $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{P(OMe)_3\}]$ and A are indicated with ∗ and Δ, respectively.

We propose for A the chemical formula $[Ru(OH)_2(\eta^6\text{-}p\text{-cymene})\{P(OMe)_2(OH)\}]$ on the basis of:

(i) In the ^{1}H NMR spectrum, the signal corresponding to OMe integrates for 6 hydrogens.

(ii) The presence of one equivalent of free MeOH has been detected.

(iii) ^{1}H NMR data are consistent with a plane of symmetry in the molecule.

(iv) The same species A is detected in the reaction of [$RuCl_2$(η^6-*p*-cymene){$P(OMe)_2(OH)$}][3] with NaOH in D_2O.

10. References

[1] B. Lastra-Barreira, J. Díez, P. Crochet, *Green Chem.* **2009**, *11*, 1681.

[2] a) M. A. Bennett, A. K. Smith, *J. Chem. Soc., Dalton Trans.* **1974**, , 233; b) S. A. Serron, S. P. Nolan, *Organometallics* **1995**, *14*, 4611; c) E. Hodson, S. J. Simpson, *Polyhedron* **2004**, *23*, 2695.

[3] Prepared from [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] and dimethylphosphite.