Supplementary Material (ESI) for Green Chemistry


# Supporting Information

# Highly water-soluble arene-ruthenium(II) complexes: application to catalytic isomerization of allylic alcohols in aqueous medium.

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**1. Preparation and characterization of [$RuCl_2(\eta^6$-*p*-cymene){$P(O^iPr)_3$}], 3c.** A solution of the dimer [{RuCl($\mu$-Cl)($\eta^6$-*p*-cymene)}$_2$] (0.175 g, 0.300 mmol) and $P(O^iPr)_3$ (205 μL, 0.838 mmol) in 25 ml of $CH_2Cl_2$ was stirred for 1 h at room temperature. After evaporation to dryness, the resultant residue was washed with a 3:1 mixture of hexane:diethyl ether (5 x 30 ml) and dried in vacuo, affording **3c** as a red solid. Yield: 0.217 g (72%). $^{31}P\{^1H\}$ NMR, $CDCl_3$, $\delta$: 107.5 (s). $^1H$ NMR, $CDCl_3$, $\delta$: 5.49 and 5.35 (both d, 2 H each, $^3J_{HH}$ = 5.9, CH, cymene), 4.90-4.82 (m, 3 H, OC*H*$Me_2$), 2.87 (sept, 1 H, $^3J_{HH}$ = 6.9, C*H*$Me_2$, cymene), 2.12 (s, 3 H, Me, cymene), 1.30 (d, 18 H, $^3J_{HH}$ = 6.2, OCH*Me*$_2$), 1.24 (d, 6 H, $^3J_{HH}$ = 6.9, CH*Me*$_2$, cymene). $^{13}C\{^1H\}$ NMR, $CDCl_3$, $\delta$: 107.7 (s, C of cymene), 100.9 (s, C of cymene), 88.8 (d, $^2J_{PC}$ = 3.2 CH of cymene), 88.7 (d, $^2J_{PC}$ = 2.4, CH of cymene), 71.1 (d, $^2J_{PC}$ = 7.2, O*C*H$Me_2$), 30.4 (s, *C*H$Me_2$), 23.8 (d, $^3J_{PC}$ = 4.0, OCH*Me*$_2$), 21.8 (s, CH*Me*$_2$), 17.9 (s, Me of cymene). Anal. Calcd for $C_{19}H_{35}Cl_2O_3PRu$: C, 44.12; H, 7.01. Found: C, 44.36; H, 6.86.

**2. X-ray crystal structure determination of complexes 2a-b.** The most relevant crystallographic and refinement data are given in Tables S1 (**2a**) and S3 (**2b**). Selected bond distance and angle values are given in Tables S2 (**2a**) and S4 (**2b**). Diffraction data were recorded on a Nonius KappaCCD single crystal diffractometer using Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). The data were collected the oscillation method, with 1º oscillation and 80 s exposure time per frame, and a crystal-to-detector distance of 35 mm. The data collection strategy was calculated with the program Collect.[1] Data reduction and cell refinement were performed using the programs HKL Denzo and Scalepack.[2] Absorption correction was applied by means of SORTAV.[3]

The software package WINGX was used for space group determination, structure solution and refinement.[4] Crystal structures were solved by direct methods, using the program SIR-2004.[5] Anisotropic least-squares refinement was carried out with SHELXL-97.[6] All non-hydrogen atoms were anisotropically refined. For **2a**, the hydrogen atoms were geometrically placed riding on their parent atoms with isotropic displacement parameters set to 1.2 times the $U_{eq}$ of the atoms to which they are attached (1.5 for methyl groups). For **2b**, the coordinates of H atoms were found from different Fourier maps, and included in a refinement with isotropic parameters. The function minimized was $([\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)]^{½}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ ($a$ and $b$ values are shown in Tables S1 and S3) with $\sigma^2(F_o^2)$ from counting statistics and $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[7] Geometrical calculations were made with PARST.[8] Crystallographic plots were made with PLATON.[9] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nº CCDC 728240 (**2a**) and 728241 (**2b**). The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

**Table S1.** Crystal data and structure refinement for **2a**.

| | | |
|---|---|---|
| Empirical formula | $C_{11}H_{19}Cl_2O_5PRu$ | |
| Formula weight | 434.20 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit Cell dimensions | a = 6.9850(6) Å | $\alpha$ = 80.825(4)º |
| | b = 7.3150(6) Å | $\beta$ = 81.027(4)º |
| | c = 16.9400(16) Å | $\gamma$ = 63.636(5)º |
| Volume | 762.05(12) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.892 $g/cm^3$ | |
| F(000) | 436 | |
| Crystal size | 0.1 x 0.10 x 0.05 $mm^3$ | |
| Theta range for data collection | 2.45-25.38 | |
| Reflections collected | 9619 | |
| Independent reflections | 2771 | |
| Weight function (*a*, *b*) | 0.0586, 0 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0364, wR2 = 0.0948 | |
| R indices (all data) | R1 = 0.0460, wR2 = 0.0991 | |

**Table S2**: Selected bond distance and angle values for **2a**.

| **Bond distances (Å)** | | **Bond angles (º)** | |
|---|---|---|---|
| Ru-Cl(1) | 2.4145(10) | C*-Ru-Cl(1) | 122.41(3) |
| Ru-Cl(2) | 2.4024(11) | C*-Ru-Cl(2) | 125.79(3) |
| Ru-P | 2.2948(12) | C*-Ru-P | 130.60(3) |
| Ru-C* | 1.7330(4) | Cl(1)-Ru-Cl(2) | 88.86(4) |
| C(6)-O(1) | 1.345(5) | Cl(1)-Ru-P | 90.53(4) |
| | | Cl(2)-Ru-P | 86.18(4) |
| | | C(6)-O(1)-C(7) | 117.8(3) |
| **Torsion angles** | | | |
| C(1)-C(6)-O(1)-C(7) | -1.9(6) | | |

C* = centroid of the arene ring (C(1), C(2), C(3), C(4), C(5) and C(6) carbon atoms).

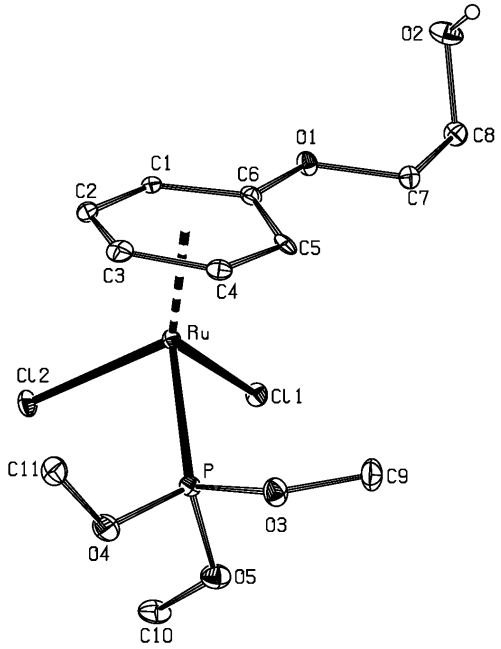



**Figure S1**. ORTEP type view of the structure of $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OMe)_3]$ (**2a**). Hydrogen atoms, except OH one, are omitted for clarity. Thermal ellipsoids are drawn at 20% probability level.

**Table S3.** Crystal data and structure refinement for **2b**.

| | | |
|---|---|---|
| Empirical formula | $C_{14}H_{25}Cl_2O_5PRu$ | |
| Formula weight | 476.28 | |
| Temperature | 150(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/c$ | |
| Unit Cell dimensions | a = 7.6034(1) Å | $\alpha = 90^o$ |
| | b = 14.0769(2) Å | $\beta = 109.371(1)^o$ |
| | c = 18.3180(3) Å | $\gamma = 90^o$ |
| Volume | 1849.63(5) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.710 $g/cm^3$ | |
| F(000) | 968 | |
| Crystal size | 0.5 x 0.15 x 0.1 $mm^3$ | |
| Theta range for data collection | 1.87-25.23 | |
| Reflections collected | 9264 | |
| Independent reflections | 3301 | |
| Weight function (*a*, *b*) | 0.0676, 1.1315 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0307, wR2 = 0.0861 | |
| R indices (all data) | R1 = 0.0379, wR2 = 0.1162 | |

**Table S4**: Selected bond distance and angle values for **2b**.

| **Bond distances (Å)** | | **Bond angles (º)** | |
|---|---|---|---|
| Ru-Cl(1) | 2.4128(8) | C*-Ru-Cl(1) | 124.61(2) |
| Ru-Cl(2) | 2.4061(8) | C*-Ru-Cl(2) | 124.24(2) |
| Ru-P | 2.2786(9) | C*-Ru-P | 129.80(2) |
| Ru-C* | 1.7181(2) | Cl(1)-Ru-Cl(2) | 87.34(3) |
| C(6)-O(1) | 1.338(4) | Cl(1)-Ru-P | 87.79(3) |
| | | Cl(2)-Ru-P | 90.44(3) |
| | | C(6)-O(1)-C(7) | 121.4(3) |
| **Torsion angles** | | | |
| C(1)-C(6)-O(1)-C(7) | 2.1(5) | | |

C* = centroid of the arene ring (C(1), C(2), C(3), C(4), C(5) and C(6) carbon atoms).

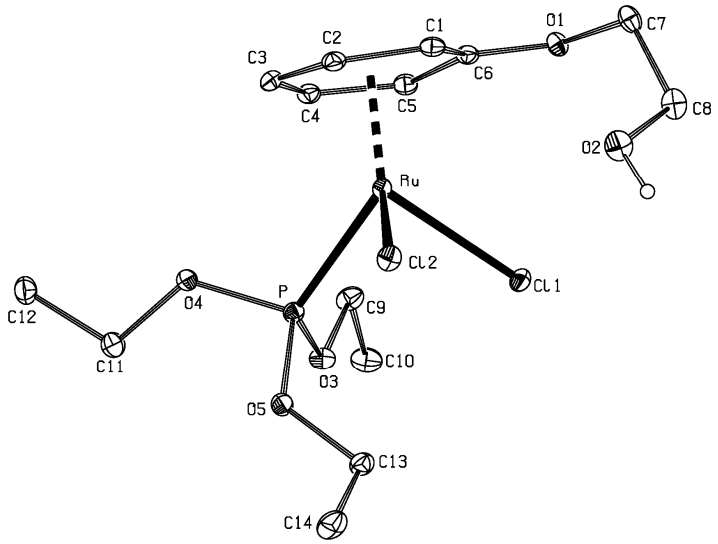



**Figure S2**. ORTEP type view of the structure of $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OEt)_3]$ (**2b**). Hydrogen atoms, except OH one, are omitted for clarity. Thermal ellipsoids are drawn at 20% probability level.

**3. Behavior of complexes 2a-c in water.**

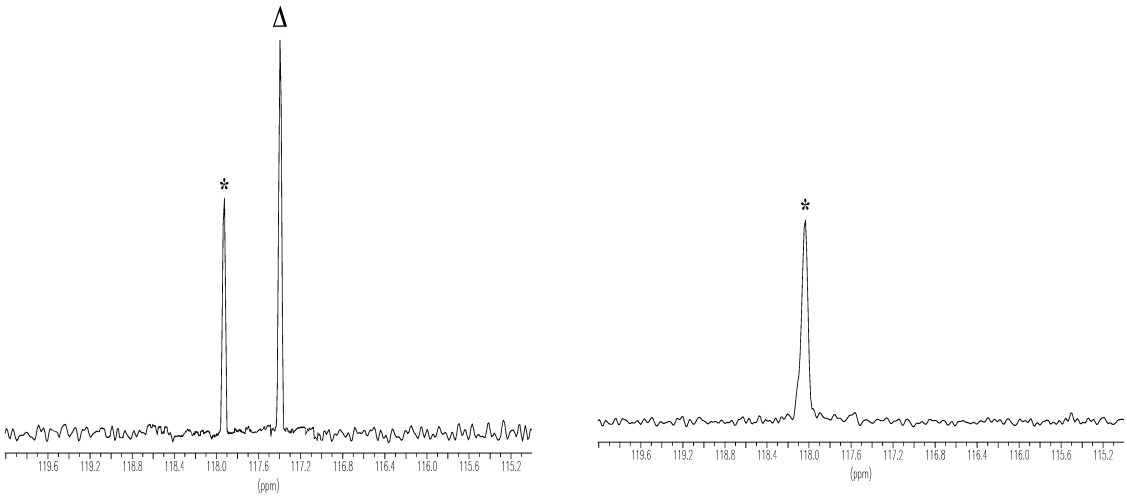
When complexes $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OR)_3\}]$ (R = Me (**2a**), Et (**2b**), $^i$Pr (**2c**)) were dissolved in $D_2O$ a mixture of $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OR)_3\}]$ and $[RuCl(H_2O)(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OR)_3\}][Cl]$ is observed by NMR spectroscopy.

***Characterization of $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OMe)_3\}]$ (2a) and $[RuCl(H_2O)(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OMe)_3\}][Cl]$ (2a') in water.*** Data for **2a**: $^{31}P\{^1H\}$ NMR, $D_2O$, $\delta$: 125.3 (s). $^1H$ NMR, $D_2O$, $\delta$: 6.55 (m, 2 H, $CH_{meta}$), 6.02 (d, 2 H, $^3J_{HH}$ = 5.7, $CH_{ortho}$), 5.68 (t, 1 H, $^3J_{HH}$ = 5.3, $CH_{para}$), 4.71 (m, 2 H, $OCH_2$), 4.36 (m, 2 H, $OCH_2$), 4.16 (d, 9 H, $^3J_{PH}$ = 11.4, Me). Data for **2a'**: $^{31}P\{^1H\}$ NMR, $D_2O$, $\delta$: 123.9 (s). $^1H$ NMR, $D_2O$, $\delta$: 6.28 (t, 1 H, $^3J_{HH}$ = 5.9, $CH_{para}$), 6.18 (m, 1 H, $CH_{ortho}$), 6.01 (d, 1 H, $^3J_{HH}$ = 6.5, $CH_{ortho}$), 5.43 (m, 2 H, $CH_{meta}$), 4.38 (m, 2 H, $OCH_2$), 4.03 (m, 2 H, $OCH_2$), 3.84 (m, 9 H, Me). Molar conductivity in water: $\Lambda_M$ = 79 $\Omega.cm^2.mol^{-1}$.

***Characterization of $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}]$ (2b) and $[RuCl(H_2O)(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}][Cl]$ (2b') in water.*** Data for **2b**: $^{31}P\{^1H\}$ NMR, $D_2O$, $\delta$: 118.0 (s). $^1H$ NMR, $D_2O$, $\delta$: 6.12 (broad s, 2 H, $CH_{meta}$), 5.58 (broad s, 2 H, $CH_{ortho}$), 5.22 (broad s, 1 H, $CH_{para}$), 4.35 (broad s, 2 H, $OCH_2$), 4.15 (m, 6 H, C*H*$_2$Me), 4.00 (broad s, 2 H, $OCH_2$), 1.35 (t, 9 H, $^3J_{HH}$ = 6.2, Me). Data for **2b'**: $^{31}P\{^1H\}$ NMR, $D_2O$, $\delta$: 117.4 (s). $^1H$ NMR, $D_2O$, $\delta$: 6.12 (m, 1 H, $CH_{meta}$), 6.00 (m, 1 H, $CH_{meta}$), 5.84 (dt, 1 H, $^3J_{HH}$ = 6.4, $^4J_{HH}$ = 2.0, $CH_{ortho}$), 5.27 (dd, 1 H, $^3J_{HH}$ = 6.4, $^4J_{PH}$ = 2.0, $CH_{ortho}$), 5.23 (t, 1 H, $^3J_{HH}$ = 5.2, $CH_{para}$), 4.26 (t, 2 H, $^3J_{HH}$ = 3.6, $OCH_2$), 4.07 (dq, 6 H, $^3J_{PH}$ = 14.4, $^3J_{HH}$ = 6.8, C*H*$_2$Me), 3.90 (m, 2 H, $OCH_2$), 1.24 (dt, 9 H, $^4J_{PH}$ = $^3J_{HH}$ = 6.8, $CH_2$*Me*). Molar conductivity in water: $\Lambda_M$ = 74 $\Omega.cm^2.mol^{-1}$.

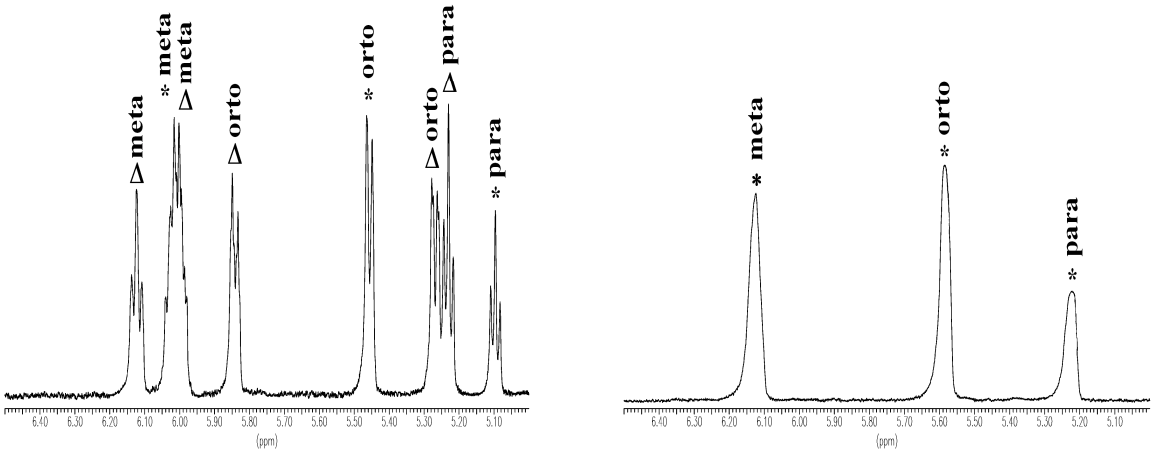
***Characterization of [RuCl$_2$($\eta^6$-C$_6$H$_5$OCH$_2$CH$_2$OH){P(O$^i$Pr)$_3$}] (2c) and [RuCl(H$_2$O)($\eta^6$-C$_6$H$_5$OCH$_2$CH$_2$OH){P(O$^i$Pr)$_3$}][Cl] (2c') in water.*** Data for **2c**: $^{31}$P{$^1$H} NMR, D$_2$O, $\delta$: 111.5 (s). $^1$H NMR, D$_2$O, $\delta$: 6.08 (m, 2 H, CH$_{meta}$), 5.37 (d, 2 H, $^3J_{HH}$ = 4.8, CH$_{ortho}$), 5.00 (t, 1 H, $^3J_{HH}$ = 5.2, CH$_{para}$), 4.66 (m, 3 H, C*H*Me$_2$), 4.22 (m, 2 H, OCH$_2$), 3.90 (m, 2 H, OCH$_2$), 1.27 (m, 18 H, CH*Me$_2$*). Data for **2c'**: $^{31}$P{$^1$H} NMR, D$_2$O, $\delta$: 111.2 (s). $^1$H NMR, D$_2$O, $\delta$: 6.01 (m, 1 H, CH$_{meta}$), 5.97 (m, 1 H, CH$_{meta}$), 5.77 (d, 1 H, $^3J_{HH}$ = 6.4, CH$_{ortho}$), 5.21 (d, 1 H, $^3J_{HH}$ = 5.6, CH$_{ortho}$), 5.13 (t, 1 H, $^3J_{HH}$ = 5.2, CH$_{para}$), 4.66 (m, 3 H, C*H*Me$_2$), 4.25 (m, 2 H, OCH$_2$), 3.90 (m, 2 H, OCH$_2$), 1.29 (m, 18 H, CH*Me$_2$*). Molar conductivity in water: $\Lambda_M$ = 47 Ω.cm$^2$.mol$^{-1}$.

***NMR spectra of 2b/2b' in D$_2$O.***




**(a)** **(b)**

**Figure 1:** $^{31}$P{$^1$H} NMR of **2b** in D$_2$O without NaCl (part a) and with NaCl (part b). Signals due to [RuCl$_2$($\eta^6$-C$_6$H$_5$OCH$_2$CH$_2$OH){P(OEt)$_3$}] (**2b**) and [RuCl(H$_2$O)($\eta^6$-C$_6$H$_5$OCH$_2$CH$_2$OH){P(OEt)$_3$}][Cl] (**2b'**) are indicated with ∗ y Δ, respectively.




**(a)** **(b)**

**Figura 2**: Detail of $^1$H NMR of **2b** in $D_2O$ without NaCl (part a) and with NaCl (part b). Signals due to $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}]$ (**2b**) and $[RuCl(H_2O)(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}][Cl]$ (**2b'**) are indicated with ∗ y Δ, respectively.

## 4. Catalytic redox isomerization of allylic alcohols in THF.

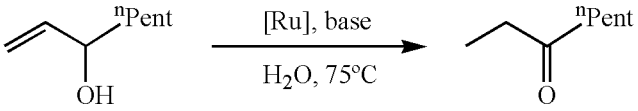



**Table S5**. Isomerization of 1-octen-3-ol into 3-octanone catalyzed by complexes $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)(L)]$ (**2a-e**).[a]

| Catalyst [L] | Time | Yield (%)[b] | TOF ($h^{-1}$)[c] |
|---|---|---|---|
| **2a** $[P(OMe)_3]$ | 5 min | > 99 | 1200 |
| **2b** $[P(OEt)_3]$ | 5 min | > 99 | 1200 |
| **2c** $[P(O^iPr)_3]$ | 5 min | > 99 | 1200 |
| **2d** $[P(OPh)_3]$ | 4 h | > 99 | 25 |
| **2e** $[PPh_3]$ | 20 min | > 99 | 300 |

[a] Reactions carried out at 75ºC using 4 mmol of 1-octen-3-ol, 1 mol% of Ru, 5 mol% of $KO^tBu$ and 20 mL of THF. [b] Determined by GC analyses. [c] TOF = Turn Over Frequency, ((mol of product/mol of catalyst)/time), calculated at the time indicated in each case.

## References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