

Electronic Supplementary Information

Functionalized arene-ruthenium(II) complexes: dangling vs. tethering side chain

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1. General methods

2. Preparation of $[\text{RuCl}(\eta^6\text{-}\kappa^1\text{(O)-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})(\text{PPh}_3)][\text{SbF}_6]$ (5c[SbF_6]).

3. X-ray crystal structure determination of complexes $2[\text{SbF}_6]_2$, $3[\text{SbF}_6]$ and $5\text{a}[\text{SbF}_6]$.

4. Behavior of precursors $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5\text{XCH}_2\text{CH}_2\text{OH})\{\text{P}(\text{OEt})_3\}]$ (X = O or CH₂) in water (NMR data).

5. Relative energies of $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5\text{-X-CH}_2\text{CH}_2\text{OH})\{\text{P}(\text{OMe})\}]$ (X = O (1M), CH₂ (4M)) in function of the dihedral angle C_{ortho}-C_{ipso}-X-C_(CH₂).

6. Cartesian coordinates and total energies of model complexes 1M and 4M.

7. References

1. General methods. The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers with the exception of compounds $[\text{RuCl}_2(\eta^6:\kappa^1(O)\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})]$,^{1,2} $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{OH})(\text{PR}_3)]$ ($\text{PR}_3 = \text{P}(\text{OPh})_3$ (**1a**), $\text{P}(\text{OEt})_3$ (**1b**), PPh_3 (**1c**))³ and $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})(\text{PPh}_3)]$ (**4c**),² which were prepared by following the method reported in the literature. The C, H elemental analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Infrared spectra were recorded with a Perkin-Elmer 1720-XFT spectrometer. NMR spectra were performed with a Bruker DPX300 instrument at 300 MHz (^1H), 121.5 MHz (^{31}P) or 75.4 MHz (^{13}C) using SiMe_4 or 85% H_3PO_4 as standards. Cyclovoltammetric measurements were performed at 20°C with a “ μ Autolab type III” apparatus equipped with a three-electrode system. Platinum disk electrode, spiral shaped platinum wire and silver wire were used as working-, counter- and reference-electrodes, respectively. CV experiments were carried out with CH_2Cl_2 solutions of the appropriate complex (0.5×10^{-3} M) and $[\text{N}^n\text{Bu}_4][\text{PF}_6]$ (0.1 M) as electrolyte. Formal CV potentials (E°) are referenced relative to potential of the ferrocinium/ferrocene couple ($E^\circ = 0.184$ V) run under identical conditions ($E^\circ = E^\circ(\text{complex}^+/\text{complex}) - E^\circ([\text{Cp}_2\text{Fe}]^+ / [\text{Cp}_2\text{Fe}])$). A scan rate of 0.5V/s has been employed.

2. Preparation of $[\text{RuCl}(\eta^6:\kappa^1(O)\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})(\text{PPh}_3)][\text{SbF}_6]$ (5c** $[\text{SbF}_6]$)**

A solution of **4c** (0.100 g, 0.18 mmol) in 20 mL of dichloromethane was treated with AgSbF_6 (0.072 g, 0.21 mmol, dissolved in 1 mL of MeOH). After stirring 0.5 h at room temperature, the suspension was filtered on Kieselguhr, and the filtrate was evaporated

to dryness. The residue was washed 3 times with 10 mL of diethylether and the resultant yellow solid was dried in vacuum. Yield: 0.110 g (81 %). Anal. Calcd for $C_{27}H_{27}ClF_6OPRuSb$: C, 42.08; H, 3.53. Found: C, 41.78; H, 3.71. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ : 28.3 (s). 1H NMR, $CDCl_3$, δ : 7.78 - 7.36 (m, 15 H, PPh_3), 5.38 (d, 2 H, $^3J_{HH} = 5.9$, CH_{ortho}), 5.15 (apparent t, 2 H, $^3J_{HH} \approx ^3J_{HH} \approx 5.6$, CH_{meta}), 4.55 (td, 1 H, $^3J_{HH} = 5.4$, $^3J_{PH} = 2.1$, CH_{para}), 3.80 (very broad s, CH_2OH), 2.82 (t, 2 H, $^3J_{HH} = 7.2$, $PhCH_2$), 1.98 (m, 2 H, CH_2CH_2OH), OH not observed. IR, $\nu_{OH} = 3456\text{ cm}^{-1}$. The spectroscopic data of compound **5c**[SbF_6] are very similar to those of the BF_4 -salt reported previously.²

3. X-ray crystal structure determination of compounds 2[SbF₆]₂, 3[SbF₆] and 5a[SbF₆]. Single crystals suitable for X-ray diffraction analyses were obtained by slow diffusion of diethylether through saturated solutions of **2[SbF₆]₂**, **3[SbF₆]** or **5a[SbF₆]** in acetone. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publications Nos. CCDC 908513 (**2[SbF₆]₂**), 908514 (**3[SbF₆]**), 908515 (**5a[SbF₆]**). Copies of the data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif. The most relevant crystal and refinement data are collected in Tables S1, S3 and S5. Diffraction data of compound **2[SbF₆]₂** were recorded on a Nonius KappaCCD single crystal diffractometer, using Mo-K α radiation ($\lambda = 0.71073$ Å). Images were collected at a 35 mm fixed crystal-detector distance, using the oscillation method, with 1° oscillation and 50 s exposure time per frame. Data collection strategy was calculated with the program Collect.⁴ Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack.⁵ A semi-empirical absorption correction was applied using the program SORTAV.⁶ For derivatives **3[SbF₆]** and **5a[SbF₆]**, data collection was performed on a Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu-K α radiation ($\lambda = 1.5418$ Å). Images were collected at a 63 mm fixed crystal-detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (1.5-5 s for **3[SbF₆]** and 2-15 s for **5a[SbF₆]**). Data collection strategy was calculated with the program *CrysAlis^{Pro} CCD*.⁷ Data reduction and cell refinement were performed with the program *CrysAlis^{Pro} RED*.⁷ An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program *CrysAlis^{Pro} RED*.⁷ In all cases, the software package WINGX⁸ was used for space group determination, structure solution and refinement. The structure of complex **2[SbF₆]₂** was solved by direct methods using SIR92.⁹ For **3[SbF₆]** and **5a[SbF₆]**, the structures were solved by Patterson interpretation and phase expansion using DIRDIF.¹⁰ The crystal of **3[SbF₆]**

and **5a[SbF₆]** contains, respectively, two diethylether and one acetone molecules of solvation per formula unit. Isotropic least-squares refinement on F^2 using SHELXL97¹¹ was performed. During the final stages of the refinements, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined. The hydrogen atoms were geometrically located 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), (except H1O for **5a[SbF₆]**, the coordinates of this hydrogen atom were found from different Fourier maps and included in a refinement with isotropic parameters). The function minimized was $([\sum w F_o^2 - F_c^2]/\sum w(F_o^2))^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (a and b values are collected in Tables S1, S3 and S5) with $\sigma(F_o^2)$ from counting statistics and $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography.¹² Geometrical calculations were made with PARST.¹³ The crystallographic plots were made with PLATON.¹⁴

Table S1. Crystal data and structure refinement details for **2[SbF₆]₂**.

Compound 2[SbF₆]₂	
Empirical formula	C ₅₂ H ₅₀ Cl ₂ F ₁₂ O ₁₀ P ₂ Ru ₂ Sb ₂
Formula weight	1641.4
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 2 ₁ /c
<i>Unit cell dimensions</i>	
a (Å)	9.9387(3)
b (Å)	11.8480(4)
c (Å)	24.2871(7)
α (°)	90
β (°)	92.775(2)
γ (°)	90
Volume (Å ³)	2856.5(1)
Z	2
Calculated density (g.cm ⁻¹)	1.908
F(000)	1608
Crystal size (mm)	0.25 x 0.20 x 0.10
Theta range for data collected	1.91 to 25.36°
Reflections collected	18346
Independent reflections	5227 [R(int) = 0.037]
Completeness to theta max	100.0%
Data / restraints / parameters	5227 / 0 / 370
Weight function (a, b)	0.0620, 0.0
Final R indices [I>2σ(I)]	
R ₁ ^[a]	0.0479
wR ₂ ^[b]	0.1234
R indices (all data)	
R ₁ ^[a]	0.0721
wR ₂ ^[b]	0.1459
Largest diff. peak and hole	1.695 and -1.109 e.Å ³
^[a] R ₁ = Σ(F _o - F _c)/Σ F _o . ^[b] wR ₂ = {Σ[w(F _o ² - F _c ²) ²]/Σ[w(F _o ²) ²]} ^{1/2} .	

Table S2. Selected bond lengths (Å) and angles (°) for **2[SbF₆]₂**.

Bond lengths		Bond angles	
Ru(1)-Cl(1)	2.429(1)	Cl(1)-Ru(1)-Cl(1a)	79.91(5)
Ru(1)-Cl(1a)	2.436(1)	Cl(1)-Ru(1)-P(1)	88.75(5)
Ru(1)-P(1)	2.284(2)	Cl(1a)-Ru(1)-P(1)	92.93(5)
Ru(1)-C*	1.7488(4)	Cl(1)-Ru(1)-C*	128.66(4)
C(4)-O(1)	1.327(7)	P(1)-Ru(1)-C*	127.56(4)
O(1)-C(7)	1.451(8)	Cl(1a)-Ru(1)-C*	124.93(4)
C(8)-O(2)	1.421(9)	Ru(1)-Cl(1)-Ru(1a)	100.09(5)
Ru(1)-C(1)	2.229(6)	C(4)-O(1)-C(7)	119.3(5)
Ru(1)-C(2)	2.183(5)		
Ru(1)-C(3)	2.214(5)	Torsion angles	
Ru(1)-C(4)	2.340(6)	C(3)-C(4)-O(1)-C(7)	-0.6(8)
Ru(1)-C(5)	2.302(6)	P(1)-Ru(1)-C*-C(4)	131.3
Ru(1)-C(6)	2.228(6)		

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

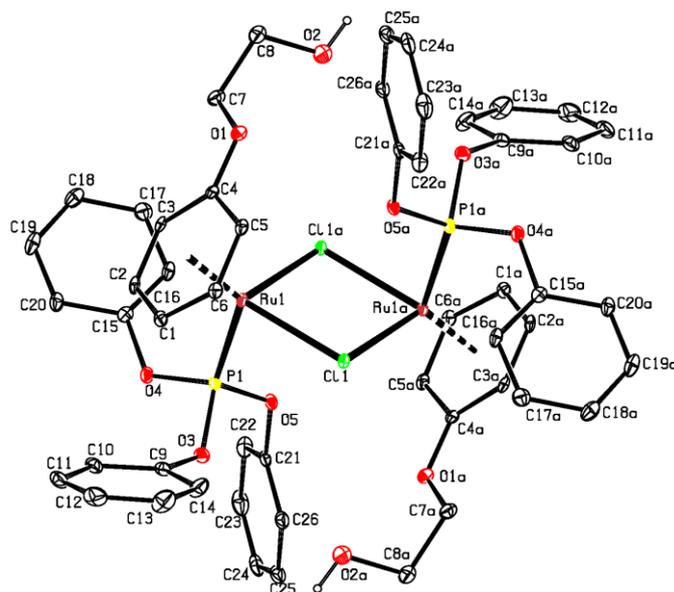


Table S3. Crystal data and structure refinement details for **3[SbF₆]**.

Compound 3[SbF₆]	
Empirical formula	C ₅₂ H ₅₀ Cl ₃ F ₆ O ₄ P ₂ Ru ₂ Sb·2OC ₄ H ₁₀
Formula weight	1493.34
Temperature (K)	100(2)
Wavelength (Å)	1.5418
Crystal system	Monoclinic
Space group	C 2/c
<i>Unit cell dimensions</i>	
a (Å)	31.342(1)
b (Å)	14.4711(7)
c (Å)	15.0960(5)
α (°)	90
β (°)	114.850(4)
γ (°)	90
Volume (Å ³)	6213.0(4)
Z	4
Calculated density (g.cm ⁻¹)	1.597
F(000)	3008
Crystal size (mm)	0.316 x 0.085 x 0.037
Theta range for data collected	3.11 to 66.98°
Reflections collected	17101
Independent reflections	5479 [R(int) = 0.0401]
Completeness to theta max	99.2%
Data / restraints / parameters	5479 / 0 / 341
Weight function (a, b)	0.0805, 0
Final R indices [I>2σ(I)]	
R ₁ ^[a]	0.0423
wR ₂ ^[b]	0.1165
R indices (all data)	
R ₁ ^[a]	0.0526
wR ₂ ^[b]	0.1206
Largest diff. peak and hole	1.885 and -2.202 e.Å ³
^[a] R ₁ = Σ(F _o - F _c)/Σ F _o . ^[b] wR ₂ = {Σ[w(F _o ² - F _c ²) ²]/Σ[w(F _o ²) ²]} ^{1/2} .	

Table S4. Selected bond lengths (Å) and angles (°) for **3[SbF₆]**.

Bond length		Bond angles	
Ru(1)-Cl(1)	2.4271(8)	Cl(2)-Ru(1)-Cl(1)	91.45(3)
Ru(1)-Cl(2)	2.414(1)	Cl(1)-Ru(1)-P(1)	86.80(4)
Ru(1)-P(1)	2.341(1)	Cl(2)-Ru(1)-P(1)	86.28(4)
Ru(1)-C*	1.722(3)	Cl(1)-Ru(1)-C*	124.82(2)
C(4)-O(1)	1.341(8)	Cl(2)-Ru(1)-C*	124.38(3)
O(1)-C(7)	1.429(9)	P(1)-Ru(1)-C*	130.53(3)
C(8)-O(2)	1.414(9)	Ru(1)-Cl(1)-Ru(1a)	117.59(6)
Ru(1)-C(1)	2.215(5)	C(4)-O(1)-C(7)	119.6(6)
Ru(1)-C(2)	2.164(4)		
Ru(1)-C(3)	2.174(5)	Torsion angles	
Ru(1)-C(4)	2.304(5)	C(3)-C(4)-O(1)-C(7)	4.6(9)
Ru(1)-C(5)	2.267(5)	P(1)-Ru(1)-C*-C(4)	139.9
Ru(1)-C(6)	2.184(4)		

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

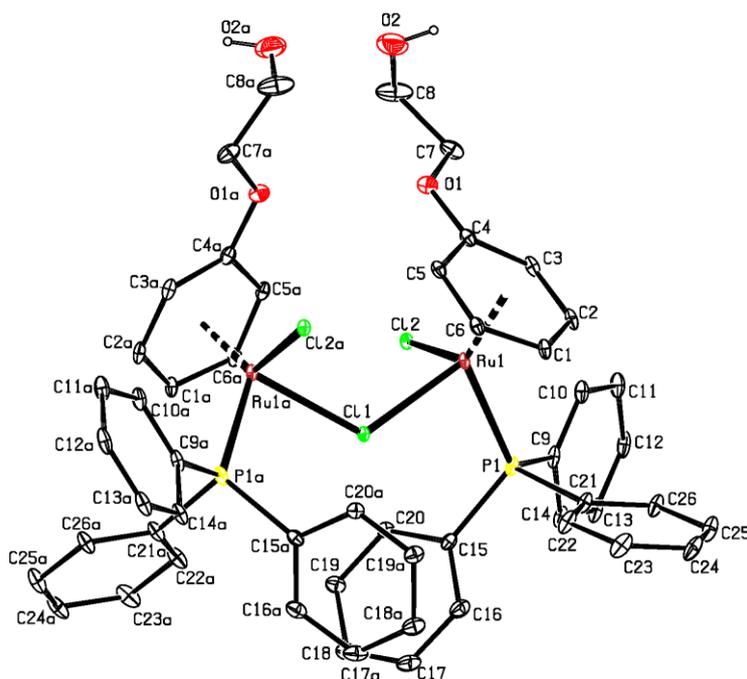


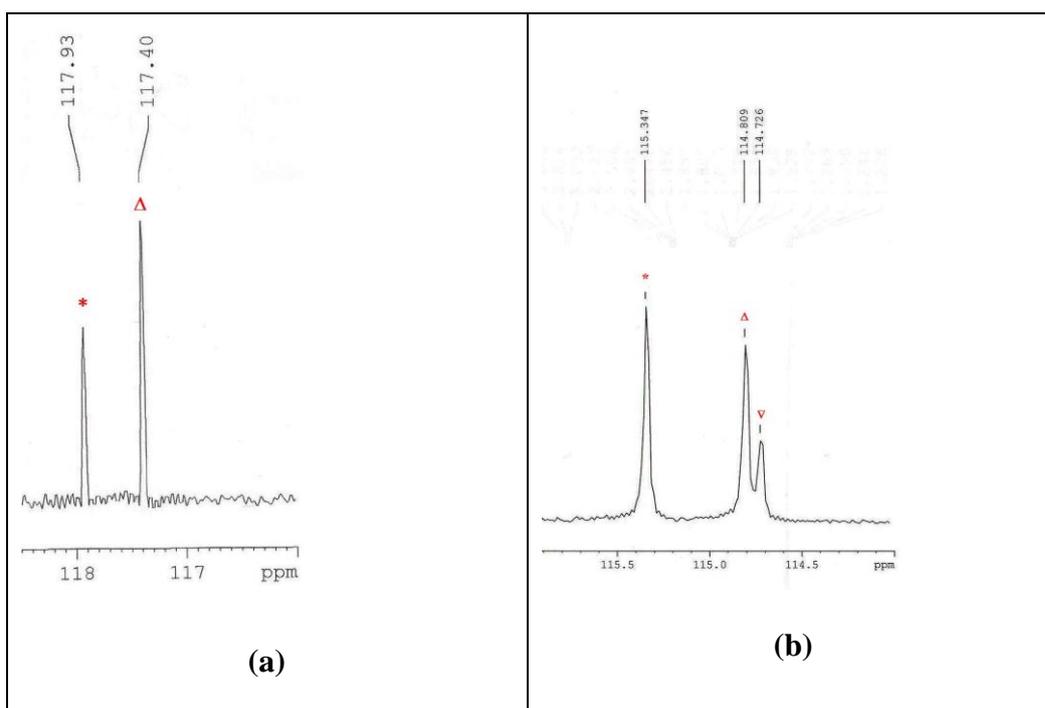
Table S5. Crystal data and structure refinement details for **5a[SbF₆]**.

Compound 5a[SbF₆]	
Empirical formula	C ₂₈ H ₂₃ ClF ₆ O ₄ PRuSb·OC ₂ H ₁₀
Formula weight	876.80
Temperature (K)	293(2)
Wavelength (Å)	1.5418
Crystal system	Monoclinic
Space group	P21/n
<i>Unit cell dimensions</i>	
a (Å)	11.7393(1)
b (Å)	19.5779(2)
c (Å)	15.0206(1)
α (°)	90
β (°)	99.505(1)
γ (°)	90
Volume (Å ³)	3404.80(5)
Z	4
Calculated density (g.cm ⁻¹)	1.710
F(000)	1736
Crystal size (mm)	0.167 x 0.127 x 0.087
Theta range for data collected	3.74 to 73.98°
Reflections collected	23902
Independent reflections	6878 [R(int) = 0.0218]
Completeness to theta max	99.5 %
Data / restraints / parameters	6878 / 11 / 392
Weight function (a, b)	0.099, 7.3304
Final R indices [I > 2σ(I)]	
R ₁ ^[a]	0.0583
wR ₂ ^[b]	0.1673
R indices (all data)	
R ₁ ^[a]	0.0607
wR ₂ ^[b]	0.1701
Largest diff. peak and hole	2.422 and -1.824 e.Å ⁻³
^[a] R ₁ = Σ(F _o - F _c)/Σ F _o . ^[b] wR ₂ = {Σ[w(F _o ² - F _c ²) ²]/Σ[w(F _o ²) ²]} ^{1/2} .	

4. Behavior of precursors $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5\text{XCH}_2\text{CH}_2\text{OH})\{\text{P}(\text{OEt})_3\}]$ ($\text{X} = \text{O}$ or CH_2) in water.

Aqueous solutions of $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{OH})\{\text{P}(\text{OEt})_3\}]$ (**1b**) and $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})\{\text{P}(\text{OEt})_3\}]$ (**4b**) were prepared with 20 mg of **1b** or **4b** in 0.6 mL of D_2O , and ^1H and $^{31}\text{P}\{^1\text{H}\}$ spectra were recorded on a Bruker DPX300 apparatus.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectra:



(a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **1b**, recorded in D_2O . Resonances attributed to compounds $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{OH})\{\text{P}(\text{OEt})_3\}]$ and $[\text{RuCl}(\text{D}_2\text{O})(\eta^6\text{-C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{OH})\{\text{P}(\text{OEt})_3\}][\text{Cl}]$ are labelled with * and Δ , respectively. (b) $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **4b**, recorded in D_2O . Resonances attributed to derivatives $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})\{\text{P}(\text{OEt})_3\}]$, $[\text{RuCl}(\text{D}_2\text{O})(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})\{\text{P}(\text{OEt})_3\}][\text{Cl}]$ and $[\text{RuCl}(\eta^6\text{-}\kappa^1\text{O})\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})\{\text{P}(\text{OEt})_3\}][\text{Cl}]$ are labelled with *, Δ and ∇ , respectively.

^1H (and $^{13}\text{C}\{^1\text{H}\}$) NMR data are in complete agreement with the presence of both $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{OH})\{\text{P}(\text{OEt})_3\}]$ and $[\text{RuCl}(\text{D}_2\text{O})(\eta^6\text{-C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{OH})\{\text{P}(\text{OEt})_3\}][\text{Cl}]$ in the sample (a) and with the presence of $[\text{RuCl}_2(\eta^6\text{-}$

$C_6H_5CH_2CH_2CH_2OH\{P(OEt)_3\}$, $[RuCl(D_2O)(\eta^6-C_6H_5CH_2CH_2CH_2OH)\{P(OEt)_3\}][Cl]$ and $[RuCl(\eta^6:\kappa^1(O)-C_6H_5CH_2CH_2CH_2OH)\{P(OEt)_3\}][Cl]$ in the sample (b). Data are the following:

Spectroscopic data of $[RuCl_2(\eta^6-C_6H_5OCH_2CH_2CH_2OH)\{P(OEt)_3\}]$.

$^{31}P\{^1H\}$ NMR, D_2O , δ : 118.0 (s).

1H NMR, D_2O , δ : 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, $OCCH_2$), 4.15 (m, 6 H, CH_2CH_3), 4.00 (broad s, 2 H, OCH_2), 1.35 (t, 9 H, $^3J_{HH} = 6.2$, CH_2CH_3), the OH signal was not observed.

Spectroscopic data of $[RuCl(D_2O)(\eta^6-C_6H_5OCH_2CH_2CH_2OH)\{P(OEt)_3\}][Cl]$.

$^{31}P\{^1H\}$ NMR, D_2O , δ : 117.4 (s).

1H NMR, D_2O , δ : 6.12 (m, 1 H, CH_{meta}), 6.00 (m, 1 H, CH_{meta}), 5.84 (d, 1 H, $^3J_{HH} = 6.4$, 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, $^3J_{PH} = 14.4$, $^3J_{HH} = 6.8$, CH_2CH_3), 3.90 (m, 2 H, OCH_2), 1.24 (dt, 9 H, $^4J_{PH} = ^3J_{HH} = 6.8$, CH_2CH_3), the OH signal was not observed.

Spectroscopic data of $[RuCl_2(\eta^6-C_6H_5CH_2CH_2CH_2CH_2OH)\{P(OEt)_3\}]$.

$^{31}P\{^1H\}$ NMR, D_2O , δ : 115.3 (s).

1H NMR, D_2O , δ : 6.12 (m, 2 H, CH_{meta}), 6.01 (d, 2 H, $^3J_{HH} = 5.7$, CH_{ortho}), 5.85 (m, 1 H, CH_{para}), 4.35 (dq, 6 H, $^3J_{PH} = 7.1$, $^3J_{HH} = 7.1$, $POCH_2$), 3.92 (t, 2 H, $^3J_{HH} = 6.5$, CH_2OH), 2.76 (t, 2 H, $^3J_{HH} = 7.5$, $PhCH_2$), 2.16 (m, 2 H, CH_2), 1.55 (t, 3 H, $^3J_{HH} = 7.1$, CH_3), the OH signal was not observed.

$^{13}C\{^1H\}$ NMR, D_2O , δ : 113.7 (d, $^2J_{PC} = 7.1$, C_{ipso}), 89.7 (d, $^2J_{PC} = 7.0$, CH_{meta} or CH_{ortho}), 89.4 (s, CH_{meta} or CH_{ortho}), 81.6 (s, CH_{para}), 63.5 (d, $^2J_{PC} = 6.0$, $POCH_2$), 60.8 (s, CH_2OH), 30.9 and 29.1 (both s, $PhCH_2CH_2$), 15.3 (d, $^3J_{PC} = 6.3$, CH_3).

Spectroscopic data of [RuCl(D₂O)(η^6 -C₆H₅CH₂CH₂CH₂CH₂OH){P(OEt)₃}] [Cl].

³¹P{¹H} NMR, D₂O, δ : 114.8 (s).

¹H NMR, D₂O, δ : 5.87-5.76 (m, 3 H, CH_{arene}), 5.63 (m, 1 H, CH_{arene}), 5.59 (m, 1 H, CH_{arene}), 4.35 (m, 6 H, POCH₂), 3.62 (t, 2 H, ³J_{HH} = 6.3, CH₂), 2.49 (m, 2 H, CH₂), 1.86 (m, 2 H, CH₂), 1.55 (m, 3 H, CH₃), the OH signal was not observed.

¹³C{¹H} NMR, D₂O, δ : 114.1 (d, ²J_{PC} = 7.1, C_{ipso}), 91.3 (d, ²J_{PC} = 9.1, CH meta or CH_{ortho}), 89.2 and 87.0 (s, CH_{meta} or CH_{ortho}), 84.8 (d, ²J_{PC} = 5.0, CH_{meta} or CH_{ortho}), 80.9 (s, CH_{para}), 63.8 (d, ²J_{PC} = 6.2, POCH₂), 60.7 (s, CH₂OH), 30.8 and 29.1 (both s, PhCH₂CH₂), 15.3 (d, ³J_{PC} = 6.3, CH₃).

Spectroscopic data of [RuCl(η^6 : κ^1 (O)-C₆H₅OCH₂CH₂CH₂OH){P(OEt)₃}] [Cl].

³¹P{¹H} NMR, D₂O, δ : 114.7 (s).

¹H NMR, D₂O, δ : 6.43 (m, 1 H, CH_{arene}), 6.28 (m, 1 H, CH_{arene}), 5.94 (m, 1 H, CH_{arene}), 5.50 (m, 1 H, CH_{arene}), 5.19 (m, 1 H, CH_{arene}), 4.35 (m, 6 H, POCH₂), 4.10 (m, 1 H, CH₂), 3.51 (m, 1 H, CH₂), 3.12 (m, 1 H, CH₂), 2.66 (m, 1 H, CH₂), 2.39 (m, 1 H, CH₂), 1.86 (m, 1 H, CH₂), 1.61 (m, 3 H, CH₃), the OH signal was not observed.

¹³C{¹H} NMR, D₂O, δ : 103.3 (d, ²J_{PC} = 10.1, CH_{ortho} or CH_{meta}), 84.8 (d, ²J_{PC} = 17.1, CH_{ortho} or CH_{meta}), 86.7 and 82.1 (both s, CH_{meta}), 73.3 (CH_{para}), 64.0 (s, CH₂OH), 28.6 and 27.1 (both s, PhCH₂CH₂), 15.3 (d, ³J_{PC} = 6.3, CH₃).

Signal attributions have been made with the help of ¹H-¹H and ¹H-¹³C correlations NMR spectroscopy and on the basis of the following observations:

(a) When NaCl was added to aqueous solution of **1b**, only the signals corresponding to the dichloro-complex [RuCl₂(η^6 -C₆H₅OCH₂CH₂OH){P(OEt)₃}] were observed. In particular, under these conditions the ³¹P{¹H} NMR spectra showed only one singlet resonance at 117.9 ppm.

(b) When NaCl was added to aqueous solution of **4b**, only the signals corresponding to the dichloro-complex $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})\{\text{P}(\text{OEt})_3\}]$ were observed. In particular, under these conditions the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showed only one singlet resonance at 115.3 ppm.

(c) NMR spectra of aqueous solution of $[\text{RuCl}_2(\eta^6:\kappa^1(\text{O})\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})\{\text{P}(\text{OEt})_3\}][\text{SbF}_6]$ showed signals corresponding to the tethered cation $[\text{RuCl}_2(\eta^6:\kappa^1(\text{O})\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})\{\text{P}(\text{OEt})_3\}]^+$ and the aquo-derivative $[\text{RuCl}(\text{D}_2\text{O})(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})\{\text{P}(\text{OEt})_3\}]^+$.

5. Relative energies of $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_5\text{-X-CH}_2\text{CH}_2\text{OH})\{\text{P}(\text{OMe})\}]$ (X = O, CH₂) in function of the dihedral angle C_{ortho}-C_{ipso}-X-C(CH₂).

Table S7. Relative energies, C_{ipso}-O bond distances and C_{ipso}-O bond order as a function of the θ values.^a

θ	$E_{\text{rel}} / \text{kcal mol}^{-1}$	$r(\text{C-O}) / \text{\AA}$	C-O Wiberg Index
0	0.0	1.337	1.093
9.2	-0.2	1.337	1.092
15	-0.1	1.337	1.091
30	1.0	1.340	1.082
45	2.8	1.344	1.066
60	3.5	1.349	1.043
90	4.3	1.358	1.001

All data have been computed at the BP86/def2-SVP level. ^a $\theta = \text{C}_{\text{ortho}}\text{-C}_{\text{ipso}}\text{-O-C}$ dihedral angle.

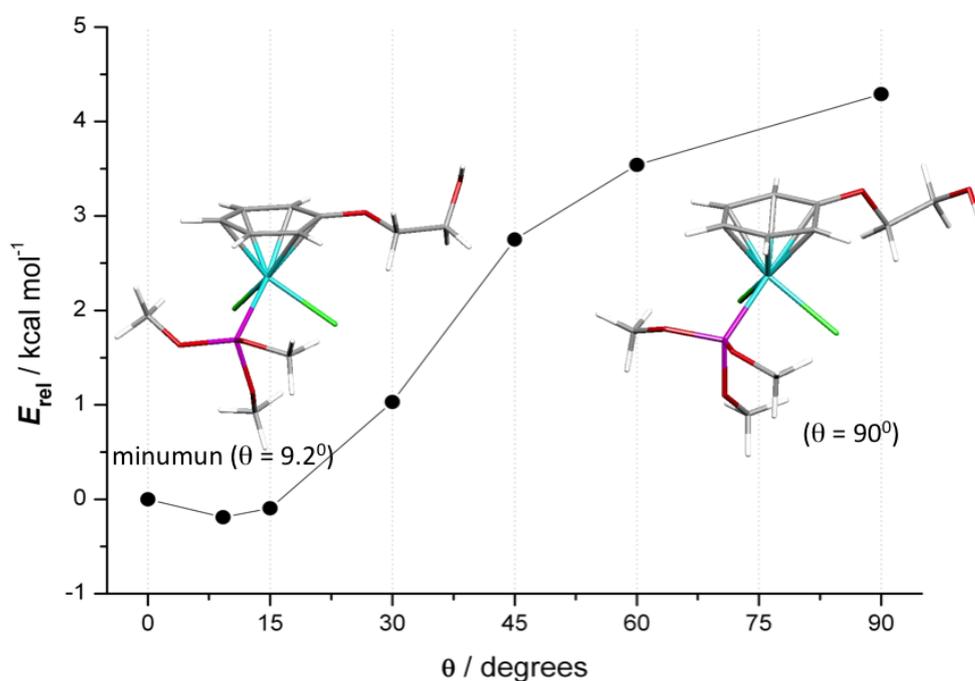
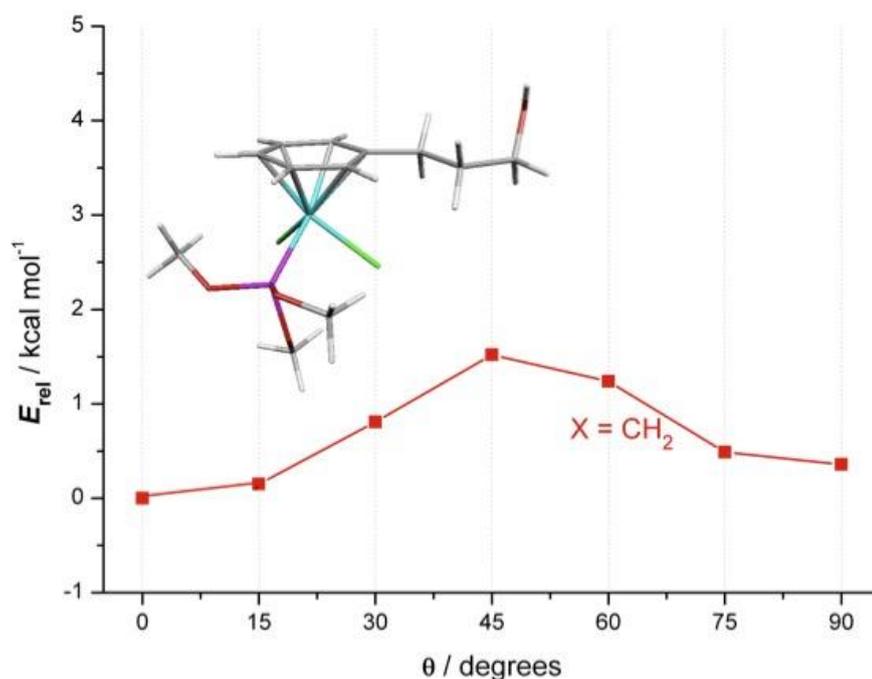


Table S8. Relative energies, $C_{\text{ipso}}\text{-CH}_2$ bond distances and $C_{\text{ipso}}\text{-CH}_2$ bond order as a function of the θ values.^a

θ	$E_{\text{rel}} / \text{kcal mol}^{-1}$	$r(\text{C-CH}_2) / \text{\AA}$	C-CH_2 Wiberg Index
0	0.0	1.513	1.027
15	0.2	1.512	1.028
30	0.8	1.512	1.028
45	1.5	1.512	1.027
60	1.2	1.515	1.022
75	0.5	1.515	1.014
90	0.4	1.515	1.014

All data have been computed at the BP86/def2-SVP level. ^a $\theta = C_{\text{ortho}}\text{-C}_{\text{ipso}}\text{-CH}_2\text{-C}$ dihedral angle.



6. Cartesian coordinates and total energies of model complexes 1M and 4M.

Cartesian coordinates (in Å) and total energies (in a. u., ZPVE included) of all the stationary points discussed in the text. All calculations have been performed at the BP86/def2-SVP level of theory.

1M: E= -2162.471666

C	1.560215000	-2.066960000	0.331937000
H	2.071924000	-2.376901000	1.252871000
C	0.350509000	-2.699613000	-0.098510000
H	-0.075647000	-3.504166000	0.519819000
C	-0.329561000	-2.290434000	-1.283554000
H	-1.235511000	-2.810043000	-1.622695000
C	0.136512000	-1.101652000	-1.943998000
H	-0.423339000	-0.688341000	-2.797576000
C	1.329263000	-0.424680000	-1.511369000
H	1.657627000	0.481016000	-2.036508000
C	2.087195000	-0.963075000	-0.407558000
C	3.658275000	0.859828000	-0.410917000
H	2.836468000	1.591304000	-0.246024000
H	3.894675000	0.800594000	-1.500195000
C	4.895244000	1.262237000	0.383477000
H	5.116951000	2.330216000	0.130867000
H	4.641748000	1.232162000	1.463594000
C	-0.947390000	2.744697000	-1.850188000
H	-0.061025000	2.613102000	-1.192440000
H	-1.521459000	3.626614000	-1.498153000
H	-0.623142000	2.910238000	-2.896936000
C	-2.765000000	1.925873000	1.890144000

H	-1.855371000	1.670317000	2.468242000
H	-3.555881000	1.174255000	2.088935000
H	-3.128703000	2.934108000	2.169754000
C	-3.675397000	-1.386267000	-0.724295000
H	-3.477471000	-1.878735000	-1.701153000
H	-4.755718000	-1.485152000	-0.497296000
H	-3.086004000	-1.864444000	0.085485000
Cl	0.618502000	1.356790000	1.342826000
Cl	-1.530388000	-1.195662000	2.017853000
O	3.221879000	-0.431933000	0.058986000
O	6.008573000	0.409007000	0.203383000
H	6.312780000	0.504592000	-0.718844000
O	-1.783300000	1.573894000	-1.849300000
O	-3.400809000	0.016905000	-0.807243000
O	-2.466110000	1.995124000	0.483994000
P	-1.977257000	0.742607000	-0.438299000
Ru	-0.182115000	-0.563698000	0.113673000

4M: E= -2126.574145

C	1.443965000	-2.140292000	0.294822000
H	1.878680000	-2.533466000	1.225571000
C	0.217162000	-2.698798000	-0.207439000
H	-0.269543000	-3.510964000	0.353438000
C	-0.390140000	-2.202206000	-1.395870000
H	-1.309341000	-2.656970000	-1.789494000
C	0.166927000	-1.018840000	-1.993369000
H	-0.342419000	-0.542486000	-2.845445000
C	1.364296000	-0.427983000	-1.474775000
H	1.753362000	0.488732000	-1.936918000
C	2.033710000	-1.006184000	-0.333736000
C	3.831576000	0.872404000	-0.385440000
H	3.095493000	1.700076000	-0.289634000
H	3.991788000	0.703894000	-1.476787000
C	5.163578000	1.308604000	0.241992000
H	5.500878000	2.265391000	-0.227288000
H	5.015769000	1.519149000	1.323092000
C	-1.003369000	2.748895000	-1.850175000
H	-0.090522000	2.603391000	-1.233165000
H	-1.560993000	3.624403000	-1.458432000
H	-0.722860000	2.931895000	-2.906290000
C	-2.789333000	1.916677000	1.911867000
H	-1.872717000	1.666443000	2.481112000
H	-3.574217000	1.160693000	2.117958000
H	-3.156090000	2.922869000	2.194744000
C	-3.727369000	-1.389598000	-0.671213000
H	-3.576335000	-1.901543000	-1.646385000
H	-4.799079000	-1.468717000	-0.399333000
H	-3.114562000	-1.864700000	0.122591000
Cl	0.577840000	1.365989000	1.325621000
Cl	-1.525506000	-1.192144000	2.017828000
O	6.172480000	0.305237000	0.179233000
H	6.386803000	0.169142000	-0.763389000
O	-1.841778000	1.579078000	-1.837465000
O	-3.434745000	0.006959000	-0.792829000
O	-2.503616000	1.987625000	0.503287000
P	-2.015830000	0.742763000	-0.429212000
Ru	-0.196237000	-0.556927000	0.095853000
C	3.272991000	-0.391049000	0.276941000
H	4.070908000	-1.166509000	0.296997000
H	3.034495000	-0.163741000	1.339629000

7. References

- (1) Although this compound has been initially described as the dimer [$\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})\}_2$], its monomeric structure, at least in solid state, has been recently evidenced. See, Čubrilo, J.; Hartenbach, I.; Schleid, T.; Winter, R. F. Z. *Anorg. Allg. Chem.* **2006**, 632, 400.
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