Electronic Supplementary Information for Dalton Transactions

Supporting Information

Chiral phosphonite, phosphite and phosphoramidite η^6-arene-ruthenium(II) complexes: application to the kinetic resolution of allylic alcohols.

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Contents

1. X-ray crystal structure determination of complexes 1a, 1b, 3b and 3c. Suitable single crystal of **1a·¼CH$_2$Cl$_2$**, **1b·CH$_2$Cl$_2$**, **3b** and **3c** for X-ray diffraction analyses were obtained by slow diffusion of hexane (**1b**, **3b**, **3c**) or diethylether (**1a**) into a concentrated solution of the appropriate complex in dichloromethane. The most relevant crystallographic and refinement data are given in Tables S1 (**1a·¼CH$_2$Cl$_2$**), S3 (**1b·CH$_2$Cl$_2$**), S5 (**3b**) and S7

(**3c**). Selected bond distance and angle values are given in Tables S2 (**1a·¼CH$_2$Cl$_2$**), S4 (**1b·CH$_2$Cl$_2$**), S6 (**3b**) and S8 (**3c**). For complexes **1b·CH$_2$Cl$_2$** and **3c**, diffraction data were recorded on a Oxford Diffraction Xcalibur Nova single crystal diffractometer using Cu-Kα radiation (λ = 1.5418 Å). The data were collected through the oscillation method, with 1º oscillation and variable exposure time per frame (4-20 s), and a crystal-to-detector distance of 65 mm. The data collection strategy was calculated with the program CrysAlis Pro CCD.[1] Data reduction and cell refinement were performed using the program CrysAlis Pro RED.[1] Empirical absorption correction was applied by means of SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.[1] For derivatives **1a·¼CH$_2$Cl$_2$** and **3b**, diffraction data were recorded on a Nonius KappaCCD single crystal diffractometer using Mo-Kα radiation (λ = 0.71073 Å). The data were collected through 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.[2] Data reduction and cell refinement were performed using the programs HKL Denzo and Scalepack.[3] Semi-empirical absorption correction was applied by means of SORTAV.[4]

In all the cases, the software package WINGX was used for space group determination, structure solution and refinement.[5] Crystal structure of **3c** was solved by direct methods using the program SIR92.[6] For compounds **1a·¼CH$_2$Cl$_2$**, **1b·CH$_2$Cl$_2$** and **3b**, crystal structures were solved by Patterson interpretation and phase expansion using DIRDIF.[7] Isotropic least-square refinement on F^2 was carried out with SHELXL-97.[8] During the final stage of the refinements, all the positional parameters and the anisotropic temperature factors of all non-hydrogen atoms were refined. The hydrogen atoms were geometrically located and their coordinates were refined riding on their parent atomswith 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 complexes **1a·¼CH$_2$Cl$_2$** and **1b·CH$_2$Cl$_2$**, the maximum residual electron density is located near to heavy

atoms and CH_2Cl_2 solvent, respectively. 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 given in Tables S1, S3, S5 and S7) with $\sigma(F_o^2)$ from counting statistic and $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[9] Geometrical calculations were made with PARST.[10] Crystallographic plots were made with PLATON.[11] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nº CCDC 769455 (**1a·¼CH$_2$Cl$_2$**), CCDC 769456 (**1b·CH$_2$Cl$_2$**), CCDC 769457 (**3b**) and CCDC 769458 (**3c**). 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 **1a·¼CH$_2$Cl$_2$**.

Empirical formula	$C_{32}H_{23}Cl_2O_2PRu \cdot \frac{1}{4}CH_2Cl_2$	
Formula weight	663.68	
Temperature	150(2) K	
Wavelength	1.5418 Å	
Crystal system	triclinic	
Space group	P-1	
Unit Cell dimensions	a = 11.5207(2) Å	α = 80.3851(10)º
	b = 14.5067(3) Å	β = 89.6249(2)º
	c = 16.9585(3) Å	γ = 84.3682(12)º
Volume	2780.79(9) Å^3	
Z	4	
Calculated density	1.585 g/cm^3	
F(000)	1338	
Crystal size	0.15 x 0.15 x 0.12 mm^3	
Theta range for data collection	2.64º to 70.14º	
Reflections collected	39888	
Independent reflections	10255 [R(int) = 0.0464]	
Completeness to theta = 70.14	97.0%	
Data / restraints / parameters	10255 / 1 / 703	
Weight function (*a*, *b*)	0.1004, 4.9948	
Final R indices [I>2sigma(I)]	R_1 = 0.0459, wR_2 = 0.1363[a]	
R indices (all data)	R_1 = 0.0586, wR_2 = 0.1646[a]	
Largest diff. peak and hole	1.071 and -1.161 e.Å^{-3}	

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$.

Table S2. Selected bond distance and angle values for **1a·¼CH_2Cl_2**.

Bond distances (Å)		**Bond angles (º)**	
Ru-C*	1.7110(4)	C*-Ru-Cl(1)	125.43(4)
Ru-Cl(1)	2.3904(14)	C*-Ru-Cl(2)	126.38(3)
Ru-Cl(2)	2.3980(11)	C*-Ru-P	131.86(3)
Ru-P	2.2659(11)	Cl(1)-Ru-Cl(2)	88.38(5)
O(1)-P	1.625(3)	Cl(1)-Ru-P	85.99(4)
O(2)-P	1.615(3)	Cl(2)-Ru-P	84.37(4)
C(21)-P	1.793(5)	O(1)-P-O(2)	102.57(16)
		O(1)-P-C(21)	97.25(19)
		O(2)-P-C(21)	106.91(19)

C* = centroid of the benzene ring (C(27), C(28), C(29), C(30), C(31) and C(32) carbon atoms).

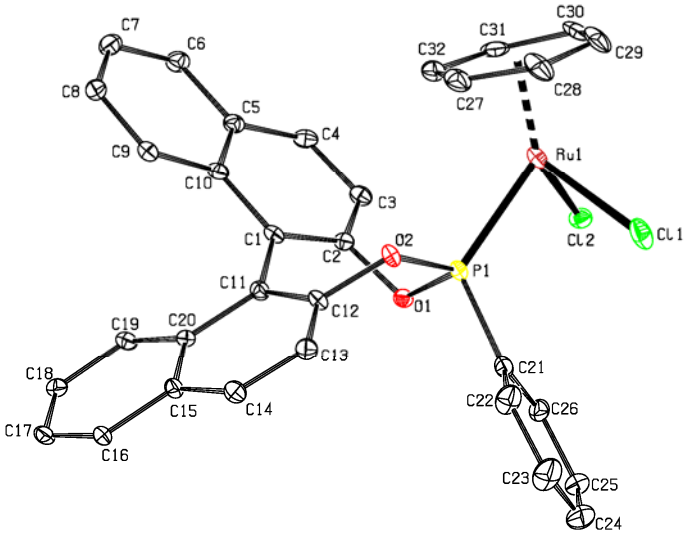


Table S3. Crystal data and structure refinement for **1b·CH_2Cl_2**.

Empirical formula	$C_{32}H_{23}Cl_2O_3PRu \cdot CH_2Cl_2$	
Formula weight	743.37	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	triclinic	
Space group	P-1	
Unit Cell dimensions	a = 9.8464(4) Å	α = 70.902(3)º
	b = 11.4973(3) Å	β = 81.985(3)º
	c = 15.3719(5) Å	γ = 65.405(3)º
Volume	1495.22(9) $Å^3$	
Z	2	
Calculated density	1.651 g/cm^3	
F(000)	748	
Crystal size	0.14 x 0.07 x 0.04 mm^3	
Theta range for data collection	3.04º to 73.99º	
Reflections collected	15171	
Independent reflections	5575 [R(int) = 0.0197]	
Completeness to theta =73.99	91.7%	
Data / restraints / parameters	5575 / 0 / 379	
Weight function (*a*, *b*)	0.1266, 2.7167	
Final R indices [I>2sigma(I)]	R_1 = 0.0496, wR_2 = 0.1611[a]	
R indices (all data)	R_1 = 0.0560, wR_2 = 0.1848[a]	
Largest diff. peak and hole	1.191 and -2.214 e.$Å^{-3}$	

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$.

Table S4. Selected bond distance and angle values for **1b·CH_2Cl_2**.

Bond distances (Å)		**Bond angles (º)**	
Ru-C*	1.7038(4)	C*-Ru-Cl(1)	124.49(4)
Ru-Cl(1)	2.3975(13)	C*-Ru-Cl(2)	127.53(4)
Ru-Cl(2)	2.3968(13)	C*-Ru-P	128.92(4)
Ru-P	2.2540(13)	Cl(1)-Ru-Cl(2)	87.34(5)
O(1)-P	1.609(4)	Cl(1)-Ru-P	90.17(5)
O(2)-P	1.607(4)	Cl(2)-Ru-P	85.10(5)
O(3)-P	1.580(4)	O(1)-P-O(2)	102.62(19)
		O(1)-P-O(3)	99.86(19)
		O(2)-P-O(3)	102.78(19)

C* = centroid of the benzene ring (C(27), C(28), C(29), C(30), C(31) and C(32) carbon atoms).

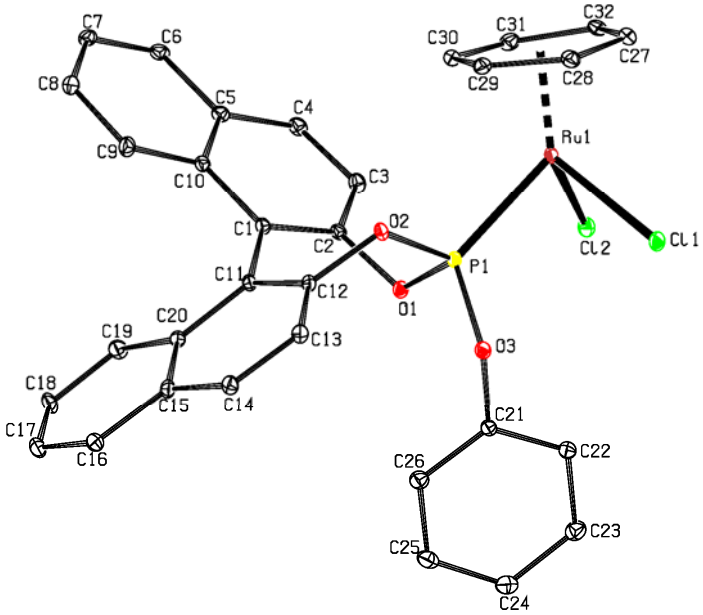


Table S5. Crystal data and structure refinement for **3b**.

Empirical formula	$C_{35}H_{29}Cl_2O_3PRu$	
Formula weight	700.52	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P n a 21	
Unit Cell dimensions	a = 13.4193(3) Å	α = 90º
	b = 18.7656(2) Å	β = 90º
	c = 11.9365(2) Å	γ = 90º
Volume	3005.86(9) $Å^3$	
Z	4	
Calculated density	1.548 g/cm^3	
F(000)	1424	
Crystal size	0.17 x 0.15 x 0.10 mm^3	
Theta range for data collection	1.87º to 25.35º	
Reflections collected	18991	
Independent reflections	2896 [R(int) = 0.030]	
Completeness to theta = 25.35	99.9%	
Data / restraints / parameters	2896 / 0 / 382	
Weight function (*a*, *b*)	0.0596, 0.00	
Final R indices [I>2sigma(I)]	R_1 = 0.0283, wR_2 = 0.0757[a]	
R indices (all data)	R_1 = 0.0375, wR_2 = 0.1009[a]	
Largest diff. peak and hole	0.765 and -0.716 e.$Å^{-3}$	

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$.

Table S6. Selected bond distance and angle values for **3b**.

Bond distances (Å)		**Bond angles (º)**	
Ru-C*	1.740(12)	C*-Ru-Cl(1)	125.9(9)
Ru-Cl(1)	2.4106(18)	C*-Ru-Cl(2)	125.0(6)
Ru-Cl(2)	2.3894(18)	C*-Ru-P	128.5(3)
Ru-P	2.2372(16)	Cl(1)-Ru-Cl(2)	87.20(8)
O(1)-P	1.614(4)	Cl(1)-Ru-P	89.62(6)
O(2)-P	1.599(4)	Cl(2)-Ru-P	87.97(7)
O(3)-P	1.609(4)	O(1)-P-O(2)	102.8(2)
		O(1)-P-O(3)	98.8(2)
		O(2)-P-O(3)	98.6(2)

C* = centroid of the mesitylene ring (C(27), C(28), C(29), C(30), C(31) and C(32) carbon atoms).

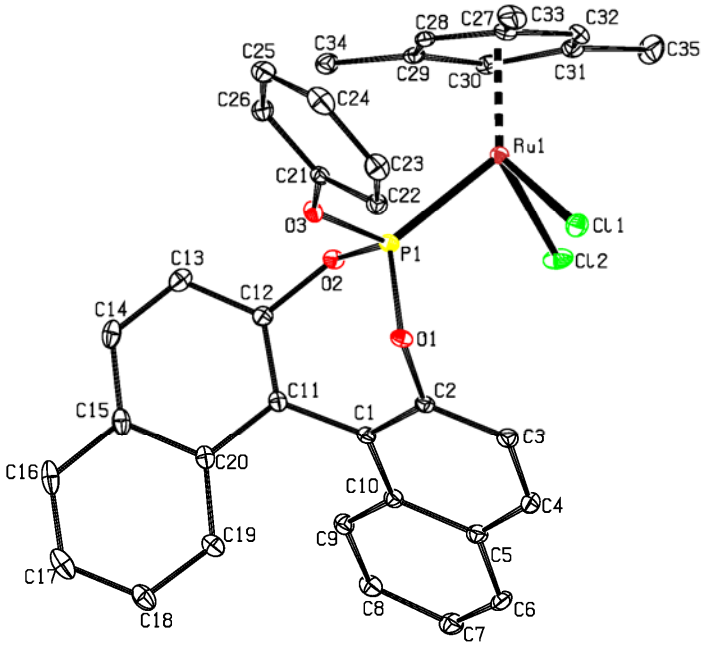


Table S7. Crystal data and structure refinement for **3c**.

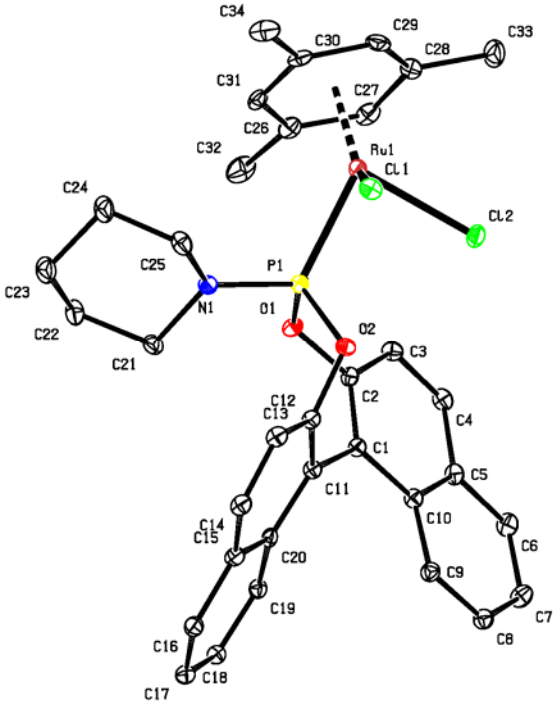
Empirical formula	$C_{34}H_{34}Cl_2NO_2PRu$	
Formula weight	691.56	
Temperature	293(2) K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit Cell dimensions	a = 12.0637(4) Å	α = 90º
	b = 8.3804(3) Å	β = 95.135(3)º
	c = 15.1019(5) Å	γ = 90º
Volume	1520.65(9) $Å^3$	
Z	2	
Calculated density	1.510 g/cm^3	
F(000)	708	
Crystal size	0.143 x 0.058 x 0.017 mm^3	
Theta range for data collection	2.94º to 74.00º	
Reflections collected	11273	
Independent reflections	4576 [R(int) = 0.0459]	
Completeness to theta = 74.00	99.5%	
Data / restraints / parameters	4576 / 0 / 373	
Weight function (*a*, *b*)	0.0596, 1.000	
Final R indices [I>2sigma(I)]	$R_1 = 0.0382$, $wR_2 = 0.0984$[a]	
R indices (all data)	$R_1 = 0.0480$, $wR_2 = 0.1069$[a]	
Largest diff. peak and hole	0.619 and -0.691 e.$Å^{-3}$	

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$.

Table S8. Selected bond distance and angle values for **3c**.

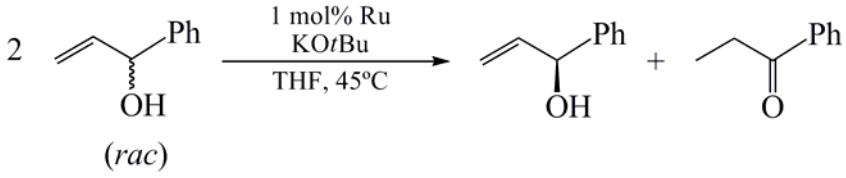
Bond distances (Å)		**Bond angles (º)**	
Ru-C*	1.73(2)	C*-Ru-Cl(1)	127.7(4)
Ru-Cl(1)	2.4165(16)	C*-Ru-Cl(2)	124.7(3)
Ru-Cl(2)	2.3917(16)	C*-Ru-P	130.5(6)
Ru-P	2.2618(11)	Cl(1)-Ru-Cl(2)	87.82(7)
O(1)-P	1.619(4)	Cl(1)-Ru-P	84.94(6)
O(2)-P	1.625(5)	Cl(2)-Ru-P	87.03(6)
N(1)-P	1.650(5)	O(1)-P-O(2)	100.6(2)
		O(1)-P-N(1)	97.7(2)
		O(2)-P-N(1)	110.3(2)

C* = centroid of the mesitylene ring (C(26), C(27), C(28), C(29), C(30), and C(31) carbon atoms).



2. Optimization of the catalytic activity

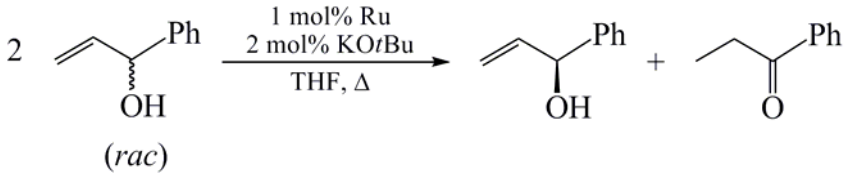
Table S9. Kinetic resolution of 1-phenyl-2-propen-1-ol by complex (*R*)-**2a** using different quantities of base.[a]



Quantity of KO*t*Bu	Time	Alcohol (%)[b,c]	e.e. (%)[c]
1 mol%	1.5 h	95	< 0.5 %
1 mol%	5 h	90	2 (S)
1 mol%	16 h	89	2 (S)
2 mol%	1.5 h	63	10 (S)
2 mol%	3 h	48	13 (S)
2 mol%	9 h	18	19 (S)
3 mol%	0.25 h	77	4 (S)
3 mol%	0.5 h	50	6 (S)
3 mol%	5 h	22	7 (S)
5 mol%	0.25 h	51	4 (S)
5 mol%	5 h	45	5 (S)
5 mol%	16 h	45	5 (S)

[a] Reactions carried out at 45ºC using 4 mmol of 1-phenyl-2-propen-1-ol, 1 mol% of (*R*)-**2a**, the indicated quantity of KO*t*Bu, and 20 mL of THF. [b] Allylic alcohol remaining. [c] Determined by GC, absolute configuration of the major enantiomer indicated in parenthesis.

Table S10. Kinetic resolution of 1-phenyl-2-propen-1-ol by complex (*R*)-**2a** at different temperatures.[a]



Temperature	Time	Alcohol (%)[b,c]	e.e. (%)[c]
25ºC	16 h	98	not determined
35ºC	4 h	83	7 (S)
35ºC	16 h	71	8 (S)
45ºC	3 h	48	13 (S)
55ºC	1.75 h	52	8 (S)
55ºC	3 h	27	11 (S)

[a] Reactions carried out at the temperature indicated, using 4 mmol of 1-phenyl-2-propen-1-ol, 1 mol% of (*R*)-**2a**, 2 mol% of KO*t*Bu, and 20 mL of THF. [b] Allylic alcohol remaining. [c] Determined by GC, absolute configuration of the major enantiomer indicated in parenthesis.

3. References

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