

Formation of racemic crystals of transition metal complexes by grinding 1:1 mixtures of enantiomeric crystals

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Experimental

Optical Resolution of the Metal Complexes. The chiral metal complexes were optically resolved using potassium antimony tartrate ($K_2[Sb_2\{(+)\text{-tartrate}\}_2]\cdot 3H_2O$) as a resolving reagent. A typical procedure for resolving $[Ru(bpy)_3]^{2+}$ ion is as follows.

The chloride salt of the complex (710 mg, 1 mmol) was dissolved in 50 mL of pure water. A solution of potassium antimony tartrate (670 mg (1 mmol) in 25 mL water, dissolved by warming the solution) was added to the solution. Upon leaving the solution at r.t., dark red crystals precipitated. The obtained crystals were nearly pure Λ - $[Ru(phen)_3][Sb_2\{(+)\text{-tartrate}\}_2]$, and the supernatant contained only Δ - $[Ru(phen)_3]^{2+}$. The crystals (**I**) and the solution (**II**) were separated by filtration. The crystals of the Λ -isomer (**I**) were dissolved using 100 mL of a hot sodium hydroxide solution (0.05 M). After filtration to remove the white precipitates of an antimony salt, a solution of $NaPF_6$ (5 g in 20 mL) was added drop by drop into the solution until no more precipitates generate. Orange precipitates formed were collected and washed with water. The hexafluorophosphate salt of Δ -isomer was obtained from the solution (**II**) by adding the $NaPF_6$ solution. The obtained enantiopure salts were further purified by repeated recrystallization from acetone–water solution (1:5) by slow evaporation of the solvents at ambient temperature.

Optical purity of the resolved complexes was analyzed using HPLC. The estimated optical purities (= enantiomer excesses) were 96.0% for Λ - $[Ru(phen)_3](PF_6)_2$, 95.3% for Δ - $[Ru(phen)_3](PF_6)_2$, 98.9% for Λ - $[Os(phen)_3](PF_6)_2$, and 98.5% for Δ - $[Os(phen)_3](PF_6)_2$.

Crystallization for X-ray Diffraction Experiments. Single crystals suitable for X-ray diffraction experiments were obtained from aqueous solutions.

Grinding and Annealing of Crystal Mixtures. Crystals of each optical isomer were separately ground in an agate mortar with an agate pestle by hands. The ground crystals were dried in vacuum at 70 °C over night. The dried crystals of the isomers were combined and co-ground in a dry box under dry nitrogen in an agate mortar with an agate pestle by hands for a few minutes. The ground mixture was transferred onto a slide glass and heated on a hot plate in the dry box at 250 °C for 30 min. It was transferred back again into the

mortar, ground again at room temperature, and heated again on the slide glass at 250 °C for 30 min. The grinding-and-heating procedure was repeated once more (total of 3 times). Extra repeating did not induce any further progress in crystallization.

TG-DTA and DSC Analyses. Seiko Instruments TG-DTA 6200 and DSC 6200 systems were used for measuring thermal properties of the crystals. TG-DTA and DSC measurements were performed under a flow of dry nitrogen.

HPLC analysis. For analyzing the optical purity of the resolved complexes, a column of Chiralcel OD-RH (Daicel; 4.6 mm I.D. × 15 mm) was used. The chromatography was operated at 35 °C. A mixture of 0.1 M NaPF₆ aq. solution and acetonitrile (50:50 by volume) was used as the eluent. For analyzing the mixtures of Δ -[Ru(phen)₃](PF₆)₂ and Λ -[Os(phen)₃](PF₆)₂, two tandem columns of the Chiralcel OD-RH (30 mm in the total length) were used and the chromatography was operated at 15 °C. A mixture of 0.1 M NaPF₆ aq. solution and acetonitrile (55:45 by volume) was used as the eluent.

Results

Structure of the Crystal of the Chiral Ruthenium Complex. The structure of the chiral crystal from an organic solution was reported, which contained acetonitrile and diethylether.¹ However, no chiral crystal from aqueous solutions was reported. We obtained single crystals suitable for X-ray diffraction experiments from aqueous solutions. The freshly prepared crystals analyzed at 100 K contained 3 molecules of water in an asymmetric unit of the crystal structure (Figure S1, left). However, the structure obtained for the single crystal dried in air at 298 K did not obtain water (Figure S1, right). The packing diagrams are very much similar to each other, except that water is not observed in the structure at 298 K and that the unit cell volume is larger at the higher temperature (Table S1). As a result, density of the crystal was significantly lower at the higher temperature.

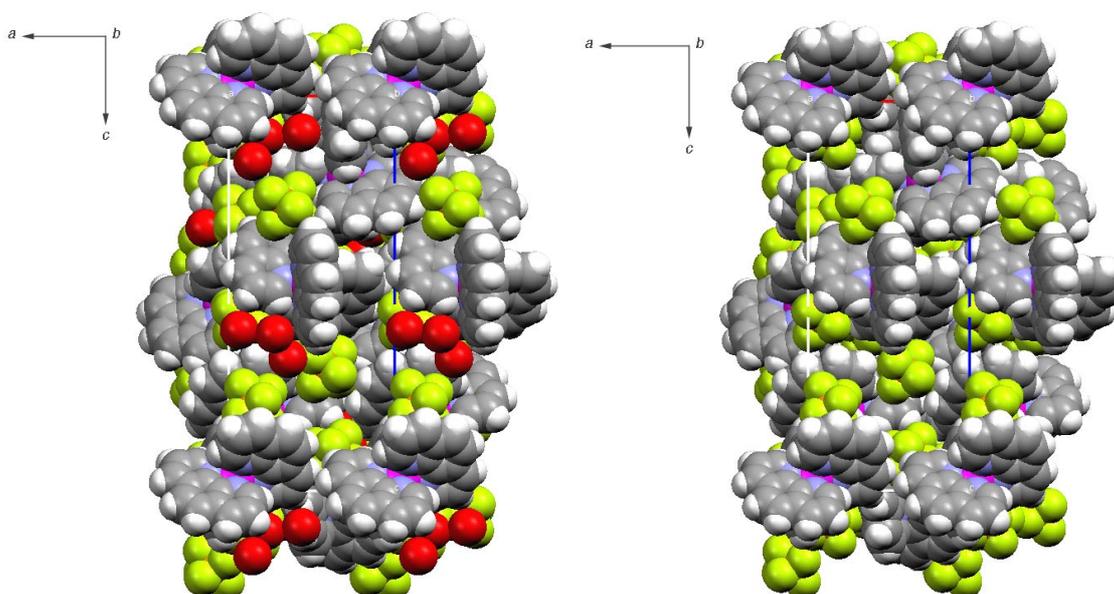


Figure S1. Single-crystal structures of Λ -[Ru(phen)₃](PF₆)₂ crystals at 100 K (left) and at 298 K (right). Red

balls are oxygen atoms of water.

The chiral crystal was composed of helical columns of the chiral complex, with one of the ligands stacked with each other (Figure S2). The helical column has a similar structure to that described for the chiral crystal containing organic solvents,¹ although its symmetry was lower (2_1 helix; not 4_1 (4_3) helix).

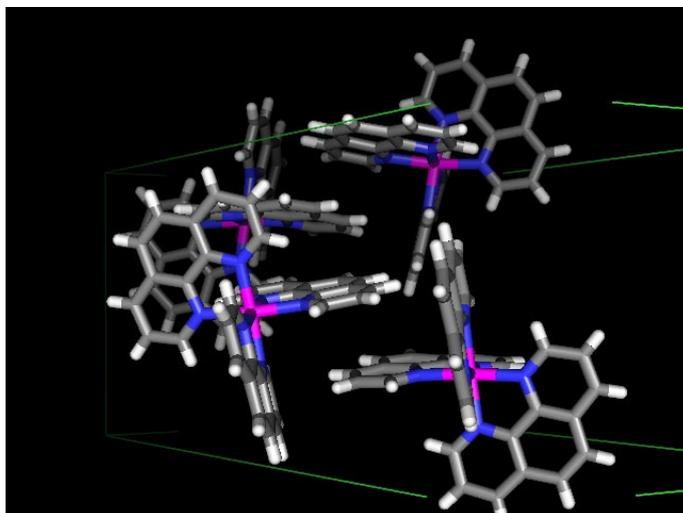


Figure S2. Crystal structure of Λ -[Ru(phen)₃]₂(PF₆)₄·3H₂O. A helical column of [Ru(phen)₃]²⁺ ions running along *a* axis.

Structure of the Crystal of the Racemic Ruthenium Complex. The structure of the racemic crystal of [Ru(phen)₃](PF₆)₂ was reported.² X-ray diffraction measurement was performed at 293 K. The resolved structure has no water (space group *C2/c*). However, our X-ray diffraction analysis of freshly prepared single crystal at 100 K indicated that the crystal contained water. The symmetry of the crystal was lower at the low temperature (space group *Cc*). In the structure at r. t., waters are lost from the lattice and cavities are left. Packing of the other ions in the structures at 100 K and 298 K are very much similar to each other (Figure S3).

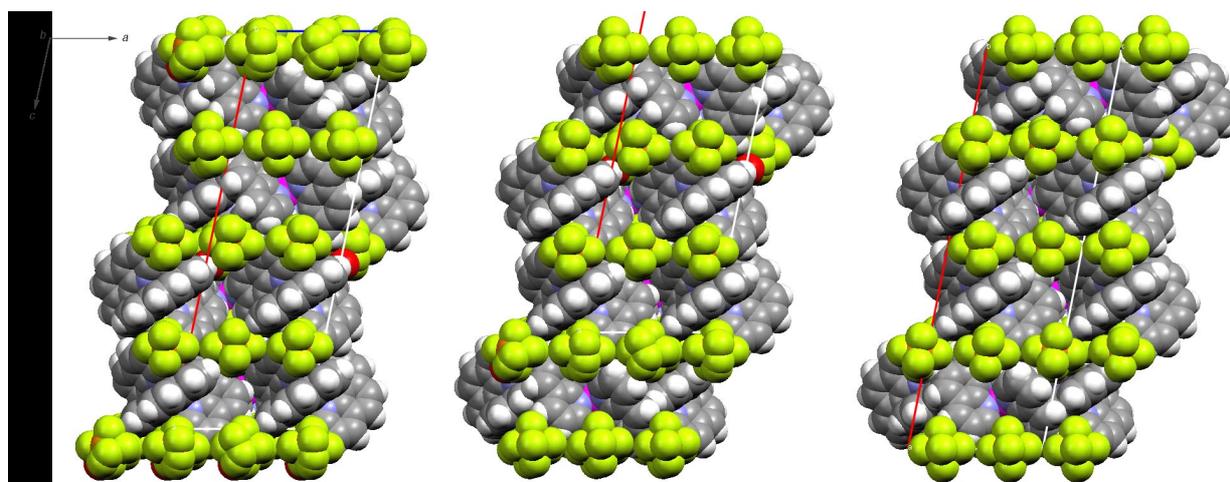


Figure S3. Single-crystal structures of $\square\square\square$ -[Ru(phen)₃](PF₆)₂ crystals at 100 K (left and middle) and at 298 K (right). Red balls are oxygen atoms of water. In the figures in the middle and at the right, the volumes containing corresponding molecules are shown.

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Racemic crystal of $[\text{Ru}(\text{phen})_3](\text{PF}_6)_2$ was composed of alternating layers of $[\text{Ru}(\text{phen})_3]^{2+}$ and PF_6^- . Each layer contained both enantiomers (Figure S1).

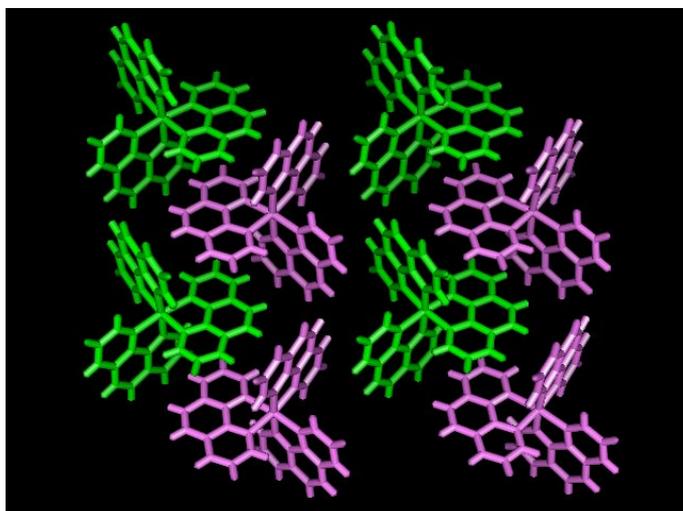


Figure S4. Crystal structure of *rac*- $[\text{Ru}(\text{phen})_3]_2(\text{PF}_6)_4 \cdot \text{H}_2\text{O}$. Top view of the sheet of $[\text{Ru}(\text{phen})_3]^{2+}$ ions parallel to *bc* plane. Color code: Λ -isomer, green; Δ -isomer, violet.

Crystal Structure of the Salt of Osmium Complex. Crystals of $[\text{Os}(\text{phen})_3](\text{PF}_6)_2$ were isomorphous to the corresponding crystals of the ruthenium complex. Selected parameters are listed in Tables S1.

Table S1. Crystallographic parameters for the single crystals of [M(phen)₃](PF₆)₂ (M = Ru, Os).

	1	2	3	4
Compound	Λ-[Ru(phen) ₃] ₂ (PF ₆) ₄	Λ-[Ru(phen) ₃] ₂ (PF ₆) ₄ ·3H ₂ O	<i>r</i> □□-[Ru(phen) ₃](PF ₆) ₂	<i>r</i> □□-[Ru(phen) ₃] ₂ (PF ₆) ₄ ·H ₂ O
CCDC code			ZUZSIW^a	
Empirical formula	C ₇₂ H ₄₈ F ₂₄ N ₁₂ P ₄ Ru ₂	C ₇₂ H ₅₄ F ₂₄ N ₁₂ O ₃ P ₄ Ru ₂	C ₃₆ H ₂₄ F ₁₂ N ₆ P ₂ Ru	C ₇₂ H ₅₀ F ₂₄ N ₁₂ OP ₄ Ru ₂
Formula weight	1863.24	1917.30	931.62	1881.26
Temperature / K	298(2)	100(2)	298(2),	100(2)
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁	<i>C</i> 2/ <i>c</i>	<i>C</i> <i>c</i>
<i>a</i> / Å	13.1694(16)	12.9342(13)	37.042(3),	36.810(3)
<i>b</i> / Å	17.940(2)	17.6216(18)	16.0714(14),	15.7955(12)
<i>c</i> / Å	32.024(4)	31.042(3)	12.0759(10),	12.1174(9)
<i>α</i> / deg	90.00	90.00	90.00	90.00
<i>β</i> / deg	90.00	90.00	101.023(2),	101.6810(10)
<i>γ</i> / deg	90.00	90.00	90.00	90.00
<i>U</i> / Å ³	7566.1(15)	7075.2(12)	7056.4(10),	6899.6(9)
<i>D</i> _c / g cm ⁻³	1.636	1.800	1.754,	1.811
<i>Z</i>	4	4	8	4
<i>μ</i> □□□□	0.595	0.642	0.638,	0.654
No. of reflections				
measured	47632	51702	21581	20932
unique	17473	17596	8101	12059
<i>I</i> > 2σ(<i>I</i>)	7879	13893	5674	12030
<i>R</i> _{int}	0.0647	0.0455	0.0382	0.0163
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0401	0.0324	0.0517	0.0347
<i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0613	0.0574	0.1248	0.0849
	5	6	7	8
Compound ^a	Λ-[Os(phen) ₃] ₂ (PF ₆) ₄	Λ-[Os(phen) ₃] ₂ (PF ₆) ₄ ·3H ₂ O	<i>r</i> □□-[Os(phen) ₃](PF ₆) ₂	<i>r</i> □□-[Os(phen) ₃] ₂ (PF ₆) ₄ ·H ₂ O
Our code				
Empirical formula	C ₇₂ H ₄₈ F ₂₄ N ₁₂ Os ₂ P ₄	C ₇₂ H ₅₄ F ₂₄ N ₁₂ O ₃ Os ₂ P ₄	C ₃₆ H ₂₄ F ₁₂ N ₆ OsP ₂	C ₇₂ H ₅₀ F ₂₄ N ₁₂ OOS ₂ P ₄
Formula weight	2041.50	2095.56	1020.75	2059.52
Temperature / K	298(2)	100(2)	298(2)	100(2)
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁	<i>C</i> 2/ <i>c</i>	<i>C</i> <i>c</i>
<i>a</i> / Å	13.1878(13)	13.0513(10)	36.943(4)	36.6813(19)
<i>b</i> / Å	17.9354(16)	17.7690(14)	16.1178(15)	15.8390(8)
<i>c</i> / Å	32.058(3)	31.426(3)	12.1037(11)	12.1451(6)
<i>α</i> / deg	90.00	90.00	90.00	90.00
<i>β</i> / deg	90.00	90.00	100.993(2)	101.6650(10)
<i>γ</i> / deg	90.00	90.00	90.00	90.00
<i>U</i> / Å ³	7582.7(12)	7288.0(10)	7074.7(11)	6910.5(6)
<i>D</i> _c / g cm ⁻³	1.788	1.910	1.917	1.980
<i>Z</i>	4	4	8	4
<i>μ</i> □□□□	3.543	3.692	3.798	3.890
No. of reflections				
measured	47279	46061	21362	21341
unique	17377	16877	8093	10791
<i>I</i> > 2σ(<i>I</i>)	11599	13679	6898	10539
<i>R</i> _{int}	0.0717	0.0771	0.0228	0.0264
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0553	0.0503	0.0312	0.0313
<i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.1066	0.0927	0.0764	0.0756

^a J. Breu, A. J. Stoll, *Acta Crystallogr., Sect. C*, 1996, **52**, 1174–1177.

TG and DTA of the Crystal Mixtures of Δ - and Λ -[Ru(phen)₃](PF₆)₂. A 1:1 mixture of the crystals of Δ - and Λ -[Os(phen)₃](PF₆)₂ was ground in an agate mortar. Thermal properties of the co-ground crystals were analyzed using TG-DTA and DSC systems. The co-grinding was performed either in atmosphere or in a dry box (Figure S5, top) under a flow of dry nitrogen (Figure S5, bottom) to investigate the effect of atmospheric humidity.

Before starting heating, the system was equilibrated at 50 °C until constant weight was obtained. During this equilibration procedure, significant (a few percent) loss in weight was observed only for the sample prepared in atmosphere. A small continuous loss in weight was observed in a wide range of temperature up to 420 °C. At this temperature, decomposition of the Ru complex occurred. The TG curves for the slow continuous loss in weight did not differ between wet and dry samples. Therefore, the slow continuous loss in weight must be due to a partial decomposition of the metal complex or removal of some small impurity (physically adsorbed or included in the lattice); not due to release of water. At the transformation temperature (205–220 °C), no discontinuous change in weight was observed (Figure S5, top right and bottom right). This also supports that water does not play any role in the transformation of the crystals.

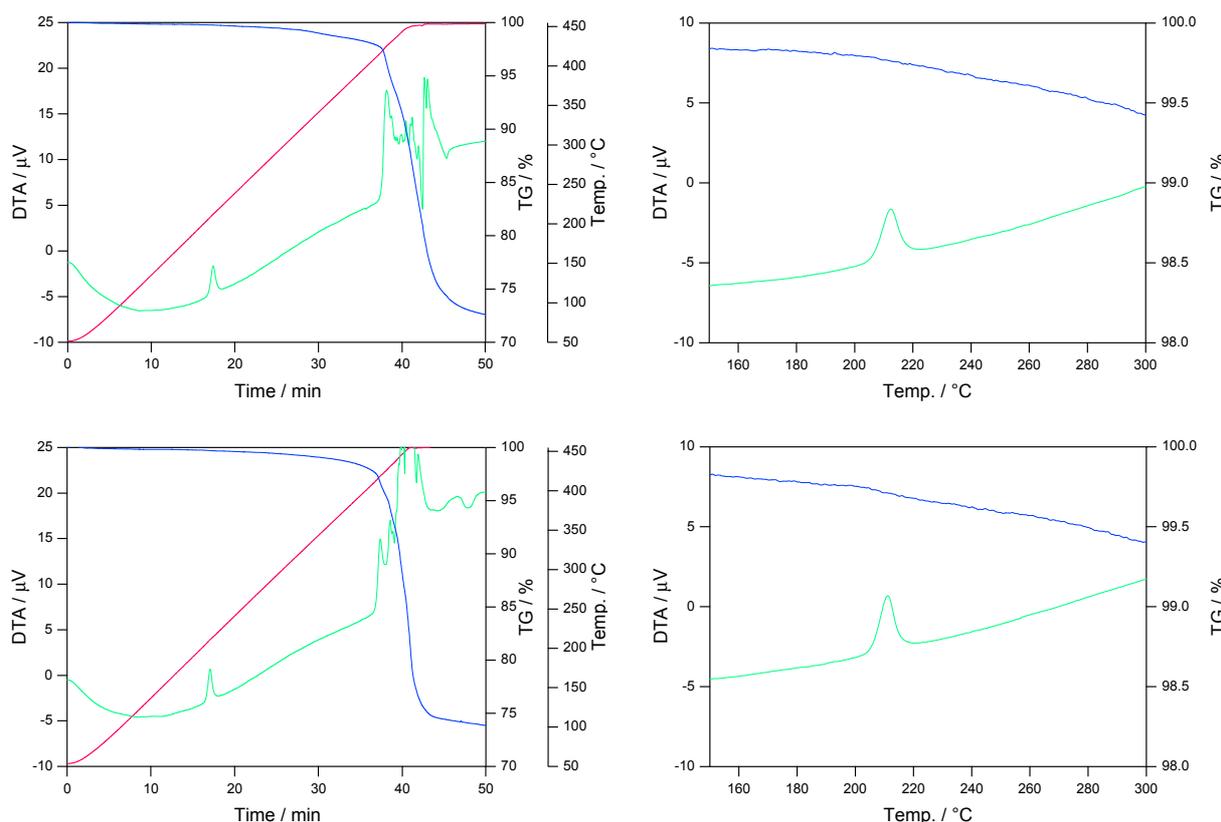


Figure S5. DTA and TG curves for the powder co-ground in a dry box under a flow of dry nitrogen (top), and for the powder co-ground in air (bottom). Right figures show DTA and TG curves around the crystal transformation temperature.

Grinding and Annealing of the Crystal Mixtures of Δ -[Ru(phen)₃](PF₆)₂ and Λ -[Os(phen)₃](PF₆)₂.

A 1:1 mixture of the crystals of Δ -[Ru(phen)₃](PF₆)₂ and Λ -[Os(phen)₃](PF₆)₂ was ground in an agate mortar

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and subsequently heated at 250 °C for 30 min. This process was followed using powder X-ray diffraction experiments (Figure S6). Upon grinding at room temperature, only broad diffraction peaks were observed. However, upon heating at 250 °C, new diffraction peaks occurred. The pattern of the new peaks was nearly the same as those for the crystals of the racemic compounds of $[\text{Ru}(\text{phen})_3](\text{PF}_6)_2$ and $[\text{Os}(\text{phen})_3](\text{PF}_6)_2$. An HPLC analysis using a chiral stationary phase indicated that both species did not racemize at all upon heating at 250 °C. The product mixture contained only Δ - $[\text{Ru}(\text{phen})_3]^{2+}$ and Λ - $[\text{Os}(\text{phen})_3]^{2+}$ (Figure S7). The product was a pseudo-racemic compound of Δ - $[\text{Ru}(\text{phen})_3](\text{PF}_6)_2$ and Λ - $[\text{Os}(\text{phen})_3](\text{PF}_6)_2$, but not a mixture of the racemic compounds of $[\text{Ru}(\text{phen})_3](\text{PF}_6)_2$ and $[\text{Os}(\text{phen})_3](\text{PF}_6)_2$.

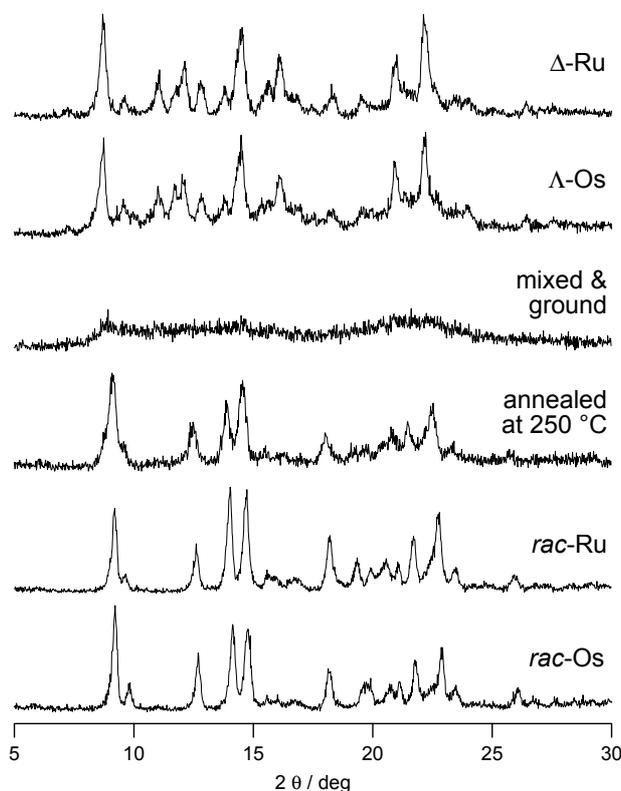


Figure S6. X-ray diffraction patterns for the mixtures of Δ - $[\text{Ru}(\text{phen})_3](\text{PF}_6)_2$ and Λ - $[\text{Os}(\text{phen})_3](\text{PF}_6)_2$.

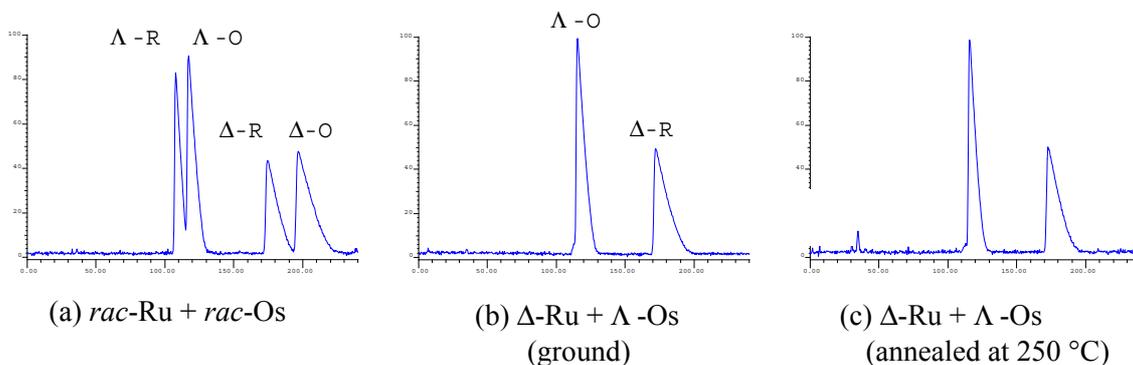


Figure S7. HPLC chromatograms of the mixtures of $[\text{Ru}(\text{phen})_3](\text{PF}_6)_2$ and $[\text{Os}(\text{phen})_3](\text{PF}_6)_2$.

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- 2 J. Breu and A. J. Stoll, *Acta Crystallogr., Sect. C*, 1996, **52**, 1174–1177.