Synthesis and Catalytic Properties of a Very Latent Selenium-Chelated Ruthenium Benzylidene Olefin Metathesis Catalyst

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Supporting Information

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Experimental Details

General Remarks: unless otherwise noted, all materials were purchased from commercial suppliers and used as received. All reactions requiring exclusion of oxygen and moisture were carried out in dry glassware with dry solvents (purified using MBraun SPS) under a dry and oxygen-free atmosphere using Schlenk technique. The bottles with ruthenium catalysts were stored under argon atmosphere, but no special precautions were taken to avoid air or moisture exposure in the moment of extracting catalysts from the bottles.

Nuclear Magnetic Resonance (NMR): NMR (¹H and ¹³C) spectra were recorded on Agilent Mercury 400 MHz spectrometer at ambient temperature with CDCl₃ or CD₂Cl₂ used as a solvent. Chemical shifts (δ) are given in parts per million (ppm) downfield from tetramethylsilane with a residual non-deuterated solvent peak used as a reference: CDCl₃ (δH = 7.26 ppm, δC = 77.16 ppm), CD₂Cl₂ (δH = 5.32 ppm, δC = 53.84 ppm). Coupling constants (J) are reported in hertz (Hz) and refer to H,H-couplings. The following abbreviations are used in order to indicate the multiplicity of the signal: s (singlet), d (doublet), t (triplet), q (quartet), quin (quinart), sext (sextet), hept (heptet), dd (doublet of doublet), dt (doublet of triplet), ddd (doublet of doublet of doublet) etc., bs (broad signal), m (multiplet). The obtained data was processed with the software MestReNova.

Gas Chromatography (GC): GC measurements were carried out using PerkinElmer Clarus 580 employing InertCap 5MS-Sil column and helium as a carrier gas.

Infrared Spectroscopy (IR): IR spectra were recorded using JASCO FT/IR-6200 spectrometer. The substances were examined as a film or in the solution. Wavenumbers (υ) are reported in cm⁻¹. The obtained data was processed with the software Omni32.

Ultraviolet-Visible Spectroscopy (UV-Vis): UV-Vis spectra were recorded using Thermo Fischer Scientific Evolution 300 UV-Vis spectrophotometer in 10.00 mm QS cuvettes. Wavelengths (λ) are reported in nanometers (nm), whereas absorbance (A) is given in absorbance units (a.u.). Scan speed was set to 600 nm/min, range 300 – 500 nm, bandwidth 1 nm and data interval 1 nm.

High Resolution Mass Spectrometry (HRMS): HRMS measurements were carried out using AutoSpec Premier spectrometer.

Column Chromatography (CC): CC was performed using Merck Millipore silica gel (60, particle size 0.043 – 0.063 nm).

Thin Layer Chromatography (TLC): TLC was performed using Merck Silica Gel 60 F254 precoated aluminum sheets. Substances were visualized using UV-light (254 or 365 nm) or by stains after KMnO₄/K₂CO₃/NaOH reagent treatment (aqueous solution).

Size Exclusion Chromatography (SEC or GPC): Number-average molecular weights (Mn), weight-average molecular weight (Mw), and molecular weight distribution (Mw/Mn) were determined by a specialized laboratory at the University of Warsaw (Dr. Elżbieta Megiel, Faculty of Chemistry, Poland), using a Schimadzu Nexera’s high-pressure liquid chromatograph (Shimadzu Corporation) in THF at 40 °C with a flow rate of 1.0 mL.min⁻¹. Two columns placed in series were used: ReproGel 1000 and 10000, (Dr. Maisch) 5 μm, 300 mm x 8 mm. Samples were detected with a refractive index detector.
using a Shimadzu model RID-20A. The system was calibrated using poly(styrene) standards (PSS GmbH) in the range of molecular weights 2.09-323 kDa. Molecular weight analysis by Size Exclusion Chromatography (SEC) has been performed from samples dissolved in THF (1 mg/mL) followed by filtration on Pall PTFE membrane filters (0.2 μm); 20 uL injections were applied. The polymers were analyzed after the removal of the catalyst and unreacted monomers by precipitation of the polymers and filtration with methanol.
Synthesis of the Ligand

Scheme S1. Synthesis of bromostyrene derivative 2 via Wittig olefination.

Ethyltriphenylphosphonium bromide (8.7 g, 23.1 mmol, 2.3 equiv.) and potassium tert-butoxide (2.7 g, 23.1 mmol, 2.3 equiv.) were placed in an oven-dried flask. 20 mL of anhydrous THF was added. Reaction mixture was stirred at room temperature for 30 minutes. Then the mixture was cooled down to -78 °C and appropriate aldehyde 1 (1.9 g, 10.1 mmol, 1 equiv.) was added dropwise. Stirring was continued over 2 h at rt. The reaction mixture was quenched with saturated aqueous solution of NH₄Cl (50 mL) and the THF was removed under reduced pressure. DCM (50 mL) was added and the layers were separated. Aqueous phase was extracted with DCM (2 x 50 mL). Organic layer was dried over anhydrous MgSO₄ and afterwards, the solid was filtered off and the organic solution was concentrated by the evaporation of DCM. Crude product was purified using quick column chromatography (stationary phase: SiO₂, eluent: DCM) in order to remove triphenylphosphine oxide from the alkene. The product was obtained as a yellow oil (1.81 g, 91%) and can be used without further purification.

It is possible to further purified compound 2 by distillation using Kugelrohr apparatus (p ~ 10 mbar, T = 145 °C) to give pure product 2 (1.55 g, 78%, E/Z = 1.7:1).

**Major Isomer (E):** ¹H NMR (400 MHz, CDCl₃) δ: 7.53 (dd, J = 8.0, 1.3 Hz, 1H), 7.47 (dd, J = 7.8, 1.7 Hz, 1H), 7.27 – 7.20 (m, 1H), 7.06 (ddd, J = 7.9, 7.3, 1.7 Hz, 1H), 6.74 (dq, J = 15.7, 1.8 Hz, 1H), 6.19 (dq, J = 15.6, 6.7 Hz, 1H), 1.93 (dd, J = 6.7, 1.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ: 137.8, 132.9, 130.1, 129.0, 128.2, 127.5, 126.9, 123.1, 18.8.

**Minor Isomer (Z):** ¹H NMR (400 MHz, CDCl₃) δ: 7.59 (dd, J = 8.0, 2.5 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.13 – 7.08 (m, 1H), 6.49 (dq, J = 11.4, 1.7 Hz, 1H), 5.90 (dq, J = 11.4, 7.1 Hz, 1H), 1.79 (dd, J = 7.1, 1.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ: 137.5, 132.7, 130.8, 129.5, 128.3, 128.2, 126.9, 124.2, 14.5.
Scheme S2. Synthesis of selenium-containing ligand 3 via selenium insertion with subsequent alkylation.

In an glovebox filled with argon, a 25 mL round-bottom flask was charged with Mg (finely ground, 26 mg, 1.1 mmol, 1.1 equiv.), lithium chloride (4.8 mg, 0.1 mmol, 0.1 equiv.) and THF (3 mL). To the resulting suspension, the solution of bromostyrene derivative 2 (200 mg, 1.0 mmol, 1.0 equiv.) in THF (2 mL) was added dropwise. The reaction was stirred at room temperature until the complete consumption of magnesium (leading to a clear colorless to pale yellow solution). The Grignard reagent was thus formed and gray Se (80 mg, 1.0 mmol, 1.0 equiv.) was added in one portion while stirring vigorously. The dark suspension of selenium in the reaction mixture turned rapidly (after 5 minutes) into a homogeneous clear orange solution indicating the full conversion of selenium. The flask was taken outside of the glovebox and 2-iodopropane (509 mg, 3 mmol, 3 equiv.) was added to the reaction mixture. After the addition of alkylating agent, a precipitate appears instantly leading to a grey to yellow turbid suspension. The reaction mixture was stirred at room temperature overnight and afterwards water was added (5 mL). The product was extracted with DCM (3 x 10 mL). The organic phases were combined, washed with brine and dried over anhydrous Na$_2$SO$_4$. The volatiles were removed under reduced pressure and the yellow oil was dried overnight under high vacuum (1·10$^{-3}$ mbar). The product 3 was obtained as yellow oil (177.6 mg, 74%, E/Z = 1.7:1) and can be used without further purification.

**Major Isomer (E):** $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.55 (dd, $J = 7.7$, 1.1 Hz, 1H), 7.47 (dd, $J = 7.8$, 1.2 Hz, 1H), 7.13 (m, 2H), 6.95 and 6.79 (dd, $J = 15.6$, 1.5 Hz, 1H), 6.22 – 6.04 (m, 1H), 3.41 (sept, $J = 6.8$ Hz, 1H), 1.91 (dd, $J = 6.6$, 1.7 Hz, 3H) 1.39 (d, $J = 6.8$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ: 141.2, 135.8, 131.4, 127.9, 127.6, 127.1, 126.8, 33.9, 24.2, 18.8, 14.5, 14.4. $^{77}$Se NMR (76 MHz, CDCl$_3$) δ: 368.82.

**Minor Isomer (Z):** $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.55 (dd, $J = 7.7$, 1.1 Hz, 1H), 7.47 (dd, $J = 7.8$, 1.2 Hz, 1H), 7.26 – 7.01 (m, 2H), 6.63 and 6.56 (dd, $J = 11.5$, 1.6 Hz, 1H), 3.45 (sept, $J = 6.8$ Hz, 1H), 1.77 (dd, $J = 7.0$, 1.8 Hz, 3H), 1.40 (d, $J = 6.8$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ: 140.12, 134.04, 130.5, 127.94, 127.27, 127.1, 33.2, 24.1, 18.8, 14.5, 14.4. $^{77}$Se NMR (76 MHz, CDCl$_3$) δ: 379.53.

**HRMS (ESI):** calculated mass for C$_{12}$H$_{17}$Se [M+H]$^+$: 241.0490; found: 241.0490(3).
Synthesis of the Ruthenium Complex

Dry Schlenk vessel was charged with ruthenium complex Ind-II (100 mg, 0.105 mmol, 1 equiv.) under argon atmosphere. Then, 15 mL of anhydrous toluene was added, resulting in a deep red solution. Selenium-containing styrene 3 (62 mg, 0.315 mmol, 3 equiv.) and anhydrous CuCl (15 mg, 0.158 mmol, 1.5 equiv.) were added to the reaction mixture and then it was stirred for 3 hours after heating up to 80 °C. Complete conversion of Ind-II catalyst was observed using TLC (stationary phase: SiO2, eluent: EtOAc/n-hexane 10:90 v/v, Rf,Ind-II = 0.39, Rf,Ru8 = 0) after that time. All the volatiles were removed under reduced pressure and the crude product was purified using column chromatography (stationary phase: SiO2, eluent: EtOAc/n-hexane from 20:80 to 80:20 v/v). Product complex Ru8 was obtained as a green solid (67 mg, 81%).

1H NMR (400 MHz, CD2Cl2) δ: 17.47 (s, 1H), 7.52 – 7.41 (m, 2H), 7.20 (ddd, J = 7.7, 5.4, 3.0 Hz, 1H), 7.12 (s, 1H), 7.01 (s, 1H), 6.89 (s, 1H), 6.83 (d, J = 7.5 Hz, 1H), 5.94 (s, 1H), 4.25 – 3.72 (m, 5H), 2.67 (s, 1H), 2.53 (s, 1H), 2.47 (s, 1H), 2.36 (s, 1H), 2.15 (s, 1H), 1.54 (d, J = 4.4 Hz, 4H), 1.30 (t, J = 5.0 Hz, 2H), 1.02 (d, J = 6.8 Hz, 1H). 13C NMR (101 MHz, CD2Cl2) δ: 8284.6, 215.0, 157.5, 140.3, 140.2, 138.4, 137.8, 136.8, 135.4, 132.4, 131.8, 130.7, 129.8, 129.7, 129.6, 129.2, 128.7, 124.9, 51.6, 51.3, 36.4, 23.7, 21.9, 21.1, 20.9, 20.3, 20.1, 18.7, 17.8. 77Se NMR (76 MHz, CD2Cl2) δ: 518.9.
X-Ray Data Collection and Structure Refinement

Good quality single-crystals of Ru8 was selected for the X-ray diffraction experiments at $T = 100(2)$ K. Diffraction data were collected on the Agilent Technologies SuperNova Dual Source diffractometer with MoKα ($\lambda = 0.71073$) radiation using CrysAlis RED software. The analytical numerical absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid, implemented in SCALE3 ABSPACK scaling algorithm, were applied. The structural determination procedure was carried out using the SHELX package. The structures were solved with direct methods and then successive least-square refinement was carried out based on the full-matrix least-squares method on $F^2$ using the SHELXL program. All H-atoms were positioned geometrically with C–H equal to 0.93, 0.96, 0.97 and 0.98 Å for the aromatic, methyl, methylene and methine H-atoms, respectively. The H-atoms were constrained to ride on their parent atoms with $U_{iso}(H) = xU_{eq}(C)$, where $x = 1.2$ for the aromatic, methylene and methine H-atoms, and 1.5 for the methyl H-atoms, respectively. Additionally, several distinct peaks on the difference Fourier map of Ru8 were indicating the presence of a disordered solvent molecule/s. However, all of the attempts to propose reasonable model of disorder have failed. Therefore, the solvent contribution was removed by applying the appropriate MASK procedure in the Olex2 program. Calculated total solvent accessible volume / cell was 919.0 Å³ occupied by 184.8 electrons per unit cell. The figures for this publication were prepared using Olex2 and ORTEP-3 programs.

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3. G. M. Sheldrick, Acta Crystallogr. Sect. A 2008, 64, 112.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Cryst. 2009, 42, 339.
5. L. J. Farrugia, J. Appl. Cryst. 2012, 45, 849.
Table S1. Crystal data and structure refinement details for Ru8.

| Compound | Ru8 |
|----------|-----|
| Empirical formula | C$_{31}$H$_{38}$Cl$_2$N$_2$RuSe |
| Formula weight | 689.56 |
| Temperature/K | 100(2) |
| Crystal system | Monoclinic |
| Space group | I2/a |
| $a$/Å | 16.6540(2) |
| $b$/Å | 16.4089(2) |
| $c$/Å | 26.2915(3) |
| $\alpha$/° | 90 |
| $\beta$/° | 95.3149(11) |
| $\gamma$/° | 90 |
| Volume/Å$^3$ | 7153.86(15) |
| $Z$ | 8 |
| $\rho_{\text{calc}}$/g/cm$^3$ | 1.280 |
| $\mu$/mm$^{-1}$ | 1.624 |
| $F$(000) | 2800.0 |
| Crystal size/mm$^3$ | 0.33 × 0.18 × 0.13 |
| Radiation | MoKα ($\lambda = 0.71073$) |
| 2$\theta$ range for data collection/° | 4.524 to 52.742 |
| Index ranges | -20 ≤ h ≤ 20, |
| Reflections collected | -20 ≤ k ≤ 20, |
| Independent reflections | -32 ≤ l ≤ 32 |
| Data/restraints/parameters | 47448 |
| Goodness-of-fit on $F^2$ | 7316 [$R_{	ext{int}} = 0.0267$] |
| Final $R$ indexes [$\geq 2\sigma (I)$] | $R_{\text{sigma}} = 0.0175$ |
| Final $R$ indexes [all data] | 7316/0/342 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.35/-1.30 |
**Figure S1.** ORTEP diagram of Ru8 with 50% probability ellipsoids; hydrogen atoms were omitted for clarity.
### Table S2. Bond lengths for Ru8.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| C1   | N1   | 1.345(4) | C15  | C16  | 1.379(5) |
| C1   | N2   | 1.339(4) | C16  | C20  | 1.513(5) |
| C1   | Ru24 | 2.022(3) | C16  | C21  | 1.515(5) |
| C2   | C3   | 1.524(5) | C17  | C18  | 1.397(5) |
| C2   | N1   | 1.478(4) | C18  | C21  | 1.515(5) |
| C3   | N2   | 1.481(4) | C22  | C23  | 1.459(5) |
| C4   | C5   | 1.401(5) | C22  | Ru24 | 1.825(3) |
| C4   | C9   | 1.405(5) | C23  | C24  | 1.404(5) |
| C4   | N1   | 1.425(4) | C23  | C28  | 1.391(4) |
| C5   | C6   | 1.384(5) | C24  | C25  | 1.381(6) |
| C5   | C10  | 1.508(5) | C25  | C26  | 1.390(6) |
| C6   | C7   | 1.404(6) | C26  | C27  | 1.390(7) |
| C7   | C8   | 1.378(7) | C27  | C28  | 1.387(5) |
| C7   | C11  | 1.524(7) | C28  | Se1  | 1.927(3) |
| C8   | C9   | 1.367(7) | C29  | C30  | 1.500(5) |
| C9   | C12  | 1.513(6) | C29  | C31  | 1.528(6) |
| C13  | C14  | 1.408(4) | C29  | Se1  | 1.991(4) |
| C13  | C18  | 1.396(5) | C11  | Ru24 | 2.3821(9) |
| C13  | N2   | 1.429(4) | C12  | Ru24 | 2.374(1) |
| C14  | C15  | 1.373(5) | Ru24 | Se1  | 2.4479(7) |
| C14  | C19  | 1.508(5) |      |      |          |

### Table S3. Values of valence angles for Ru8.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| N1   | C1   | N2   | 108.4(3)| C22  | C23  | C24  | 122.1(3)|
| N1   | C1   | Ru24 | 118.4(2)| C22  | C23  | C28  | 119.2(3)|
| N2   | C1   | Ru24 | 133.0(2)| C24  | C23  | C28  | 118.7(3)|
| C2   | C3   | N2   | 103.2(3)| C23  | C24  | C25  | 120.1(3)|
| C5   | C4   | C9   | 121.2(3)| C24  | C25  | C26  | 120.5(4)|
| C5   | C4   | N1   | 118.5(3)| C25  | C26  | C27  | 120.2(4)|
| C9   | C4   | N1   | 120.3(3)| C26  | C27  | C28  | 119.1(4)|
| C4   | C5   | C6   | 117.7(3)| C23  | C28  | C27  | 121.4(3)|
| C4   | C5   | C10  | 120.9(3)| C23  | C28  | Se1  | 113.9(2)|
| C6   | C5   | C10  | 121.3(3)| C27  | C28  | Se1  | 124.5(3)|
| C5   | C6   | C7   | 121.3(4)| C30  | C29  | C31  | 112.2(3)|
| C6   | C7   | C8   | 118.8(4)| C30  | C29  | Se1  | 111.6(2)|
| C6   | C7   | C11  | 119.0(4)| C31  | C29  | Se1  | 104.9(3)|
| C8   | C7   | C11  | 122.2(4)| C1   | N1   | C2   | 113.3(3)|
| C7   | C8   | C9   | 121.9(4)| C1   | N1   | C4   | 121.7(3)|
| C4   | C9   | C8   | 118.4(4)| C2   | N1   | C4   | 124.3(3)|
| C4   | C9   | C12  | 121.5(4)| C1   | N2   | C3   | 112.6(3)|

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The table below lists the torsion angles for Ru8.

| A  | B  | C  | D  | Angle/° | A  | B  | C  | D  | Angle/° |
|----|----|----|----|---------|----|----|----|----|---------|
| N2 | C1 | N1 | C2 | -2.9(4) | N2 | C13| C18| C17| 176.7(3) |
| N2 | C1 | N1 | C4 | 167.5(3) | N2 | C13| C18| C21| -2.2(5)  |
| Ru24| C1 | N1 | C2 | 171.9(2) | C14| C13| N2 | C1 | -95.0(4) |
| Ru24| C1 | N1 | C4 | -17.7(4) | C14| C13| N2 | C3 | 92.6(4)  |
| N1  | C1  | N2  | C3  | -1.9(4)  | C18| C13| N2 | C1 | 90.4(4)  |
| N1  | C1  | N2  | C13 | -174.7(3)| C18| C13| N2 | C3 | -82.0(4) |
| Ru24| C1  | N2  | C3  | -175.7(2)| C13| C14| C15| C16| 0.1(5)   |
| Ru24| C1  | N2  | C13 | 11.5(5)  | C19| C14| C15| C16| -176.6(3)|
| N1  | C1  | Ru24| C22| -175.0(2)| C14| C15| C16| C17| 1.4(5)   |
| N1  | C1  | Ru24| C11| -84.5(2) | C14| C15| C16| C20| -179.0(3)|
| N1  | C1  | Ru24| C12| -3.6(4)  | C15| C16| C17| C18| -1.0(5)  |
| N1  | C1  | Ru24| Se1 | 99.7(2)  | C20| C16| C17| C18| 179.4(3) |
| N2  | C1  | Ru24| C22| -1.7(3)  | C16| C17| C18| C13| -0.8(5)  |
| N2  | C1  | Ru24| C11| 88.8(3)  | C16| C17| C18| C21| 178.1(3) |
| N2  | C1  | Ru24| C12| 169.7(2) | Ru24| C22| C23| C24| -177.7(3)|
| N2  | C1  | Ru24| Se1 | -87.0(3) | Ru24| C22| C23| C28| 3.1(5)   |
| N1  | C2  | C3  | N2  | -6.5(3)  | C23| C22| Ru24| C1 | -96.5(3) |
| C3  | C2  | N1  | C1  | 6.2(3)   | C23| C22| Ru24| C1 | 174.6(3) |
| C3  | C2  | N1  | C4  | -163.9(3)| C23| C22| Ru24| C12| 87.4(3)  |
| C2  | C3  | N2  | C1  | 5.6(3)   | C23| C22| Ru24| Se1| -4.8(3)  |
| C2  | C3  | N2  | C13 | 179.2(3) | C22| C23| C24| C25| -178.8(3)|
| C9  | C4  | C5  | C6  | -8.8(5)  | C28| C23| C24| C25| 0.4(5)   |
| C9  | C4  | C5  | C10 | 168.0(3) | C22| C23| C28| C27| 177.4(3) |
| N1  | C4  | C5  | C6  | 174.2(3) | C22| C23| C28| Se1 | 1.8(4)   |
| N1  | C4  | C5  | C10 | -9.0(5)  | C24| C23| C28| C27| -1.9(5)  |
| C5 | C4 | C9 | C8 | 9.5(6) | C24 | C23 | C28 | Se1 | -177.4(2) |
|----|----|----|----|--------|-----|-----|-----|-----|------------|
| C5 | C4 | C9 | C12| -167.4(4) | C23 | C24 | C25 | C26 | 0.5(6) |
| N1 | C4 | C9 | C8 | -173.6(4) | C24 | C25 | C26 | C27 | -1.2(6) |
| N1 | C4 | C9 | C12| 9.5(6) | C25 | C26 | C27 | C28 | -0.1(7) |
| C5 | C4 | N1 | C1 | -83.2(4) | C26 | C27 | C28 | C23 | 2.3(6) |
| C5 | C4 | N1 | C2 | 86.1(4) | C26 | C27 | C28 | Se1 | 177.4(3) |
| C9 | C4 | N1 | C1 | 99.7(4) | C23 | C28 | Se1 | C29 | -116.0(3) |
| C9 | C4 | N1 | C2 | -91.0(4) | C23 | C28 | Se1 | Ru24 | -4.0(2) |
| C4 | C5 | C6 | H6 | -178.7 | C27 | C28 | Se1 | C29 | 68.6(3) |
| C4 | C5 | C6 | C7 | 1.4(6) | C27 | C28 | Se1 | Ru24 | -179.5(3) |
| C10 | C5 | C6 | C7 | -175.4(4) | C30 | C29 | Se1 | C28 | -58.4(3) |
| C5 | C6 | C7 | C8 | 5.3(7) | C30 | C29 | Se1 | Ru24 | -158.4(2) |
| C5 | C6 | C7 | C11| -175.6(4) | C31 | C29 | Se1 | C28 | 179.9(3) |
| C6 | C7 | C8 | C9 | -4.7(7) | C31 | C29 | Se1 | Ru24 | 79.9(3) |
| C11 | C7 | C8 | C9 | 176.2(4) | C1 | Ru24 | Se1 | C28 | 101.4(1) |
| C7 | C8 | C9 | C4 | -2.5(7) | C1 | Ru24 | Se1 | C29 | -153.4(1) |
| C7 | C8 | C9 | C12| 174.4(4) | C22 | Ru24 | Se1 | C28 | 4.2(1) |
| C18 | C13 | C14 | C15| -2.1(5) | C22 | Ru24 | Se1 | C29 | 109.3(1) |
| C18 | C13 | C14 | C19| 174.7(3) | C1 | Ru24 | Se1 | C28 | -4.0(4) |
| N2 | C13 | C14 | C15| -176.4(3) | C1 | Ru24 | Se1 | C29 | 101.2(4) |
| N2 | C13 | C14 | C19| 0.4(5) | C2 | Ru24 | Se1 | C28 | -103.7(1) |
| C14 | C13 | C18 | C17| 2.4(5) | C2 | Ru24 | Se1 | C29 | 1.5(1) |
| C14 | C13 | C18 | C21| -176.5(3) |
Figure S2. Superimposed molecules of Ru8 obtained by us and Ru8 (CCDC 790618) obtained by the group of Lemcoff. The hydrogen atoms are omitted for clarity.

Figure S3. Superimposed molecules of Ru8 obtained by us and Ru4 (CCDC 689901) obtained by the group of Lemcoff. The hydrogen atoms are omitted for clarity.

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7 A. Ben-Asuly, E. Tzur, C. E. Diesendruck, M. Sigalov, I. Goldberg, N. G. Lemcoff, *Organometallics* **2008**, *27*, 811.
Activation of Ru8 and Catalytic Activity

Demonstration of Ru8 Latency

Scheme S4. RCM reaction of 4 as a method for Ru catalysts activity assessment.

Procedure: In a glovebox filled with argon, diene 4 (48.5 mg, 50 µL, 0.2 mmol, 1 equiv.) was added to a solution of Ru8 (1.38 mg, 0.002 mmol, 1 mol%) in C₆D₆ (0.4 mL) in a screw cap NMR tube. The NMR tube was taken outside of the glovebox and the reaction mixture was stirred at 20 °C for the required time. Data was recorded using 32 scans with a D1 delay time minimum of 1 s between each pulse. Progress of the reaction was monitored through the disappearance of the methylene signals of 4 (2.63 ppm) and the growth of the methylene proton signal of the product 5 (3.01 ppm). After the time of 1 month, the conversion of the diene 4 to the corresponding cycloalkene derivative 5 was not observable.

Figure S4. ^1H NMR spectra of reaction mixture at t₀ (top) and after the time of one month (bottom) in benzene.
Activation of Ru8 in CD$_2$Cl$_2$ with UV-Irradiation

![Scheme S5. Cis-trans isomerization of Ru8 in DCM with UV-irradiation.]

In a glovebox filled with argon, a screw cap NMR tube was charged with Ru8 (5 mg, 0.0072 mmol) in CD$_2$Cl$_2$ (0.5 mL). The NMR tube was taken outside of the glovebox and placed in a UV-reactor. Data was recorded using 32 scans with a D1 delay time minimum of 1 s between each pulse. Progress of the reaction was monitored through the disappearance of the benzylidene signal of cis-Cl$_2$Ru8 (17.46 ppm) and the growth of the benzylidene signal of trans-Cl$_2$Ru8 (17.72 ppm).

![Figure S5. $^1$H NMR spectra of Ru8 in CD$_2$Cl$_2$ at t$_0$ (top) and after 3 h of UV-irradiation (bottom).]
**Activation of Ru8 in C₆D₆ with UV-Irradiation**

![Chemical structure of Ru8](image)

**Scheme S6. Cis-trans isomerization of Ru8 in benzene-d₆ with UV-irradiation.**

In a glovebox filled with argon, a screw cap NMR tube was charged with Ru8 (5 mg, 0.0072 mmol) in C₆D₆ (0.5 mL). The NMR tube was taken outside of the glovebox and placed in a UV-reactor. Data was recorded using 32 scans with a D1 delay time minimum of 1 s between each pulse. Progress of the reaction was monitored through the disappearance of the benzylidene signal of cis-Cl₂Ru8 (17.46 ppm) and the growth of the benzylidene signal of trans-Cl₂Ru8 (17.72 ppm).

![NMR spectra](image)

**Figure S6.** ¹H NMR spectra of Ru8 in C₆D₆ at t₀ (top) and after 3 h of UV-irradiation (bottom).
Procedure: In a glovebox filled with argon, diene 4 (48.5 mg, 50 µL, 0.2 mmol, 1 equiv.) was added to a solution of Ru8 (1.38 mg, 0.002 mmol, 0.1 mol%) in C6D6 (0.4 mL) in a screw cap NMR tube. The NMR tube was taken outside of the glovebox and the reaction mixture was heated in an oil bath at 80 °C for the required time. Data was recorded using 32 scans with a D1 delay time minimum of 5 s between each pulse. Progress of the reaction was monitored through the disappearance of the methylene signals of 4 (2.63 ppm) and the growth of the methylene proton signal of the product 5 (3.01 ppm).

Figure S7. Progress of the RCM reaction of 4 in benzene-d6 at 80 °C monitored by 1H NMR.
Figure S8. Progress of the RCM reaction of 4 in benzene-$d_6$ at 80 °C monitored by $^1$H NMR.
Activity of Ru8 in RCM Reactions with Thermal Activation in C₆D₅CD₃

Scheme S8. RCM reaction of 4 promoted by Ru8 complex at increased temperature.

Procedure: In a glovebox filled with argon, diene 4 (48.5 mg, 50 µL, 0.2 mmol, 1 equiv.) was added to a solution of Ru8 (1.38 mg, 0.002 mmol, 0.1 mol%) in deuterated toluene (0.4 mL) in a screw cap NMR tube. The NMR tube was taken outside of the glovebox and the reaction mixture was heated in an oil bath at 80 °C for the required time. Data was recorded using 32 scans with a D1 delay time minimum of 5 s between each pulse. Progress of the reaction was monitored through the disappearance of the methylene signals of 4 (2.63 ppm) and the growth of the methylene proton signal of the product 5 (3.01 ppm).

Figure S9. Progress of the RCM reaction of 4 promoted by Ru8 in deuterated toluene at 80 °C monitored by ¹H NMR.
Procedure: In a glovebox filled with argon, diene 4 (48.5 mg, 50 µL, 0.2 mmol, 1 equiv.) was added to a solution of Ru8 (1.38 mg, 0.002 mmol, 0.1 mol%) in deuterated toluene (0.4 mL) in a screw cap NMR tube. The NMR tube was taken outside of the glovebox and the reaction mixture was heated in an oil bath at 110 °C for the required time. Data was recorded using 32 scans with a D1 delay time minimum of 5 s between each pulse. Progress of the reaction was monitored through the disappearance of the methylene signals of 4 (2.63 ppm) and the growth of the methylene proton signal of the product 5 (3.01 ppm).

**Scheme S9.** RCM reaction of 4 promoted by Ru8 complex at increased temperature.

**Figure S10.** Progress of the RCM reaction of 4 promoted by Ru8 in deuterated toluene at 110 °C monitored by ¹H NMR.
Figure S11. $^1$H NMR spectra of a crude mixture of 4 in presence of Ru8 in toluene at 110 °C at t=0 (top) and t= 4 h (bottom).

Figure S12. Partial $^1$H NMR spectra (benzylidene region) of a crude mixture of 4 in presence of Ru8 in toluene at 110 °C at t=0 (top) and t= 4 h (bottom).
Activity of Ru8 in RCM Reactions with Photochemical Activation in DCM

Scheme S10. RCM reaction of 4 promoted by Ru8 complex under irradiation.

Procedure: In a glovebox filled with argon, diene 4 (48.5 mg, 50 µL, 0.2 mmol, 1 equiv.) was added to a solution of Ru8 (1.38 mg, 0.002 mmol, 0.1 mol%) in CD2Cl2 (0.4 mL) in a screw cap NMR tube. The NMR tube was taken outside of the glovebox and placed in the UV photoreactor (λ = 365 nm) for a required time. Data was recorded using 32 scans with a D1 delay time minimum of 1 s between each pulse. Progress of the reaction was monitored through the disappearance of the methylene signals of 4 (2.63 ppm) and the growth of the methylene proton signal of the product 5 (3.01 ppm).

Figure S13. Progress of the RCM reaction of 4 promoted by Ru8 in DCM under UV irradiation (365 nm) monitored by 1H NMR.
Activity of Ru8 in RCM Reactions with Photochemical Activation in Benzene

Scheme S11. RCM reaction of 4 promoted by Ru8 complex under irradiation.

Procedure: In a glovebox filled with argon, diene 4 (48.5 mg, 50 µL, 0.2 mmol, 1 equiv.) was added to a solution of Ru8 (1.38 mg, 0.002 mmol, 0.1 mol%) in C6D6 (0.4 mL) in a screw cap NMR tube. The NMR tube was taken outside of the glovebox and placed in the UV photoreactor (λ = 365 nm) for a required time. Data was recorded using 32 scans with a D1 delay time minimum of 1 s between each pulse. Progress of the reaction was monitored through the disappearance of the methylene signals of 4 (2.63 ppm) and the growth of the methylene proton signal of the product 5 (3.01 ppm).

Figure S14. Progress of the RCM reaction of 4 promoted by Ru8 in benzene-d6 under UV irradiation (365 nm) monitored by 1H NMR.
**Figure S15.** $^1$H NMR spectra of a crude mixture of 4 in presence of Ru8 in benzene under light irradiation at t=0 (top), t=3 h (middle) and t= 7 h bottom.

**Figure S16.** Partial $^1$H NMR spectra of a crude mixture of 4 in presence of Ru8 in benzene under light irradiation at t=0 (top), t=3 h (middle) and t= 10 h bottom.
Polymerization Reactions Catalyzed by Ru8

Polymerization of Cyclooctene (COE)

Scheme S12. ROMP polymerization of COE promoted by Ru8 catalyst.

15 mL vial equipped with a screw cap was charged with substrate COE (323 mg, 385 µL, 2.93 mmol, 1 equiv.). Unless the reaction was carried out in neat, an appropriate solvent (6 mL) was added (DCM or toluene). To the resulting solution mesitylene (353 mg, 407 µL, 2.93 mmol, 1 equiv.) was added as internal standard followed by the addition of Ru8 catalyst stock solution in DCM (1 M, 0.3 mL, 0.303 mg, 0.44 µmol, 150 ppm, 0.0150 mol%). For the reactions carried out in neat conditions, the solvent (DCM) was removed under the reduced pressure before photochemical activation. The vial was then placed in the UV-reactor (365 nm) or in heated oil bath (80 °C) and was left for a required time affording a highly viscous solution. NMR of this crude solution was recorded and highlighted the presence of the polymer. The resulting polymer was precipitated out with acetone and methanol then filtered off. In the case of reaction in neat, the solid was washed with hexane and DCM and filtered. The filtrate was analyzed by 1H NMR to assess the conversion of the reaction.

In case of reaction with 10 ppm of Ru8, the following conditions has been used:
To a 15 mL screw capped vial containing COE (840 mg, 1000 µL, 7.62 mmol, 1 equiv.), mesitylene (916 mg, 1056 µL, 7.62 mmol, 1 equiv.) was added as internal standard followed by the addition of Ru8 catalyst stock solution in DCM (1 mg/mL, 0.050 mL, 0.05 mg, 0.076 µmol, 10 ppm, 0.0010 mol%).

Table S5. Results of ROMP reactions involving COE as a substrate.

| Entry | Solvent | Ru8 [ppm] | Activation | t [h] | conv. [%] | Aspect | M_n,th [kDa] | M_n [Da] | M_w [Da] | PDI |
|-------|---------|-----------|------------|-------|-----------|--------|--------------|----------|----------|-----|
| 1.    | neat    | 10        | hv         | 20    | 82        | elastic rubber | 9 900     | 21 528   | 56 934   | 2.64 |
| 2.    | 150     |           | 1         | 99    |           |         | 726        | 173 961  | 302 767  | 1.74 |
| 3.    | 150     | 80 °C     | 72        | 99    |           |         | 726        | 127 272  | 974 892  | 7.66 |
| 4.    | DCM     | 150       | hv         | 2     | 37        | -       | -           | -        | -        | -   |
| 5.    | 150     |           | 20        | 37    | -         |         | 271        | 6445     | 14578    | 2.26 |
| 6.    | toluene | 150       |           | 12    | 99        | Foam    | 726        | 188439   | 188.4    | 2.21 |
Figure S17. Pictures of the polyCOE obtained from the reaction of COE (1.0 equiv.) with 10 ppm of Ru8 in neat with light activation.

Figure S18. GPC traces of the polyCOE obtained from the reaction of COE (1.0 equiv.) with 150 ppm of Ru8 in neat with light activation.
Figure S19. GPC traces of the polyCOE obtained from the reaction of COE (1.0 equiv.) with 150 ppm of Ru8 in toluene with light activation.

Figure S20. GPC traces of the polyCOE obtained from the reaction of COE (1.0 equiv.) with 150 ppm of Ru8 in neat with heat activation.
Figure S21. GPC traces of the polyCOE obtained from the reaction of COE (1.0 equiv.) with 150 ppm of Ru8 in DCM with light activation.

Figure S22. GPC traces of the polyCOE obtained from the reaction of COE (1.0 equiv.) with 10 ppm of Ru8 in neat with light activation.
Polymerization of Dicyclopentadiene (DCPD)

Scheme S13. ROMP polymerization of DCPD promoted by Ru8 catalyst under UV irradiation.

15 mL vial equipped with a screw cap was charged with DCPD (500 mg, 3.67 mmol, 1 equiv.) and mesitylene (441 mg, 508 µL, 3.67 mmol, 1 equiv.) as internal standard. To the resulting mixture was added Ru8 catalyst stock solution (1 M, 0.38 mL, 0.378 mg, 0.55 µmol, 150 ppm, 0.0150 mol%). The solvent (DCM) was removed under the reduced pressure before photochemical activation. The vial was then placed in the UV-reactor (365 nm) and was left for a required time affording a transparent solid polymer (hard and odorless). The table containing the results of conducted ROMP reactions is presented below.

In case of reaction with 10 ppm of Ru8, the following conditions has been used:
To a 15 mL screw capped vial containing DCPD (1200 mg, 8.8 mmol, 1 equiv.), mesitylene (1058 mg, 1220 µL, 8.8 mmol, 1 equiv.) was added as internal standard followed by the addition of Ru8 catalyst stock solution in DCM (1 mg/mL, 0.06 mL, 0.06 mg, 0.08 µmol, 10 ppm, 0.0010 mol%).

Table S6. Results of ROMP reactions involving dicyclopentadiene as a substrate.

| Entry | Solvent | Ru [ppm] | t [h] | conv. [%] | Aspect       |
|-------|---------|----------|-------|-----------|-------------|
| 1.    | neat    | 10       | 6     | 71        | transparent soft rubber |
| 2.    | neat    | 10       | 12    | 84        | transparent soft rubber |
| 3.    | neat    | 150      | 1     | 99        | transparent hard rubber |

Figure S23. Pictures of polyDCPD obtained from the reaction of DCPD (1.0 equiv.) in neat with light activation with a) 150 ppm of Ru8 b) 10 ppm of Ru8.
Polymerization of Norbornene

Scheme S14. ROMP polymerization of norbornene promoted by Ru8 catalyst under UV irradiation.

15 mL vial equipped with a screw cap was charged with substrate 6 (276 mg, 2.93 mmol, 1 equiv.). Unless the reaction was carried out in neat, an appropriate solvent (6 mL) was added (DCM or toluene). To the resulting solution mesitylene (353 mg, 407 µL, 2.93 mmol, 1 equiv.) was added as internal standard followed by the addition of Ru8 catalyst stock solution in DCM (1 M, 0.3 mL, 0.303 mg, 0.44 µmol, 150 ppm, 0.0150 mol%). For the reactions carried out in neat conditions, the solvent (DCM) was removed under the reduced pressure before photochemical activation. The vial was then placed in the UV-reactor (365 nm) or in heated oil bath (80 °C) and was left for a required time affording a highly viscous solution. NMR of this crude solution was recorded. The resulting polymer was precipitated out with acetone and methanol then filtered off. In the case of reaction in neat, the solid was washed with hexane and DCM and filtered. The filtrate was analyzed by 1H NMR to assess the conversion of the reaction.

In case of reaction with 10 ppm of Ru8, the following conditions has been used: To a 15 mL screw capped vial containing 6 (1026 mg, 10.9 mmol, 1 equiv.), mesitylene (1310 mg, 1510 µL, 10.9 mmol, 1 equiv.) was added as internal standard followed by the addition of Ru8 catalyst stock solution in DCM (1 mg/mL, 0.075 mL, 0.075 mg, 0.11 µmol, 10 ppm, 0.0010 mol%).

| Entry | Solvent | Ru [ppm] | t [h] | conv. [%] | Aspect | \(M_n\), theo [Da] | \(M_n\) [Da] | \(M_w\) [Da] | PDI |
|-------|---------|----------|-------|----------|--------|------------------|--------------|--------------|-----|
| 1.    | neat    | 10       | 12    | 99       | colorless rubber | 9325/800    | 318/624     | 650/241   | 2.04 |
| 2.    |    | 150    | 1     | 99       | grey solid     | 621/720     | -            | -          | -   |
| 3.    | DCM    | 150     | 20    | 91       | grey solid     | 571/480     | 25/410      | 656/97    | 2.59 |
Figure S24. GPC traces of the polynorbornene obtained from the reaction of 6 (1.0 equiv.) with 10 ppm of Ru8 in neat with light activation.

Figure S25. GPC traces of the polynorbornene obtained from the reaction of 6 (1.0 equiv.) with 10 ppm of Ru8 in DCM with light activation.
Polymerization of Cycloocta-1,5-diene (COD)

Scheme S15. ROMP polymerization of cyclooctadiene promoted by Ru8 catalyst.

15 mL vial equipped with a screw cap was charged with substrate COD (324 mg, 367 µL, 2.93 mmol, 1 equiv.). Unless the reaction was carried out in neat, an appropriate solvent (6 mL) was added (DCM or toluene). To the resulting solution mesitylene (353 mg, 407 µL, 2.93 mmol, 1 equiv.) was added as internal standard followed by the addition of Ru8 catalyst stock solution in DCM (1 M, 0.3 mL, 0.303 mg, 0.44 µmol, 150 ppm, 0.0150 mol%). For the reactions carried out in neat conditions, the solvent (DCM) was removed under the reduced pressure before photochemical activation. The vial was then placed in the UV-reactor (365 nm) or in heated oil bath (80 °C) and was left for a required time affording a highly viscous solution. NMR of this crude solution was recorded and highlighted the presence of the polymer polyCOD, which was subsequently precipitated out with acetone and then filtered off. Despite the flexibility of the obtained material, it can be broken easily on elongation. The filtrate was analyzed by NMR spectroscopy to determine the conversion of the substrate. The table containing the results of conducted ROMP reactions is presented below.

Table S8. Results of ROMP reactions involving COD as a substrate. N.D. = not detected.

| Entry | Solvent | Ru [ppm] | Activation | t [h] | conv. [%] | Aspect | M_{n,theoretical} [Da] | M_n [Da] | M_w [Da] | PDI |
|-------|---------|----------|------------|------|----------|--------|---------------------|--------|---------|-----|
| 1.    | neat    | 150      | hv         | 6    | 68       | elastic rubber | -      | N.D    | N.D | N.D |
| 2.    |         | 150      | 80 °C      | 72   | 0        | -      | -      | -      | -   | -   |
| 3.    | DCM     | 150      | hv         | 20   | 0        | -      | -      | -      | -   | -   |
Self Cross-Metathesis of Methyl Oleate (MO)

Methyl oleate (MO) (341 μL, 1 mmol) was introduced into a 1.5 mL screw-capped vial. The air in the flask was replaced by argon. The catalyst Ru8 (0.69 mg, 0.001 equiv., 1 μmol, 0.1 mol% or 0.35 mg, 0.5 μmol, 0.05 mol%) was added as DCM solution (1 mg/mL). The solvent (DCM) was evaporated from the vessel under reduced pressure followed by refilling the vial with argon atmosphere before placing the vial in a UV-reactor. Then, the reaction mixture was irradiated for 14 h. After this time, a solution of SnatchCat was added and the reaction mixture was diluted in toluene. The resulting solution was injected to the GC-MS.

Calculation of % of isomerization:

\[
\%_{iso} (C_{18}) = \frac{... + % (C_{18} - 1) + % (C_{18} + 1) + \ldots}{... + % (C_{18} - 1) + % (C_{18}) + % (C_{18} + 1) + \ldots} \times 100
\]

\[
\%_{iso} (MO) = \frac{... + % (MO - 1) + % (MO + 1) + \ldots}{... + % (MO - 1) + % (MO) + % (MO + 1) + \ldots} \times 100
\]

\[
\%_{iso} (DE) = \frac{... + % (DE - 1) + % (DE + 1) + \ldots}{... + % (DE - 1) + % (DE) + % (DE + 1) + \ldots} \times 100
\]

Global %iso = \frac{\%_{iso} (C_{18}) + \%_{iso} (MO) + \%_{iso} (DE)}{3}

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D. Butilkov, A. Frenklah, I. Rozenberg, S. Kozuch, N. G. Lemcoff, "ACS Catal. 2017, 7, 7634."
Calculation of selectivity toward C=C bond shifting:

\[
Selectivity \ (C_{18}) = \frac{\%(C_{18})}{\ldots + \% (C_{18} - 1) + \% (C_{18}) + \% (C_{18} + 1) + \ldots} \times 100
\]

\[
Selectivity \ (MO) = \frac{\% (MO)}{\ldots + \% (MO - 1) + \% (MO) + \% (MO + 1) + \ldots} \times 100
\]

\[
Selectivity \ (DE) = \frac{\% (DE)}{\ldots + \% (DE - 1) + \% (DE) + \% (DE + 1) + \ldots} \times 100
\]

\[
Global \ Selectivity = \frac{Selectivity \ (C_{18}) + Selectivity \ (MO) + Selectivity \ (DE)}{3}
\]

*Table S9. GC-MS chromatogram analysis of self-CM of MO with Ru8.*

| Compound | R.T. (min) | Corr. area | % total |
|----------|------------|------------|---------|
|          | 1000 ppm of Ru8 |           |         |
| Z-C18    | 9.986      | 24310.65   | 2.44    |
| E-C18    | 10.029     | 57824.65   | 5.79    |
| Z-Imp    | 11.128     | 11587.71   | 1.16    |
| E-Imp    | 11.213     | 18193.05   | 1.82    |
| Z-MO     | 12.666     | 598067.81  | 59.92   |
| E-MO     | 12.693     | 158880.77  | 15.92   |
| Z-DE     | 14.986     | 25075.30   | 2.51    |
| E-DE     | 15.022     | 69665.84   | 6.71    |
|          | 500 ppm of Ru8 |           |         |
| Z-C18    | 9.984      | 29994.57   | 2.49    |
| E-C18    | 10.028     | 74072.23   | 6.16    |
| Z-Imp    | 11.124     | 12595.86   | 1.05    |
| E-Imp    | 11.209     | 21613.80   | 1.80    |
| Z-MO     | 12.667     | 716577.19  | 59.59   |
| E-MO     | 12.691     | 196341.23  | 16.33   |
| Z-DE     | 14.982     | 30115.75   | 2.50    |
| E-DE     | 15.019     | 80346.05   | 6.68    |
|          | 1000 ppm dark control |       |         |
| E-Imp    | 11.116     | 12193.41   | 1.86    |
| Z-Imp    | 11.201     | 16013.88   | 2.45    |
| E-MO     | 12.656     | 601909.25  | 92.01   |
| Z-MO     | 12.801     | 12264.73   | 1.87    |
Figure S26. Chromatogram of self-CM of MO promoted by 1000 ppm of Ru8 under light irradiation.
Figure S27. Chromatogram of self-CM of MO promoted by 500 ppm of Ru8 under light irradiation.
Figure S28. Chromatogram of self-CM of MO promoted by 500 ppm of Ru8 in the dark.
NMR Spectra of New Compounds
Figure S29. $^1$H NMR spectrum of 3 in CDCl$_3$. 

$^1$H NMR spectrum of 3 in CDCl$_3$. 

- Figure S29. $^1$H NMR spectrum of 3 in CDCl$_3$. 

S40
$^{13}$C NMR spectrum of 3 in CDCl$_3$. 

Figure S30. $^{13}$C NMR spectrum of 3 in CDCl$_3$. 

S41
Figure S31. 2D NMR HSQC spectrum of 3 in CDCl₃.
Figure S32. $^{77}$Se NMR spectrum of 3 in CDCl$_3$. 
Figure S33. $^1$H NMR spectrum of Ru8 in CD$_2$Cl$_2$. 

$^1$H NMR spectrum of Ru8 in CD$_2$Cl$_2$.
$^{13}$C NMR spectrum of Ru8 in CD$_2$Cl$_2$.

Figure S34. $^{13}$C NMR spectrum of Ru8 in CD$_2$Cl$_2$. 
Figure S35. 2D NMR spectrum COSY of Ru8 in CD$_2$Cl$_2$. 

S46
Figure S36. 2D NMR spectrum HSQC of Ru8 in CD$_2$Cl$_2$. 

2D NMR spectrum HSQC of Ru8 in CD$_2$Cl$_2$. 

S47
Figure S37. Partial 2D NMR spectrum HSQC of Ru8 in CD2Cl2.
Figure S38. Partial 2D NMR spectrum HSQC of Ru8 in CD$_2$Cl$_2$. 

Partial 2D NMR spectrum HSQC of Ru8 in CD$_2$Cl$_2$
$^{77}\text{Se}$ NMR spectrum of Ru8 in CD$_2$Cl$_2$. 

Figure S39. $^{77}\text{Se}$ NMR spectrum of Ru8 in CD$_2$Cl$_2$. 
Figure S40. Superimposition of the $^{77}$Se NMR spectra of 3 (top) and Ru8 (bottom).