

# Supporting Information

## A solvent-responsive coordination cage

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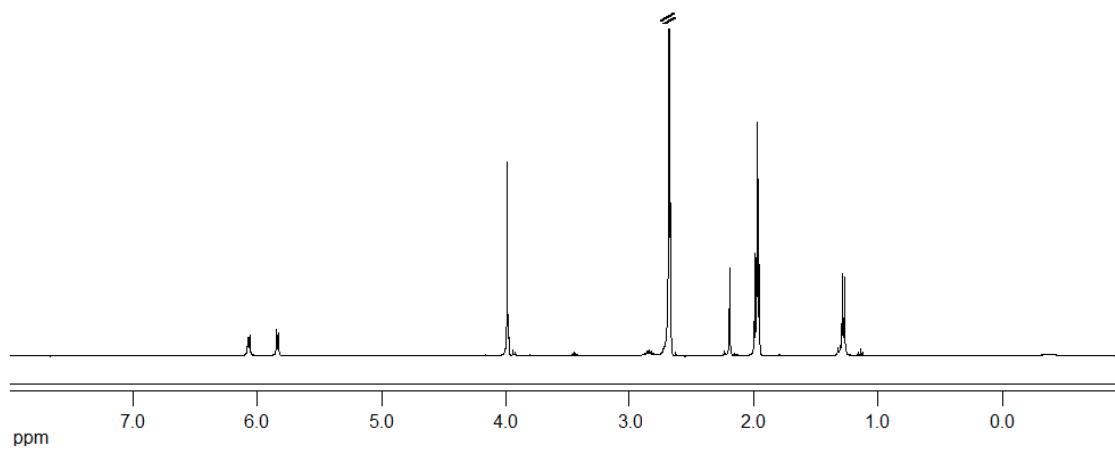
**1. General:** [(cymene)RuCl<sub>2</sub>]<sub>2</sub><sup>1</sup> and tetra(4-pyridylphenyl)ethylene (**2**)<sup>2</sup> were synthesized according to previously published procedures. 3,4-Dimethoxyfuran-2,5-dicarboxylic acid was obtained from Aldrich. All solvents were dried using a solvent purification system from Innovative Technologies, Inc. All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. NMR spectra were measured on a Bruker Avance DPX-400 (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 100 MHz) spectrometer. Combustion analyses were performed with a Thermo Scientific Flash 2000 Organic Elemental Analyzer.

**2. Synthesis of complex 1:** Silver acetate (75 mg, 0.45 mmol) was added to a stirred solution of [(cymene)RuCl<sub>2</sub>]<sub>2</sub> (62 mg, 0.10 mmol) in acetonitrile (20 mL). After stirring for 2 h at room temperature under protection of light, AgCl was removed by filtration via celite. 3,4-Dimethoxy-2,5-furandicarboxylic acid (43 mg, 0.20 mmol) was added to the filtrate and the mixture was stirred for 3 h at 50 °C. The volume was reduced to 10 mL and 0.5 mL water was added. The mixture was stirred for 1 h at 40 °C. The product precipitated in the form of a yellow powder upon addition of diethyl ether (20 mL) and pentane (3 mL). The precipitate was isolated, washed with diethyl ether (30 mL) and pentane (20 mL), and dried under vacuum (78 mg, 81%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN/D<sub>2</sub>O, 100:2, 298 K): δ 6.07 (d, *J* = 6.0 Hz, 4H, CH<sub>arom</sub>, cymene), 5.83 (d, *J* = 6.0 Hz, 4H, CH<sub>arom</sub>, cymene), 3.99 (s, 12H, OCH<sub>3</sub>), 2.84 (sept, *J* = 6.8 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.19 (s, 6H, CH<sub>3</sub>, cymene), 1.27 (d, *J* = 6.8 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN/D<sub>2</sub>O, 100:2, 298 K): δ 164.2, 143.5, 134.1, 96.5 (2C), 81.6, 80.5, 61.1, 30.9, 21.5, 18.0. Anal. Calcd. for C<sub>38</sub>H<sub>45</sub>NO<sub>15</sub>Ru<sub>2</sub>: C, 47.65; H, 4.74; N, 1.46. Found: C, 47.30; H, 4.34; N, 1.33. Single crystals were obtained by slow vapor diffusion of pentane into a solution of complex **1** in dichloromethane/acetonitrile (1:1).

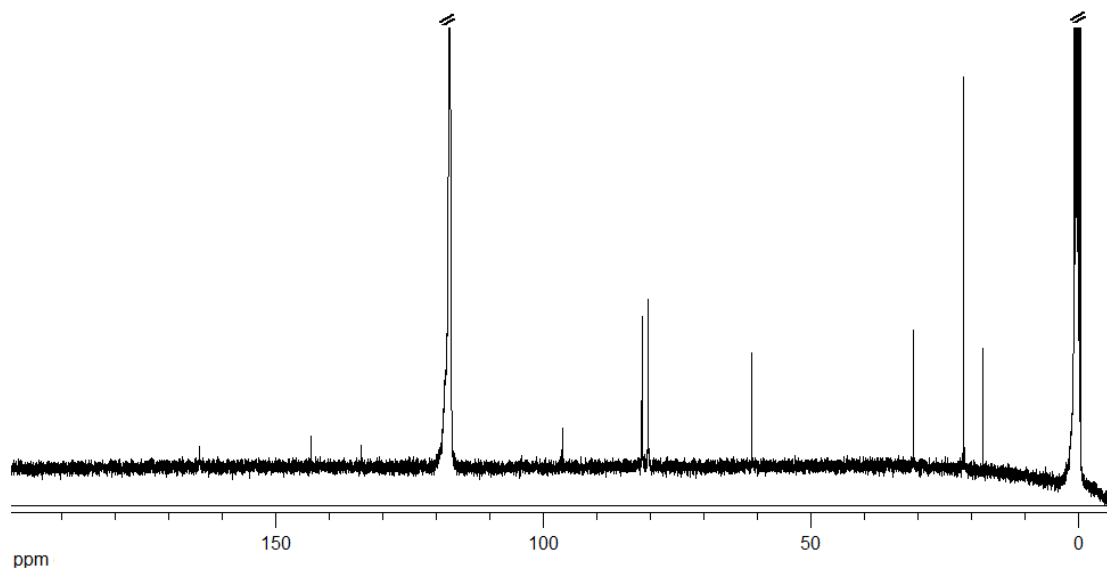
**3. Synthesis of complex 3:** A solution of complex **1** (30 mg, 31 μmol) and tetra-(4-pyridylphenyl)ethylene (10.2 mg, 16 μmol) in CHCl<sub>3</sub> (14 mL) was stirred for 4.5 h at 55 °C. Subsequently, the solvent was reduced to 5 mL under reduced pressure. Cage **3** precipitated in the form of an orange powder upon addition of diethyl ether (20 mL). The precipitate was isolated, washed with diethyl ether (20 mL) and pentane (20 mL), and dried under vacuum (24 mg, 57%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ 8.89 (d, *J* = 6.4 Hz, 16H, CH<sub>arom</sub>), 7.23 (m, 32H, CH<sub>arom</sub>), 6.92 (d, *J* = 8.0 Hz, 16H, CH<sub>arom</sub>), 6.29 (m, 16H, CH<sub>arom</sub>, cymene), 5.70 (d, *J* = 6.0

Hz, 8H, CH<sub>arom</sub>, cymene), 5.67 (d,  $J = 5.6$  Hz, 8H, CH<sub>arom</sub>, cymene), 4.20 (s, 24H, OCH<sub>3</sub>), 4.12 (s, 24H, OCH<sub>3</sub>), 2.67 (m, 8H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.76 (s, 24H, CH<sub>3</sub>, cymene), 1.22 (d,  $J = 7.2$  Hz, 24H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.21 (d,  $J = 6.8$  Hz, 24H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  166.34, 166.31, 154.2, 149.1, 144.1, 144.0, 143.8, 139.4, 135.6, 134.3, 134.0, 132.1, 126.9, 122.9, 99.4, 96.7, 86.5, 77.2, 61.5, 61.2, 31.2, 22.6, 18.2 (the diastereotopic groups of the cymene  $\pi$ -ligand are not resolved in the <sup>13</sup>C NMR spectrum). Anal. Calcd. for C<sub>236</sub>H<sub>224</sub>N<sub>8</sub>O<sub>56</sub>Ru<sub>8</sub>·4CHCl<sub>3</sub>: C, 53.84; H, 4.29; N, 2.09. Found: C, 54.04; H, 4.80; N, 2.44. Single crystals were obtained by slow vapor diffusion of pentane into a solution of complex **3** in CHCl<sub>3</sub>.

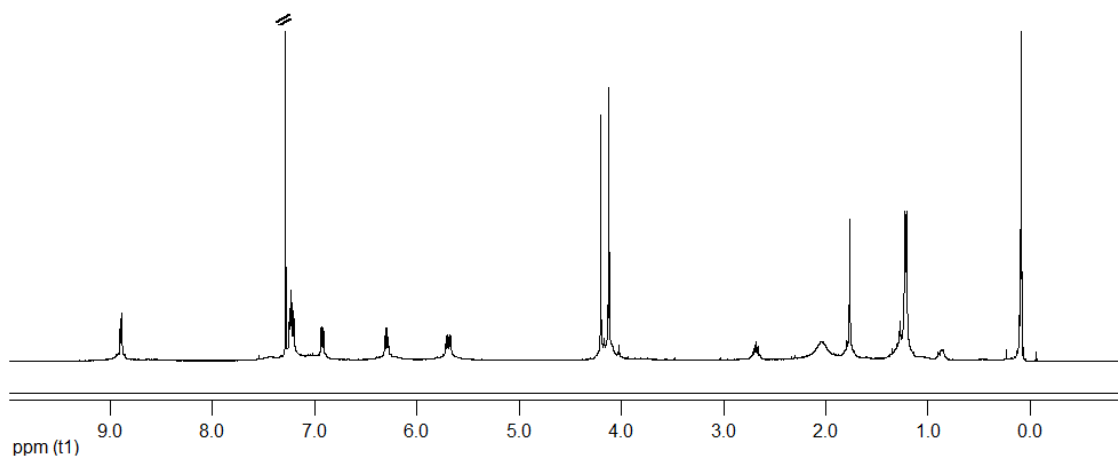
**4. Synthesis of complex 4:** A solution of complex **1** (30 mg, 31  $\mu$ mol) and tetra-(4-pyridylphenyl)ethylene (10.2 mg, 16  $\mu$ mol) in CH<sub>2</sub>Cl<sub>2</sub> (14 mL) was stirred for 3.5 h at 41 °C. Subsequently, the solvent was reduced to 5 mL under reduced pressure. Complex **4** precipitated in the form of an orange powder upon addition of diethyl ether (15 mL) and pentane (10 mL). The precipitate was isolated, washed with diethyl ether (20 mL) and pentane (20 mL), and dried under vacuum. (33 mg, 79%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  8.66 (d,  $J = 6.8$  Hz, 8H, CH<sub>arom</sub>), 7.28 (d,  $J = 6.8$  Hz, 8H, CH<sub>arom</sub>), 7.15 (d,  $J = 8.4$  Hz, 8H, CH<sub>arom</sub>), 6.99 (d,  $J = 8.4$  Hz, 8H, CH<sub>arom</sub>), 6.28 (d,  $J = 5.6$  Hz, 8H, CH<sub>arom</sub>, cymene), 5.91 (d,  $J = 5.6$  Hz, 8H, CH<sub>arom</sub>, cymene), 4.07 (s, 24H, OCH<sub>3</sub>), 2.82 (sept,  $J = 7.2$  Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.97 (s, 12H, CH<sub>3</sub>, cymene), 1.24 (d,  $J = 7.2$  Hz, 24H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  165.2, 153.6, 149.3, 143.8, 143.7, 143.3, 135.8, 133.8, 131.5, 126.9, 123.6, 100.9, 96.2, 82.4 (br), 79.8 (br), 61.3, 30.6, 22.5, 18.2. Anal. Calcd. for C<sub>118</sub>H<sub>112</sub>N<sub>4</sub>O<sub>28</sub>Ru<sub>4</sub>·3CH<sub>2</sub>Cl<sub>2</sub>: C, 53.96; H, 4.42; N, 2.08. Found: C, 53.88; H, 4.80; N, 2.20. Single crystals were obtained by slow vapor diffusion of pentane into a solution of complex **4** in dichloromethane.



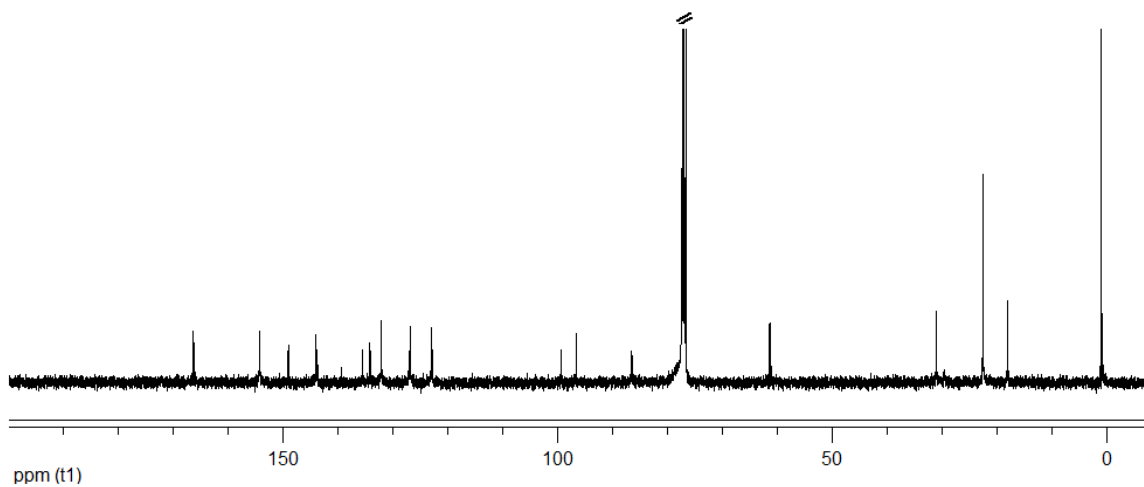
**Figure S1.**  $^1\text{H}$  NMR spectrum of complex **1** ( $\text{CD}_3\text{CN}/\text{D}_2\text{O}$ ; 100:2).



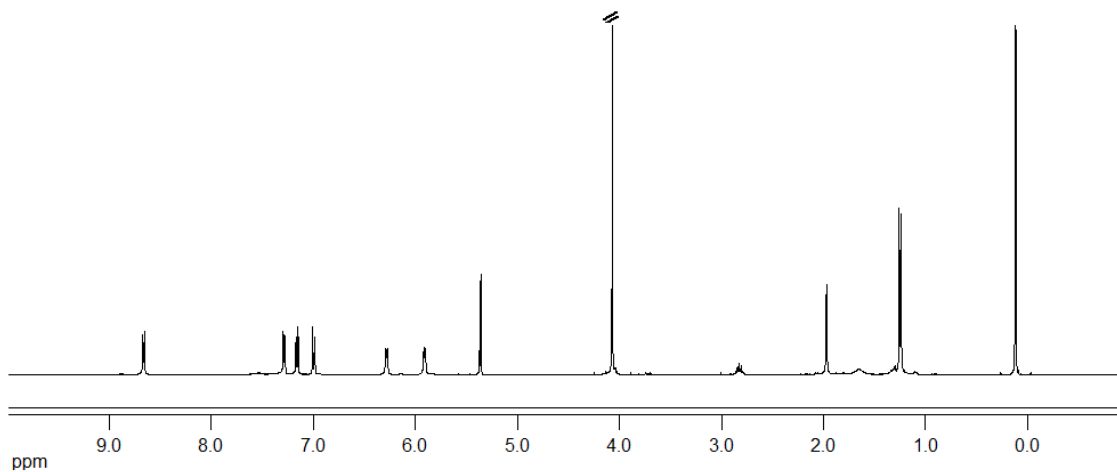
**Figure S2.**  $^{13}\text{C}$  NMR spectrum of complex **1** ( $\text{CD}_3\text{CN}/\text{D}_2\text{O}$ ; 100:2).



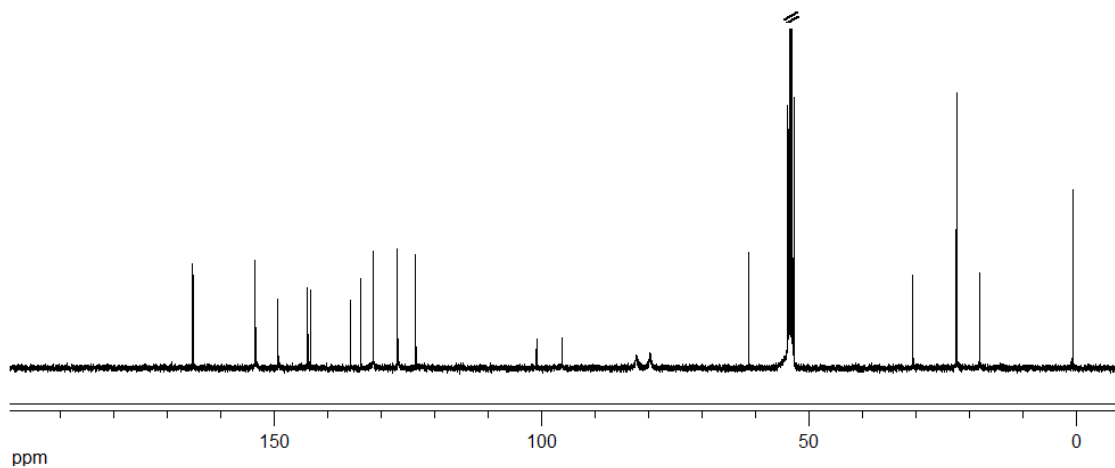
**Figure S3.**  $^1\text{H}$  NMR spectrum of complex **3** ( $\text{CDCl}_3$ ).



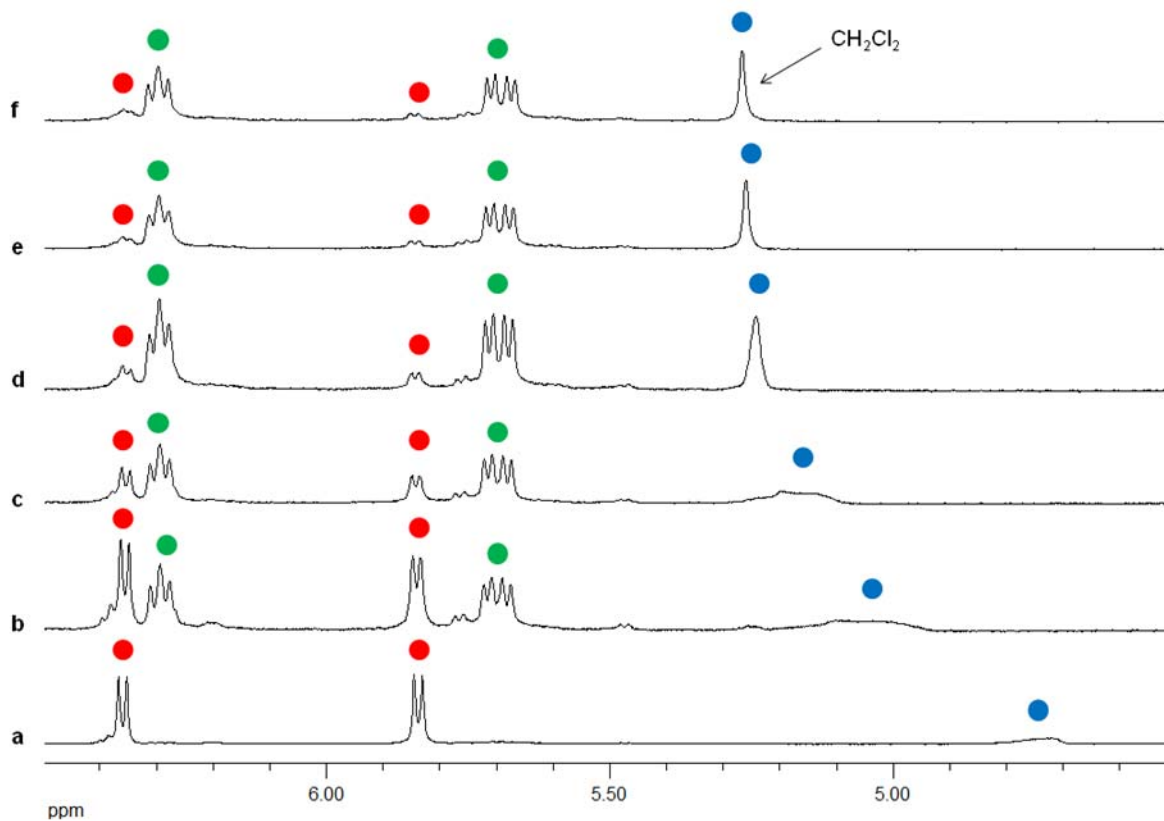
**Figure S4.**  $^{13}\text{C}$  NMR spectrum of complex **3** ( $\text{CDCl}_3$ ).



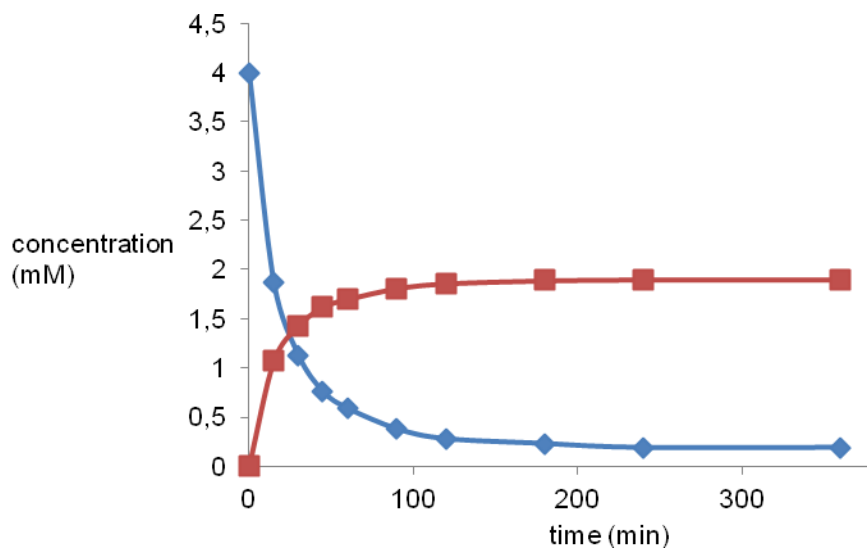
**Figure S5.**  $^1\text{H}$  NMR spectrum of complex **4** ( $\text{CD}_2\text{Cl}_2$ ).



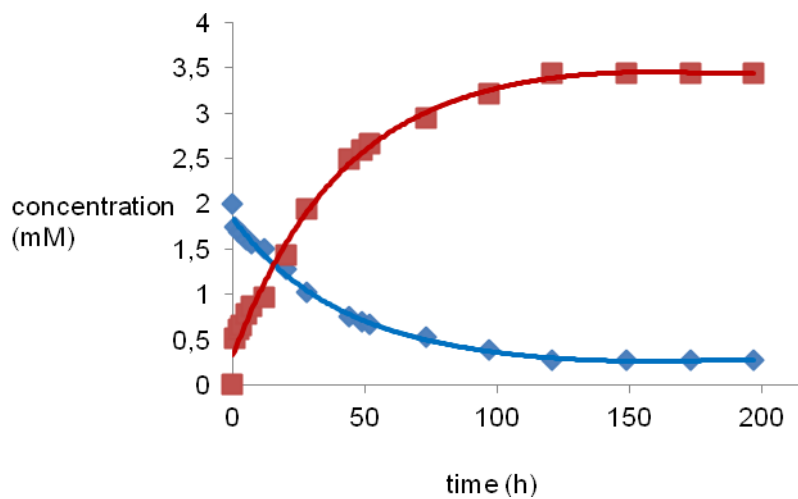
**Figure S6.**  $^{13}\text{C}$  NMR spectrum of complex **4** ( $\text{CD}_2\text{Cl}_2$ ).



**Figure S7.** Part of the <sup>1</sup>H NMR spectra of complex **4** (4.0 mM) in CDCl<sub>3</sub>. The spectra were recorded after tempering at 50°C for 0 min (a), 30 min (b), 1 h (c), 2 h (d), 3 h (e), and 6 h (f). Heating at 50 °C in CDCl<sub>3</sub> induces a rearrangement of complex **4** (●) in complex **3** (●). In parallel, the broad signal of bound CH<sub>2</sub>Cl<sub>2</sub> (●) sharpens and moves to its 'normal' position at δ = 5.31 ppm.



**Figure S8.** Time course for the conversion of complex 4 ( $[4]_{\text{init.}} = 4.0 \text{ mM}$ ; ■) into complex 3 (◆) at 50 °C in  $\text{CDCl}_3$ .



**Figure S9.** Time course for the conversion of complex 3 ( $[3]_{\text{init.}} = 2.0 \text{ mM}$ ; ◆) into complex 4 (■) at 38 °C in  $\text{CD}_2\text{Cl}_2$ .



**6. Single crystal X-ray analyses:** Selected structure refinement details can be found in Table S1. Diffraction intensity data were collected using either MoK $\alpha$  radiation on a four-circle kappa goniometer equipped with a Nonius-Bruker Apex II CCD. Data were reduced by EvalCCD.<sup>3</sup> Absorption corrections were applied to all data sets. All structures were solved using conventional heavy atom methods and refined using full-matrix least-squares on  $F^2$ . The hydrogen atoms were placed in calculated positions using the riding model with  $U_{\text{iso}} = aU_{\text{eq}}$  (where  $a$  is 1.5 for methyl hydrogen atoms and 1.2 for others). Refinement and geometrical calculations were carried out on all structures with SHELXTL.<sup>4</sup> In all cases, scattering contributions from some residual diffuse electron density (i.e. disordered solvent) were removed using the SQUEEZE routine in PLATON.<sup>5</sup>

**Table S1.** Crystallographic data and structure refinement details for the complexes **1**, **3**, and **4**.

	<b>1</b>	<b>3</b>	<b>4</b>
Empirical formula	C <sub>40</sub> H <sub>46</sub> N <sub>2</sub> O <sub>14</sub> Ru <sub>2</sub>	C <sub>236</sub> H <sub>224</sub> N <sub>4</sub> O <sub>56</sub> Ru <sub>8</sub> ·23CHCl <sub>3</sub>	C <sub>118</sub> H <sub>112</sub> N <sub>4</sub> O <sub>28</sub> Ru <sub>4</sub> ·4CH <sub>2</sub> Cl <sub>2</sub>
Formula weight	980.93	7622.26	2778.10
Temperature / K	100(2)	100(2)	100(2)
Wavelength / Å	0.71073	0.71073	0.71073
Space group	C2/c	P-1	P-1
Unit cell dimensions / Å	<i>a</i> = 23.769(3) <i>b</i> = 15.938(3) <i>c</i> = 13.3495(11) $\alpha$ = 90° $\beta$ = 102.022(9)° $\gamma$ = 90°	<i>a</i> = 16.0499(16) <i>b</i> = 24.504 (4) <i>c</i> = 26.963(4) $\alpha$ = 70.041(10)° $\beta$ = 77.399(12)° $\gamma$ = 81.696(9)°	<i>a</i> = 12.0083(18) <i>b</i> = 15.379(4) <i>c</i> = 20.855(3) $\alpha$ = 85.969(16)° $\beta$ = 78.367(10)° $\gamma$ = 87.615(16)°
Volume / Å <sup>3</sup>	4946.5(11)	9699(2)	3767.0(12)
<i>Z</i>	4	1	1
Calculated density / g cm <sup>-3</sup>	1.317	1.305	1.225
Absorption coefficient / mm <sup>-1</sup>	0.668	0.835	0.596
<i>F</i> (000)	2000	3830	1416
Crystal size / mm	0.44 × 0.17 × 0.11	0.48 × 0.32 × 0.22	0.43 × 0.32 × 0.20
Measured $\theta$ range	3.04 to 27.50	3.02 to 22.99	3.13 to 25.03°
Limiting indices	-30 ≤ <i>h</i> ≤ 30 -20 ≤ <i>k</i> ≤ 20 -17 ≤ <i>l</i> ≤ 17	-17 ≤ <i>h</i> ≤ 17 -26 ≤ <i>k</i> ≤ 26 -28 ≤ <i>l</i> ≤ 29	-14 ≤ <i>h</i> ≤ 13 -18 ≤ <i>k</i> ≤ 18 -24 ≤ <i>l</i> ≤ 24
Reflections collected / unique	38422 / 5677	113529 / 26459	59170 / 13042
<i>R</i> <sub>int</sub>	0.0413	0.0612	0.0437
Data / restraints / parameters	5677 / 0 / 262	26459 / 698 / 1796	13042 / 392 / 828
Goodness of fit on <i>F</i> <sup>2</sup>	1.064	1.480	1.211
<i>R</i> indices [ <i>I</i> ≥ 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0269 <i>wR</i> <sub>2</sub> = 0.0729	<i>R</i> <sub>1</sub> = 0.1234 <i>wR</i> <sub>2</sub> = 0.3466	<i>R</i> <sub>1</sub> = 0.0904 <i>wR</i> <sub>2</sub> = 0.1965
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0310 <i>wR</i> <sub>2</sub> = 0.0759	<i>R</i> <sub>1</sub> = 0.1571 <i>wR</i> <sub>2</sub> = 0.3818	<i>R</i> <sub>1</sub> = 0.0977 <i>wR</i> <sub>2</sub> = 0.1993
Final Fourier residuals	0.475 and -0.752 e Å <sup>-3</sup>	2.670 and -2.953 e Å <sup>-3</sup>	1,271 and -1.809 e Å <sup>-3</sup>

## 7. References:

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- [2] P. P. Kapadia, J. C. Widen, M. A. Magnus, D. C. Swenson and F. C. Pigge, *Tetrahedron Lett.* 2011, **52**, 2519.
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- [4] (a) G. M. Sheldrick, *SHELXTL*; University of Göttingen: Göttingen, Germany, 1997; (b) Bruker AXS, Inc.: Madison, WI, 1997.
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