

Supporting information

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Molecular Switches Based on Dinuclear N-Heterocyclic Carbene Ruthenium(II) Complexes

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1. Temperature-dependent NMR spectra of 2c and 2d

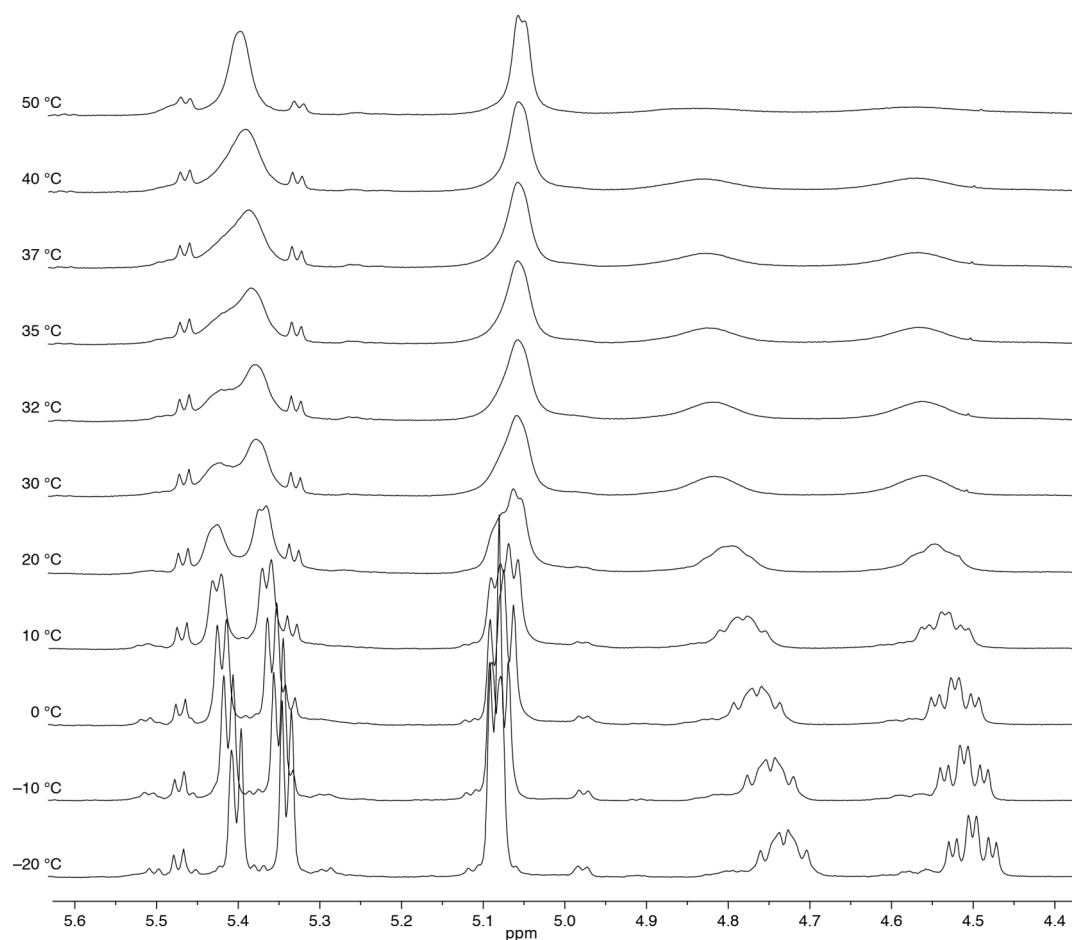


Figure S1. Variable temperature NMR spectra of complex **2c** recorded on a Varian 500 MHz spectrometer. The coalescence temperature in the manuscript was measured on a 400 MHz spectrometer (allowing straight comparison with monometallic systems). The energy barrier for rotation is independent of the NMR frequency: T_c for the cymene $C_{ar}-H$ protons (δ_H 5.41 and 5.34) on the 500 MHz spectrometer is 308 K, thus giving $\Delta G^\ddagger = 64.0(\pm 0.4) \text{ kJ mol}^{-1}$

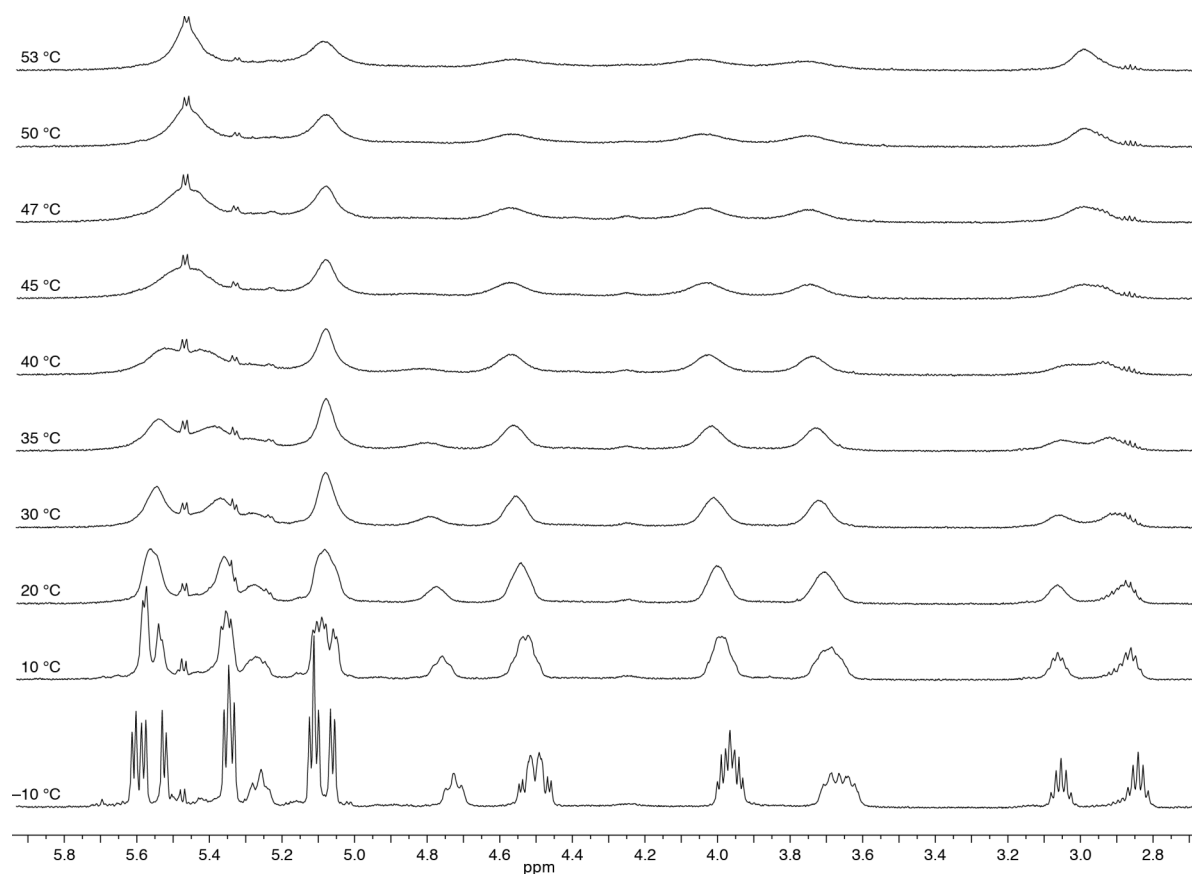


Figure S2. Variable temperature NMR spectra of complex **2d** recorded on a Varian 500 MHz spectrometer. The coalescence temperature in the manuscript was measured on a 400 MHz spectrometer (allowing straight comparison with monometallic systems). The energy barrier for rotation is independent of the NMR frequency: T_c for the cymene CHMe_2 protons (δ_{H} 3.04 and 2.81) on the 500 MHz spectrometer is 320 K, thus giving $\Delta G^\ddagger = 63.8(\pm 0.4) \text{ kJ mol}^{-1}$.

2. Discussion of the proton-mediated isomerization of **6**

We propose the following presumably acid-mediated epimerization of **6** prior to decomposition (Scheme S1). Spectroscopic analyses of **6** do not permit unambiguous assignment of the complex as either *meso*- or *rac*-isomer (Fig. S3).

Scheme S1

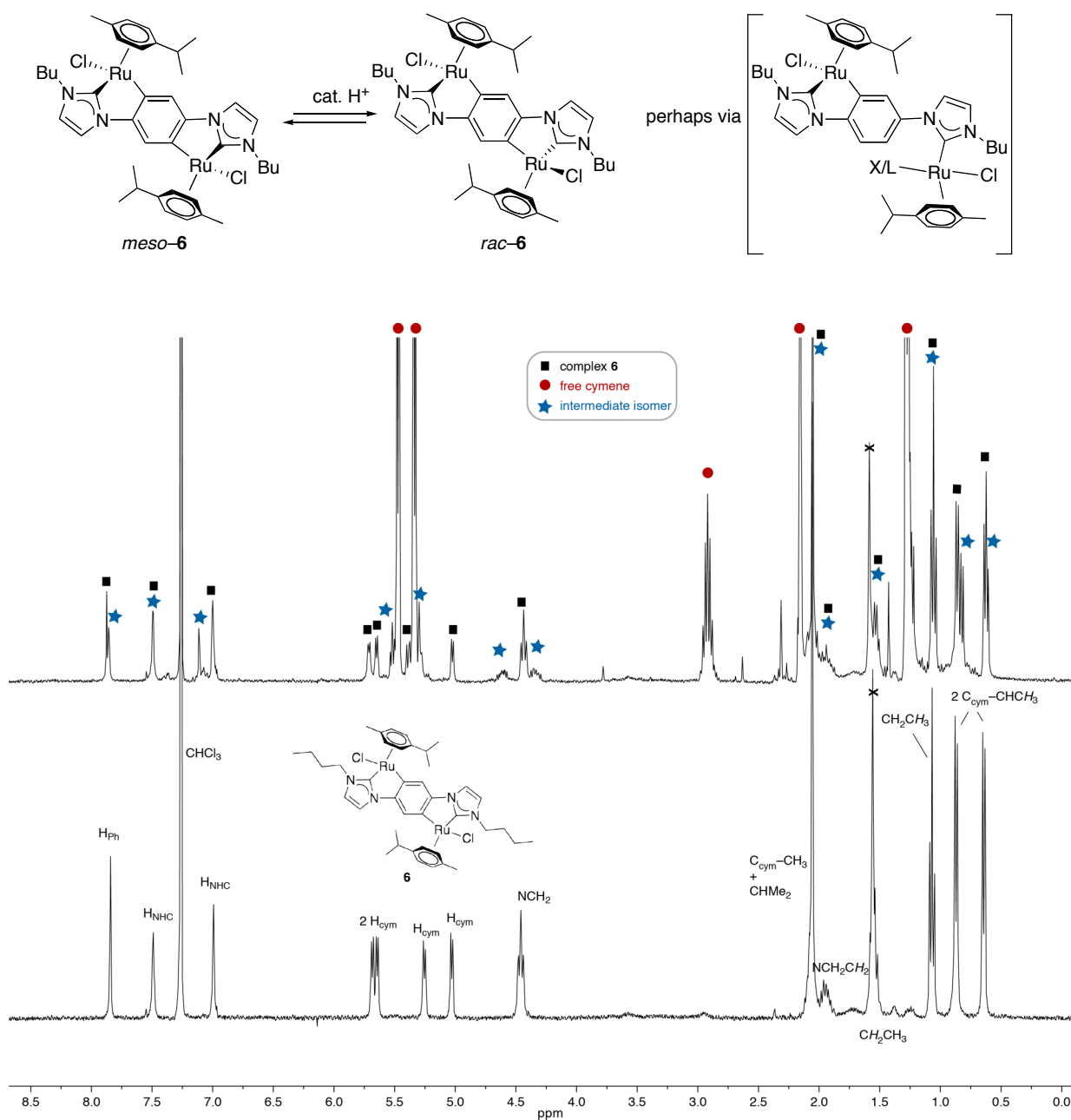


Figure S3. Pertinent ^1H NMR spectra of freshly prepared **6** (bottom, stereochemistry at Ru ambiguous) and of a mixture in CDCl_3 comprising **6** and an intermediate, tentatively assigned to an epimer of **6** (top, see also Scheme S1), and free cymene originating from complex decomposition.

3. Deconvolution of the DPV signals for **2a** and **2b**

Deconvolutions were performed by superimposition of multiple DPV signals of **3**. Good fits were obtained when assuming two one-electron oxidations at +1.15 V and +1.24 V for **2a** and a subsequent two-electron oxidation at +1.41 V (Fig. S4a). For **2b**, similar treatment revealed a two-electron oxidation at +1.13 V followed by two one-electron oxidations at +1.21 V and +1.31 V (Fig. S4b).

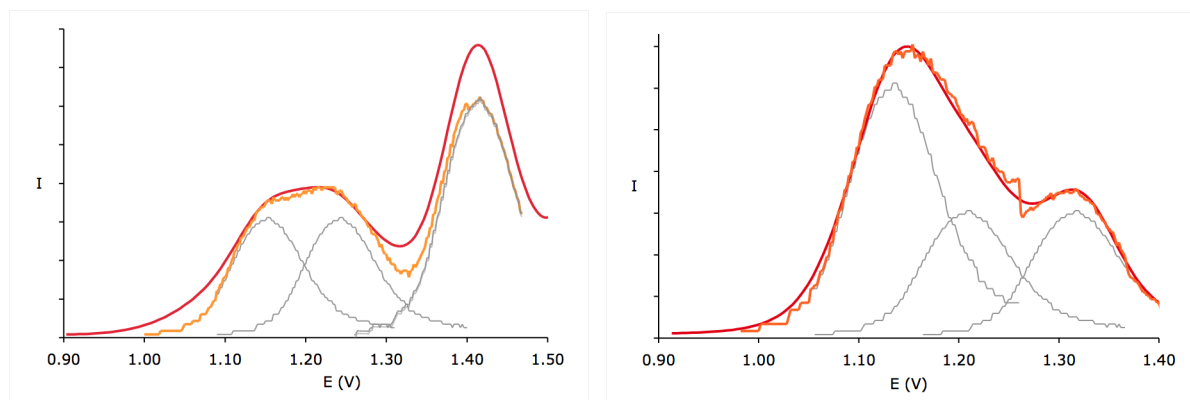


Figure S4. Deconvolution of the DPV data for **2a** (a) and **2b** (b). Red curves correspond to the measured data, orange curves to the sum of the fits of the single oxidation events (gray).

4. Spectroelectrochemical investigations on the stability of model complex **3**

Further support for a partially irreversible oxidation of the Ru^{II} center in **3** was obtained from spectroelectrochemical analyses. In the reduced form, complex **3** features a CT band at $\lambda_{\text{max}} = 406$ nm (Figure S5a). Oxidation at 1.15 V for 5 min produced a new species that is characterized by a shoulder at around 350 nm and a new CT band at $\lambda_{\text{max}} = 639$ nm, tentatively attributed to **3**⁺. Continuous oxidation at 1.15 V for further 15 min resulted in a decrease of the shoulder and the CT band and concomitantly, a new band appeared at $\lambda_{\text{max}} = 444$ nm. Subsequent reduction generated a species with absorption properties slightly different from those of the parent compound **3** (*e.g.*, $\lambda_{\text{max}} = 413$ nm). Similarly, when two redox cycles were recorded consecutively, the absorbance at 639 nm diminished to ~30% in the second cycle (Figure S5b). Such a result is consistent with only a small portion of the electrochemically generated Ru^{III} species being reduced back to the original Ru^{II} complex **3** in the reductive step of the first cycle. These observations strongly support an EC mechanism.

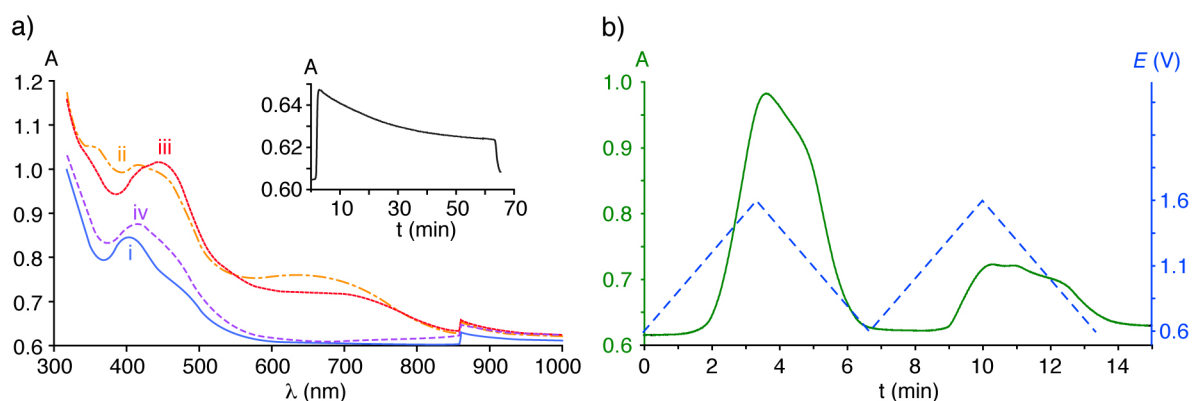


Figure S5. a) UV-Vis spectra of a 20 mM CH_2Cl_2 solution of **3** i) before electrolysis, ii) upon oxidation at 1.15 V for 5 min, iii) upon oxidation at 1.15 V for 15 min, iv) upon reduction at 0.1 V for 10 min in an OTTLE cell. The inset shows the gradual decay of the absorbance at 639 nm upon continuous oxidation of a 2 mM solution of **3** at 1.3 V for 60 min; b) change of absorbance at 639 nm upon two consecutive redox cycles performed on a 20 mM CH_2Cl_2 solution of **3** between 0.6–1.6 V (solid line, left y-scale), and applied potential-time profile (dashed line, right y-scale).

5. Crystallographic details

Complex **2a** crystallized with two centrosymmetric complex molecules in the asymmetric unit. The butyl groups of the ligand in one of the complex molecules were disordered. The carbon atoms involved were refined with occupancies of 0.5/0.5. Complex **2d** crystallized with three quarters of a molecule of Et_2O per molecule of complex. In addition, the isopropyl and methyl groups of the *p*-cymene ligands underwent considerable thermal motion. The situation was not improved when attempts were made to split the atoms. Furthermore, a region of disordered electron density (274 electrons for a void of 901 \AA^3) was removed using the SQUEEZE routine in PLATON: Equated to 0.75 Et_2O per molecule of complex. Finally, the crystal appeared to be a twin and this was dealt with using the TWINROTMAX routine in PLATON; the final BASF was 0.06318. Complex **5** crystallized with two complex cations, two chloride anions and three water molecules (H atoms not localized) per asymmetric unit. In each of the independent complex molecules, one butyl group was found to be disordered (occupancies 0.5/0.5). The crystal of **5** was of very low quality (broad reflections and poorly diffracting), which resulted in relatively high R values, high thermal parameters and low precision in the geometrical parameters. Further details on data collection and refinement parameters are collected in Table S1. CCDC No. 771526 (**2a**), 771527 (**2d**), and 771528 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data for complexes **2a**, **2d**, and **5**

	2a	2d	5
color, shape	orange plate	red rod	yellow block
crystal size/mm	0.40 × 0.30 × 0.10	0.45 × 0.24 × 0.22	0.45 × 0.40 × 0.35
empirical formula	C ₃₅ H ₅₂ Cl ₄ N ₄ Ru ₂	C ₃₈ H ₅₈ Cl ₄ N ₄ Ru ₂ × 0.75 Et ₂ O	C ₃₀ H ₄₀ Cl ₂ N ₄ Ru × 1.5 H ₂ O
Fw	872.75	970.41	655.65
<i>T</i> /K	173(2)	173(2)	173(2)
cryst syst	Orthorhombic	Orthorhombic	Monoclinic
space group	<i>Pbcn</i> (No. 60)	<i>Pccn</i> (No. 56)	<i>P</i> 2 ₁ /n (No. 14)
unit cell			
<i>a</i> /Å	18.6314(9)	30.4955(19)	18.0226(10)
<i>b</i> /Å	16.0854(8)	30.6288(15)	17.5343(6)
<i>c</i> /Å	24.9485(11)	9.5047(4)	20.5361(10)
<i>α</i> /deg	90	90	90.00
<i>β</i> /deg	90	90	103.179(4)
<i>γ</i> /deg	90	90	90.00
<i>V</i> /Å ³	7476.9(6)	8877.8(8)	6318.8(5)
<i>Z</i>	8	8	8
<i>D</i> _{calc} /g cm ⁻³	1.551	1.452	1.378
<i>μ</i> /mm ⁻¹ (Mo K _α)	1.124	0.956	0.696
rflens total, unique	80683, 6693	8406, 8406	81231, 11276
<i>R</i> _{int}	0.089	0.065	0.102
rflens obsd [<i>I</i> > 2σ(<i>I</i>)]	4717	5470	7724
transmission range	0.683–0.728	0.911–1.078	0.647–0.914
no. paras, restraints	404, 4	404, 5	677, 12
<i>R</i> ^{a)} <i>R</i> _w ^{b)}	0.034, 0.067	0.089, 0.258	0.121, 0.384
GOF ^{c)}	0.891	1.020	1.449
min/max resid density /e Å ⁻³	–1.388, 0.824	–0.906, 1.467	–1.084, 2.859

a) $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ for all $I > 2\sigma(I)$; b) $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$; c) final BASF parameter 0.06318 for **2d**