Supporting Information for:

A redox-switchable catalyst with an ‘unplugged’ redox tag

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General considerations

N,N'-Bis(3-propylimidazole)-1,4,5,8-naphthalenediimide (I),
N,N'-bis(1-n-butyl-3-propylimidazolium)-1,4,5,8-naphthalenediimide ([1A](Br)_2) and N,N'-bis(1-benzyl-3-propylimidazolium)-1,4,5,8-naphthalenediimide ([1B](Br)_2) were prepared as described in the literature. All other reagents were used as received from the commercial suppliers. Anhydrous solvents were dried using a solvent purification system (SPS M BRAUN) or purchased and degassed prior to use by purging them with dry argon or nitrogen. Column chromatography was performed using silica gel (60-120 mesh). NMR spectra were recorded on a Bruker 400 or 300 MHz, chemical shifts (δ) are expressed in ppm using the residual proton resonance of the solvent as an internal standard. All coupling constants (J) are expressed in hertz (Hz). Signals marked with an asterisk (*) in the NMR spectra correspond to Apiezon brand H grease. Infrared spectra (FTIR) were performed on a Bruker Equinox 55 spectrometer with a spectral window of 4000-400 cm⁻¹. Mass spectra (ESI-MS) were collected from m/z 0 – 1500 in Micromass Quatro LC instrument. UV-Visible absorption spectra were recorded on a Varian Cary 300 BIO spectrophotometer using dry and degassed CH₂Cl₂ under ambient conditions. Emission spectra were recorded on a modular Horiba FluoroLog-3 spectrofluorometer employing CH₂Cl₂.
1. Synthesis and characterization of compounds

**Scheme S1.** Synthesis of NDI-NHC complexes 2-4

**General procedure for the synthesis of NDI-NHC complexes 2 and 3.** Silver oxide (1.2 equiv.) was added to a solution of the corresponding NDI-bis-imidazolium salt ([1A](Br)₂ or [1B](Br)₂) (1 equiv.) in dichloromethane (100 mL). The mixture was stirred at 40°C overnight. After this time, [M(COD)Cl]₂ (M = Rh or Ir, 1 equiv.) was added to the resulting suspension. The mixture was stirred at 40°C for 4 hours and filtered through Celite. The solvent was removed under vacuum and the crude product was purified by column chromatography using dichloromethane and dichloromethane/acetone mixtures as eluent.

**Synthesis and characterization of 2A.** Complex 2A was prepared employing the general procedure by reacting bis-imidazolium salt [1A](Br)₂ (100 mg, 0.132 mmol), Ag₂O (36.8 mg, 0.159 mmol) and [RhCl(COD)]₂ (65.2 mg, 0.132 mmol). Complex 2A was isolated as a dark-yellow solid in 91% yield (131 mg).

**1H NMR (400 MHz, CDCl₃):** δ 8.69 (s, 4H, C₆HNDI), 6.98-6.94 (m, 2H, C₆Himid), 6.83-6.80 (m, 2H, C₆Himid), 4.93-4.74 (m, 4H; 2H C₆Hcod and 2H, NNDIC₆H₂), 4.53-4.33 (m, 8H; 2H C₆Hcod, 4H NC₆H₂), 4.30 (t, 4H, 3JH-H = 6.7 Hz, NNDIC₆H₂), 3.32-3.09 (m, 4H, C₆Hcod), 2.49-2.17 (m, 12H; 8H C₆Hcod and 4H NC₆H₂), 1.97-1.62 (m, 12H; 8H C₆Hcod and 4H NC₆H₂), 1.44-1.35 (m, 8H, NNDIC₆H₂), 0.95 (t, 6H, 3JH-H = 7.3 Hz, NC₆H₂)

**13C{¹H} NMR (101 MHz, CDCl₃):** 182.0 (d, 1JRh-C = 51.2 Hz, Rh-Carbene), 163.0 (C=O), 130.9 (CH₆NDI), 128.6 (C₂NDI), 126.7 (C₂NDI), 120.5 (CH₆NDI), 120.0 (CH₆NDI), 98.1 (d, 3JRh-C = 3.1 Hz, Rh-CH₆cod), 97.7 (Rh-CH₆cod),
Synthesis and characterization of 2B. Complex 2B was prepared employing the general procedure by reacting bis-imidazolium salt 1B (100 mg, 0.121 mmol), Ag₂O (33.7 mg, 0.145 mmol) and [RhCl(COD)]₂ (59.7 mg, 0.121 mmol). Complex 2B was isolated as a dark-yellow solid in 85% yield (119 mg). ¹H NMR (300 MHz, CDCl₃): δ 8.77 (s, 4H, CH₉NDI), 7.36-7.29 (m, 10H, CH_Bn), 6.99 (t, 2H, 3J_H-H = 2.0 Hz, CH_imid), 6.68 (d, 2H, 3J_H-H = 1.9 Hz, CH_imid), 5.82 (d, 2H, 2J_H-H = 15.0 Hz, CH₂_Bn), 5.65 (d, 2H, 2J_H-H = 15.0 Hz, CH₂_Bn), 4.99-4.83 (m, 4H; 2H CH_cod and 2H N₉NDI_2CH₂CH₂CH₂N_imid), 4.64-4.46 (m, 4H; 2H CH_cod and 2H N₉NDI_2CH₂CH₂CH₂N_imid), 4.38 (t, 4H, 3J_H-H = 6.7 Hz, N₉NDI_2CH₂CH₂CH₂N_imid), 3.38-3.17 (m, 4H, CH_cod), 2.61-1.67 (m, 20H; 16H CH₂_cod and 4H N₉NDI_2CH₂CH₂CH₂N_imid). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 183.2 (d, 1J_Rh-C = 51.1 Hz, Rh-Carbene), 163.1 (C=O), 136.5 (C₉NDI), 131.1 (CH₉NDI), 129.0 (CH_Bn), 128.3 (CH_Bn), 128.2 (CH_Bn), 126.8 (C₉NDI), 120.9 (CH_imid), 120.6 (CH_imid), 98.6 (d, 1J_Rh-C = 6.8 Hz, Rh-CH_cod), 98.4 (dd, 1J_Rh-C = 7.1, 2.3 Hz, Rh-CH_cod), 68.5 (dd, 1J_Rh-C = 14.4, 2.1 Hz, Rh-CH_cod), 68.1 (dd, 1J_Rh-C = 14.4, 2.0 Hz, Rh-CH_cod), 54.7 (CH₂_Bn), 48.7 (N₉NDI_2CH₂CH₂CH₂N_imid), 38.5 (N₉NDI_2CH₂CH₂CH₂N_imid), 33.4 (CH₂_cod), 32.6 (N₉NDI_2CH₂CH₂CH₂N_imid), 29.7 (CH₂_cod), 29.2 (CH₂_cod), 28.7 (CH₂_cod). ESI-MS (20V, m/z): 1119.31 [M-Cl]⁺.

Synthesis and characterization of 3A. Complex 3A was prepared employing the general procedure by reacting bis-imidazolium salt 1A (100 mg, 0.132 mmol), Ag₂O (36.8 mg, 0.159 mmol) and [IrCl(COD)]₂ (88.7 mg, 0.132 mmol). Complex 3A was isolated as a dark-yellow solid in 86% yield (144 mg). ¹H NMR (400 MHz, CDCl₃): δ 8.73 (s, 4H CH₉NDI), 7.01-6.96 (m, 2H, CH_imid), 6.86-6.82 (m, 2H, CH_imid), 4.79-4.65 (m, 2H, N₉NDI_2CH₂CH₂CH₂N_imid), 4.46-4.18 (m, 12H; 2H CH_cod, 2H N₉NDI_2CH₂CH₂CH₂N_imid, 4H NCH₂CH₂CH₂CH₃, 4H N₉NDI_2CH₂CH₂CH₂N_imid), 3.96-3.77 (m, 2H, CH_cod), 2.92-2.85 (m, 2H, CH_cod), 2.82-2.74 (m, 2H, CH_cod), 2.49-2.35 (m, 2H, CH₂_cod), 2.33-2.22 (m, 2H, CH₂_cod), 2.22-1.51 (m, 20H; 12H CH₂_cod, 4H N₉NDI_2CH₂CH₂CH₂N_imid and 4H NCH₂CH₂CH₂CH₃), 1.43-1.33 (m, 4H, NCH₂CH₂CH₂CH₃), 0.95 (t, 6H, 3J_H-H = 8.7 Hz, NCH₂CH₂CH₂CH₃). ¹³C{¹H} NMR (101
quantitative yields. The solvent was removed under reduced pressure, giving the desired carbonyl derivatives in high yield, starting from complex 3A.

**Synthesis and characterization of 3B.** Complex 3B was prepared employing the general procedure by reacting bis-imidazolium salt 1B (100 mg, 0.121 mmol), Ag₂O (33.7 mg, 0.145 mmol) and [IrCl(COD)]₂ (81.3 mg, 0.121 mmol). Complex 3B was isolated as a dark-orange solid in 82% yield (133 mg). The compound was characterized by NMR and ESI-MS. The NMR spectra showed characteristic signals for the imidazole and carbene moieties.

**Synthesis and characterization of 4A.** Complex 4A was isolated as a yellow-orange solid starting from complex 3A. The compound was characterized by NMR and ESI-MS, providing detailed information about the structure and purity of the product. The synthesis and characterization of 4A were crucial for the further applications of the carbonyl derivatives.
7.3 Hz, NCH₂CH₂CH₂CH₃). ¹³C{¹H} (101 MHz, CDCl₃): δ 180.0 (Ir-C carbene), 172.5 (Ir-CO), 166.9 (Ir-CO), 162.0 (C=O), 130.1 (CH₉NDI), 127.7 (Cq_NDI), 125.8 (Cq_NDI), 120.2 (CHimid), 120.2 (CHimid), 50.2 (NNDIC₂CH₂CH₂Nimid), 36.8 (NNDIC₂CH₂CH₂Nimid), 31.7 (NNDIC₂CH₂CH₂Nimid), 28.4 (NCH₂CH₂CH₂CH₃), 18.7 (NCH₂CH₂CH₂CH₃), 12.6 (NCH₂CH₂CH₂CH₃). ESI-MS (20V, m/z): 1125.23 [M-Cl]+. IR (CH₂Cl₂): 2002 (νIr-CO) and 2080 (νIr-CO) cm⁻¹.

**Synthesis and characterization of 4B.** Complex 4B was isolated as a yellow-orange solid starting from complex 3B. ¹H NMR (400 MHz, CDCl₃): δ 8.78 (s, 4H, CHNDI), 7.42-7.27 (m, 10H, CHBn), 7.15 (d, 2H, 2J_H-H = 2.0 Hz, CHimid), 6.87 (d, 2H, 2J_H-H = 2.0 Hz, CHimid), 5.47 (d, 4H, CH₂Bu), 4.53-4.41 (4H, NNDIC₂CH₂CH₂CH₂Nimid), 4.33 (t, 3J_H-H = 6.6 Hz, NNDIC₂CH₂CH₂CH₂Nimid), 2.46-2.39 (m, 4H, NNDIC₂CH₂CH₂CH₂Nimid). ESI-MS (20V, m/z): 1193.17 [M-Cl]+. IR (CH₂Cl₂): 1999 (νIr-CO) and 2081 (νIr-CO) cm⁻¹.

**Synthesis of [NDI-(NHC)₂][W(CO)₅]₂**

Silver oxide (28 mg, 0.12 mmol) was added to a solution of [1A](Br)₂ (75.0 mg, 0.1 mmol) in dichloromethane (50 mL). The mixture was stirred at 40°C overnight and then was filtered through Celite. The solvent was removed under vacuum and the crude product was dissolved in dry dichloromethane (15 mL). W(CO)₆ (70 mg, 0.2 mmol) and Me₃NO (15 mg, 0.2 mmol) were dissolved in THF (10 mL) and the resulting solution was stirred for 20 min. The resulting solution containing [W(CO)₅(THF)] was added to the Ag-NHC solution under the exclusion
of light. The mixture was stirred at 40°C for 40 hours and filtered through Celite. The solvent was removed under vacuum and the crude product was purified by column chromatography using dichloromethane as eluent. $^1$H NMR (300 MHz, CDCl$_3$): δ 8.78 (s, 4H, $CH_\text{NDI}$), 7.18 (d, 2H, $^2$$J_{H-H}$ = 1.98 Hz, $CH_\text{imid}$), 7.06 (d, 2H, $^2$$J_{H-H}$ = 1.98 Hz, $CH_\text{imid}$), 4.42-4.38 (m, 8H, 4H $N_\text{imid}CH_2CH_2CH_2N$, 4H $NCH_2CH_2CH_2$CH$_3$), 4.18 (t, 4H, $^3$$J_{H-H}$ = 8.07 Hz $N_\text{NDI}CH_2CH_2CH_2N_\text{imid}$), 2.32 (q, 4H, $^4$$J_{H-H}$ = 8.01 Hz), 1.83-1.66 (m, 4H), 1.51-1.38 (m, 4H), 0.98 (t, 6H, $^3$$J_{H-H}$ = 8.7 Hz, $NCH_2CH_2CH_2$CH$_3$). $^{13}$C{$^1$H} NMR $^{13}$C NMR (126 MHz, CDCl$_3$) δ 201.1 (W-$C_{\text{carbene}}$), 198.3 (W-$CO$), 179.8 (W-$CO$), 163.4(C=$O_{\text{NDI}}$), 131.6 (C-H$_{\text{NDI}}$), 127.2 (C$_q$NDI), 127.0 (C$_q$NDI), 121.6(C-H$_{\text{imid}}$), 121.0 (C-H$_{\text{imid}}$), 53.3 (N$_{\text{NDI}}CH_2CH_2CH_2N_\text{imid}$), 51.3(N$_{\text{imid}}CH_2CH_2CH_2N_\text{NDI}$), 38.5 (N$_{\text{imid}}CH_2CH_2CH_2$CH$_3$), 33.8 (N$_{\text{imid}}CH_2CH_2CH_2$N$_{\text{NDI}}$), 33.1 (NCH$_2$CH$_2$CH$_2$CH$_3$), 20.33 (NCH$_2$CH$_2$CH$_2$CH$_3$), 14.12 (NCH$_2$CH$_2$CH$_2$CH$_3$).
2. Spectroscopic data

2.1 $^1$H, $^{13}$C{$^1$H} and HSQC NMR spectra of 2A in CDCl$_3$

**Figure S1.** $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 2A

**Figure S2.** $^{13}$C{$^1$H} spectrum (101 MHz, CDCl$_3$) of 2A
Figure S3. $^1$H-$^{13}$C HSQC spectrum (400 MHz, CDCl$_3$) of 2A
2.2 $^1$H, $^{13}$C{$^1$H} and HSQC NMR spectra of 2B in CDCl$_3$

**Figure S4.** $^1$H NMR spectrum (300 MHz, CDCl$_3$) of 2B

**Figure S5.** $^{13}$C{$^1$H} spectrum (75 MHz, CDCl$_3$) of 2B
Figure S6. $^1$H-$^{13}$C HSQC spectrum (400 MHz, CDCl$_3$) of 2B
2.3 $^1$H, $^{13}$C{$^1$H} and HSQC NMR spectra of 3A in CDCl$_3$

**Figure S7.** $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 3A

**Figure S8.** $^{13}$C{$^1$H} spectrum (101 MHz, CDCl$_3$) of 3A
Figure S9. $^1$H-$^{13}$C HSQC spectrum (400 MHz, CDCl$_3$) of 3A
2.4 $^1\text{H}$, $^{13}\text{C}[^1\text{H}]$ and HSQC NMR spectra of 3B in CDCl$_3$

**Figure S10.** $^1\text{H}$ NMR spectrum (400 MHz, CDCl$_3$) of 3B

**Figure S11.** $^{13}\text{C}[^1\text{H}]$ spectrum (101 MHz, CDCl$_3$) of 3B
Figure S12. $^1$H-$^{13}$C HSQC spectrum (400 MHz, CDCl$_3$) of 3B
2.5 $^1$H, $^{13}$C{$^1$H} NMR spectra of 4A in CDCl$_3$

Figure S13. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 4A

Figure S14. $^{13}$C{$^1$H} spectrum (101 MHz, CDCl$_3$) of 4A
2.6 $^1$H, $^{13}$C{${}^1$H} NMR spectra of 4B in CDCl$_3$

Figure S15. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 4B

Figure S16. $^{13}$C{${}^1$H} spectrum (101 MHz, CDCl$_3$) of 4B
Figure S17. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 5

Figure S18. $^{13}$C{${^1}$H} spectrum (125 MHz, CDCl$_3$) of 5.
3. X-ray crystallography

X-Ray Diffraction studies for complex 3B. Single crystals for X-Ray studies of 3B were obtained by slow evaporation of a concentrated solution of the complex in chloroform. Diffraction data was collected on an Agilent SuperNova diffractometer equipped with an Atlas CCD detector using Cu-Kα radiation (\( \lambda = 1.54184 \) Å). Single crystals were mounted on a MicroMount® polymer tip (MiteGen) in a random orientation. Absorption corrections based on Gaussian methods. Using Olex2, the molecular structure of the compound was solved by Charge Flipping in Superflip, and refined by least squares with the ShelXL refinement package. Key details of the crystals and structure refinement data are summarized in Supplementary Table S1. Further crystallographic details may be found in the CIF files, which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The reference number for complex 3B was assigned as 2170148.

Table S1. Summary of crystal data, data collection, and structure refinement details of 3B

<table>
<thead>
<tr>
<th>3B</th>
<th>3B</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{58}H_{56}Cl_{8}Ir_{2}N_{6}O_{4}</td>
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<tr>
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<tr>
<td>Temperature/K</td>
<td>200.1(9)</td>
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<td>C2/c</td>
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<td>a/Å</td>
<td>26.1313(9)</td>
</tr>
<tr>
<td>b/Å</td>
<td>18.4166(6)</td>
</tr>
<tr>
<td>c/Å</td>
<td>16.7444(5)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>92.392(3)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å(^3)</td>
<td>8051.2(5)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
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4. Photophysical properties

Figure S19. UV-Vis and emission spectra ($\lambda_{\text{exc}} = 361$ nm) of complex [1A](Br)$_2$, recorded in CH$_2$Cl$_2$ at a concentration of 1.0x10$^{-5}$ M.

Figure S20. UV-Vis and emission spectra ($\lambda_{\text{exc}} = 361$ nm) of complex [1B](Br)$_2$, recorded in CH$_2$Cl$_2$ at a concentration of 2.0x10$^{-5}$ M.
**Figure S21.** UV-Vis and emission spectra ($\lambda_{\text{exc}} = 361\ \text{nm}$) of complex 2A, recorded in CH$_2$Cl$_2$ at a concentration of $2.0 \times 10^{-5}\ \text{M}$

**Figure S22.** UV-Vis and emission spectra ($\lambda_{\text{exc}} = 361\ \text{nm}$) of complex 2B, recorded in CH$_2$Cl$_2$ at a concentration of $2.0 \times 10^{-5}\ \text{M}$
**Figure S23.** UV-Vis and emission spectra ($\lambda_{\text{exc}} = 361$ nm) of complex 3A, recorded in CH$_2$Cl$_2$ at a concentration of 2.0x10$^{-5}$ M

**Figure S24.** UV-Vis and emission spectra ($\lambda_{\text{exc}} = 361$ nm) of complex 3B, recorded in CH$_2$Cl$_2$ at a concentration of 2.0x10$^{-5}$ M
Table S2. Summary of the photophysical properties of the NDI-derived compounds[^a]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{abs}}$ [nm]</th>
<th>$\lambda_{\text{NDI}}$ [nm]</th>
<th>$\lambda_{\text{em, max}}$ [nm]</th>
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<tbody>
<tr>
<td><a href="Br">1A</a>$_2$</td>
<td>237.0, 361.0, 381.0</td>
<td>362.0, 381.0</td>
<td>406.0</td>
</tr>
<tr>
<td><a href="Br">1A</a>$_2$</td>
<td>237.1, 362.5, 381.0</td>
<td>362.5, 381.0</td>
<td>408.0</td>
</tr>
<tr>
<td>2A</td>
<td>236.3, 294.1, 343.1, 360.4, 381.0</td>
<td>360.4, 381.0</td>
<td>411.9</td>
</tr>
<tr>
<td>2B</td>
<td>236.1, 291.4, 343.0, 360.4, 380.9</td>
<td>360.4, 380.9</td>
<td>405.9</td>
</tr>
<tr>
<td>3A</td>
<td>236.6, 343.6, 360.4, 380.7, 419.2</td>
<td>360.4, 380.7</td>
<td>406.9</td>
</tr>
<tr>
<td>3B</td>
<td>236.3, 343.4, 360.5, 380.7, 420.6</td>
<td>360.5, 380.7</td>
<td>435.0</td>
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</table>

[^a]: Measurements were performed in dry and degassed CH$_2$Cl$_2$ under ambient conditions
5. Electrochemical studies

5.1. Electrochemical measurements

Electrochemical studies were carried out by using an Autolab Potentiostat, Model PGSTAT101 and three-electrode cell, controlled with NOVA 2.1.4 software. The cell was equipped with platinum working and counter electrodes, as well as a silver wire pseudoreference electrode. In all experiments, [N(nBu)₄][PF₆] (0.1M in dry CH₂Cl₂) was used as the supporting electrolyte with an analyte concentration of approximately 1 Mm. Measurements were performed at 25, 50, 100, 250 and 500 mV/s scan rates. All scans were referenced to the ferrocenium/ferrocene (Fc⁺/Fc) couple at 0 V. Ohmic drop was minimized by minimizing the distance between the working and reference electrodes. The residual ohmic drop was estimated by positive feedback and compensated at 85%.

**Figure S25.** Cyclic voltammogram of [1A](Br)₂ at different scan rates  
**Figure S26.** Cyclic voltammogram of [1B](Br)₂ at different scan rates
Figure S27. Cyclic voltammogram of 2A at different scan rates

Figure S28. Cyclic voltammogram of 2B at different scan rates

Figure S29. Cyclic voltammogram of 2A at 25 mV/s scan rate showing the irreversible oxidation wave

Figure S30. Cyclic voltammogram of 2B at 100 mV/s scan rate showing the irreversible oxidation wave
**Figure S31.** Cyclic voltammogram of 3A at different scan rates

**Figure S32.** Cyclic voltammogram of 3B at different scan rates

**Figure S33.** Cyclic voltammogram of 3A at 100 mV/s scan rate showing the irreversible oxidation wave

**Figure S34.** Cyclic voltammogram of 3B at 100 mV/s scan rate showing the irreversible oxidation wave
Figure S35. Cyclic voltammogram of 4A at different scan rates

Figure S36. Cyclic voltammogram of 4B at different scan rates

Table S3. Electrochemical properties of compounds 1, 2, 3 and 4[a]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}^2$/V/$\Delta$E (mV)[b]</th>
<th>$E_{1/2}^1$/V/$\Delta$E (mV)</th>
<th>$E_{pa}$ (V)[c]</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="Br">1A</a>$_2$</td>
<td>-1.30/71</td>
<td>-0.92/75</td>
<td>-</td>
</tr>
<tr>
<td><a href="Br">1B</a>$_2$</td>
<td>-1.29/71</td>
<td>-0.92/71</td>
<td>-</td>
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<tr>
<td>2A</td>
<td>-1.53</td>
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<td>2B</td>
<td>-1.47</td>
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<td>3A</td>
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<td>3B</td>
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<td>4A</td>
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<tr>
<td>4B</td>
<td>-1.41</td>
<td>-0.97/75</td>
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</tr>
</tbody>
</table>

[a]Measurements performed at a scan rate of 100 mVs$^{-1}$ and referenced vs. ferrocenium/ferrocene.
[b]The second reduction event is an irreversible process for complexes 2, 3 and 4, the value indicated in the table corresponds to the cathodic peak potential ($E_{pc}$).
[c]The oxidation event is an irreversible process for complexes 2 and 3, the value indicated in the table corresponds to the anodic peak potential ($E_{pa}$).
5.2 Spectroelectrochemical measurements

Spectroelectrochemical (SEC) measurements were performed using a gastight, optically transparent thin-layer solution cell fabricated by Prof. Hartl at the University of Reading (Reading, U.K.), as described previously. The SEC cell contained a masked Au-minigrid working electrode (32 wires/cm), a Pt-gauze auxiliary electrode, and an Ag-wire pseudo-reference electrode and had CaF$_2$ windows. In each experiment, electrochemical reduction of the species of interest ([Analyte] = 3 mM for IR experiments and 0.25 mM for UV-vis experiments, [N(nBu)$_4$][PF$_6$] = 250 mM in CH$_2$Cl$_2$ (under nitrogen atmosphere)).

![Figure S37. IR-SEC monitoring of the reduction of 4A in CH$_2$Cl$_2$. Lines represent the spectra of the starting (red), singly-reduced (blue) and doubly-reduced (black) species.](image-url)
**Figure S38.** Infrared difference spectra resulting from the IR-SEC reduction of 4A in CH$_2$Cl$_2$. The electrochemical reduction was performed applying progressively lower potentials with a Au working electrode, Pt counter electrode, and Ag wire pseudo-reference electrode.

**Figure S39.** IR difference spectra resulting from the IR-SEC reduction of [NDI-(NHC)$_2$][W(CO)$_5$]$_2$ in CH$_2$Cl$_2$ (0.25 M [N(nBu)$_4$][PF$_6$]). The electrochemical reduction was performed applying progressively lower potentials with a Au working electrode, Pt counter electrode, and Ag wire pseudo-reference. The frequencies in blue refer to the neutral complex, while those in red are due to the doubly-reduced complex.
Figure S38. FT-IR spectra resulting from the IR-SEC reduction of \([\text{IrCl(IBu)(CO)}_2]\) (IBu = 1,3-di-n-butylimidazole-2-ylidene) (5mM) and N,N'-dibutyl-1,4,5,8-naphthalenetetracarboxylic acid diimide (5mM) in \(\text{CH}_2\text{Cl}_2\) (TBAPF$_6$ 0.25M). The electrochemical reduction was performed applying progressively lower potentials with a Au working electrode, Pt counter electrode, and Ag wire pseudo-reference electrode.
**Figure S38.** UV-vis SEC monitoring of the reduction of salt [1A](Br)2 in CH2Cl2. Lines represent the spectra of the starting (black), singly-reduced (red) and doubly-reduced (blue) species.

**Figure S39.** UV-vis SEC monitoring of the reduction of 3A in CH2Cl2. Lines represent the spectra of the starting (black), singly-reduced (red) and doubly-reduced (blue) species.
6. Catalytic studies: cyclization of acetylenic carboxylic acids

![Chemical structure](image)

All the catalytic experiments and manipulations were conducted under nitrogen atmosphere. Complex [Fe(ƞ5-C5H4COMe)Cp][BF4]8 was prepared according to the literature procedure. All other reagents were purchased from commercial sources and used as received. For this study, complexes 2A and 3A were employed as model catalysts.

**Cyclization of 4-pentynoic acid to γ-methylene-γ-butyrolactone.** In a high pressure Schlenk tube fitted with a Teflon cap, the corresponding catalyst (0.05 mol % to 0.4 mol % based on metal) was added to a 0.33 M solution of 4-pentynoic acid (0.5 mmol) and 1,3,5-trimethoxybenzene (0.5 mmol) in CD3CN. The mixture was heated at 80 °C. Yields were determined by 1H-NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. γ-Methylene-γ-butyrolactone was isolated as the only product. Spectroscopic data were consistent with those reported in the literature. 1H NMR (400 MHz, CD3CN): δ 4.65-4.63 (m, 1H, C=CCH2), 4.30-4.28 (m, 1H, C=CCH2), 2.88-2.83 (m, 2H, CH2), 2.65-2.61 (m, 2H, CH2).

**Cyclization of 5-hexynoic acid to 6-methylidenetetrahydro-2-pyrone.** In a high pressure Schlenk tube fitted with a Teflon cap, the corresponding catalyst (0.1 mol % or 1 mol % based on metal) was added to a 0.083 M solution of 5-hexynoic acid (0.125 mmol) and 1,3,5-trimethoxybenzene (0.125 mmol) in CD3CN. The mixture was heated at 80 °C. Yields were determined by 1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. 6-Methylidenetetrahydro-2-pyrone, was obtained as the only product. Spectroscopic data were consistent with those reported in the literature. 1H NMR (400 MHz, CD3CN): δ 4.56-4.57 (m, 1H, C=CCH2), 4.32-4.30 (m, 1H, C=CCH2), 2.60 (t, 2H, JH-H = 6.8 Hz, CH2), 2.52-2.48 (m, 2H, CH2), 1.87-1.80 (m, 2H, CH2).

Table S4 shows the rate constants calculated by plotting the concentration of the product (γ-methylene-γ-butyrolactone) versus time, assuming a zero order reaction with respect to substrate, at different catalyst (2A) loadings (Figure S39). Figure S40 shows the plot of the
initial rates versus the concentrations of catalyst 2A that allows to calculate a first reaction order in catalyst.

Figure S40. Formation of the product (γ-methylene-γ-butyrolactone) over time varying the catalyst (2A) loading assuming zero order reaction.

Table S4. Rate constants assuming zero order reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst loading (mol% Rh)</th>
<th>Rate constants (*10^6Ms^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
<td>1.49</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>2.31</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>3.64</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>8.66</td>
</tr>
</tbody>
</table>
**Figure S41.** Dependence of the ln of the rate constants on the ln of catalyst (2A) concentration. Determination of the order with respect to catalyst 2A.

Reactivity of the catalysts in the presence of cobaltocene and decamethylcobaltocene.

The experiments were carried out as explained above for the cyclization of 4-pentynoic and 5-hexynoic acids, adding 1.3 equivalents of cobaltocene ([CoCp₂]) to the reaction mixture. The evolution of the reaction was monitored by ¹H NMR spectroscopy collecting a small aliquot at the desired times, using 1,3,5-trymethoxybenzene as internal standard. Figure S41 plots the time-dependent reaction profiles for the cyclization of 4-pentynoic acid in the presence of 0.1 mol% of 2A with and without cobaltocene. Figure S42 plots the time-dependent reaction profiles for the cyclization of 5-hexynoic acid in the presence of 1 mol% of 3A with and without cobaltocene.

In two independent experiments, the cyclization of 4-pentynoic and 5-hexynoic acids was carried out using 3A and 2.3 equivalents of decamethylcobaltocene ([CoCp*₂]). The reactions were allowed to evolve for the desired times. The product yields are shown in Table S5. The data shown allows a comparison of the catalytic behavior of 3A in the absence of any redox additive, and in the presence of [CoCp₂] and [CoCp*₂].
Figure S42. Time-dependent reaction profiles for the cyclization of 4-pentynoic acid in the presence of 0.1 mol% of 2A with (blue) and without (orange) addition of cobaltocene. The reactions were carried out in CD$_3$CN, with an initial concentration of 4-pentynoic acid of 0.33 M.

Figure S43. Time-dependent reaction profile for the cyclization of 5-hexynoic acid in the presence of 1 mol% of 3A with (blue line) and without (orange line) addition of cobaltocene. The reactions were carried out in CD$_3$CN, with an initial concentration of 5-hexynoic acid of 0.083 M.
**Redox switching experiments.** In a high pressure Schlenk tube fitted with a Teflon cap, complex 3A (0.1 mol % based on metal) was added to a 0.33 M solution of 4-pentyonoic acid (0.5 mmol) and 1,3,5-trimethoxybenzene (0.5 mmol) in CD$_3$CN. The mixture was heated at 80 °C. The reaction was monitored for 2 hours collecting a small aliquot at the desired times. The reductant cobaltocene was then added to the reaction mixture under nitrogen. After collecting data for 60 minutes, 1.5 equivalent (with respect to the catalyst) of a chemical oxidant, namely [Fe(η$_5$-C$_5$H$_4$COCH$_3$)Cp][BF$_4$] ([Fe'](BF$_4$)), was added to the reaction mixture under nitrogen. The reaction was monitored for further 180 minutes collecting a small aliquot at the desired times. The evolution of the reaction was monitored by $^1$H NMR using 1,3,5-trymethoxybenzene as internal standard.

![Graph showing the cyclization of 4-pentyonoic acid with 0.1 mol% of 3A and sequential additions of [Cp$_2$Co] and acetyl ferrocenium tetrafluoroborate, [Fe'](BF$_4$) (blue solid dots). The plots showing the evolution of the reaction using 0.1 mol% of 3A (orange solid dots) and 3A+[CoCp$_2$] (grey solid dots) are also shown for comparison.](image)

**Figure S44.** Plot showing the cyclization of 4-pentyonoic acid with 0.1 mol% of 3A and sequential additions of [Cp$_2$Co] and acetyl ferrocenium tetrafluoroborate, [Fe'](BF$_4$) (blue solid dots). The plots showing the evolution of the reaction using 0.1 mol% of 3A (orange solid dots) and 3A+[CoCp$_2$] (grey solid dots) are also shown for comparison.
Table S5. Cyclization of 4-pentynoic and 5-pentynoic acids using 3A as catalyst.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkynoic Acid</th>
<th>Cat. Load (Mol%)</th>
<th>Additive</th>
<th>t [h]</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-pentynoic</td>
<td>0.1</td>
<td>none</td>
<td>5</td>
<td>15.5</td>
</tr>
<tr>
<td>2</td>
<td>4-pentynoic</td>
<td>0.1</td>
<td>[CoCp₂]</td>
<td>2.5</td>
<td>&gt;99.0</td>
</tr>
<tr>
<td>3</td>
<td>4-pentynoic</td>
<td>0.1</td>
<td>[CoCp*₂]</td>
<td>7</td>
<td>73</td>
</tr>
<tr>
<td>4</td>
<td>5-hexynoic</td>
<td>1</td>
<td>none</td>
<td>24</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>5</td>
<td>5-hexynoic</td>
<td>1</td>
<td>[CoCp₂]</td>
<td>5</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>5-hexynoic</td>
<td>1</td>
<td>[CoCp₂]</td>
<td>7</td>
<td>82</td>
</tr>
<tr>
<td>7</td>
<td>5-hexynoic</td>
<td>1</td>
<td>[CoCp*₂]</td>
<td>7</td>
<td>48</td>
</tr>
</tbody>
</table>

*a*The reactions were carried out in acetonitrile at 80°C, with an initial concentration of 4-alkynoic acid of 0.33 M. The amount of cobaltocene and decamethylcobaltocene was 1.3 or 2.3 equivalents with respect to 3A, respectively. Yields were determined by ¹H-NMR spectroscopy, using 1,3,5-trimethoxybenzene as integration standard.
7. References