## Supporting Information

# Facile Concerted Proton-Electron Transfers in a Ruthenium Terpyridine-4'Carboxylate Complex with a Long Distance between the Redox and Basic Sites 

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## I. General Experimental

Unless otherwise noted, all reagents were purchased from Aldrich and solvents from Fisher. $\mathrm{RuCl}_{3} \bullet \mathrm{H}_{2} \mathrm{O}$ was purchased from Strem, ${ }^{n} \mathrm{BuOH}$ was purchased from J. T. Baker. Acetonitrile was purchased from Burdick and Jackson (low-water brand) and stored in an argonpressurized stainless steel drum plumbed directly into a glovebox. The syntheses of $\mathbf{R u}{ }^{\text {II }} \mathbf{C O O H}$ and $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}$ and all kinetics studies were performed under $\mathrm{N}_{2}$, but purification, electrochemistry, $\mathrm{p} K_{\mathrm{a}}$ determination, and most characterizations of $\mathbf{R u} \mathbf{u}^{\mathrm{II}} \mathbf{C O O H}$ and $\mathbf{R u}^{\mathbf{I I}} \mathbf{C O O}^{-}$ were performed under air. UV-Visible spectra were obtained using a Hewlett-Packard 8453 diode array spectrophotometer. Elemental analyses were performed by Atlantic Microlab, Inc.

## II. Syntheses

$\left[\left(\eta^{6} \text {-cymene }\right) \mathrm{RuCl}\right]_{2}(\mu-\mathrm{Cl})_{2}{ }^{1}$ and $\left[\left(p-\mathrm{BrC}_{6} \mathrm{H}_{4}\right)_{3} \mathrm{~N}^{++}\right]\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{4}{ }^{-}\right]^{2}$ were prepared following literature procedures. Tri-p-tolylaminium hexafluorophosphate $\left(\left[\mathrm{N}(\mathrm{tol})_{3}{ }^{++}\right] \mathrm{PF}_{6}{ }^{-}\right)$is a known compound, ${ }^{3}$ but caused decomposition in the synthesis of $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}$ unless it was made with the procedure given below.

Sodium 2,2':6', $\mathbf{2}^{\prime \prime}$-terpyridine-4'-carboxylate ( $\left[\mathbf{N a}^{+}\right]$tpyCOO ${ }^{-}$). Following a modified literature procedure, ${ }^{4} 1.953 \mathrm{~g} 4^{\prime}$-chloro-2, $2^{\prime}: 6^{\prime}, 2^{\prime \prime}$-terpyridine ( 7.29 mmol ), $0.261 \mathrm{~g} \mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}_{2}$ ( 0.372 mmol ), and 7.8 mL of ${ }^{n} \mathrm{Bu}_{3} \mathrm{~N}$ were dissolved in $40 \mathrm{~mL}{ }^{n} \mathrm{BuOH}$ in a 1000 mL bomb. The mixture was degassed using two freeze-pump-thaw cycles, and CO was bubbled through at 1 atm for 4 min while stirring. The bomb was sealed, and the lower part was heated at $125{ }^{\circ} \mathrm{C}$ for 20 hours. The solution was continuously stirred for another 16 hours at room temperature, and the container was carefully opened to air. The solvent was reduced to 15 mL on a rotovap, washed five times with saturated $\mathrm{NH}_{4} \mathrm{Cl}(\mathrm{aq})$, and filtered through a fine frit. The filtrate was mixed with 29 mL of 2 M NaOH in $\mathrm{H}_{2} \mathrm{O}$, and heated at $50-60^{\circ} \mathrm{C}$ for 5 hours, forming a white precipitate. The solution was cooled at $-35^{\circ} \mathrm{C}$ for 40 minutes, then filtered and washed with cold $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and diethyl ether. The fluffy white solid was dried in vacuo, giving 1.19 g of $\left[\mathbf{N a}^{+}\right] \mathbf{t p y C O O}{ }^{-}(55 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $\mathrm{D}_{2} \mathrm{O}$ ) $\delta: 7.45(\mathrm{t}, 2 \mathrm{H}), 7.94(\mathrm{t}, 2 \mathrm{H}), 8.15(\mathrm{~d}, 2 \mathrm{H}), 8.28(\mathrm{~s}, 2 \mathrm{H}), 8.55(\mathrm{~d}, 2 \mathrm{H})$. ESI/MS ${ }^{+}(m / z): 278.3[\text { tpyCOOH }+\mathrm{H}]^{+}$, and ESI/MS ${ }^{-}(m / z): 276.1[\text { tpyCOO }]^{-}$.
$\mathbf{R u}$ (dipic)(tpyCOOH) ( $\left.\mathbf{R u}^{\text {II }} \mathbf{C O O H}\right)$. Following the preparation of the unsubstituted derivative, ${ }^{5}\left[\left(\eta^{6} \text {-cymene }\right) \mathrm{RuCl}\right]_{2}(\mu-\mathrm{Cl})_{2}(0.505 \mathrm{~g}, 0.825 \mathrm{mmol})$ and $\left[\mathrm{Na}^{+}\right] \mathrm{tpyCOO}^{-}(0.494 \mathrm{~g}, 1.65$ mmol ) were dissolved in 15 mL of MeOH . The solution became bright purple, and was stirred for $\sim 3$ minutes. An in situ solution of disodium pyridine-2,6-dicarboxylate was prepared, from 0.277 g of pyridine-2,6-dicarboxylic acid ( 1.66 mmol ), 4.5 mL of 0.79 M aqueous NaOH , and 9 mL MeOH ), and added to the Ru solution. The mixture was stirred under $\mathrm{N}_{2}$ for one hour at 60 ${ }^{\circ} \mathrm{C}$, and a black precipitate formed. The solution was cooled at $-35^{\circ} \mathrm{C}$ for 30 minutes, and filtered in air using a glass frit. The precipitate was dissolved in 11 mL of deionized $\mathrm{H}_{2} \mathrm{O}$, and $221 \mu \mathrm{~L}$ of 12 M HCl was added. The fine precipitate was collected immediately on a glass frit,
(1) Hodson, E.; Simpson, S. J. Polyhedron, 2004, 23, 2695-2707.
(2) O’Connor, A. R.; Nataro, C.; Golen, J. A.; Rheingold, A. L. J. Organometallic Chem., 2004, 689, 2411.
(3) Connelly, N. G.; Geiger, W. E. Chem. Rev., 1996, 96, $877-910$.
(4) El-ghayoury, A.; Zeissel, R. Tetrahedron Lett. 1998, 39, 4473-4476.
(5) Nishiyama, H.; Shimada, T.; Itoh, H.; Sugyama, H.; Motoyama, Y. Chem. Commun. 1997, 18631864.

and the solid was washed with small amounts of cold water and THF, followed by diethyl ether. The solid was dried in vacuo, giving 0.587 g of $\mathbf{R u} \mathbf{u}^{\mathrm{II}} \mathbf{C O O H}(65 \%$ yield, Equation S 1$)$.
${ }^{1} H$ NMR (DMF- $d_{7}$ ) $\delta: 7.82\left(\mathrm{t}, 2 \mathrm{H}_{\mathrm{D}}\right), 8.03\left(\mathrm{~d}, 2 \mathrm{H}_{\mathrm{C}}\right), 8.25\left(\mathrm{t}, 2 \mathrm{H}_{\mathrm{E}}\right), 8.58\left(\mathrm{~d}, 2 \mathrm{H}_{\mathrm{B}}\right), 8.65\left(\mathrm{t}, 1 \mathrm{H}_{\mathrm{A}}\right)$, $9.20\left(\mathrm{~d}, 2 \mathrm{H}_{\mathrm{F}}\right), 9.44\left(\mathrm{~s}, 2 \mathrm{H}_{\mathrm{G}}\right)$. Peak assignments were made using COSY and NOESY NMR (Figure S1). ESI/MS ${ }^{+}(\mathrm{m} / \mathrm{z}): 544.3[\mathrm{M}]^{+}$, and ESI/MS ${ }^{-}(\mathrm{m} / \mathrm{z}): 543.2[\mathrm{M}-\mathrm{H}]^{-}$, and $499.5\left[\mathrm{M}-\mathrm{H}^{+}-\right.$ $\left.\mathrm{CO}_{2}\right]^{-}$. UV-Visible spectrum in DMF: $\lambda_{\max }=531 \mathrm{~nm}\left(\varepsilon_{531}=12,000 \pm 300 \mathrm{M}^{-1} \mathrm{~cm}^{-1}\right)$. In MeCN : $\lambda_{\text {max }}=527 \mathrm{~nm}\left(\varepsilon_{527} \sim 13,000 \mathrm{M}^{-1} \mathrm{~cm}^{-1}\right)$. In MeCN , it is difficult to dissolve $\mathbf{R u}{ }^{\mathrm{II}} \mathbf{C O O H}$ quantitatively due to its low solubility; based on the titrations with DBU discussed in Section SIII, $\left[\varepsilon_{527}\left(\mathbf{R u}{ }^{\text {II }} \mathbf{C O O H}\right) / \varepsilon_{527}\left(\mathbf{R u}^{\text {II }} \mathbf{C O O}^{-}\right)\right]_{\text {MeCN }}=1.4$ so $\varepsilon_{527}\left(\mathbf{R u}{ }^{\text {II }} \mathbf{C O O H}\right)_{\text {MeCN }} \sim 13,000 \mathrm{M}^{-1} \mathrm{~cm}^{-1}$. Elemental analysis: Calculated for $\mathrm{C}_{23} \mathrm{H}_{14} \mathrm{~N}_{4} \mathrm{O}_{6} \mathrm{Ru} \bullet \mathrm{H}_{2} \mathrm{O}, \mathrm{C}: 49.20$, $\mathrm{H}: 2.87$, N: 9.98; Found: C: $49.52, \mathrm{H}: 2.90, \mathrm{~N}: 10.09$. The presence of water in this sample was indicated by a broad peak in a ${ }^{1} \mathrm{H}$ NMR spectrum taken in dry DMF- $d_{7}$.
$\left[{ }^{n} \mathbf{N B u}_{4}{ }^{+}\right]\left[\mathbf{R u}\left(\right.\right.$ dipic) $\left.\left(\mathbf{t p y C O O}^{-}\right)\right]\left(\mathbf{R u}^{\mathrm{II}} \mathbf{C O O}^{-}\right)$. To a solution of $\mathbf{R u}{ }^{\text {II }} \mathbf{C O O H}(0.125 \mathrm{~g}, 0.395$ mmol ) in 40 mL DMF, $500 \mu \mathrm{~L}$ of 1 M tetra- $n$-butylammonium hydroxide ( ${ }^{n} \mathrm{Bu}_{4} \mathrm{NOH}$ ) in MeOH ( 0.500 mmol ) was added. After stirring for 1 minute, the mixture was added dropwise to 700 mL diethyl ether, and the purple/black precipitate was collected on a glass frit (excess $\mathrm{Et}_{2} \mathrm{O}$ was required for precipitation). This solid was dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, and fine needle crystals were grown from slow diffusion of a $1: 1$ solution of $\mathrm{Et}_{2} \mathrm{O}: n$-hexane at $10^{\circ} \mathrm{C}$. A poor crystal structure was obtained of these crystals, which indicated the presence of three water molecules. Suitable X-ray quality crystals were grown by slow diffusion of $\mathrm{Et}_{2} \mathrm{O}$ into a solution of $\mathbf{R u}^{\mathrm{II}} \mathbf{C O O}^{-}$in MeCN at $10{ }^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{3} \mathrm{CN}\right) ~ \delta: 7.33(\mathrm{t}, 2 \mathrm{H}), 7.63(\mathrm{~d}, 2 \mathrm{H}), 7.84(\mathrm{t}, 2 \mathrm{H}), 8.19(\mathrm{t}, 1 \mathrm{H}), 8.27(\mathrm{~d}, 2 \mathrm{H}), 8.54(\mathrm{~d}$, $2 \mathrm{H}), 9.10(\mathrm{~s}, 2 \mathrm{H}) . \mathrm{ESI} / \mathrm{MS}^{+}(\mathrm{m} / \mathrm{z}): 545.0[\mathrm{M}+2 \mathrm{H}]^{+}, 242.2\left[\mathrm{NBu}_{4}\right]^{+}$, and ESI/MS $(\mathrm{m} / \mathrm{z}): 542.9$ $[\mathrm{M}]^{-}$. UV-vis $\left(\mathrm{CH}_{3} \mathrm{CN}\right)$ : $\lambda_{\max }=520 \mathrm{~nm}\left(\varepsilon_{520}=9400 \pm 400 \mathrm{M}^{-1} \mathrm{~cm}^{-1}\right) ; 587 \mathrm{~nm}$ (shoulder; $\varepsilon_{587}=$ $\left.7200 \pm 200 \mathrm{M}^{-1} \mathrm{~cm}^{-1}\right) . \quad \varepsilon_{527}=9500 \pm 300 \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ was used to calculate $\varepsilon_{527}$ for $\mathbf{R u}{ }^{\text {II }} \mathbf{C O O H}$.

Elemental analysis: Calculated for $\mathrm{C}_{39} \mathrm{H}_{49} \mathrm{~N}_{5} \mathrm{O}_{6} \mathrm{Ru} \bullet \mathrm{H}_{2} \mathrm{O}, \mathrm{C}: 58.26, \mathrm{H}: 6.40, \mathrm{~N}: 8.72$; Found: C: $58.06, \mathrm{H}: 6.31, \mathrm{~N}: 8.70$. The small water peak in $\mathrm{CD}_{3} \mathrm{CN}$ broadened out completely in the presence of $\mathbf{R u} \mathbf{u}^{\mathbf{I I}} \mathbf{C O O}^{-}$, indicating that water could be in fast exchange with $\mathbf{R u}^{\mathbf{I I}} \mathbf{C O O}^{-}$and making it impossible to quantify how much water was in the sample.


Figure S1. ${ }^{1} \mathrm{H}$ COSY NMR with peak assignments for $\mathbf{R u}{ }^{\text {II }} \mathbf{C O O H}$ in DMF- $d_{7}$. Peaks can be fully assigned because coupling was seen between $\mathrm{H}_{\mathrm{G}}$ and $\mathrm{H}_{\mathrm{F}}$ in a NOESY NMR spectrum.
$\left[\mathbf{N}(\text { tol })_{3}{ }^{\cdot+}\right] \mathbf{P F}_{6}{ }^{-}$. Following literature precedent, ${ }^{2,6} 0.168 \mathrm{~g} \mathrm{AgPF}_{6}(0.664 \mathrm{mmol})$ and 0.195 g tritolylamine ( 0.678 mmol ) were dissolved in $20 \mathrm{~mL} \mathrm{CH} \mathrm{Cl}_{2}$ in a swivel frit apparatus covered in foil, and the solution turned dark blue over several minutes. To ensure that the reaction went to completion, $0.043 \mathrm{~g} \mathrm{I}_{2}(0.169 \mathrm{mmol})$ in $9 \mathrm{~mL} n$-hexane was added to the solution under a flow of $\mathrm{N}_{2}$, and allowed to stir for 40 minutes and filtered. The volume was reduced to $\sim 10 \mathrm{~mL}$, and 50 $\mathrm{mL} n$-hexane was added to precipitate a royal blue powder. After drying in vacuo, 0.250 g of $\left[\mathrm{N}(\mathrm{tol})_{3}{ }^{\cdot+}\right] \mathrm{PF}_{6}{ }^{-}$was collected in $85 \%$ yield.
(6) Barton, D. H. R.; Haynes, R. K.; Leclerc, G.; Magnus, P. D.; Menzies, I. D. J. Chem. Soc., Perkin Trans 1, 1975, 2055-2065.


Ru ${ }^{\text {III }} \mathbf{C O O}$. Following equation S 2 , a swivel frit apparatus with a fine filter was charged with $\mathbf{R u}^{\text {II }} \mathbf{C O O}^{-}(0.190 \mathrm{~g}, 0.242 \mathrm{mmol})$ and $\sim 15 \mathrm{~mL} \mathrm{CH}_{2} \mathrm{Cl}_{2}$ was vacuum-transferred in. A solution of $\left[\mathrm{N}(\mathrm{tol}){ }_{3}{ }^{+{ }^{+}} \mathrm{PF}_{6}{ }^{-}(0.160 \mathrm{~g}, 0.370 \mathrm{mmol})\right.$ in $\sim 5 \mathrm{~mL} \mathrm{CH} \mathrm{Cl}_{2}$ was syringed into the solution over 1 min . The volume was reduced to $\sim 2 \mathrm{~mL}$, and the fine brown precipitate was collected and washed with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and pentane. The solid was dried in vacuo for 30 minutes and then stored under $\mathrm{N}_{2}$ at $-35^{\circ} \mathrm{C}$, giving 0.094 g of $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}$ ( $72 \%$ yield). ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{3} \mathrm{CN}\right.$ ): (all broad singlets) $-37.9(2 \mathrm{H}),-15.8(2 \mathrm{H}),-2.4(2 \mathrm{H}), 1.4(2 \mathrm{H}), 7.3(2 \mathrm{H}), 9.6(1 \mathrm{H}), 14.6(2 \mathrm{H})$ (Figure S2). ESI/MS ${ }^{+}(\mathrm{m} / \mathrm{z}): 544.1[\mathrm{M}+\mathrm{H}]^{+}$. Generating $\mathbf{R u} \mathbf{u}^{\mathrm{III}} \mathbf{C O O}$ in situ from titrations of $\mathbf{R u}^{\mathrm{II}} \mathbf{C O O}^{-}$with $\left[\left(p-\left(\mathrm{BrC}_{6} \mathrm{H}_{4}\right)_{3} \mathrm{~N}^{++}\right]\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{4}{ }^{-}\right]\right.$gave a UV-Visible spectrum with a shoulder at $435 \mathrm{~nm}\left(\varepsilon_{435}=3400\right.$ $\pm 700 \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ ). Elemental analysis: Calculated for $\mathrm{C}_{23} \mathrm{H}_{14} \mathrm{~N}_{4} \mathrm{O}_{6} \mathrm{Ru} \bullet 4 \mathrm{H}_{2} \mathrm{O}, \mathrm{C}: 44.88, \mathrm{H}: 3.44, \mathrm{~N}$ : 9.11; Found: $\mathrm{C}: 45.18, \mathrm{H}: 2.83, \mathrm{~N}: 8.82$. The presence of water in this sample was indicated by a broad peak in a ${ }^{1} \mathrm{H}$ NMR spectrum taken in dry MeCN . Due to the thermal instability of $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}$, further attempts at drying $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}$ only showed more decomposition by elemental analysis.


Figure S2. ${ }^{1} \mathrm{H}$ NMR of $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}$ in $\mathrm{CD}_{3} \mathrm{CN}$. In order to see the paramagnetic peaks, the delay time was set to 0.1 sec , the acquisition time to 0.1 sec , and $\geq 600$ scans were obtained. The seven peaks for $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}$ are labeled, and a broad peak can be seen for $\mathrm{H}_{2} \mathrm{O}$ at $\delta \cong 2$.

## III. $\mathrm{pK} \mathbf{K}_{\text {a }}$ Determination for $\mathrm{Ru}^{\text {II }} \mathrm{COOH}$ in MeCN

Titration of $\mathbf{R u}^{\mathbf{I I}} \mathbf{C O O}^{-}$with the weak acid benzoic acid ( $\mathrm{PhCOOH}, \mathrm{p} K_{\mathrm{a}, \mathrm{PhCOOH}}=20.7 \pm$ $0.1^{7}$ ) forms $\mathbf{R u}^{\text {II }} \mathbf{C O O H}$ and $\left({ }^{n} \mathrm{NBu}_{4}{ }^{+}\right)\left(\mathrm{PhCOO}^{-}\right)$in equilibrium. To a solution of 2 mL of 0.033 $\mathrm{mM} \mathrm{Ru}{ }^{\text {II }} \mathbf{C O O}^{-}$in MeCN was added 5.7 equiv ( $3 \mu \mathrm{~L}$ ) of $\mathrm{PhCOOH}(0.126 \mathrm{M})$ up to 114 equiv total. Changes in the optical spectra were monitored after each addition at 527 nm (Figure S3), and corrected for volume additions. The concentrations of $\mathbf{R u}{ }^{\mathbf{I I}} \mathbf{C O O H}$ and $\mathbf{R u}^{\mathbf{I I}} \mathbf{C O O}^{-}$were determined from the optical spectra using eq S3, where A is the absorbance at 527 nm over the course of the reaction and $\mathrm{b}=1 \mathrm{~cm}$ is the path length. The mass balance for the reaction (eq S4) was confirmed by back-titrating with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) to form $\mathbf{R u}^{\text {II }} \mathbf{C O O}^{-}$quantitatively). Therefore, the calculated concentrations are $\left[\mathbf{R u}^{\mathbf{I I}} \mathbf{C O O}^{-}\right]_{\text {calc }}=\{\mathrm{A}-$ $\left.\varepsilon_{\text {RuCOOH }}\left[\mathrm{Ru}^{\mathrm{II}}\right]_{\text {total }}\right\} /\left(\varepsilon_{\text {RuCOO- }}-\varepsilon_{\text {RuCOOH }}\right)$, and $\left[\mathbf{R u} \mathbf{u}^{\mathrm{II}} \mathbf{C O O H}\right]_{\text {calc }}=\left\{\mathrm{A}-\varepsilon_{\text {RuCOO- }}\left[\mathrm{Ru}^{\mathrm{II}}\right]_{\text {total }}\right\} /\left(\varepsilon_{\text {RuCOOH }}-\right.$ $\left.\varepsilon_{\text {Rucoo- }}\right)$.

$$
\begin{align*}
A & =b\left\{\varepsilon_{\text {RuCOOH }}\left[R u^{I I} \mathrm{COOH}\right]+\varepsilon_{\text {RuCOO- }}\left[\mathrm{Ru}^{I I} \mathrm{COO}^{-}\right]\right\}  \tag{S3}\\
{\left[R u^{I I}\right]_{\text {total }} } & =\left[R u^{\text {II }} \mathrm{COO}^{-}\right]_{\text {initial }}=\left[\mathrm{Ru}^{\text {II } \mathrm{COOH}]+\left[\mathrm{Ru}^{\text {II }} \mathrm{COO}^{-}\right]}\right.  \tag{S4}\\
K_{\text {eq }} & =\frac{\left[\mathrm{Ru}^{I I} \mathrm{COOH}\right]\left[\left[^{n} \mathrm{NBu}_{4}^{+}\right]\left[\mathrm{PhCOO}^{-}\right]\right]}{\left[\mathrm{Ru}^{I I} \mathrm{COO}^{-}\right][\mathrm{PhCOOH}]} \tag{S5}
\end{align*}
$$



Figure S3. Change in absorbance at 527 nm upon addition of PhCOOH to a 0.033 mM solution of $\mathbf{R u}^{\mathbf{I I}} \mathbf{C O O}^{-}$in MeCN .


Figure S4. Plot of $\left[\mathrm{Ru}^{\mathrm{II}} \mathbf{C O O H}\right]^{2} /\left[\mathrm{Ru}^{\mathrm{II}} \mathrm{COO}^{-}\right]$ vs. $[\mathrm{PhCOOH}]$ for the equilibrium titration:
$\mathbf{R u}^{\mathrm{II}} \mathbf{C O O}^{-}+\mathrm{PhCOOH} \rightarrow \mathbf{R u}^{\text {II }} \mathbf{C O O H}+$ $\left({ }^{n} \mathrm{NBu}_{4}{ }^{+}\right)\left(\mathrm{PhCOO}^{-}\right)$, where $\left[\left({ }^{n} \mathrm{NBu}_{4}^{+}\right)\left(\mathrm{PhCOO}^{-}\right)\right]$ $=\left[\mathbf{R u}{ }^{\text {II }} \mathbf{C O O H}\right]$. The slope of the plot is $K_{\text {eq }}$.
(7) Acid-Base Dissociation Constants in Dipolar Aprotic Solvents, Chemical Data Series, No. 35; Izutsu, K. Ed.; Blackwell Scientific Publications: London, 1990.
$\left[\mathbf{R u}^{\text {II }} \mathbf{C O O H}\right]$ is assumed to be equal to $\left[\left({ }^{n} \mathrm{NBu}_{4}{ }^{+}\right)\left(\mathrm{PhCOO}^{-}\right)\right]$, so $K_{\text {eq }}$ (eq S5) can be calculated by plotting $\left[\mathbf{R} \mathbf{u}^{\text {II }} \mathbf{C O O H}\right]^{2} /\left[\mathbf{R u}^{\text {II }} \mathbf{C O O}^{-}\right]$vs. $[\mathrm{PhCOOH}]$, giving $K_{\text {eq }}=(6.1 \pm 0.3) \times 10^{-3}$ (Figure S4). The $\mathrm{p} K_{\mathrm{a}}$ of $\mathbf{R} \mathbf{u}^{\text {II }} \mathbf{C O O H}$ in MeCN equals $\left\{\mathrm{p} K_{\mathrm{a}, \mathrm{PhCOOH}}-\left[-\log \left(K_{\mathrm{eq}}\right)\right]\right\}$, giving $\mathrm{p} K_{\mathrm{a}}\left(\mathbf{R} \mathbf{u}^{\text {II }} \mathbf{C O O H}\right)=$ $18.5 \pm 0.1$. This value was verified by titrations of $0.008 \pm 0.002 \mathrm{mM} \mathrm{Ru}{ }^{\text {II }} \mathbf{C O O H}$ with 4 dimethylaminopyridine (DMAP) using a similar procedure, yielding $K_{\mathrm{eq}}=0.34 \pm 0.07$. Using the $\mathrm{p} K_{\mathrm{a}}$ of DMAP- $\mathrm{H}^{+}\left(17.95 \pm 0.03^{8}\right)$, this gives $\mathrm{p} K_{\mathrm{a}}\left(\mathbf{R} \mathbf{u}^{\text {II }} \mathbf{C O O H}\right)=18.4 \pm 0.1$.

## Titrations of $\mathrm{Ru}^{\mathrm{II}} \mathbf{C O O H}$ with a strong base

Titrations of 2 mL of a 0.0055 mM solution of $\mathbf{R} \mathbf{u}^{\mathrm{II}} \mathbf{C O O H}$ in MeCN with 0.17 equiv $(5.5 \mu \mathrm{~L})$ of the strong base DBU $(0.334 \mathrm{mM})$ were monitored by UV-vis spectroscopy at 527 nm . Up to 1.17 equiv of DBU were added, although the spectrum stopped changing after 1.0 equiv, giving $\mathrm{A}_{527, \text { initial }} / \mathrm{A}_{527, \text { final }}$ (the ratio of absorbances at the beginning and end of the titrations) of 1.4. Addition of the weak acid pentafluorophenol (in excess) regenerated $\mathbf{R u} \mathbf{u}^{\mathbf{I I}} \mathbf{C O O H}$ in $95 \pm$ $2 \%$ yield ( $\mathbf{R u}^{\mathbf{I I}} \mathbf{C O O H}$ decomposed in the presence of stronger acids).

[^0]
## IV. Electrochemistry



Figure S5. Cyclic voltammogram for $\mathbf{R u} \mathbf{C O O}^{-}$in $\mathrm{MeCN}\left(\mathrm{Cp}_{2} \mathrm{Fe}^{+/ 0}\right.$ is 0.10 V vs. $\mathrm{Ag} / \mathrm{AgNO}_{3}$ on the scale given).

Table S1. Cyclic voltammetry for $\mathbf{R u} \mathbf{u}^{\text {II }} \mathbf{C O O H}$ and $\mathbf{R u}^{\mathbf{I I}} \mathbf{C O O}^{-}$in MeCN and DMF. ${ }^{a}$

|  | $E_{1 / 2}(\mathrm{~V})$ | $E_{\mathrm{p}, \mathrm{c}}-E_{\mathrm{p}, \mathrm{a}}(\mathrm{mV})$ | $\Delta E_{1 / 2}(\mathrm{~V})^{b}$ |
| :---: | :---: | :---: | :---: |
| Ru' ${ }^{\text {II }} \mathbf{C O O H} / \mathrm{MeCN}$ | $\sim 0.21{ }^{\text {c }}$ | 100 |  |
| $\mathbf{R u}^{\text {II }} \mathbf{C O O}^{-} / \mathrm{MeCN}$ | 0.047 | 84 | $\left\{\sim 0.16^{\text {c }}\right.$ |
| $\mathbf{R u}{ }^{\text {II }} \mathbf{C O O H} / \mathrm{DMF}$ | 0.156 | 77 |  |
| $\mathbf{R u}^{\text {II }} \mathbf{C O O}^{-} / \mathrm{DMF}$ | 0.026 | 73 | $\{0.130$ |

The $\Delta E_{1 / 2}$ of 0.13 V implies that the $\mathrm{p} K_{\mathrm{a}}$ s of the $\mathrm{Ru}^{\text {II }}$ and $\mathrm{Ru}^{\text {III }}$ species differ by 2.2 units since $\Delta \mathrm{p} K_{\mathrm{a}}=\mathrm{p} K_{\mathrm{a}, \mathrm{M}(\mathrm{II})}-\mathrm{p} K_{\mathrm{a}, \mathrm{M}(\mathrm{III})}=\Delta E_{1 / 2} / 0.059 \mathrm{~V}$ (from a thermochemical cycle ${ }^{25}$ ).

## V. X-ray Crystal Structure of $\left[\mathrm{NBu}_{4}{ }^{+}\right] \mathbf{R u}^{\mathrm{II}} \mathbf{C O O}^{-}$

X-ray crystallography was performed by the Small Molecule X-ray Crystallography Facility, Department of Chemistry and Biochemistry, University of California, San Diego.

A purple rod $0.10 \times 0.10 \times 0.04 \mathrm{~mm}$ in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at $100(2) \mathrm{K}$ using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 5 seconds per frame using a scan width of $0.5^{\circ}$. Data collection was $99.1 \%$ complete to 67.00 。in $\theta$. A total of 25463 reflections were collected covering the indices, $-18 \leq h \leq 24,-10 \leq k \leq 10,-24 \leq l \leq 24.6552$ reflections were found to be symmetry independent, with an $R_{\text {int }}$ of 0.0221 . Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $\mathrm{P} 2_{1} / \mathrm{n}$ (No. 14). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SIR-2004) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97.

Positional and thermal disorder can be seen for the ${ }^{n} \mathrm{Bu}_{4} \mathrm{~N}^{+}$cation (Figure S6). The positionally distorted $n$-butyl arm was modeled using partial occupancies.


Figure S6. ORTEP of $\mathbf{R u}^{\text {II }} \mathbf{C O O}^{-}$shown with disordered ${ }^{n} \mathrm{Bu}_{4} \mathrm{~N}^{+}$cation, with ellipsoids at $50 \%$ probability.

Table S2. Crystal data and structure refinement for $\left[\mathrm{NBu}_{4}{ }^{+}\right] \mathbf{R u}^{\mathbf{I I}} \mathbf{C O O}^{-}$

| Empirical formula | $\mathrm{C}_{39} \mathrm{H}_{49} \mathrm{~N}_{5} \mathrm{O}_{6} \mathrm{Ru}$ |
| :---: | :---: |
| Formula weight | 784.90 |
| Temperature (K) | 100(2) |
| Wavelength ( $\AA$ ) | 1.54178 |
| Crystal description/color | purple rod |
| Crystal system, space group | Monoclinic, $\mathrm{P}_{1} / \mathrm{n}$ |
| Unit cell dimensions ( $\AA$, ${ }^{\circ}$ ) | $a=20.4473$ (10) $\quad \alpha=90$ |
|  | $b=8.5753(4) \quad \beta=95.704(2)$ |
|  | $c=20.7023(11) \quad \gamma=90$ |
| Volume ( $\AA^{3}$ ) | 3612.0(3) |
| Z , Calculated density ( $\mathrm{Mg} / \mathrm{m}^{3}$ ) | 4, 1.443 |
| Absorption coefficient ( $\mathrm{mm}^{-1}$ ) | 3.956 |
| F(000) | 1640 |
| Crystal size ( $\mathrm{mm}^{3}$ ) | $0.10 \times 0.10 \times 0.04$ |
| Theta range for data collection ( ${ }^{\circ}$ ) | 4.29 to 68.24 |
| Index ranges | $-18 \leq h \leq 24,-10 \leq k \leq 10,-24 \leq l \leq 24$ |
| Reflections collected / unique | $25463 / 6552\left[R_{\text {int }}=0.0221\right]$ |
| Completeness to theta | $67.00^{\circ} 99.1 \%$ |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.8578 and 0.6931 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 6552 / 0 / 491 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | $S=1.055$ |
| Final R indices [ $\mathrm{I}>2 \sigma(\mathrm{I})$ ] | $* R 1=0.0334, w R 2=0.0769$ |
| R indices (all data) | $R 1=0.0378, * w R 2=0.0790$ |
| Largest diff. peak and hole (e/ $\AA^{3}$ ) | 0.630 and -0.510 |

Table S3. Selected bond lengths $(\AA)$ and Angles ( ${ }^{\circ}$ ) for $\mathbf{R u}^{\text {II }} \mathbf{C O O}^{-}$

|  | Length | Angle |  |
| :--- | :--- | :--- | :---: |
| Ru-N1 | $1.964(2)$ | O1-C1-O2 | $125.2(3)$ |
| Ru-N2 | $2.053(2)$ | O3-C7-O4 | $125.5(3)$ |
| Ru-N3 | $1.957(2)$ | O5-C23-O6 | $128.2(2)$ |
| Ru-N4 | $2.066(2)$ | O1-Ru1-N1 | $78.50(8)$ |
| Ru-O1 | $2.1031(19)$ | O1-Ru1-N2 | $87.23(8)$ |
| Ru-O3 | $2.0988(19)$ | O3-Ru1-N1 | $78.59(8)$ |
| C23-O5 | $1.249(3)$ | O3-Ru1-N4 | $87.38(8)$ |
| C23-O6 | $1.249(3)$ | N2-Ru1-N3 | $79.53(9)$ |
| C7-O3 | $1.289(3)$ | N3-Ru1-N4 | $79.11(9)$ |
| C7-O4 | $1.230(3)$ |  |  |
| C1-O1 | $1.291(3)$ |  |  |
| C1-O2 | $1.236(3)$ |  |  |

## VI. Thermochemical Cycle and BDFE Determination



Figure S7. Thermochemical cycle for $\mathbf{R u}{ }^{\mathbf{I I}} \mathbf{C O O H}$ CPET to $\mathbf{R u}{ }^{\mathbf{I I I}} \mathbf{C O O}$.

From above, $\mathrm{p} K_{\mathrm{a}}\left(\mathbf{R} \mathbf{u}^{\mathbf{I I}} \mathbf{C O O H}\right)=18.5 \pm 0.1$ and $E_{1 / 2}\left(\mathbf{R u}^{\text {III/II }} \mathbf{C O O}^{-}\right)=0.047 \pm 0.020 \mathrm{~V}$.

Converting to free energies, and accounting for $C_{\mathrm{G}}\left(54.9 \pm 1.0 \mathrm{kcal} \mathrm{mol}^{-1}\right.$, for $\mathrm{H}^{+} \rightarrow \mathrm{H}^{+}+e^{-}$in $\mathrm{MeCN}){ }^{9}$

$$
\begin{aligned}
& \operatorname{BDFE}\left(\mathbf{R} \mathbf{u}^{\text {II }} \mathbf{C O O H}\right)=23.1\left(E_{1 / 2}\right)+1.37\left(p \mathrm{~K}_{\mathrm{a}}\right)+C_{\mathrm{G}} \\
& \operatorname{BDFE}\left(\mathbf{R} \mathbf{u}^{\mathrm{II}} \mathbf{C O O H}\right)=81 \pm 1 \mathrm{kcal} \mathrm{~mol}^{-1}
\end{aligned}
$$

(9) The Thermodynamics of Organometallic Systems Involving Electron-transfer Paths, Tilset, M.; Electron Transfer in Chemistry 2, Organic Molecules, Organometallic and Inorganic Molecules; Balzani, V. Ed.; Wiley-VCH: Weinheim (Federal Republic of Germany), 2001; pp. 677-713.

## VII. Possible Stepwise Pathways for $\mathbf{R u}^{\text {III }} \mathbf{C O O}+{ }^{t} \mathbf{B u}_{3} \underline{\mathbf{A r O H}^{\prime}}$

The $\mathrm{p} K_{\mathrm{a}}$ of ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}$ is 17.8 in DMSO. ${ }^{10} \mathrm{p} K_{\mathrm{a}}$ values in MeCN are $10.2 \pm 0.3 \mathrm{p} K_{\mathrm{a}}$ units higher than in DMSO, ${ }^{11}$ so $\mathrm{p} K_{\mathrm{a}}\left({ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}\right)_{\mathrm{MeCN}}=28.0 \pm 0.3$ in MeCN . The $E_{1 / 2}$ in $\mathrm{MeCN} v s$. $\mathrm{Cp}_{2} \mathrm{Fe}^{+/ 0}$ for ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}^{+/ / 0}$ is $1.18 \pm 0.02 \mathrm{~V}^{12}$ The $\mathrm{p} K_{\mathrm{a}}\left(\mathbf{R u}{ }^{\text {II }} \mathbf{C O O H}\right)=18.5 \pm 0.1$ (Section III) can be converted to $\mathrm{p} K_{\mathrm{a}}\left(\mathbf{R u}^{\text {III }} \mathbf{C O O H}^{+}\right)=16.3 \pm 0.5$ using $\Delta \mathrm{p} K_{\mathrm{a}}=2.2 \pm 0.5{ }^{13}$ From Table S1, $E_{1 / 2}\left(\mathbf{R u}^{\text {III/II }} \mathbf{C O O}^{0 /-}\right)=0.047 \pm 0.020 \mathrm{~V}$.

The ground state free energies for the initial reactions of the stepwise pathways, proton transfer from ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}$ to $\mathbf{R u}{ }^{\mathbf{I I I}} \mathbf{C O O}$ in $\mathrm{MeCN}\left(\Delta G^{\circ}{ }_{\mathrm{PT}}\right)$ and electron transfer from ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}$ to $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}$ in $\mathrm{MeCN}\left(\Delta G^{\circ}{ }_{\text {ет }}\right)$, can be calculated with equations S 6 and S 7 below. Figure S 8 illustrates that $\Delta G^{\circ}{ }_{\text {ET }}$ and $\Delta G^{\circ}{ }_{\mathrm{PT}}$ are significantly larger than the barrier for the reaction, $\Delta G^{\ddagger}{ }_{1}$.

$$
\begin{gather*}
\Delta G^{\circ}{ }_{\mathrm{PT}}=1.37\left[\mathrm{p} K_{\mathrm{a}}\left({ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}\right)-\mathrm{p} K_{\mathrm{a}}\left(\mathbf{R u}^{\mathrm{III}} \mathbf{C O O H}^{+}\right)\right]=+16.1 \pm 0.8 \mathrm{kcal} \mathrm{~mol}^{-1}  \tag{S6}\\
\Delta G^{\circ}{ }_{\mathrm{ET}}=-23.06\left[E\left(\mathbf{R u}^{\mathrm{III} / \mathrm{II}} \mathbf{C O O}^{0 /-}\right)-E\left({ }^{\mathrm{t}} \mathrm{Bu}_{3} \mathrm{ArOH}^{+/ 0}\right)\right]=+26.1 \pm 0.7 \mathrm{kcal} \mathrm{~mol}^{-1} \tag{S7}
\end{gather*}
$$



Figure S8. A schematic energy surface (not to scale) for the reaction of $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}+{ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}$, showing that the $\Delta G^{\circ}$ for the pathways with initial PT or ET are significantly larger than the $\Delta G^{\ddagger}$ for the CPET pathway.

[^1]
## VIII. Reactivity Studies

Reaction of Ru" ${ }^{\text {III }} \mathbf{C O O}+{ }^{t} \mathrm{Bu}_{3} \mathbf{A r O H} \rightarrow \mathrm{Ru}^{\text {II }} \mathbf{C O O H}+{ }^{t} \mathrm{Bu}_{3} \mathbf{A r O}{ }^{-}$
A solution of $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}(0.0234 \mathrm{mM})$ was generated by adding $150 \mu \mathrm{~L}$ of a 0.517 mM solution of $\left[\left(p-\mathrm{BrC}_{6} \mathrm{H}_{4}\right)_{3} \mathrm{~N}^{++}\right]\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{4}{ }^{-}\right]$to $0.0255 \mathrm{mM} \mathrm{Ru}{ }^{\text {II }} \mathbf{C O O}^{-}$in MeCN . This solution was titrated with 0.1 equiv ( $3.4 \mu \mathrm{~L}$ aliquots) of a 1.28 mM solution of ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}$, and the change in absorbance was followed by UV-visible spectroscopy at 527 nm . A total of 1.9 equiv of ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}$ were added, although the spectrum did not change significantly after $0.7 \pm 0.1$ equiv. The resulting spectrum is shown in Figure S 9 (A) along with the known spectra of $\mathbf{R u}{ }^{\text {II }} \mathbf{C O O H}$ and ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArO}^{\cdot} .{ }^{14}$ Analysis of these spectra indicated a ca. $67 \%$ yield of $\mathbf{R u}{ }^{\text {II }} \mathbf{C O O H}$ (some decomposition was seen due to the long timescale of the titrations, and the source of the decomposition is discussed below). Figure S 9 (B) shows the closeness of (solid line) the final reaction spectrum ( $\varepsilon_{\text {reaction }}$ ) minus $\left\{0.67 \times \varepsilon_{t \mathrm{Bu} 3 \mathrm{ArO}}.\right\}$ with (dot-dash line) the spectrum expected for a $67 \%$ yield of $\mathbf{R u} \mathbf{I I}^{\text {II }} \mathbf{C O O H},\left\{0.67 \times \varepsilon_{\text {RuCOOH }}\right\}$.


Figure S9. (A) UV-Visible spectra (in $\varepsilon, \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ ) of the final reaction solution for $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}$ $+{ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH} \rightarrow \mathbf{R} \mathbf{u}^{\text {II }} \mathbf{C O O H}+{ }^{t} \mathrm{Bu}_{3} \mathrm{ArO}^{\cdot}\left(\varepsilon_{\text {reaction }}\right.$, solid line $)$; the spectrum of $\mathbf{R u}{ }^{\text {II }} \mathbf{C O O H}$ ( $\varepsilon_{\mathrm{Ru}(I I) \mathrm{COOH}}$, dot-dash line, -- ); and ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArO}^{*}\left(\varepsilon_{\text {tBu3ArO}}\right.$., dotted line,---).
(B) Final reaction spectrum from (A) minus $0.67 \times$ the spectrum of ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArO}^{\circ}$ (solid line, $\left\{\varepsilon_{\text {reaction }}\right.$ $\left.-\left(0.67 \times \varepsilon_{t \text { Bu3ArO }}.\right)\right\}$, overlaid with $0.67 \times$ the spectrum of $\mathbf{R u} \mathbf{u}^{\text {II }} \mathbf{C O O H}$ (dot-dash line, $\{0.67 \times$ $\left.\left.\varepsilon_{\mathrm{Ru}(\mathrm{II}) \mathrm{COOH}}\right\}\right)$.
(14) Manner, V. W.; Markle, T. F.; Freudenthal, J.; Roth, J. P.; Mayer, J. M. Chem. Commun. 2008, 256-258.

## In situ generation of $\mathrm{Ru}^{\text {III }} \mathbf{C O O}$, and discussion of decomposition

A 0.0242 mM solution of $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}$ was generated in situ by adding $110 \mu \mathrm{~L}$ of 0.620 $\mathrm{mM}\left[\left(p-\mathrm{BrC}_{6} \mathrm{H}_{4}\right)_{3} \mathrm{~N}^{\cdot+}\right]\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{4}{ }^{-}\right]$to a 0.0255 mM solution of $\mathbf{R u}^{\mathbf{I I}} \mathbf{C O O}^{-}$in MeCN , and the change in absorbance was followed by UV-visible spectroscopy. Reduction of this in situ $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}$ with $18 \mu \mathrm{~L}$ of a solution of 3.41 mM decamethylferrocene ( $\mathrm{Fc}^{*}$ ) in MeCN gave a spectrum which suggests $77 \% \mathbf{R u}^{\text {II }} \mathbf{C O O}^{-}$and $23 \% \mathbf{R u}^{\text {II }} \mathbf{C O O H}$. The formation of $\mathbf{R u}{ }^{\text {II }} \mathbf{C O O H}$ could be due to a decomposition pathway which involves $\mathbf{R u}{ }^{\text {III }} \mathbf{\mathbf { O O H } ^ { + }}$.

The reaction of $\mathbf{R u}{ }^{\mathbf{I I I}} \mathbf{C O O H}{ }^{+}$and ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}$ has also been examined. To a solution of $0.023 \mathrm{mM} \mathrm{Ru}{ }^{\text {III }} \mathbf{C O O H}^{+}$(generated in situ from $\left.\mathbf{R u}^{\text {II }} \mathbf{C O O H}+\left[\left(p-\mathrm{BrC}_{6} \mathrm{H}_{4}\right)_{3} \mathrm{~N}^{\bullet+}\right]\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{4}{ }^{-}\right]\right), 8$ equiv of ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}$ were added (to make $\left[{ }^{t} \mathrm{Bu} u_{3} \mathrm{ArOH}\right]_{\text {initial }}=0.182 \mathrm{mM}$ ) and the change in optical spectra was monitored. This reaction occurred with $t_{1 / 2} \sim 2 \mathrm{~min}$, which is a much longer timescale than seen for the reaction of $\mathbf{R u}{ }^{\mathbf{I I I}} \mathbf{C O O}$ with ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}$. The final spectrum of this reaction mixture had $\lambda_{\text {max }}=500 \mathrm{~nm}\left(\varepsilon_{500} \sim 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}\right)$, which is significantly different than the spectrum of $\mathbf{R u}{ }^{\mathbf{I I}} \mathbf{C O O H}$. It is therefore possible that the less than quantitative yield of $\mathbf{R u} \mathbf{u}^{\text {II }} \mathbf{C O O H}$ in reaction (1) on the stopped-flow timescale (Figure S10) is due to some of the $\mathrm{Ru}\left(\right.$ III ) material being protonated and therefore reacting much more slowly with ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}$.

## IX. Stopped Flow Kinetics

The kinetics of the reaction of $\mathbf{R u}{ }^{\mathbf{I I I}} \mathbf{C O O}+{ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}$ in MeCN were measured under pseudo first-order conditions using an OLIS RSM-1000 stopped-flow. The appearance of $\mathbf{R u}{ }^{\text {II }} \mathbf{C O O H}\left(\lambda_{\max } 527 \mathrm{~nm}\right.$ ) was observed within a second (Figure S10). The full spectra as a function of time were analyzed with Specfit ${ }^{\mathrm{TM}}$ global analysis software. The reaction was shown to be first order in ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}$ (Table S4, Figure S11), and first order in $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}$ (the same rate constant was obtained when varying [Ru $\left.{ }^{\mathbf{I I I}} \mathbf{C O O}\right]$ from 0.0077 mM to 0.023 mM ). Reactions were performed both with isolated $\mathbf{R u} \mathbf{u}^{\mathbf{I I I}} \mathbf{C O O}$, and with $\mathbf{R u}{ }^{\mathbf{I I I}} \mathbf{C O O}$ generated in situ from $\mathbf{R u}^{\text {II }} \mathbf{C O O}^{-}+\left[\left(p-\mathrm{BrC}_{6} \mathrm{H}_{4}\right)_{3} \mathrm{~N}^{\mathbf{+}}\right]\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{4}^{-}\right]$, with no differences in the derived rate constants. The stopped-flow reactions give a yield of $77 \pm 10 \%$. These reactions were performed as a function of temperature, from $15-50^{\circ} \mathrm{C}$, in order to obtain the Eyring parameters shown in Figure S12.


Figure S10. (Left) Stack plot showing optical spectra of the reaction of Ru ${ }^{\text {III }} \mathbf{C O O}(0.023 \mathrm{mM})$ with ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}(0.21 \mathrm{mM})$; the growing absorbance is due to $\mathbf{R u}{ }^{\mathrm{II}} \mathbf{C O O H}$. (Right) Absorbance at 527.5 nm over 1 sec , superimposed with the pseudo first order fit.

Table S4. Pseudo first-order $k_{\text {obs }}$ in MeCN at $298 \mathrm{~K} v s$. [ ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}$ ].

| $\left[{ }^{t} \mathbf{B u}_{3} \mathbf{A r O H}\right](\mathbf{m M})$ | $\boldsymbol{k}_{\mathbf{0 b s}}\left(\mathbf{s}^{\mathbf{- 1}}\right)$ | $\left.{ }^{\boldsymbol{t}} \mathbf{B u}_{\mathbf{3}} \mathbf{A r O H}\right](\mathbf{m M})$ | $\boldsymbol{k}_{\mathbf{0 b s}}\left(\mathbf{s}^{\mathbf{- 1}}\right)$ |
| :---: | :---: | :---: | :---: |
| 0.095 | 2.2 | 0.21 | 5.3 |
| 0.13 | 2.7 | 0.23 | 5.5 |
| 0.15 | 3.5 | 0.26 | 5.3 |
| 0.18 | 4.1 | 0.31 | 6.9 |



Figure S11. Pseudo first order plot for $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}+{ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}$, with a slope of $k_{1 \mathrm{H}}$ $=(2.3 \pm 0.2) \times 10^{4} \mathrm{M}^{-1} \mathrm{~s}^{-1}$.


Figure S12. Eyring plot for the reaction of $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}$ with ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}$ from $15-50^{\circ} \mathrm{C}$. $\Delta H^{\ddagger}=3.5 \pm 1.4 \mathrm{kcal} \mathrm{mol}^{-1}$ and $\Delta S^{\ddagger}=-27 \pm 5 \mathrm{cal}$ $\mathrm{mol}^{-1} \mathrm{~K}^{-1}$.

## Isotope effect

The kinetics of the reaction of $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}+{ }^{t} \mathrm{Bu}_{3} \mathrm{ArOD}$ were measured in MeCN with $0.2 \% \mathrm{CD}_{3} \mathrm{OD}$ under pseudo first order conditions (Table S5, Figure S13). To check whether the presence of up to $0.2 \%$ methanol had an effect on the reaction, a stopped flow experiment with $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}(0.017 \mathrm{mM})+{ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}(0.10 \mathrm{mM})$ was performed with $0.2 \% \mathrm{CH}_{3} \mathrm{OH}$ present. The derived second order rate constant of $(2.1 \pm 0.2) \times 10^{4} \mathrm{M}^{-1} \mathrm{sec}^{-1}$ was within error of $k_{1 \mathrm{H}}$. The percent yield of products for the reaction of $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}+{ }^{t} \mathrm{Bu}_{3} \mathrm{ArOD}$ was within $5 \%$ of the control experiment.

Table S5. Pseudo first order $k_{\text {obs }}$ in MeCN at $298 \mathrm{~K} v s$. [ ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArOD}$ ].

| $\left[{ }^{t} \mathbf{B u}_{3} \mathbf{A r O D}\right](\mathbf{m M})$ | $\boldsymbol{k}_{\text {obs }}\left(\mathbf{s}^{\mathbf{- 1}}\right)$ | $\left.{ }^{t}{ }^{t} \mathbf{B u} \mathbf{u}_{\mathbf{3}} \mathbf{A r O D}\right](\mathbf{m M})$ | $\boldsymbol{k}_{\text {obs }}\left(\mathbf{s}^{\mathbf{- 1}}\right)$ |
| :---: | :---: | :---: | :---: |
| 0.10 | 0.38 | 0.22 | 0.85 |
| 0.13 | 0.41 | 0.24 | 0.71 |
| 0.16 | 0.43 | 0.27 | 0.97 |
| 0.20 | 0.58 | 0.30 | 1.0 |



## X. Reactivity with $\mathrm{Ru}^{\text {III }} \mathbf{C O O}+$ TEMPOH

## Possible Stepwise Pathways for Ru ${ }^{\text {III }} \mathbf{C O O}+$ TEMPOH

The $\mathrm{p} K_{\mathrm{a}}$ of TEMPOH is $31.0 \pm 0.2$ in DMSO. ${ }^{15}$ For O-H acids in MeCN, $\mathrm{p} K_{\mathrm{a}}(\mathrm{MeCN})=11.80+$ $0.884 \times \mathrm{p} K_{\mathrm{a}}(\mathrm{DMSO})^{16}$ to give $\mathrm{p} K_{\mathrm{a}}(\mathrm{TEMPOH})=39 \pm 1$ in MeCN . The $E_{1 / 2}$ for $\mathrm{TEMPOH}^{0 / \bullet}$ in MeCN is $0.71 \pm 0.02 \mathrm{~V}$ (converted from $\mathrm{Ag} / \mathrm{AgNO}_{3}$ to $\mathrm{FeCp}_{2}{ }^{0 /+}$ by subtracting 0.088 V ). ${ }^{17}$
(15) Bordwell, F. G.; Liu, W. Z. J. Am. Chem. Soc. 1996, 118, 10819-10823.
(16) Kutt, A.; Leito, I.; Kaljurand, I.; Soovali, L.; Vlasov, V. M.; Yagupolskii, L. M.; Koppel, I. A. J. Org. Chem. 2006, 71, 2829-2838.

The possible stepwise pathways were determined using the same method as that described in Section VII above, yielding $\Delta G^{\circ}{ }_{\mathrm{PT}}=+31 \pm 2 \mathrm{kcal} \mathrm{mol}^{-1}$ and $\Delta G^{\circ}{ }_{\text {ET }}=+15.3 \pm 0.7 \mathrm{kcal} \mathrm{mol}^{-1}$, both of which are significantly higher than $\Delta G^{\ddagger}$ TEMPOH $\left(10.3 \pm 0.1 \mathrm{kcal} \mathrm{mol}^{-1}\right)$.

## Stopped-flow experiments

The kinetics of the reaction of $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}+\mathrm{TEMPOH}$ in MeCN were measured under second order conditions using an OLIS RSM-1000 stopped-flow instrument, as described above. The appearance of $\mathbf{R u} \mathbf{u}^{\text {II }} \mathbf{C O O H}$ ( $\lambda_{\max } 527 \mathrm{~nm}$ ) was observed within seconds, and all reactions gave $80 \pm 10 \%$ yield of products. The full spectra were analyzed as discussed in Section IX, and shown to be first order in TEMPOH (Table S6) and first order in $\mathbf{R u}{ }^{\mathbf{I I I}} \mathbf{C O O}$ (the same rate constant was obtained when varying [ $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}$ ] from 0.014 to 0.026 mM ). The average second order rate constant is $k_{\text {TEMPOH }}=(2.0 \pm 0.6) \times 10^{5} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ (Figure S14).

Table S6. Second order rate constants ( $k$ ) in MeCN at $298 \mathrm{~K} v$. [TEMPOH].

| [TEMPOH] (mM) | $\boldsymbol{k}\left(\mathbf{M}^{-1} \mathbf{s}^{-1}\right)$ | [TEMPOH] (mM) | $\boldsymbol{k}\left(\mathbf{M}^{-1} \mathbf{s}^{-1}\right)$ |
| :---: | :---: | :---: | :---: |
| 0.0229 | $2.2 \times 10^{5}$ | 0.114 | $1.9 \times 10^{5}$ |
| 0.0280 | $1.7 \times 10^{5}$ | 0.127 | $1.6 \times 10^{5}$ |
| 0.0308 | $2.0 \times 10^{5}$ | 0.191 | $2.2 \times 10^{5}$ |
| 0.0763 | $1.7 \times 10^{5}$ | 0.267 | $2.4 \times 10^{5}$ |
|  |  | 0.294 | $2.2 \times 10^{5}$ |



Figure S14. Second order $k$ versus [TEMPOH] for $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}+$ TEMPOH, giving an average second order rate constant of $k_{\text {TEMPOH }}=(2.0 \pm 0.6) \times 10^{5} \mathrm{M}^{-1} \mathrm{~s}^{-1}$. A line is drawn at the mean.
(17) Semmelhack, M. F.; Chou, C. S.; Cortes, D. A. J. Am. Chem. Soc. 1983, 105, 4492-4494.

## XI. Selected Oxidants and BDEs of the X-H Bonds They Form

The list of bond dissociation enthalpies (BDEs) of strong organic and metal hydrogen atom abstractors given below is not complete but does show some of the strongest oxidants for CPET and HAT reactions. BDEs are used for consistency, because most of the older literature values are reported this way. As described in Section VI, Ru ${ }^{\text {III }} \mathbf{C O O}$ forms an O-H BDFE of 81 kcal $\mathrm{mol}^{-1}$, or a BDE of $\sim 86 \mathrm{kcal} \mathrm{mol}^{-1}$, using the conversion of $4.6 \mathrm{kcal} \mathrm{mol}^{-1}$ in $\mathrm{MeCN} .^{18}$
(a) $\left.\left[\mathrm{Ru}^{\mathrm{IV}} \text { (bpy) }\right)_{2}(\mathrm{py}) \mathrm{O}\right]^{2+}$, 84; Moyer, B. A.; Meyer, T. J. J. Am. Chem. Soc. 1978, 100, 36013603; Bryant, J. R.; Mayer, J. M. J. Am. Chem. Soc. 2003, 125, 10351-10361. (b) $\left[\mathrm{Fe}^{\text {III }}\{2,6-\right.$
 Stack, T. D. P. J. Am. Chem. Soc. 2002, 124, 83-96. (c) $\left[\mathrm{Mn}^{\mathrm{III}}(\mathrm{L}) \mathrm{O}\right]^{2-}(\mathrm{L}=\operatorname{tris}[(N$-tert-butylureaylato)- $N$-ethyl ]aminato), $77\left(\left[\mathrm{Mn}^{\mathrm{IV}}(\mathrm{L}) \mathrm{O}\right]^{-}\right.$and $\left[\mathrm{Fe}^{\mathrm{IV}}(\mathrm{L}) \mathrm{O}\right]^{-}, 110$ and 115 but not isolated); Gupta, R.; Borovik, A. S. J. Am. Chem. Soc. 2003, 125, 13234-13242. (d) $\left[\mathrm{Fe}^{\mathrm{IV}}\right.$ (NAd) $\{$ phenyltris(1-mesitylimidazol-2-ylidene)borate) $\left.\}\right] \mathrm{OTf}, \quad 92.2$ (BDFE $=87.6$, converted to number for $\mathrm{BDE}^{18}$ ); Nieto, I.; Ding, F.; Bontchev, R. P.; Wang, H.; Smith, J. M. J. Am. Chem. Soc. 2008, 130, 2716-2717 and references therein. (e) $\left[\mathrm{Mn}^{\mathrm{III}}\{2,6-\mathrm{bis}(\mathrm{bis}(2-\right.$ pyridyl)methoxymethane)-pyridine $\}(\mathrm{OH})]^{2+}, \mathrm{BDE}=82 \mathrm{kcal} \mathrm{mol}{ }^{-1}$ in MeCN: Goldsmith, C. R.; Cole, A. P.; Stack, T. D. P. J. Am. Chem. Soc. 2005, 127, 9904-9912. (f) $\mathrm{Mn}^{\mathrm{VII}} \mathrm{O}^{4-}, \mathrm{BDE}=80$ $\mathrm{kcal} \mathrm{mol}{ }^{-1}$ in $\mathrm{H}_{2} \mathrm{O} ;\left[\mathrm{Mn}_{2}(\mu-\mathrm{O})_{2}(1,10-\text { phenanthroline })_{4}\right]^{3+}, \mathrm{BDE}=79 \mathrm{kcal} \mathrm{mol}^{-1}$ in MeCN: Mayer, J. M. Acc. Chem. Res. 1998, 31, 441-450. (g) $\left[\mathrm{Tp}^{t \mathrm{Bu}, \mathrm{Me}}-\mathrm{Cr}^{\mathrm{IV}} \mathrm{O}\left(\mathrm{py}^{\prime} \mathrm{H}\right)\right]^{+}\left(\mathrm{Tp}^{t \mathrm{Bu}, \mathrm{Me}}=\right.$ hydrotris(3-tert-butyl-5-methylpyrazolyl)borate, py'H = 3-tert-butyl-5-methylpyrazole), $\mathrm{BDE}>75.3 \mathrm{kcal}$ $\mathrm{mol}^{-1}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ : Qin, K.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. J. Am. Chem. Soc. 2002, 124, 14008-14009. (h) $\left[\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})(\mathrm{N} 4 \mathrm{Py})\right]^{2+}$ and $\left[\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})(\mathrm{Bn}-\text { tpen })\right]^{2+}(\mathrm{N} 4 \mathrm{Py}=N, N-b i s(2-$ pyridylmethyl)- $N$-bis(2pyridyl)methylamine, Bn-tpen $=N$-benzyl- $N, N^{\prime}, N^{\prime}$-tris(2-pyridylmethyl)ethylenediamine) oxidize $\mathrm{C}-\mathrm{H}$ bonds of cyclohexane ( $\mathrm{BDE} \approx 99.3 \mathrm{kcal} \mathrm{mol}^{-1}$ ) in MeCN: Kaizer, J.; Klinker, E. J.; Oh, N. Y.; Rohde, J.-U.; Song, W. J.; Stubna, A.; Kim, J.; Münck, E.; Nam, W.; Que, L., Jr. J. Am. Chem. Soc. 2004, 126, 472-473. (i) There are many organic oxidants with high BDE’s, for instance: ${ }^{t} \mathrm{Bu}_{2} \mathrm{C}=\mathrm{NO}^{*}$, 79.2; Pratt, D. A.; Blake, J. A.; Mulder, P.; Walton, J. C.; Korth, H.-G.; Ingold, K. U. J. Am. Chem. Soc. 2004, 126, 10667-10675. (j) ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArO}^{\bullet}$, 80.1; Mulder, P.; Korth, H.-G.; Pratt, D. A.; DiLabio, G. A.; Valgimigli, L.; Pedulli, G. F.; Ingold, K. U. J. Phys. Chem. A, 2005, 109, 2647-2655.
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## XII. Terminology for PCET, HAT and CPET

The term 'proton-coupled electron transfer' (PCET) was probably first coined by T. J. Meyer in his pioneering work in this area in the 1980s. ${ }^{19}$ Over time, this term has come to encompass a very wide range of processes, including electron transfer reactions modulated by hydrogen bond interfaces (that may or may not involve proton transfer) ${ }^{20}$ to long range redox events of not-yet defined mechanism ${ }^{21}$ to small organic reactions such as phenoxyl radical + phenol that were historically called hydrogen atom transfer. ${ }^{22}$ In response to this, Savéant et al. recently proposed that reactions that involve concerted transfer of a proton and an electron (in one kinetic step) should be termed concerted proton-electron transfer (CPET). ${ }^{23}$ A classic example of CPET is the oxidation of tyrosine Z in Photosystem II, where the proton and electron appear to transfer in a single step involving long-range electron transfer to the oxidized chlorophyll and proton transfer to a nearby histidine. ${ }^{24}$

In our current view, ${ }^{25} \mathrm{CPET}$ reactions that involve movement of $\mathrm{H}^{+}$and $e^{-}$from one donor to one acceptor, that can be written $\mathrm{XH}+\mathrm{Y} \rightarrow \mathrm{X}+\mathrm{HY}$, should be called hydrogen atom transfer (HAT) reactions. In this view, HAT is one type of CPET. We understand that this differs from the distinction between HAT and PCET that one of us put forward in [22], and we apologize for the confusion. We now feel that this distinction, while interesting, can be problematic. For instance, the classical reaction ${ }^{t} \mathrm{BuOOH}+\mathrm{PhO}{ }^{\circ}$ could be described as HAT in the forward direction but PCET in the reverse, or HAT from the perspective of ${ }^{t} \mathrm{BuOOH}$ but PCET from the view of the phenol. In addition, trying to make this distinction can separate reactions that are not so different. For example, our studies of reactions that remove $\mathrm{H}^{+}+e^{-}$(三 $\mathrm{H}^{*}$ ) from dihydroanthracene have found that rate constants typically correlate well with the $\Delta G^{\circ}$ of reaction, regardless of whether they would fit into an HAT or "PCET" category (e.g., ${ }^{t} \mathrm{BuOO}$ • vs. iron complexes)..$^{25,26}$ We have thus come to use the term HAT for any reaction where $\mathrm{H}^{+}$and $e^{-}$move from a single donor to a single acceptor.

Meyer has advocated a different definition of HAT, that it should be restricted to processes where $\mathrm{H}^{+}$and $e^{-}$"are transferred from the same chemical bond." ${ }^{24}$ Under this specific

[^2]definition, the reactions of $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}$ with TEMPO-H and xanthene would be considered HAT even though the proton and electron are separated by $6.9 \AA$ in the product. The reverse reaction, however, would be PCET and not HAT. Similarly, by this definition toluene + phenoxyl would be HAT in the forward direction but not in the reverse direction. It seems odd to have different names for the same reaction in opposite directions. In addition, this definition would exclude from HAT all reactions of, for instance, phenols and ascorbate - because the $\mathrm{H}^{+}$is lost from a $\sigma$ bond in the molecular plane to form a radical in which the SOMO is of $\pi$ symmetry. ${ }^{23,22,25,27}$ To classify reactions of ${ }^{t} \mathrm{Bu}_{3} \mathrm{ArOH}$ would require knowing the ground state location of the phenolic proton: if the proton is in the molecular plane the reactions would be PCET but if sterics force the proton to lie well out of the plane (with a C-C-O-H tortion angle of $90^{\circ}$ ), then its reactions would be HAT. We hope that these examples illustrate the difficulties in applying a definition based on, for instance, whether $\mathrm{H}^{+}$and $e^{-}$"are transferred from the same chemical bond."

We feel that it would be unfortunate to classify the reactions of $\mathbf{R u}{ }^{\text {III }} \mathbf{C O O}$ ( or ${ }^{t} \mathrm{BuO}^{*}$ or any other H-abstractor) as HAT with some substrates and PCET with others, in the absence of experimental evidence for a difference. We have used CPET in this communication to describe the overall reactivity but we believe that all of our reactions in this communication could be more specifically defined as HAT.
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