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. RuCl₃•H₂O was purchased from Strem, "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 **Ru^{II}COOH** and **Ru^{III}COO** and all kinetics studies were performed under N₂, but purification, electrochemistry, pK_a determination, and most characterizations of **Ru^{II}COOH** and **Ru^{II}COO** 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

 $[(\eta^6-cymene)RuCl]_2(\mu-Cl)_2^1$ and $[(p-BrC_6H_4)_3N^{+}][B(C_6F_5)_4^-]^2$ were prepared following literature procedures. Tri-*p*-tolylaminium hexafluorophosphate ($[N(tol)_3^{+}]PF_6^-$) is a known compound,³ but caused decomposition in the synthesis of **Ru**^{III}COO unless it was made with the procedure given below.

Sodium 2,2':6',2"-terpyridine-4'-carboxylate ([Na⁺]tpyCOO⁻). Following a modified literature procedure,⁴ 1.953 g 4'-chloro-2,2':6',2"-terpyridine (7.29 mmol), 0.261 g Pd(PPh₃)₂Cl₂ (0.372 mmol), and 7.8 mL of "Bu₃N were dissolved in 40 mL "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 °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 NH₄Cl (aq), and filtered through a fine frit. The filtrate was mixed with 29 mL of 2 M NaOH in H₂O, and heated at 50-60 °C for 5 hours, forming a white precipitate. The solution was cooled at -35 °C for 40 minutes, then filtered and washed with cold CH₂Cl₂ and diethyl ether. The fluffy white solid was dried *in vacuo*, giving 1.19 g of [Na⁺]tpyCOO⁻ (55% yield). ¹H NMR (D₂O) δ : 7.45 (t, 2H), 7.94 (t, 2H), 8.15 (d, 2H), 8.28 (s, 2H), 8.55 (d, 2H). ESI/MS⁺ (*m/z*): 278.3 [tpyCOOH+H]⁺, and ESI/MS⁻ (*m/z*): 276.1 [tpyCOO]⁻.

Ru(dipic)(tpyCOOH) (Ru^{II}COOH). Following the preparation of the unsubstituted derivative, 5 [(η^{6} -*cymene*)RuCl]₂(μ -Cl)₂ (0.505 g, 0.825 mmol) and [Na⁺]tpyCOO⁻ (0.494 g, 1.65 mmol) were dissolved in 15 mL of MeOH. The solution became bright purple, and was stirred for ~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 N₂ for one hour at 60 °C, and a black precipitate formed. The solution was cooled at -35 °C for 30 minutes, and filtered in air using a glass frit. The precipitate was dissolved in 11 mL of deionized H₂O, and 221 µL 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, 1863– 1864.



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 $\mathbf{Ru}^{II}\mathbf{COOH}$ (65% yield, Equation S1).

¹H NMR (DMF- d_7) δ : 7.82 (t, 2H_D), 8.03 (d, 2H_C), 8.25 (t, 2H_E), 8.58 (d, 2H_B), 8.65 (t, 1H_A), 9.20 (d, 2H_F), 9.44 (s, 2H_G). Peak assignments were made using COSY and NOESY NMR (Figure S1). ESI/MS⁺ (*m/z*): 544.3 [M]⁺, and ESI/MS⁻ (*m/z*): 543.2 [M–H]⁻, and 499.5 [M–H⁺– CO₂]⁻. UV-Visible spectrum in DMF: $\lambda_{max} = 531$ nm ($\varepsilon_{531} = 12,000 \pm 300 \text{ M}^{-1} \text{ cm}^{-1}$). In MeCN: $\lambda_{max} = 527$ nm ($\varepsilon_{527} \sim 13,000 \text{ M}^{-1} \text{ cm}^{-1}$). In MeCN, it is difficult to dissolve **Ru**^{II}COOH quantitatively due to its low solubility; based on the titrations with DBU discussed in Section SIII, [ε_{527} (**Ru**^{II}COOH)/ ε_{527} (**Ru**^{II}COO⁻)]_{MeCN} = 1.4 so ε_{527} (**Ru**^{II}COOH)_{MeCN} ~ 13,000 M⁻¹ cm⁻¹. Elemental analysis: Calculated for C₂₃H₁₄N₄O₆Ru•H₂O, C: 49.20, H: 2.87, N: 9.98; Found: C: 49.52, H: 2.90, N: 10.09. The presence of water in this sample was indicated by a broad peak in a ¹H NMR spectrum taken in dry DMF- d_7 .

["NBu₄⁺][Ru(dipic)(tpyCOO⁻)] (Ru^{II}COO⁻). To a solution of Ru^{II}COOH (0.125 g, 0.395 mmol) in 40 mL DMF, 500 μ L of 1 M tetra-*n*-butylammonium hydroxide ("Bu₄NOH) 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 Et₂O was required for precipitation). This solid was dissolved in CH₂Cl₂, and fine needle crystals were grown from slow diffusion of a 1:1 solution of Et₂O:*n*-hexane at 10 °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 Et₂O into a solution of Ru^{II}COO⁻ in MeCN at 10 °C.

¹H NMR (CD₃CN) δ : 7.33 (t, 2H), 7.63 (d, 2H), 7.84 (t, 2H), 8.19 (t, 1H), 8.27 (d, 2H), 8.54 (d, 2H), 9.10 (s, 2H). ESI/MS⁺ (*m*/*z*): 545.0 [M+2H]⁺, 242.2 [NBu₄]⁺, and ESI/MS⁻(*m*/*z*): 542.9 [M]⁻. UV-vis (CH₃CN): $\lambda_{\text{max}} = 520 \text{ nm} (\epsilon_{520} = 9400 \pm 400 \text{ M}^{-1} \text{ cm}^{-1})$; 587 nm (shoulder; $\epsilon_{587} = 7200 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$). $\epsilon_{527} = 9500 \pm 300 \text{ M}^{-1} \text{ cm}^{-1}$ was used to calculate ϵ_{527} for **Ru^{II}COOH**.

Elemental analysis: Calculated for $C_{39}H_{49}N_5O_6Ru \cdot H_2O$, C: 58.26, H: 6.40, N: 8.72; Found: C: 58.06, H: 6.31, N: 8.70. The small water peak in CD₃CN broadened out completely in the presence of **Ru^{II}COO**⁻, indicating that water could be in fast exchange with **Ru^{II}COO**⁻ and making it impossible to quantify how much water was in the sample.



Figure S1. ¹H COSY NMR with peak assignments for $\mathbf{Ru}^{II}\mathbf{COOH}$ in DMF- d_7 . Peaks can be fully assigned because coupling was seen between H_G and H_F in a NOESY NMR spectrum.

 $[N(tol)_{3}^{++}]PF_{6}^{-}$. Following literature precedent,^{2,6} 0.168 g AgPF₆ (0.664 mmol) and 0.195 g tritolylamine (0.678 mmol) were dissolved in 20 mL CH₂Cl₂ 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 g I₂ (0.169 mmol) in 9 mL *n*-hexane was added to the solution under a flow of N₂, and allowed to stir for 40 minutes and filtered. The volume was reduced to ~10 mL, and 50 mL *n*-hexane was added to precipitate a royal blue powder. After drying *in vacuo*, 0.250 g of $[N(tol)_{3}^{++}]PF_{6}^{-}$ 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^{III}COO. Following equation S2, a swivel frit apparatus with a fine filter was charged with **Ru^{III}COO**⁻ (0.190 g, 0.242 mmol) and ~15 mL CH₂Cl₂ was vacuum-transferred in. A solution of $[N(tol)_{3}^{++}]PF_{6}^{--}$ (0.160 g, 0.370 mmol) in ~5 mL CH₂Cl₂ was syringed into the solution over 1 min. The volume was reduced to ~2 mL, and the fine brown precipitate was collected and washed with CH₂Cl₂ and pentane. The solid was dried *in vacuo* for 30 minutes and then stored under N₂ at -35°C, giving 0.094 g of **Ru^{III}COO** (72% yield). ¹H NMR (CD₃CN): (all broad singlets) -37.9 (2H), -15.8 (2H), -2.4 (2H), 1.4 (2H), 7.3 (2H), 9.6 (1H), 14.6 (2H) (Figure S2). ESI/MS⁺ (*m/z*): 544.1 [M+H]⁺. Generating **Ru^{III}COO** *in situ* from titrations of **Ru^{II}COO**⁻ with [(*p*-(BrC₆H₄)₃N⁺⁺][B(C₆F₅)₄⁻] gave a UV-Visible spectrum with a shoulder at 435 nm (ε_{435} = 3400 ± 700 M⁻¹ cm⁻¹). Elemental analysis: Calculated for C₂₃H₁₄N₄O₆Ru•4H₂O, C: 44.88, H: 3.44, N: 9.11; Found: C: 45.18, H: 2.83, N: 8.82. The presence of water in this sample was indicated by a broad peak in a ¹H NMR spectrum taken in dry MeCN. Due to the thermal instability of **Ru^{III}COO**, further attempts at drying **Ru^{III}COO** only showed more decomposition by elemental analysis.



Figure S2. ¹H NMR of **Ru**^{III}**COO** in CD₃CN. In order to see the paramagnetic peaks, the delay time was set to 0.1 sec, the acquisition time to 0.1 sec, and ≥ 600 scans were obtained. The seven peaks for **Ru**^{III}**COO** are labeled, and a broad peak can be seen for H₂O at $\delta \approx 2$.

III. pK_a Determination for Ru^{II}COOH in MeCN

Titration of $\mathbf{Ru}^{II}\mathbf{COO}^{-}$ with the weak acid benzoic acid (PhCOOH, $pK_{a,PhCOOH} = 20.7 \pm 1000$ (0.1^7) forms **Ru^{II}COOH** and ("NBu₄⁺)(PhCOO⁻) in equilibrium. To a solution of 2mL of 0.033 mM Ru^{II}COO⁻ in MeCN was added 5.7 equiv (3 µL) of PhCOOH (0.126 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 Ru^{II}COOH and Ru^{II}COO⁻ were determined from the optical spectra using eq S3, where A is the absorbance at 527 nm over the course of the reaction and b = 1 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 $Ru^{II}COO^{-}$ quantitatively). Therefore, the calculated concentrations are $[Ru^{II}COO^{-}]_{calc} = \{A - A^{-}\}$ $\epsilon_{\text{RuCOOH}}[\text{Ru}^{\text{II}}]_{\text{total}}/(\epsilon_{\text{RuCOO-}} - \epsilon_{\text{RuCOOH}}), \text{ and } [\text{Ru}^{\text{II}}\text{COOH}]_{\text{calc}} = \{A - \epsilon_{\text{RuCOO-}}[\text{Ru}^{\text{II}}]_{\text{total}}\}/(\epsilon_{\text{RuCOOH}} - \epsilon_{\text{RuCOOH}})$ ε_{RuCOO-}).

$$A = b \left\{ \varepsilon_{RuCOOH} \left[Ru^{II} COOH \right] + \varepsilon_{RuCOO-} \left[Ru^{II} COO^{-} \right] \right\}$$
(S3)

$$\begin{bmatrix} Ru^{II} \end{bmatrix}_{total} = \begin{bmatrix} Ru^{II}COO^{-} \end{bmatrix}_{initial} = \begin{bmatrix} Ru^{II}COOH \end{bmatrix} + \begin{bmatrix} Ru^{II}COO^{-} \end{bmatrix}$$
(S4)

$$K_{eq} = \frac{\left[Ru^{II}COOH\right]\left[\left[{}^{n}NBu_{4}^{+}\right]\left[PhCOO^{-}\right]\right]}{\left[Ru^{II}COO^{-}\right]\left[PhCOOH\right]}$$
(S5)



7 10⁻⁶ 0 0.0004 0.0008 0.0012 [PhCOOH] (M)

upon addition of PhCOOH to a 0.033 mM solution of **Ru^{II}COO**⁻ in MeCN.



⁽⁷⁾ Acid-Base Dissociation Constants in Dipolar Aprotic Solvents, Chemical Data Series, No. 35; Izutsu, K. Ed.; Blackwell Scientific Publications: London, 1990.

[**Ru**^{II}**COOH**] is assumed to be equal to [(^{*n*}NBu₄⁺)(PhCOO⁻)], so K_{eq} (eq S5) can be calculated by plotting [**Ru**^{II}**COOH**]²/[**Ru**^{II}**COO**⁻] vs. [PhCOOH], giving $K_{eq} = (6.1 \pm 0.3) \times 10^{-3}$ (Figure S4). The p K_a of **Ru**^{II}**COOH** in MeCN equals {p $K_{a,PhCOOH} - [-log(K_{eq})]$ }, giving p K_a (**Ru**^{II}**COOH**) = 18.5 ± 0.1. This value was verified by titrations of 0.008 ± 0.002 mM **Ru**^{II}**COOH** with 4dimethylaminopyridine (DMAP) using a similar procedure, yielding $K_{eq} = 0.34 \pm 0.07$. Using the p K_a of DMAP-H⁺ (17.95 ± 0.03⁸), this gives p K_a (**Ru**^{II}**COOH**) = 18.4 ± 0.1.

Titrations of Ru^{II}COOH with a strong base

Titrations of 2 mL of a 0.0055 mM solution of $\mathbf{Ru}^{II}\mathbf{COOH}$ in MeCN with 0.17 equiv (5.5 µL) of the strong base DBU (0.334 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 $A_{527,initial}/A_{527,final}$ (the ratio of absorbances at the beginning and end of the titrations) of 1.4. Addition of the weak acid pentafluorophenol (in excess) regenerated $\mathbf{Ru}^{II}\mathbf{COOH}$ in 95 ± 2% yield ($\mathbf{Ru}^{II}\mathbf{COOH}$ decomposed in the presence of stronger acids).

⁽⁸⁾ Kaljurand, I.; Kütt, A.; Sooväli, L.; Rodima, T.; Mäemets, V.; Leito, I.; Koppel, I. A. J. Org. Chem., **2005**, 70, 1019 – 1028.

IV. Electrochemistry



Figure S5. Cyclic voltammogram for $\mathbf{Ru}^{II}\mathbf{COO}^{-}$ in MeCN (Cp₂Fe^{+/0} is 0.10 V vs. Ag/AgNO₃ on the scale given).

Table S1. Cyclic voltammet	ry for Ru^{II}COOH and Ru^I	^I COO ⁻ in MeCN and DMF. ^a
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	$E_{1/2}(V)$	$E_{\rm p,c} - E_{\rm p,a} ({\rm mV})$	$\Delta E_{1/2} \left(\mathbf{V} \right)^{b}$
Ru ^{II} COOH /MeCN	~0.21 °	100	
Ru ^{II} COO ⁻ /MeCN	0.047	84	{~0.16°
Ru ^{II} COOH /DMF	0.156	77	
Ru ^{II} COO ⁻ /DMF	0.026	73	{ 0.130

^{*a*} $E_{1/2}$ values in V vs. $Cp_2Fe^{+/0}$. ^{*b*} $\Delta E_{1/2} = E_{1/2}(\mathbf{Ru}^{II}\mathbf{COOH}) - E_{1/2}(\mathbf{Ru}^{II}\mathbf{COO}^{-})$. ^{*c*} Due to poor solubility, $E_{1/2}$ and $\Delta E_{1/2}$ are approximate.

The $\Delta E_{1/2}$ of 0.13 V implies that the p K_a s of the Ru^{II} and Ru^{III} species differ by 2.2 units since $\Delta pK_a = pK_{a,M(II)} - pK_{a,M(III)} = \Delta E_{1/2}/0.059$ V (from a thermochemical cycle²⁵).

V. X-ray Crystal Structure of [NBu₄⁺]Ru^{II}COO⁻

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 $0.10 \times 0.10 \times 0.04$ mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) 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° . Data collection was 99.1% complete to 67.00_{\circ} in θ . A total of 25463 reflections were collected covering the indices, $-18 \le h \le 24$, $-10 \le k \le 10$, $-24 \le l \le 24$. 6552 reflections were found to be symmetry independent, with an R_{int} of 0.0221. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P2₁/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 ${}^{n}Bu_{4}N^{+}$ cation (Figure S6). The positionally distorted *n*-butyl arm was modeled using partial occupancies.



Figure S6. ORTEP of $\mathbf{Ru}^{II}\mathbf{COO}^{-}$ shown with disordered ${}^{n}\mathbf{Bu}_{4}N^{+}$ cation, with ellipsoids at 50% probability.

Table 52. Crystal data and structure refiner	
Empirical formula	$C_{39}H_{49}N_5O_6Ru$
Formula weight	784.90
Temperature (K)	100(2)
Wavelength (Å)	1.54178
Crystal description/color	purple rod
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions (Å, °)	$a = 20.4473(10)$ $\alpha = 90$
	$b = 8.5753(4)$ $\beta = 95.704(2)$
	$c = 20.7023(11)$ $\gamma = 90$
Volume (Å ³)	3612.0(3)
Z, Calculated density (Mg/m^3)	4, 1.443
Absorption coefficient (mm ⁻¹)	3.956
F(000)	1640
Crystal size (mm ³)	$0.10 \times 0.10 \times 0.04$
Theta range for data collection (°)	4.29 to 68.24
Index ranges	$-18 \le h \le 24, -10 \le k \le 10, -24 \le l \le 24$
Reflections collected / unique	$25463 / 6552 [R_{int} = 0.0221]$
Completeness to theta	67.00° 99.1%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8578 and 0.6931
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6552 / 0 / 491
Goodness-of-fit on F^2	S = 1.055
Final R indices $[I > 2\sigma(I)]$	*R1 = 0.0334, wR2 = 0.0769
R indices (all data)	R1 = 0.0378, *wR2 = 0.0790
Largest diff. peak and hole $(e/Å^3)$	0.630 and -0.510

Table S2. Crystal data and structure refinement for [NBu₄⁺]**Ru**^{II}**COO**⁻

	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)
С7–ОЗ	1.289 (3)	N3-Ru1-N4	79.11 (9)
С7–О4	1.230 (3)		
C101	1.291 (3)		
C1–O2	1.236 (3)		

Table S3. Selected bond lengths (Å) and Angles (°) for $Ru^{II}COO^{-}$

VI. Thermochemical Cycle and BDFE Determination



Figure S7. Thermochemical cycle for Ru^{II}COOH CPET to Ru^{III}COO.

From above, $pK_a(\mathbf{Ru}^{II}\mathbf{COOH}) = 18.5 \pm 0.1$ and $E_{1/2}(\mathbf{Ru}^{III/II}\mathbf{COO}^{-}) = 0.047 \pm 0.020$ V.

Converting to free energies, and accounting for C_G (54.9 ± 1.0 kcal mol⁻¹, for H[•] \rightarrow H⁺ + e^- in MeCN):⁹

BDFE(**Ru**^{II}**COOH**) = $23.1(E_{1/2}) + 1.37(pK_a) + C_G$ BDFE(**Ru**^{II}**COOH**) = $81 \pm 1 \text{ kcal mol}^{-1}$

⁽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 Ru^{III}COO + ^tBu₃ArOH

The p K_a of ^{*t*}Bu₃ArOH is 17.8 in DMSO.¹⁰ p K_a values in MeCN are 10.2 ± 0.3 p K_a units higher than in DMSO,¹¹ so p K_a (^{*t*}Bu₃ArOH)_{MeCN} = 28.0 ± 0.3 in MeCN. The $E_{1/2}$ in MeCN vs. Cp₂Fe^{+/0} for ^{*t*}Bu₃ArOH^{+/0} is 1.18 ± 0.02 V.¹² The p K_a (**Ru**^{II}COOH) = 18.5 ± 0.1 (Section III) can be converted to p K_a (**Ru**^{III}COOH⁺) = 16.3 ± 0.5 using $\Delta pK_a = 2.2 \pm 0.5$.¹³ From Table S1, $E_{1/2}$ (**Ru**^{III/II}COO^{0/-}) = 0.047 ± 0.020 V.

The ground state free energies for the initial reactions of the stepwise pathways, proton transfer from 'Bu₃ArOH to **Ru**^{III}COO in MeCN (ΔG°_{PT}) and electron transfer from 'Bu₃ArOH to **Ru**^{III}COO in MeCN (ΔG°_{ET}), can be calculated with equations S6 and S7 below. Figure S8 illustrates that ΔG°_{ET} and ΔG°_{PT} are significantly larger than the barrier for the reaction, ΔG^{\ddagger}_{1} .

$$\Delta G^{\circ}_{PT} = 1.37[pK_a(^{t}Bu_3ArOH) - pK_a(Ru^{III}COOH^{+})] = +16.1 \pm 0.8 \text{ kcal mol}^{-1}$$
(S6)

$$\Delta G^{\circ}_{\rm ET} = -23.06[E(\mathbf{Ru}^{\mathbf{III/II}}\mathbf{COO}^{\mathbf{0/-}}) - E(^{t}\mathbf{Bu}_{3}\mathbf{ArOH}^{\mathbf{+/0}})] = +26.1 \pm 0.7 \text{ kcal mol}^{-1}$$
(S7)



Figure S8. A schematic energy surface (not to scale) for the reaction of $\mathbf{Ru}^{III}\mathbf{COO} + {}^{t}\mathbf{Bu}_{3}\mathbf{ArOH}$, showing that the ΔG° for the pathways with initial PT or ET are significantly larger than the ΔG^{\ddagger} for the CPET pathway.

⁽¹⁰⁾ Bordwell, F. G.; Cheng, J.-P. J. Am. Chem. Soc. 1991, 113, 1736-1743.

⁽¹¹⁾ Kolthoff, I. M.; Chantooni, Jr., M. K. J. Phys. Chem. 1976, 80, 1306-1310.

⁽¹²⁾ Osako, T.; Ohkubo, K.; Taki, M.; Tachi, Y.; Fukuzumi, S.; Itoh, S. J. Am. Chem. Soc. 2003, 11027–11033.

⁽¹³⁾ From Table S1, $\Delta E_{1/2} = 0.13$ V, which can be converted to $\Delta pK_a = 2.2 \pm 0.5$ using a thermochemical cycle: $\Delta pK_a = pK_{a,M(II)} - pK_{a,M(III)} = \Delta E_{1/2}/0.059$ V.

VIII. Reactivity Studies

Reaction of $Ru^{III}COO + {}^{t}Bu_3ArOH \rightarrow Ru^{II}COOH + {}^{t}Bu_3ArO^{\bullet}$

A solution of $\mathbf{Ru^{III}COO}$ (0.0234 mM) was generated by adding 150 µL of a 0.517 mM solution of $[(p\text{-BrC}_6\text{H}_4)_3\text{N}^+][B(C_6\text{F}_5)_4^-]$ to 0.0255 mM $\mathbf{Ru^{II}COO^-}$ in MeCN. This solution was titrated with 0.1 equiv (3.4 µL aliquots) of a 1.28 mM solution of ${}^{t}\text{Bu}_3\text{ArOH}$, and the change in absorbance was followed by UV-visible spectroscopy at 527 nm. A total of 1.9 equiv of ${}^{t}\text{Bu}_3\text{ArOH}$ were added, although the spectrum did not change significantly after 0.7 ± 0.1 equiv. The resulting spectrum is shown in Figure S9 (A) along with the known spectra of $\mathbf{Ru^{II}COOH}$ and ${}^{t}\text{Bu}_3\text{ArO}^{-14}$ Analysis of these spectra indicated a ca. 67% yield of $\mathbf{Ru^{II}COOH}$ (some decomposition was seen due to the long timescale of the titrations, and the source of the decomposition is discussed below). Figure S9 (B) shows the closeness of (solid line) the final reaction spectrum ($\varepsilon_{\text{reaction}}$) minus {0.67 × $\varepsilon_{tBu3ArO}$.} with (dot-dash line) the spectrum expected for a 67% yield of $\mathbf{Ru^{II}COOH}$, {0.67 × $\varepsilon_{tRuCOOH}$ }.



Figure S9. (A) UV-Visible spectra (in ε , M⁻¹ cm⁻¹) of the final reaction solution for **Ru**^{III}COO + 'Bu₃ArOH \rightarrow **Ru**^{II}COOH + 'Bu₃ArO' ($\varepsilon_{reaction}$, solid line); the spectrum of **Ru**^{II}COOH ($\varepsilon_{Ru(II)COOH}$, dot-dash line, --); and 'Bu₃ArO' ($\varepsilon_{tBu3ArO}$, dotted line,---). (B) Final reaction spectrum from (A) minus 0.67 × the spectrum of 'Bu₃ArO' (solid line, { $\varepsilon_{reaction} - (0.67 \times \varepsilon_{tBu3ArO})$ }, overlaid with 0.67 × the spectrum of **Ru**^{II}COOH (dot-dash line, {0.67 × $\varepsilon_{Ru(II)COOH}$ }).

⁽¹⁴⁾ Manner, V. W.; Markle, T. F.; Freudenthal, J.; Roth, J. P.; Mayer, J. M. Chem. Commun. 2008, 256–258.

In situ generation of Ru^{III}COO, and discussion of decomposition

A 0.0242 mM solution of $\mathbf{Ru^{III}COO}$ was generated *in situ* by adding 110 µL of 0.620 mM [$(p-BrC_6H_4)_3N^{++}$][B(C₆F₅)₄⁻] to a 0.0255 mM solution of $\mathbf{Ru^{II}COO^{-}}$ in MeCN, and the change in absorbance was followed by UV-visible spectroscopy. Reduction of this *in situ* **Ru^{III}COO** with 18 µL of a solution of 3.41 mM decamethylferrocene (Fc^{*}) in MeCN gave a spectrum which suggests 77% **Ru^{II}COO**⁻ and 23% **Ru^{II}COOH**. The formation of **Ru^{II}COOH** could be due to a decomposition pathway which involves **Ru^{III}COOH**⁺.

The reaction of $\mathbf{Ru}^{III}\mathbf{COOH}^+$ and ${}^{t}\mathbf{Bu}_3\mathbf{ArOH}$ has also been examined. To a solution of 0.023 mM $\mathbf{Ru}^{III}\mathbf{COOH}^+$ (generated *in situ* from $\mathbf{Ru}^{II}\mathbf{COOH} + [(p-BrC_6H_4)_3N^{*+}][B(C_6F_5)_4^-])$, 8 equiv of ${}^{t}\mathbf{Bu}_3\mathbf{ArOH}$ were added (to make [${}^{t}\mathbf{Bu}_3\mathbf{ArOH}]_{initial} = 0.182$ mM) and the change in optical spectra was monitored. This reaction occurred with $t_{1/2} \sim 2$ min, which is a much longer timescale than seen for the reaction of $\mathbf{Ru}^{III}\mathbf{COO}$ with ${}^{t}\mathbf{Bu}_3\mathbf{ArOH}$. The final spectrum of this reaction mixture had $\lambda_{max} = 500$ nm ($\varepsilon_{500} \sim 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), which is significantly different than the spectrum of $\mathbf{Ru}^{II}\mathbf{COOH}$. It is therefore possible that the less than quantitative yield of $\mathbf{Ru}^{II}\mathbf{COOH}$ in reaction (1) on the stopped-flow timescale (Figure S10) is due to some of the Ru(III) material being protonated and therefore reacting much more slowly with ${}^{t}\mathbf{Bu}_3\mathbf{ArOH}$.

IX. Stopped Flow Kinetics

The kinetics of the reaction of $\mathbf{Ru^{III}COO} + {}^{t}Bu_{3}ArOH$ in MeCN were measured under pseudo first-order conditions using an OLIS RSM-1000 stopped-flow. The appearance of $\mathbf{Ru^{II}COOH}$ (λ_{max} 527 nm) was observed within a second (Figure S10). The full spectra as a function of time were analyzed with SpecfitTM global analysis software. The reaction was shown to be first order in ${}^{t}Bu_{3}ArOH$ (Table S4, Figure S11), and first order in $\mathbf{Ru^{III}COO}$ (the same rate constant was obtained when varying [$\mathbf{Ru^{III}COO}$] from 0.0077 mM to 0.023 mM). Reactions were performed both with isolated $\mathbf{Ru^{III}COO}$, and with $\mathbf{Ru^{III}COO}$ generated *in situ* from $\mathbf{Ru^{II}COO^{-} + [(p-BrC_{6}H_{4})_{3}N^{*+}][B(C_{6}F_{5})_{4}^{-}]$, with no differences in the derived rate constants. The stopped-flow reactions give a yield of 77 ± 10%. These reactions were performed as a function of temperature, from 15 – 50 °C, in order to obtain the Eyring parameters shown in Figure S12.



Figure S10. (Left) Stack plot showing optical spectra of the reaction of $Ru^{III}COO$ (0.023 mM) with ^{*t*}Bu₃ArOH (0.21 mM); the growing absorbance is due to $Ru^{II}COOH$. (Right) Absorbance at 527.5 nm over 1 sec, superimposed with the pseudo first order fit.

[^t Bu ₃ ArOH] (mM)	$k_{\rm obs}~({\rm s}^{-1})$	[^t Bu ₃ ArOH] (mM)	$k_{\rm obs}~({\rm s}^{-1})$
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

Table S4. Pseudo first-order k_{obs} in MeCN at 298 K vs. [^tBu₃ArOH].





Figure S11. Pseudo first order plot for Figure S12. Eyring plot for the reaction of **Ru**^{III}COO + ^tBu₃ArOH, with a slope of k_{1H} = (2.3 ± 0.2) × 10⁴ M⁻¹s⁻¹. **Ru**^{III}COO with ^tBu₃ArOH from 15 - 50°C. $\Delta H^{\ddagger} = 3.5 \pm 1.4 \text{ kcal mol}^{-1} \text{ and } \Delta S^{\ddagger} = -27 \pm 5 \text{ cal}$ mol⁻¹ K⁻¹.

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Isotope effect

The kinetics of the reaction of $\mathbf{Ru}^{III}\mathbf{COO} + {}^{t}\mathbf{Bu}_{3}\mathbf{ArOD}$ were measured in MeCN with 0.2% CD₃OD 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 $\mathbf{Ru}^{III}\mathbf{COO}$ (0.017 mM) + ${}^{t}\mathbf{Bu}_{3}\mathbf{ArOH}$ (0.10 mM) was performed with 0.2% CH₃OH present. The derived second order rate constant of (2.1 ± 0.2) × 10⁴ M⁻¹ sec⁻¹ was within error of k_{1H} . The percent yield of products for the reaction of $\mathbf{Ru}^{III}\mathbf{COO} + {}^{t}\mathbf{Bu}_{3}\mathbf{ArOD}$ was within 5% of the control experiment.

[^t Bu ₃ ArOD] (mM)	$k_{\rm obs}$ (s ⁻¹)	[^t Bu ₃ ArOD] (mM)	$k_{\rm obs}~({\rm s}^{-1})$
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

Table S5. Pseudo first order k_{obs} in MeCN at 298 K vs. [^tBu₃ArOD].



Figure S13. Pseudo first order plot for **Ru**^{III}**COO** + ^{*t*}Bu₃ArOD in MeCN with 0.2% CD₃OD, with a slope of $k_{1D} = (3.0 \pm 0.4) \times 10^3 \text{ M}^{-1}\text{s}^{-1}$.

X. Reactivity with Ru^{III}COO + TEMPOH

Possible Stepwise Pathways for Ru^{III}COO + TEMPOH

The p K_a of TEMPOH is 31.0 ± 0.2 in DMSO.¹⁵ For O-H acids in MeCN, p K_a (MeCN) = 11.80 + 0.884 × p K_a (DMSO)¹⁶ to give p K_a (TEMPOH) = 39 ± 1 in MeCN. The $E_{1/2}$ for TEMPOH^{0/+•} in MeCN is 0.71 ± 0.02 V (converted from Ag/AgNO₃ to FeCp₂^{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 $\Delta G^{\circ}_{PT} = +31 \pm 2 \text{ kcal mol}^{-1}$ and $\Delta G^{\circ}_{ET} = +15.3 \pm 0.7 \text{ kcal mol}^{-1}$, both of which are significantly higher than $\Delta G^{\ddagger}_{TEMPOH}$ (10.3 ± 0.1 kcal mol}^{-1}).

Stopped-flow experiments

The kinetics of the reaction of $\mathbf{Ru^{III}COO}$ + TEMPOH in MeCN were measured under second order conditions using an OLIS RSM-1000 stopped-flow instrument, as described above. The appearance of $\mathbf{Ru^{II}COOH}$ (λ_{max} 527 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 $\mathbf{Ru^{III}COO}$ (the same rate constant was obtained when varying [$\mathbf{Ru^{III}COO}$] from 0.014 to 0.026 mM). The average second order rate constant is $k_{\text{TEMPOH}} = (2.0 \pm 0.6) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (Figure S14).

Table S6. Second order rate constants (k) in MeCN at 298 K vs. [TEMPOH].

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



Figure S14. Second order *k* versus [TEMPOH] for **Ru**^{III}**COO** + TEMPOH, giving an average second order rate constant of $k_{\text{TEMPOH}} = (2.0 \pm 0.6) \times 10^5 \text{ M}^{-1}\text{s}^{-1}$. 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**^{III}COO forms an O-H BDFE of 81 kcal mol⁻¹, or a BDE of ~86 kcal mol⁻¹, using the conversion of 4.6 kcal mol⁻¹ in MeCN.¹⁸

(a) [Ru^{IV}(bpy)₂(py)O]²⁺, 84; Moyer, B. A.; Meyer, T. J. J. Am. Chem. Soc. **1978**, 100, 3601– 3603; Bryant, J. R.; Mayer, J. M. J. Am. Chem. Soc. 2003, 125, 10351-10361. (b) [Fe^{III}{2,6bis(bis(2-pyridyl)methoxymethane)-pyridine}(OMe)]²⁺, 83.5; Goldsmith, C. R.; Jonas, R. T.; Stack, T. D. P. J. Am. Chem. Soc. 2002, 124, 83–96. (c) $[Mn^{III}(L)O]^{2-}$ (L = tris[(N²-tertbutylureaylato)-N-ethyl]aminato), 77 ([Mn^{IV}(L)O]⁻ and [Fe^{IV}(L)O]⁻, 110 and 115 but not isolated); Gupta, R.; Borovik, A. S. J. Am. Chem. Soc. 2003, 125, 13234-13242. (d) $[Fe^{IV}(NAd) \{phenyltris(1-mesitylimidazol-2-ylidene)borate)\}]OTf, 92.2 (BDFE = 87.6,$ converted to number for BDE¹⁸); Nieto, I.; Ding, F.; Bontchev, R. P.; Wang, H.; Smith, J. M. J. Am. Chem. Soc. 2008, 130, 2716-2717 and references therein. (e) [Mn^{III}{2,6-bis(bis(2pyridyl)methoxymethane)-pyridine}(OH)]²⁺, BDE = 82 kcal mol⁻¹ in MeCN: Goldsmith, C. R.; Cole, A. P.; Stack, T. D. P. J. Am. Chem. Soc. 2005, 127, 9904–9912. (f) $Mn^{VII}O^{4-}$, BDE = 80 kcal mol⁻¹ in H₂O; $[Mn_2(\mu-O)_2(1,10\text{-phenanthroline})_4]^{3+}$, BDE = 79 kcal mol⁻¹ in MeCN: Mayer, J. M. Acc. Chem. Res. **1998**, 31, 441–450. (g) $[Tp^{tBu,Me}-Cr^{IV}O(py'H)]^+$ $(Tp^{tBu,Me} = hydrotris(3$ *tert*-butyl-5-methylpyrazolyl)borate, py'H = 3-tert-butyl-5-methylpyrazole), BDE > 75.3 kcal mol⁻¹ in CD₂Cl₂: Qin, K.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. J. Am. Chem. Soc. **2002**, 124, 14008–14009. (h) $[Fe^{IV}(O)(N4Py)]^{2+}$ and $[Fe^{IV}(O)(Bn-tpen)]^{2+}$ (N4Py = N,N-bis(2pyridylmethyl)-*N*-bis(2pyridyl)methylamine, Bn-tpen = N-benzyl-N, N', N'-tris(2-pyridylmethyl)ethylenediamine) oxidize C-H bonds of cyclohexane (BDE \approx 99.3 kcal 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: 'Bu₂C=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) ^tBu₃ArO[•], 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 mechanism²¹ 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 CPET reactions that involve movement of H⁺ and e^- from one donor to one acceptor, that can be written XH + Y \rightarrow X + 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 'BuOOH + PhO' could be described as HAT in the forward direction but PCET in the reverse, or HAT from the perspective of '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 H⁺ + e^- (= H⁺) from dihydroanthracene have found that rate constants typically correlate well with the ΔG° of reaction, regardless of whether they would fit into an HAT or "PCET" category (*e.g.*, 'BuOO' vs. iron complexes).^{25,26} We have thus come to use the term HAT for any reaction where 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 H^+ and e^- "are transferred from the same chemical bond."²⁴ Under this specific

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⁽²⁰⁾ Cukier, R. I.; Nocera, D. G. Annu. Rev. Phys. Chem. 1998, 49, 337-369.

⁽²¹⁾ Stubbe, J.; Nocera, D. G.; Yee, C. S.; Chang, M. C. Y. Chem. Rev. 2003, 103, 2167.

⁽²²⁾ Mayer, J. M.; Hrovat, D. A.; Thomas, J. L.; Borden, W. T. J. Am. Chem. Soc. 2002, 124, 11142–11147.

⁽²³⁾ Costentin, C.; Evans, D. H.; Robert, M.; Savéant, J.-M.; Singh, P. S. J. Am. Chem. Soc. 2005, 127, 12490–12491.

⁽²⁴⁾ Meyer, T. J.; Huynh, M. H. V.; Thorp, H. Angew. Chem. Int. Ed. 2007, 46, 5284-5304.

⁽²⁵⁾ Mayer, J. M. Annu. Rev. Phys. Chem. 2004, 55, 363-390.

⁽²⁶⁾ Mayer, J. M. Acc. Chem. Res. 1998, 31, 441-450.

definition, the reactions of **Ru^{III}COO** with TEMPO-H and xanthene would be considered HAT even though the proton and electron are separated by 6.9 Å 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 H⁺ is lost from a σ bond in the molecular plane to form a radical in which the SOMO is of π symmetry.^{23,22,25,27} To classify reactions of ^{*t*}Bu₃ArOH 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°), then its reactions would be HAT. We hope that these examples illustrate the difficulties in applying a definition based on, for instance, whether H⁺ and *e*⁻ "are transferred from the same chemical bond."

We feel that it would be unfortunate to classify the reactions of **Ru^{III}COO** (or ^{*t*}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.

 ^{(27) (}a) Free Radicals Kochi, J. K., Ed.; Wiley: New York: 1973. (b) Mayer, J. M. Acc. Chem. Res. 1998, 31, 441–450.