

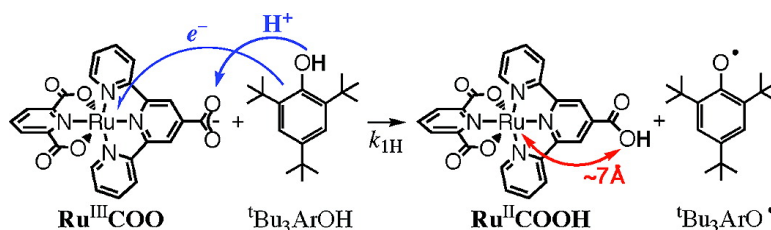
Communication

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## 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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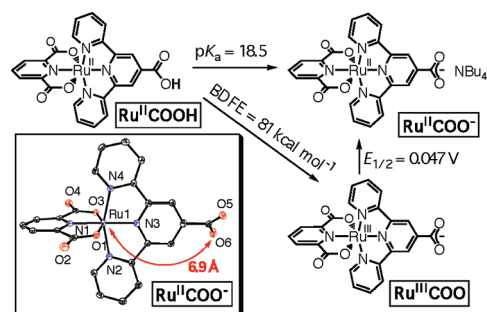
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Reactions that involve transfer of both a proton and an electron are important in a wide range of chemical and biochemical processes.<sup>1</sup> When the two particles transfer in a single step from a donor to an acceptor,  $\text{XH} + \text{Y} \rightarrow \text{X} + \text{YH}$ , such reactions are termed concerted proton–electron transfer (CPET) or, in certain cases, hydrogen atom transfer (HAT); the exact definition of these terms is a matter of continuing discussion.<sup>2</sup> This reactivity has been observed even when the proton and electron-accepting (or donating) sites are separated, as in reactions of phenols, ascorbate, and many transition metal species.<sup>1</sup> Within this framework, a CPET process has *four* relevant distances: the distances traveled by the electron and by the proton, and the separations of the  $\text{H}^+$  and  $e^-$  in the donor and in the acceptor. CPET reactions in which at least one of these distances is long have been implicated in photosystem II and class 1 ribonucleotide reductases,<sup>3</sup> and the distance dependence of pure electron transfer has long been studied.<sup>4</sup> We have reported HAT and CPET reactions of iron and ruthenium complexes with imidazole or related ligands, in which  $\text{H}^+$  transfers to or from a nitrogen that is three bonds and  $\sim 4 \text{ \AA}$  distant from the metal center where the redox change primarily occurs.<sup>5–7</sup> Even with this separation, the rate constants typically correlate well with those for related organic processes.<sup>1c,e</sup> This report describes studies of ruthenium terpyridine-4'-carboxylate complexes in which the basic site is  $\sim 6.9 \text{ \AA}$  removed from the metal center to probe how this distance affects CPET reactivity.<sup>8</sup>

The protonated ruthenium(II) complex,  $\text{Ru}^{\text{II}}(\text{pydic})(\text{tpyCOOH})$  ( $\text{Ru}^{\text{II}}\text{COOH}$ , Scheme 1), is prepared as a dark purple solid from  $[(\eta^6\text{-cymene})\text{RuCl}(\mu\text{-Cl})_2]$ , sodium 2,2':6',2''-terpyridine-4'-carboxylate ( $\text{tpyCOONa}$ ), followed by disodium pyridine-2,6-dicarboxylate ( $\text{Na}_2\text{pydic}$ ) and then aqueous  $\text{HCl}$ , in a modification of a related procedure.<sup>9,10</sup> Treating a DMF solution of  $\text{Ru}^{\text{II}}\text{COOH}$  with  ${}^n\text{Bu}_4\text{NOH}$  (1 M in MeOH) gives the deprotonated Ru(II) complex,  ${}^n\text{Bu}_4\text{N}[\text{Ru}^{\text{II}}(\text{pydic})(\text{tpyCOO})]$  ( $\text{Ru}^{\text{II}}\text{COO}^-$ ).  $\text{Ru}^{\text{II}}\text{COO}^-$  and  $\text{Ru}^{\text{II}}\text{COOH}$  have been characterized by  $^1\text{H}$  NMR, ESI/MS, UV–vis spectroscopy, elemental analyses, and an X-ray crystal structure of  $\text{Ru}^{\text{II}}\text{COO}^-$  (Scheme 1,  ${}^n\text{Bu}_4\text{N}^+$  not shown).<sup>10</sup> The structure shows an anion with the expected distorted octahedral geometry, containing two planar, meridional tridentate ligands. The carboxylate oxygen atoms (the site of proton binding) are  $6.9 \text{ \AA}$  from the ruthenium(II) center, and the carboxylate ( $\text{CO}_2$ ) plane is rotated  $53^\circ$  from its connected pyridine ring.

Cyclic voltammograms of  $\text{Ru}^{\text{II}}\text{COO}^-$  in MeCN show a chemically reversible oxidation at  $E_{1/2} = 0.047 \pm 0.02 \text{ V}$  vs  $\text{FcP}_2^{+/0}$ . Chemical oxidation of  $\text{Ru}^{\text{II}}\text{COO}^-$  ( $\lambda_{\text{max}} = 520 \text{ nm}$ ,  $\epsilon = 9400 \pm 400 \text{ M}^{-1} \text{ cm}^{-1}$ ) with  $[(p\text{-BrC}_6\text{H}_4)_3\text{N}^+][\text{B}(\text{C}_6\text{F}_5)_4^-]$ <sup>10</sup> yields zwitterionic  $\text{Ru}^{\text{III}}(\text{pydic})(\text{tpyCOO})$  ( $\text{Ru}^{\text{III}}\text{COO}$  [the carboxylate is

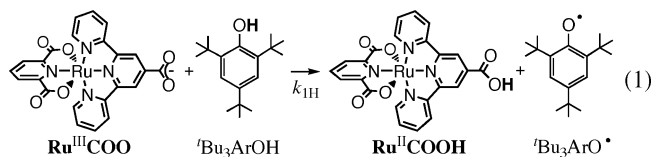
Scheme 1



anionic but the overall complex is neutral]) ( $\lambda_{\text{max}} = 435 \text{ nm}$ ,  $\epsilon = 3400 \pm 700 \text{ M}^{-1} \text{ cm}^{-1}$ ). Addition of dexamethylferrocene as a reductant regenerates  $\text{Ru}^{\text{II}}\text{COO}^-$  in 77% yield, along with 23%  $\text{Ru}^{\text{II}}\text{COOH}$  by UV–visible spectroscopy.  $\text{Ru}^{\text{III}}\text{COO}$  has been isolated from  $\text{Ru}^{\text{II}}\text{COO}^-$  plus  $[(p\text{-tol})_3\text{N}^+]\text{PF}_6^-$  and has been fully characterized. Its  $^1\text{H}$  NMR spectrum in  $\text{CD}_3\text{CN}$  shows seven paramagnetically shifted resonances (2:1:2:2:2:2:2) from  $\delta$  15 to  $-38 \text{ ppm}$ .<sup>10</sup> A typical in situ generated solution of  $\text{Ru}^{\text{III}}\text{COO}$  decomposes  $\sim 16\%$  over 5 h under a  $\text{N}_2$  atmosphere.

$\text{Ru}^{\text{II}}\text{COOH}$  and  $\text{Ru}^{\text{III}}\text{COO}$  differ by  $\text{H}^+ + e^-$  (a hydrogen atom). The O–H bond dissociation free energy (BDFE) for  $\text{Ru}^{\text{II}}\text{COOH}$  in MeCN is  $81 \pm 1 \text{ kcal mol}^{-1}$ , using the thermochemical cycle in Scheme 1 ( $\text{BDFE} = 23.1E_{1/2} + 1.37\text{p}K_a + C_G$ <sup>5d</sup>). The  $\text{p}K_a$  of  $\text{Ru}^{\text{II}}\text{COOH}$  in MeCN is  $18.5 \pm 0.1$ , determined by titrating  $\text{Ru}^{\text{II}}\text{COO}^-$  with benzoic acid ( $\text{p}K_a = 20.7$ <sup>11</sup>). This is a large BDFE, corresponding to a bond dissociation enthalpy of  $86 \text{ kcal mol}^{-1}$  (ignoring any entropic effects),<sup>5d</sup> making  $\text{Ru}^{\text{III}}\text{COO}$  among the thermodynamically strongest hydrogen atom acceptors that have been isolated.<sup>10,12</sup>

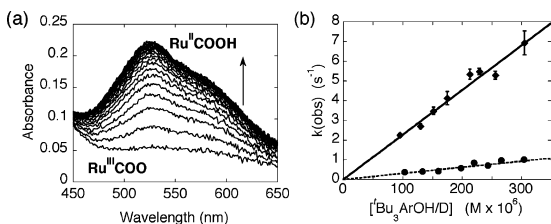
$\text{Ru}^{\text{III}}\text{COO}$  reacts rapidly with excess 2,4,6-tri-*tert*-butylphenol ( ${}^t\text{Bu}_3\text{ArOH}$ ) in MeCN to form  $\text{Ru}^{\text{II}}\text{COOH}$  and  ${}^t\text{Bu}_3\text{ArO}^\bullet$ , both in  $77 \pm 10\%$  yield based on UV–visible spectra (eq 1).<sup>10</sup> This reaction



is a net transfer of  $\text{H}^\bullet$ . On the basis of the BDFEs of  $\text{Ru}^{\text{II}}\text{COOH}$  and  ${}^t\text{Bu}_3\text{ArOH}$  ( $77 \pm 1 \text{ kcal mol}^{-1}$ ),<sup>13</sup> eq 1 has  $\Delta G^\circ_{1\text{H}} = -4 \text{ kcal mol}^{-1}$ . The reaction has been monitored under pseudo first-order conditions, following the growth of the strong absorbance of  $\text{Ru}^{\text{II}}\text{COOH}$  ( $\lambda_{\text{max}} = 527 \text{ nm}$ ). Stopped-flow rapid-scanning UV–vis spectrophotometry gives a second-order rate constant of  $k_{1\text{H}} = (2.3 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  (Figure 1;  $\Delta G^\ddagger_{1\text{H}} = 11.5 \pm 0.1 \text{ kcal}$

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**Figure 1.** Kinetic data for  $\text{Ru}^{\text{III}}\text{COO} + {}^t\text{Bu}_3\text{ArOH}$  in MeCN (eq 1): (a) optical spectra over 1 s showing the appearance of  $\text{Ru}^{\text{II}}\text{COOH}$ ; (b) plot of first-order  $k_{\text{obs}}$  versus  $[{}^t\text{Bu}_3\text{ArOH}]$  ( $\blacklozenge$ ,  $k_{\text{IH}}$ ) and versus  $[{}^t\text{Bu}_3\text{ArOD}]$  ( $\bullet$ ,  $k_{\text{ID}}$ ).

$\text{mol}^{-1}$ ).<sup>10,13</sup> Eyring analysis (288–323 K) gives  $\Delta H_{\text{IH}}^\ddagger = 3.5 \pm 1.4 \text{ kcal mol}^{-1}$  and  $\Delta S_{\text{IH}}^\ddagger = -27 \pm 5 \text{ cal mol}^{-1} \text{ K}^{-1}$  at 298 K. The analogous reaction with  ${}^t\text{Bu}_3\text{ArOD}$  is considerably slower,  $k_{\text{ID}} = (3.0 \pm 0.4) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  (Figure 1), indicating  $k_{\text{IH}}/k_{\text{ID}} = 7.7 \pm 1.2$ .<sup>14</sup>

There are three possible mechanistic pathways for reaction 1. The  $\text{H}^+$  and  $e^-$  could transfer from  ${}^t\text{Bu}_3\text{ArOH}$  to  $\text{Ru}^{\text{III}}\text{COO}$  in a single kinetic step (CPET) or by pathways with two separate kinetic steps. Initial electron transfer (to form the intermediates  $\text{Ru}^{\text{II}}\text{COO}^- + {}^t\text{Bu}_3\text{ArOH}^+$ ) and initial proton transfer (to form  $\text{Ru}^{\text{III}}\text{COOH}^+ + {}^t\text{Bu}_3\text{ArO}^-$ ) are ruled out on thermochemical grounds: the ground-state free energy changes of the initial steps,  $\Delta G_{\text{ET}}^\circ = +26.1 \pm 0.7 \text{ kcal mol}^{-1}$  and  $\Delta G_{\text{PT}}^\circ = +16.1 \pm 0.8 \text{ kcal mol}^{-1}$ ,<sup>10,13</sup> are larger than the observed free energy barrier,  $\Delta G_{\text{IH}}^\ddagger = 11.5 \pm 0.1 \text{ kcal mol}^{-1}$  (and  $\Delta G^\ddagger \geq \Delta G^\circ$ ). Thus reaction 1 proceeds via concerted transfer of  $\text{H}^+$  to the carboxylate and  $e^-$  to the ruthenium, in a single kinetic step. The primary  $k_{\text{IH}}/k_{\text{ID}}$  of 7.7 is also most consistent with such a CPET pathway, as  $k_{\text{H}}/k_{\text{D}}$  would likely be close to 1 for ET or for PT between O atoms.

$\text{Ru}^{\text{III}}\text{COO}$  also abstracts a hydrogen atom from the hydroxylamine TEMPOH (BDFE =  $66.5 \pm 0.5 \text{ kcal mol}^{-1}$ )<sup>5d,6,7</sup> to form the stable nitroxyl radical TEMPO $\cdot$  and  $\text{Ru}^{\text{II}}\text{COOH}$ , as determined by NMR and UV–visible spectroscopies. Stopped-flow kinetics experiments, as above, yielded  $k_{\text{TEMPOH}} = (2.0 \pm 0.6) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  ( $\Delta G_{\text{TEMPOH}}^\ddagger = 10.2 \pm 0.2 \text{ kcal mol}^{-1}$ ). Thermochemical arguments analogous to those given above indicate a similar concerted pathway for this reaction.<sup>10</sup> Preliminary experiments suggest that  $\text{Ru}^{\text{III}}\text{COO}$  also can remove  $\text{H}^\cdot$  from the weak C–H bond in xanthenes (BDE =  $75.5 \pm 2 \text{ kcal mol}^{-1}$ )<sup>15</sup> to form  $\text{Ru}^{\text{II}}\text{COOH}$  and bixanthenyl (by UV–vis and GC/MS).

The thermochemical affinity of  $\text{Ru}^{\text{III}}\text{COO}$  for  $\text{H}^\cdot$  will only lead to CPET reactivity if there is communication between the redox Ru and the basic oxygens 6.9 Å away. One crude measure of this communication or coupling is the thermochemical interaction between these sites, as indicated by the difference between the  $E_{1/2}$  values for  $\text{Ru}^{\text{II}}\text{COOH}$  versus deprotonated  $\text{Ru}^{\text{II}}\text{COO}^-$ :  $\Delta E_{1/2} = 0.13 \text{ V}$  in DMF (used because of low solubility in MeCN).<sup>16</sup> Analogous  $\Delta E_{1/2}$  values range from 0.3 to 0.5 V for Fe, Co, and Ru imidazole and biimidazole complexes, which each have three bonds and  $\pi$ -conjugation between the metal and basic site.<sup>17</sup> Additionally, there are Ru oxo/hydroxo complexes with  $\Delta E_{1/2} > 1.1 \text{ V}$ .<sup>1d,12a</sup> The small  $\Delta E_{1/2}$  for  $\text{RuCOO}(\text{H})$  could be a result of the long distance between the metal and carboxyl site or to decreased resonance stabilization of the carboxylate anion in  $\text{Ru}^{\text{III}}\text{COO}$  relative to, for instance, an imidazole ligand. Still, even though the thermochemical data imply less communication between the redox and basic sites, CPET reactivity is still facile.

In conclusion, we have designed and isolated three new complexes in a system with six bonds and a distance of 6.9 Å between the redox-active and basic sites. The small shift of the redox potential on protonation ( $\Delta E_{1/2}$ ) indicates that communication between the Ru and the carboxylate

group is decreased relative to other systems. Despite the separation and decreased communication,  $\text{Ru}^{\text{III}}\text{COO}$  readily removes a hydrogen atom from  ${}^t\text{Bu}_3\text{ArOH}$  and TEMPOH. Kinetic and thermochemical data indicate that this reaction proceeds by concerted transfer of  $\text{H}^+$  and  $e^-$  (CPET). These reactions appear to be similar to other  $\text{H}^+/e^-$  transfers to metal complexes, including cytochrome P450 compound I and iron biimidazolines, that have traditionally been termed hydrogen atom transfer (HAT).<sup>1d,5–7,10,18</sup> This study is the first to show that the separation in the acceptor can be as large as 6.9 Å without preventing such reactivity. Modifications of the terpyridine ligand are currently underway to increase the distance between the Ru and the basic site, to further probe the effect of redox center/basic site communication on CPET (HAT) rate constants.

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**Supporting Information Available:** Details for the syntheses, kinetic measurements, and crystal structure, and additional analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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