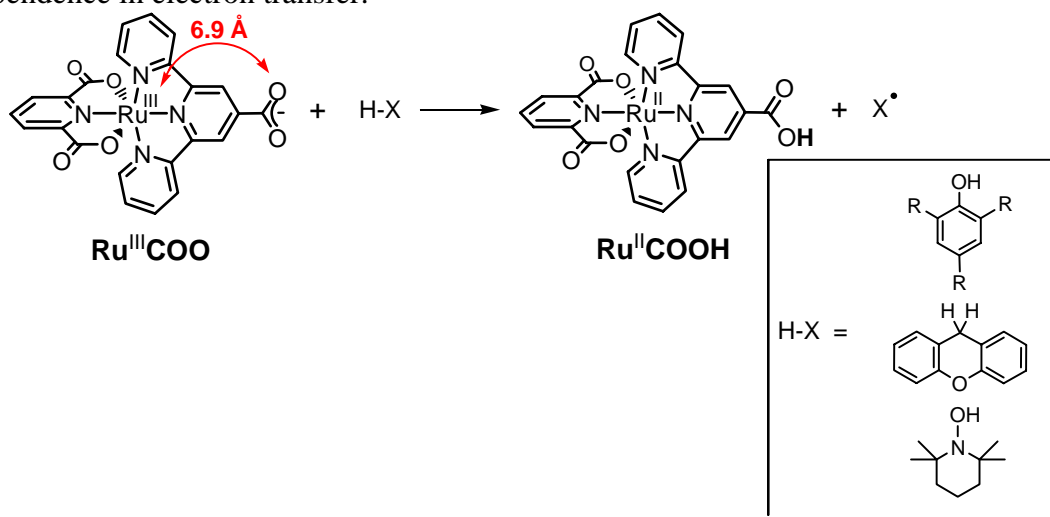


CONCERTED PROTON-ELECTRON TRANSFERS IN RUTHENIUM TERPYRIDINE CARBOXYLATE COMPLEXES: INCREASING THE DISTANCE BETWEEN THE METAL AND BASIC SITE

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Coupling electron transfer to proton transfer is key to converting solar energy to chemical fuels, and more generally in a wide range of chemical and biochemical processes. Electron transfers can also occur through hydrogen bonded interfaces: in solar cells, Graetzel's Ru(II) carboxy-polypyridyl sensitizers are anchored to a TiO₂ surface, and the protonation state of the carboxy groups greatly affects the electronic properties of the sensitized TiO₂ nanoparticles.¹ Although electron transfers have been thoroughly studied over many decades, the fundamentals of proton-coupled electron transfer (PCET) are still being worked out.

In order to understand how the distance between the electron and proton-accepting sites affects PCET reactivity, we have designed and synthesized a ruthenium complex with a terpyridine-4'-carboxylate ligand, in which there are six bonds between the redox-active Ru and the basic carboxylate. A crystal structure of the deprotonated Ru(II) complex, Ru^{II}COO⁻, shows a distance of 6.9 Angstroms between the metal and basic sites. The Ru(III) complex (Ru^{III}COO) has been isolated, and oxidizes hydrogen atom donors such as 2,4,6-tri-tert-butylphenol by removal of e⁻ and H⁺ to form 2,4,6-tri-tert-butylphenoxyl radical and Ru^{II}COOH (see Figure below). Thermochemical analysis indicates that this reaction occurs by *concerted* (one-step) transfer of the proton and electron despite the 6.9 Angstrom distance between Ru and the H⁺-accepting oxygen. To further understand how the reactivity has been affected by the distance dependence, current work is focused on further increasing the distance between the Ru and basic site by inserting a phenyl group between the terpyridine and the carboxylate. This is the first study to address the distance dependence of the proton and electron accepting sites in PCET reactivity, and may serve as a compliment to the extensive studies of distance dependence in electron transfer.



(1) Angelis, F. D.; Fantacci, S.; Selloni, A.; Nazeeruddin, M. K.; Graetzel, M. *J. Am. Chem. Soc.* **2007**, *119*, 14156–14157.