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Reversible Electrochemical Generation of a Rhodium(II) Porphyrin: Thwarting Disproportionation with Weakly Coordinating Anions

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We report electrochemical generation of a stable Rh(II) porphyrin ($Rh^{II}(F_{28}TPP)$) from a four-coordinate Rh(I) precursor $[Rh^{I}(F_{28}TPP)]^{-}$ dissolved in weakly coordinating electrolyte solutions. This work provides the first example of an unambiguously reversible one-electron electrochemical oxidation of a Rh^{I}(por), and demonstrates that electrochemical oxidation can be performed under conditions that are compatible with alkane activation. These studies begin to classify those media capable of supporting a stable Rh^{II}(por), and those that induce disproportionation.

Selective functionalization of saturated C−H bonds under mild conditions remains a significant challenge in organometallic chemistry.[1,2] Sterically hindered Rh(II) porphyrins (Rh^{II}(por)) are one class of late transition metal complexes that have been shown to activate light alkanes, particularly methane, reversibly at room temperature and low (1 atm) pressure.[3−5] Of late, we have shown that electron-deficient rhodium porphyrins, such as $Rh^{II}(F_{28}TPP)$, can so stabilize the Rh(I) oxidation state that methylrhodium complexes can act as electrophiles in alkyl-transfer reactions, providing a route to direct alkane functionalization at low temperature.[6]

Exploitation of Rh(II) porphyrins in catalytic alkane functionalization schemes is hindered by the propensity of these species to undergo rapid irreversible reactions to form catalytically incompetent products. Kadish et al. have argued that this instability is due to dimerization of the Rh^{II}(por) metalloradical that occurs upon loss of an axial ligand,[7−12] but Saveant et al. have described it in terms of a disproportionation reaction that is coupled to the loss of a ligand from an electrogenerated Rh(II) intermediate.[13,14] Wayland has suggested that undesirable disproportionation of certain Rh^{II}(por) to Rh^{I}(por) and Rh^{III}(por) is driven by the favorable thermodynamics associated with binding an axial ligand to the Rh(III) product.[15,16] Finally, Collman and Boulatov have recently provided some clarification by showing how triethylphosphine ligands can be used to stabilize the Rh(II) state of octaethylporphyrin.[17]

We ultimately wished to determine the role of axial ligation on the stability and reactivity of $Rh^{II}(F_{28}TPP)$. Given this goal, it seemed logical to determine first the electrochemical behavior of $Rh^{II}(F_{28}TPP)$ in the absence of strong ligands. This seemed essential if we were to interpret chemical steps coupled to electron-transfer events in more complex media. We report here the electrochemical generation of $Rh^{II}(F_{28}TPP)$ from four-coordinate $[Rh^{I}(F_{28}TPP)]^{-}$ dissolved in weakly coordinating electrolyte solutions. Our results clearly demonstrate that a stable Rh^{II}(por) can be generated electrochemically from a stable Rh^{I}(por) precursor. Furthermore, this approach has enabled us to determine the formal potential for the $Rh^{II}(F_{28}TPP)/[Rh^{I}(F_{28}TPP)]^{-}$ couple where the rhodium is nominally four-coordinate in both oxidation states. We believe this value will prove to be a benchmark for interpreting more complicated reaction mechanisms featuring rhodium porphyrins.

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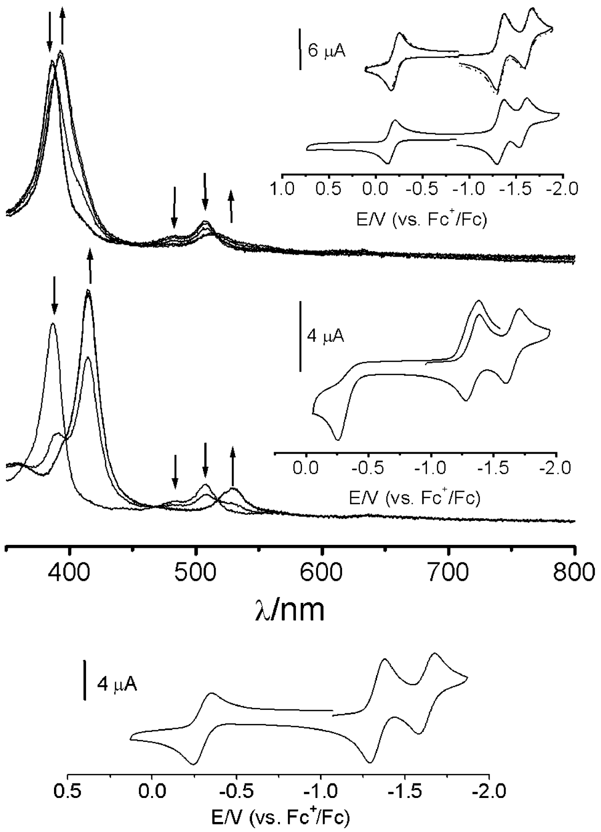

Figure 1. Cyclic voltammograms and thin layer spectroelectrochemistry of the oxidation of $Rh^{I}(F_{28}TPP)^-$ in DFB containing 0.1 M $TBAPF_6$ (top) and in DFB containing 0.1 M TBACl (middle). Cyclic voltammogram in DFB containing 1.4 M THF and 0.1 M $TBAPF_6$ (bottom). CV experimental conditions: glassy carbon working electrode, silver wire pseudo reference electrode, Pt counter electrode, sweep rate = 100 mV/s.

Cyclic voltammograms of the cobaltocenium salt of $[Rh^{I}(F_{28}TPP)]^-$ ($[Co^{III}(Cp)_2]^+[Rh^{I}(F_{28}TPP)]^-$, **1**) dissolved in 1,2-difluorobenzene[18] (DFB) are shown in Figure 1. The synthesis of **1** has been reported previously.[6] In the presence of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (Figure 1, top) three reversible electrochemical processes were observed: $Rh^{II}(F_{28}TPP)/[Rh^{I}(F_{28}TPP)]^-$, -0.214 V; $[Co^{III}(Cp)_2]^+/[Co^{II}(Cp)_2]$, -1.336 V; and $[Rh^{I}(F_{28}TPP)]^-/[Rh^{I}(F_{28}TPP)]^{-2}$, -1.629 V. The $[Co^{III}(Cp)_2]^+/[Co^{II}(Cp)_2]$ couple serves as a convenient one-electron internal reference that is present at the same concentration as $[Rh^{I}(F_{28}TPP)]^-$. We measure the formal potential for the $[Co^{III}(Cp)_2]^+/[Co^{II}(Cp)_2]$ couple to be -1.336 V vs the $[Fe^{III}(Cp)_2]^+/[Fe^{II}(Cp)_2]$ couple in DFB and -1.325 V in benzene, values that are in good agreement with that determined in acetonitrile (-1.35 ± 0.01 V) by Stojanovic and Bond.[19]

The voltammetric wave at -0.214 V in Figure 1 (top) can be definitively assigned to the $Rh^{II}(F_{28}TPP)/[Rh^{I}(F_{28}TPP)]^-$ couple. The one-electron response is nearly reversible and is not coupled to any other reactions on this time scale. Digital simulation, shown as the dashed line in Figure 1, is consistent with the assignment of this electrode reaction as a one-electron process.[20,21] Spectroelectrochemical data gathered for this process also show clean generation of $Rh^{II}(F_{28}TPP)$ from $[Rh^{I}(F_{28}TPP)]^-$; three isosbestic points are observed, and the transition wavelengths for $Rh^{II}(F_{28}TPP)$ are identical to those for photochemically generated $Rh^{II}(F_{28}TPP)$ in the same media.

Electrochemical and redox titration experiments were also conducted in benzene. Because of the less polar nature of this solvent, a higher concentration of electrolyte (1.0 M tetrahexylammonium hexafluorophosphate, $THAPF_6$) was required to overcome solution resistance problems. Reversible behavior for the $Rh^{II}(F_{28}TPP)/[Rh^{I}(F_{28}TPP)]^-$ couple (-0.161V) in benzene was observed. Titration of a benzene solution of **1** (1.0 M $THAPF_6$) with ferrocenium hexafluorophosphate was followed by monitoring the UV−vis spectrum in the Soret region. A plot of moles of $Rh^{II}(F_{28}TPP)$ produced vs moles of added ferrocenium gave a straight line with a slope of 1.05, verifying the one-electron nature of this oxidation. Finally, the absorbance spectrum for the oxidized product is again indistinguishable from photochemically generated $Rh^{II}(F_{28}TPP)$ dissolved in a benzene solution containing 1.0 M $THAPF_6$.

In contrast to the reversible electrochemical oxidation of $[Rh^{I}(F_{28}TPP)]^-$ seen when $TBAPF_6$ is the supporting electrolyte, $TBAClO_4$ and TBACl electrolyte solutions lead to more complex behavior. The voltammogram in Figure 1 (middle) (0.1 M TBACl, DFB) shows a single (apparently) irreversible oxidation at approximately -0.34 V. In addition, a new reduction peak that is not present in the initial ramp toward negative potentials appears only after the process or processes associated with the oxidation at -1.27 V. This response is consistent with what is expected if the following equilibrium is coupled to the initial electron-transfer event.

$$2Rh^{II}(por) + X^- \rightleftarrows Rh^{III}(por)X + Rh^{I}(por)^- \qquad (1)$$

When the equilibrium in eq 1 lies far to the right, disproportionation driven by chloride generates Rh(III) and Rh(I) species, and the latter is rapidly oxidized to give a net oxidation by two electrons. It is clear that the interaction between $[Rh^{III}(F_{28}TPP)]^+$ and Cl^- in this solvent is significant, and for our purposes undesirable, because it is associated with the rapid depletion of $Rh^{II}(F_{28}TPP)$. Verification that $[Rh^{I}(F_{28}TPP)]^-$ and $[Rh^{III}(F_{28}TPP)]^+$ are the stable oxidation states of this rhodium porphyrin in DFB solutions containing chloride is again obtained by spectroelectrochemistry. Oxidation of $[Rh^{I}(F_{28}TPP)]^-$ generates a single new species; the UV−vis spectrum is consistent with that of $[Rh^{III}(F_{28}TPP)]^+$. Likewise, addition of TBACl to a $Rh^{II}(F_{28}TPP)$ solution (DFB, 0.1 M $TBAPF_6$) results in conversion of $Rh^{II}(F_{28}TPP)$ to $[Rh^{III}(F_{28}TPP)]^+$ and $[Rh^{I}(F_{28}TPP)]^-$.

The cyclic voltammetry is more interesting (and more complex) when neutral donor ligands, such as water or THF, are present in DFB solutions (0.1 M $TBAPF_6$). Cyclic voltammograms of such solutions still exhibit a reversible

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$Rh^{II}(F_{28}TPP)/[Rh^{I}(F_{28}TPP)]^{-}$ couple at nearly the same potential as that observed in the absence of the added ligand (Figure 1, bottom). The chemically or electrochemically generated $Rh^{II}(F_{28}TPP)$ persists for hours under these conditions, indicating a thermodynamic, rather than merely kinetic, stability of this oxidation state in the presence of these ligands. In contrast, under the same conditions, pyridine and benzonitrile induce disproportionation when present at concentrations equivalent to that of the rhodium complex. Taken together, these data show that select sets of potential nucleophiles are compatible with stable Rh^{II}(por) species, and that disproportionation can be driven by either ion-pairing or coordination events.

This work provides the first example of an unambiguously reversible one-electron electrochemical oxidation of a Rh^{I}(por), and demonstrates that electrochemical oxidation can be performed under conditions that are compatible with alkane activation. In addition, these studies begin to classify those media capable of supporting a stable Rh^{II}(por), and those that induce disproportionation; in DFB and benzene, the weakly coordinating counterion PF_6^- supports the Rh(II) oxidation state, whereas Cl^- and ClO_4^- do not. Although no detailed mechanistic information regarding the affinities of various counterions for $Rh^{III}(F_{28}TPP)^+$ can yet be derived from this work, use of eq 1 in conjunction with formal potentials for the four-coordinate species does provide a thermodynamic framework for our ongoing mechanistic studies of ligand exchange reactions convolved with $Rh^{II}(F_{28}TPP)$-based alkane functionalization strategies.

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Supporting Information Available: Details regarding (1) materials and methods, (2) determination of formal redox potentials, (3) parameters for cyclic voltammetric digital simulation, and (4) solvent and counterion effects upon voltammetry. This material is available free of charge via the Internet at http://pubs.acs.org.

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