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# Cobalt *meso*-Tetrakis(*N*-methyl-4-pyridiniumyl)porphyrin Becomes a Catalyst for the Electroreduction of $O_2$ by Four Electrons When $[(NH_3)_5Os]^{n+}$ ($n = 2, 3$) Groups Are Coordinated to the Porphyrin Ring

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In a series of recent reports[1−9] evidence has been offered to support the proposal that coordination of $(NH_3)_5Ru^{2+}$ groups to ligand sites introduced on the *meso* positions of certain cobalt porphyrins enhances their abilities to act as electrocatalysts for the reduction of $O_2$ to $H_2O$. The enhancement is believed to be the result of back-bonding by the Ru(II) centers into the pendant ligands and the cobalt porphyrin to which they are linked.[3−9] The catalytic mechanism that has been proposed[5] leaves the coordinated Ru centers in their +2 oxidation state as the $O_2$ molecule coordinated to the Co(II) center of the porphyrin in the activated complex is reduced via electron-transfer from the electrode surface. Intramolecular electron-transfer from the Ru(II) centers to the coordinated $O_2$ is not consistent with the experimental data.[3,5] To obtain additional information about the importance of back-bonding in enhancing the catalytic activity of these cobalt porphyrins, we sought to use Os(III) in place of Ru(II) as the source of the back-donation. Os(III), unlike Ru(III), exhibits substantial back-bonding capabilities,[10−12] but Os(III) is a much weaker thermodynamic reductant than Ru(II).[13] Thus, we reasoned that any increase in the catalytic activity of cobalt porphyrins that might result from the attachment of Os(III) centers to the porphyrin ring could be confidently attributed to back-bonding effects free of any contributions from intramolecular electron-transfer. The results of experiments designed to test this speculation are described in this report.

## Experimental Section

**Materials.** *meso*-Tetrakis(*N*-methyl-4-pyridiniumyl)porphyrin tosylate was obtained from Aldrich. Cobalt(II) was inserted into the ring using a published procedure.[14] Stock solutions of the porphyrin were prepared in aqueous acid (0.05 M $CF_3SO_3H$). The Co(II) was air-oxidized to Co(III) in the stock solution. $OsO_4$ (Aldrich) was the starting material used to prepare $[Os(NH_3)_5(OTf)](OTf)_2$ (OTf = trifluoromethanesulfonate) using published procedures[15−17] except that the microcrystalline final product was separated by centrifugation instead of filtration. Other chemicals were reagent grade and were used as received. Laboratory distilled water was further purified by passage through a purification train (MilliQ Plus).

**Apparatus and Procedures.** Electrochemical measurements were conducted with conventional cells and instrumentation. Edge plane pyrolytic graphite electrodes (Union Carbide) were mounted on stainless steel rotation shafts using heat shrinkable tubing. Their surfaces were roughened by abrasion with moist 600 grit SiC paper. All potentials are reported with respect to a saturated calomel electrode. Experiments were conducted at the ambient laboratory temperature, 22 ± 2 °C.

## Results

**Formation of an Adduct of $(NH_3)_5Os^{2+}$ with Cobalt *meso*-Tetrakis(*N*-methyl-4-pyridiniumyl)porphyrin ($[CoP(py\text{-}CH_3)_4]^{4+}$).** There is extensive previous literature on the coordination of $(NH_3)_5Os^{2+}$ groups to $\pi$-acid ligands.[12,18−28] Most of the coordination chemistry was carried out in non-aqueous solvents in the presence of a large excess of the ligand and a metallic reducing agent (Zn or Mg). However, there have been a few reports of the formation of complexes in aqueous solution.[26−28] In these cases, the source of Os(II) was $[Os(NH_3)_5(OTf)](OTf)_2$, which was reduced with Zn(Hg). The immediate product of the reduction in aqueous media was assumed to be $[Os(NH_3)_5(OH_2)]^{2+}$, but Call et al. have recently suggested that another, yet to be identified, intermediate is present in such solutions and participates in complex formation reactions.[29] We attempted to coordinate $(NH_3)_5Os^{2+}$ groups to the water-soluble porphyrin, $[CoP(py\text{-}CH_3)_4]^{4+}$, by adding excesses of an aqueous solution of $[Os(NH_3)_5(OTf)](OTf)_2$ that had been reduced with Zn(Hg) to a deaerated solution of the oxidized porphyrin, $[CoP(py\text{-}CH_3)_4]^{5+}$, in 0.05 M $CH_3SO_3H$. The oxidized porphyrin was rapidly reduced to $[CoP(py\text{-}CH_3)_4]^{4+}$ by the excesses of Os(II) that were present. The resulting mixture was allowed to react for 30−60 min. Changes in the color of the solution indicated that a reaction was occurring. A freshly roughened EPG electrode was dipped into the reaction solution after various reaction times. The spontaneous, irreversible adsorption of the porphyrin onto the EPG surface[9] produced a coating that was examined by cyclic voltammetry after the electrode was removed, washed, and transferred to a pure supporting electrolyte solution. Shown in Figure 1 are the results of a series of such experiments in which the ratio of Os(II) to the cobalt porphyrin in the reaction solution was gradually increased. The voltammogram in Figure 1A is the response from the bare EPG electrode. It contains only the broad feature near +0.30 V which arises from the reduction and oxidation of the graphite surface. In Figure 1B is shown the response obtained after the electrode was dipped in a 0.35 mM solution of [CoP(py-

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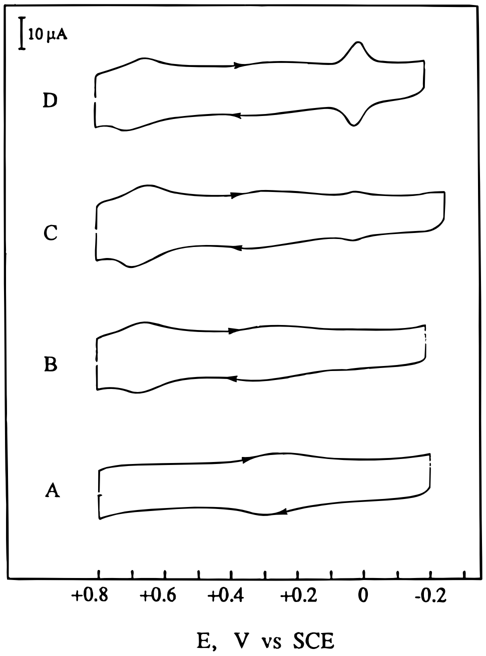

**Figure 1.** Cyclic voltammograms of EPG electrodes (0.32 $cm^2$) in pure supporting electrolyte, 0.125 M $HClO_4$: (A) freshly polished electrode; (B) freshly polished electrode that was dipped into a 0.35 mM solution of $[CoP(py\text{-}CH_3)_4]^{5+}$ for 10 min, washed, and transferred to the pure supporting electrolyte; (C) as in B except the electrode was dipped for 10 min into a solution containing 0.35 mM $[CoP(py\text{-}CH_3)_4]^{4+}$, 0.70 mM $[Os(NH_3)_5(OH_2)]^{2+}$, and 0.35 mM $[Os(NH_3)_5(OH_2)]^{3+}$ that had been allowed to react for 30 min; (D) as in C except the dipping solution contained 1.40 mM $[Os(NH_3)_5(OH_2]^{2+}$. Scan rate: 50 mV $s^{-1}$. The quantity of porphyrin spontaneously adsorbed on each electrode was ca. 1.7 × $10^{-10}$ mol $cm^{-2}$.

$CH_3)_4]^{5+}$ before transfer to the 0.125 M $HClO_4$ supporting electrolyte. The new feature centered at 0.65 V corresponds to the Co(III)/Co(II) couple of the adsorbed porphyrin.[30] The response in Figure 1C was obtained when the EPG electrode was dipped into a solution containing 0.35 mM $[CoP(py\text{-}CH_3)_4]^{4+}$, 0.70 mM Os(II) and 0.35 mM Os(III) (produced by the reduction of $[CoP(py\text{-}CH_3)_4]^{5+}$) which had been allowed to react for 30 min. A new, reversible feature can be discerned in the voltammogram near 0.05 V. When this experiment was repeated with a reaction solution that contained 0.35 mM $[CoP(py\text{-}CH_3)_4]^{4+}$, 1.40 mM Os(II), and 0.35 mM Os(III), the response shown in Figure 1D was obtained. The feature near 0.05 V is now very prominent. It must originate from an Os couple that is bound to the electrode surface by the spontaneously adsorbing cobalt porphyrin because no such feature resulted when the electrode was dipped into an identical solution of Os(II) that contained none of the porphyrin. Thus, the Os(II) complex must be coordinated to the adsorbed porphyrin. The formal potential of the $[Os(NH_3)_5(OH_2)]^{3+/2+}$ couple in water is −0.97 V vs SCE.[31] The much more positive potential of the response from what we presume to be an $(NH_3)_5Os^{III}/(NH_3)_5Os^{II}$ couple in Figure 1D is consistent with coordination of the Os center to a $\pi$-accepting ligand.[17,32] The position of the couple in Figure 1D is not far from the formal potential estimated by Harman and co-workers for the $[(NH_3)_5Os(\eta^2\text{-pyrrole})]^{3+/2+}$ couple in acetonitrile (−0.13 V vs SCE).[12,23] In the case of the pyrrole complex, the voltammetry is irreversible in that no cathodic wave is observed during the reductive half of the voltammetric cycle.[33] However, reversible behavior is obtained with several derivatives of pyrrole.[20] Thus, we assign the reversible couple near 0.05 V in Figure 1D to an $[(NH_3)_5OsL]^{3+/2+}$ couple where L is the porphyrin ring and $\eta^2$-coordination of the $(NH_3)_5Os^{2+}$ center to a double bond is likely. $\eta^2$-Coordination of the $(NH_3)_5Os^{2+}$ to the *N*-methylpyridine ring is also a possibility,[22] but electrochemical oxidation of the corresponding $(NH_3)_5Os(N\text{-methylpyridinium})^{3+}$ complex is irreversible and leads to rapid loss of the ligand from the osmium coordination sphere.[22] The reversible and stable voltammetric response in Figure 1D therefore seems much more likely to correspond to $\eta^2$-coordination of the $(NH_3)_5Os$ centers to the porphyrin ring.

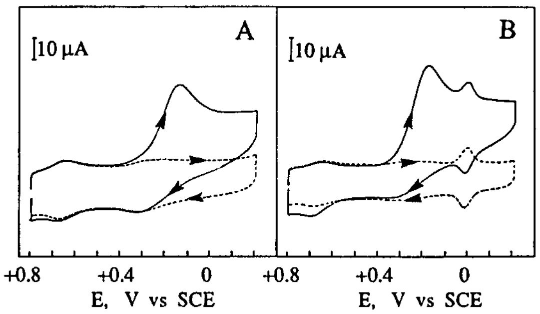

**Figure 2.** Cyclic voltammograms for the reduction of $O_2$ at EPG electrodes as catalyzed by ca. 1.7 × $10^{-10}$ mol $cm^{-2}$ of adsorbed (A) $[CoP(py\text{-}CH_3)_4]^{4+}$ or (B) $(NH_3)_5Os{-}[CoP(py\text{-}CH_3)_4]$ containing ca. 2.3 $Os(NH_3)_5$ groups per porphyrin ring: solid lines, air-saturated solution; dashed lines,: argon-saturated solution. Supporting electrolyte: 0.125 M $HClO_4$. Scan rate: 50 mV $s^{-1}$.

The magnitude of the peak currents of the reversible couple near 0.05 V in Figure 1D did not increase significantly when the experiment was repeated with higher concentrations of Os(II) in the reaction mixtures. The ratio of the areas for the voltammetric responses from the Co(III)/Co(II) and the Os(III)/Os(II) couples was used to estimate the average number of Os(II) centers coordinated to each adsorbed cobalt porphyrin. In three replicate experiments the average ratio of Os to Co was 2.3 ± 0.3. Because the exact composition of the species present in the reaction mixture from which the cobalt porphyrin was adsorbed was unknown, the molecules on the electrode surface could include some to which fewer than two, and others to which more than two, Os(II) centers were coordinated. Attempts to prepare purified samples of the Os(II)−cobalt porphyrin complex are currently in progress. However, it proved instructive to test the catalytic activity of the electrode coatings obtained by adsorption from the reaction solution before its components were separated.

**Catalysis of the Electroreduction of $O_2$ by Adsorbed $(NH_3)_5Os{-}[CoP(py\text{-}CH_3)_4]$.** The effect of the coordination of $(NH_3)_5Os$ groups to the cobalt porphyrin on its electrocatalytic activity toward the reduction of $O_2$ was examined by cyclic and rotating disk voltammetry. The solid curve in Figure 2A is a cyclic voltammogram for the reduction of $O_2$ at an EPG electrode on which $[CoP(py\text{-}CH_3)_4]^{4+}$ was adsorbed. (The dashed curve is the response obtained in the absence of $O_2$.) The reduction of $O_2$ at the bare EPG electrode begins near −0.4 V, so the adsorbed porphyrin catalyzes the reduction of $O_2$ at much more positive potentials, but the reduction proceeds only to $H_2O_2$.[30,34]

In Figure 2B are shown the analogous responses obtained at an electrode on which the $(NH_3)_5Os{-}[CoP(py\text{-}CH_3)_4]$ complex was adsorbed. The catalyzed reduction of $O_2$ begins at about

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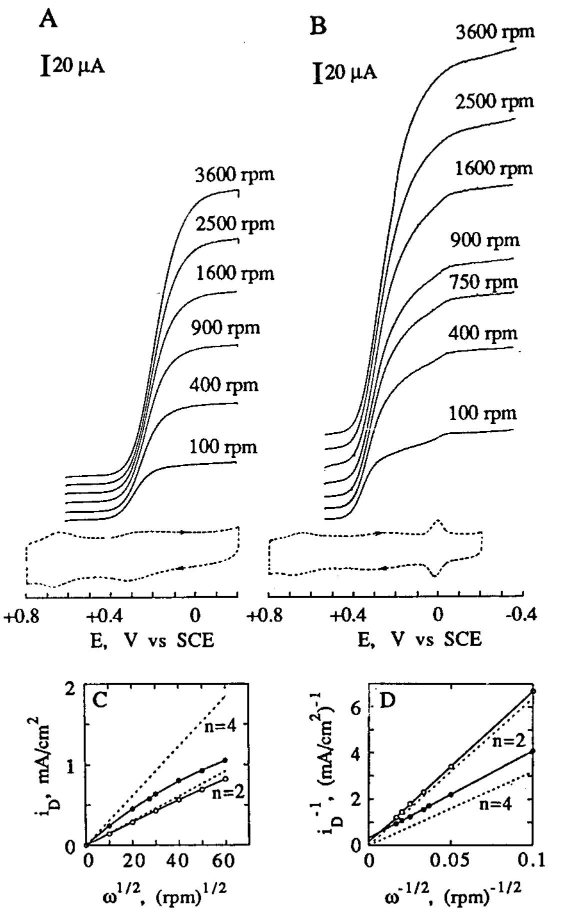

**Figure 3.** Reduction of $O_2$ at a rotating EPG disk electrode on which about $1.7 \times 10^{-10}$ mol cm$^{-2}$ of $[CoP(py\text{-}CH_3)_4]^{4+}$ or $(NH_3)_5Os-[CoP(py\text{-}CH_3)_4]$ containing ca. 2.3 $Os(NH_3)_5$ groups per porphyrin ring was adsorbed. Supporting electrolyte: 0.125 M $HClO_4$ saturated with air. (A) Current−potential curves for the electrode coated with $[CoP(py\text{-}CH_3)_4]^{4+}$ recorded at the indicated rotation rates and a scan rate of 5 mV s$^{-1}$. The dashed curve shows the response of the adsorbed catalyst in the absence of $O_2$ at a scan rate of 50 mV s$^{-1}$. (B) As in A except the catalyst was $(NH_3)_5Os-[CoP(py\text{-}CH_3)_4]$. (C) Levich plots of the plateau currents in A (solid circles) and B (open circles) vs the electrode (rotation rate)$^{1/2}$. The dashed lines are the calculated responses for the diffusion−convection-controlled reduction of $O_2$ by two or four electrons. (D) Koutecky−Levich plots of the data from C. Plateau currents were estimated by drawing tangents to the central portions of the two plateaus. They correspond, approximately, to potentials of 0.2 V (first plateau) and −0.2 V (second plateau).

the same potential as with the nonosmiumated porphyrin, but the peak current is somewhat larger. A more quantitative comparison of the difference between the two types of catalysts was obtained by means of rotating disk voltammetry. Current−potential curves for the reduction of $O_2$ at a rotating disk electrode on which $[CoP(py\text{-}CH_3)_4]^{4+}$ or $(NH_3)_5Os-[CoP(py\text{-}CH_3)_4]$ was adsorbed are shown in Figure 3A,B. Larger plateau currents are obtained with the latter cobalt porphyrin both before and after the coordinated $(NH_3)_5Os$ centers are reduced from Os(III) to Os(II). Levich and Koutecky−Levich plots[35,36] of the plateau currents from Figure 3A and Figure 3B are shown in Figure 3C and Figure 3D. The slopes of the plots for the $[CoP(py\text{-}CH_3)_4]^{4+}$ catalyst show that the reduction of $O_2$ involves only two electrons while those for the $(NH_3)_5Os-[CoP(py\text{-}CH_3)_4]$ complex correspond to ca. 3.4 electrons per $O_2$ molecule. Even at potentials where the coordinated $Os(NH_3)_5$ complex is present as Os(III), e.g., 0.15 V, the currents correspond to more than 2.5 electrons per $O_2$ molecule, which indicates that a four-electron reduction pathway is available in parallel with the usual two-electron reduction pathway.

## Discussion

The results presented in Figure 3 demonstrate that coordination of $(NH_3)_5Os^{3+/2+}$ to $[CoP(py\text{-}CH_3)_4]^{4+}$ enhances the catalytic activity of the adsorbed porphyrin toward the electroreduction of $O_2$ by four electrons. This finding supports the idea that back-bonding by the Os complex is the source of the enhanced catalytic activity of the adsorbed porphyrin. The increase in the reduction current that results when the $(NH_3)_5Os^{3+}$ is converted to $(NH_3)_5Os^{2+}$ is also in accord with this mechanistic scheme because of the greater extent of $\pi$-donation by Os(II) compared with Os(III).[12,32] The evidence against the cycling of the coordinated $(NH_3)_5Os$ centers between their +3 and +2 oxidation states during the catalytic cycle at potentials less positive than 0.05 V, where the resting oxidation state of the Os is Os(II), includes the lack of dependence of the peak potentials for the coordinated $(NH_3)_5Os^{3+/2+}$ couple on the presence of $O_2$ (Figure 2B). If the coordinated $(NH_3)_5Os^{2+}$ groups were rapidly oxidized by $O_2$, the cathodic peak for the reduction of $(NH_3)_5Os^{3+}$ in the solid curve in Figure 2B would appear at potentials more positive than that where it occurs in the absence of $O_2$ (dashed curve in Figure 2B), but no such shift is observed.

In our previous studies, in which $(NH_3)_5Ru^{2+}$ groups were coordinated to 4-cyanophenyl or 4-pyridine ligands attached to the *meso* portion of cobalt porphyrins, at least three $(NH_3)_5Ru^{2+}$ groups were necessary to convert the cobalt porphyrin from a two-electron to a four-electron catalyst.[3,4] The results of the present study suggest that fewer than three $(NH_3)_5Os^{3+}$ groups coordinated to $[CoP(py\text{-}CH_3)_4]^{4+}$ may be sufficient to produce a four-electron catalyst despite the weaker back-bonding of $(NH_3)_5Os^{3+}$ compared to $(NH_3)_5Ru^{2+}$.[12,32] The greater potency of $(NH_3)_5Os^{3+}$ than of $(NH_3)_5Ru^{2+}$ in promoting a four-electron reduction pathway for $O_2$ seems likely to be the result of the coordination of the Os complex directly to the porphyrin ring. Transmission of the back-bonding electron density to the $O_2$ molecule coordinated to the Co(II) center of the porphyrin in the activated complex, believed to be the key element in the enhancement of the four-electron reduction pathway,[3−9] would be expected to be more efficient when the back-bonding metal is coordinated directly to the porphyrin ring rather than to the "distal" end of a pendant ligand such as 4-pyridine or 4-cyanophenyl. The detailed mechanism through which back-bonding from $(NH_3)_5Ru^{2+}$, $(NH_3)_5Os^{3+}$, and $(NH_3)_5Os^{2+}$ into the cobalt porphyrin ring enhances the rate of the four-electron electroreduction of $O_2$ remains to be elucidated. However, neither the parent cobalt porphyrins nor their ruthenated or osmiumated derivatives are active catalysts for the electroreduction of $H_2O_2$ to $H_2O$, and one may speculate that back-bonding acts to delay the release of the partially reduced, coordinated (and possibly activated) $O_2$ species from the Co center of the porphyrin so that it can accept additional electrons from the electrode before it escapes into the acidic solution as $H_2O_2$ and cannot be further reduced.

## Conclusion

The primary conclusions that resulted from this study are summarized in Figure 4 in which cyclic voltammograms in the absence of $O_2$ for three cobalt porphyrins adsorbed on an EPG electrode (dashed curves) are compared with the current−potential curves obtained when the same electrode is used as a

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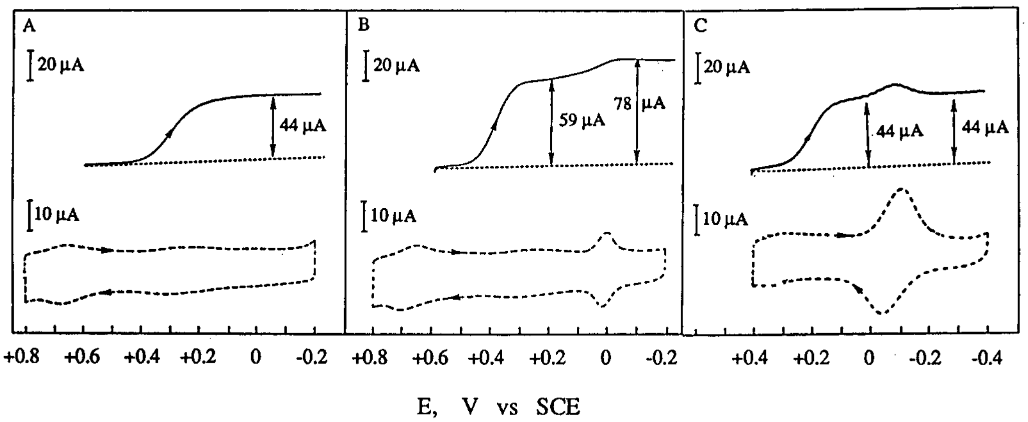

**Figure 4.** Comparison of the reduction of $O_2$ at rotated EPG disk electrodes coated with three different cobalt porphyrin catalysts. The solid lines are current−potential curves for the reduction of $O_2$ recorded at a rotation rate of 100 rpm and a scan rate of 5 mV $s^{-1}$. The dashed curves are the responses of the adsorbed catalysts in the absence of $O_2$ recorded with a scan rate of 50 mV $s^{-1}$. Supporting electrolyte: 0.125 M $HClO_4$. The adsorbed catalysts were (A) $[CoP(py\text{-}CH_3)_4]^{4+}$; (B) $(NH_3)_5Os{-}[CoP(py\text{-}CH_3)_4]$; and (C) $[CoP(pyRu(edta))_4]^{4-}$; data are from ref 3.

rotating disk in the presence of $O_2$. In Figure 4A the reduction of $O_2$ catalyzed by $[CoP(py\text{-}CH_3)_4]^{4+}$ yields a plateau current of 44 $\mu$A at a rotation rate of 100 rpm, which corresponds to a diffusion−convection-controlled two-electron reduction. When the adsorbed porphyrin has $(NH_3)_5Os$ coordinated to it (Figure 4B), a plateau current that exceeds the two-electron limit is obtained at potentials where the Os is present as Os(III). At potentials where the Os is converted to Os(II), the current reaches 90% of the value corresponding to the diffusion−convection-controlled four-electron reduction of $O_2$. In Figure 4C the adsorbed porphyrin is cobalt *meso*-tetrakis(4-pyridyl)-porphyrin to which four (edta)Ru complexes (edta = ethylenediaminetetraacetate) are coordinated. The plateau current corresponds only to the two-electron reduction of $O_2$ both before and after the $(edta)Ru^{III}$ centers are reduced to $(edta)Ru^{II}$. Note that the formal potential of the $(edta)Ru^{-/2-}$ couples coordinated to the pyridine ligands of the porphyrin is about 50 mV more negative than that of the $(NH_3)_5Os^{3+/2+}$ groups coordinated to the porphyrin in Figure 4B. The four $(edta)Ru^{II}$ centers are ineffective in promoting the four-electron reduction of $O_2$ despite their greater reducing strength while the smaller number of more weakly reducing $(NH_3)_5Os^{3+/2+}$ centers are effective (Figure 4B). The striking difference in catalytic activity correlates with the relative back-bonding strengths of the coordinated metal complexes but not with their relative reducing strengths. This result, combined with those presented in previous studies,[3−9] provides strong evidence of the importance of back-bonding in determining the catalytic activities toward the electroreduction of $O_2$ of this class of ruthenium- and osmium-modified cobalt porphyrins. The possibility that the increased electron density in the porphyrin ring resulting from the presence of coordinated, back-bonding metals might also be provided by suitable metal-free substituents on the porphyrin ring is suggested by these results. Preliminary experiments to test this possibility have been encouraging.[37]

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