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# Electron and Ligand Transfer Reactions between Cyclometallated Platinum(II) Compounds and Thallium(III) Carboxylates

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*The relative redox potentials of amine adducts of tetra(*p*-isopropylphenyl)porphinatocarbonylruthenium(II) have been measured in order to study the dependence of porphyrin ring oxidation on axial base. The potentials observed for aromatic heterocyclic amines vary over a range of 0.09 volts; are dependent on the π-base and hydrogen bond donor strength of the amine; and are independent of base strength and steric bulk of the ligand. These results indicate that tension in the imidazole linkage is not a mechanism for protein control on porphyrin ring oxidations and that changes in the hydrogen bonding of the bound imidazole may be a mechanism for controlling porphyrin ring redox potential. The potentials observed for aliphatic amines were constant to within experimental uncertainty and independent of the hydrogen bond donor strength of the axial ligand. The latter result indicates that hydrogen bonding effects are transmitted via the π-bonds of the metal porphyrin complex. A direct correlation between the axial ligand dependence of porphyrin ring and metal center oxidation has been found and this implies that the same mechanisms may be operative in either porphyrin ring or metal center oxidation.*

## Introduction

Electrochemical studies of porphinatocarbonylruthenium(II)*, $Ru^{II}COP$, have shown that this metal porphyrin undergoes two facile one electron oxidations, eqns. 1 and 2 [1–3].

$$Ru^{II}COP \rightarrow Ru^{II}COP^{+\cdot} + e^- \quad (1)$$

$$Ru^{II}COP^{+\cdot} \rightarrow Ru^{III}COP^{+2} + e^- \quad (2)$$

*The abbreviation $Ru^{II}COP$ will be used for porphinatocarbonylruthenium(II) and $Ru^{II}COPL$ for the Lewis base adduct. For specific porphines the following abbreviations have been used: i-Pr-TPP, tetra(*p*-isopropylphenyl)porphine; TPP, tetraphenylporphine; and OEP, octaethylporphine. Also tetrahydrofuran has been abbreviated as THF.

The product of the first oxidation, $Ru^{II}COP^{+\cdot}$, is stable on an extended time scale and this species has been characterized by optical and ESR spectroscopy as a π-cation radical [1]. $Ru^{II}COP$ also forms 1:1 adducts with amines and NMR spectroscopy has been used to determine the structure and stability of a number of these adducts [4–6]. Here this metal porphyrin has been used as a model for studying axial ligand effects on porphyrin ring oxidation and the stability of porphyrin π-cation radicals. Such information is pertinent to accessing the role of the protein [7–10] and π-cations [11, 12] in heme protein redox chemistry. Previous studies of porphyrin ring oxidations have investigated the dependence of the porphyrin ring redox potential on electronegativitiy and oxidation state of the central metal [13], substituent groups on the porphyrin ring [14–16], and solvent [14, 16]. Work on axial ligand effects has shown that the ground state configuration of the π-cation radical is sensitive to the co-ordinating strength of the counter anion [11]. The amine adducts selected for study here examine the influence of imidazole on porphyrin ring redox potential, the mechanisms for protein control on porphyrin ring oxidation potential and the transmission path for hydrogen bonding effects in metal porphyrins.

Studies of redox potentials of iron(II) and osmium(II) porphyrins have shown that imidazole as compared to other nitrogen bases lowers the stability of the metal center to oxidation [17, 18]. By correlating the observed redox potentials with amine structure, the influence of imidazole on metal center oxidations has been explained as resulting from the π-base and hydrogen bond donor properties of the imidazole ligand [18]. The electrochemical data also indicate that the magnitude of the imidazole effect is a weak function of the imidazole–metal bond strength in the osmium(II) porphyrins [18]. In this work, the effects of systematic variations in the π-base, hydrogen bond donor, and coordinating strength of the axial ligand on porphyrin ring redox potential have been measured. On this basis correlations similar to those obtained for metal center oxidation have been developed and the axial ligand

dependence of porphyrin ring and metal center oxidations have been compared. These variations in axial ligand have also been used to determine if tension in the imidazole linkage or changes in the hydrogen bonding of coordinated imidazole are plausible mechanisms for protein control on porphyrin ring oxidations. Both tension in the imidazole linkage and changes in hydrogen bonding to the coordinated imidazole have been proposed as mechanisms for allosteric effects in hemoglobin [19–22]. Mashiko and co-workers have observed that oxidation of an iron porphyrin model of cytochrome C occurs with no significant change in metal–axial ligand bond length [10].

Variations in the hydrogen bonding to the coordinated imidazole ligand have been observed to change the axial ligand exchange rate and spectra of iron porphyrins [23–25]. Stein and co-workers have presented evidence from Raman spectroscopy that hydrogen bonding increases the $\pi$-base strength of the imidazole ligand [26]. Support for this conclusion can be found in the calculations of Del Bene and Cohen [27]. These calculations show that when imidazole functions as the donor in an imidazole-water hydrogen bond, the $\pi$-density at the immine N is increased. The transmission path for hydrogen bonding effects has been investigated in this work by measuring the effects of increasing the hydrogen bond donor strength in aliphatic amines and by comparing the effects of increased hydrogen bond and $\pi$-base strength for amines which can form $\pi$-bonds with the ruthenium(II) center.

## Results

Relative redox potentials for $Ru^{II}CO$(i-Pr-TPP)L oxidation were measured using cyclic voltammetry. Consistent with eqns. 1 and 2, two waves were observed and the half-wave potentials are presented in Table I. These potentials are not corrected for liquid junction potentials and have an estimated uncertainty of 0.01 volts for the first wave and 0.02 volts for the second wave. For the first oxidation the anodic and cathodic peak currents are equal to within experimental uncertainty and the anodic and cathodic peak separations range between 0.06 and 0.08 volts. The lower limit of this range is characteristic of a one electron diffusion controlled electron transfer. Peak separations above 0.06 V are attributed to uncompensated solution resistance. The second oxidation wave shows similar properties except the anodic and cathodic peak separations range between 0.06 volts and 0.10 volts. The site of the first oxidation was established by carrying out controlled potential electrolysis for the imidazole, pyridine and THF adducts at a potential between the first and second waves. The visible spectra of the oxidation products are similar to that observed by Brown and co-workers for the analogous $Ru^{II}CO$(TPP) adducts [1]. Brown and co-workers characterized this oxidation product as $Ru^{II}CO(TPP)L^{\cdot}$ by visible and ESR spectroscopy [1]. The similar spectra observed for the $Ru^{II}CO$-(i-Pr-TPP)L adducts studied here demonstrates that the $\pi$-cation radicals produced by the first oxidation have the same ground state configuration [11].

Table I also presents the structures of the amines studied in this work and the base site coordinated to the ruthenium(II) center in the multiple base site amines. The site of coordination in imidazole and the substituted imidazoles has been assigned by Faller and co-workers [6]. For 3-aminopyridine coordination at the ring N has been established using the NMR method developed by Faller and co-workers [6]. This establishes the assigned structure for 4-aminopyridine and 4-dimethylaminopyridine as in these derivatives the ring N is a stronger base relative to the amine N on electronic grounds. Also, the amine N is sterically hindered in 4-dimethylaminopyridine. For the 3-hydroxypyridine, 3-hydroxylaniline, and 4-hydroxypiperidine adducts, co-ordination at the amine N is consistent with the observation that alcohols co-ordinate weakly to the ruthenium(II) center and are readily replaced by amines [4–6].

The half-wave potentials presented in Table I sample the relative stabilities of the species $Ru^{II}$-$CO$(i-Pr–TPP)$L^{\cdot}$ and $Ru^{II}CO$(i-Pr-TPP)L if the ligand is coordinated under the conditions of these experiments [28]. Co-ordination for the 2-methylimidazole adduct was established by titrating a sample of RuCO(i-Pr-TPP)THF with 2-methylimidazole. A half-wave potential within experimental uncertainty of that for a sample of RuCO(i-Pr–TPP)-2-methylimidazole was observed when the mole ratio of 2-methylimidazole/RuCO(i-Pr-TPP)THF was 0.90. This experiment also provides evidence that the imidazole, 1-methylimidazole, 1-acetylimidazole, pyridine, 3-aminopyridine, 3-hydroxypyridine, 4-aminopyridine, 4-dimethylaminopyridine, 4-methylpyridine, benzylamine, and 3-hydroxyaniline are coordinated to the ruthenium(II) center under the conditions of these experiments. These amines do not sterically interact with the porphyrin ring and the base strengths of these amines exceed the base strength of pyrazole. Faller and co-workers have shown that the RuCOP-pyrazole adduct is more stable to dissociation than RuCOP-2, 4-dimethylimidazole [6] and their data also show that stability to dissociation is directly proportional to base strength for sterically unhindered amines [6]. The RuCO(i-Pr–TPP)-1,2-dimethylimidazole adduct has been assumed to be co-ordinated on the basis of the structural similarity to 2-methylimidazole. Co-ordination of 4-hydroxypiperidine to $Ru^{II}$(i-Pr-TPP) has

been established by NMR. This also establishes the co-ordination of diethylamine as molecular models indicate comparable steric interactions between porphyrin ring and axial ligand for these systems.

The identification of the product of the second oxidation as $Ru^{II}CO(i\text{-}Pr\text{-}TPP)^{+2}$ is less certain. By determining the dependence of porphyrin ring oxidation potential on ring substituents and the difference between half wave potentials for the first and second waves, Rillema and co-workers have assigned the site of the second oxidation as the ruthenium(II) center in a number of $Ru^{II}COP$ porphyrins [3]. The difference in half-wave potentials for the oxidations observed here ranges beween 0.44 volts and 0.58 volts. These differences are significantly greater than the average of 0.30 volts observed in porphyrins where both oxidations are known to occur at the porphyrin ring [11]. Hence the data in Table I support the tentative assignment of the site of the second oxidation as the metal center. Further work on this assignment is in progress and only the axial ligand dependence of the first porphyrin ring oxidation will be discussed.

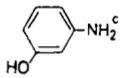
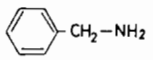
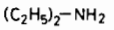
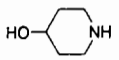
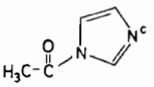
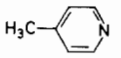
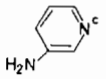
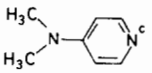
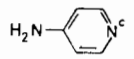
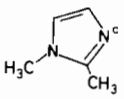
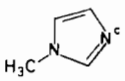
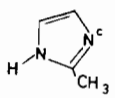
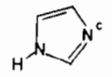
## Discussion

The observed half-wave potentials in Table I have been ordered on the basis of the reduction potential for the couple $Ru^{II}CO(P)L^{+}/Ru^{II}CO(P)L$, eqn. 1. This ordering of potentials shows that the stability of the porphyrin ring to oxidation varies over a range of 0.09 volts. This range is approximately 20% of the porphyrin ring redox potential range observed for $M^{II}OEP$ porphyrins with variations in the divalent center [13] and 25% of the range observed in M(p-R-TPP) porphyrins with variations in the substituent group, R [14–16]. Although qualitative in nature, this comparison suggests that exchange of a histidine residue for a lysine residue or the reverse represents a way to control the stability of the porphyrin ring to oxidation. Furthermore, the observed potentials for the first porphyrin ring oxidation show that the imidazole adduct is less stable to oxidation than the benzylamine adduct. This indicates that a histidine residue bound to the iron center in a heme protein would stabilize a porphyrin $\pi$-cation radical more than a lysine residue. This result suggests that if oxidation of iron(II) porphyrins occurs via a $\pi$-cation radical mechanism [7, 8, 11] the imidazole adduct would be the most rapidly oxidized.

The potentials in Table I show no dependence on adduct stability to dissociation and hence on base strength or steric bulk of the axial ligand. For example, Faller and co-workers have measured the relative stability constants for the pyrazole, 4-methylpyridine and benzylamine adducts and their results show the stability increases in the given order [6]. The porphyrin ring redox potentials for these adducts agree to within experimental uncertainty. These adducts also illustrate the independence of porphyrin ring redox potential on base strength of the axial ligand as the pKBs for pyrazole, 4-methylpyridine and benzylamine are respectively 11.52, 7.97, and 4.65. This range of base constants includes all other ligands studied here regardless of porphyrin ring redox potentials. The weak dependence of porphyrin ring redox potentials on steric interactions between the porphyrin ring and axial ligand is demonstrated by the close agreement between the potentials observed for the imidazole and 2-methylimidazole or 1-methylimidazole and 1,2-dimethylimidazole adducts. Substitution of a methyl group in the 2 position in imidazole is known to stretch, bend and weaken the metal imidazole bond as the result of steric interaction between the porphyrin ring and axial ligand [6, 29, 30].

The observed potentials for the 1-substituted imidazoles and the amino substituted pyridines can be used to show that increasing the $\pi$-base strength of the axial ligand lowers the stability of the porphyrin ring to oxidation. Consider first, the 1-methylimidazole and 1-acetylimidazole adducts which show a difference in porphyrin ring stability of 0.05 volts with the 1-acetylimidazole adduct being more stable to oxidation. A methyl group is electron releasing by inductance while the acetyl group withdraws electrons by both inductance and resonance. Then the 1-acetylimidazole ligand is both a weaker $\sigma$ and $\pi$-base than 1-methylimidazole. Since the observed potentials are independent of $\sigma$-base strength, the difference in potentials between these adducts is attributed to the difference in $\pi$-base strength of the 1-methylimidazole and 1-acetylimidazole ligands. The order of the potentials and $\pi$-base strengths for these ligands indicates an inverse correlation between $\pi$-base strength and porphyrin ring stability to oxidation. The amino substituted pyridines show similar behavior and confirm these conclusions. For example, the 4-dimethylaminopyridine adduct is less stable to porphyrin ring oxidation than the pyridine adduct by 0.04 volts. The dimethylamino group in the 4 position is strongly electron releasing by resonance and 4-dimethylaminopyridine is as a result a stronger $\pi$-base than pyridine. Also the resonance electron releasing properties of the amino group can be blocked by shifting the amino group from the 4-position to the 3-position. This explains the difference and order of potentials observed for the 4-aminopyridine and 3-aminopyridine adducts. The potentials observed for 4-methylpyridine and pyridine adducts agree to within experimental error. This further demonstrates that the observed potentials do not depend on a base strength and that the axial ligand dependence of porphyrin ring oxidation is not affected by inductive effects of substituent groups on the axial ligand.

TABLE I. Half-wave Potentials for Amine Adducts of Tetra(p-isopropylphenyl)porphinatocarbonylruthenium(II) in $CCl_2H_2$, 0.1 *M* TBAHP.[a]

| Ligand | Structure | Potential (Wave 1)[b] | Potential (Wave 2)[b] |
|---|---|---|---|
| Tetrahydrofuran |  | 0.46 v | 0.99 v |
| 3-Hydroxyaniline |  | 0.46 v | 0.99 v |
| Benzylamine |  | 0.46 v | 0.95 v |
| Diethylamine |  | 0.46 v | 0.94 v |
| 4-Hydroxypiperidine |  | 0.46 v | 0.97 v |
| Pyrazole |  | 0.46 v | 0.90 v |
| 1-Acetylimidazole |  | 0.45 v | 0.96 v |
| Pyridine |  | 0.44 v | 0.99 v |
| 4-Methylpyridine |  | 0.44 v | 0.99 v |
| 3-Aminopyridine |  | 0.44 v | 0.99 v |
| 3-Hydroxypyridine |  | 0.41 v | 0.92 v |
| 4-Dimethylaminopyridine |  | 0.40 v | 0.94 v |
| 4-Aminopyridine |  | 0.40 v | 0.94 v |
| 1,2-Dimethylimidazole |  | 0.40 v | 0.94 v |
| 1-Methylimidazole |  | 0.40 v | 0.93 v |
| 2-Methylimidazole |  | 0.37 v | 0.95 v |
| Imidazole |  | 0.37 v | 0.95 v |

[a]Tetra-n-butylammonium hexafluorophosphate, TBAHP. [b]Reference electrode, $Ag/AgNO_3$ (0.1 *M* in $CH_3CN$). [c]Lewis base site coordinated to metal center.

The observed potentials for the imidazole and 1-methylimidazole or the 3-substituted pyridine adducts can be used to show that increasing the hydrogen bond donor strength lowers the stability of the porphyrin ring to oxidation. For example, the 1-methylimidazole adduct is more stable to porphyrin ring oxidation than the imidazole adduct by 0.03 volts. This difference is attributed to the methyl group blocking the hydrogen bond donor capacity of the co-ordinated imidazole ligand and not to any differences in $\pi$-base strength of two ligands as the methyl group is electron releasing by induction. In a similar manner, hydrogen bond donor strength can be used to explain the difference and order of potentials for the 3-hydroxypyridine and 3-aminopyridine adducts. 3-Hydroxypyridine is a stronger hydrogen bond donor than 3-aminopyridine. Neither group will change the $\pi$-base strength of the pyridine ligand as the resonance electron releasing properties of these groups are blocked in the 3 position and inductive effects of substituent groups have been shown to be negligible in other pyridine adducts. Then consistent with expectations based on hydrogen bond donor strength the 3-hydroxypyridine adduct is observed to be less stable to porphyrin ring oxidation than the 3-aminopyridine adduct by 0.03 volts. The amino substituted pyridines also show that under the conditions of this experiment the amino group does not form sufficiently strong hydrogen bonds to change the porphyrin ring redox potential. For example, the dimethylaminopyridine adduct with no hydrogen bond donor capacity and the 4-aminopyridine adduct with hydrogen bond donor capacity are observed to have porphyrin ring redox potentials which agree to within experimental uncertainty. A similar observation is made with the 3-aminopyridine and pyridine adducts.

The potentials observed for the aliphatic amines provide evidence that the effect of hydrogen bonding to the co-ordinated ligand is transmitted through the $\pi$-bonding of the metal porphyrin complex. On the basis of the hydrogen bond donor strength of the hydroxy group, the 4-hydroxypiperidine and 3-hydroxyaniline adducts would be expected to show a porphyrin ring redox potential lower than other aliphatic amine adducts. However, the porphyrin ring redox potentials for these adducts and all other aliphatic amine adducts agree to within experimental uncertainty. This behavior is attributed to the absence of overlap between the axial ligand and ruthenium center in these adducts. This observation is consistent with the hypothesis that hydrogen bonding to the co-ordinated imidazole increases the $\pi$-base strength of the bond ligand [26]. Further support for this hypothesis comes from the observation that the hydrogen bond donor strength or the $\pi$-base strength of the ligand are both inversely correlated with the stability of the porphyrin ring to oxidation.

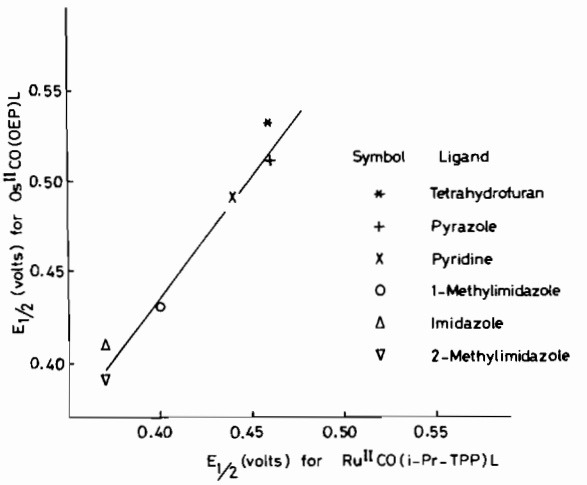



Fig. 1. Comparison of relative half-wave potentials for amine adducts of octaethylporphinatocarbonylosmium(II), $Os^{II}$-CO(OEP) and tetra(*p*-isopropylphenylporphinatocarbonyl-ruthenium(II), $Ru^{II}CO$(i-Pr-TPP). The solvent for both systems is dichloromethane and the supporting electrolyte is tetra-n-butylammonium hexafluorophosphate.

Buchler and co-workers have reported relative redox potentials for amine adducts of $Os^{II}(OEP)L$ under conditions similar to those used in these experiments [18]. This porphyrin undergoes oxidation at the metal center [2] and Fig. 1 presents a comparison of the axial ligand dependence of these potentials with the axial ligand dependence of the potentials observed here for $Ru^{II}CO$(i-Pr-TPP)L. The linearity of the free energy plot shows that metal center and porphyrin ring oxidation depend on the same factors. The slope of the line defined by these points is greater than unity indicating that metal center oxidation is more sensitive to variations in the axial ligand than the porphyrin ring.

## Conclusions

The amine adducts of $Ru^{II}CO$(i-Pr-TPP) have been found to be useful models for probing axial ligand effects on porphyrin ring oxidation. The observed range of porphyrin ring redox potentials was 0.09 volts and this range has been shown to be sufficient for the protein to control porphyrin ring redox potential by exchange of a histidine residue for a lysine residue (or the reverse). This conclusion uses imidazole and benzylamine respectively as models for the residues of histidine and lysine. The potentials also show that the imidazole adduct is the most easily oxidized and imply that binding a histidine residue as compared to a lysine residue would promote the formation of $\pi$-cation radicals.

The redox potentials for substituted imidazole and pyridine adducts have been found to be dependent on the $\pi$-base and hydrogen bond donor strength of the axial ligand. The dependence on the hydrogen bond donor strength indicates that changes in hydrogen bonding to the co-ordinated imidazole may be a mechanism for protein control on porphyrin $\pi$-cation radical stability. The data also show that stretching and bending the imidazole-ruthenium(II) bond as sampled by 2-methylimidazole [6, 29, 30] does not change the porphyrin ring redox potential. This indicates that tension in the imidazole linkage is not a mechanism for control porphyrin $\pi$-cation radical stability.

Examination of the potentials for aliphatic amines shows that introduction of strong hydrogen bond donor groups into these amines does not change the porphyrin ring redox potential. This is consistent with the transmission of hydrogen bonding effects through the $\pi$-bonding of the porphyrin complex and the hypothesis that hydrogen bonding increases the $\pi$-base strength of the imidazole ligand [26]. The latter conclusion is also supported by the result that porphyrin ring stability to oxidation is inversely correlated with the $\pi$-base strength or hydrogen bond donor strength of the axial ligand.

The redox potentials for $Ru^{II}CO$(i-Pr-TPP)L and $Os^{II}CO$(OEP)L show the same qualitative dependence on axial ligand. This shows that porphyrin ring and metal center oxidation depend on the same factors and that protein control on either porphyrin ring or metal center oxidation may occur by the same mechanism. The redox potentials for $Os^{II}CO$(OEP)L oxidation are quantitatively more sensitive to changes in the axial ligand than the potentials for $Ru^{II}CO$(i-Pr-TPP)L. The implication of this observation is that the imidazole linkage is a more efficient control unit for electron transfer from the metal center than the porphyrin ring. This conclusion and all other conclusions with regard to the imidazole linkage may be sensitive to the metal center and porphyrin ring substitutions used in this work. The sensitivity of the axial ligand effects observed here to these substitutions is currently being investigated.

## Experimental

*Solvents*

The dichloromethane used in the cyclic voltammetry experiments was distilled from 4 Å molecular sieves under nitrogen. Tetrahydrofuran, THF, was distilled from sodium/benzophenone under nitrogen. All other solvents were reagent grade and used as provided by suppliers.

*Axial Ligands*

Imidazole and 2-methylimidazole were sublimed and stored in a desiccator. Pyrazole was crystallized from cyclohexane, dried under vacuum, and stored in a desiccator. Benzylamine was vacuum distilled. 4-Methylpyridine was distilled from sodium hydroxide. All other ligands were used as obtained from suppliers.

*Supporting Electrolyte*

Tetra-n-butylammonium hexafluorophosphate, TBAHP, was prepared by dissolving 12.2 g of tetra-n-butylammonium bromide in approximately 25 ml of water and 7.0 grams of potassium hexafluorophosphate in 200 ml of water. The two solutions were mixed and tetra-n-butylammonium hexafluorophosphate precipitated immediately. The precipitate was collected, washed with water, then recrystallized twice from ethanol/water (1:1). The crystals were dried under vacuum for at least two days and stored in a vacuum desiccator.

*Porphine*

Tetra(*p*-isopropylphenyl)porphine was prepared by literature methods [5, 32].

*Tetra(*p*-isopropylphenyl)porphinatocarbonyltetrahydrofuranruthenium(II)*

The ruthenium was inserted into i-Pr-TPP following the procedure of Tsutsui and co-workers [4]. In this procedure, dodecacarbonylruthenium and porphine are refluxed in benzene under nitrogen. The product, $Ru^{II}CO$(i-Pr-TPP)L, was separated from the starting materials by chromatography on dry high activity alumina. Benzene, dichloromethane, and dichloromethane/acetone were used as eluting solutions. The final product, $Ru^{II}CO$(i-Pr-TPP)THF, was then obtained by recrystallization from THF/n-hexane. The dodecacarbonylruthenium was prepared using literature methods [32].

*Amine Adducts of tetra(*p*-isopropylphenyl)porphinatocarbonylruthenium(II)*

$Ru^{II}CO$(i-Pr-TPP)THF and excess amine were dissolved in dichloromethane. Methanol was added and the solution concentrated under a stream of nitrogen until crystallization occurred. The micro-crystals were collected by centrifuging and then washed with methanol. The adduct was dried under a stream of nitrogen and then vacuum.

*Electrochemistry*

Cyclic voltammetry was carried out under nitrogen with approximately millimolar solutions of the adduct under study. The solvent was freshly distilled dichloromethane and the concentration of the supporting electrolyte was 0.10 *M*. The measurements employed a standard three electrode system; a PAR 174A Polarographic Analyzer with a Wavetek Function generator or a custom made potentiostat using an Exar 2206 K function generator; and a

Hewlett Packard X–Y recorder or a storage oscilloscope fitted with a Polaroid camera. The working and counter electrodes were platinum wires. The reference electrode was an $Ag/Ag^+$ electrode which was 0.10 *M* $AgNO_3$ in acetonitrile. This electrode was connected to the solution under study using a Vycor salt bridge. Solution resistance was compensated using a positive feedback circuit which was adjusted by the procedure of Whitson and co-workers [33].

For the titration of RuCo(i-Pr-TPP)THF by 2-methylimidazole, the 2-methylimidazole solution was made from freshly prepared supporting electrolyte solution and the titration was carried out under nitrogen saturated with dichloromethane vapor.

Controlled potential electrolysis was carried out under conditions similar to the cyclic voltammetry studies except for the following differences. Platinum plates were used as working and counter electrodes and the counter electrode was separated from the solution being electrolyzed by a Vycor salt bridge. Aliquots of the solution being electrolyzed were taken as the electrolysis progressed and the visible spectrum of the aliquot was recorded.

*NMR*

Proton NMR spectra were run using a Brucker 270 MHz spectrometer operating in a Fourier transfer mode. The samples were approximately millimalor in RuCO(i-Pr-TPP)L with deuterochloroform as a solvent. A sample of RuCO(i-Pr-TPP)3-aminopyridine was run in dichloromethane. No solvent dependence of the chemical shifts was observed.

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